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Reactions of Peroxydisulphuryl Difluoride and Halogen Fluorosulphates with Organic Compounds

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The literature data on the reactions of peroxydisulphuryl difluoride and halogenofluorosulphates with various classes of organic compounds and on the methods of synthesis and properties of the above reagents are surveyed and described systematically. Attention is concentrated on the possibility of selective reactions which apparently predetermine the subsequent extensive employment of peroxydisulphuryl difluoride and halogen fluorosulphates for synthetic purposes. The bibliography includes 226 references.

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I. INTRODUCTION

Peroxydisulphuryl difluoride $(OSO_2F)_2$ and halogen fluorosulphates $HalOSO_2F$, which were first synthesised at the end of the 1950's and the beginning of the 1960's[1-7], have comparatively recently attracted the attention of organic chemists as exceptionally active reagents permitting in a number of instances reactions which had not been feasible hitherto and a deeper understanding of the nature of the reactivities of many organic compounds, including those which had been previously regarded as the most inert.

Peroxydisulphuryl difluoride and halogen fluorosulphates are genetically related although their reactivities are to some extent different.

Peroxydisulphuryl difluoride—the peroxide of fluorosulphonic acid—differs from the majority of the known peroxides by the complete absence of explosive properties and a high stability in a pure state. By virtue of its structure, it is capable of supplying the $\dot{O}SO_2F$ radical, and is usually regarded as one of the most effective radical reagents. However, direct oxidations, which have been most thoroughly investigated in the case of inorganic substances, are also known.

Halogen fluorosulphates are mixed anhydrides of the corresponding halogen oxy-acids (for example hypochlorous and hypobromous) and fluorosulphonic acid. The name "halogenofluorosulphates" is used together with "halogen fluorosulphate".

In view of the similarity of the electronegativities of the fluorine atom and the fluorosulphate group, reactions of the radical type are more characteristic of fluorine fluorosulphate. In chlorine, bromine, and iodine fluorosulphates the halogen atoms carry a positive charge as a result of polarisation, so that these compounds are extremely effective electrophiles.

Since peroxydisulphuryl difluoride has been hitherto an essential precursor of halogen fluorosulphates (except fluorine fluorosulphate), its properties have naturally been investigated to a greater extent.

To ensure a compact exposition of the relevant data, in addition to the nomenclature generally adopted (such as, for example, the term methyl fluorosulphate CH_3OSO_2F), in a number of instances, as in the majority of original communications, the fluorosulphate group has been treated as a substituent: for example, bis(fluorosulphato)dichloromethane $CCl_2(OSO_2F)_2$ and tetrakis(fluorosulphato)methane $C(OSO_2F)_4$.

Individual questions of the chemistry of peroxydisulphuryl difluoride and halogen fluorosulphates have been dealt with in a number of publications[8-10], but sufficiently complete surveys are not available and in the present review an attempt has been made to make good this deficiency.

II. PROPERTIES OF PEROXYDISULPHURYL DIFLUORIDE AND HALOGEN FLUOROSULPHATES

Peroxydisulphuryl difluoride and chlorine and bromine fluorosulphates are low-boiling liquids, fluorine fluorosulphate is a gas, and iodine fluorosulphate and bromine and iodine trisfluorosulphates are readily fusible substances (see Table). The infrared and Raman spectra[3,11,22-29] as well as ^{19}F NMR spectra[3,7,12,30-36] of the above compounds have been studied in detail.

The high reactivity of peroxydisulphuryl difluoride is due to the ease of its dissociation into radicals[3,14-19,37]:

$$S_2O_6F_2 \rightleftarrows 2OSO_2F \cdot$$

The molar dissociation energies of the O—O bond in peroxydisulphuryl difluoride and of the O—Hal bond in chlorine and fluorine fluorosulphates are listed in the Table. A calculation has been performed for the fluorosulphate radical by the LCAO-MO SCF method[38] and studies have been made of its infrared spectrum[39], its absorption spectrum in the visible region[14,15,40-42], and its fluorescence spectrum excited by laser radiation[43-46].

Solutions of peroxydisulphuryl difluoride in fluorosulphonic acid are not conducting[47], in contrast to solutions of, for example, iodine fluorosulphate[13].

Peroxydisulphuryl difluoride and halogen fluorosulphates are highly reactive compounds. They are best stored (except fluorine fluorosulphate) in sealed glass tubes, when no changes are observed in the specimen even after several months. The majority of the reactions can be carried out in

apparatus made of Pyrex glass, but at elevated temperatures quartz, Teflon, stainless steel, nickel, and monel metal are usually employed.

Certain physicochemical properties of peroxydisulphuryl difluoride and halogen fluorosulphates*.

Compound	M.p., °C	B.p., °C**	d_4, g cm^{-3} (t, °C)	References	E, kJ mol^{-1}	λ_{vap}, kJ mol^{-1}	Trouton's constant	References
$(FSO_2O)_2$	−55.4	67.1	1.6450 (35.5)	[3]	92.048***	31.882	22.4	[3]
$FOSO_2F$	−158.5	−31.3	—	[2]	138.072±1.225	—	—	[20]
$ClOSO_2F$ ****	−84.3	45.1	1.711 (20)	[7]	188.280±6.276	32.049	24.0	[7, 21]
$BrOSO_2F$ *****	−31.5	117.3	2.238 (25)	[12]	—	36.275	22.05	[6]
$Br(OSO_2F)_3$	59	—	—	[6]	—	—	—	—
$IOSO_2F$	51.5	200	—	[13]	—	—	—	—
$I(OSO_2F)_3$	32.2	—	—	[6]	—	—	—	—

*Note: E is the dissociation energy of the O–O or O–Hal bonds and λ_{vap} is the latent heat of evaporation.

**At 760 mmHg.

***Other values of E: 91.221 ± 0.628 kJ mol^{-1};[14] 94.487 kJ mol^{-1};[15] 112.968 kJ mol^{-1};[16] 104.60 kJ mol^{-1};[17] 93.722 ± 3.766 kJ mol^{-1}.[18,19]

****According to the results of Schack and Wilson[11], the boiling point is 43.4 °C, λ_{vap} = 31.610 kJ mol^{-1}, and Trouton's constant is 23.8.

*****According to the results of Roberts and Cady[6], the boiling point is 120.5 °C and d_4^{25} = 2.600 g cm^{-3}.

In contrast to organic compounds, peroxydisulphuryl difluoride and chlorine, bromine, and iodine fluorosulphates are insensitive to external influences (impact, brief contact with an open flame) and to changes in phase state, but fluorine fluorosulphate has shown a high tendency towards explosive decomposition even at temperatures below 0°C[48], which is apparently characteristic of liquefied $FOSO_2F$. The usual thermal decomposition of fluorine fluorosulphate at 236–263 °C leads to sulphuryl fluoride and oxygen[49], while in the presence of chlorine at 90–110 °C the products are peroxydisulphuryl difluoride, chlorine monofluoride, and a small amount of chlorine fluorosulphate[50]. Both reactions have been studied kinetically and the calculated data agree satisfactorily with experiment[51].

Both peroxydisulphuryl difluoride and halogen fluorosulphates react vigorously at room temperature with traces of moisture, benzene, acetone, and other organic compounds (sometimes with inflammation). Liquid chlorine fluorosulphate and peroxydisulphuryl difluoride ignite incompletely fluorinated greases. At low temperatures peroxydisulphuryl difluoride is much less reactive than chlorine and particularly bromine fluorosulphate. Peroxydisulphuryl difluoride therefore tends to accumulate in the reaction mass in many instances; as the temperature is raised, this can be the cause of a vigorous reaction and ejection of the mixture. Peroxydisulphuryl difluoride behaves analogously also in water containing ice, where it is initially precipitated as the lower layer.

The facts presented indicate the highly corrosive nature of the reagents; experiments employing them require reliable protection from atmospheric moisture, are potentially dangerous, must be carried out with adequate caution, and protective measures must be taken.

In order to increase the selectivity of the reactions, usually reduced temperatures (down to −100 °C), inert (highly fluorinated) solvents, very slow mixing of the reactants (for example, by diffusion *in vacuo*), and similar procedures are used. The method of generating peroxydisulphuryl difluoride *in situ* by an electrochemical method is apparently extremely promising[52–54].

In a more detailed consideration of the properties of peroxydisulphuryl difluoride and halogen fluorosulphates one must emphasise that they react vigorously with many elements (the reactions of peroxydisulphuryl difluoride with the halogens described in the next section) and their hydrides, oxides, peroxides, and salts.

Peroxydisulphuryl difluoride readily oxidises sulphur[55–57], selenium[58,59], tellurium[60,61], and antimony[62], complex cations being formed in the first stage, for example[56,57]:

$$2S_8 + (OSO_2F)_2 \xrightarrow[HSO_3F]{t^\circ} S_{16}^{+2}(OSO_2F^-)_2 \quad \text{(red soln)}$$

$$S_8 + (OSO_2F)_2 \xrightarrow[HSO_3F]{0^\circ} S_8^{+2}(OSO_2F^-)_2 \quad \text{(blue soln)}$$

Many salts of fluorosulphonic acid, including complex salts, have been obtained by treating metals and their oxides or salts with peroxydisulphuryl difluoride (data up to 1972 inclusive have been surveyed in a review[9]) or halogen fluorosulphates; vigorous research is being continued[63–73], for example, the following methods of synthesis have been proposed[67,73]:

$$Ag + (OSO_2F)_2 \rightarrow Ag(OSO_2F)_2$$

$$Au + BrOSO_2F \rightarrow Br_3[Au(SO_3F)_4]$$

Fluorine fluorosulphate readily fluorinates not only salts[74], bromine[7], and iodine[75], but also xenon at 170–180 °C[76]:

$$FOSO_2F \xrightarrow{CsOSF_5} SF_5OF$$

$$FOSO_2F \xrightarrow{I_2} IF_3(OSO_2F)_2 + (OSO_2F)_2$$

$$FOSO_2F \xrightarrow{Xe} XeF_2 + (OSO_2F)_2$$

Peroxydisulphuryl difluoride reacts vigorously with ammonia, hydrogen sulphide, and hydrogen chloride[77]; chlorine fluorosulphate also readily reacts with the last substance[78]:

$$HCl + ClOSO_2F \rightarrow Cl_2 + HSO_3F$$

The main products of the reactions of peroxydisulphuryl difluoride[79–82] and fluorine[83], chlorine[78], and bromine[82] fluorosulphates with nitrogen oxide, tetroxide, and pentoxide, as well as the reactions of peroxydisulphuryl difluoride with nitryl and nitrosyl chlorides[82] are nitryl and nitrosyl fluorosulphates, for example:

$$HalOSO_2F + N_2O_4 \rightarrow NO_2OSO_2F + HalNO_2 \quad (Hal = F, Cl)$$

$$(OSO_2F)_2 + 2ClNO_2 \rightarrow 2NO_2OSO_2F + Cl_2$$

Peroxydisulphuryl difluoride interacts vigorously with tetrafluorohydrazine[84,85]:

$$(OSO_2F)_2 + N_2F_4 \rightarrow 2F_2NOSO_2F$$

The substitution of halogen atoms in chlorosulphonic acid[86], chlorosulphonyl isocyanate[87], and phosphoryl bromide[88] or chloride[89] on treatment with chlorine fluorosulphate, bromine fluorosulphate, or peroxydisulphuryl difluoride yielded the corresponding fluorosulphates:

$$ClSO_2NCO + BrOSO_2F \xrightarrow{20^\circ} FSO_2OSO_2NCO$$

$$Br_3PO + (OSO_2F)_2 \rightarrow (FSO_2O)_3PO + Br(OSO_2F)_3$$

SO_2Cl_2,[89] SOClF,[55] and $SeOCl_2$[90] react analogously. The reaction with *N*-chlorosulphinylamine is more complex[91]:

$$ClNSO + ClOSO_2F \rightarrow Cl_2 + SO_2F_2 + SO(OSO_2F)_2 + N_2 + S_2O_5F_2 + SO_2 + ClN(SO_2F)_2 + Cl_2NSO_2F \ .$$

Chlorine[92,93] and bromine[94] fluorosulphates have been used to prepare chlorine and bromine perchlorates:

$$NO_2ClO_4 + BrOSO_2F \rightarrow BrOClO_3 \ .$$

Peroxydisulphuryl difluoride only oxidises phosphorus trifluoride, thionyl fluoride, and carbon monoxide[55,95,96], but adds to arsenic trifluoride[97], sulphur dioxide[5,55,98,99], and sulphur tetrafluoride[55,99]; in the presence of potassium fluoride, a mixed peroxide can be obtained from thionyl tetrafluoride[100]:

$$(OSO_2F)_2 \xrightarrow{AsF_3} AsF_3(OSO_2F)_2 \ ; \quad \xrightarrow{SO_2} F_2S_2O_6 \ ; \quad \xrightarrow{SF_4} F_4S(OSO_2F)_2 \ ; \quad \xrightarrow{OSF_4,\ KF} F_5SOOSO_2F \ .$$

The reactions with CO,[95,96] SO_2,[98,99] and SF_4[99] have been studied by kinetic methods.

Fluorine fluorosulphate[75,101–104] and (even at room temperature) chlorine fluorosulphate[78] readily combine with sulphur dioxide and carbon monoxide:

$$HalOSO_2F \xrightarrow{SO_2} HalSO_2OSO_2F \ ; \quad \xrightarrow{CO} HalCOOSO_2F \ ;$$
$$Hal = F, Cl \ .$$

The kinetics of the reactions involving SO_2[101] and CO[103,104] have been investigated at 60–120 °C and 30–90 °C respectively.

Peroxydisulphuryl difluoride and fluorine fluorosulphate could not be made to add to difluorodiazine[105].

On interaction with peroxydisulphuryl difluoride, metal carbonyls form fluorosulphonate salts of different composition[55,106,107], for example:

$$W(CO)_6 + (OSO_2F)_2 \rightarrow WO(SO_3F)_4 \ .$$

Although the reagents considered belong to the class of the most vigorous oxidants, nevertheless a detailed study has been made of the possibility of increasing the oxidation state of the halogen atoms in halogen fluorosulphates. The interaction of peroxydisulphuryl difluoride with OF_2,[32,108] ClO_2,[109] I_2O_4 and I_2O_5,[110–112] $(SF_5O)_2$,[113] and $(SeF_5O)_2$[114] has also been investigated, for example:

$$(OSO_2F)_2 + (SF_5O)_2 \rightarrow 2SF_5OOSO_2F \ .$$

Chlorine (but not bromine) fluorosulphate readily interacts with ozone at 0 °C[115]:

$$ClOSO_2F + O_3 \rightarrow O_2ClOSO_2F \ .$$

Chlorine oxide difluoride has also been used to oxidise chlorine fluorosulphate[116]. Treatment of iodine fluorosulphate with chlorine and bromine yielded the fluorosulphates $IHal_2OSO_2F$ and $I_2HalOSO_2F$ (Hal = Cl or Br)[13,117]; the interaction of ICl_2OSO_2F and IBr_2OSO_2F leads to $IBrClOSO_2F$.[118]

The above main types of reactions of peroxydisulphuryl difluoride and halogen fluorosulphates (oxidation, introduction of the fluorosulphate group, or halogenation and addition to unsaturated compounds) are as a rule also characteristic of reactions with organic compounds.

III. METHODS OF SYNTHESIS OF PEROXYDISULPHURYL DIFLUORIDE AND HALOGEN FLUOROSULPHATES

Peroxydisulphuryl difluoride and halogen fluorosulphates have not as yet become readily available and widely used reagents but the methods of their synthesis have been developed and described in fair detail.

The historical aspects of the early methods of synthesis have been examined in other reviews[8,9], which also present data (partly supplemented in the review of Gillespie and Morton[119] and certain publications[27,120]) concerning related compounds containing the $Br_n^+SO_3F^-$ (n = 2,3) and $I_n^+SO_3F^-$ (n = 2–7) polycations.

The fluorination of sulphur trioxide with fluorine in the presence of silver difluoride still apparently remains the most suitable procedure for the synthesis of peroxydisulphuryl difluoride[121,122]:

$$SO_3 + F_2 \xrightarrow{AgF_2;\ 150°} (OSO_2F)_2 + FOSO_2F \ .$$

The reaction has been carried out repeatedly[1–4,48,55,100,121,123]; its main disadvantage is the possibility of the formation of the potentially dangerous fluorine fluorosulphate[48,122]. By varying the conditions, the latter can be isolated as the main product[2–4]. It has been recommended that small amounts of peroxydisulphuryl difluoride be obtained[9] at 170 °C under static conditions without a catalyst[100]. It is apparently more desirable to employ for this purpose the complex salt $CsAgF_4$[124]:

$$CsAgF_4 + SO_3 \xrightarrow{25°} (OSO_2F)_2 + CsAg(OSO_2F)_3 \ .$$

The methods of synthesis of peroxydisulphuryl difluoride by the electrolysis of fluorosulphonic acid in the presence of potassium fluorosulphate *in vacuo* at −23 °C (current yield 55%)[123], by the photochemical fluorination of sulphur trioxide with fluorine[125–127], and by the fluorination of copper or nickel fluorosulphates at 200 °C[123] are evidently not of preparative interest [with the exception of the generation of $(OSO_2F)_2$ *in situ*[52–54]]. The above photochemical reactions and the interaction of oxygen fluorides with sulphur trioxide[127–129] and particularly sulphur dioxide[128,130] lead to the formation not only of fluorine fluorosulphate but also of fluorine peroxyfluorosulphate $FOOSO_2F$. Fluorine fluorosulphate and sulphuryl fluoride have been obtained by the photochemical fluorination of $F_2S_2O_6$.[131]

Photochemical[108] or thermal[5,132] fluorination of peroxydisulphuryl difluoride leads to fluorine fluorosulphate whose treatment with sulphur trioxide at 90–300 °C[3,20,55] or with ultraviolet radiation[126,127,133] regenerates peroxydisulphuryl difluoride:

$$(OSO_2F)_2 \underset{+SO_3}{\overset{+F_2}{\rightleftharpoons}} 2FOSO_2F \ .$$

The fluorination of sulphur trioxide and fluorosulphonic acid with xenon fluorides[76,134–139], chromium pentafluoride[140], uranium hexfluoride[141,142], and trifluoromethyl hypofluorite[143], the decomposition of silver fluorosulphate[67], the reactions described above[75,76], and the oxidation of fluorosulphonic acid in accordance with the scheme[144]

$$HSO_3F + O_2^+[AsF_6]^- \rightarrow (OSO_2F)_2$$

are fairly exotic methods of synthesis of peroxydisulphuryl difluoride.

Very pure fluorine fluorosulphate is formed on decomposition of tetrafluoroammonium fluorosulphate[145]:

$$NF_4OSO_2F \xrightarrow{10°} NF_3 + FOSO_2F \ .$$

Chlorine, bromine, and iodine fluorosulphates are obtained by treating peroxydisulphuryl difluoride with the corresponding halogens:

$$(OSO_2F)_2 + Hal_2 \rightarrow 2HalOSO_2F \ ; \quad Hal=Cl, Br, I \ .$$

The reaction with chlorine requires fairly severe conditions—the mixture of reactants must be heated in an autoclave for 5 days at 125 °C[7]; the process kinetics have been investigated[21]. It has been shown comparatively recently with the aid of spectra that, in solution in fluorosulphonic acid, chlorine interacts with $(OSO_2F)_2$ even at room temperature[146]. Bromine[6,12] and iodine[6,13,119] react at 25 °C and, depending on the molar ratios, it is possible to obtain either mono or tris-fluorosulphates of bromine or iodine:

$$(OSO_2F)_2 + Br_2 \rightarrow BrOSO_2F \underset{+Br_2}{\overset{+(OSO_2F)_2}{\rightleftharpoons}} Br(OSO_2F)_3 \ .$$

It follows from the foregoing that in the general case the ease of synthesis of halogen fluorosulphates is determined by the availability of peroxydisulphuryl difluoride. It is of interest to note that the interaction of iodine monochloride with peroxydisulphuryl difluoride leads to iodine trisfluorosulphate[55]:

$$ICl + (OSO_2F)_2 \rightarrow I(OSO_2F)_3 + Cl_2 \ .$$

Another pathway leading to the formation of the above reagents is based on the synthesis of chlorine fluorosulphate by the addition of chlorine monofluoride to sulphur trioxide[11,35,147,148]:

$$ClF + SO_3 \rightarrow ClOSO_2F \ .$$

The initial substances are condensed at −196 °C and are slowly heated to room temperature[11,35,148]. Ultraviolet irradiation of the chlorine fluorosulphate formed in almost quantitative yield gives rise to peroxydisulphuryl difluoride (yield 94–97%)[11,149] and treatment with bromine produces bromine fluorosulphate in 93% yield[148]:

$$ClOSO_2F \begin{cases} \xrightarrow{h\nu} (OSO_2F)_2 + Cl_2 \ ; \\ \xrightarrow{Br_2} BrOSO_2F \ . \end{cases}$$

The report of the possible formation of chlorine fluorosulphate in the reaction of nitryl chloride with the anhydride of fluorosulphonic acid[150] has not been reliably confirmed.

Thus the methods of synthesis of peroxydisulphuryl difluoride and halogen fluorosulphates are not complex and these substances can be readily obtained in any laboratory where studies with fluorine or fluorides are prosecuted.

IV. SUBSTITUTION OF HYDROGEN AND HALOGEN ATOMS AND CERTAIN FUNCTIONAL GROUPS

In view of the highly corrosive nature of peroxydisulphuryl difluoride and halogen fluorosulphates, the study of their reactions with organic compounds was begun in relation to the fully halogenated derivatives. Already at the beginning of the 1960's, it was shown that both peroxydisulphuryl difluoride[55] and bromine[6,12] and iodine[13] fluorosulphates react vigorously with carbon tetrachloride at room temperature to form phosgene:

$$CCl_4 \begin{cases} \xrightarrow{(OSO_2F)_2} COCl_2 + O(SO_2F)_2 + Cl_2 \ ; \\ \xrightarrow{2BrOSO_2F} COCl_2 + O(SO_2F)_2 + 2BrCl \ . \end{cases}$$

The above reactions can be regarded formally as direct oxidation, but one cannot rule out the possibility also of the intermediate formation and then decomposition of bis(fluorosulphato)dichloromethane. The latter hypothesis was soon confirmed and, depending on the reactant ratio, mono-, bis-, tris-, and tetrakis-(fluorosulphato)methanes were obtained at −22 °C[89]:

$$CCl_4 \xrightarrow[-BrCl]{+BrOSO_2F} CCl_n(OSO_2F)_{4-n} \ ; \quad n = 0-3$$

The second chlorine atom in carbon tetrachloride is apparently somewhat more readily substituted by the fluorosulphato-group using bromine fluorosulphate, since bis-(fluorosulphato)dichloromethane is formed together with the mono(fluorosulphato)-derivative even in the presence of a fivefold excess of carbon tetrachloride[89].

Further study of the reactivity of the above reagents showed that substitution by the fluorosulphato-group of the hydrogen atoms in alkanes, including hydrogen-containing polychlorofluoroalkanes but not bromoalkanes, and also in the OH, NH, NH_2, and similar groups is most characteristic of peroxydisulphuryl difluoride. Chlorine and bromine fluorosulphates are more effective for the substitution of halogen atoms (sometimes even fluorine atoms) by the fluorosulphato-group. The chlorinating (brominating) effect of these fluorosulphates in reactions with alkanes is not usually manifested, but this rule does not extend to functional groups and aromatic compounds.

Here one must bear in mind that the fluorosulphonic acid formed on substitution of hydrogen atoms by peroxydisulphuryl difluoride frequently tends to cause the degradation of the reaction products. On the other hand, the substitution of halogen atoms on treatment with chlorine and bromine fluorosulphates is accompanied by the liberation of the corresponding halogen or mixed halogen, which can be removed much more readily.

Next we shall consider the interactions of peroxydisulphuryl difluoride and then of the halogen fluorosulphates with various bonds and groups.

A. Aliphatic Compounds

1. Substitution of Hydrogen Atoms in Alkanes and Substituted Alkanes

Peroxydisulphuryl difluoride successfully substitutes the hydrogen atom in methylene chloride by the fluorosulphato-group even at −25 °C[77]. The attempt to substitute the second hydrogen atom was unsuccessful and only phosgene was isolated, in contrast to the interaction with methyl fluorosulphate, where bis(fluorosulphato)methane is formed smoothly and with a high yield[77]:

$$(OSO_2F)_2 \begin{cases} \xrightarrow{CH_2Cl_2} CHCl_2OSO_2F \xrightarrow{(OSO_2F)_2} COCl_2 \ ; \\ \xrightarrow{CH_3OSO_2F} CH_2(OSO_2F)_2 \ . \end{cases}$$

The reaction with methylene chloride has been carried out in trichlorofluoromethane; in the absence of the latter, vigorous explosions were observed.

Fairly unambiguous results are apparently achieved when peroxydisulphuryl difluoride is used at the instant of formation in electrolysis. Thus, by bubbling methane into the anodic compartment of the electrolytic cell containing a 1 M solution of potassium fluorosulphate in fluorosulphonic acid, it is possible to obtain selectively methyl fluorosulphate (yield 1–61%) or bis(fluorosulphato)methane (yield 6–63%), depending on the current density, temperature, and the degree of dispersion of the gas streams[52–54]:

$$CH_4 \xrightarrow[KSO_4F/HSO_4F]{(OSO_2F)_2} CH_3OSO_2F + CH_2(OSO_2F)_2 \ .$$

Analogous results have been obtained also for ethane[52,53]. The process kinetics have been investigated[54], suggesting a radical reaction mechanism.

Under these conditions, acetone is cleaved, bis(fluorosulphato)methane is formed from acetic acid, and in propionic acid the hydrogen atom in the β-position is substituted by the fluorosulphato-group, which leads to the relatively unstable β-fluorosulphatopropionic acid[52]:

$$(OSO_2F)_2 \mid KSO_3F/HSO_3F \mid \begin{cases} \xrightarrow{(CH_3)_2CO} MeOSO_2F + CH_2(OSO_2F)_2 + CH_3C(O)OSO_2F \\ \xrightarrow{C_2H_5COOH} FSO_2OCH_2CH_2COOH \xrightarrow[-HSO_3F]{-25^\circ} CH_2{=}CHCOOH \end{cases}$$

It was shown for the first time in 1972[151] that peroxydisulphuryl difluoride is effective even in relation to the primary hydrogen atoms in monohydrochloro- fluoro- and monohydroperfluoro-alkanes, which are exceptionally inert as regards radical substitution[77,151]. The reaction has been achieved with dichlorofluoro- and trifluoro-methanes, monohydroperfluoroethane[77], and monohydroperfluoropropane[151] at room temperature or with heating to 40–50 °C, for example:

$$CF_3(CF_2)_2H + (OSO_2F)_2 \rightarrow CF_3(CF_2)_2OSO_2F + HSO_3F .$$

The secondary hydrogen atoms in 2-chloro-2-hydro- and 2-hydroperfluoro-propanes are substituted even more readily (at 5–10 °C) by the fluorosulphato-group, but only hexafluoroacetone has been obtained from 2,2-dihydrohexafluoropropane[152]:

$$(CF_3)_2CH_2 + (OSO_2F)_2 \rightarrow (CF_3)_2CO .$$

The selectivity of the action of peroxydisulphuryl difluoride in relation to the hydrogen atom is indicated by the successful substitution of the latter in difluoronitromethane[153], α-hydroperfluoropropionitrile[152], ω-hydroperfluoroheptanonitrile[151], and 1-hydrotetrafluoroethylsulphur pentafluoride and 2-hydrohexafluoro-2-propylsulphur pentafluoride[154]:

$$(OSO_2F)_2 \begin{cases} \xrightarrow{O_2NCF_2H} O_2NCF_2OSO_2F \\ \xrightarrow{H(CF_2)_6CN} FSO_2O(CF_2)_6CN \\ \xrightarrow{(CF_3)_2CHSF_5} (CF_3)_2C(SF_5)OSO_2F \end{cases}$$

Treatment of 2,2,2-trifluoroethylsulphur pentafluoride with two moles of peroxydisulphuryl difluoride led only to trifluoroacetyl fluoride[154]:

$$CF_3CH_2SF_5 + (OSO_2F)_2 \rightarrow CF_3C(=O)F .$$

There is no doubt about the radical nature of the reactions considered, but no examples of the dimerisation of the hydrocarbon radicals formed as a result of the abstraction of a hydrogen atom by the fluorosulphate radical have been noted.

According to the authors[151], they obtained proof that such radicals really exist by treating a film of the vinylidene fluoride–perfluoropropene copolymer with gaseous peroxydisulphuryl difluoride at 50 °C, which makes it possible to introduce into the specimen a fairly large number of fluorosulphato-groups (the sulphur content was 7.21%). Even after the removal of these groups by treatment with aqueous pyridine, the polymer remained rigid and insoluble in acetonitrile, which is explained by its "cross-linked" nature[151].

Peroxydisulphuryl difluoride also readily interacts with the potassium salts of bromodinitromethane[153] and dinitroacetonitrile[100]. A radical-ion reaction mechanism has been put forward[100]:

$$\dot{O}SO_2F + [NCC(NO_2)_2]^- \xrightarrow{-SO_2F^-} [NCC(NO_2)_2]^{\cdot} \xrightarrow{\dot{O}SO_2F} NCC(NO_2)_2OSO_2F .$$

As mentioned above, halogen fluorosulphates are inert with respect to the CH bond at the usual temperatures but vigorously substitute halogens. The only exception is apparently fluorine fluorosulphate, which reacts with chloroform in the gas phase even at −78 °C to form dichloromethyl fluorosulphate (80%) and trichlorofluoromethane (13%)[155]:

$$FOSO_2F + CHCl_3 \rightarrow CHCl_2OSO_2F + CFCl_3 .$$

Although in the main the process is directed towards the substitution of a halogen atom, the substitution of a hydrogen atom by fluorine under these conditions cannot in all probability be accounted for by the effect of chlorine monofluoride.

Chlorine fluorosulphate has been used successfully to chlorinate nitroform and dinitroacetonitrile salts[153]:

$$ClOSO_2F + KC(NO_2)_3 \rightarrow ClC(NO_2)_3 .$$

2. Substitution of Halogen Atoms in Halogenoalkanes and Carboxylic and Sulphonic Acid Chlorides

In contrast to the reactions discussed above, peroxydisulphuryl difluoride substitutes selectively the bromine atoms in methyl bromide[77] and in 1-bromopropane[156] by the fluorosulphato-group at room or a reduced temperature:

$$(OSO_2F)_2 + CH_3Br \rightarrow CH_3OSO_2F + BrOSO_2F + Br_2 .$$

In all probability, in this case peroxydisulphuryl difluoride substitutes bromine atoms only in the first instants, since the bromine fluorosulphate formed is much more reactive in the process. The bromine evolved readily interacts with peroxydisulphuryl difluoride, generating bromine fluorosulphate. These factors explain both the selectivity of the above reactions and the ease of substitution of the bromine atoms in other bromine-containing compounds.

Thus peroxydisulphuryl difluoride successfully substitutes the bromine atoms in bromotrifluoro-[157], dibromodifluoro-, tribromofluoro-, and tetrabromo-methanes[158]. In the last two examples carbonyl compounds are formed, including the relatively unstable carbonyl bisfluorosulphate[158]:

$$(OSO_2F)_2 \begin{cases} \xrightarrow{CBr_3F} FC(OSO_2F)_3 + FC(O)OSO_2F \\ \xrightarrow{CBr_4} OC(OSO_2F)_2 + CO_2 + S_2O_5F_2 \end{cases}$$

The reaction has also been extended to bromotris(difluoroamino)methane[159], 3-bromoheptafluoro-2-butanone[160], and trifluoroacetyl bromide[161]:

$$(OSO_2F)_2 \begin{cases} \xrightarrow{(F_2N)_3CBr} (F_2N)_3COSO_2F \\ \xrightarrow{CF_3C(O)CFBrCF_3} CF_3C(O)CF(CF_3)OSO_2F \\ \xrightarrow{CF_3C(O)Br} CF_3C(O)OSO_2F + CF_3OSO_2F \end{cases}$$

Chlorine atoms are substituted by peroxydisulphuryl difluoride with much more difficulty. As mentioned above, the only compounds which react under comparatively mild conditions are carbon tetrachloride (phosgene is formed at 25 °C[55]) and trichlorofluoromethane (20 days, 40 °C[142]). The chlorine atom in chlorotrifluoromethane could be substituted by the fluorosulphato-group only by heating the reactants at 150 °C and a pressure of 304×10^5 N m^{-2} for five days[157]. It has been shown spectroscopically[146] that 1,1,2-trichlorotrifluoroethane also reacts at 150 °C and only in the presence of fluorosulphonic acid. Peroxydisulphuryl difluoride substitutes the difluoroamino-group in difluoroaminocarbonyl chloride[162]:

$$(OSO_2F)_2 \begin{cases} \xrightarrow{CCl_3F} CCl_2FOSO_2F \\ \xrightarrow[HSO_3F]{CClF_2CCl_2F} CClF_2CClFOSO_2F \\ \xrightarrow{ClC(O)NF_2} ClC(O)OSO_2F + F_2NOSO_2F \end{cases}$$

The single example of the substitution of the chlorine atom in chloroform by fluorine fluorosulphate was described above[155].

Chlorine fluorosulphate has been used successfully even at temperatures below 0 °C to synthesise chloromethyl and chloroethyl fluorosulphates from methylene chloride and dichloroethane[86,163]. Treatment of *sym*-tetrachloroethane with two moles of chlorine fluorosulphate leads to a mixture of 1,1- and 1,2-bis(fluorosulphato)dichloroethanes in proportions of 3:1[164]:

$$ClOSO_2F \xrightarrow{ClCH_2CH_2Cl} ClCH_2CH_2OSO_2F \ ;$$
$$ClOSO_2F \xrightarrow{Cl_2CHCHCl_2} Cl_2CHCH(OSO_2F)_2 + FSO_2OCHClCHClOSO_2F \ .$$

At −40 °C chlorine fluorosulphate substitutes selectively the chlorine atom in alkyl monochloroacetates by the fluorosulphato-group[86,163]:

$$ClOSO_2F + ClCH_2COOR \rightarrow FSO_2OCH_2COOR \ .$$

The esters of fluorosulphatoacetic acid formed are relatively unstable at room temperature but, by virtue of their high reactivity, can be used *in situ* in further syntheses[86].

In the presence of fluorosulphonic acid, chlorine fluorosulphate substitutes vigorously the first chlorine atom in 1,1,2-trichlorotrifluoroethane by the fluorosulphato-group even at room temperature (with a small exothermic heat change)[165]:

$$CClF_2CCl_2F + ClOSO_2F \rightarrow CClF_2CClFOSO_2F + Cl_2 \ .$$

This indicates a much greater effectiveness of chlorine fluorosulphate in relation to the C–Hal bonds compared with peroxydisulphuryl difluoride, since the latter undergoes an analogous reaction only at 150 °C.[146]

Dichlorodifluoromethane and *sym*-tetrachlorodifluoroethane react analogously; at 70–85 °C it is possible to substitute two or three chlorine atoms in these compounds, while at 120 °C all the chlorine atoms and one fluorine atom are substituted in *sym*-tetrachlorodifluoroethane[146,165]:

$$ClOSO_2F \xrightarrow{CClF_2CCl_2F,\ 85°} CClF_2CF(OSO_2F)_2 \ ;$$
$$ClOSO_2F \xrightarrow{CCl_2FCCl_2F,\ 85°} FSO_2OCClFCF(OSO_2F)_2 \xrightarrow[120°]{ClOSO_2F} (FSO_2O)_2CFC(O)OSO_2F \ .$$

It must be emphasised that the substitution takes place smoothly only in the presence of fluorosulphonic acid, the employment of which as the solvent tends to reduce the reaction temperature[146,165].

The role of fluorosulphonic acid† apparently reduces to enhancing the polarisation of the chlorine atom in chlorine fluorosulphate. A study of ^{19}F NMR spectra showed that, after mixing in equimolar proportions, the individual signals of chlorine fluorosulphate (−112.2 p.p.m. relative to CF_3COOH) and fluorosulphonic acid (−119 p.p.m.) disappear and a single signal (broadened singlet) appears at −116.1 p.p.m.[86] An equimolar mixture of chlorine fluorosulphate and fluorosulphonic acid can be separated into its components almost quantitatively by fractionation[86]. It may be that the halogen is substituted via a one-electron transfer mechanism[86]:

$$Cl{-}O{-}SO_2F + H^+ + SO_3F^- \rightarrow Cl{-}\overset{+}{O}(H){-}SO_2F + SO_3F^- \ ;$$

$$R{:}\rightarrow Cl + Cl \overset{\delta+}{:} O(H){-}SO_2F \rightarrow \dot{R} + \cdot\overset{+}{O}(H){-}SO_2F + Cl_2$$

$$ROSO_2F \xleftarrow[-HSO_3F]{SO_3F^-} R{-}\overset{+}{O}(H){-}SO_2F \ .$$

Subsequently it was shown that the reactivity of chlorine fluorosulphate increases significantly also after the addition of bromine[166,167]. This involves the substitution of the primary chlorine atom in chloropentafluoroethane and 1,2-dichlorohexafluoropropane sulphato-group, while in 1,2-dichlorotetrafluoroethane one or both chlorine atoms are substituted depending on the conditions[167]:

$$ClOSO_2F + ClCF_2CF_2Cl \xrightarrow[130°,\ 5\ days]{Br_2} ClCF_2CF_2OSO_2F \xrightarrow[140°,\ 14\ days]{ClOSO_2F,\ Br_2} FSO_2OCF_2CF_2OSO_2F \ .$$

Without the addition of bromine, the chlorine atoms in these compounds are not substituted either by peroxydisulphuryl difluoride or chlorine fluorosulphate[166,167]. The authors naturally explained the effectiveness of bromine by the formation of bromine fluorosulphate *in situ* (cf. Schack and Wilson[148]) and its subsequent regeneration during the reaction.

The chlorine atoms in 2-chlorotetrafluoroethyltrifluoromethyl ether[166] and, with catalysis by fluorosulphonic acid, in chlorocarbonyl fluorosulphate[146] and C_2–C_9 perfluoroacyl chlorides[86,168] have also been substituted by the fluorosulphato-group following the addition of bromine:

$$ClOSO_2F \xrightarrow[110°]{CF_3OCF_2CF_2Cl,\ Br_2} CF_3OCF_2CF_2OSO_2F + Cl_2 \ ;$$
$$ClOSO_2F \xrightarrow[30°]{ClC(O)OSO_2F,\ HSO_3F} S_2O_5F_2 + CO_2 + Cl_2 \ ;$$
$$ClOSO_2F \xrightarrow[20–60°]{CF_3C(O)Cl,\ HSO_3F} CF_3C(O)OSO_2F + Cl_2 \ .$$

The fluorides of perfluorocarboxylic acids are much less reactive and the mixed anhydride of perfluoropelargonic and fluorosulphonic acid has been obtained in only a low yield by heating the corresponding acid fluoride with chlorine fluorosulphate (28 h at 80 °C), the reaction being catalysed by fluorosulphonic acid[86].

As was to be expected, the bromine atom in bromoperfluoroalkanes reacts with chlorine fluorosulphate more readily than the chlorine atom. The primary bromine atoms in perfluorinated bromo- and 1,2-dibromoethanes and also in 1,2- and 1,3-dibromopropanes are substituted at 25 °C (after 21–24 days); at 50–65 °C both primary bromine atoms of dibromoperfluoroalkanes react[167]:

$$ClOSO_2F \xrightarrow[65°,\ 2\ days]{BrCF_2CF_2Br,} \underset{64\%}{FSO_2OCF_2CF_2OSO_2F} + \underset{31\%}{ClCF_2CF_2OSO_2F} \ ;$$
$$ClOSO_2F \xrightarrow[50°,\ 11\ days]{Br(CF_2)_3Br,} \underset{57\%}{FSO_2O(CF_2)_3OSO_2F} + \underset{10\%}{Cl(CF_2)_3OSO_2F} \ .$$

The secondary bromine atoms in 1,2-dibromo- and 2-bromoperfluoro-propanes are not substituted under these conditions[167].

As mentioned above, bromine fluorosulphate substitutes by perfluorosulphato-groups all the chlorine atoms in carbon tetrachloride[89]. Mixtures of mono- and bis-(fluorosulphato)-derivatives are formed from trichlorofluoromethane at −55 °C and from oxalyl chloride at −2 °C.[89] Chlorocarbonyl

† Chlorosulphonic acid interacts with chlorine fluorosulphate and is converted into fluorosulphonic acid[86].

fluorosulphate has been obtained by the reaction of bromine fluorosulphate with a sevenfold excess of phosgene at −65 °C, but only the difluoroamino-group is substituted in difluoroaminocarbonyl chloride[162]:

$$BrOSO_2F \xrightarrow{CCl_3F} CCl_2FOSO_2F + CClF(OSO_2F)_2 \ ;$$
$$BrOSO_2F \xrightarrow{ClC(O)C(O)Cl} ClC(O)C(O)OSO_2F + FSO_2OC(O)C(O)OSO_2F \ ;$$
$$BrOSO_2F \xrightarrow{ClC(O)NF_2} ClC(O)OSO_2F + N_2F_4 \ .$$

The above facts clearly show that bromine fluorosulphate is more reactive towards the C−Cl bond than not only peroxydisulphuryl difluoride but also chlorine fluorosulphate.

In conclusion, one should note that bromine fluorosulphate has been used successfully to substitute the chlorine atoms in methanesulphonyl[169] and trifluoromethanesulphonyl chlorides[170] by the fluorosulphato-group. Methanesulphonyl fluorosulphate proved to be metastable; at 80 °C it decomposes into methanesulphonyl fluoride and sulphur trioxide[169]:

$$BrOSO_2F \xrightarrow{CH_3SO_2Cl} CH_3SO_2OSO_2F \xrightarrow{80^\circ} CH_3SO_2F + SO_3 \ ;$$
$$BrOSO_2F \xrightarrow{CF_3SO_2Cl} CF_3SO_2OSO_2F \ .$$

3. *Reactions with Alcohols and Carboxylic Acids*

The reactions of peroxydisulphuryl difluoride with alcohols have attracted the attention of investigators as possible ways of synthesising organic peroxides and mixed peroxides (of the type [illegible]), the potential initiators of radical

The yield of fluorosulphuryl trifluoromethyl peroxide does not exceed 50%, since in the presence of potassium and particularly caesium fluoride it can decompose approximately under the conditions of its synthesis[100]:

$$CsF + CF_3OOSO_2F \xrightarrow{25^\circ,\ 2\ h} CsOCF_3 + SO_2F_2 + O_2 \ .$$

Fluorosulphuryl perfluoroisopropyl peroxide decomposes during storage in glass vessels at room temperature[100], while fluorosulphonyl perfluoro-t-butyl peroxide decomposes only on heating to 100 °C[173]:

$$(CF_3)_3COOSO_2F \rightarrow CF_3OSO_2F + (CF_3)_2CO \ .$$

The above facts show that the radical-ion mechanism proposed[100] for the reactions of peroxydisulphuryl difluoride with anions is apparently not fully justified at least for perfluoroalkyl alkoxides. This can be seen particularly clearly in relation to perfluoro-t-alkyl alcohols and the corresponding alkoxides. Not even traces of the mixed peroxide or the corresponding perfluoro-t-alkoxy-radicals could be detected in reactions with alcohols[77] as a consequence of the ready decomposition of the perfluoro-t-alkoxy-radical via the mechanism

$$C_2F_5C(CF_3)_2OH + \dot{O}SO_2F \rightarrow C_2F_5C(CF_3)_2\dot{O} + HSO_3F \ ;$$
$$C_2F_5C(CF_3)_2\dot{O} \rightarrow (CF_3)_2CO + \dot{C}F_5 \ ;$$
$$C_2F_5C(CF_3)_2\dot{O} \rightarrow C_2F_5C(O)CF_3 + \dot{C}F_3 \ ;$$
$$\dot{C}F_5 + (OSO_2F)_2 \rightarrow C_2F_5OSO_2F + \dot{O}SO_2F \ ;$$
$$\dot{C}F_3 + (OSO_2F)_2 \rightarrow CF_3OSO_2F + \dot{O}SO_2F \ .$$

All the final compounds presented in the above scheme have been identified; perfluoroethyl fluorosulphate and trifluoro-

Bearing in mind that only trifluoromethyl fluorosulphate is formed also in the reaction of peroxydisulphuryl difluoride with sodium trifluoroacetate[100], it is apparently hardly possible to expect an acceptable stability of fluorosulphuryl trifluoroacetyl peroxide even if the latter is formed under these conditions.

The reactions of chlorine and bromine fluorosulphates with alcohols and carboxylic acids began to be investigated only recently. The interaction of chlorine fluorosulphate with polyfluoroalcohols in dichlorodifluoromethane or 1,1,2-trichlorotrifluoroethane at −30°– −15 °C leads to the corresponding hypochlorites[175]:

$$ClOSO_2F + RCH_2OH \rightarrow RCH_2OCl + HSO_3F \ ;$$
$$R = H(CF_2)_n,\ O_2NCF_2;\ n = 2, 4, 6 \ .$$

The yield of hypochlorites does not exceed 40%, apparently as a consequence of decomposition under the influence of fluorosulphonic acid and the acid sulphates formed from the corresponding alcohols as side products. In the absence of water and acid impurities, such hypochlorites are fairly stable, particularly higher hypochlorites[175]. However, treatment of 2,2-dinitropropanediol with chlorine fluorosulphate led to the isolation of only dichlorodinitromethane in a low yield[153].

It has been noted[176] that chlorine fluorosulphate chlorinates trifluoro- and chlorodifluoro-acetic acids as well as their salts more effectively than chlorine monofluoride at temperatures between −78° and −45 °C. The hypochlorites of these acids are volatile and tend to decompose with detonation even at a pressure of the pure substance in a vacuum system of ~ 40 mmHg; they have been fairly fully characterised[176] and have been used successfully *in situ* for the synthesis (at −78 °C) of chloroperfluoro-esters[176,177] and perfluoroalkyl halides[167,178]. Perfluorodicarboxylic acids have also been introduced into the latter reaction[167,178]. Bromine fluorosulphate reacts similarly[167,178]:

$$ClOSO_2F \xrightarrow{CF_3COOH} CF_3CC(O)OCl \begin{cases} \xrightarrow{CF_2=CFCF_3} CF_3COOCF_2CClFCF_3 \ ; \\ \xrightarrow[25°]{} CF_3Cl \ ; \end{cases}$$
$$ClOSO_2F + CF_2(CF_2COOH)_2 \rightarrow Cl(CF_2)_3Cl + Cl(CF_2)_2COF + Cl(CF_2)_3OSO_2F \ ;$$
$$BrOSO_2F + C_2F_5COONa \rightarrow C_2F_5Br \ .$$

4. *Reactions with Peroxides, Ethers, Carboxylic Acid Anhydrides, and Certain Other Compounds*

Peroxydisulphuryl difluoride is inert with respect to perfluoroalkyl ethers up to 140 °C[166] and does not interact with perfluoroepoxypropane[151].

Bis(trifluoromethyl) peroxide reacts with peroxydisulphuryl difluoride only at fairly high temperatures (up to 240 °C)[179, 180], forming the corresponding mixed peroxide; the process kinetics have been studied in the range 185–230 °C[179]. The same peroxide has been obtained from bis(trifluoromethyl) trioxide in a yield of 87% at a temperature as low as 75 °C[181]:

$$(OSO_2F)_2 \begin{cases} \xrightarrow{CF_3OOCF_3} CF_3OOSO_2F \ ; \\ \xrightarrow{CF_3OOOCF_3} CF_3OOSO_2F \ . \end{cases}$$

The reaction involving difluorophosphoryl trifluoromethyl peroxide CF_3OOPOF_2 at room temperature was found to entail only a slow decomposition to COF_2, POF_3, etc.[182]

The anhydrides of perfluorinated mono- and di-carboxylic acids react with peroxydisulphuryl difluoride slowly at 25 °C and rapidly at 100 °C, forming mixed anhydrides of fluorosulphonic and carboxylic acids and also perfluoroalkyl fluorosulphates, which, together with carbon dioxide, are apparently the products of the decomposition of the mixed peroxides of fluorosulphonic and carboxylic acids[183]:

$$(OSO_2F)_2 \begin{cases} \xrightarrow{(CF_3CO)_2O} CF_3COOSO_2F + CF_3OSO_2F + CO_2 \ ; \\ \xrightarrow{OCOCF_2CF_2CO} FSO_2OCF_2CF_2COOSO_2F + CO_2 \ . \end{cases}$$

In another study[184] only fluoroalkyl fluorosulphates were isolated in an analogous reaction; in this case difluoromethyl fluorosulphate was obtained from difluoroacetic acid anhydride with retention of the hydrogen atom.

Chlorine fluorosulphate and trifluoroacetic anhydride give rise to a mixed anhydride (yield 80–85%) and chlorotrifluoromethane[167]:

$$ClOSO_2F + (CF_3CO)_2O \rightarrow CF_3COOSO_2F + CClF_3 + CO_2 \ .$$

Other reactions accompanied by the rupture of carbon–carbon bonds include the interaction between peroxydisulphuryl difluoride and oxalyl chloride[162] and also the substitution of the cyano-group in ethyl cyanodinitroacetate by a chlorine atom on treatment with chlorine fluorosulphate at temperatures between −20° and −30 °C[153]:

$$(OSO_2F)_2 + ClC(O)C(O)Cl \rightarrow ClCOOSO_2F \ ;$$
$$ClOSO_2F + NCC(NO_2)_2COOC_2H_5 \rightarrow ClC(NO_2)_2COOC_2H_5 \ .$$

Dichlorodinitromethane has been obtained in a low yield from ethyl chlorodinitroacetate on treatment with $ClOSO_2F$.[153]

In addition it has been shown that peroxydisulphuryl difluoride readily substitutes the methyl groups in organotin compounds[185]:

$$(OSO_2F)_2 + (CH_3)_4Sn \rightarrow (CH_3)_2Sn(OSO_2F)_2 + (CH_3)_3SnOSO_2F \ .$$

5. *Substitution of Hydrogen or Halogen Atoms in Amines, Imines, Halogenoimines, and Carboxylic Acid Amides*

Peroxydisulphuryl difluoride smoothly substitutes the hydrogen atom in bis(trifluoromethyl)amine by the fluorosulphato-group[77]. Hexafluoroacetone imine reacts in a more complex manner; together with substitution, the imine undergoes oxidative dimerisation and peroxydisulphuryl difluoride apparently adds to the resulting diazadiene[77]:

$$(OSO_2F)_2 \begin{cases} \xrightarrow{(CF_3)_2NH} (CF_3)_2NOSO_2F \ ; \\ \xrightarrow{(CF_3)_2C=NH} (CF_3)_2C(NOSO_2F)N=C(CF_3)_2 + \\ \quad + FSO_2OC(CF_3)_2N=NC(CF_3)_2OSO_2F \ . \end{cases}$$

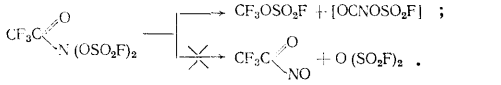
The reactions take place at temperatures as low as 0–25 °C and are clearly of a radical type. In contrast to this, the sodium salt of fluorosulphurylcarbamoyl fluoride reacts slowly with peroxydisulphuryl difluoride only at 70 °C and the yield of the final product is only 17%[186]:

$$(OSO_2F)_2 + Na^+[FSO_2NCOF]^- \rightarrow FSO_2N(OSO_2F)COF \ .$$

The reaction of peroxydisulphuryl difluoride with perfluorocarboxylic acid amides is extremely unusual[187]. In the presence of $(OSO_2F)_2$ a suspension of the initial amide in 1,1,2-trichlorotrifluoroethane dissolves fully at temperatures as low as −30– −25 °C, but fluorosulphonic acid precipitates from solution only after several hours, usually after the temperature of the mixture approaches room temperature[187]:

$$RC(O)NH_2 + 2(OSO_2F)_2 \rightarrow RC(O)N(OSO_2F)_2 + 2HSO_3F \ ;$$
$$R = CF_3,\ C_3F_7,\ C_6F_{13} \ .$$

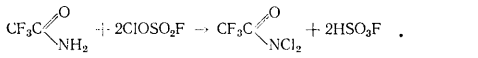
Although the amount of the fluorosulphonic acid formed is consistent with stoichiometry, *N*,*N*-bis(fluorosulphato)amides have been obtained in yields less than 25%, because, under the conditions of the synthesis and on isolation, they decompose into perfluoroalkyl fluorosulphate and possibly fluorosulphatoisocyanate. The expected perfluoroacylnitroso-compounds and pyrosulphuryl difluorides could not be isolated in this reaction[187]:



Chlorine and bromine fluorosulphates have been used successfully even at reduced temperatures to substitute fluorine[187] and chlorine[77] atoms respectively in hexafluoroacetone *N*-halogenoimines by the fluorosulphato-group, for example:

$$ClOSO_2F + (CF_3)_2C{=}NF \rightarrow (CF_3)_2C{=}NOSO_2F \ .$$

Also at reduced temperatures, chlorine fluorosulphate vigorously substitutes the hydrogen atoms in the amides of trifluoroacetic and heptafluorobutyric acids by chlorine:



However, the yields of *N*,*N*-dichloroamides are low, possibly as a consequence of the formation of fluorosulphonic acid[163,189].

B. Aromatic Compounds

As early as 1971, Merrill reported[156] at the VIth International Symposium on the Chemistry of Fluorine that a hydrogen atom in benzene can be substituted by the fluorosulphato-group on treatment with peroxydisulphuryl difluoride in trichlorofluoromethane at −45 °C:

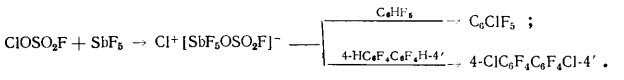
$$(OSO_2F)_2 + C_6H_6 \rightarrow C_6H_5OSO_2F \ .$$

Toluene, which is substituted in the ring, reacts even more vigorously, but the position of the fluorosulphato-group relative to the methyl group has not been established[77].

Chlorine fluorosulphate proved to be a unique chlorinating agent for benzene. At a temperature as low as −100 °C and for the molar ratio $ClOSO_2F:C_6H_6 = 1:1.5$, hexachlorobenzene was obtained unexpectedly in a yield of ~ 80%[190]:

$$ClOSO_2F + C_6H_6 \rightarrow C_6Cl_6 \ .$$

The complex of chlorine fluorosulphate with antimony pentafluoride has been used successfully to chlorinate pentafluorobenzene and octafluorobiphenyl[191]:

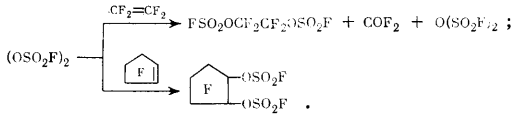


Iodine fluorosulphate interacts vigorously with pyridine, but the yellow solid formed decomposes rapidly and is converted into a brown oil, whose structure has not been established[13].

V. ADDITION OF PEROXYDISULPHURYL DIFLUORIDE AND HALOGEN FLUOROSULPHATES TO UNSATURATED COMPOUNDS

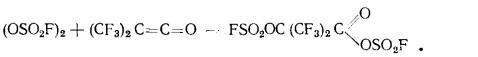
1. Addition to Carbon–Carbon Multiple Bonds

The addition of peroxydisulphuryl difluoride to carbon–carbon double bonds was achieved for the first time in 1961 in relation to tetrafluoroethylene and perfluorocyclopentene[55]:



The olefin, diluted with nitrogen, was added slowly *in vacuo* (~ 125 mmHg) to peroxydisulphuryl difluoride. A slight increase of the rate of supply of tetrafluoroethylene led to a rapid increase of temperature and the formation of a brown gas in the reactor, which, according to the authors[55], might have indicated the appearance of free radicals. At the same time the appearance of a solid white powder in the gas connections and on the walls of the vessel was observed; up to 5% of tetrafluoroethylene was oxidised to carbonyl fluoride[55].

Subsequently the corresponding vicinal bis(fluorosulphato)-polyfluoroalkanes were obtained from chlorotrifluoroethylene[157], perfluoropropene[151,192], perfluorobutene[157,192,193], perfluorocyclobutene[192], 1,2-dichlorohexafluorocyclopentene[151], and perfluoro-derivatives of pent-2-ene and hex-2-enes[193]. Peroxydisulphuryl difluoride adds just as readily to trichloroethylene (the hydrogen atom is not then substituted)[156] and also to bis(trifluoromethyl)keten[194]:



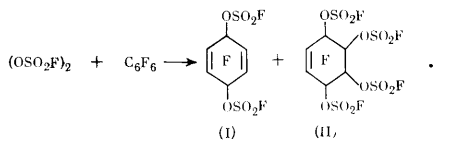
The above reactions were as a rule carried out at room temperature and, more rarely, with slight heating§. The radical nature of these reactions is confirmed not only by the clear signs of the polymerisation of tetrafluoroethylene[55] but also by the fact that a mixture of perfluoro-derivatives of bis(fluorosulphato)propane and bis(fluorosulphato)hexanes is formed from hexafluoropropene (in yields of 63 and 22% respectively)[151]:



Under very mild conditions (at −78 °C), peroxydisulphuryl difluoride adds to vinyl chloride and fluoride, but the compounds formed decompose on heating to room temperature[157].

The addition of peroxydisulphuryl difluoride to alkenes takes place non-stereospecifically. A mixture of *cis*- and *trans*-isomers is formed from 1,2-dichlorohexafluorocyclopentene[151], while acyclic internal C_4–C_6 *trans*-perfluoroolefins give rise to a mixture of *erythro*- and *threo*-isomers[193].

The exceptionally high reactivity of peroxydisulphuryl difluoride was manifested in its interaction with perfluorobenzene. It was found that the latter behaves in this instance as an unsaturated compound and readily combines with fluorosulphato-groups at 0–5 °C[195]:



One must note that the reaction is preferably carried out in an inert solvent, for example, in 1,1,2-trichlorotrifluoroethane, since in its absence there is an abrupt increase of temperature and pressure, which can lead to the ejection of the reaction mass[195]. At the beginning 1,4-addition of

§ The authors[151] note that, on heating a mixture of 1,2-dichlorohexafluorocyclopentene and peroxydisulphuryl difluoride from −30° to ~ 15 °C, a vigorous uncontrollable reaction is observed; satisfactory yields have been obtained only by adding the peroxide to the olefin heated to 50 °C.

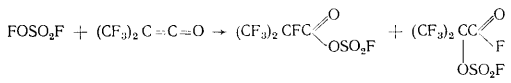
peroxydisulphuryl difluoride to perfluorobenzene takes place preferentially, but, even when an excess of perfluorobenzene by a factor of 1,5 together with 1,4-bis(fluorosulphato)perfluorocyclohexa-2,5-diene (I) is used, up to 10% of 1,2,3,4-tetrakis(fluorosulphato)perfluorocyclohex-5-ene (II) is formed. Possibly this can be explained by the fact that either the diene (I) is more reactive than hexafluorobenzene or by the partial 1,2-addition of peroxydisulphuryl difluoride, the conjugated diene being naturally more reactive. The hexene (II) as well as hexakis(fluorosulphato)perfluorohexane¶ can be obtained in quantitative yields using the corresponding molar amounts of the reactants, but the reaction with the third mole of peroxydisulphuryl difluoride is usually completed only after 5–6 h at 20–25 °C[195]:

$$3\,(OSO_2F)_2 + C_6F_6 \rightarrow C_6F_6(OSO_2F)_6 \ .$$

Halogen fluorosulphates add to alkenes still more vigorously than peroxydisulphuryl difluoride. The reagents diluted with nitrogen were initially combined *in vacuo* at room temperature. As a result, the corresponding fluorosulphonate esters were obtained from tetrafluoroethylene in a high yield[7]:

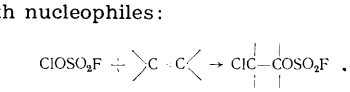
$$HalOSO_2F + CF_2{=}CF_2 \rightarrow HalCF_2CF_2OSO_2F \ ;$$
$$Hal{=}F,\ Cl,\ Br \ .$$

Fluorine fluorosulphate adds just as readily to tetrachloroethylene and perfluorocyclopentene[7], trichloroethylene (at −78 °C)[155], and a mixture of the *cis*- and *trans*-isomers of perfluorobut-2-ene[161]. A mixture of regioisomers has been obtained from bis(trifluoromethyl)keten in yields of 87 and 13%[194]:



However, β-fluoroethyl fluorosulphate could not be isolated from the products of the reaction of fluorine fluorosulphate and ethylene (*in vacuo* at −50 °C)[7].

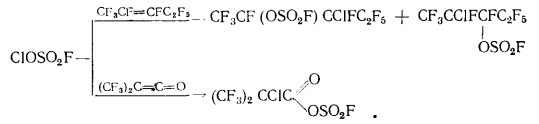
Apart from tetrafluoroethylene, fluoro- and chlorofluoroolefins are absorbed, as reported for the first time in 1973[196,197], by liquid chlorine fluorosulphate with a large exothermic effect at a temperature as low as 0–20 °C. On the basis of qualitative observations, the authors[196,197] reached the preliminary conclusion that the reactivity of the above olefins in the reaction with liquid chlorine fluorosulphate increases in the sequence which corresponds to their interaction with nucleophiles:



Continuation of research on these lines showed that chlorine fluorosulphate adds vigorously to trichloroethylene at temperatures between −50° and −55 °C[164], to tetrachloroethylene at −20 °C[78], and to trifluoroethylene, chlorotrifluoroethylene, perfluoropropene†, bis(trifluoromethyl)-keten[199], and *trans*-perfluorohex-2-ene[200] at temperatures as low as −65°–−70 °C, i.e. at the limit corresponding to the freezing of the mixture of reactants. However, it has been suggested[197] that the slow reaction of liquid chlorine fluorosulphate with tetrafluoroethylene is probably due to the poor solubility of the latter, since tetrafluoroethylene reacts with solutions of chlorine fluorosulphate in dichlorodifluoromethane or in 2-chlorotetrafluoroethyl fluorosulphate at a very high rate and a temperature as low as −70 °C[199]. Heating to 50–60 °C is required only for addition to 1,1-bis(fluorosulphonyl)difluoroethylene[201]:

$$ClOSO_2F + (FSO_2)\,C{=}CF_2 \rightarrow (FSO_2)_2\,CClCF_2OSO_2F \ .$$

Mixtures of regioisomers have been obtained in reactions with trifluoroethylene[199], chlorotrifluoroethylene[197,198], and *trans*-perfluoropent-2-ene[200], which can be explained in all probability by competition between the electronic and steric factors (the relative yields depend very little on the process temperature[199]). However, in contrast to the reaction with fluorine fluorosulphate[194], only one isomer is obtained from bis(trifluoromethyl)keten[199]:



In the presence of a perfluorocarboxylic acid, the interaction of chlorine fluorosulphate with perfluoropropene leads to a mixture of 2-chloroperfluoropropyl fluorosulphate and 2-chloroperfluoropropyl perfluorocarboxylate, the yield of the latter increasing with increasing excess of the acid[199]:

$$ClOSO_2F + CF_3CF{=}CF_2 \xrightarrow{C_3F_7COOH} CF_3CClFCF_2OSO_2F + C_3F_7COOCF_2CClFCF_3 \ .$$

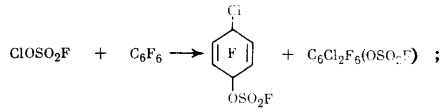
In the light of recent data[176,177], one cannot rule out the possibility that the formation of the ester is preceded by a stage involving the formation of the acyl hypochlorite.

At −100 °C chlorine fluorosulphate adds readily to ethylene[199] and at −30– −25 °C to acetylene, whose triple bond is fully saturated[164,189]:

$$ClOSO_2F + CH{\equiv}CH \rightarrow CHCl_2CH\,(OSO_2F)_2 + FSO_2OCHClCHClOSO_2F \ .$$

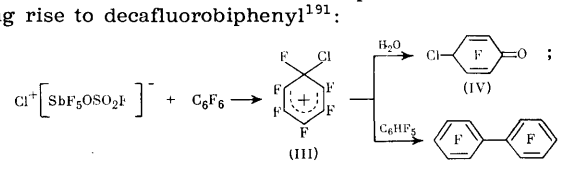
Symmetrical bis(fluorosulphato)dichloroethane was then obtained only in the form of an admixture (5–7%)[164].

Like peroxydisulphuryl difluoride but at an even lower temperature (between −20° and −25 °C), chlorine fluorosulphate reacts with perfluorobenzene[195]. The interaction with one mole also results in the formation of a 1,4-substituted cyclohexadiene containing an admixture (up to 10%) of a tetrasubstituted cyclohexene#. The latter as well as a hexasubstituted cyclohexane can be isolated in almost quantitative yields[195]:



$$3ClOSO_2F + C_6F_6 \longrightarrow C_6Cl_3F_6(OSO_2F)_3 \ .$$

The benzenium ion (III) can be generated by treating hexafluorobenzene with the complex of chlorine fluorosulphate and antimony pentafluoride, the hydrolysis of the ion yielding the ketone (IV) and its reaction with pentafluorobenzene giving rise to decafluorobiphenyl[191]:



¶ A mixture of stereoisomers is formed in both cases[195].

† The reaction has been carried out successfully also at −45 °C.[198]

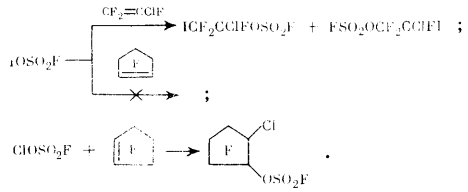
A complex mixture of regio- and stereo-isomers[195].

As already mentioned, bromine fluorosulphate adds exceptionally readily to tetrafluoroethylene[7] and also to hexafluoropropene[198] and perfluorobut-2-ene[160]. As in the case of chlorine fluorosulphate, the reaction with chlorotrifluoroethylene results in the formation of two regioisomers[160]. The product of the addition of bromine fluorosulphate to vinyl fluoride proved to be unstable[160].

The possibility of the addition of iodine fluorosulphate to alkenes was reported almost simultaneously by Fokin in Venice[189,202] and by Schack and Christe in San Francisco[203]. Iodine fluorosulphate is much less reactive in these reactions than fluorine, chlorine, or bromine fluorosulphates and interacts only slowly at 20–40 °C with tetrafluoroethylene, hexafluoropropene[202–204], partly fluorinated propenes, and vinylidene fluoride[205]. 2-Iodoperfluoroisobutyl fluorosulphate has been obtained in a yield less than 30% only after keeping the mixture of reactants at 20–25 °C for three weeks, but iodine fluorosulphate adds relatively easily to bis(trifluoromethyl)keten[205]:

$$IOSO_2F \left\{ \begin{array}{l} \xrightarrow{(CF_3)_2C=CF_2} (CF_3)_2CICF_2OSO_2F \ ; \\ \xrightarrow{(CF_3)_2C=C=O} (CF_3)_2CIC(O)OSO_2F \ . \end{array} \right.$$

Mixtures of regioisomers have been obtained from chlorotrifluoroethylene[203,205] and trifluoroethylene[205]. Iodine fluorosulphate does not add to perfluorocyclobutene[205] and perfluorocyclopentene[203], but chlorine fluorosulphate reacts readily with perfluorocyclopentene[203]:



2. Addition to Nitrogen–Carbon Multiple Bonds

Peroxydisulphuryl difluoride does not interact with perfluoro-2-azapropene[9] and perfluoro-2-azabut-1-ene[206]. The addition to pentafluoroguanidine is accompanied by the substitution of the difluoroamino-groups by fluorosulphato-groups[207,208], while the addition to fluorosulphonyl isocyanate under the influence of ultraviolet radiation is accompanied by the elimination of sulphur trioxide[209]:

$$(OSO_2F)_2 \left\{ \begin{array}{l} \xrightarrow{(F_2N)_2C=NF} (FSO_2O)_3CNFOSO_2F \ ; \\ \xrightarrow[FSO_2NCO,\,h\nu]{} FSO_2N(OSO_2F)C(=O)F + SO_3 \ . \end{array} \right.$$

Peroxydisulphuryl difluoride reacts under mild conditions with diazadienes—conjugated[77] and even those where the double bonds are separated by a sulphur atom[210]:

$$(OSO_2F)_2 \left\{ \begin{array}{l} \xrightarrow{(CF_3)_2C=NN=C(CF_3)_2} FSO_2OC(CF_3)_2N=NC(CF_3)_2OSO_2F \ ; \\ \xrightarrow{(CF_3)_2C=NSN=C(CF_3)_2} FSO_2OC(CF_3)_2N=S=NC(CF_3)_2OSO_2F \ . \end{array} \right.$$

The interaction of peroxydisulphuryl difluoride with chlorocyanogen and trifluoroacetonitrile at 80 °C is completed by the complete saturation of the triple bond, which the authors[211] explain by the intermediate formation of the nitrene (V), for example, via the mechanism

$$CF_3C\equiv N + \dot{O}SO_2F \rightarrow FSO_2OC(CF_3)=\dot{N} \ ;$$
$$FSO_2OC(CF_3)=\dot{N} + \dot{O}SO_2F \rightarrow \underset{(V)}{(FSO_2O)_2C(CF_3)\ddot{N}} \ ;$$
$$(FSO_2O)_2C(CF_3)\ddot{N} + (OSO_2F)_2 \rightarrow (FSO_2O)_2C(CF_3)N(OSO_2F)_2 \ .$$

In contrast to peroxydisulphuryl difluoride, chlorine and bromine fluorosulphates add exceptionally readily to perfluoro-2-azabut-1-ene[206] and pentafluoroguanidine[207,212]:

$$ClOSO_2F \left\{ \begin{array}{l} \xrightarrow{C_2F_5N=CF_2} C_2F_5NClCF_2OSO_2F \ ; \\ \xrightarrow{FN=C(NF_2)_2} FNClC(NF_2)_2OSO_2F \ . \end{array} \right.$$

Chlorine fluorosulphate interacts just as vigorously with trifluoromethyl, fluoroformyl, and trifluoroacetyl isocyanates[213], but fluorine fluorosulphate reacts with fluorosulphonyl isocyanate only under ultraviolet irradiation[209]:

$$ClOSO_2F + CF_3C(=O)NCO \rightarrow CF_3C(=O)NClC(=O)OSO_2F \ ;$$
$$FOSO_2F + FSO_2NCO \xrightarrow{h\nu} FSO_2N(OSO_2F)C(=O)F \ .$$

Despite the clear difference between the reaction mechanisms[209,213], the mode of addition indicated corresponds rigorously to the polarity of the reactants.

Only one mole of chlorine fluorosulphate adds easily to the nitriles of perfluorocarboxylic[168] and nitroperfluorocarboxylic[153] acids (at −40°–−30 °C) (in contrast to the reactions with peroxydisulphuryl difluoride[211]), for example:

$$ClOSO_2F + C_3F_7CN \rightarrow \underset{(VI)}{C_3F_7C(=NCl)OSO_2F} \ .$$

Treatment of the chloroimine (VI) with the second mole of chlorine fluorosulphate leads solely to the perfluoroacyl fluorosulphate and the anhydride of fluorosulphonic acid, approximately half of the chloroimine (VI) being converted. This can apparently be accounted for by the fact that the dichloroamine (VII) formed reacts with chlorine fluorosulphate more readily than the chloroimine (VI), splitting off the anhydride of fluorosulphonic acid and possibly nitrogen trichloride[168]:

$$C_3F_7C(=NCl)OSO_2F \xrightarrow{ClOSO_2F} \underset{(VII)}{[C_3F_7C(OSO_2F)_2NCl_2]} \xrightarrow{ClOSO_2F}$$
$$\rightarrow C_3F_7C(=O)OSO_2F + O(SO_2F)_2 + [NCl_3] \ .$$

Analogous results have been obtained also for the reactions of the nitriles of perfluorocarboxylic acids with two moles of chlorine fluorosulphate[168].

VI. OXIDATION OF CERTAIN NITROGEN-, SULPHUR-, SELENIUM-, AND IODINE-CONTAINING ORGANIC COMPOUNDS AS WELL AS CARBOXYLIC ACIDS

It is fairly difficult to achieve selective oxidation by the reagents considered, but in a series of instances this has been clearly demonstrated.

Peroxydisulphuryl difluoride oxidises almost quantitatively (yield 98%) bis(trifluoromethyl)hydroxylamine to bis(trifluoromethyl)nitroxide[77], from which only trifluoromethyl

fluorosulphate is formed subsequently, as from trifluoronitrosomethane[184]:

$$(OSO_2F)_2 + (CF_3)_2NOH \rightarrow (CF_3)_2NO \xrightarrow{(OSO_2F)_2} CF_3OSO_2F ,$$
$$(OSO_2F)_2 + CF_3NO \rightarrow CF_3OSO_2F .$$

Treatment of 2-nitrotetrafluoronitrosoethane with chlorine fluorosulphate leads to a chloroalkane and nitrosyl fluorosulphate[189]. An unstable, possibly salt-like, intermediate is apparently formed in the first stage and then decomposes under the usual conditions[189]:

$$R_FNO + ClOSO_2F \rightarrow R_FCl + NOSO_3F .$$

Trifluoromethanethiol is not oxidised unambiguously by peroxydisulphuryl difluoride, the product being a disulphide (yield 30%), from which trifluoromethyl fluorosulphate was subsequently obtained[77]. On the other hand, trifluorothioloacetic acid is converted qualitatively (for a molar reactant ratio of 2:1) into the corresponding disulphide, whose further treatment with peroxydisulphuryl difluoride yields trifluoroacetyl fluorosulphate[77]:

$$(OSO_2F)_2 \begin{cases} \xrightarrow{CF_3SH} (CF_3S)_2 + O(SO_2F)_2 + SO_2 + S ; \\ \xrightarrow{(CF_3S)_2} CF_3OSO_2F + SO_2 + S ; \\ \xrightarrow{2CF_3C(O)SH} [CF_3C(O)S]_2 \xrightarrow{(OSO_2F)_2} CF_3C(O)OSO_2F + O(SO_2F)_2 + SO_2 + S . \end{cases}$$

The reaction of chlorine fluorosulphate with perfluoroalkyl and pentafluorophenyl diselenides is accompanied by the dissociation of the selenium–selenium bond[214]:

$$(CF_3Se)_2 + ClOSO_2F \rightarrow CF_3SeOSO_2F .$$

Only trifluoromethyl fluorosulphate was obtained initially from trifluoroiodomethane on treatment with peroxydisulphuryl difluoride[158] or chlorine fluorosulphate[165]:

$$ClOSO_2F + CF_3I \rightarrow CF_3OSO_2F .$$

However, in 1977 Naumann reported[215] that tervalent iodine compounds (VIII) are formed from perfluoroalkyl iodides and chlorine fluorosulphate in accordance with the mechanism

$$ClOSO_2F + R_FI \rightarrow [R_FICl OSO_2F] \xrightarrow{ClOSO_2F} \underset{(VIII)}{R_FI(OSO_2F)_2} .$$

Further study of this reaction showed that alkyl iodides are converted, on reaction with peroxydisulphuryl difluoride[204] or chlorine fluorosulphate[167] at a temperature as low as −50– −40 °C, into cream-coloured or white solid compounds of type (VIII), which decompose into alkyl fluorosulphates and iodine fluorosulphate when the alkyl radical has a straight-chain structure. Only perfluoroisopropyliodine bisfluorosulphate (m.p.101 °C) proved to be stable; on the basis of Raman spectra, the authors[167] attributed the dimeric structure (IX) to this substance:

$$RI \xrightarrow[[ClOSO_2F]]{(OSO_2F)_2} \underset{(VIII)}{RI(OSO_2F)_2} \xrightarrow{\sim 30-\ -20^\circ} ROSO_2F + IOSO_2F ;$$
$$R = CH_3,\ CF_3,\ C_3F_7,\ C_7F_{15}$$
$$(CF_3)_2CFI + ClOSO_2F \rightarrow \underset{(IX)}{\{[(CF_3)_2CF]_2I\}^+[I(SO_3F)_4]^-} .$$

Peroxydisulphuryl difluoride has been used successfully to synthesise iodine tristrifluoromethanesulphonate[216], but it was not possible to oxidise iodosyl trifluoromethanesulphonate to iodyl trifluoromethanesulphonate by this reagent as a consequence of the cleavage of the carbon–sulphur bond[112]:

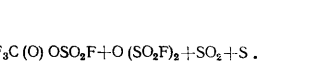
$$(OSO_2F)_2 \begin{cases} \xrightarrow{CF_3SO_3H,\ I_2} (CF_3SO_2O)_3I ; \\ \xrightarrow{CF_3SO_2OIO} CF_3OSO_2F . \end{cases}$$

It must be emphasised that apparently fairly extensive possibilities arise in processes of the type considered when peroxydisulphuryl difluoride is used *in situ*, i.e. in its electrochemical generation directly in the reaction mixture. Perfluoroalkyl fluorosulphates have been obtained by this method from perfluoroalkyl iodides in high yields and mono- and bis-fluorosulphates have been obtained from the di-iodo-derivatives[217], for example:

$$C_4F_9I \xrightarrow[HSO_3F/KSO_3F]{\text{electrolysis}} C_4F_9OSO_2F .$$

Carboxylic acids undergo mild oxidation to lactones (via fluorosulphato-substituted acids), from which cyclic unsaturated ketones are formed on keeping in the electrolyte for a longer period (up to 48 h)[218,219]. Unambiguous and readily reproducible results have been obtained for valeric and higher aliphatic acids as well as ω-cyclohexyl-substituted propionic and butyric acids. However, a mixture of 3- and 4-fluorosulphates (in proportions of 3:4) is obtained from the unsubstituted butyric acid, the yield of lactones being low and unstable. The sequence of transformations can be represented schematically as follows[219]:

$$RR'CH(CH_2)_nCOOH + HSO_3F \rightarrow FSO_3^- + RR'CH(CH_2)_nCO_2H_2^+ \rightarrow$$
$$\xrightarrow{(OSO_2F)_2} FSO_2OCRR'(CH_2)_nCO_2H_2^+ \rightarrow$$



R and R′ = H, alkyl, or cycloalkyl; n = 2 or 3.

The xenon difluoride–fluorosulphonic acid system, in which peroxydisulphuryl difluoride is formed[135–138] (see above), has been used to generate radical-cations from perfluoro-derivatives of naphthalene and biphenyl[139].

VII. CONCLUSION

The data described show that the reactions of peroxydisulphuryl difluoride and halogen fluorosulphates have been more widely investigated at present in relation to inorganic than organic compounds, this being confirmed also by the number of the corresponding publications. The very small number of kinetic studies, particularly on organic substances, is striking. Nevertheless the available information already provides an idea concerning the exceptionally high and extremely novel reactivity of the reagents considered and also about their extensive synthetic possibilities.

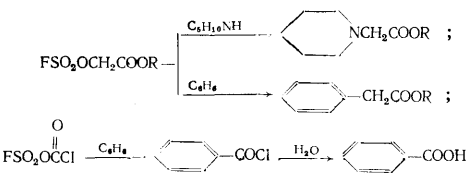
There is apparently no doubt about the radical nature of the absolute majority of the reactions of peroxydisulphuryl difluoride. The unusually high reactivity of the fluorosulphate radical is indicated, for example, by its ability to saturate perfluorobenzene completely at room temperature[195], whereas the analogous reaction of bis(trifluoromethyl)nitroxide requires prolonged heating at 120 °C.[220] Facts such as the necessity to add fluorosulphonic acid in order to substitute the chlorine atom in 1,1,2-trichlorotrifluoroethane[146] and also the substitution of the fluorosulphato-group in the ring and not the methyl group of toluene at temperatures below 0 °C are clear exceptions[77].

Except for fluorine fluorosulphate, which reacts via both radical and ionic mechanisms, halogen fluorosulphates are extremely vigorous electrophiles. Thus, despite the generally known inertness of perfluoro-olefins, particularly higher perfluoro-olefins, to the action of electrophiles, chlorine fluorosulphate adds readily to these compounds at temperatures as low as −65– −70 °C regardless of their structure[199] and at room temperature it adds to all the bonds of perfluorobenzene[195]. Chlorine fluorosulphate is apparently one of the strongest chlorinating agents, having a

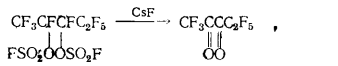
positively polarised chlorine atom, since, for example, its ability to chlorinate benzene to perchlorobenzene at −100 °C has no analogies in other systems[190].

The "anomalies" enumerated undoubtedly require further thought and study using modern methods of physicochemical analysis, possibly also as regards the reaction kinetics, in order to elucidate the true mechanisms of these phenomena.

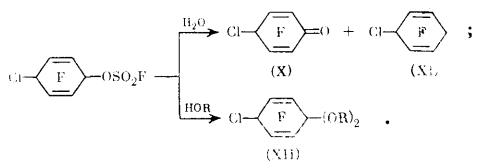
The possibility of introducing fluorosulphato-groups into various classes of organic compounds either by the addition of peroxydisulphuryl difluoride and halogen fluorosulphates to multiple carbon–carbon and carbon–nitrogen bonds§ or by the substitution of hydrogen, halogen, or certain functional groups. The fluorosulphato-group, which is one of the most readily eliminated groups, can be substituted in its turn by other functional groups on treatment with nucleophiles. The high reactivity of alkyl and acyl fluorosulphates is indicated, for example, by the alkylation of not only amines but also of benzene, even at reduced temperatures in the absence of a catalyst, by the relatively unstable fluorosulphatoacetate esters *in situ*[86,221] and also by the acylation of benzene by chlorocarbonyl fluorosulphate under approximately similar conditions[78]:



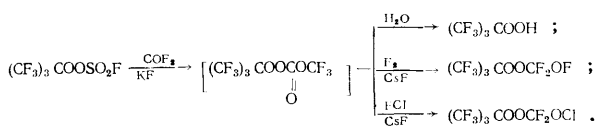
Primary perfluoroalkyl fluorosulphates are readily converted into the corresponding derivatives of perfluorocarboxylic acids, while the secondary compounds are converted into carbonyl compounds, for example into α-diketones[193]:



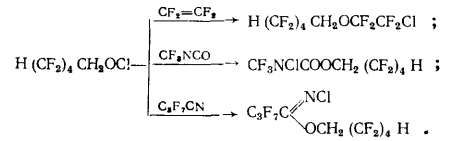
The diene (XI) is formed together with the ketone (X) from 4-chloroperfluoro-2,5-cyclohexadienyl fluorosulphate on hydrolysis, while treatment with alcohols leads to the stable ketals (XII)[222]:



Peroxy-compounds which could not be synthesised previously have been obtained from perfluoro-t-butylfluorosulphuryl peroxide[174,223]:



The hypochlorites derived from polyfluoro-alcohols, obtained by chlorination with chlorine fluorosulphate, also exhibit a high reactivity; they readily add to multiple carbon–carbon and carbon–nitrogen bonds[175,224]:



In conclusion we should like to emphasise that at present increasing attention is being devoted to the study of the properties and reactivities of the hypohalite derivatives of other strong acids such as nitric[10], perchloric[10,92–94], and trifluoromethanesulphonic[225,226]. Although many of these are much less stable than halogen fluorosulphates (for example, it has been recommended[226] that $ClOSO_2CF_3$ and $BrOSO_2CF_3$ are not heated above 0 °C), these compounds too are being used to an increasing extent in organic synthesis[10,225,226].

§ One cannot rule out the possibility that perfluoroazaalkenes do not react with peroxydisulphuryl difluoride[9,206] merely because of their poor solubility, as was observed previously in the reaction of tetrafluoroethylene with chlorine fluorosulphate[199].

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