REACTIONS OF SULFUR FLUORIDES AND OTHER FLUORIDES

BY

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TO MY MOTHER

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INTRODUCTION

Since 1950 there have been rapid developments in sulfur fluorine chemistry especially in the chemistry of sulfur fluorides containing carbon, nitrogen or oxygen. Several detailed reviews [1-5] and articles on sulfur fluorine chemistry have been published [6-11]. A brief review of the sulfur fluorine chemistry of various oxidation states relevant to the present work is given below.

Sulfur in the oxidation state+2

The compounds (1) FSSF (2) SF_2 and (3) RSF are examples of this class.

Disulfur difluoride

FSSF is thermally less stable than its isomer thiothionyl fluoride SSF_2. FSSF is formed by the reaction of sulfur vapour with AgF or HgF_2 and is easily separated by distillation from its isomer.

$$S + AgF \longrightarrow FSSF$$

Microwave data show the structure given in Fig. I.

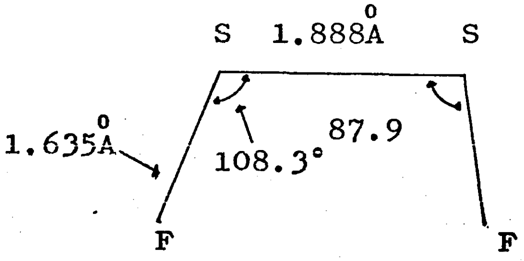


Fig. I

Sulfur difluoride

SF_2 has been detected by its mass spectrum [14]. Unstable SF_2 is formed in the reaction of SCl_2 vapour with HgF_2 at extremely low pressure.

$$SCl_2 + HgF_2 \longrightarrow SF_2 + HgCl_2$$

The microwave spectrum [15] shows that the molecule has C_{2v} symmetry. The structure is given in Fig. 2.

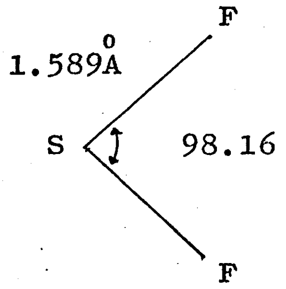


Fig. 2

Its dipole moment is found to be 1.05D

Sulfenyl fluorides

The first FSR compound to be described was $(CF_3)_2CFSF$ [16] which does not attack dry glass. CaF_2 fluorinates AgSCN, yielding among other products, F_2NCF_2SF [17]. Further sulfenyl fluorides of the type $FS\text{-}CF_nCl_{3-n}$, where n=0, 1,2,3 have been characterised by their ^{19}F n.m.r. and I.R. spectra. These compounds are unstable intermediate species formed by the fluorination of CCl_3SCl, $CFCl_2SCl$ and CF_2ClSCl with KSO_2F [18]. The reaction of CF_3SCl with mercury fluoride yields CF_3SF [19].

$$2\ CF_3SCl + HgF_2 \longrightarrow 2\ CF_3SF + HgCl_2$$

CF_3SF dimerises to $CF_3SF_2SCF_3$ in the liquid state. The compound CF_3SF reacts rapidly with metals, e.g. Mg, Cu or Hg, to give metal fluorides and CF_3SSCF_3.

$$2CF_3SF + M \longrightarrow MF_2 + CF_3SSCF_3$$

CF_3SF disproportionates at room temperature according to the equation.

$$3\ CF_3SF \longrightarrow CF_3SF_2SCF_3 + CF_3SF \longrightarrow CF_3SSCF_3 + CF_3SF_3.$$

Sulfur in oxidation state +4

The compounds that are discussed in this section are SSF_2, SF_4, derivatives containing sulfur carbon bonds, derivatives containing sulfur nitrogen bonds, and SOF_2.

Of these compounds, SF_4 and derivatives containing S-C bonds are discussed in more detail in Chapters I, II and III.

Thiothionyl fluoride

SSF_2 is formed by the fluorination of S_2Cl_2 or by the passage of NF_3 through molten sulfur.

$$S_2Cl_2 + 2KSO_2F \longrightarrow S{=}SF_2 + 2\ KCl + SO_2 \qquad [20]$$

$$3S + NF_3 \xrightarrow{400^\circ} S{=}SF_2 + N{=}SF \qquad [21]$$

Figure (3) shows the structure of SSF_2 determined from its microwave spectrum.

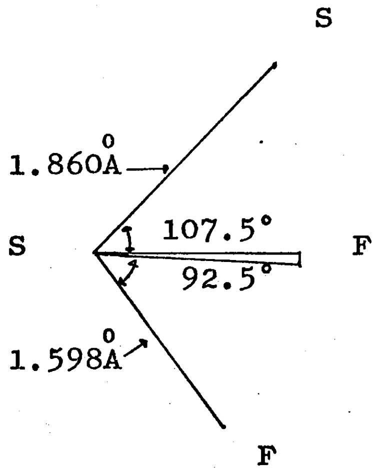


Fig. 3 Structure of $S{=}SF_2$

Anhydrous hydrogen fluoride or boron trifluoride cause disproportionation.

e.g. $S{=}SF_2 + BF_3 \longrightarrow BF_3 . SF_4 + 3S$

Sulfur tetrafluoride, SF_4

SF_4 is of great importance because of its reactivity with amine, carbonyl, silyl, nitrile and other groups. A short review of the reactions of SF_4 is given in Chapter I.

SF_4 derivatives containing sulfur nitrogen bonds

This section covers the following series of compounds:

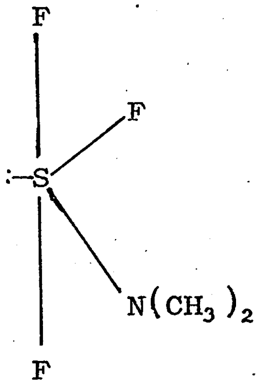
(1) R_2NSF_3 (2) $R{-}N{=}SF_2$ (3) $R{-}N{=}S(F){-}NR_2$ (4) $R{-}N{=}S(F)R$ and (5) $N{\equiv}SF$

R_2NSF_3 (dialkylaminosulfur trifluorides):

The compounds R_2NSF_3 [$R=CH_3, C_2H_5$] are prepared by the following route: [22 and 23].

$$R_2N\text{-}SiMe_3 + SF_4 \longrightarrow R_2N\text{-}SF_3 + Me_3SiF$$

The ^{19}F n.m.r. spectrum of $(CH_3)_2NSF_3$ at low temperatures suggests a trigonal bipyramidal structure with the two fluorine atoms in the axial sites and one fluorine atom, the lone pair of electrons and the dimethylamino group in the equatorial sites.



[22]

Fig. 4 Proposed structure for $(CH_3)_2N\text{-}SF_3$

$R\text{-}N=SF_2$ can be prepared by the following routes:

(i) via cyanides, cyanates or thiocyanates e.g.

$$R\text{-}C\equiv N + SF_4 \longrightarrow RCF_2N=SF_2 \qquad [24]$$

(ii) via amines or amides

$$3\ RNH_2 + SF_4 \longrightarrow R{-}N{=}SF_2 + 2RNH_3^{+}F^{-}$$ [25]

(iii)via compounds containing silyl groups

$$RN[SiMe_3]_2 + SF_4 \longrightarrow R{-}N{=}SF_2 + 2F\ SiMe_3$$ [26]

(iv) by cleavage or addition reactions of imino sulfur difluorides.

$$O{=}C(F) - N{=}SF_2 + Cl_2 + CsF \longrightarrow Cl{-}N{=}SF_2 + COF_2 + CsCl$$ [27]

The structure of the compound $Cl{-}N{=}SF_2$ as determined by electron diffraction is shown in Fig. 5 [28].

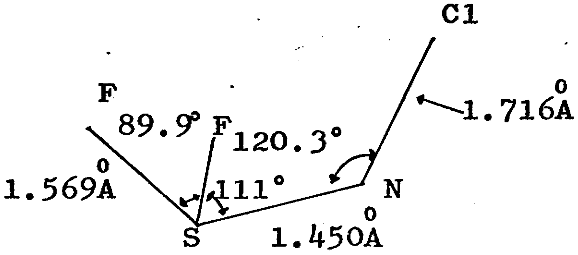


Fig. 5 Structure of $ClNSF_2$

<u>Aminosulfur fluoride imides</u>:

The compound $N{\equiv}C{-}N{=}S(F)NR_2$ contains both a sulfur nitrogen single bond and a sulfur nitrogen double bond, Attempts at substitution of one fluorine atom in sulfur difluoride imides by a dialkylamino group has been unsuccessful [23]. Aminosulfur fluoride imides are prepared by the following method.

$$\begin{array}{l} Me_3Si - N{=}C{=}N{-}Si(CH_3)_3 \;+\; F_3S{-}NR_2 \\ \qquad\qquad\qquad \downarrow \\ \qquad\qquad N{\equiv}C{-}N{=}S(F)NR_2 \;+\; 2FSiMe_3 \end{array} \qquad [23]$$

Alkylsulfur fluoride imides, $R{-}N{=}S(F)R'$, contain instead of the dialkyl amino group in the preceding compounds an alkyl group. These are prepared as follows:

$$R{-}N{=}SF_2 \;+\; F_2C{=}C(F)CF_3 \xrightarrow{CsF} R{-}N{=}S(F)CF(CF_3)_2 \qquad [29]$$

Where $R{=}CF_3$ or C_2F_5

Thiazyl fluoride $N{\equiv}SF$ can be prepared by several methods, the best of these being.

(a) $NF_3 + 3S \xrightarrow{400^\circ} N{\equiv}SF + S{=}SF_2$ [21]

(b) $O{=}C(F){-}N{=}SF_2 \xrightarrow[CsF]{20^\circ} N{\equiv}SF + O{=}CF_2$ [27]

(c) $Hg(N{=}SF_2)_2 \xrightarrow[\text{High vacuum}]{110^\circ} 2N{\equiv}SF + HgF_2$ [30]

Method (c) is especially useful, since unstable NSF may conveniently be kept in the form of the mercury compound from which it can be generated in a very pure state.

Thionyl fluoride:

SOF_2 is the most familiar example of an oxyfluoride of sulfur and was first reported in 1896 [31]. A number of methods are known for its synthesis, usually involving metathetical exchange of fluoride with thionyl chloride. Dropwise addition of thionyl chloride on to a slurry of sodium fluoride in acetonitrile results in a high yield of thionyl fluoride [32].

$$SOCl_2 + 2NaF \longrightarrow SOF_2 + 2NaCl$$

The intermediate in these metathetical reactions is thionyl chloride fluoride S(O)FCl, which can be isolated from the reaction of iodine pentafluoride and thionyl chloride [33]. Thionyl chloride fluoride reacts with mercury and undergoes disproportionation at room temperature to thionyl chloride and thionyl fluoride.

$$2\,SOClF \longrightarrow SOF_2 + SOCl_2$$

Thionyl fluoride has a pyramidal structure based on a tetrahedral arrangement of four pairs of electrons one of which is a lone pair [35] Fig. 6.

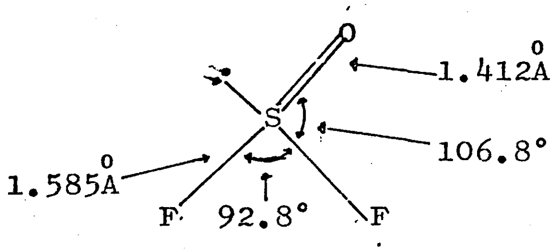


Fig. 6 Structure of thionyl fluoride

Sulfur in the oxidation state+6

SF_6 - sulfur hexafluoride: SF_6 can be obtained by the fluorination of elemental sulfur.

$$S + 3F_2 \longrightarrow SF_6 \qquad [36]$$

SF_6 in a very pure state is available by electrochemical fluorination of H_2S in anhydrous liquid HF [37].
By virtue of its dielectric properties and its chemical and physiological inertness, SF_6 is of importance in the electrical industry and refrigeration. The inactivity of SF_6 is due less to its thermodynamic [38], than to its kinetic properties [Dissociation energy - $D(SF_5-F) = 75.92$ Kcal/mole].
SF_6 has highly symmetrical octahedral structure [S-F bond distance 1.564Å] and is kinetically stable which prevent any nucleophilic reagents from attacking the molecule [39]. However, by irradiation of SF_6 in an aqueous buffered solution a reaction with hydrated electrons can be detected.

$$SF_6 + e^-aq \xrightarrow{pH.6.5} F^- H_3O^+, SO_4^{-2} \qquad [40]$$

The reaction of SF_6 with oxygen can be initiated by electrical explosion of extremely small masses of platinum or copper in SF_6 and oxygen mixtures.

$$SF_6 + \tfrac{1}{2}O_2 \longrightarrow O{=}SF_4 + F_2 \qquad [41]$$

SF_6 derivative containing sulfurnitrogen double bonds

The only known sulfur tetrafluoride imide of the type $R{-}N{=}SF_4$ is $CF_3N{=}SF_4$ which can be produced in the following manner.

$$\begin{tikzcd}
N{\equiv}CCl + SF_5Cl \arrow[r] & F_5S{-}N{=}CCl_2 \arrow[r, "+2\ NaF", "-2NaCl"'] & F_5S{-}N{=}CF_2 \arrow[d, "+HF"] \\
{[42]} & F_4S{=}N{-}CF_3 & F_5S{-}N(H)CF_3 \arrow[l, "{+225^\circ, +KF}"', "-HF"]
\end{tikzcd}$$

Thionyltetrafluoride SOF_4:

SOF_4 is made by the oxidation of SF_4 with oxygen in the presence of NO_2 as a catalyst.

$$O_2 + 2SF_4 \xrightarrow[NO_2]{200^\circ} 2\ O{=}SF_4 \qquad [43]$$

SOF_4 can also be prepared by the fluorination of SOF_2.

$$S(O)F_2 + F_2 \longrightarrow O{=}SF_4 \qquad [44]$$

The structure of SOF_4 is a trigonalbipyramid where oxygen occupies an equatorial position. The recent revised data based on electron diffraction is given in Fig. 7.[45]

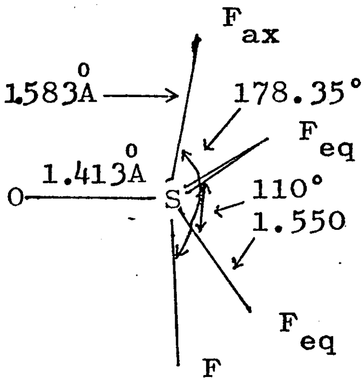


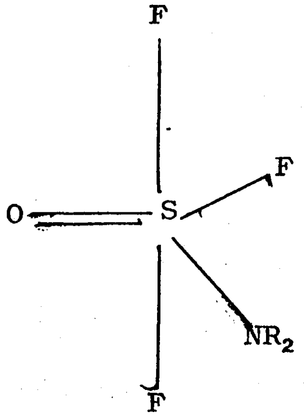
Fig. 7 Structure of $S(O)F_4$

Like SF_4, $S(O)F_4$ can be used to form new sulfur fluorine compounds.

$S(O)F_4$ reacts with silylamino compounds to produce $R_2N{-}S(O)F_3$.

$$O{=}SF_4 + R_2N{-}Si(CH_3)_3 \longrightarrow R_2N{-}S({=}O)F_3 + FSi(CH_3)_3 \qquad [23]$$

Analysis of the ^1H and ^{19}F n.m.r. spectra confirm trigonal-bipyramidal structures for the $R_2N{-}S({=}O)F_3$ molecules with the new substituent in the equatorial position as shown in Fig. 8.



Complete substitution of all the fluorine atoms of $S(O)F_4$ was effected by cleavage of the Si-O bond.

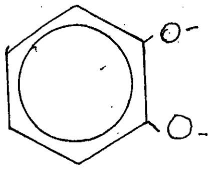
$$PhOSiMe_3 + S(O)F_4 \longrightarrow PhOS(O)F_3 + Me_3SiF$$

$$2PhOSiMe_3 + S(O)F_4 \longrightarrow (PhO)_2S(O)F_2 + 2Me_3SiF \qquad [46]$$

$$2\overset{*}{C}_6H_4OO(SiMe_3)_2 + S(O)F_4 \longrightarrow C_6H_4OOS(O)OOC_6H_4 + 2Me_3SiF$$

The ^{19}F n.m.r. spectra of the compounds $PhOS(O)F_3$, $(PhO)_2S(O)F_2$ show the general preference for equatorial substitution in the trigonalbipyramid geometry.

* Where C_6H_4OO is



General Experimental Procedures

Standard vacuum procedures were used throughout, using pyrex glass apparatus. Involatile liquids and solids were handled in a dry, oxygen free nitrogen atmosphere.

Infrared spectra were measured on Perkin Elmer 257, and 457 spectrophotometers. Infrared spectra of gasses were recorded using 5 cm and 10 cm gas cells fitted with KBr windows. Solution spectra were recorded using KBr, semi-permanent cells from R.I.I.C. Liquid Film Spectra were obtained using KBr plates. Solid spectra were recorded as mulls with Nujol using KBr plates. Normal abbreviations to denote band shapes and intensities are used viz. s=strong, m=medium, w=weak, v=very, br=broad, sh=shoulder etc. Proton magnetic resonance shifts were measured in ppm. relative to tetramethylsilane $(CH_4)_4Si$, fluorine magnetic resonance shifts relative to trichlorofluoromethane CCl_3F. Peak multiplets are abbreviated as d=doublet, t=triplet, bs=broad singlet, s=singlet etc.

NMR spectra were obtained from a Perkin Elmer R10 spectrometer at 60 MHz for proton, 56.5 MHz for fluorine using a probe temperature of 33°C.

Variable temperature n.m.r. spectra were obtained from a Jeol 100 spectrometer.

Mass Spectra were recorded at 70 ev (if not otherwise mentioned)using an A.E.I. MS12 spectrometer. A cold inlet system was used where possible and failing this the heated inlet was used, or the sample applied directly to the probe.

Elemental analysis were performed by Bernhardt microanalytical laboratory.

C H A P T E R I

REACTIONS OF SULFUR TETRAFLUORIDE

SUBSTITUTION REACTIONS OF SF_4

INTRODUCTION:

The first successful synthesis and characterization of SF_4 was by the direct fluorination of a thin film of sulfur on a cooled surface [47].

$$S + 2F_2 \longrightarrow SF_4$$

Nowadays sulfur tetrafluoride is readily prepared in excellent yield from sulfur dichloride and fluoride ion e.g. from NaF in acetonitrile in pyrex apparatus [48].

$$3\,SCl_2 + 4NaF \xrightarrow{CH_3CN} SF_4 + S_2Cl_2 + 4NaCl$$

SF_4 thus formed can easily be separated from most impurities by trap to trap distillation system. The gas however always contains impurities such as SOF_2 and SiF_4 formed by the hydrolysis of SF_4 and because of the close boiling points of the two gases SF_4 and SOF_2, it is difficult to separate them by ordinary fractionation techniques. Pure SF_4 can be obtained by adduct formation with BF_3 thus allowing the pumping-away of the SOF_2 and other impurities. SF_4 can be liberated by metal fluorides which displace it from the BF_3 [49].

$$BF_3SF_4 + NaF \longrightarrow SF_4 + NaBF_4$$

SF_4 has a high value of Trouton's constant 27.1 (Trouton's constant is the ratio of the molar heat of evaporation of the liquid to its boiling point on the absolute scale; for normal liquids the value is 23) that suggests some association of the molecules in the liquid phase [50]. From the microwave spectrum and from electron diffraction studies it is known that the structure of SF_4 is trigonal bipyramidal with the two axial positions occupied by fluorines with the lone pair equatorial [51a]. The electron diffraction data of SF_4 show the detailed structure given in Fig. 9 [51b].

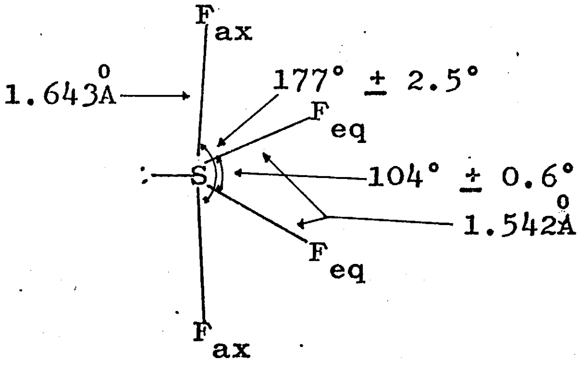


Fig. 9 Structure of SF_4

Gillespie has discussed the shape of sulfur tetrafluoride in terms of repulsive interaction between the electron pairs and considered that a trigonal bipyramid arrangement of five electron pairs around the sulfur in the geometry has minimum repulsive interactions [52]. The rather gross derivations from regular trigonal-bipyramid geometry have been explained by the different amounts of s,p,d hybridization in the axial and equatorial bonds [57]. In SF_4, the hybridization can be described as $SP_3d_{z^2}$, where two axial bonds have 'pd' character whereas the two equatorial bonds are of 'sp' types; as such the equatorial S-F bond distance is shorter than that of the axial S-F. The NMR spectrum of SF_4 has been studied extensively [53-55]. Cotton et al reported that the spectrum at -100°C consisted of two triplets [53], in agreement with the trigonal bipyramidal structure in which the lone pair of electrons on sulfur occupies an equatorial site. The spectrum obtained at -101°, has been carefully analysed as an A_2B_2 system by Gillespie's group [54]. The spectrum consists of the expected pair of triplets of doublets (i.e. 12 lines) with $\Delta\nu = 2935$ Hz measured at 56.4 MHz, and $J = 76.3 \pm 0.3$ Hz.

Muetterties and Phillips [55] published the results of more extensive experiments carried out between 23° and -98°. It was shown that fluorine interchange occurred, the fluorines becoming equivalent (single-line spectrum) at 23°. The activation energy for this exchange process was calculated to be 4.5 ± 0.8 Kcal mole^{-1}, and experiments at various concentrations of SF_4 indicated that the kinetics of the process were of an order greater than unity. A possible intermolecular exchange mechanism involving a fluorine bridge was put forward for the exchange process [Fig. 11].

The infrared and Raman spectral data of the gas were consistent with the trigonal bipyramid structure [56] [57]. Thermodynamic functions have been calculated from the spectroscopic data [58].

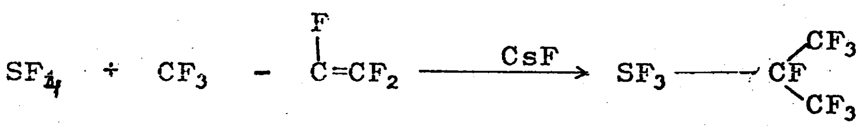
An early impetus on sulfur tetrafluoride chemistry was its remarkable character as reagent for the selective replacement of a carbonyl oxygen with fluorine in organic compounds [50].

$$>C=O \quad + \quad SF_4 \longrightarrow \; >CF_2 \quad + \quad SOF_2$$

This reaction has a broad scope and is effective with a variety of carbonyl compounds. SF_4 also fluorinates a number of metal oxides and sulfides to fluorides [50]. Sulfur tetrafluoride forms complexes with Lewis acids e.g. $SF_4.SbF_5$, $SF_4.BF_3$ and $SF_4.PF_5$. Initially the structure of these adducts were formulated as simple acid base complexes $[F_4S \rightarrow BF_3]$, however it is now generally accepted that SF_4 is only a relatively weak donor molecule, and from recent studies the adducts are considered to become [59,60].

e.g. $SF_3^{+}BF_4^{-}$

SF_4 reacts with perfluoroalkenes in the presence of CsF as catalyst as below [61].



$$SF_4 + CF_3-CF=CF_2 \xrightarrow{CsF} SF_3-CF(CF_3)_2$$

$$SF_4 \quad + \quad F_2C=CF_2 \xrightarrow{CsF} SF_3CF_2CF_3$$

With CF_3OF and SF_5OF, SF_4 undergoes oxidative addition to CF_3OSF_5, SF_5OSF_5 [62].

$$CF_3OF + SF_4 \longrightarrow CF_3OSF_5$$
$$SF_5OF + SF_4 \longrightarrow SF_5OSF_5$$
$$SF_4 + N_2F_2 \longrightarrow SF_5NF_2$$

SF_4 can easily be oxidized to the S(VI) oxidation state. With F_2, it gives SF_6 with Cl_2 in the presence of CsF, it produces SF_5Cl and with oxygen, in the presence of NO_2, it is oxidized to $SF_4(=O)$. [63, 42, 43].

$$SF_4 + F_2 \longrightarrow SF_6$$
$$SF_4 + Cl_2 + CsF \longrightarrow SF_5Cl + CsCl$$
$$SF_4 + O_2 \xrightarrow{NO_2} S(O)F_4$$

With amines or silylamines, SF_4 is substituted.

$$RNH_2 + SF_4 \longrightarrow RN{=}SF_2 \qquad [25]$$

$$(R_3Si)_2NR + SF_4 \longrightarrow RN{=}SF_2 \qquad [26]$$

The first monosubstituted derivative of SF_4 was prepared by Si-N bond cleavage.

$$SF_4 + Me_3SiNMe_2 \longrightarrow SF_3NMe_2 + Me_3SiF \qquad [22]$$

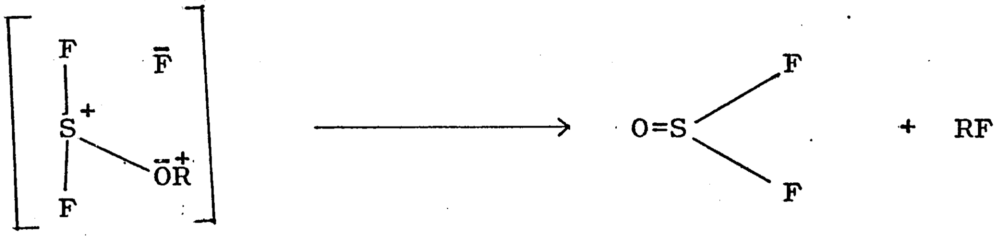
Substitution in SF_4 through Si-O bond breaking was also successful.

$$SF_4 + Me_3SiOPh \longrightarrow SF_3OPh + Me_3SiF \qquad [64]$$

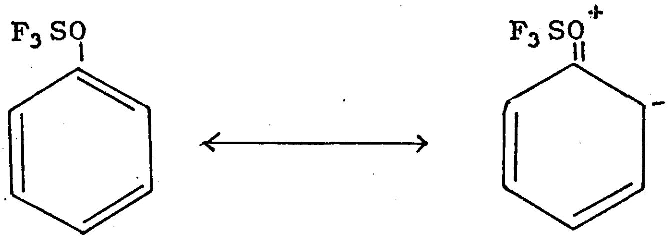
REACTIONS OF SF_4 WITH SILOXY DERIVATIVES

From bond energy data (Si-O=108 Kcal/mole [65], S-F=78 Kcal/mole [66] S-O=63 Kcal/mole [67] and Si-F 137 Kcal/mole [65]), it is clear that the replacement of fluorine atoms from SF_4 by the cleavage of Si-O bond is thermodynamically a favourable reaction. However, the stability of SF_3OR thus formed largely depends on the group R. In the attempted preparation of alkoxy derivatives of SF_4 by the above method, it was found that the reaction was fast and the products were Me_3SiF, RF and SOF_2 [68]. It was presumed that the reaction proceded through intermediate formation of SF_3OR that rapidly decomposed to SOF_2 and RF as in the following:

$$SF_4 \quad + \quad Me_3SiOR\ [R=CH_3 \text{ or } C_2H_5] \longrightarrow [SF_3OR] \quad + \quad Me_3SiF$$



The stability of the S-O-C bond would depend on the group attached to carbon which might counteract the tendency of the sulfur atom to form a double bond with oxygen. The successful formation of 2,fluoro,2,2,dinitro,ethoxy sulfur trifluoride [69] $FC(NO_2)_2CH_2OSF_3$ indicates that one fluorine atom and two nitro (strong electron withdrawing) groups increase the stability of the COS system. The successful preparation of phenoxysulfur trifluoride is also another good example of π-overlap between the aromatic ring system and p'orbitals of the oxygen atom may stabilize the C-O bond.



The present work designed to prepare new substituted aryloxy derivatives of sulfur tetrafluoride is an attempt to observe the effect of the substituents of the benzene on the overall stability. The substituents used are:

Me, (ortho, meta and para), Cl (meta, para), F (ortho, meta, para), NO_2 (para), CF_3 (para).

New compounds are prepared by the reactions:

$$SF_4 + Me_3SiORx \longrightarrow SF_3ORx + Me_3SiF$$

$$SF_4 + 2Me_3SiORx \longrightarrow SF_2(ORx)_2 + 2Me_3SiF$$

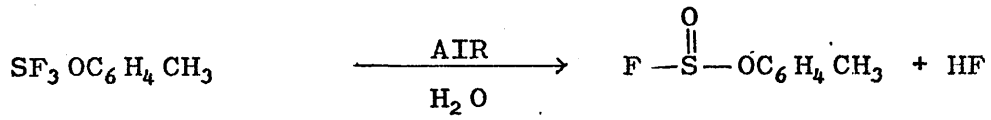
where $Rx = MeC_6H_4$, $Cl\ C_6H_4$, FC_6H_4

Reactions: $SF_4/Me_3SiOC_6H_4CH_3$ [ortho, meta and para, molar ratio 1:1].

Using an excess of sulfur tetrafluoride, trimethyl tolyloxy silane reacts readily well below room temperature to give monosubstituted derivatives of SF_4. The reaction is fast and exothermic.

$$Me_3SiOC_6H_4CH_3 \quad + \quad SF_4 \longrightarrow SF_3OC_6H_4CH_3 \quad + Me_3SiF$$

$SF_3OC_6H_4CH_3$, (ortho, meta and para) tolyloxy sulfur trifluorides are non volatile liquids, readily hydrolysed in air.



$$SF_3OC_6H_4CH_3 \xrightarrow[H_2O]{AIR} F-\overset{\overset{\displaystyle O}{\|}}{S}-OC_6H_4CH_3 \quad + HF$$

The substituted thionyl derivatives, $F-\overset{\overset{O}{\|}}{S}-OC_6H_4CH_3$, have been characterized by their ^{19}F n.m.r. spectra and their mass spectra (Chapter IV).

$SF_3OC_6H_4CH_3$ (ortho) is unstable at room temperature and decomposes to an unidentified coloured mass. $SF_3OC_6H_4CH_3$ (meta, para) slowly disproportionate at room temperature to give $SF_2(OC_6H_4CH_3)_2$ and SF_4.

$$2\ SF_3OC_6H_4CH_3 \longrightarrow SF_2(OC_6H_4CH_3)_2 \quad + SF_4$$

On heating above 75°C, $SF_3OC_6H_4CH_3$ (meta, para) decomposes to SOF_2, SF_4 and an unidentified coloured mass.

$$SF_3OC_6H_4CH_3 \xrightarrow{\Delta} SOF_2 \quad + SF_4 \quad + \text{solid}$$

The formation of SF_4 in the above reaction suggests the possible mode of decomposition to be:

$$\begin{aligned} SF_3OC_6H_4CH_3\ \text{(meta + para)} \xrightarrow[75°C]{\Delta}\ & SF_2(OC_6H_4CH_3)_2 \quad + SF_4 \\ & \qquad\qquad SOF_2 \quad + \text{coloured mass} \end{aligned}$$

$SF_4/CH_3C_6H_4OSiMe_3$ [ortho, meta and para ratio 1:2]

In the case of ortho $MeC_6H_4OSiMe_3$, the reaction with SF_4 in a 2:1 molar ratio produces not $(CH_3C_6H_4O)_2SF_2$ but an unidentified coloured mass. With meta and para $CH_3C_6H_4OSiMe_3$, SF_4 reacts readily at 20°C to produce Me_3SiF and white solid identified as $SF_2(OC_6H_4CH_3)_2$. The reactions are fast and exothermic.

$$SF_4 + 2Me_3SiOC_6H_4CH_3 \longrightarrow SF_2(OC_6H_4CH_3)_2 + 2Me_3SiF$$

$SF_2(OC_6H_4CH_3)_2$ readily hydrolyze in air to give $S(=O)(OC_6H_4CH_3)_2$, confirmed by mass spectrum.

$$SF_2(OC_6H_4CH_3)_2 \xrightarrow[H_2O]{air} S(=O)(OC_6H_4CH_3)_2 + 2HF$$

On heating above 80°C, $SF_2(OC_6H_4CH_3)_2$ decompose to $S(O)F_2$ and coloured masses.

$$SF_2(OC_6H_4CH_3)_2 \xrightarrow{\Delta} SOF_2 + \text{coloured mass}$$

$SF_4/FC_6H_4OSiMe_3$ (ortho, meta and para, molar ratio 1:1)

In a 1:1 molar ratio, SF_4 reacts smoothly with $FC_6H_4OSiMe_3$ below room temperature. The reaction is fast and exothermic.

$$SF_4 + FC_6H_4OSiMe_3 \longrightarrow SF_3OC_6H_4F + Me_3SiF$$

$SF_3OC_6H_4F$ is readily hydrolysed in air to HF and $FC_6H_4OS(=O)F$ identified by ^{19}F n.m.r. and mass spectrum.

$$SF_3OC_6H_4F \xrightarrow[H_2O]{air} FC_6H_4OS(=O)F + HF$$

Of the three $FC_6H_4OSF_3$ (ortho, meta and para), the ortho-fluorophenoxysulfur trifluoride is stable for some hours at room temperature, but slowly decomposes to an unidentified coloured mass over a long time. The meta and para fluorophenoxy sulfur trifluorides disproportionate at room temperature to $SF_2(OC_6H_4F)_2$ and SF_4.

$$SF_3OC_6H_4F \longrightarrow SF_2(OC_6H_4F)_2 + SF_4$$

On heating above 80° $SF_3OC_6H_4F$ (meta and para) decompose to SF_4, SOF_2 and unidentified coloured masses.

$$SF_3OC_6H_4F \xrightarrow{\Delta} S(O)F_2 + SF_4 + \text{coloured mass}$$

$SF_4/FC_6H_4OSiMe_3$ [ortho, meta and para] molar ratio 1:2.

The reactions are successful in producing new compounds in the case of meta and para fluorophenoxytrimethylsilane. The reaction of $\underline{o}$-$FC_6H_4OSiMe_3$ with SF_4 in a 2:1 molar ratio does not produce $SF_2(OC_6H_4F$-$\underline{o})_2$ but gives an unidentified coloured mass. The reactions however go smoothly in the case of meta and para fluorophenoxytrimethylsilane at room temperature to give Me_3SiF and $SF_2(OC_6H_4F)_2$, colourless liquids, m.p. ~30°C.

$$SF_4 \quad + \quad FC_6H_4OSiMe_3 \longrightarrow SF_2(OC_6H_4F)_2 \; + \; Me_3SiF$$

$SF_2(OC_6H_4F)_2$, meta and para, are readily hydrolysed in air to produce HF and $S(=O)(OC_6H_4F)_2$ identified by their mass spectra.

$$SF_2(OC_6H_4F)_2 \; + \; H_2O \longrightarrow S(=O)(OC_6H_4F)_2 \; + \; 2HF$$

On heating above 100°C, $SF_2(OC_6H_4F)_2$ give SOF_2 and unidentified coloured masses.

$$SF_2(OC_6H_4F)_2 \xrightarrow{\Delta} S(O)F_2 \; + \text{ coloured mass}$$

$SF_4/ClC_6H_4OSiMe_3$ [ortho, meta and para] molar ratio 1:1

With an excess of SF_4, chlorophenoxytrimethylsilane reacts well below room temperature. The reaction at 20°C is vigorous and exothermic.

$$SF_4 \; + \; Cl\;C_6H_5OSiMe_3 \longrightarrow SF_3OC_6H_4Cl \; + \; Me_3SiF$$

ortho $ClC_6H_4OSF_3$ is very unstable and isolation of the compound is not possible and physical properties could not be recorded.

$SF_3OC_6H_4Cl$ are readily hydrolysed in moisture to give HF and $FS(=O)OC_6H_4Cl$, identified by mass spectrum.

$$SF_3OC_6H_4Cl(meta,para) + H_2O \longrightarrow FS(=O)OC_6H_4Cl + HF.$$

On heating above 80°C, $SF_3OC_6H_4Cl$ decomposes to SOF_2, SF_4 and unidentified coloured masses.

$$SF_3OC_6H_4Cl \xrightarrow{\Delta} S(=O)F_2 + SF_4 + \text{coloured mass}$$

$SF_3OC_6H_4Cl$ meta and para disproportionate at room temperature to $SF_2(OC_6H_4Cl)_2$ and SF_4.

$$SF_3OC_6H_4Cl \longrightarrow SF_2(OC_6H_4Cl)_2 + SF_4$$

$SF_4/Me_3SiOC_6H_4Cl$ [ortho, meta and para] molar ratio 1:2. The reaction between ortho-$ClC_6H_4OSiMe_3$ and SF_4 in a 2:1 molar ratio produces an unidentified coloured mass. SF_4 and $ClC_6H_4OSiMe_3$ (meta and para) in 1:2 molar ratios react at room temperature to give Me_3SiF and white solids identified as $SF_2(OC_6H_4Cl)_2$.

$$SF_4 + 2ClC_6H_4OSiMe_3 \longrightarrow SF_2(OC_6H_4Cl)_2 + 2Me_3SiF$$

$SF_2(OC_6H_4Cl)_2$,meta and para are hydrolysed in the atmosphere to HF and $S(=O)(OC_6H_4Cl)_2$, identified by mass spectrometry.

$$SF_2(OC_6H_4Cl)_2 \xrightarrow{H_2O} S(=O)(OC_6H_4Cl)_2 + 2HF$$

On heating above 80°C, $SF_2(OC_6H_4Cl)_2$ decompose to SOF_2 and an unidentified coloures mass.

$$SF_2(OC_6H_4Cl)_2 \xrightarrow{\Delta} S(O)F_2 + \text{coloured mass}$$

SF_4/$\underline{p}NO_2C_6H_4OSiMe_3$, molar ratio 1:1

With an excess of SF_4, $\underline{p}NO_2C_6H_4OSiMe_3$ reacts at room temperature to produce a reddish solid, identified as $SF_2(OC_6H_4NO_2\underline{p})_2$.

$$SF_4 + O_2NC_6H_4OSiMe_3 \longrightarrow SF_2(OC_6H_4NO_2\underline{p})_2 + Me_3SiF$$

The reddish solid is insoluble in CCl_4, H_2O, CCl_3F and CH_3CN. The mass spectrum shows a product $S(=O)(OC_6H_4NO_2\underline{p})_2$ presumably formed by the hydrolysis of $SF_2(OC_6H_4NO_2\underline{p})_2$. The compound $SF_2(OC_6H_4NO_2)_2$ characterized by elemental analysis. Because of the difficulty in getting the compound in a solution, an n.m.r. spectrum was not recorded.

SF_4/$\underline{p}CF_3C_6H_4OSiMe_3$, molar ratio 1:1.

Excess SF_4 and $\underline{p}CF_3C_6H_4OSiMe_3$ reacts readily at room temperature to produce Me_3SiF and a slightly coloured solid $SF_2(OC_6H_4CF_3)_2$, confirmed by its n.m.r. spectrum and by elemental analysis.

$SF_4 + Me_3SiOC_6H_4CF_3 \longrightarrow SF_2(OC_6H_4CF_3)_2 + Me_3SiF$

The compound hydrolysed slowly in air to HF and $S(=OC_6H_4CF_3)_2$, identified by mass spectroscopy.

$SF_2(OC_6H_4CF_3)_2 + H_2O \longrightarrow S(=O)(OC_6H_4CF_3)_2 + HF$

$SF_4/Me_3SiOC_6F_5$, molar ratio 1:1

With an excess of SF_4, pentafluorophenoxytrimethylsilane reacts at room temperature in six hours. After pumping off the volatiles SF_4 (excess) and Me_3SiF, a crystalline solid which sublimes at room temperature under vacuum is left in the vessel. The compound is confirmed by its ^{19}F n.m.r. spectrum, elemental analysis and infrared spectrum as $SF(OC_6F_5)_3$.

$SF_4 + Me_3SiOC_6F_5 \longrightarrow SF(OC_6F_5)_3 + Me_3SiF$

$SF(OC_6F_5)_3$ is hydrolysed in air to HF and an oily unidentified liquid.

$SF_4/1,2\text{-}C_6H_4(OSiMe_3)_2$ molar ratio 2:1

SF_4 and 1,2 bis(trimethylsiloxy)benzene react at room temperature after shaking for several hours to give a totally substituted SF_4 derivative - 70% yield.

$SF_4 + Me_3SiOC_6H_4OSiMe_3 \longrightarrow C_6H_4OOSOOC_6H_4 + Me_3SiF$

$C_6H_4OOSOOC_6H_4$ is a faintly yellowish coloured product. The compound $S(OOC_6H_4)_2$ has been crystallised from CCl_4.

$S(OOC_6H_4)_2$ hydrolyses in a moist atmosphere to catechol.

[illegible] arative stab[illegible] at room temperature based on

[illegible] rvations can be drawn as follows:

[illegible] > $pCH_3C_6H_4$[illegible] > [illegible]OSF_3

[illegible] lated to the [illegible] the [illegible]

[illegible] to be the [illegible]

Other than [illegible]

of the Si-OH [illegible]

DISCUSSION

[illegible]

[illegible] ervations [illegible] made,

while comparing [illegible] relative rate of [illegible]

in the [illegible]

[illegible]H_4OSF_3 > [illegible] > $pCH_3C_6H_4$[illegible] > [illegible]

$C_6H_5OSF_3$ > [illegible]$C_6H_4OSF_3$

[illegible] confirmed [illegible]

[illegible] is confirmed [illegible] present

[illegible] and is also believed to occur by the [illegible]

[illegible]

Of all the SF_3ORX compounds prepared the *ortho* substituted phenoxy sulfurtrifluorides are the least stable. Of the $SF_3ORX[X = oF, oMe, oCl]$ *ortho*-$ClC_6H_4OSF_3$ could not be obtained for physical studies. Their comparative stability at room temperature based on simple observations can be shown as follows:

$$\underline{o}FC_6H_4OSF_3 > \underline{o}CH_3C_6H_4OSF_3 > \underline{o}ClC_6H_4OSF_3$$

Steric factors related to the size of the substituent are presumed to be the reason for this instability.

Other than $\underline{o}FC_6H_4OSF_3$, $\underline{o}MeC_6H_4OSF_3$, $\underline{o}ClC_6H_4OSF_3$, all of the SF_3ORX compounds disproportionate at room temperature to $SF_2(ORX)_2$ and SF_4.

$$2SF_3ORX \longrightarrow SF_2(ORX)_2 + SF_4$$

It is observed that increasing temperature and impurities such as HF accelerate the disproportionation.

Although no quantitative study on the rate of disproportionation of the compounds SF_3ORX was made, from simple observation the relative rate of disproportionation is in the order:

$$\underline{m}FC_6H_4OSF_3 > \underline{m}ClC_6H_4OSF_3 > \underline{p}FC_6H_4OSF_3 > \underline{p}ClC_6H_4OSF_3$$

$$\underline{m}CH_3C_6H_4OSF_3 > \underline{p}CH_3C_6H_4OSF_3$$

Darragh reported an uncharacterized solid in his preparation of SF_3OPh [68]; the solid is confirmed in present work as $SF_2(OPh)_2$ and is also believed to occur by the disproportionation of SF_3OPh.

Since HF catalyses the disproportionation, the mechanism possibly involves the following ionic intermediates.

$$SF_3ORX \longrightarrow SF_3^+ + \bar{O}RX$$

$$\bar{O}RX + SF_3ORX \longrightarrow SF_2(ORX)_2 + F^-$$

$$\bar{F} + SF_3^+ \longrightarrow SF_4$$

If this is true a strong electron withdrawing group on the benzene ring should strongly favour ionisation of the type:

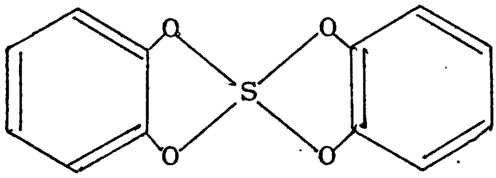
$$SF_3ORX \longrightarrow SF_3^+ + \bar{O}RX$$

The reactions of p-$NO_2C_6H_4OSiMe_3$ and p-$CF_3C_6H_4OSiMe_3$ with excess of SF_4 produce $SF_2(OC_6H_4X)_2$ where X=p-NO_2 or p-CF_3. The failure to obtain a compound of the type SF_3ORX[X=p-NO_2, p-CF_3] is probably because of their high rate of disproportionation to $SF_2(ORX)_2$.

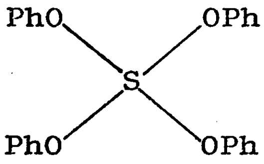
The compounds $SF_2(ORX)_2$ are in general more stable thermally than SF_3ORX irrespective of their physical state e.g. liquid or solid. This enhanced stability of the disubstituted derivatives of SF_4 is in common with cases where R is a fluoroalkyl group [70].

The reactions of $XC_6H_4OSiMe_3$ (where X= ortho, meta, para; Me, F, Cl) with SF_4 in the molar ratio of 3:1 or 4:1 have been studied but no tris or tetrakis substituted derivative of SF_4 obtained in these cases. $SF(OC_6F_5)_3$ is an unique example of the trisubstituted derivative of sulfur tetrafluoride. $(PhO)_3SF$ has been reported [64] but the characterization of the compound was not complete. $SF(OC_6F_5)_3$ is crystalline in nature. An X-ray crystal study would be of great interest.

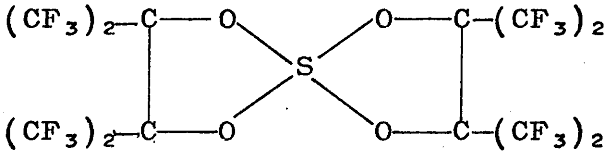
$S(O_2C_6H_4)_2$, bis-1,2-dioxybenzene ortho-sulfite is one of three compounds where sulfur is linked single bondedly to four oxygen atom. Previously reported ortho sulfites are tetraphenoxyorthosulfites [64] and perfluoropinacolate [71] prepared by the action of disodium perfluoropinacolate on sulfur dichloride.



bis-1,2-Dioxybenzeneorthosulfite

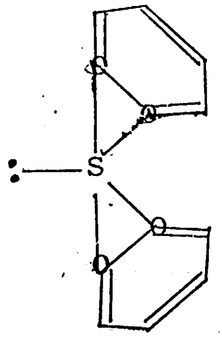


Tetraphenoxyortho-sulfite



Perfluoropinacolate

The structure of $S(OOC_6H_4)_2$ is not known. The analogous compound in PF_5 chemistry was prepared by reacting PF_5 with $(Me_3Si)_2OOC_6H_4$ and the geometry of the compound was confirmed as trigonalbipyramid by the ^{19}F n.m.r. spectrum with the single fluorine forced to occupy the equatorial position [72]. Although in $S(O_2C_6H_4)_2$, no helpful information on the geometry of the compound can be obtained by the ^1H n.m.r. spectrum, the geometry of the compound could be derived from a trigonal bipyramid where the lone pair of electrons occupy the equatorial position.



Possible structure of bis-1,2-dioxybenzene<u>ortho</u>sulfite.

^{19}F n.m.r. spectra

Introduction

The observed range of chemical shifts for fluorine nuclei are much larger than the range of hydrogen shifts; for example the ^{19}F resonance in the molecule UF_6 is at 955 ppm to the downfield of HF. These large chemical shifts arise because of the importance of paramagnetic terms for the electron localised on the fluorine nucleus.

Table IA ^{19}F Chemical Shifts in Binary Fluorides [75]

Compound	CCl_3F ppm	Compound	CCl_3F
NF_3	-146.5	CF_4	+66.6
ClF_3	-114.5, -2.5	BF_4^-	+149.5
BrF_3	+34.2	SiF_4	+161.8
PF_3	+36.3	GeF_4	177.5
AsF_3	+43.5	IF_5	-59.5, -17.3
SbF_3	+54.6	PF_5	+77.8
SF_4	-116.5, -69.5		
SeF_4	-62.5		
TeF_4	+27.1		

The importance of the paramagnetic effect arises from the presence of 'p' electrons in the fluorine atom which on molecule formation can depart considerably from spherical symmetry. The paramagnetic term will be negligible in the spherical fluoride ion where the paramagnetic effect is zero; whereas in the fluorine molecule (F_2) the paramagnetic effect is large with the result that the resonance of fluorine gas is 630 ppm to the downfield of HF. The magnitude of the effect is dependent on the degree of ionic character in the bond and this has been shown consistent with the observation of ^{19}F chemical shifts found in an extensive series of binary fluorides. These shifts are linearly dependent on the electronegativity Table-IA (Pauling) of the atom bonded to the fluorine [73].

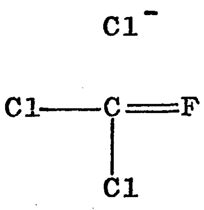
The ^{19}F chemical shift of nitrosyl fluoride, O=N-F has an exceptionally low value [-55 ppm from F_2 -428 ppm from CCl_3F] which is surprising in view of the predominantly ionic nature of the N-F bond [74]. The large paramagnetic contribution to the fluorine shielding has been explained by the presence of a low-lying electronic state of suitable symmetry for mixing with the ground state by the magnetic field. Thus the qualitative correlation between bond ionic character and fluorine chemical shifts is only valid if the molecules in a series have similar energy separation between the ground state and low lying excited electronic states.

In the halofluorocarbon derivatives the chemical shifts in the fluorine nuclei move in the opposite direction to that expected from electronegativity (Table 1) [75]

Table 1 [75]

Compounds	CF_4 ext
CH_3F	+210.0
CH_2F_2	+80.0
CHF_3	+18.0
CF_4	00
$CFCl_3$	-76.2
CF_2Cl_2	-60.2
CF_3Cl	-36.8
CF_4	00

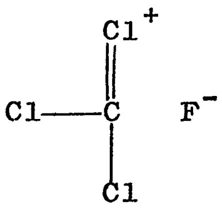
The ^{19}F shifts of the fluoromethanes (Table 1) follow the trend expected from electronegativity, where successive replacement of protons by fluorine atoms moves the ^{19}F shifts to lower field because of increased deshielding of the fluorine by an increasing inductive effect. The reverse trend of the chemical shifts in the case of chlorofluoromethanes has been explained by postulating the presence of double bonded structures and ionic species of the type:



$\mathrm{Cl{-}\overset{\overset{\displaystyle Cl^-}{}}{\underset{\underset{\displaystyle Cl}{|}}{C}}{=}F}$

(I)

and



$\mathrm{Cl{-}\overset{\overset{\displaystyle Cl^+}{\|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}\quad F^-}$

(II)

It is assumed that fluorine atoms are more able to form double bonds than chlorine atoms and type I structure plays a more important part than other structure in the molecule. Inductive effects are small in these molecules, hence double bonded structures of type I become the dominant shielding factor for the fluorine nuclei. This results in the C-F bonds decreasing in ionicity as the fluorine substitution decreases.

Changing the oxidation state of the element attached to the fluorine in binary fluorides usually results in more shielding of the fluorine nuclei (Table 2).

Table 2 [75]

Compound	F(CCl_3F)
PF_3	+26.7
PF_5	+78.3
SF_4	-62.0
SF_6	-48.0

This change has been attributed to the need for the use of higher energy 'd' orbitals in the higher valence state.

Table 3 The ^{19}F nmr parameters of the monoderivatives of SF_4

Compounds	Temp.	δF equatorial	δF axial	J_{FeFa} Hz	δFa-Fe
SF_3OPh [64]	R.T.	-30.5(t)	-79.1(d)	67.7	48.6
SF_3Ph [76]	-40°C	+25.8(t)	-72.2(d)	53	98
SF_3NMe_2 [22]	-100°C	-29 (t)	-58(d)	58	29
SF_3NEt_2 [23]	-84°C	-37.2(t)	-54.1(d)	62	16.9

Chemical shifts relative to CCl_3F, t = triplet, d = doublet, R.T. = Room temperature.

Table 4 The ^{19}F nmr parameters of SF_3ORX, reference CCl_3F (int)

Compound.	Temp.	δF eq.	δFax.	δC-F	J_{Fe-Fa} Hz	δFa-Fe
$SF_3OC_6H_4CH_3$(ortho)	R.T.	-31.2(t)	-76.2(d)	-	84	45
$SF_3OC_6H_4CH_3$(meta)	R.T.	-31.3(t)	-78.8(d)	-	76	47.5
$SF_3OC_6H_4CH_3$(para)	R.T.	-30.3(t)	-78.6(d)	-	72	48.3
$SF_3OC_6H_4Cl$ (para)	-20°C	-30.5(t)	-79.0(d)	-	75	49.5
$SF_3OC_6H_4Cl$ (meta)	-20°C	-31.0(t)	-79.2(d)	-	74	48.2
$SF_3OC_6H_4F$ (ortho)	R.T.	-31.4(t)	-77.4(d)	128	77	46
$SF_3OC_6H_4F$ (meta)	-36°C	-30.3(t)	-82.0 (d)	107.7	76	51.7
$SF_3OC_6H_4F$ (para)	-20°C	-30.1(t)	-78.8(d)	111	75	48.7

R.T. = Room temperature, t = triplet, d = doublet.

^{19}F spectra of SF_3ORX compounds

^{19}F nmr spectra are the most important tools in the characterization of the compounds SF_3ORX. The spectra consist of one doublet of intensity two and a triplet of intensity one arising from first order coupling between the two magnetically different fluorine atoms in trigonalbipyramid geometry. This is similar to the published spectra of other mono derivatives of SF_4 (Table 3). Other than $FC_6H_4OSF_3$ (<u>meta</u> and <u>para</u>) and $ClC_6H_4OSF_3$ (<u>meta</u> and <u>para</u>), the compounds SF_3ORX do not show exchange of fluorine atoms at room temperature. The spectra of $FC_6H_4OSF_3$ (meta) is discussed later in this chapter. Although the spectra of SF_3ORX compounds are consistent with trigonalbipyramid geometry, because of the geometry axial or equatorial substitution could not be distinguished from the ^{19}F nmr spectra. However, the evidence from the reported ^{19}F nmr spectra of R_2PF_3 and R_3PF_2 [77] indicate that the chemical shift of the axial fluorine atoms occurs downfield relative to the equatorial fluorine atoms. Accordingly an equatorial substitution is found here since the doublet of intensity two is at lower field than the triplet of intensity one. Gillespie's electron pair repulsion theory also suggests an equatorial substitution by a large group since that will experience less repulsion from other atoms. The geometry of the compound can then be described as a trigonalbipyramid where the lone pair and 'ORX' group occupy the equatorial position (Fig. 11).

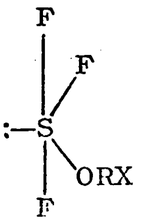


Fig. 11
Structure of SF_3ORX

Table 5 Chemical Shifts of monosubstituted fluorobenzenes. Reference CCl_3F

Substituents	δF ortho	δF meta	δF para	References
I	90.7	111.4	115.2	[75]
Br	108.5	111.6	116.3	[75]
Cl	116.7	111.9	116.4	[75]
F	139.9	110.9	120.4	[75]
OH	139	110.9	120.4	[75]
OMe	136.4	-	125.5	[75]
OEt	135.7	112.7	125.5	[75]
$OS(O)F_3$	129.4	108.7	112.3	[46]
OSF_3	128	107.7	111	this work
OSF_2	-	108.7	112	this work

C-F Chemical Shifts.

Substitution in the benzene molecule influences the *ortho*, *meta* and *para* positions to the substituents in different ways. The *ortho* position is influenced by a combination of inductive, resonance and steric effects and the *para* position mainly by resonance effects. Several workers have examined the ^{19}F nmr spectra of fluorobenzene derivatives in an attempt to obtain information about the electron distribution in aromatic systems [75]. In most cases the *ortho* substituted fluorine is the most shielded followed by the *para* and *meta* substituted fluorine atoms. The shielding of ^{19}F nucleus in the *ortho* fluorohalobenzenes decreases with the decrease in electronegativity of the halogen substituents in the series F, Cl, Br and I. This deshielding is said to arise from the Van der Waals interactions of the more bulky halogen atom with the adjacent fluorine atom inducing intermolecular electric effects.

The SF_3O group deshields fluorine atoms in all three positions but the *meta* and *para* fluorines are comparatively more de-shielded. According to the previous discussion the deshielding of the *meta* and *para* fluorine atoms indicates the SF_3O group imparts considerable electron withdrawing effect on the benzene ring.

Variable temperature ^{19}F nmr spectrum

Table 3 shows that apart from SF_3OPh, known ^{19}F nmr spectra of monoderivatives of SF_4 (other than fluoroalkyl derivatives) are temperature dependent. For SF_3OPh, the spectrum was not studied above 30°C but at room temperature non-equivalence of fluorine atoms was observed. In the present work, in a series of substituted aryloxysulfur trifluorides, it is found that the ^{19}F nmr spectra of $FC_6H_4OSF_3$ (<u>meta</u> and <u>para</u>), $ClC_6H_4OSF_3$ (<u>meta</u> and <u>para</u>) show different chemical shifts for non-equivalent fluorine atoms but that fine structure due to interaction between magnetically different fluorine atoms is not observed at 20°C. On cooling to -20°C to -30°C, coupling is observed. This observation is consistent with a slow exchange of fluorine atoms between the two sites of the trigonal bipyramidal structure. Apparently [55] this behaviour appears as an intermediate situation of a fast exchange system as in SF_4 where the coalescence temperature is -84°C but at -60°C the distinct signals without fine structure is observed for the two magnetically different fluorine atoms. At -60°C a slow exchange of the fluorine atoms continues.

In a recent investigation of SF_3NR_2 compounds, it was observed that impurity such as HF, present due to slight hydrolysis, could bring about collapse of the fine structure due to coupling between different types of fluorine atoms [78]. Anticipating this possibility, the present compounds were dried over dry NaF for several hours and were transferred to NMR tubes in a vacuum line by slow distillation.

The spectrum of liquid $FC_6H_4OSF_3$ between -30°C and +65°C (Fig A) confirm the slow exchange of the fluorine atoms of the liquid. It is assumed that other SF_3ORX compounds will also have temperature dependent ^{19}F nmr

THE 19F NMR SPECTRUM OF $mFC_6H_4OSF_3$
over the temperatures −30°C to +60°C

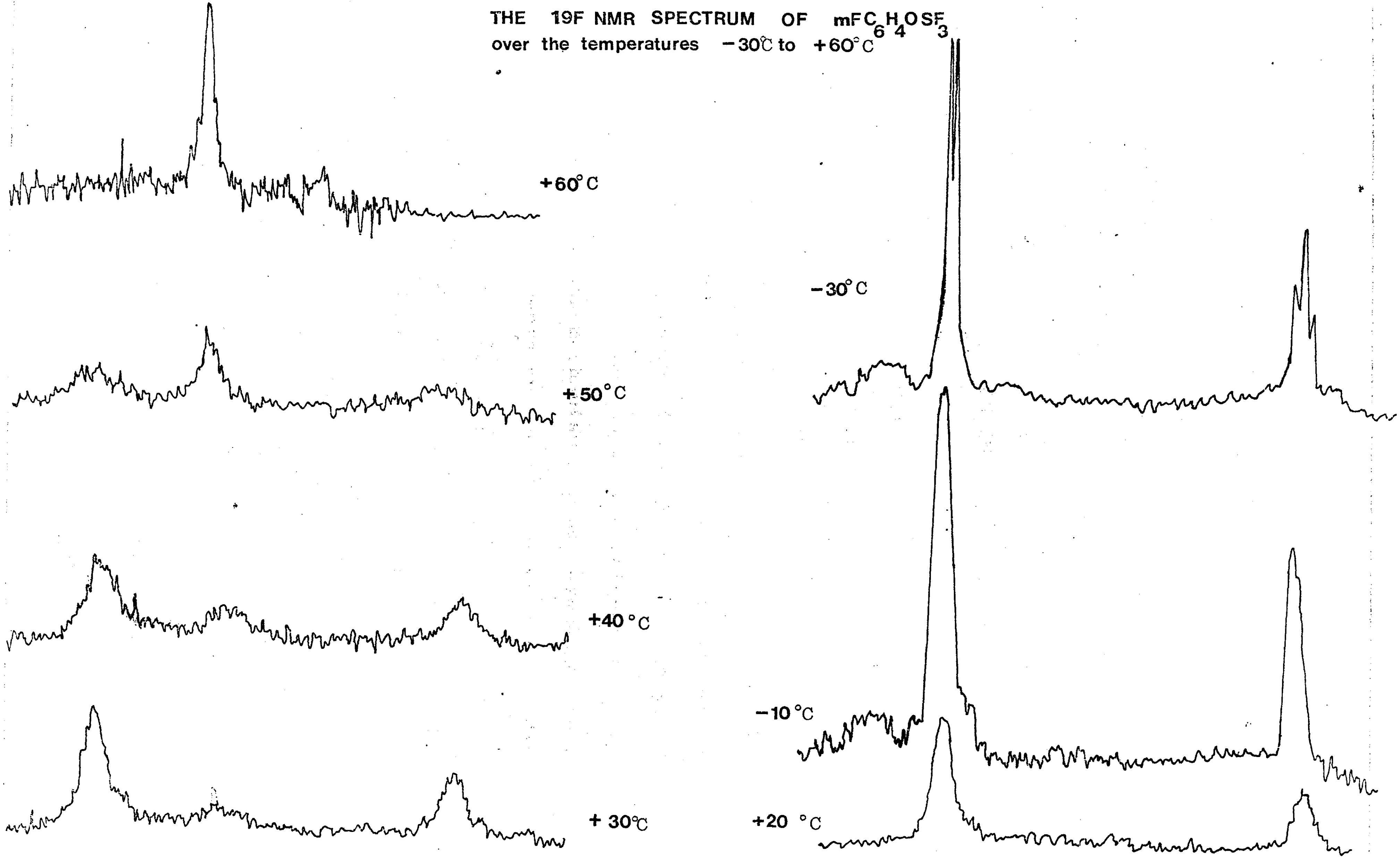


Fig - A

spectra but this has not been investigated.

The coalescence temperatures of $m\text{FC}_6\text{H}_4\text{OSF}_3$ in different dilution and in various solvents are given in Table 6.

Table 6

Dilution %	Solvent	*Coalescence temperatures
neat	-	-30°C
20	CCl_4	-10 to -8°C
20	CH_3CN	-10 to -8°C
20	CCl_3F	-10 to -8°C
50	CCl_4	+20°C
50	CH_3CN	+20°C
50	CCl_3F	+20°C

* Temperature at which spin coupling colapses

As is clear from the table, the coalescence temperature depends on the concentration but is apparently independent of the dielectric constant of the solvent which suggests an intermolecular mechanism for the exchange process.

The experiments on the ^{19}F nmr spectra at different concentrations of SF_4 [55] also indicate an intermolecular mechanism for the exchange process. Muetterties <u>et al</u> [55] have put forward a possible mechanism involving a fluorine bridge for this reaction. (Fig. 12).

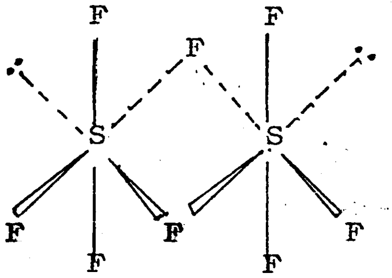


Fig. 11

Redington and Berney [79] in their study on low temperature infrared spectra of SF_4 proposed an intramolecular mechanism as in PF_5 [77] for the exchange process. However, a recent infrared investigation on SF_4 supported an intermolecular mechanism involving fluorine bridge [80].

The present compounds SF_3ORX, being mono derivatives of SF_4 might be expected to have a similar mechanism for the exchange process. Hence an intermediate dimer of the type (Fig. 11) is proposed for the intermolecular exchange mechanism of SF_3ORX compounds.

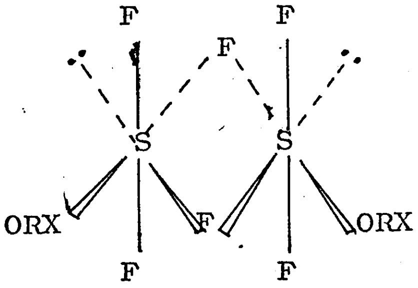


Fig. 12.

A further possibility - an ionic intermediate of the type $XROSF_4^-$ in the intermolecular exchange reaction cannot be ruled out particularly since HF [78] accelerates the exchange process. But in a conductivity measurements on a series of halogen fluorides ClF_3, BrF_3 and IF_5 (which demonstrate similar mechanism for fluorine exchange), the conductivities were found inconsistent with the rate of fluorine exchange [81]. Thus in halofluorides, the mechanism for fluorine exchange appears not to be through ionic intermediates. It is probable that the situation in SF_4 and in its derivatives is similar.

Table 7 ^{19}F Chemical shifts of $SF_2(ORX)_2$ compounds CCl_3F (int) reference

Compound	Temp.	δSF_2	δCF	Reference
1. $SF_2(OC_6H_5)_2$	R.T.	-67.4 (b.s)	-	[64]
2. $SF_2(OC_6H_4CH_3\underline{p})_2$	R.T.	-66.3 (b.s)	-	
3. $SF_2(OC_6H_4CH_3\underline{m})_2$	R.T.	-67.7 (b.s)	-	
4. $SF_2(OC_6H_4Cl\text{-}\underline{p})_2$	R.T.	-71.2 (b.s)	-	
5. $SF_2(OC_6H_4Cl\underline{m})_2$	R.T.	-70.0 (b.s)	-	
6. $SF_2(OC_6H_4F\underline{p})_2$	R.T.	-69.0 (b.s)	+112	
7. $SF_2(OC_6H_4F\underline{m})_2$	R.T.	-69.2 (b.s)	+108.7	
8. $SF_2(OC_6H_4CF_3)_2$	R.T.	-72.0 (b.s)	δCF_3 + 62 ppm	

b.s = broad singlet

^{19}F Spectra of $SF_2(ORX)_2$ Compounds

The compounds $SF_2(ORX)_2$ show a single signal for the SF_2 fluorine atoms. The spectra are in general broad in nature which suggest some sort of exchange continuing at room temperature. For $SF_2(OC_6H_4F)_2$- meta and para, the spectra at room temperature are broad, but on cooling to -30°C give sharp signals. This change of shape of the spectrum with change of temperature is consistent with an intermolecular exchange of fluorine atoms as in SF_4 and possibly in $SF_3(OR)$ derivatives.

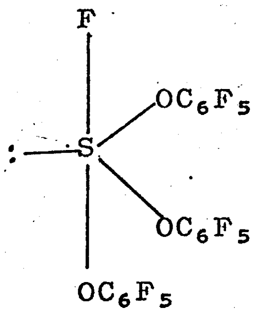
By comparison with the spectra of SF_3ORX derivatives the chemical shifts of the fluorine atoms indicate that the two fluorine atoms are in axial positions of a trigonalbipyramid geometry. The upfield shift of the axial fluorine atoms from SF_3ORX compounds (table-4) may be due to the difference of electronegativities of a fluorine atom and ORX group. Of the different $SF_2(ORX)_2$ compounds, maximum deshielding of SF_2 fluorine atoms occurs in $SF_2(OC_6H_4CF_3)_2$ where the trifluoromethyl group applies a strong electronwithdrawing effect to the oxygen atom. This shift is consistent with electronegativity correlations. The other compounds in general agree with the nature of the substituents and their electronwithdrawing capabilities with the deshielding of fluorine atoms. Chemical shifts of the C-F fluorines are discussed already. The CF_3 in $SF_2(OC_6H_4CF_3)_2$ shows a single fluorine signal at +62 ppm ($Me_3SiOC_6H_4CF_3$ $CF_3 = + 61.00$).

$SF(OC_6F_5)_3$

The ^{19}F Chemical Shifts

Compound	Solvent	Temp.	δSF	CF
$SF(OC_6F_5)_3$	CCl_4	R.T.	-67.4	+152(ortho) +155.2(para) +162.4(meta)

The chemical shift of the SF fluorine atom in $SF(OC_6F_5)_3$ is consistent with an axial fluorine in trigonal bipyramid by comparison with the shifts of the axial fluorins of $SF_2(OC_6H_4X)_2$. Discussion on C_6F_5 group is given in Chapter II.



Proposed structure of $SF(OC_6F_5)_3$

Table 8

^1H NMR Spectra

Compounds	Temp	C_6H_4	δH
1. $SF_3OC_6H_4CH_3$(ortho)	R.T.	-6.8(m)	-1.95
2. $SF_3OC_6H_4CH_3$(meta)	R.T.	-7.0(m)	-2.1(b.s)
3. $SF_3OC_6H_4CH_3$(para)	R.T.	-6.9(b.s)	-1.95
4. $SF_3OC_6H_4Cl$(para)	R.T.	-7.25(quartet A_2B_2)	
5. $SF_3OC_6H_4Cl$(meta)	R.T.	-7.3(m)	
6. $SF_3OC_6H_4F$(ortho)	R.T.	-7.3(m)	
7. $SF_3OC_6H_4F$(meta)	R.T.	-7.38(m)	
8. $SF_3OC_6H_4F$(para)	R.T.	-7.16(quartet A_2B_2)	
9. $SF_2(OC_6H_4CH_3m)_2$	R.T.	-7.01(b.s.)	-1.96
10. $SF_2(OC_6H_4CH_3p)_2$	R.T.	-6.9 (b.s.)	-2.1
11. $SF_2(OC_6H_4Clp)_2$	R.T.	-7.28(quartet A_2B_2)	
12. $SF_2(OC_6H_4Clm)_2$	R.T.	-7.38(m)	
13. $SF_2(OC_6H_4Fp)_2$	R.T.	-7.05(quartet A_2B_2)	
14. $SF_2(OC_6H_4Fm)_2$	R.T.	-7.3(m)	
15. $SF_2(OC_6H_4CF_3p)$	R.T.	-7.4 (quartet A_2B_2)	

m = multiplet, b.s = broad singlet

For compounds 1, 2, 3, 9 and 10 the chemical shifts at -1.95 ppm, -2.1ppm -1.95 ppm, -1.96ppm and 2.1 ppm are due the CH_3 group attached to the benzene ring. The other chemical shifts are typical aromatic protons.

In a series of either SF_3O or SF_2 compounds, the change of the chemical shifts is apparently solely due to the nature of the substituents on the benzene ring. The electronegative elements or group deshields the protons where CH_3 being electron releasing group increases the shielding of the protons.

Compound $S(O_2C_6H_4)_2$ Room Temp. $\delta H=-6.95$ (b) T.M.S. ext. A single peak at -6.95 ppm is consistent with aromatic protons. The spectrum does not give any information on the structure of the compound.

Infrared spectra: SF_3ORX compounds

The infrared spectra of SF_3ORX compounds do not have much value for characterisation or for determining structure. The aromatic group and the probable low symmetry of the molecules make the spectra complex with many bands. An attempt has been made to assign some of the more important bands including νC-H, νC=C νCOS and νS-F. Full details of the spectra are given in the experimental section.

C-H Stretching Modes:

All of the compounds show a medium to weak absorption near 3000 cm^{-1} which are assigned to C-H stretching modes.

The absorptions at 2930 cm^{-1} and 2873 cm^{-1} in $SF_3OC_6H_4CH_3$(meta) and at 2924 cm^{-1} in $SF_3OC_6H_4CH_3$(para) are assigned to the CH_3 group of the benzene ring.

Table 9

Compounds	frequencies cm^{-1}	Assignments
1. $SF_3OC_6H_4CH_3$(meta)	3075, 3030, 2930, 2873	C-H ring stretching CH_3
2. $SF_3OC_6H_4CH_3$(para)	3075, 3037 2924	C-H ring '' CH_3
3. $SF_3OC_6H_4Cl$(meta)	3098, 3076	C-H ring ''
4. $SF_3OC_6H_4Cl$(para)	3131, 3098	C-H ring ''
5. $SF_3OC_6H_4F$(ortho)	3108, 3074	C-H ring ''
6. $SF_3OC_6H_4F$(meta)	3086 (br)	C-H ring ''
7. $SF_3OC_6H_4F$(para)	3121, 3095	C-H ring ''

δ C=C ring skeletal modes

An aromatic group absorbs in the region of 1600 cm^{-1} to 1500 cm^{-1} for its ring skeletal stretching modes [93]. Absorptions near 1600 cm^{-1} to 1500 cm^{-1} are prominent in all the compounds. The following assignments are made for ring skeletal stretching modes.

Table 10

Compound	δC=C ring cm^{-1}
$SF_3OC_6H_4CH_3$(para)	1595, 1495
$SF_3OC_6H_4CH_3$(meta)	1618, 1585
$SF_3OC_6H_4Cl$(meta)	1621, 1521
$SF_3OC_6H_4Cl$(para)	1600, 1515
$SF_3OC_6H_4F$(ortho)	1616,1600,1493
$SF_3OC_6H_4F$(meta)	1607, 1475
$SF_3OC_6H_4F$(para)	1601, 1500.

An electronegative substitution on the benzene ring appears to shift the bands to higher frequency. However an exception is found in the case of <u>m</u>$CH_3C_6H_4OSF_3$

COS <u>Stretching Modes</u>: Absorptions near 1200 cm^{-1} are prominent in all the compounds. COS groups are reported to have absorption in this region [82] and assignments are made on that basis.

<u>Table 11</u>

Compounds	νCOS cm^{-1}
$SF_3OC_6H_4CH_3$(<u>meta</u>)	1223
$SF_3OC_6H_4CH_3$(<u>para</u>)	1225
$SF_3OC_6H_4Cl$(<u>meta</u>)	1261
$SF_3OC_6H_4Cl$(<u>para</u>)	1241
$SF_3OC_6H_4F$(<u>ortho</u>)	1250
$SF_3OC_6H_4F$(<u>meta</u>)	1244
$SF_3OC_6H_4F$(<u>para</u>)	1239

S-F <u>Vibrational Modes</u>: On the basis of the published infrared spectra of CF_3SF_3 [83], SF_5X [84], $SF_3C_6H_5$ [76], the following strong absorptions are assigned to S-F vibrational modes.

Table 12

Compound	S-F Vibrational Modes cm^{-1}	Reference
$SF_3OC_6H_5$	845	[64]
$SF_3C_6H_5$	807	[76]
SF_3NMe_2	993,769	[22]
SF_3CF_3	851, 755, 711	[83]
$SF_3OC_6H_4CH_3$ (<u>para</u>)	905, 825, 620	this work
$SF_3OC_6H_4CH_3$ (<u>meta</u>)	920, 811, 622	this work
$SF_3OC_6H_4Cl$ (<u>para</u>)	907, 765, 639	this work
$SF_3OC_6H_4Cl$ (<u>meta</u>)	928, 756, 650	this work
$SF_3OC_6H_4$ (<u>ortho</u>)	909, 800, 651	this work
$SF_3OC_6H_4F$(<u>meta</u>)	953, 811, 663	this work
$SF_3OC_6H_4F$(<u>para</u>)	907, 765, 639	this work

Of the three vibrational modes, the first two are assigned to asymmetric and symmetric stretching modes and the third one as a deformation mode.

<u>$SF_2(ORX)_2$ Compounds:</u>

In $SF_2(ORX)_2$ compounds, absorptions at about 3000 cm^{-1} (medium), 1600 cm^{-1}, 1500 cm^{-1} (strong), 1200 cm^{-1} (s), 800 cm^{-1} to 600 cm^{-1} (s) are assigned as discussed previously to C-H, C=C ring skeletal, COS and S-F vibrational modes respectively. The S-F vibrational modes are assigned on the observation of the changes after hydrolysis. Detailed infrared spectra are given in the experimental section.

Table 13 Assignments of some bands (IR) of $SF_2(ORX)_2$ compounds.

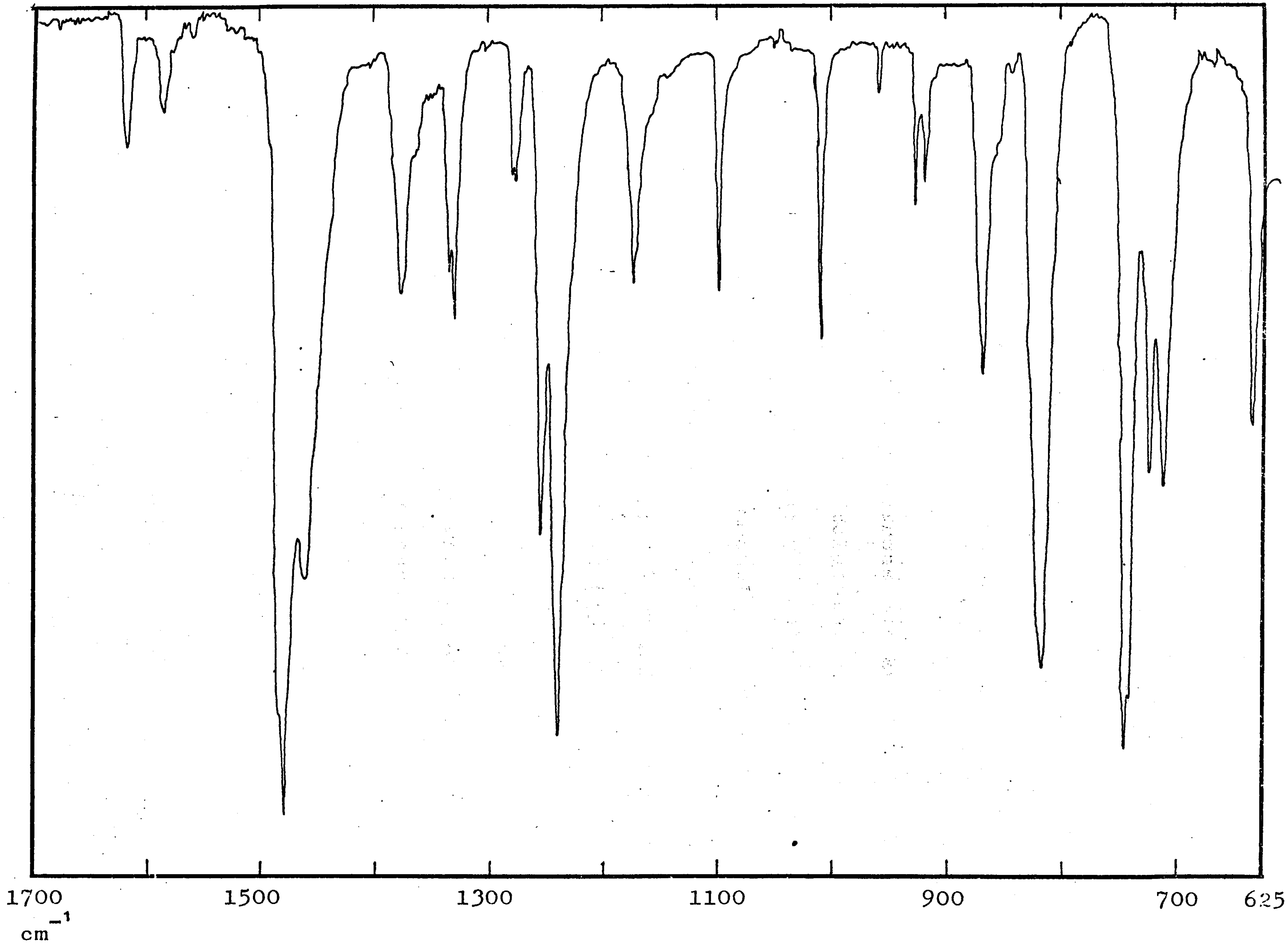
Compound	νC-H cm^{-1}	νC=C ring cm^{-1}	νCOS cm^{-1}	νS-F cm^{-1}
$SF_2(OC_6H_4CH_3\underline{m})_2$	3060	1615, 1585	1230	815, 685
$SF_2(OC_6H_4CH_3\underline{p})_2$	3038	1500	1170	825, 680
$SF_2(OC_6H_4Cl\underline{m})_2$	3102, 3072	1602, 1521	1258	803, 621
$SF_2(OC_6H_4Cl\underline{p})_2$	3133, 3110	1600, 1515	1245	808, 647
$SF_2(OC_6H_4F\underline{m})_2$	3100, 3085	1606, 1487	1249	806, 666
$SF_2(OC_6H_4F\underline{p})_2$	3123, 3084	1599, 1494	1232	811, 618
$SF_2(OC_6H_4NO_2\underline{p})_2$	3110, 3085	1615, 1582	1235	780, 695

Compound $S(OOC_6H_4)_2$:

The compound $S(O_2C_6H_4)_2$ has absorptions due to √C-H at 3078 cm^{-1} and 3030 cm^{-1}, √C=C ring at 1619 cm^{-1} (s) and 1585 cm^{-1} (m), and strong bands at 1242 cm^{-1}, 1100 cm^{-1}, 870 cm^{-1}, 820 cm^{-1}, 749 cm^{-1} and 725 cm^{-1} which may be due to COS and S-O vibrational modes.

$(C_6F_5O)_3SF$:

Absorptions at 1653 cm^{-1} and 1518 cm^{-1} (v.s.) are assigned to the √C=C ring modes and very strong absorption at 999 cm^{-1} to √C-F modes.



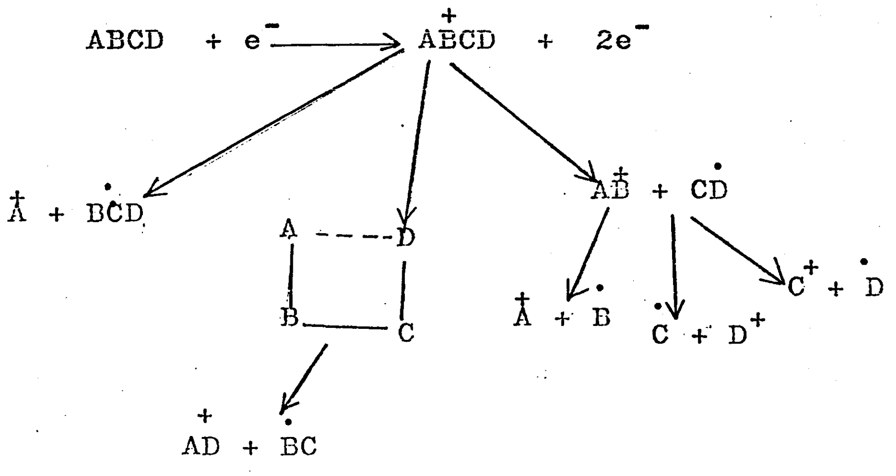
Infrared Spectrum Of $C_6H_4OOSOOC_6H_4$ (Nujol)

Mass Spectrum: General Discussion

When a molecule M is bombarded by electrons of moderate energy, ionization occurs as shown:

$$M + e^- \longrightarrow M^+ + 2e^-$$

This will occur when the bombarding electron has an energy equal to or higher than the ionization potential of the molecule [85]. It is considered that any one of the valence electrons has an equal probability of being removed from the molecule. The excess energy is then distributed over the molecule. When it is concentrated in sufficient amount in any bond, then that bond may break. The electron energies commonly used in mass spectrometers (70 e.v.) are usually far in excess of molecular ionization potentials (15 e.v. for organic species) in order to obtain reproducible spectra. Such high energies must cause ruptures of many bonds in a polyatomic molecule, mass spectra are therefore rather complex and consist of many peaks corresponding to the large number of different fragments which can be formed from any one molecule. Some processes which could occur by an electron impact on the hypothetical molecule ABCD are shown below.



Each bond cleavage leads to a positive fragment and a neutral one. The latter may be a radical or uncharged molecule. The principal ion fragment peaks in the mass spectrum of a particular polyatomic molecule should correspond to the most stable ion products of the most favourable reaction pathways. The factors that can stabilize an ionic product include the following:

(1) electron sharing from a neighbouring group such as in an amine

$$\overset{+}{C}H_2 - NH_2 \longleftrightarrow CH_2 = NH_2$$

This occurs most commonly, where there is a hetero atom that contains non-bonding outer shell electrons, such as nitrogen, or oxygen or sulfur.

$$R'-CH_2-\overset{+}{O}-R \longrightarrow R' + CH_2=\overset{+}{O}-R$$

$$R-CH_2-\overset{+}{O}-R \longrightarrow R'-CH_2-O+R^+$$

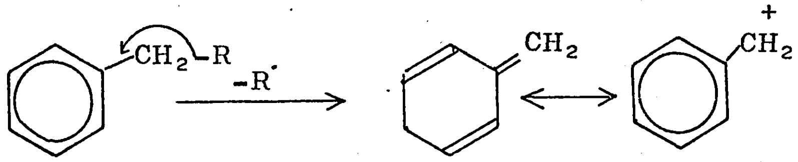
This stabilization by electron sharing from the hetero atoms is generally in the order of their Lewis base strengths, that is

$$N > S > O > Cl \quad [86]$$

(2) A resonance effect such as in allyl cation

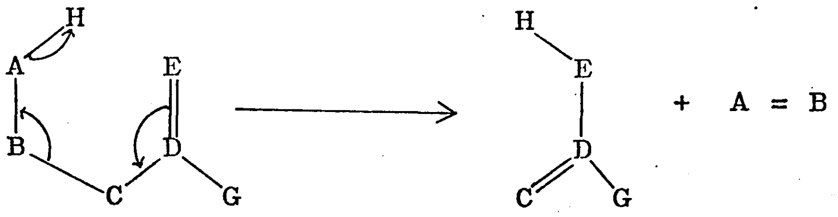
$$\overset{+}{C}H_2 - CH = CH_2 \longleftrightarrow CH_2 = CH_2 - \overset{+}{C}H_2$$

In the spectra of substituted aromatic compounds, resonance stabilizes the benzyl ion.



(3) Inductive effects such as in the tert-butyl carbonium ion. In addition to the influence of ion stabilization, inductive release and withdrawal of electrons as well as polarizability can markedly influence bond cleavages.

Rearrangements usually occur with the simultaneous rupture of more than one bond. This is only energetically feasible when the energy demand of such a fragmentation is balanced by the simultaneous formation of particles of low energy content i.e. neutral molecules. Many molecules achieve this by the formation of as many new bonds as are broken. In most cases this accompanied by the migration of a hydrogen atom from one part of the molecule to another. The most common type of rearrangement involves the intramolecular migration of hydrogen atoms in molecules containing heteroatoms [87]. The general scheme of these 'McLafferty type' rearrangements are illustrated below. The atoms A, B, C. D, and E, and the group G can vary widely as long as the conditions of the multiple bond between D and E, and the availability of γ-hydrogen are fulfilled.



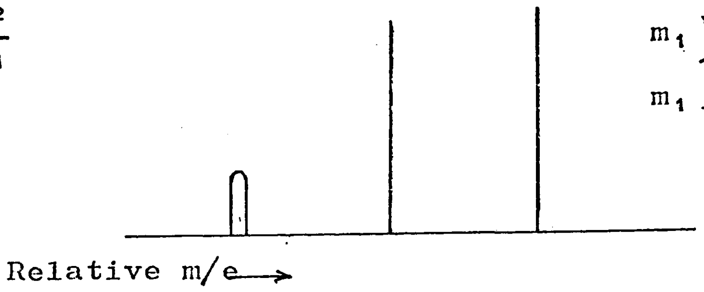
Compounds exhibiting McLafferty-type rearrangements include ketones, aldehydes, amides and substituted aromatic systems.

Metastable peaks: Some of the ions found in the ionization chamber of the mass spectrometer are metastable. They are sufficiently stable to be withdrawn in large numbers from the ionization chamber. but their half life is only of the order of 10^{-6} sec and many of them dissociate during their passage to the collector. While some of these ions of mass m_1, say reach the collector without decomposition, others decompose to give an ion of m_2, before leaving the chamber, Peaks corresponding to both the initial and final masses, (m_1 and m_2) of the metastable transition will therefore appear in the mass spectrum. The metastable peak is observed as a weak diffuse peak, generally not located at an integral mass number. It arises because some of the ions are initially accelerated as mass M_1 but after the decomposition they are accelerated as m_2. As a result the particles are not recorded as m_1 or m_2 but as a broad 'metastable peak' at m^* Where

$$m^* = \frac{m^2}{m_1}$$

$m_1 \rangle m_2$

$m_1 \rightarrow m_2 + m_3$



The assignment of a metastable peak to two other peaks in the spectrum is very useful since it can then be assumed with reasonable certainty that the fragment of mass m_2 arises in a one step decomposition from the species of mass m_1. Further the indication of such a process may be taken as an indication that a particular group m_3 exists as an entity in the molecule m_1. In short metastable transitions permit a direct observation of an actual fragmentation process.

Mass Spectra of SF_3ORX Compounds

Table 14

p$CH_3C_6H_4OSF_3$: 196$\overset{+}{M}$ 28.57, 177 $SF_2OC_6\overset{+}{H}_4CH_3$ 0.2, 158 $SFOC_6\overset{+}{H}_4CH_3$ 14.28, 107 $OC_6\overset{+}{H}_4CH_3$ 100, 91 $C_6\overset{+}{H}_4CH_3$ 28.57, 89 $S\overset{+}{F}_3$ 66.6, 70 $S\overset{+}{F}_2$ 26.6, 51$S\overset{+}{F}$ 73.3

m$CH_3C_6H_4OSF_3$: 196$\overset{+}{M}$ 24.6, 177 $SF_2OC_6\overset{+}{H}_4CH_3$ 2.24, 158 $SFO\overset{+}{C}_6H_4CH_3$ 3.37, 107 $OC_6\overset{+}{H}_4CH_3$ 100 91 $C_6\overset{+}{H}_4CH_3$ 79.7, 89 $S\overset{+}{F}_3$ 78.15, 70 $S\overset{+}{F}_2$ 21.91, 51 $S\overset{+}{F}$ 57.30

m$ClC_6H_4OSF_3$: 216$\overset{+}{M}$ 8.1, 197 $SF_2\overset{+}{O}C_6H_4Cl$ 3.0, 178 $SFO\overset{+}{C}_6H_4Cl$ 2.1, 159 $SOC_6H_4\overset{+}{C}l$ 2.75, 127 OC_6H_4Cl 100 111 C_6H_4Cl 71, 89 $S\overset{+}{F}_3$ 35, 70 $S\overset{+}{F}_2$ 5, 51 $S\overset{+}{F}$ 4

p$ClC_6H_4OSF_3$: 216$\overset{+}{M}$ 8.5, 197 $SF_2OC_6H_4Cl$ 7.1, 178 $SFOC_6\overset{+}{H}_4Cl$ 4.0, 159 $SOC_6H_4\overset{+}{C}l$ 3.0, 127 $OC_6\overset{+}{H}_4Cl$ 100, 111 $C_6\overset{+}{H}_4Cl$ 93, 89 $S\overset{+}{F}_3$ 44, 70 $S\overset{+}{F}_2$ 6, 51 $S\overset{+}{F}$ 4

o$FC_6H_4OSF_3$: 200$\overset{+}{M}$ 17.2, 181 $SF_2OC_6H_4F$ 5.1, 162 $FC_6H_4O\overset{+}{S}F$ 1.1, 143 $SOC_6\overset{+}{H}_4F$ 0.7, 111 $FC_6\overset{+}{H}_4O$ 100, 95 $FC_6\overset{+}{H}_4$ 64, 59 $S\overset{+}{F}_3$ 62.3, 70 $S\overset{+}{F}_2$ 7.5, 51 $S\overset{+}{F}$ 6.1

m$FC_6H_4OSF_3$: 200$\overset{+}{M}$ 9.16, 181 $SF_2\overset{+}{O}C_6H_4F$ 6.25, 162 $SFOC_6\overset{+}{H}_4F$ 2.50 143 $SOC_6\overset{+}{H}_4F$ 2.75, 111 $OC_6\overset{+}{H}_4F$ 100, 95 $C_6\overset{+}{H}_4F$ 75, 89 $S\overset{+}{F}_3$ 35, 70 $S\overset{+}{F}_2$ 4.16, 51 $S\overset{+}{F}$ 3.41

p$FC_6H_4OSF_3$: 200$\overset{+}{M}$ 9.48, 181 $SF_2OC_6\overset{+}{H}_4F$ 13.7, 162 $SFO\overset{+}{C}_6H_4F$ 8.16. 143 $SO\overset{+}{C}_6H_4F$ 3.7, 111 $OC_6\overset{+}{H}_4F$ 100, 95 $C_6\overset{+}{H}_4F$ 91.8, 89 $S\overset{+}{F}_3$ 42.8, 70 $S\overset{+}{F}_2$ 5.1, 51 $S\overset{+}{F}$ 4.1.

Metastable Peaks	m^*	m_1	m_2
$SF_3OC_6H_4CH_3$(para + meta)	58.41	196	107
$SF_3OC_6H_4F$ (ortho, meta + para)	61.6	200	111
$SF_3OC_6H_4Cl$ (meta + para)	76.4	216	117

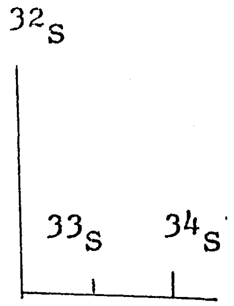
m^* = found and calculated values.

Discussion of the mass spectra of SF_3ORX Compounds

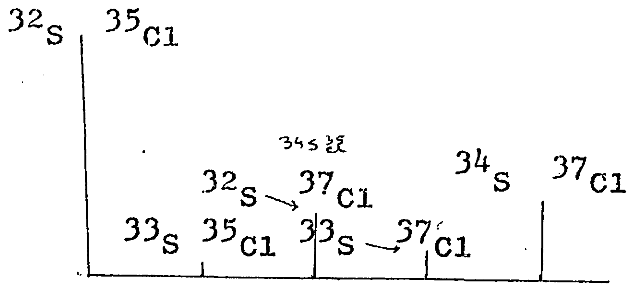
The compounds of SF_3ORX while relatively involatile have sufficient vapour pressure for mass spectra to be observed using a cold inlet for the mass spectrometer although as SF_3ORX compounds disproportionate at room temperature to SF_4 and $SF_2(ORX)_2$, in a cold inlet system SF_4 and its fragments dominate the mass spectra. However using a direct probe the SF_3ORX compounds give mass spectra which unequivocally characterise the materials. $SF_2(ORX)_2$ decomposed in the heated inlet or in the atmosphere when applied to the probe directly. The spectra in the latter case show only the diaryl sulfite resulting from hydrolysis.

$$(ArO)_2SF_2 + H_2O \longrightarrow (ArO)_2SO + 2HF$$

Mass measurements have not been made for SF_3ORX compounds, but the spectra are highly characteristic as they give the standard sulfur isotopic patterns. For elemental sulfur, the distribution of sulfur isotopes is 95.1% ^{32}S, 0.74% ^{33}S, 4.2% ^{34}S, and 0.16% ^{36}S. The latter isotope ^{36}S is not usually observed, but the others are readily identified. The spectra of the chlorophenoxysulfur trifluoride are further complicated by chlorine isotope patterns, the isotopic abundances being 75% ^{25}Cl and 25% ^{37}Cl. In these compounds the abundances quoted for fragments containing sulfur and chlorine refer to the $^{32}S^{35}Cl$ species and those containing chloride atoms refer to the ^{35}Cl species.



Sulfur pattern



S-Cl pattern

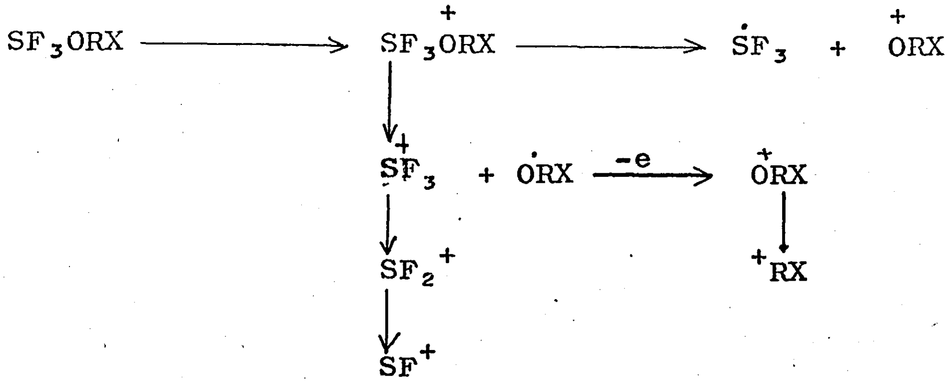
The mass spectral data of the aryloxysulfur trifluorides are given in table-14. The relative abundance of the molecular ion is moderately high in comparison with the other fragments. The increased stabilization of the parent ion of the aryloxysulfur trifluorides probably arises from the ease of withdrawal of the positive charge by the mesomeric effect of the benzene rings.

Metastable peaks involve the following transition in all the SF_3ORX compounds.

$$SF_3ORX \xrightarrow{-SF_3} \overset{+}{S}F_3 + \dot{O}RX, \quad \dot{S}F_3 + \overset{+}{O}RX$$

These metastable peaks and the relative abundance of $XR\overset{+}{O}$ and $SF_3{}^{+}$ ions strongly indicate that the breakdown of the parent ion involves the cleavage of the S-O bond and not the C-O bond. The same observation was made in $S(O)F_3ORX$ compounds [92]. The mesomeric release of electrons from Me, F or Cl to the aromatic ring would appear to stabilize the $\overset{+}{O}RX$ ion by neutralizing the charge.

The metastable peaks and mass spectral data indicate the following mechanism for major breakdown of ions.



and so on

Compound $S(O_2C_6H_4)_2$

248M 2.5, 172 $C_6H_4O_2\overset{+}{S}O_2$ 1.25, 156 $C_6H_4O\overset{+}{O}$ 509.84, 140 $C_6H_4\overset{+}{O}OS$ 51.5, 108 $C_6H_4\overset{+}{O}O$ 100, 92 $C_6\overset{+}{H}_4O$ 23.43, 80 $\overset{+}{C}_5H_4O$ 100, 64 $\overset{+}{C}_5H_4$ 43.75

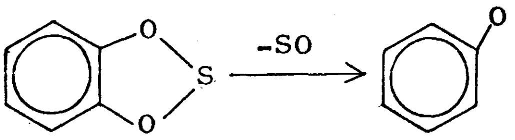
Metastable peaks

m^*	m_1	m_2
60.45	140	92
44.52	92	64

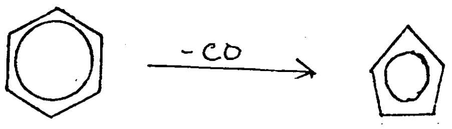
m^* = found and calculated values.

The parent ion and the fragments such as $C_6H_4O_2S\overset{+}{O}_2$, $C_6H_4OOS\overset{+}{O}$, $C_6\overset{+}{H}_4OO$, of the parent ion strongly support the proposed structure of the compound. The fragmentation pattern is also a strong indication of the monomeric nature of the compound.

The metastable peaks correspond to the following transitions:

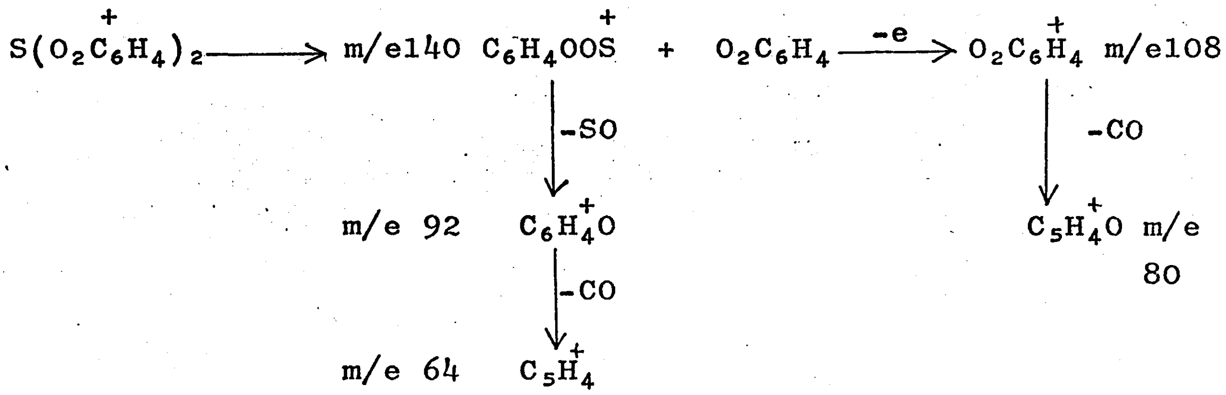


140 m/e 90 m/e



92 m/e 64

The metastable peaks and relative abundances of ions suggest the following mechanism for the major breakdown.



The transition between m/e 108 and m/e 80 is not accompanied by metastable peaks, but the absence of a peak corresponding to $C_6H_4^+$ and the presence of $C_5H_4\overset{+}{O}$ indicate the possible elimination of CO in the transition state.

$SF(OC_6F_5)_3$

The mass spectrum of the compound $SF(OC_6F_5)_3$ does not produce any useful information. The only identifiable peak is $O\overset{+}{C}_6F_5$, others are peaks containing fluorocarbons.

EXPERIMENTAL

Preparations were carried out in pyrex vessels fitted with teflon stopcocks. The silyl compound was pipetted into the reaction vessel under an atmosphere of dry nitrogen. The reaction vessel was then cooled to -196°C and the stoichiometric amount of SF_4 required for reaction was weighed in via the vacuum line. Liquid products were distilled where possible from the reaction vessel in vacuum and involatile liquids and solids were transferred in the dry box.

Reagents:

Silyl compounds were prepared by standard methods outlined in the table. Many of the silyl ethers have not been previously reported in the literature. The silyl ethers were identified by ^1H n.m.r. All liquid samples were stored over 4A molecular sieves until required. Me_3SiCl was obtained from Midland silicones; alcohols and non-fluorine containing phenols were obtained from B.D.H., pFC_6H_4OH, mFC_6H_4OH, oFC_6H_4OH, C_6H_5OH and $CF_3C_6H_4OH$ were obtained from Pierce Chemical Co. SF_4 was obtained from Peninsular Chem. Research. The gas was purified where necessary by distilling over dry NaF.

TABLE

Preparation of Silicon Compounds

Compound	Method	Reference	B.pts.
Me_3SiORh	$Me_3SiCl/PhOH$	88	182-3/760 mm
$\underline{p}Me_3SiOC_6H_4CH_3$	$Me_3SiCl/\underline{p}HOC_6H_4Me$	-	196-8/758 mm
$\underline{m}Me_3SiOC_6H_4CH_3$	$Me_3SiCl/\underline{m}HOC_6H_4Me$	-	195-7/742 mm
$\underline{o}Me_3SiOC_6H_4CH_3$	$Me_3SiCl/\underline{o}HOC_6H_4Me$	-	194-6/755 mm
$\underline{p}Me_3SiOC_6H_4Cl$	$Me_3SiCl/\underline{p}HOC_6H_4Cl$	-	204-5/761 mm
$\underline{m}Me_3SiOC_6H_4Cl$	$Me_3SiCl/\underline{m}HOC_6H_4Cl$	-	212-3/750 mm
$\underline{p}Me_3SiOC_6H_4F$	$Me_3SiCl/\underline{p}HOC_6H_4F$	-	175-6/741 mm
$\underline{m}Me_3SiOC_6H_4F$	$Me_3SiCl/\underline{m}HOC_6H_4F$	-	178-9/750 mm
$\underline{o}Me_3SiOC_6H_4F$	$Me_3SiCl/\underline{o}HOC_6H_4F$	-	179-180/760 mm
$\underline{p}Me_3SiOC_6H_4NO_2$	$(Me_3Si)_2NH/\underline{p}HOC_6H_4NO_2$	-	89-90/0.2 mm
$\underline{p}Me_3SiOC_6H_4CF_3$	$(Me_3Si)_2NH/\underline{p}HOC_6H_4CF_3$	-	80-81/0.1 mm
$Me_3SiOC_6F_5$	Me_3SiCl/C_6F_5OH	89	176-8/763 mm

To avoid repetition, references of the following are given:

Me_3SiF (i.r.) - 90 SiF_4 (n.m.r.) - 91 SOF_2 (i.r.) - 94

1. ortho-$Me_3SiOC_6H_4CH_3/SF_4$ 1:1 molar ratio

12.2 mmole of $Me_3SiOC_6H_4CH_3$ and 16 mmole of SF_4 were allowed to react at 20°C. The reaction started below room temperature. On fractionation Me_3SiF (12.1 mmole) was obtained at -126°C trap. The excess of SF_4 was collected in the -196°C trap. The involatile colourless liquid in the vessel was confirmed as $SF_3OC_6H_4CH_3$(ortho).

The compound $SF_3OC_6H_4CH_3$(ortho) decomposed quickly at room temperature to give unidentified coloured compounds.

	δC_6H_4	δCH_3	
^1H nmr	- 6.8 ppm	-1.95 ppm	T.M.S. ext.
	$\delta(SF)$	$\delta(SF_2)$	
^{19}F nmr	- 31.2(+)	-76.2(d)	CCl_3F int.

2. $Me_3SiOC_6H_4CH_3$(para)/SF_4 (1:1 molar ratio)

16.2 mmole of $Me_3SiOC_6H_4CH_3$ and 18 mmole of SF_4 were allowed to react at room temperature. On fractionation Me_3SiF (15.8 mmole) and excess of SF_4 were obtained at traps -126°C and -196°C respectively. The colourless involatile liquid was confirmed as $SF_3OC_6H_4CH_3$(para). Prolonged distillation was avoided since $SF_3OC_6H_4CH_3$ disproportionates to $SF_2(OC_6H_4CH_3)_2$ and SF_4.

Mol. wt.: Calculated - 196 Found (by mass spectrum) 196

^{1}H nmr : $\overset{C_6H_4}{-6.9}$ ppm, $-\overset{CH_3}{1.95}$ ppm (TMS ext)

$\delta(S\underline{F})$ $\delta(S\underline{F}_2)$

^{19}F nmr : -30.3 (triplet) -78.6 (doublet). CCl_3F

Infrared: cm^{-1}

Liquid Film: 3075(w), 2037(m), 2924(m), 1595(m), 1498(vs), 1449(sh), 1225(s), 1178(s), 1147(s), 1110(s), 1041(m), 1015(s), 905(s), 555(br,s), 825(b,s), 792(sh), 760(w), 742(s), 655(w), 620(m,br), 560(m)

3. <u>$Me_3SiOC_6H_4CH_3$(meta)/SF_4</u> (<u>1:1 molar ratio</u>)

15.5 mmole of $Me_3SiOC_6H_4CH_3$(<u>meta</u>) and 17 mmole of SF_4 reacted at room temperature to give Me_3SiF (15.8 mmole) and $SF_3OC_6H_4CH_3$, a colourless involatile liquid.

$SF_3C_6H_4CH_3$(<u>meta</u>)

<u>Mol. wt</u>: Calculated - 196 Found 196 (by mass spectrum)

<u>^{1}H nmr</u> : -7.0 ppm, - 2.1 ppm (TMS ext)

	δSF(equatorial)	δSF_2-axial	
<u>^{19}F nmr</u>:	131.3 (triplet)	-78.8(doublet)	CCl_3F int.

<u>Infrared</u>: cm^{-1}

<u>Liquid Film</u>: 3075(m), 3030(w), 2970(sh), 2930(s), 2873(m), 1618(s), 1585(s), 1489(s), 1470(w), 1385(m), 1280(w), 1265(w), 1223(vs), 1115(sh) 1125(vs), 1089(m), 1033(m), 1009(m), 998(m), 944(sh), 920(br,s), 565(m), 831(sh), 811(br,s), 790(br,s), 735(m), 722(w), 688(m), 622(s).

4. $Me_3SiOC_6H_4CH_3$(meta)/SF_4 2:1 molar ratio

17.1 mmole of $Me_3SiOC_6H_4CH_3$(meta) and 9 mmole of SF_4 were allowed to react at room temperature. After an hour, the products were fractionated 17 mmole of Me_3SiF was obtained. The white solid in the vessel was confirmed as $SF_2(OC_6H_4CH_3)_2$.

$SF_2(OC_6H_4CH_3)_2$: Mass spectrum showed a peak at 262 corresponding to $S(=O)(OC_6H_4CH_3)_2$, a hydrolysed product of $SF_2(OC_6H_4CH_3)_2$

Elemental Analysis:

Carbon - Calc. 59.1, Found: 59.22 Fluorine Calc.13.30
Found 13.50

Hydrogen - Calc. 4.92 Found 5.10

Oxygen - Calc. 11.2 Found 11.02 sulfur Calc. 11.2.
Found 11.14

^1H nmr (inCCl_4) δC_6H_4 δCH_3
-7.21 ppm -2.38 TMS ext.

^{19}F nmr (in CCl_4) δSF_2
-67.7(b.s) ppm CCl_3F int.

Infrared cm^{-1}

Nujol 3060(m), 2978(m), 2923(s), 2860(s), 1615(m), 1585(br,s), 1460(s), 1379(s), 1300(s), 1230(v.s), 1165(w), 1121(s), 1100(m), 1085(w), 1032(s), 1005(s), 995(m), 918(vs), 863(m), 815(br,s) 785(br.s), 745(m), 685(v.s), 654(m).

5. $Me_3SiOC_6H_4CH_3$(para)/SF_4 2:1 molar ratio

20.1 mmole of $Me_3SiOC_6H_4CH_3$(para) and 11 mmole of SF_4 were allowed to react at 20°C. The reaction appeared complete in an hour. On fractionation, the volatile Me_3SiF (20 mmole) was obtained at -126° trap. Excess of SF_4 was collected at -196°C trap. The white solid remaining in the vessel was identified as $SF_2(OC_6H_4CH_3)_2$.

The mass spectrum showed its highest peak at m/e 262 corresponding to $S(=O)(OC_6H_4CH_3)_2$, a hydrolysed product of $SF_2(OC_6H_4CH_3)_2$.

Elemental analysis:

Carbon calc. 59.1 Found 59.12 Oxygen calc 11.2 Found 11.20

Hydrogen calc. 4.92 Found 5.10 Fluorine calc 13.3 Found 13.37

Sulfur calc. 11.2 Found 11.21.

^1H nmr (in CCl_4)	δC_6H_4	δCH_3	
	-7.1 ppm	-2.18 ppm	TMS ext.
^{19}F nmr	δSF_2		
	-66.3 ppm (b.s) CCl_3F int.		

Infrared: cm^{-1}

Nujol	3038(m), 2925(v.s), 2848(s), 1500(s), 1460(s), 1378(s), 1300(w), 1281(w), 1230(w), 1170(s), 1149(s), 1109(m), 1040(w), 1018(s), 941(w), 875(s) 825(s), 795(s), 715(m), 680(s), 615(s)

6. $Me_3SiOC_6H_4Cl$(meta)/SF_4 1:1 molar ratio

14.8 mmole of $Me_3SiOC_6H_4Cl$ and 18 mmole of SF_4 reacted vigorously below room temperature. On fractionation in vacuum line, 14.2 mmole of Me_3SiF was obtained at -126°C. Excess SF_4 was collected at -196°C. The involatile colourless liquid in the vessel was confirmed as $SF_3OC_6H_4Cl$.

Mol.wt. Calc. 216, Found 216 (by mass spectrum)

^{1}H nmr : - 7.32(multiplet) TMS ext.

^{19}F nmr : - δ SF δ SF_2

-31.0(triplet) -79.2(d) at -25°C

Infrared cm^{-1}

liquid film 3098(m), 3076(m), 1575(s), 1518(m), 1457(s), 1430(m), 1261(m), 1172(s), 1157(m), 1076(m) 1070(m), 1001(m), 979(w), 928(s), 902(br.v.s), 857(s), 786(s), 755(m), 700(w), 670(m), 650(m), 588(br.m).

7. $Me_3SiOC_6H_4Cl$(para)/SF_4 1:1 molar ratio

13.5 mmole of $Me_3SiOC_6H_4Cl$ and 16 mmole of SF_4 were allowed to react at 20°C. The reaction started well below room temperature and was complete in a few minutes. The products were then fractionated and Me_3SiF (13.4 mmole) was obtained in the -126° trap. The excess of SF_4 was collected to the -196° trap. The involatile colourless liquid in the vessel was confirmed as $SF_3OC_6H_4Cl$(para)

Mol.Wt. Calc. 216 Found 216 (by mass spectrum)

^{1}H nmr: -7.25 (quartet A_2B_2) TMS ext.

^{19}F nmr: δ SF δ-SF_2

-30.5(triplet),-7.9 (doublet) CCl_3F int.

Infrared cm^{-1}

3131(m), 3098(m), 1754(m), 1665(s), 1509(v.v.s) 1285(m), 1241(v.s), 1155(v.v.s), 1142(m), 1091(s), 1019(m), 989(m), 932(s), 907(br.v.s.), 873(v.s), 765(s), 742(m), 685(m), 639(v.v.s).

8. Me$_3$SiOC$_6$H$_4$Cl(meta)/SF$_4$ 2:1 molar ratio

16.9 mmole of SF$_4$ Me$_3$SiOC$_6$H$_4$Cl and 10 mmole of SF$_4$ were allowed to react at +20°C for on hour. The products were fractionated. 16.8 mmole of Me$_3$SiF was obtained in the -126° trap. Excess of SF$_4$ was pumped off. The white solid in the reaction vessel was confirmed as SF$_2$(OC$_6$H$_4$Cl)$_2$.

The mass spectrum showed its highest peak at m/e 302 corresponding to S(=O)(OC$_6$H$_4$Cl)$_2$ the hydrolysis product of SF$_2$(OC$_6$H$_4$Cl)$_2$.

Elemental analysis

Carbon calc. 44.3 Found 44.29 Oxygen calc 9.84 Found 9.76
Hydrogen calc. 2.46 Found 2.47 Fluorine calc.11.69 Found 11.86
Sulfur calc. 9.84 Found 9.64 Chlorine calc 21.84 Found 21.98

^{1}H nmr: -7.32(multiplet) in CCl$_4$ solution TMS ext.
δSF$_2$

^{19}F nmr: -70 (b.s.) ppm relative to CCl$_3$F int.

Infrared: cm^{-1}

Nujol 3102(m), 3072(m), 2925(v.s), 2848(s), 1602(v.s), 1521(s), 1460(s), 1378(s), 1258(s), 1203(s), 1144(s), 1106(s), 1081(m), 1002(m), 929(s), 855(s), 803(br.s), 781(s), 751(s), 689(s), 621(br.s).

9. $Me_3SiOC_6H_4Cl$(para)SF_4 (2:1 molar ratio)

18 mmole of $Me_3SiOC_6H_4Cl$ and 10 mmole of SF_4 reacted vigorously at room temperature. The volatiles were SF_4 and Me_3SiF (17.5mmole) obtained in the -196°C and -126°C traps respectively. The white solid remaining in the vessel was confirmed as $SF_2(OC_6H_4Clp)_2$.

The mass spectrum showed its highest peak at m/e 302 corresponding to $S(=O)(OC_6H_4Cl)_2$ the hydrolysis product of $SF_2(OC_6H_4Cl)_2$.

Elemental Analysis

Carbon	Calc.	44.30	Found	44.36
Oxygen	Calc.	11.2	Found	11.2
Hydrogen	Calc.	2.46	Found	2.55
Fluorine	Calc.	11.69	Found	11.96
Chlorine	Calc.	21.84	Found	22.06
Sulfur	Calc.	9.84	Found	9.68

(Oxygen Found by subtraction)

^1H nmr -7.28 ppm (A_2B_2 quartet) TMS ext.

^{19}F nmr SF_2 -71.2 ppm (b.s) relative to CCl_3F int.

Infrared cm^{-1}

Nujoll 2133(m), 3110(m), 2925(v.s.) 2848(s)
1600(s) 1515(v.s), 1460(s) 1378(s)
1280(s) 1245(s), 1149(br.v.s), 1093(m)
1010(m) 967(s), 849(s), 808(br,s), 755(s),
735(m), 674(m), 647(br,v.s).

10. $Me_3SiOC_6H_4F$(ortho)/SF_4 1:1 molar ratio

16.5 mmole of $Me_3SiOC_6H_4F$(ortho) and 20 mmole of SF_4 were allowed to react at room temperature. The products were Me_3SiF (16.3 mmole) and $SF_3OC_6H_4F$. Excess SF_4 was trapped at -196°. $SF_3OC_6H_4F$ was a colourless liquid which distills slowly in the vacuum line. $SF_3OC_6H_4F$ was confirmed by its ^1H and ^{19}F nmr spectra, mass spectrum and infrared spectrum.

Mol.wt.: Calc. 200 Found 200 (Mass spec.).

^1H nmr: -7.3 ppm (multiplet) TMS ext.

^{19}F nmr: δSF equatorial δSF_2 axial

-31.4 (triplet) -77.4(doublet) CCl_3F int.

δCF + 128 ppm $J_{F_{eq}-F_{ax}} = 77Hz$

Infrared cm^{-1}

Liquid Film 3108(m), 3074(m), 1610(s), 1600(s), 1493(v.s)
1460(m), 1268(s), 1250(v.s), 1165(s),
1151(sh), 1097(v.s), 1026(s), 937(m),
909(s), 577(br,s), 555(m), 800 (v.s)
758(v.s), 731(m), 678(m), 651(br.s).

11. $Me_3SiOC_6H_4F$(meta)/SF_4 (1:1 molar ratio)

15.8 mmole of $Me_3SiOC_6H_4F$ and 21 mmole of SF_4 reacted smoothly at 20°C. On fractionation Me_3SiF (15.6 mmole) and excess SF_4 were obtained in the -126°C and -196°C traps respectively. The involatile colourless liquid in the vessel was confirmed as $SF_3OC_6H_4F$ meta

Mol.Wt.: Calc. 200 Found 200 (by mass spectrum)

^{1}H nmr : -7.32 ppm (multiplet) TMS ext.

^{19}F nmr: δSF equatorial δSF_2(axial)

-30.3 ppm (triplet) -82(doublet) at -30°C

CCl_3F (inter)

δCF + 107.7 $J_{F_{eq} - F_{ax}} = 75$ Hz

Infrared cm^{-1}

Liquid Film 3086 (mbr), 1607 (v.s), 1475(v.s), 1449(m), 1268(m), 1244(s), 1155(w), 1110(v.s), 1072 (m), 966(s), 953(v.s), 865(s), 811(s), 783(s), 736(m), 680(s), 663(v.s).

12. $\underline{Me_3SiOC_6H_4\,(para)/SF_4}$ (1.1 molar ratio)

17.3 mmole of $Me_3SiOC_6H_4F$ (<u>para</u>)and 21 mmole of SF_4 were allowed to react at 20°C. The reaction started below room temperature and was complete in 20 min. On slow fractionation, Me_3SiF(17.2 mmoles) and excess SF_4 were obtained in -126°and 196° respectively. The colourless involatile liquid was confirmed as $SF_3OC_6H_4F$(<u>para</u>).

Mol. wt. calculated 200. Found 200 (Mass spectrum).

<u>^{1}H n.m.r.</u>: -7.16 ppm (quartet A_2B_2) TMS ext.

<u>^{19}F n.m.r.</u>: -SF eq. SF_2-axial

-30.1 (triplet) -82 (doublet) CCl_3F int.

CF + 111.0 J_{F-F} =76Hz

<u>Infrared</u> cm^{-1}

Liquid film 3121(m), 3095(s), 1601(s), 1500(v.v.s).
1281(m), 1239(v.s), 1160(v.v.s), 1083(s)
1017(m), 905(v.s), 844(v.s), 814(v.s),
729(s), 675(m), 637(v.v.s).

13. $Me_3SiOC_6H_4F$(meta)/SF_4 2:1 molar ratio

20.0mmole of $Me_3SiOC_6H_4F$(meta) and 11 mmole of SF_4 were reacted to completion in half an hour. When the volatiles Me_3SiF (19.8 mmole) and SF_4 (excess) were distilled off, a colourless liquid left in the vessel and was confirmed as $SF_2(OC_6H_4F)_2$. The mass spectrum showed its highest peak at m/e 270 corresponding to $S(=O)(OC_6H_4F)_2$, a hydrolysed product of $SF_2(OC_6H_4F)_2$.

Elemental Analysis:

Carbon: Calc. 49.3 Found 48.9

Fluorine: Calc. 26.02 Found 26.15

Hydrogen: Calc. 2.73 Found 2.65

Sulfur: Calc.10.95 Found 10.8

Oxygen: Calc.10.95 Found 11.5

^{1}H nmr: -7.3 (multiplet) TMS ext.

^{19}F nmr: δSF_2 - 69.2(b.s.) CCl_3F int.

δCF + 108.4 ppm CCl_3F

Infrared cm^{-1}

Solution in CCl_4 0.05 molar: 3100(m) 3085(s), 3046(w), 1606(v.s), 1487(v.s), 1449(s), 1328(w), 1305(w), 1278(s), 1249(v.s), 1158(m), 1108(br.s), 1071(s), 1009(w), 962(s), 947(m), 860(s), 806(s), 779(s), 713(m) 675(m), 666(m).

14. $Me_3SiOC_6H_4F$(para)/SF_4 (2:1 molar ratio)

18 mmole of $Me_3SiOC_6H_4F$(para) and 11 mmole of SF_4 were allowed to react at room temperature. The reaction seemed to be complete in an hour. The products were then distilled and Me_3SiF(10.8 mmole) was collected in the -126° trap. The colourless liquid remaining in the vessel was confirmed as $SF_2(OC_6H_4F)_2$.

Mass spectrum showed peak at m/e 270 of $S(=O)(OC_6H_4F)_2$ corresponding to a hydrolysed product of $SF_2(OC_6H_4F)_2$

Elemental Analysis:

Carbon:	Calc.49.31	Found 49.85
Fluorine:	Calc.26.02	Found 25.8
Hydrogen:	Calc.2.73	Found 2.81
Sulfur:	Calc.10.95	Found 10.76
Oxygen:	Calc.10.9	Found 11.8 (by deduction)

^{1}H nmr: -7.3 ppm (multiplet) TMS ext.

^{19}F nmr: $\overset{-SF_2}{-69.2}$ ppm (b.s) CCl_3F (int.)

δCF + 112.0 ppm

Infrared cm^{-1}

Solution in CCl_4 (0.05 molar) 3100(m), 3085(s), 3046(w), 1606(v.s), 1487(v.s), 1449(s), 1328(w), 1305(w), 1278 (s), 1249(v.s), 1158(m), 1108(br.v.s), 1071 (s), 1009(w), 962(sh), 947(m) 860(s), 806(s), 779(s), 713(m), 675(m), 666(m)

15. $Me_3SiOC_6H_4CF_3$(para)/SF_4(1:1 molar ratio)

17 mmole of $Me_3SiOC_6H_4CF_3$(para) and 20 mmole of SF_4 reacted at 20°C in three hours. The products were Me_3SiF (17.5 mmole) and $SF_2(OC_6H_4CF_3)_2$. The latter compound was a slightly coloured solid and was confirmed by ^{19}F nmr, ^1H nmr spectroscopy and elemental analysis.

^1H nmr : -7.45 ppm (quartet A_2B_2) TMS ext.

^{19}F nmr : δSF_2 = -72.0 ppm (s) CCl_3F(int)

δCF_3 = +62 ppm

Elemental Analysis

Carbon: Calc. 42.86, Found 42.15

Fluorine: Calc. 38.77, Found 38.3

Hydrogen: Calc. 2.04, Found 2.1

Sulfur: Calc. 8.16, Found 8.25

Oxygen: Calc. 8.16, Found 9.2

16. $Me_3SiOC_6H_4NO_2$(para)/SF_4 (1:1)

14 mmole of $Me_3SiOC_6H_4NO_2$(para) and 25 mmole of SF_4 were allowed to react at room temperature for about 2 hr. The products were Me_3SiF (12 mmole) and a slightly reddish coloured solid. The solid was insoluble in H_2O, CCl_4, benzene CH_2Cl_2 and other polar solvents. In acetonitrile, the compound was very sparingly soluble but it decomposed slowly in the solvent. Because of the lack of a proper solvent an n.m.r. spectrum could not be obtained. On the basis of elemental analysis , mass spectrum and infrared spectrum the solid compound was characterized as $SF_2(OC_6H_4NO_2p)_2$.

Mass spectroscopy showed a peak at m/e 324 corresponding to $S(=O)(OC_6H_4NO_2)_2$ a hydrolysed product of $SF_2(OC_6H_4NO_2)_2$.

Elemental analysis.

Carbon:	calc. 41.61	Found 42.1
Hydrogen:	calc. 2.31	Found 2.51
Sulfur:	calc. 9.24	Found 9.3
Fluorine:	calc 10.98	Found 11.3
Nitrogen:	calc 4.09	Found 4.02
Oxygen:	calc 27.7	Found 30.8

Infrared cm^{-1}

Nujol 3110(w), 3085(w), 1615(m), 1582(s), 1525(s), 1487(m), 1449(m), 1281(m), 1235(m), 1170(s), 1138(s), 1115(s), 1006(w), 918(m), 852(s), 780(m), 749(s) 716(m), 695(m), 622(m).

17. $Me_3SiOC_6F_5/SF_4$ 1:1 molar ratio

16 mmole of $Me_3SiOC_6F_5$ and 24 mmole of SF_4 were allowed to react at 20°C for about an hour. The products were Me_3SiF (15.7 mmole) and a white crystalline solid confirmed as $SF(OC_6F_5)_3$. The excess of SF_4 and Me_3SiF were collected in -196 and -126° traps respectively.

^{19}F nmr $\delta SF = -67.4$ ppm(s)

δCF ortho = +152, para +155.2 and meta +162.4 ppm

Elemental analysis

Carbon:	Calc.36.01	Found: 35.61
Fluorine:	Calc.50.6	Found: 50.36
Sulfur:	Calc. 5.3	Found: 5.47
Oxygen:	Calc. 8.0	Found: 7.44

Infrared cm^{-1}

Solution in CCl_4 (0.05m)	1653(m) 1518(v.s), 1476(m), 1316(w), 1225(w), 1139(m), 1028(s), 999(v.v.s), 784(w), 759(m), 741(m), 732(w), 694(s), 620(s).

18. $(Me_3SiO)_2C_6H_4(1:2)/SF_4$ (1:1 molar ratio)

18 mmole of $(Me_3SiO)_2C_6H_4(1:2)$ and 50 mmole of SF_4 were allowed to react for 3 hr. On fractionation of the volatiles, excess of SF_4 and Me_3SiF (35 mmole) were collected to the -196°C and -126°C traps respectively leaving in the vessel a slightly earth coloured solid. The solid was then purified using CCl_4 as solvent and was confirmed as $S(OOC_6H_4)_2$.

Mol.Wt.: Calc. 248 Found 248 (mass spectrum)

^1H nmr: -6.95 (b.s) ppm TMS (ext).

Infrared cm^{-1}

Solution in CCl_4	3078(m), 3030(w), 1619(s), 1585(m), 1462(m), 1331(s), 1278(m), 1258(s), 1242(v.s), 1173(s), 1100(s), 1012(s), 960(w), 940(m), 930(m), 870(s), 820(v.s) 749(v.s), 725(s), 712(s), 635(s).

Elemental Analysis

Carbon calc.	58.06.	Found 57.85
Hydrogen calc.	3.22	Found 3.35
Oxygen calc.	25.8	Found 25.61
Sulfur calc.	12.9	Found 12.76.

CHAPTER II

REACTIONS OF TRIFLUOROMETHYLSULFUR TRIFLUORIDE

REACTIONS OF TRIFLUOROMETHYLSULFUR TRIFLUORIDE

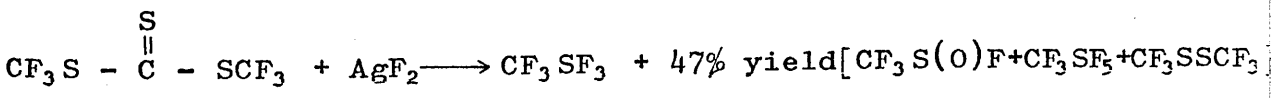
INTRODUCTION

Trifluoromethylsulfur trifluoride [95] was the first reported SF_4 derivative. It was prepared by fluorination of CS_2 in the presence of nitrogen in a metal packed fluorination reactor incorporating a concentric tube burner. CF_3SF_3 was produced along with a variety of other products including CF_4, SF_6, $C(S)F_2$, SF_4, CF_3SF_5. After purification CF_3SF_3 was identified in small yield.

$$CS_2 + F_2 \longrightarrow CF_3SF_3$$

W. A. Sheppard [76] reported a preparative route to a number of alkyl- and aryl sulfur trifluorides. Although the preparative route to arylsulfur trifluorides was fairly satisfactory, the formation of trifluoromethylsulfur trifluoride was accompanied by a number of impurities including SF_6, SF_4, CF_3SF_5 and CF_3SFO.

$$CS_2 + AgF_2 \longrightarrow CF_3SF_3 + 28\%\ \text{yield}\ [CF_3 - SF_5, SF_4, SF_6]$$



$$CF_3S - \overset{\overset{\displaystyle S}{\|}}{C} - SCF_3 + AgF_2 \longrightarrow CF_3SF_3 + 47\%\ \text{yield}[CF_3S(O)F + CF_3SF_5 + CF_3SSCF_3$$

J. M. Shreeve [97] and coworkers reported a number of methods for formation of CF_3SF_3, by fluorinating CF_3SCl and CF_3SSCF_3 using fluorinating agents such as CF_3OF, KF/CH_3CN and F_2.

(i) $2CF_3SCl + 3CF_3OF \longrightarrow 2CF_3SF_3 + Cl_2 + 3COF_2$

(ii) $CF_3SCl + KF\ [CH_3CN \text{ and } COF_2] \longrightarrow CF_3SF_3 + KCl$

(iii) $CF_3SSCF_3 + F_2 \xrightarrow[KF/N_2]{CH_3CN} CF_3SF_3 + [CF_4 + SF_6]$

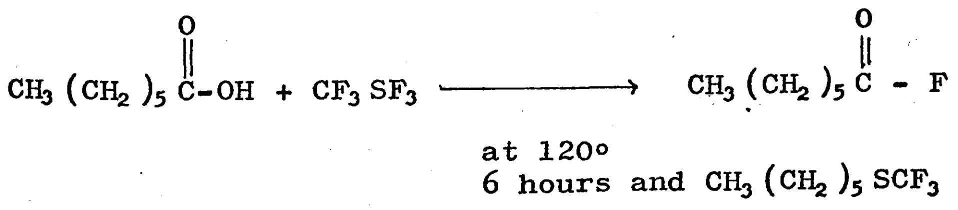
(iv) $CF_3OF + CF_3SSCF_3 \longrightarrow CF_3SF_3 + COF_2$

In the present work [96], the compound was prepared by the fluorination of CF_3SSCF_3 by AgF_2 as described by Lawless and Harman.

$$CF_3SSCF_3 + 6AgF_2 \longrightarrow 2CF_3SF_3 + 6AgF$$

The reaction was carried out in an 75 ml. steel bomb in a molar ratio of CF_3SSCF_3 to AgF_2 of 1:8. The impurities were CF_3SF_5, CF_3SFO and unreacted CF_3SSCF_3. To minimise the formation of CF_3SF_5, use of a large excess of AgF_2 was avoided. Once CF_3SF_3 is formed, it is fairly resistant to further fluorination at room temperature. Hence the reaction was maintained at -25°C for at least twenty four hours and the whole reaction was then completed in a week at 20°C. Finally, use of thoroughly dry conditions and avoidance of contact with glass minimised the formation of CF_3SFO. The purity of CF_3SF_3 was checked by i.r. and ^{19}F n.m.r. spectroscopy [96] [77]. In spite of all the precautions the compound contained small amounts of CF_3SF_5 and CF_3SFO; CF_3SF_5 was removed by distilling at -110°C under vacuum for twenty minutes. Once formed it was difficult to separate CF_3SFO but by careful vacuum distillation from a -95°C bath CF_3SFO was removed.

It has been reported that the reactions of alkyl- and arylsulfur trifluorides [76] were similar to those of sulfur tetrafluoride. Like SF_4, they are useful reagents for conversion of carbonyl and carboxyl groups to difluoromethylene and trifluoromethyl groups and considerable variation in reaction conditions was often found with different types of carbonyl and carboxyl groups. Thus for the fluorination of aromatic ketones heating at 150°C in the presence of a Lewis acid catalyst such as titanium tetrafluoride was necessary. The reaction of aliphatic aldehydes and ketones was exothermic and was best controlled by use of a solvent such as methylene chloride or acetonitrile containing a small amount of NaF powder. Carboxylic acids were treated in a container resistant to hydrogen fluoride and required heating at 120° to 150°C.



$$CH_3(CH_2)_5\overset{\overset{O}{\|}}{C}\text{-}OH + CF_3SF_3 \longrightarrow CH_3(CH_2)_5\overset{\overset{O}{\|}}{C} - F$$

$$\text{at } 120^\circ$$
$$\text{6 hours and } CH_3(CH_2)_5SCF_3$$

On hydrolysis, CF_3SF_3 gives CF_3SFO [97].

$$CF_3SF_3 + H_2O \longrightarrow CF_3SFO + 2HF$$

Trifluoromethylsulfur trifluoride [100] formed addition compounds with PF_5, PF_3, AsF_5, and SbF_5. The order of As stability inferred from the magnitude of dissociation pressures was

$$CF_3SF_3.SbF_5 > CF_3SF_3.AsF_5 > CF_3SF_3.BF_3 > CF_3SF_3.PF_5.$$

The infrared spectra of the three solid compounds $CF_3SF_3.BF_3$, $CF_3SF_3.AsF_5$ and $CF_3SF_3.SbF_5$ were interpreted as indicating that the adducts are ionic solids of the type $CF_3SF_2^+MF_{n+1}^-$

CF_3SF_3 readily reacts with dry glass to produce CF_3SFO and SiF_4 [96] and the reaction was suggested as a good method for the preparation of trifluoromethylsulfenylfluoride.

$$CF_3SF_3 + \text{glass} \longrightarrow CF_3SFO + SiF_4$$

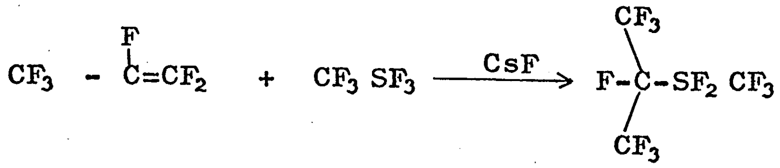
CF_3SF_3 [76] could be easily converted to CF_3SF_5 by AgF_2 at temperatures higher than 100°C.

$$CF_3SF_3 + AgF_2 \longrightarrow CF_3SF_5 + AgF$$

Trifluoromethylsulfur trifluoride [101] reacted with chlorine in the presence of CsF at room temperature to give trifluoromethylsulfur chloride tetrafluoride.

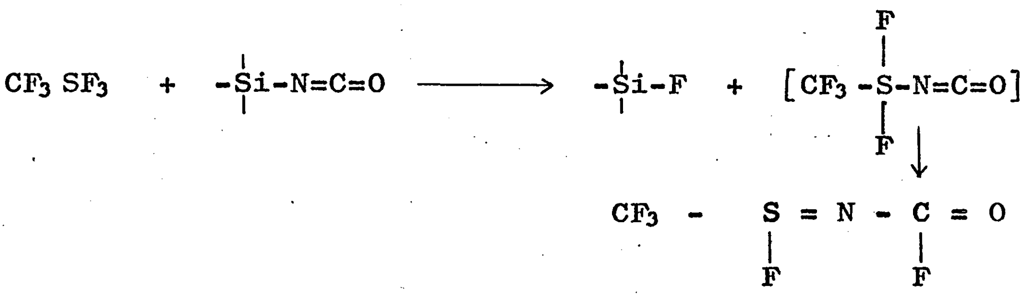
$$CF_3SF_3 + Cl_2 + CsF \longrightarrow CF_3SF_4Cl + CsCl$$

An S-F bond [16] of CF_3SF_3 added across the C=C bond of hexafluoropropene, C_3F_6, in the presence of CsF in similar reaction to that with SF_4.



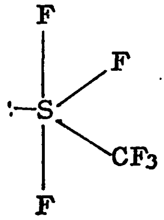
$$CF_3-CF=CF_2 + CF_3SF_3 \xrightarrow{CsF} (CF_3)_2CF-SF_2CF_3$$

Trifluoromethylsulfur trifluoride [102] reacted with a silyl isocyanate as does sulfur tetrafluoride and thionyl tetrafluoride.



$$CF_3SF_3 + \text{-Si-N=C=O} \longrightarrow \text{-Si-F} + [CF_3\text{-}SF_2\text{-N=C=O}] \longrightarrow CF_3-SF=N-CF=O$$

A low temperature [77] ^{19}F n.m.r. spectrum of CF_3SF_3 resolved the S-F fluorine resonance into two separate chemical shifts of relative intensity 2:1 separated by 100 p.p.m. By analogy with the structure of SF_4 the geometry of the compound was described as trigonal bipyramid with CF_3 and the lone pair in the equatorial position.

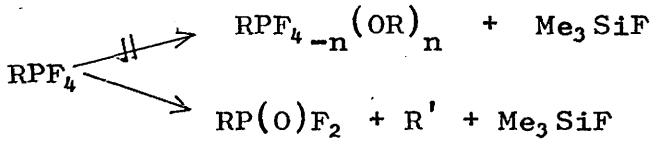


An infrared study [83] of CF_3SF_3 in the gas phase supported in the above geometry.

The compound CF_3SF_3 has b.p. -7°C and m.p. -110°C [95].

REACTIONS OF CF_3SF_3 WITH ALKOXYTRIMETHYLSILANES

Alkoxy derivatives of binary non-metal fluorides which have a tendency to form double bond to oxygen are thermally unstable. $MeOPF_4$ [105] was formed from the reaction between PF_5 and $(MeO)_3P$ but above -10°C the compound decomposed with the formation of a complex series of reaction products. Reactions of substituted derivatives of PF_5 with trimethyl alkoxy silanes produced no stable fluorophosphoranes containing an alkoxy group [61].



Similar instability [106] was found with alkoxy boron derivatives, where alkyldichloroboronates $ROBCl_2$ and dialkylchloroboronate, $(RO)_2BCl_2$ [107] decomposed readily below room temperature in accordance with the following equations.

$$3\,ROBCl_2 \longrightarrow 3RCl + BCl_3 + B_2O_3$$

$$3(RO)_2BCl \longrightarrow RCl + B(OR)_3 + B_2O_3$$

The reaction of alkoxytrimethylsilane and SF_4 produced MeF, SOF_2 and Me_3SiF [68]. The overall reaction between SF_4 and Me_3SiOR was shown to be:

$$SF_4 + Me_3SiOR \longrightarrow Me_3SiF + ROSF_3$$

$$ROSF_3 \longrightarrow RF + S(O)F_2 \qquad [R=CH_3,\ C_2H_5].$$

The reaction of CF_3SF_3 with alkoxytrimethylsilanes is similar to that of SF_4 although CF_3SF_3 reacts more slowly. In the case of SF_4, the reaction occurred below room temperature where the reaction of CF_3SF_3 took about thirty hours to complete at room temperature. The major products of the reaction were Me_3SiF, RF, $CF_3S(=O)R$ and CF_3SFO. The following steps of the reaction are probable.

$$CF_3SF_3 + Me_3SiOR \longrightarrow CF_3SF_2OR + Me_3SiF$$

$$CF_3SF_2OR \longrightarrow CF_3SFO + RF \qquad [R=CH_3,C_2H_5]$$

$$CF_3SFO + Me_3SiOR \longrightarrow CF_3(O=)S{-}OR + Me_3SiF$$

The formation of $CF_3S(=O)OR$ from a 1:1 molar ratio of reactants indicates that the secondary reaction between CF_3SFO and Me_3SiOR is faster than the reaction of CF_3SF_3 with Me_3SiOR.

Compounds of the type $CF_3(=O)OR$ where R=Me,Et have previously been prepared by the alcoholysis of the trifluoromethylsulfenylfuoride [108].

$$CF_3SFO + ROH \longrightarrow CF_3(O=)S{-}OR + HF$$

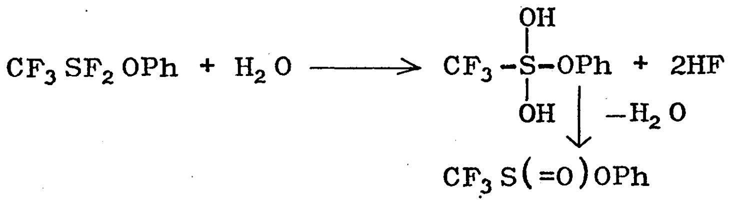
The details of the reactions between CF_3SF_3 and Me_3SiOR $[R=CH_3,C_2H_5]$ are given in the experimental section.

REACTIONS OF CF_3SF_3 WITH PHENOXYTRIMETHYLSILANE

The reaction of phenoxytrimethylsilane with CF_3SF_3 produces $PhOSF_2CF_3$. The increased stability of the phenoxy derivative compared with alkoxy has already been commented on for SF_4 and PF_5 derivatives [105, 61, 68]. $Me_3SiOC_6H_5$ reacts in three to four hours at 20°C with an excess of CF_3SF_3 to produce Me_3SiF and a colourless involatile liquid confirmed as CF_3SF_2OPh.

$$CF_3SF_3 + Me_3SiOC_6H_5 \longrightarrow CF_3SF_2OC_6H_5 + Me_3SiF$$

CF_3SF_2OPh readily hydrolyses in a moist atmosphere. From their mass spectrum the hydrolysed products are $CF_3S(O)OPh$ and HF.



$$CF_3SF_2OPh + H_2O \longrightarrow CF_3-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle OH}{|}}{S}}-OPh + 2HF \quad \Big\downarrow -H_2O \quad CF_3S(=O)OPh$$

CF_3SF_2OPh slowly decomposes to give a black decomposed product. After about ten hours it is completely decomposed to a black mass and CF_3SSCF_3 has been identified as a volatile product of the decomposition.

$Me_3SiOC_6F_5/CF_3SF_3$

A 1:1 molar ratio, CF_3SF_3 reacted with $Me_3SiOC_6F_5$ after about 3 hours to give Me_3SiF and a colourless involatile liquid identified as $CF_3SF_2OC_6F_5$.

$$CF_3SF_3 + Me_3SiOC_6F_5 \longrightarrow CF_3SF_2OC_6F_5 + Me_3SiF$$

$CF_3SF_2OC_6F_5$ readily hydrolyses in moist air to give $CF_3S(=O)OC_6F_5$, identified by its mass spectrum.

$$CF_3SF_2OC_6F_5 + H_2O \longrightarrow CF_3S(=O)OC_6F_5 + 2HF$$

The compound $CF_3SF_2OC_6F_5$ decomposes completely at room temperature over a period of ten hours to a coloured mass. CF_3SSCF_3 is identified by infrared and mass spectra as a volatile products of the decomposition.

DISCUSSION

The reaction of CF_3SF_3 and $Me_3SiOC_6H_5$ or $Me_3SiOC_6F_5$ has been attempted with 1:2 or 1:3 molar ratios of the reactants but in each case no new products occur. It seems that the two remaining fluorine atoms of $CF_3SF_2OC_6H_5$ or $CF_3SF_2OC_6F_5$ are stable towards the attack by Si-O bond. However unlike $CF_3SF_2CF_3$ [108], the compounds $CF_3SF_2OC_6H_5$ and $CF_3SF_2OC_6F_5$ are easily hydrolysed by moisture whereas $CF_3SF_2CF_3$ [108] reacts with HCl to produce the sulfoxide in pyrex only over a period of 12 hours. This latter reaction is thought to proceed through an intermediate bisfluoroalkylsulfur dichloride which is readily hydrolysed by the water formed when HF attacks the glass vessel.

$$CF_3SF_2CF_3 + 2HCl \longrightarrow CF_3SCl_2CF_3 + 2HF$$

$$4HF + SiO_2 \longrightarrow 2H_2O + SiF_4$$

$$CH_3SCl_2CF_3 + H_2O \longrightarrow CF_3S(=O)CF_3 + 2HCl$$

The enhanced stability of CF_3SF_2OPh or $CF_3SF_2OC_6F_5$ over the alkoxy derivative is due to mesomerism as discussed previously. The compounds CF_3SF_2OPh and $CF_3SF_2OC_6F_5$ decompose to give CF_3SSCF_3 (obtained as a volatile product) and an unidentified black mass. In the absence of identification of the other products of decomposition, the mechanism of the process cannot be understood but it must be remembered that CF_3SF [109] has been reported to disproportionate to CF_3SSCF_3 and CF_3SF_3.

$$3CF_3SF \longrightarrow CF_3SSCF_3 + CF_3SF_3$$

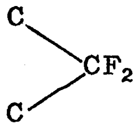
^{19}F n.m.r. Spectroscopy

^{19}F chemical shifts of the fluorocarbons

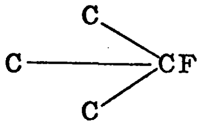
The ^{19}F chemical shifts of fluorocarbon groups of the type $-CF_3$, $\rangle CF_2$, $-\rangle CF$ occur at widely different field.

relative to CCl_3F

CF_3 = +64.5 to +86.5 p.p.m.



= +105.6 to 135.5 p.p.m. [75]



= +185.5 to +191.5 p.p.m.

Increasing substitution by fluorine causes decreasing ionic character for the C-F bond resulting in a decrease in the shielding of the fluorine nucleus. By varying the substituents to which fluoroalkyl groups are attached, variation in ^{19}F chemical shifts are obtained and such variations do not always follow the electronegativity correlation. As for example:

relative to CCl_3F

$(CF_3)_3CF$ = +77.3 p.p.m.

[135]

$(CF_3)_4C$ = +64.3 p.p.m.

CF_3 in $(CF_3)_3CF$ is more shielded than in $(CF_3)_4C$. From an electronegative point of view, the opposite direction of the shift would be expected. This anomalous behaviour has been interpreted in terms of 'repulsive deshielding' [116]. When bulky groups such as CF_3 are present in the vicinity of the fluorine atom, the repulsive interaction between the fluorine atoms and the bulky groups deshield the fluorine nucleus. This effect is also termed 'intermolecular dispersion forces' [137] described as a change in the para-magnetic contribution to the shielding due to the intermolecular dispersion forces between the bulky groups and the fluorine atoms.

Table I

relative to CCl_3F

CF_4 = +63.3 p.p.m.

CF_3Cl = +33 p.p.m.

CF_3Br = +21 p.p.m.

CF_3I = +5 p.p.m.

[136]

(Table I) Observations of the ^{19}F chemical shifts in the fluoroalkyl chloride, bromide and iodide indicate the apparent electron withdrawing power of the substituents to be $I > Br > Cl > F$.

The bulkiness of the atoms appears to offset their lower electronegativity in influencing their ability to withdraw electrons from fluorine atoms.

Table 2

The ^{19}F chemical shifts of $CF_3S(=O)OR$ and related compounds (Relative to CCl_3F)

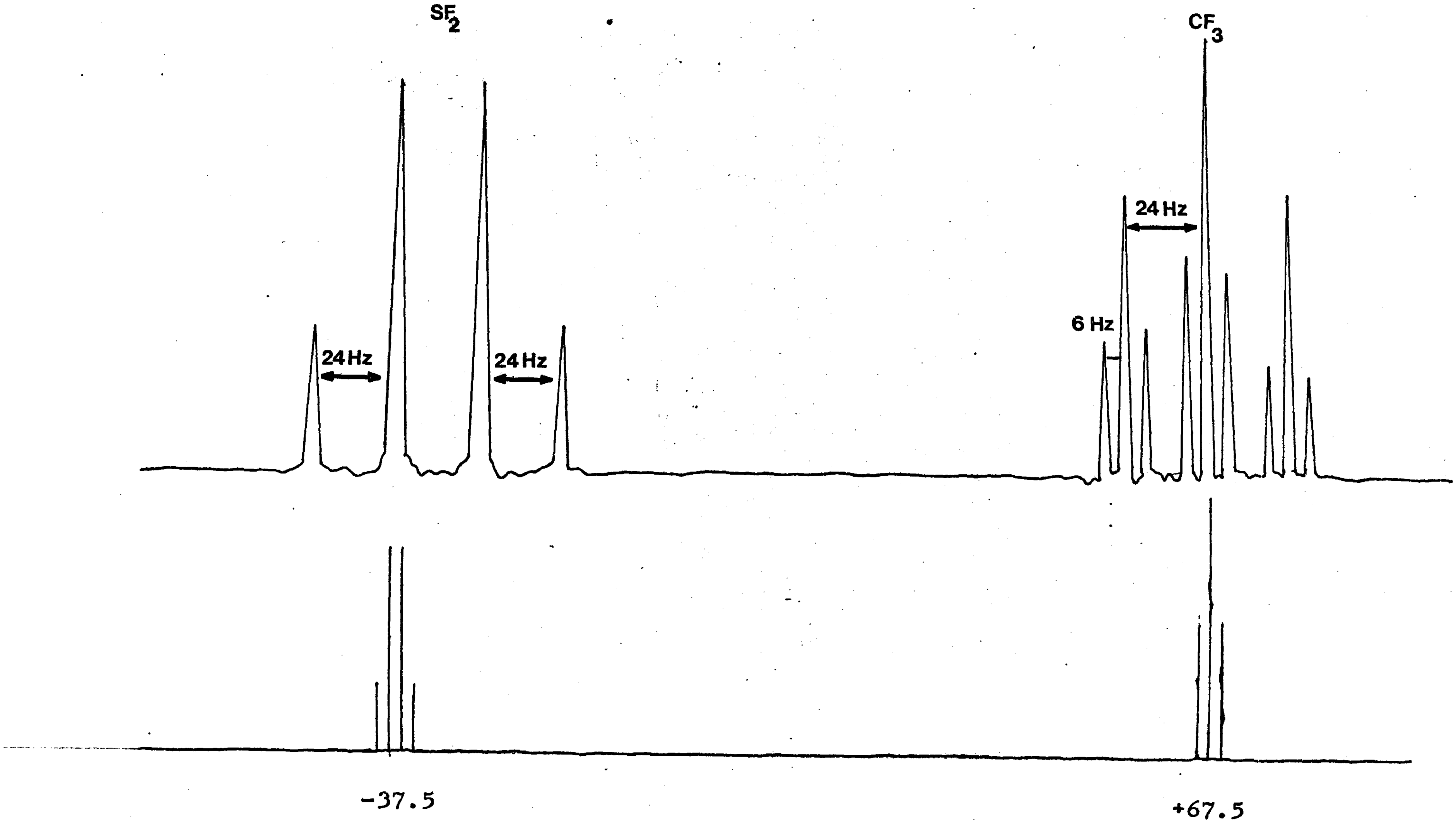
	Compounds	δCF_3	δCCF_3	δCF_2	J_{H-F}	References
1.	$CF_3S(=O)OMe$	+80.0	-	-	$J_{H-F}=1.2H_z$	Present work
2.	$CF_3S(=O)OCH_2CH_3$	+81.9	-	-	$J_{H-F}=1.2H_z$	Present work
3.	$CF_3S(=O)CF_3$	+64.5	-	-		[70]
4.	$CF_3S(=O)CF_2CF_3$	+66.7	+80.9	+116.9		[11]
5.	$CF_3S(=O)F$	+83.6	+22.1 (SF)			[96]

The chemical shifts of the CF_3 group of the compounds prepared in the present work compare well with these for similar compounds [108]. The chemical shifts of compounds $CF_3S(O)CF_3$, $CF_3S(O)CF_2CF_3$ and $CF_3S(O)F$ are (Table II) given for comparison. The shifts for the CF_3 group in (1) and (2) are reasonably comparable to that of (5) but are much higher than that of (3) and (4). The chemical shifts of the CF_3 group in $CF_3S(O)CF_3$ and $CF_3S(O)CF_2CF_3$ are at exceptionally low fields as compared with those of the other compounds in the table. This downfield shift of the CF_3 group in these compounds possibly arises from high intermolecular dispersion forces between the two perfluoroalkyl groups causing deshielding of the fluorine nuclei. This effect will be smaller in alkoxy compounds since the repulsion between the perfluoroalkyl and alkyl group will be small. The structure of the compounds $CF_3S(O)CF_3$ and $CF_3S(O)CF_2CF_3$ are likely to be similar to those of thionyl fluoride [110] which has a pyramidal structure with tetrahedral arrangement of three bonding pairs and one lone pair of electrons., The FSF angle is 92.8°. In a similar arrangement two perfluoroalkyl groups will be very close to one another.

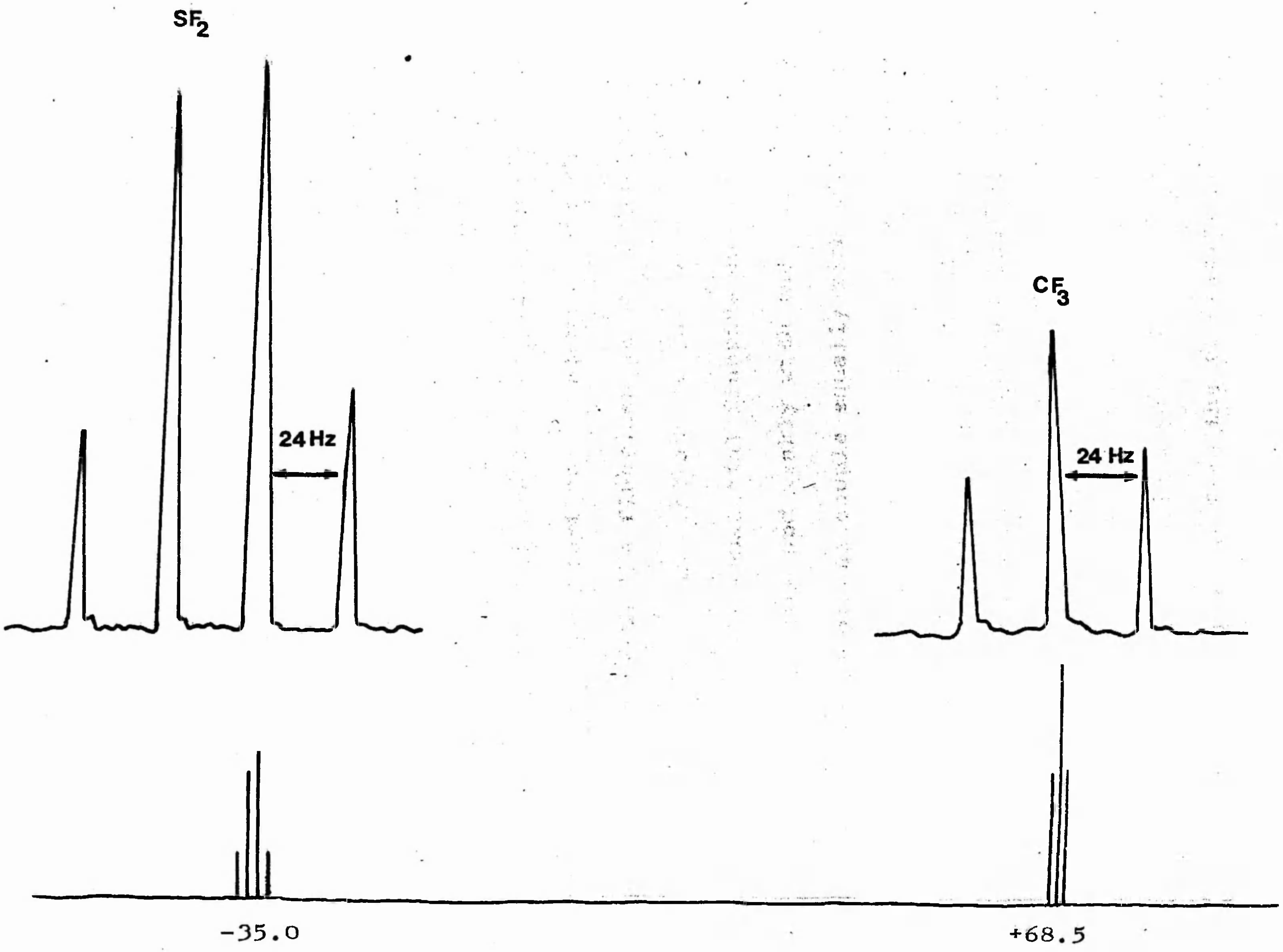
^{19}F n.m.r. chemical shifts of CF_3SF_2OPh and $CF_3SF_2OC_6F_5$

The ^{19}Fnm.r. parameters of the compounds $CF_3SF_2OC_6H_5$ and $CF_3SF_2OC_6F_5$ are completely characteristic. The two $>SF_2$ fluorine atoms are magnetically equivalent and their chemical shifts in the two compounds indicate that the

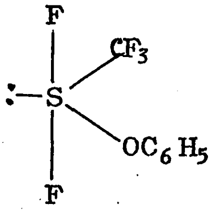
THE 19F NMR SPECTRUM OF $CF_3SF_2OC_6F_5$



THE 19F NMR SPECTRUM OF $CF_3SF_2OC_6H_5$



fluorine atoms are in axial position of a trigonal bipyramid.



The ^{19}F n.m.r. spectrum of CF_3SF_2OPh is first order of the type A_2X_3. The spectrum of $CF_3SF_2OC_6F_5$ also shows first order splitting but here the two ortho fluorines of pentafluorophenyl group couple with the CF_3 fluorine atoms although sulfurfluorine atoms do not show spin interaction with the fluorines of the pentafluorophenyl group. This is in contrast to the case of $SF_3C_6F_5$ [111] where the single equatorial fluorine couples strongly with one ortho fluorine and weakly with the other whereas the two apical fluorines couple equally with the both orthofluorines. There is however one extra bond between the fluorine atoms in the case of $CF_3SF_2OC_6F_5$.

The $>SF_2$ fluorine atoms in CF_3SF_2OPh and $CF_3SF_2OC_6F_5$ occurs at quartets interacting with the CF_3 fluorine atoms. The coupling constants in CF_3SF_3 $J_{SF_2-CF_3}$ have been measured as 24 H_z, the same as in CF_3SF_2OPh and $CF_3SF_2OC_6F_5$ (This is slightly different from the literature value for CF_3SF_3, $J_{SF_2-CF_3}$ = 22.3 H_z [102]). The chemical shifts of $>SF_2$

Table 3

^{19}F n.m.r. parameters of CF_3SF_2OPh and related compounds (relative to CCl_3F)

	Compounds	References	δCF_3	δSF_{eq}	δF_{ax}	coupling constants
1.	CF_3SF_2OPh	[Present work]	+68.5(t)	-	-35.0 (q)	$J_{SF_2-CF_3}$ =24 Hz
2.	$CF_3SF_2OC_6F_5$	[Present work]	+67.5(triplet of triplet)	-	-37.5 (q)	$J_{CF_3-F_2O}=6H_z$
3.	$CF_3SF_2CF_3$	[70]	+58	-	+14.2	$J_{SF_2-CF_3}$=19.5Hz
4.	CF_3SF_3	[Present work]	+70 (t)	+48.8(t)	-51.2 (d. of quartet)	J_{SF_2-SF} = 63.9 H_z $J_{SF_2-CF_3}$ = 24 H_z

t=triplet, q=quartet, d=doublet

axial fluorines of CF_3SF_2OPh and $CF_3SF_2OC_6F_5$ are at higher field than for CF_3SF_3 and can be explained due to the electronegativity differences of F and OC_6H_5 or OC_6F_5. $CF_3SF_2CF_3$ (3) shows an exceptionally high shift for the $>SF_2$ fluorine atoms and the value is close to the mean value of the axial and equatorial fluorine atoms of CF_3SF_3. To explain this shift a dynamic structure is suggested for $(CF_3)_2SF_2$ [77] with rapid positional exchange between axial and equatorial sites. The shifts of the CF_3 group in CF_3SF_2 OPh and $CF_3SF_2OC_6F_5$ are in agreement with the shift in CF_3SF_3 suggesting similar structures.

^{19}F n.m.r. spectra of the pentafluorophenyl group

^{19}F n.m.r. parameters of various substituted pentafluorophenyl group have been studied by various workers and correlated with the electronic interaction at the bond between substituent and the ring [112]. In addition to the ^{19}F nucleus, other nuclei (^{1}H and ^{13}C) have also been studied [113]. The pentafluorophenyl system has the advantage that the ^{19}F shifts are well separated and from the single spectra, ortho, meta and para ^{19}F n.m.r. parameters can be determined. In the absence of an isotropic and paramagnetic effects, the chemical shift seems to be a measure of the electron density at the nucleus [138]. Substituent effects on the electronic distribution can be followed from the chemical shifts of nuclei at different positions in the benzene ring. The classical concept of electronic interactions predicts changes in electron density at the ortho and para positions when the substituents exhibit resonance effects whereas changes in the electron density at the meta position are caused by an inductive effect for the substituent.

Apart from resonance and inductive effects, ortho chemical shifts are also influenced by the size of the substituent. In the table 4, the compound have a downfield shift of the ortho fluorine atom with a decrease in the electronegativity of the substituents. From the table, an increase in size of the substituent causes a downfield shift of the orthofluorine atom. This effect is described as an intermolecular Van der Waals effect [114]. Meta chemical shifts on the other hand are entirely dominated by the inductive effect of the substituent whereas in the para-chemical shifts resonance effects are prominent.

Table 4

^{19}F chemical shifts in monosubstituted perfluorobenzene relative to CCl_3F

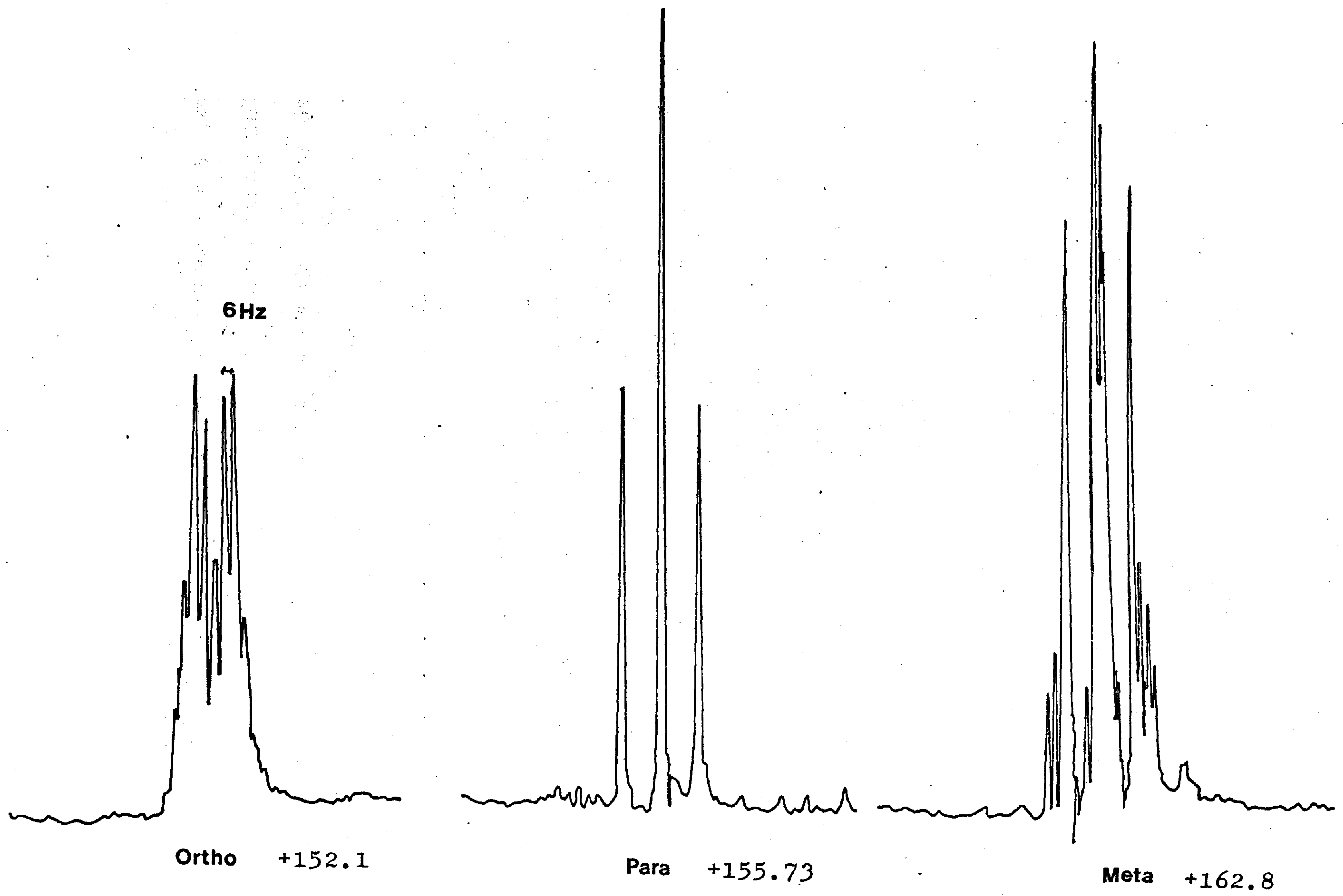
C_6F_5X substituent-X	(ortho)p.p.m.	(para)p.p.m.	(meta)p.p.m.	References
1. F	162.28	162.28	162.28	[114]
Cl	140.61	156.11	161.48	[114]
Br	132.54	154.65	160.60	[114]
I	119.18	152.53	159.65	[114]
$SnMe_3$	122.30	152.75	160.67	[114]
$HgMe_3$	121.91	153.52	160.05	[114]
C_6F_5	138.25	150.27	160.76	[114]
$NHCH_3$	161.89	173.07	165.21	[114]
H	138.89	153.50	162.05	[114]

Table 5

^{19}F chemical shifts in pentafluorophenoxy groups Relative to CCl_3F

	C_6F_5OX	(ortho)p.p.m.	(para)p.p.m.	(meta)p.p.m.	References
1.	$C_6F_5OSiMe_3$	158.7	167.6	165.1	Present work
2.	$C_6F_5OSi(C_6H_5)_3$	156.2	166.5	165	[112]
3.	$C_6F_5OGe(C_6H_5)_3$	157	169.2	166.3	[112]
4.	C_6F_5OH	164.4	171.2	165.8	[112]
5.	$(C_6F_5O)_3S(O)F$	154.0	157.2	164.2	D. S. Ross Thesis
6.	$(C_6F_5O)_3SF$	151.6	155.2	162.4	Present work
7.	$C_6F_5OSF_2CF_3$	152.1	155.73	162.8	Present work

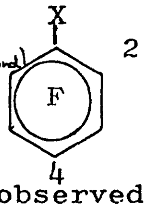
THE 19F NMR SPECTRUM OF OC_6F_5 GROUP ($CF_3SF_2OC_6F_5$)



The assignments of the spectra of compounds studied in the present work have been made by analogy with published spectra and on the basis of peak intensity. The chemical shifts of the pentafluorophenoxy groups are shown in the Table 5. It is interesting thing to note the change of the para chemical shifts of the different compounds. It has already been mentioned that the para shift is mainly dominated by the resonance effect of the ring substituent. When a substituent acts as an π-electron donor to the ring, the para fluorine nucleus becomes more shielded whereas an electron withdrawing substituent deshields the para-fluorine. In the above compounds the atom bonded to the ring is an oxygen and the change in para shifts will then indicate the extent that the atom or group attached to the oxygen influences electron donation to the ring.

From the relationship,(Assuming the relationship holds for the present compound)

$$J_{24} = -0.453\ p + 71.96 \quad [112]$$



J_{24} can be estimated from the para shift. The observed approximate value for J_{24} in $C_6F_5OSF_2CF_3$ is 1.1H_z and in $(C_6F_5O)_3SF$ 1.3 H_z but because of complexities of the spectra (parafluorine couples with two metafluorine strongly), the values are not precise. When $J_{24} = 0$ there is a balance of the substituent between π-electron donation to the ring and π electron withdrawl from the ring. A positive value indicates π withdrawl from the ring whereas a negative value (J_{24}) indicates π-donation.

For the compounds $(C_6F_5O)_3SF$ and $C_6F_5OSF_2CF_3$, values of J_{24}, +1.493 H_z and +1.67 H_z respectively are calculated from the above relationship. These values indicate that in these compounds the oxygen atom slightly withdraws electron from the ring. In other words this means that in $C_6F_5OSF_2CF_3$, the CF_3SF_2 group has imparted large electron withdrawl effect to the oxygen atom probably by π bonding to the sulfur vacant 'd' orbitals from the oxygen 'P' electrons. A similar effect may operate in $(C_6F_5O)_3SF$ where each C_6F_5 group loses electrons to the $SF(OC_6F_5)_2$ group.

'H n.m.r. spectrum

CF_3SF_2OPh δC_6H_5 = -6.7 p.p.m. T.M.S. ext

The proton spectrum of this compound is a broad singlet with no proton fluorine coupling. Relative to benzene downfield shift indicates that the protons are more deshielded. Electron withdrawing substituents deshield aromatic protons and the CF_3SF_2O is a typical such group.

INFRARED SPECTRA: (I) $CF_3SF_2OC_6H_5$ (II) $CF_3SF_2OC_6F_5$

Detailed spectra are given in the experimental section. In both the compounds, the presence of a phenoxy group makes it difficult to assign bands since the benzene nucleus shows many bands between 1600 cm^{-1} to 700 cm^{-1}. However in the compound $CF_3SF_2OC_6H_5$, the medium absorption at 3070 cm^{-1} can safely be assigned to the C-H stretching mode. The bands at 1591 cm^{-1} and 1488 cm^{-1} are assigned to ring stretching modes. CF_3SF_2OPh shows strong absorptions at 1244 cm^{-1} and 1115 cm^{-1}. Assignments are difficult since bands due to δCOS [82] and substituted benzene vibrational modes are expected in this region. However, by comparison with CF_3SF_3 [83], CF_3SF_5 [98] and $CF_3SF_2CF_3$ [70], the bands are probably assigned to C-F stretching modes. A strong absorption at 862 cm^{-1} is observed in $CF_3SF_2OC_6H_5$. A similar band at 851 cm^{-1} is observed in compound $CF_3SF_2OC_6F_5$. These are confusing since S-F stretching frequencies are recommended for this region [83] [98], the bands are retained in both cases after hydrolysis. In a study of infrared spectra of a series of covalent sulfate esters [119] bands at 800 cm^{-1} to 900 cm^{-1} were assigned to S-O stretching modes. On that basis, the present bands are also assigned to S-O stretching modes. The region 800 cm^{-1} to 600 cm^{-1} is expected to have several CF_3 deformation and F-C-F bending modes. Bands in this region are broad and could be due to the superimposition of two or more bands. However, a strong absorption at 777 cm^{-1} is observed in compound (I), but there is no similar band in compound (II). This band is assigned to a C-H out of plane mode [93]. The strong absorptions at 1722 cm^{-1} and 1520 cm^{-1} in $CF_3SF_2OC_6F_5$ are assigned to C=C ring modes.

The bands at 1257 cm^{-1}, 1228 cm^{-1} and 1109 cm^{-1} in compound (II) are assigned to C-F stretching modes. $CF_3SF_2OC_6F_5$ has a very strong absorption at 1000 cm^{-1} and there is no similar absorption in CF_3SF_2OPh. Typical values observed for the aromatic C-F modes are at 1011 cm^{-1} for C_6F_6 [117] and 983 cm^{-1} for C_6F_5N [117]. Both $CF_3SF_2OC_6H_5$ and $CF_2SF_2OC_6F_5$ have shown broad absorptions at 642 cm^{-1} and 653 cm^{-1} which disappear on hydrolysis. These bands are assigned to S-F modes.

MASS SPECTRA

Compound:

1. $CF_3S(=O)OMe$: 148M^{+}1, 117 $CF_3S^{+}(O)$ 8.1, 101$CF_3{}^{+}S$ 17.2, 79 $S(O)O^{+}Me$ 88.2, 69 CF_3^{+} 100, 64 SO_2^{+} 12.

2. $CF_3S(=O)OEt$: 162M^{+}·65, 147 $CF_3S(O)\overset{+}{O}CH_2$ 1.9, 117$CF_3\overset{+}{S}(O)$4.55, 101 $CF_3{}^{+}S$ 15.16, 93 $SO_2{}^{+}Et$ 83.3, 82 $CF_2{}^{+}S$ 2.49 69$C\overset{+}{F}_3$ 100.

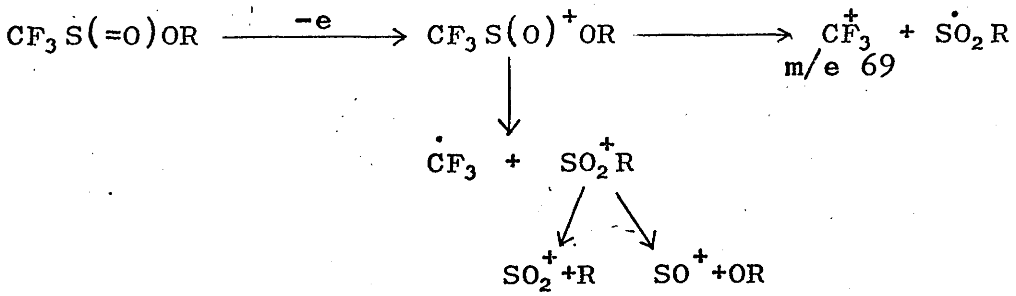
3. CF_3SF_2OPh: 228 $CF_3S(OH)_2^{+}OC_6H_5$ 0.54 226 $CF_3^{\bullet}SO_2^{+}OC_6H_5$ 7.46, 210 $CF_3\ S(O)^{+}OPh$ 2.48, 194$CF_3S\overset{+}{O}Ph$3.48,155 $CF_3\overset{+}{S}F_2O$ 10.94, 139 $CF_3\overset{+}{S}F_2$ 4.97, 120 $CF_3{}^{+}SF$ 1.24, 101 $CF_3\overset{+}{S}$ 1.19, 93 $C_6H_5\overset{+}{O}$ 21.89, 86 $\overset{+}{S}OF_2$ 69, 77 $C_6\overset{+}{H}_5$ 100, 69 $C\overset{+}{F}_3$ 54.72, 70 $\overset{+}{S}F_2$ 1.1, 64 $\overset{+}{S}O_2$ 23, 51 $S\overset{+}{F}$ 1.0.

4. $CF_3SF_2OC_6F_5$: 322 $\overset{+}{M}$ 0.27, 303 $CF_3SF^{+}OC_6F_5$ 1.0, 183 $C_6F_5\overset{+}{O}$ 3.3, 155 $C_5\overset{+}{F}_5$ 2.44, 139 $CF_3\overset{+}{S}F_2$ 16.6, 120 $CF_3\overset{+}{S}F$ 7.7, 117 $C_5F_3{}^{+}$4.5, 101 $CF_3^{+}S$ 1.0, 82 $CF_2{}^{+}S$ 16.6, 70 $S\overset{+}{F}_3$ 30, 69 CF_2^{+} 100, 51 $S\overset{+}{F}$ 32.2.

Discussion on Mass Spectra

Compounds (1) $CF_3S(=O)OMe$, (2) $CF_3S(=O)OEt$ $CF_3S(=O)OR$

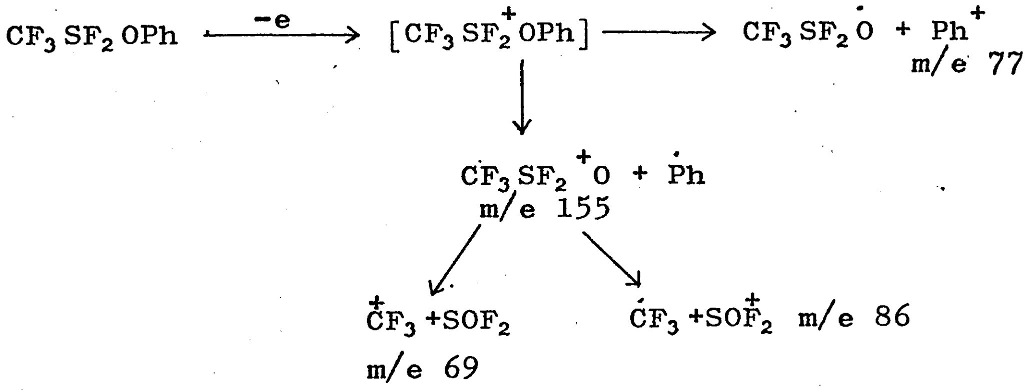
A cold inlet system was used to obtain mass spectra of the compounds $CF_3S(=O)OR$. In both the compounds molecular ion peaks were detected with low intensities. Molecular ion peaks and fragments such as CF_3^+, SO_2^+R and $CF_3\overset{+}{S}O$ support the proposed structures of the compounds. The most intense peaks are CF_3^+ and SO_2^+R which suggest the principal breakdown pathways involve the cleavage of the C-S bond rather than the S-O bond. A possible mechanism for breakdown of the ions is:



3. CF_3SF_2OPh

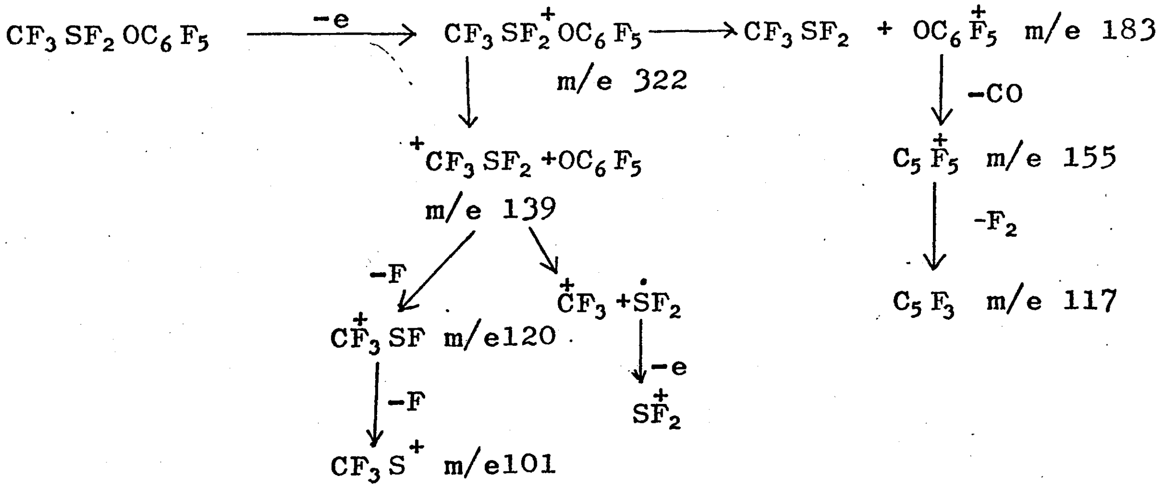
The mass spectrum was obtained using a heated inlet and direct probe systems. The parent ion is absent and the best spectrum was obtained from the heated inlet system. Although the parent ion is absent, $CF_3S(OH)_2^+OPh$ corresponding to the parent ion of the hydrolysed product of CF_3SF_2OPh was identified. This peak and peaks corresponding to ions

$CF_3SF_2\overset{+}{O}$, $CF_3\overset{+}{S}F_2$ and $C_6H_5^+$ are good evidences in favour of the proposed structure. The mass spectrum shows many peaks of low intensity but only the most intense peaks are recorded in Table. There are no peaks corresponding to ions $SF_2\overset{+}{O}Ph$ or $SF\overset{+}{O}Ph$, which indicates the breakdown of the parent ion probably involves S-O-C bond cleavage. The presence of a strong peak corresponding to a $CF_3S\overset{+}{F}_2O$ ion is strange, since in the spectra of compounds of the type SF_3ORX,, a $S\overset{+}{F}_3O$ ion is not observed [Chapter I]. The absence of any metastable ions curtails information on the mechanism of the fragmentation of ions. However based on relative abundance of the ions $CF_3SF_2\overset{+}{O}$, $C_6H_5^+$, $S\overset{+}{O}F_2$ and $C\overset{+}{F}_3$, the following breakdown mechanism can be proposed.



4. $\underline{CF_3SF_2OC_6F_5}$

A heated inlet system was used for this compound. The spectrum showed the parent ions and the parent less than one fluorine. The peak at m/e 155 is confusing, since the peak could be due to $CF_3SF_2\overset{+}{}O$ or $C_5F_5^{+}$, a possible fragment of $C_6F_5\overset{+}{O}$. The pattern does not indicate the presence of sulfur so that the assignment $C_5\overset{+}{F}_5$ was made. The absence of $C_6F_5^{+}$ could be explained by elimination of CO from a $C_6F_5\overset{+}{O}$ ion. This behaviour is common in phenoxy compounds [121] although in the absence of metastable ion, it is difficult to formulate the fragmentation pattern. The relative abundances of $CF_3\overset{+}{}SF_2$, $OC_6F_5^{+}$ and the absence of $SO\overset{+}{F}_2$ and $C_6F_5^{+}$ lead to the following breakdown mechanism.



The transition m/e 155 C_5F_5 to m/e 117 C_5F_3 is prominent in the observed spectrum of C_6F_6 [120].

EXPERIMENTAL

Me_3SiOCH_3, $Me_3SiOC_3H_5$ were obtained from Pierce Chemical Co. $Me_3SiOC_6H_5$ and $Me_3SiOC_6F_5$ were obtained as described previously. CF_3SSCF_3 was obtained from Peninsular Chemical laboratory. CF_3SF_3 was dried by condensing over NaF in a steel bomb.

Reactions:

Me_3SiOCH_3/CF_3SF_3 1:1 molar ratio:

10.5 mmoles of Me_3SiOCH_3 and 13.1 mmoles of CF_3SF_3 were allowed to react in a metallic test tube.

The reaction appeared to be complete after 12 hours. On fractionation Me_3SiF (10 mmoles), CH_3F(3.5 mmoles) and CF_3SFO (trace) (-126°C), unreacted CF_3SF_3 (-95°C) and a low volatile colourless liquid (-65°C) were obtained. A complete separation of the volatile products in the -126°C trap was not possible. The molar ratio of the volatile products was calculated from the n.m.r. spectra of the mixture. The relatively less volatile liquid at -65°C trap was identified as $CF_3S(=O)OMe$.

Mol.wt. cal. 148 Found (by mass spectrum) 148.

^1H n.m.r. $\delta OCH_3 \longrightarrow -3.66$ p.p.m. TMS ext

^{19}F n.m.r. $\delta CF_3 \longrightarrow +80$ (quartet) $_{H-F}$ 1.2 H_z

CH_3F - by n.m.r. (both ^1H and ^{19}F) Reference [75]

CF_3SFO - by infrared and ^{19}F n.m.r. Reference [96]

$Me_3SiOC_2H_5/CF_3SF_3$ 1:1 molar ratio

11 mmoles of $Me_3SiOC_2H_5$ and 14 mmoles of CF_3SF_3 were allowed to react at room temperature in a metal tube. The reaction was complete after about 10 hours. On fractionation Me_3SiF (10.1 mmoles) CF_3SFO (traces), unreacted CF_3SF_3 and C_2H_5F were obtained in -126°, -95° and -83°C traps. In the -45°C trap a colourless, fairly involatile liquid was obtained which was identified as $CF_3S(=O)OC_2H_5$.

Mol. wt. cal -162. Found 162 (by mass spectrum)

^1H n.m.r. $\delta_{CH_2} = -4.15$ p.p.m. (complex), $_{CH_3} = -1.1$ p.p.m. (triplet)

^{19}F n.m.r. $\delta_{CF_3} = +81.9$ p.p.m. CCl_3F(int)

C_2H_5F by ^1H and ^{19}F n.m.r. Reference [75]

3. <u>$CF_3SF_3/Me_3SiOC_6H_5$</u> 1:1 molar ratio

10.8 mmoles of Me_3SiOPh and 12 mmoles of CF_3SF_3 were allowed to react at room temperature for 3 to 4 hours. The products were Me_3SiF (10.2 mmoles), excess CF_3SF_3 collected in -126°C and -95°C traps respectively and an involatile colourless liquid identified as CF_3SF_2OPh. This product was identified from its Mass spectrum (the highest peak at m/e 228 corresponds to the parent ion of the hydrolysed product of $CF_3SF_2OC_6H_5$).

^1H n.m.r. δC_6H_5 = -6.7 p.p.m. (broad singlet)TMS ext.

^{19}F n.m.r. δCF_3 = +68.5 p.p.m. (triplet), δSF_2 =-35 p.p.m. (quartet) CCl_3F(int)

Infrared liquid film cm^{-1}

3070(br.m), 1591(m), 1488(s), 1461(w), 1244(v.s.) 1220(v.s.), 1165(sh), 1149(sh), 1115(v.v.s.) 1072(w), 1023(m), 909(sh), 862(br.s), 777(s), 763(m), 673(m), 642(br.s.), 600(s).

4. $Me_3SiOC_6F_5/CF_3SF_3$ 1:1 molar ratio

14 mmoles of $Me_3SiOC_6F_5$ and 16 mmoles of CF_3SF_3 were allowed to react at room temperature for 3 to 4 hours. The products were Me_3SiF (13.5 mmoles), excess CF_3SF_3 and a colourless involatile liquid which was identified as $CF_3SF_2OC_6F_5$.

Mol. wt. cal. 322 observed 322 (by mass spec.)

^{19}F n.m.r.:

δCF_3 = +67.5 p.p.m. (triplet of triplet), δSF_2 = -37.5(quartet) CCl_3F(int).

OC_6F_5 δ orthoF = +152.1 p.p.m.

δ paraF_2 = +155.73 p.p.m. CCl_3F(int)

δ metaF_2 = +162.8 p.p.m.

Infrared

liquid film cm^{-1}

1722(br.m.), 1520(br.v.s.), 1410(m), 1355(w), 1321(m), 1257(s), 1228(s), 1171(w), 1109(v.s.), 1024(s), 1000(v.v.s.), 936(w), 890(w), 851(s), 766(m), 752(m), 732(sh), 689(s), 653(br.s.).

CHAPTER III

REACTIONS OF PERFLUOROISOPROPYLSULFUR TRIFLUORIDE

REACTIONS OF $(CF_3)_2$ $CFSF_3$

INTRODUCTION

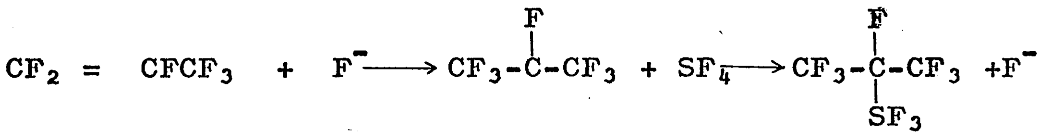
Rosenberg and Muetterties [16] reported the preparation of perfluoroalkylsulfur (IV) fluorides. When hexafluoropropene was treated with SF_4 at 150°C in the presence of CsF, the compound $(CF_3)_2CFSF_3$ resulted. In this reaction CsF acts as catalyst.

$$CF_3 - CF{=}CF_2 + SF_4 \xrightarrow[CsF]{150°C} (CF_3)_2CFSF_3$$

It was necessary to have excess SF_4 to form $(CF_3)_2CFSF_3$. With excess of hexafluoropropene, bisperfluoroisopropylsulfur difluoride was formed.

$$SF_4 + 2CF_3 - CF = CF_2 \xrightarrow[CsF]{150°C} (CF_3)\ CFSF_2CF(CF_3)_2$$

The catalytic role of CsF was ascribed to perfluorocarbanion formation and the subsequent nucleophilic attack on SF_4 [122] [123].



$$CF_2 = CFCF_3 + F^- \longrightarrow CF_3-\overset{F}{\overset{|}{C}}-CF_3 + SF_4 \longrightarrow CF_3-\underset{\underset{SF_3}{|}}{\overset{\overset{F}{|}}{C}}-CF_3 + F^-$$

Perfluoroisopropyl sulfur trifluoride $(CF_3)_2CFSF_3$ is expected to react similarly to other sulfur trifluorides [16]. It hydrolyses rapidly in air to produce $(CF_3)_2CFSFO$ and HF.

$$(CF_3)_2CFSF_3 + H_2O \longrightarrow (CF_3)_2CFS({=}O)F + 2HF$$

The controlled hydrolysis of the compound in diethylether yielded a sulfinic acid [16].

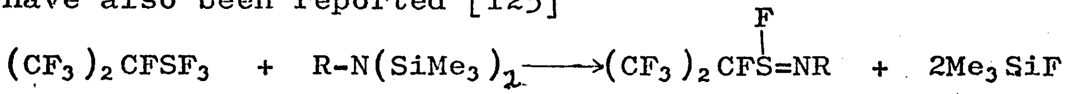
$$(CF_3)_2CFSFO + H_2O \longrightarrow (CF_3)_2CFS(O)OH + HF$$

Substitution [124] involving the initial cleavage of a Si-N bond was successful. $(CF_3)_2CFSF_3$ reacted with Me_3SiNR_2 to produce a monosubstituted derivative of $(CF_3)_2CFSF_3$.

$$(CF_3)_2CFSF_3 + Me_3SiNR_2 \longrightarrow (CF_3)_2CFSF_2NR_2 + Me_3SiF$$

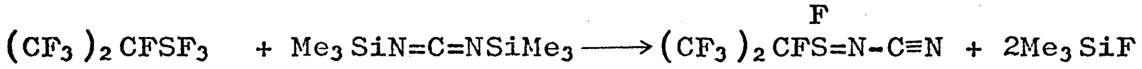
where R = CH_3, C_2H_5

The following reactions of perfluoroisopropylsulfur trifluoride have also been reported [125]



$$(CF_3)_2CFSF_3 + R\text{-}N(SiMe_3)_2 \longrightarrow (CF_3)_2CF\overset{F}{\overset{|}{S}}{=}NR + 2Me_3SiF$$

R = CH_3, $CH_3\text{-}C(O)\text{-}$

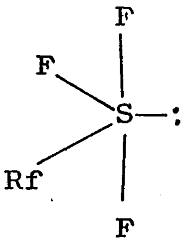


$$(CF_3)_2CFSF_3 + Me_3SiN{=}C{=}NSiMe_3 \longrightarrow (CF_3)_2CF\overset{F}{S}{=}N\text{-}C{\equiv}N + 2Me_3SiF$$

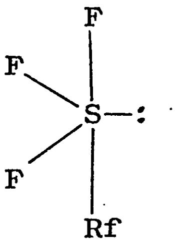
The compound $(CF_3)_2CFSF_3$ had no published infrared spectrum. In the present work, the compound showed the following absorption bands in the gas phase. The assignments of the strong absorption bands are made by analogy with the published spectra of the compounds [83] $[(CF_3)_2CF]_2SF_2$ and CF_3SF_3 [83]

Absorptions cm^{-1}	Assignments
1295 (v.s.), 1253 (v.s)	C-F stretching mode
1175, 1161	C-F stretching mode
973, 934	C-C stretching mode
839, 721	S-F stretching mode
702	SF_3 deformation

The ^{19}F nmr spectrum of $(CF_3)_2CFSF_3$ indicated a trigonal bipyramid geometry for the compound. The following two structures were considered [16].



(A)



(B)

Rf = $(CF_3)_2CF$

By analogy with the structure of SF_3ORX [Chapter I] and CF_3SF_3 [Chapter II] the ^{19}F nmr chemical shifts of SF fluorine atoms strongly support structure (A) for $(CF_3)_2CFSF_3$.

Reaction of $RfSF_3$ with alkoxytrimethylsilane $[Rf=(CF_3)_2CF]$:

The reaction between the $RfSF_3$ and $ROSiMe_3$, where R is an alkyl group does not produce a substituted derivative of the type $RfSF_2OR$. As in the case of CF_3SF_3 (Chapter II), the reactions with alkoxytrimethylsilanes result in Me_3SiF, $(CF_3)_2CFSFO$, RF and $(CF_3)_2CFS(=O)OR$. The latter compounds are probably formed by a secondary reaction between $(CF_3)_2CFSFO$ and Me_3SiOR. The following steps can be assumed:

$$(CF_3)_2CFSF_3 + Me_3SiOR \longrightarrow (CF_3)_2CFSF_2OR + Me_3SiF$$

$$(CF_3)_2CFSF_2OR \longrightarrow (CF_3)_2CFSFO + RF$$

$$(CF_3)_2CFSFO + Me_3SiOR \longrightarrow (CF_3)_2CFS(=O)OR + Me_3SiF$$

Since the reactions are carried out with a 1:1 molar ratio of the reactants, the formation of $(CF_3)_2CFS(=O)OR$ can be explained by assuming that the secondary reaction between $(CF_3)_2CFSFO$ and Me_3SiOR is faster than the reaction between $(CF_3)_2CFSF_3$ and Me_3SiOR. The reaction was attempted with both $MeOSiMe_3$ and $EtOSiMe_3$. In both cases, apart from RfSFO and Me_3SiF, similar compounds of the type RfS(=O)OR are produced. The preparation of $RfS(=O)OC_2H_5$ has been reported by ethanolysis of the acid RfS(=O)OH [16].

Details of the reactions are given in the experimental section.

Reaction of aryloxytrimethylsilane with R_fSF_3:

The reaction was attempted with a number of aryloxytrimethylsilane having substituents such as CH_3, CF_3, NO_2 in the paraposition of the benzene nucleus. Although phenoxytrimethylsilane has successfully yielded monoderivative of SF_4 and CF_3SF_3 [this work], with $(CF_3)_2CFSF_3$, no clear product is obtained. In the series of aryloxytrimethylsilanes, the reaction of $(CF_3)_2CFSF_3$ only gives a monoderivative when the benzene nucleus has strong electron withdrawing groups such as CF_3 or NO_2 in the paraposition.

Reactions:

1. $PhOSiMe_3/(CF_3)_2CFSF_3$ 1:1 molar ratio.

Using a equimolecular ratio of reactants, the reaction is allowed to stand for 12 hr at 20°C. On examining the volatile products, $(CF_3)_2CFSFO$ and Me_3SiF are identified by i.r. and n.m.r. data. The other non-volatile compounds which are coloured solid polymeric in nature are not characterized.

$$(CF_3)_2CFSF_3 + PhOSiMe_3 \longrightarrow (CF_3)_2CFSFO + Me_3SiF + \text{coloured solid}$$

2. $\underline{p}CH_3C_6H_4OSiMe_3/(CF_3)_2CFSF_3$

With an excess of $(CF_3)_2CFSF_3$, $CH_3C_6H_4OSiMe_3$ reacts at room temperature in three hours to produce products such as $(CF_3)_2CFSFO$, Me_3SiF and an unidentified coloured solid

$$(CF_3)_2CFSF_3 + \underline{p}CH_3C_6H_4OSiMe_3 \longrightarrow (CF_3)_2CFSFO + Me_3SiF + \text{black coloured solid}$$

3. $\underline{m}FC_6H_4OSiMe_3/(CF_3)_2CFSF_3$

A mixture of $(CF_3)_2CFSF_3$ and $mFC_6H_4OSiMe_3$ in equimolecular proportions reacts after twelve hours. The volatile products Me_3SiF, $(CF_3)_2CFSFO$ and $C_6H_4F_2$ were identified by ir and ^{19}F nmr spectroscopy

$$(CF_3)_2CFSF_3 + \underline{m}FC_6H_4OSiMe_3 \longrightarrow (CF_3)_2CFSFO + FC_6H_4F + Me_3SiF$$

4. $pCF_3C_6H_4OSiMe_3/(CF_3)_2CFSF_3$

With an excess of $(CF_3)_2CFSF_3$, $pCF_3C_6H_4OSiMe_3$ reacts slowly at 70° to produce $(CF_3)_2CFSF_2OC_6H_4CF_3p$. The volatile product is Me_3SiF,$(CF_3)_2CFSF_2OC_6H_4$ is a slightly reddish involatile liquid.

$(CF_3)_2CFSF_3 + pCF_3C_6H_4OSiMe_3 \rightarrow (CF_3)_2CFSF_2OC_6H_4CF_3 + Me_3SiF$

The yield of $pCF_3C_6H_4OSF_2CF(CF_3)_2$ is 30% calculated from the amount of Me_3SiF. Unreacted $Me_3SiOC_6H_4CF_3$ cannot be separated from $pCF_3C_6H_4OSF_2CF(CF_3)_2$ and hence a pure $pCF_3C_6H_4OSF_2CF(CF_3)_2$ was not obtained.

$pCF_3C_6H_4OSF_2CF(CF_3)_2$ hydrolyses in air to give HF and $(CF_3)_2CFS(=O)OC_6H_4CF_3$, identified by mass spectroscopy.

$(CF_3)_2CFSF_2OC_6H_4CF_3 + H_2O \longrightarrow (CF_3)_2CFS(=O)OC_6H_4CF_3 + 2HF$.

5. $(CF_3)_2CFSF_3/pNO_2C_6H_4OSiMe_3$

With an excess of $(CF_3)_2CFSF_3$, $pNO_2C_6H_4OSiMe_3$ reacts at 90°C. The reaction is completed in 30 hr. After fractionating off Me_3SiF and excess $(CF_3)_2CFSF_3$, the involatile red colour liquid left is confirmed as $(CF_3)_2CFSF_2OC_6H_4NO_2p$.

$(CF_3)_2CFSF_3 + pNO_2C_6H_4OSiMe_3 \longrightarrow (CF_3)_2CFSF_2OC_6H_4NO_2p + Me_3SiF$

When the compound $(CF_3)_2CFSF_2OC_6H_4NO_2p$ is exposed to air, it hydrolyses to HF and $(CF_3)_2S(=O)-OC_6H_4NO_2p$, identified by mass spectroscopy.

6. $(CF_3)_2CFSF_3/C_6F_5OSiMe_3$

Pentafluorophenoxytrimethylsilane is allowed to react at 60°C for several hours with an excess of $(CF_3)_2CFSF_3$. The i.r. spectrum of the volatile products indicate the formation of Me_3SiF. A ^{19}F n.m.r. of the almost involatile liquid shows decomposition of the pentafluoroalkyl group: The products could not be identified.

$(CF_3)CFSF_3 + C_6F_5OSiMe_3 \longrightarrow$ decomposed.

D I S C U S S I O N

The reaction of $PhOSiMe_3$ and $pCH_3C_6H_4OSiMe_3$ with $(CF_3)_2CFSF_3$ gives a number of products - two of them identified as $(CF_3)_2CFSFO$ and Me_3SiF. In the reaction of alkoxytrimethylsilane, the decomposition products are $(CF_3)_2CFSFO$, Me_3SiF and RF [where R = CH_3, C_2H_5]. If the reaction proceeds in the same way as with alkoxytrimethylsilane, fluorobenzene should have been formed. Only in the case of $mFC_6H_4OSiMe_3$ is $C_6H_4F_2$ identified among the volatile products.The reaction produces an unidentified coloured solid polymeric in nature. It seems that the reaction proceeds through intermediate formation of $RfSF_2ORX$ [where RX = -Ph, CH_3 or F substitued benzene] which subsequently decomposes to RfSFO.

$$\begin{array}{lcl} (CF_3)_2CFSFO + Me_3SiOC_6H_4X & \longrightarrow & [(CF_3)_2CFSF_2ORX] + Me_3SiF \\ & & \quad\quad\quad\downarrow \\ & & (CF_3)_2CFSFO + FC_6H_4X \end{array}$$

The failure to obtain fluorobenzene in the reaction of $PhOSiMe_3$ with $(CF_3)_2CFSF_3$ (1) and (2) $pCH_3C_6H_4OSiMe_3$ with R_fSF_3 may be explained by the occurrence of subsequent reactions among the aromatic groups. SF_3OPh decomposes on heating to produce SOF_2 [68] but no fluorobenzene is identified in the volatile products and a coloured solid is found as a residue. The stability of $pCF_3C_6H_4OSF_2CF(CF_3)_2$ and $pNO_2C_6H_4OSF_2CF(CF_3)_2$ may be explained as follows: The empty 'd' orbitals of the sulfur and filled 'p' orbitals of the oxygen tend to interact with each other in S(IV)-O compounds in which the S-O linkages are formally single bonded [126]. The increased S-O bond order reduces the C-O bond order and there is an increased tendency to cleavage of the C-O bond. In the compounds SF_3OPh [68] and CF_3SF_2OPh [Chapter II], the oxygen atom is bonded to the benzene by means of mesomerism and this counteracts the $S \Leftarrow O$ π(p-d) interaction. In $(CF_3)_2CFSF_2OPh$, the Rf group appears to impart a more negative inductive effect on the sulfur atom than the single fluorine atom and consequently the benzene ring can not effectively counteract the $S \Leftarrow O$ π(p-d) effect. The result is the formation of RfSFO i.e. S=O double bond formation. However when an oxygen atom bonded to a benzene nucleus having a strong electron withdrawing group such as CF_3 or NO_2 in the para position, there is less resultant influence on the oxygen atom because the negative inductive effect of $RfSF_2$ appears to balance π(p-d) interaction. This results in some stability for the compounds $(CF_3)_2CFSF_2OC_6H_4CF_3\underline{p}$ and $(CF_3)_2CFSF_2OC_6H_4NO_2\underline{p}$.

Nuclear Magnetic Resonance Spectroscopy

^{19}F nmr parameters of $(CF_3)_2CFS(=O)OR$ and related compounds

^{19}F nmr parameters of the compounds $(CF_3)_2CFS(O)OMe$ (1) and $(CF_3)_2CFS(O)OEt$ (2) are given in Table I. The chemical shifts of the compound (2) compare well with the reported [16] values of the same compound prepared in a different way. Compound (1) shows a simple first order AX_6 spectrum. The two CF_3 groups are equivalent and show a doublet through coupling with a single fluorine atom of $\geq CF$ group which itself is split into a septet through interaction with six fluorine atoms.

TABLE 1 (Relative to CCl_3F)

Compound	CF_3	CF	SF	Coupling Constants	Reference
1. $(CF_3)_2CFS(O)OMe$	+73.3	+184.1	-	J_{CF_3-CF} 8 Hz	This work
2. $(CF_3)_2CFS(O)OEt$	+71.3	+180.5	-	J_{CF_3-CF} 8 Hz	This work
3. $(CF_3)_3CFS(O)OH$	+72.63	+182.3	-	J_{CF_3-CF} 8 Hz	[16]
4. $(CF_3)_2CFS(O)F$	+70.6	+180.4	+10.2	- -	[97]

Compound (2) however shows a complicated ^{19}F nmr spectrum. The spectrum of the $\gtrdot$CF group shows septets as is expected for an AX_6 system. Assuming the first order treatment is applicable. The spectrum of an CF_3 group is expected to be a doublet due to the coupling with one fluorine atom of $\gtrdot$CF group. Experimentally multiplets are observed at room temperature which at -60°C give rise to quintuplets. This is explained if the molecule contains stereochemically or magnetically non equivalent CF_3 groups. A substituted ethane-type structure [16] is assumed in which non-equivalence arises from the time averaging process of energetically different isomers (Fig.). Alternatively if the configuration about 'S' is pyramidal, the two CF_3 groups are non-equivalent.

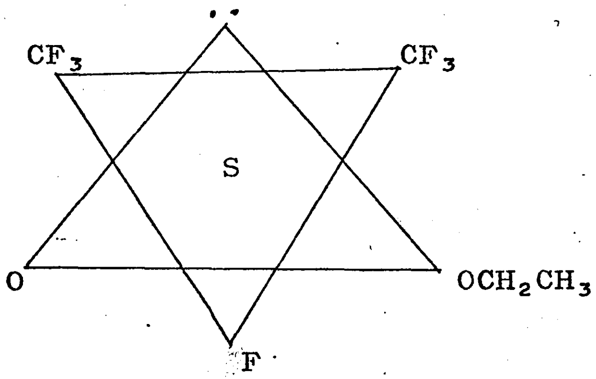


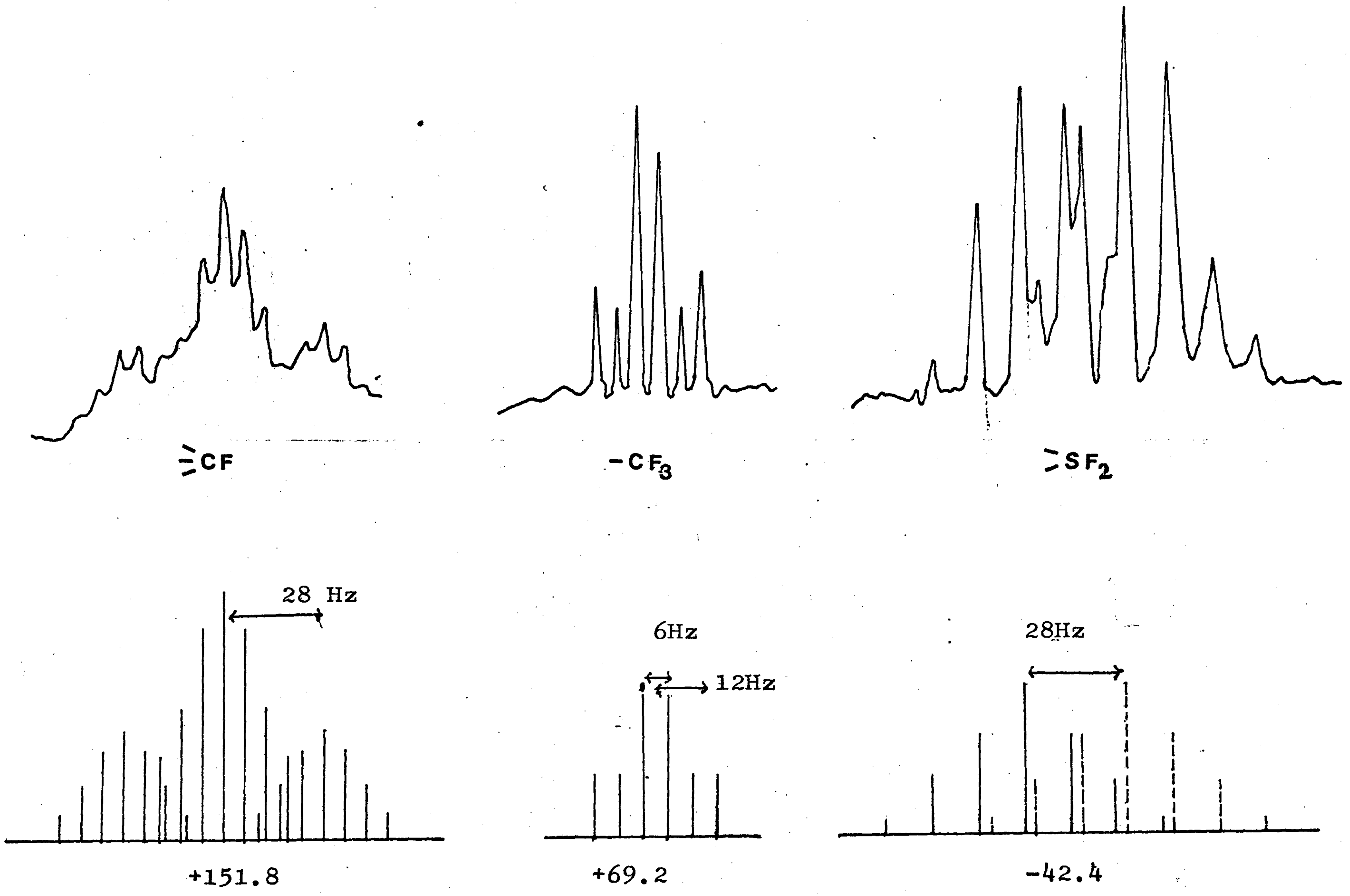
Fig.

Although eight line patterns are expected for each CF_3 group, quintuplet structures are observed as a result of overlap of peaks arising from nearby equivalent CF_3-CF_3 and CF_3-CF spin coupling.

<u>^{1}H nmr parameters of Rf-S(O)OR</u> (Rf = $(CF_3)_2CF$)

1. $(CF_3)_2CFS(O)OMe$	δ OMe= -3.66 ppm		TMS ext
2. $(CF_3)_2CFS(O)OEt$	δ CH_3= -1.1	(triplet) ppm	TMS ext
	δ CH_2= -4.15	(quartet) ppm	TMS ext

THE ^{19}FNMR OF $(CF_3)_2CFSF_2OC_6H_4NO_2p$



Compound (1) shows a single peak at -3.66 assigned to the OMe group. Compound (2) shows a triplet for the CH_3 group and a quartet for the CH_2 group which on high resolution shows complexity possibly arising from interaction with neighbouring fluorine atoms and because of magnetically non-equivalent CH_2 protons.

^{19}F nmr parameters of $RfSF_2OC_6H_4CF_3\underline{p}$ and $RfSF_2OC_6H_4NO_2\underline{p}$

$Rf = (CF_3)_2\ CF$

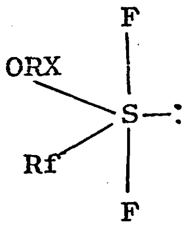
The identification of the different peaks are made by analogy with published spectra (given in the table 2) from the nature of splitting and by the measurement of intensities of the different peaks. The ^{19}F nmr spectrum of $RfSF_2OC_6H_4CF_3\underline{p}$ (1) shows peaks at -44.4, + 61.8, +68.8 and 152.1 ppm with the intensities 2,3,6 and 1 respectively which are thus assigned to $>SF_2$, CF_3C, $(CF_3)_2$ and $>CF$ fluorine atoms. The different peaks of (2) are assigned similarly. The aryl CF_3 group of (1) shows a single peak at +61.8 ppm [$SF_2(OC_6H_4CF_3)_2$ Chapter I $CF_3 = +62$ ppm]. The fluorine atoms in the $>SF_2$ groups of (1) and (2) are split in a first order manner to two superimposed septets arising from the coupling with $>CF$ fluorine atom and with six equivalent fluorine atoms in two CF_3 groups. The chemical shifts of the $>SF_2$ fluorine atoms of (1) and (2) are 17.3 and 19.3 ppm upfield relative to the value of the axial fluorine atoms of (6). This difference is consistent with the example of CF_3SF_3, CF_3SF_2OPh [Chapter II] SF_3ORX and SF_4[Chapter II] and can be explained similarly by the

TABLE 2

Compound	SF_2	CF_3	CF	CF_3C	Coupling Constants	References
1. $RfSF_2OC_6H_4CF_3\underline{p}$	-44.4	+68.8	+152.1	+61.8	J_{SF_2-CF} = 28 Hz $J_{CF_3-SF_2}$ = 12 Hz J_{CF_3-CF} = 6 Hz	
2. $RfSF_2OC_6H_4NO_2\underline{p}$	-42.4	+69.2	+151.8	-		
3. $RfSF_2NMe_2$	- 9.8	+72.7	+156.7	-	J_{SF_2-CF} = 20.3 Hz $J_{SF_2-CF_3}$ = 12.3 Hz J_{CF_3-CF} = 5 Hz	[124]
4. $RfSF_2NEt_2$	- 8.2	+72.3	+157.2	-		
5. $RfSF_2Rf$	+14	+75	+146.4		$J_{SF_2-CF_3}$ = 10 Hz J_{SF_2-CF} = 4 Hz J_{CF_3-CF} = 7.5 Hz	[16]
		$SF_{eq.}$	CF_3	CF		
6. $RfSF_3$	-61.7	+53.8	+73.7	+167.7	$J_{SF_2SF_{eq}}$ = 4.8 Hz $J_{SF_2-CF_3}$ = 1 Hz J_{SF_2-CF} = 2.8 Hz	[16]

$Rf = (CF_3)_2CF$

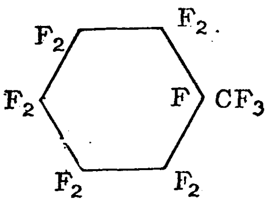
difference of the electronegativities of F and ORX groups. The chemical shifts of the $>SF_2$ fluorine atoms of (3) and (4) are at relatively high field but are consistent with the trend in SF_3NR_2 [22]. The six equivalent fluorine atoms in the CF_3 group of (1) and (2) show triplets of doublets which can be accounted for by the coupling to $>SF_2$ fluorine atoms and $\geq CF$ fluorine atom. It is interesting that there is a higher coupling constant between $>SF_2$ and CF_3 than between CF_3 and CF atoms. This behaviour is common to compounds $RfSF_2NMe_2$, $RfSF_2NEt_2$ and $RfSF_2Rf$ and is discussed latter. The $\geq CF$ fluorine atom of (1) and (2) is split into triplets each of which is split into septets in a first order spin pattern. The ^{19}F nmr parameters of compound $RfSF_2Rf$ show major differences from other disubstituted derivatives such as $RfSF_2OC_6H_4CF_3$, $RfSF_2OC_6H_4NO_2\underline{p}$, $RfSF_2NMe_2$ and $RfSF_2NEt_2$ which indicate a different geometry for $RfSF_2Rf$. An axial substitution in this compound has been suggested for the Rf group [77]. The ^{19}F nmr data of $RfSF_2OC_6H_4CF_3\underline{p}$ and $RfSF_2OC_6H_4NO_2\underline{p}$ are consistent with the presumption of trigonalbipyramidal geometry of the compounds where two substitutions occur in the equatorial position.



Structure of $RfSF_2OC_6H_4X$ [$X = CF_3\underline{p}$v $NO_2\underline{p}$]

Coupling constants [75]:

It is suggested that F-F coupling operates by both 'through bond' and 'through space' mechanisms. For atoms separated by a single bond, both mechanisms are thought to be important, whereas when the atoms are separated by a number of bonds, yet the coupling interaction between the atoms is prominent, a through space mechanism is considered the major contributing factor. In a number of examples [127] it was shown that coupling constants involving fluorine nuclei do not decrease monotonically with the number of bonds separating the interacting nuclei. For example, in the ^{19}F nmr spectrum of $(CF_3)_2NCF_2CF_3$ the fluorines of CF_2 are coupled very weakly with the adjacent CF_3 group $[J_{CF_2-CF_3} \rangle 1$ cps] but are strongly coupled to the more remote $(CF_3)_2N$ group $[J_{CF_2-NCF_3} = 16$ Hz] [128]. A similar observation was made in the ^{19}F spectrum of the CF_3 group in perfluoromethylcyclohexane $C_6F_{11}CF_3$:



$C_6F_{11}-CF_3$

The CF_3 group more strongly with the two neighbouring ring CF_2 group than with the single fluorine nucleus of the substituted carbon atom. The steric interaction in these molecules were thought to force the fluorine atoms [133] into closer proximity with each other, thereby increasing the F-F spin coupling.

Coupling constants arising from the interactions of magnetically non-equivalent fluorine atoms for compounds $RfSF_2OC_6H_4CF_3p$ and $RfSF_2OC_6H_4No_2p$ and for other compounds are given in the table 2. In all the cases CF_3 groups couple more strongly with the $>SF_2$ fluorine nuclei than with the single fluorine atom of the substituted carbon atom.By analogy with the above argument, it can be said for steric reasons the CF_3 group and $>SF_2$ fluorine atoms are closer than the single fluorine atom of the $\geq CF$ groups so that 'through space' mechanism is prominent in these compounds.

^{1}H SPECTRA

1. $pCF_3C_6H_4OSF_2CF(CF_3)_2$ δC_6H_4= -7.56(A_2B_2 quartet)ppm TMS ext.

2. $pNO_2C_6H_4OSF_2CF(CF_3)_2$ δC_6H_4= -7.93(A_2B_2 quartet)ppm TMS ext.

$pCF_3C_6H_4OSF_2CF(CF_3)_2$ and $pNO_2C_6H_4OSF_2CF(CF_3)_2$ show proton nmr spectra at -7.56 and -7.93 ppm respectively. The spectra are split into A_2B_2 quartets as is expected from substituents in the paraposition of a disubstituted aromatic ring. The large downfield shift of the protons can be explained by two factors (1) electron withdrawing effects of the CF_3 or NO_2 groups (2) and the negative inductive effect of $(CF_3)_2CFSF_2$ and the oxygen atom.

INFRARED SPECTRA

The infrared spectrum of $pCF_3C_6H_4OSF_2CF(CF_3)_2$ was not obtained since the compound could not be obtained pure. The spectrum of $pNO_2C_6H_4OSF_2CF(CF_3)_2$ however was obtained satisfactorily. The compound $pNO_2C_6H_4OSF_2CF(CF_3)_2$ shows many bands from 1600 cm^{-1} to 600 cm^{-1}, of which the most intense are assigned by analogy with published spectra of $RfSF_2Rf$ [83].

At 3128 cm^{-1} and 2991 cm^{-1}, two medium absorption bands are assigned to C-H stretching modes.

By comparison with $(CF_3)_2CFSF_2CF(CF_3)_2$ [83] bands at 1285 cm^{-1}, 1170 cm^{-1} and 1153 cm^{-1} are assigned C-F stretching modes and two absorptions at 969 cm^{-1} and 924 cm^{-1} are assigned to C-C stretching modes.

A strong absorption at 867 cm^{-1} is assigned to the S-O stretching mode as in covalent sulfate esters [119] In $(CF_3)_2CFSF_2NMe_2$ and $(CF_3)_2CFSF_2NMe_2$ [124] absorptions at 632 cm^{-1} and 629 cm^{-1} are assigned to S-F stretching modes. In CF_3SF_2OPh and $CF_3SF_2OC_6F_5$ [Chapter II], the S-F stretching frequencies occur at 700 cm^{-1} to 600 cm^{-1}. $pNO_2C_6H_4OSF_2CF(CF_3)_2$ has two broad strong bands at 655 cm^{-1} and 633 cm^{-1} which disappear on hydrolysis and are assigned to S-F stretching modes.

Compound: $pNO_2C_6H_4OSF_2CF(CF_3)_2$

Absorptions cm^{-1}	Assignments
3128	C-H stretching modes
2991	
1591	C=C ring stretching
1290	C-F stretching modes
1770	
1153	
969	C-C stretching modes
924	
867	S-O stretching modes
655	S-F stretching modes
633	

MASS SPECTRA

Mass Spectral Data

Compound 1. $(CF_3)_2CFS(O)OMe$: 248M^+1, 233 $(CF_3)_2CF^+SO_2$ 4.75, 217 $(CF_3)_2CF^+SO$ 4.75 201 $(CF_3)_2CF^+S$ 5.12, 169 $C_3F_7^+$ 6.12, 150 $C_3F_6^+$ 37.5, 131 $C_3F_5^+$ 43.75, 119 $C_2F_5^+$ 106, 100 $C_2F_4^+$ 83.75, 79 $\overset{+}{S}O_2Me$ 93.75, 69 $\overset{+}{C}F_3$ $\underline{\underline{100}}$

Compound 2. $(CF_3)_2CFS(O)OEt$: 262M^+ 1.21, 247 $(CF_3)_2CF^+SO_2CH_2$ 2.11, 233 $(\overset{+}{C}F_3)_2CFSO_2$ 2.77, 217 $(CF_3)_2CF^+SO$ 5.11, 201 $(CF_3)_2CF^+S$ 24.4, 169 $(\overset{+}{C}F_3)_2CF$ 17.7, 150 $(CF_3)_2C^+$ 32.2, 131 $C_3F_5^+$ 47.2, 119 $C_2F_5^+$ 27.7, 93 SO_2Et^+ 83.3, 78 $SO_2^+CH_2$ 32.2, 69 CF_3^+ $\underline{100}$

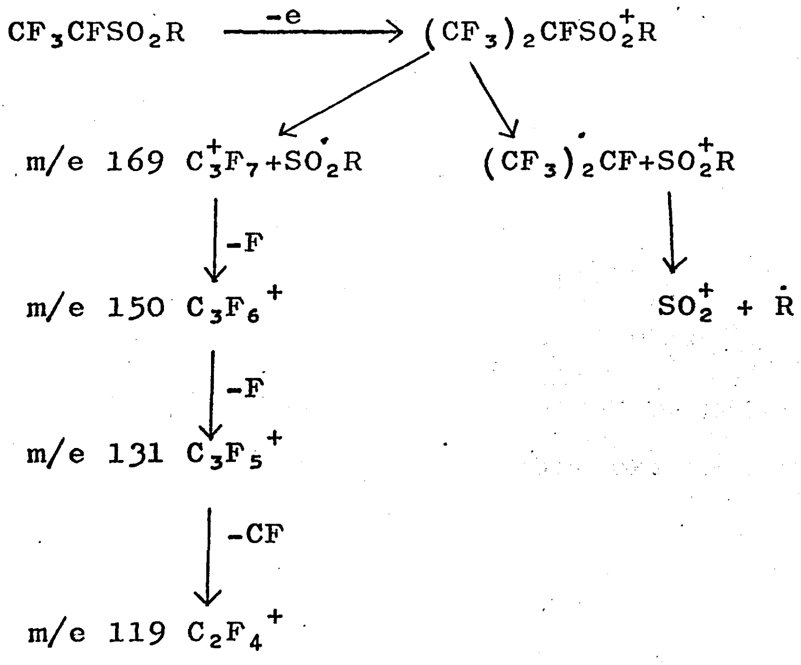
Compound 3. $(CF_3)_2CFSF_2OC_6H_4CF_3\underline{p}$: 400$M^+$ 12.8, 239 $SF_2CF^+(CF_3)_2$ 10.25, 231 $CF_3C_6H_4^+O$ 1.70, 220 $SF\overset{+}{C}F(CF_3)_2$ 2.9, 201 $SCF^+(CF_3)_2$ 9.4, 169 $(CF_3)_2^+CF$ 23.11, 151 $SC_2^+F_4$ 17.09, 150 $C_3F_6^+$ 3.24, 145 $CF_3\overset{+}{C}_6H_4$ 72.64, 131 $C_3F_5^+$ 25.64, 119 $C_2\overset{+}{F}e$ 5.98, 113 $C_3F_3^+S$ 17.94, 100 $C_2F_4^+$ 12.84, 92 $C_6H_4^+O$ 5.12, 75 $C_6H_4^+$ 72.64, 69 CF_3^+ $\underline{\underline{100}}$

Compound 4 $\underline{p}O_2NC_6H_4OSF_2CF(CF_3)_2$: 377$M^+$ 5.29, 358 $O_2NC_6H_4OSF^+CF(CF_3)_2$ 5.21, 239 $(\overset{+}{C}F_3)_2CFSF_2$ $\underline{100}$, 220 $(CF_3)_2CF^+SF$ 37.64, 201 $SCF(\overset{+}{C}F_3)_2$ 15.29, 208 $O_2NC_6H_4^+OSF_2$ 1.0, 186 $O_2N\overset{+}{C}_6H_4O_2S$ 89.41, 170 $SF_2^+CFCF_3$ 2.47, 169 $C_3^+F_7$ 27.05, 151 $SC_2F_5^+$ 34.11, 150 $C_3^+F_6$ 13.1, 138 $O_2\overset{+}{N}C_6H_4O$ 4.7, 122 $ONC_6H_4^+O$ 38.82, 113 $C_3F_3^+S$ 24.7, 100 $C_2^+F_4$ 17.64 92 $C_6H_4^+O$ 12.94, 69 CF_3^+ $\underline{80.0}$

Discussions of mass spectral data

Compound (1) and (2)

In both cases molecular ions are observed. The spectra show a dominance of the fluoroalkyl group. Molecular ions and fragments such as $C_3F_7SO_2^+$, $C_3F_7SO^+$, $C_3F_7S^+$ and $\overset{+}{SO_2}R$ strongly support the proposed structures. The most intense peaks suggest that the principal pathways for breakdown involve C-S bond rather than S-O bond cleavage. A possible mechanism for breakdown of the compounds is:



Compound (3) and (4)

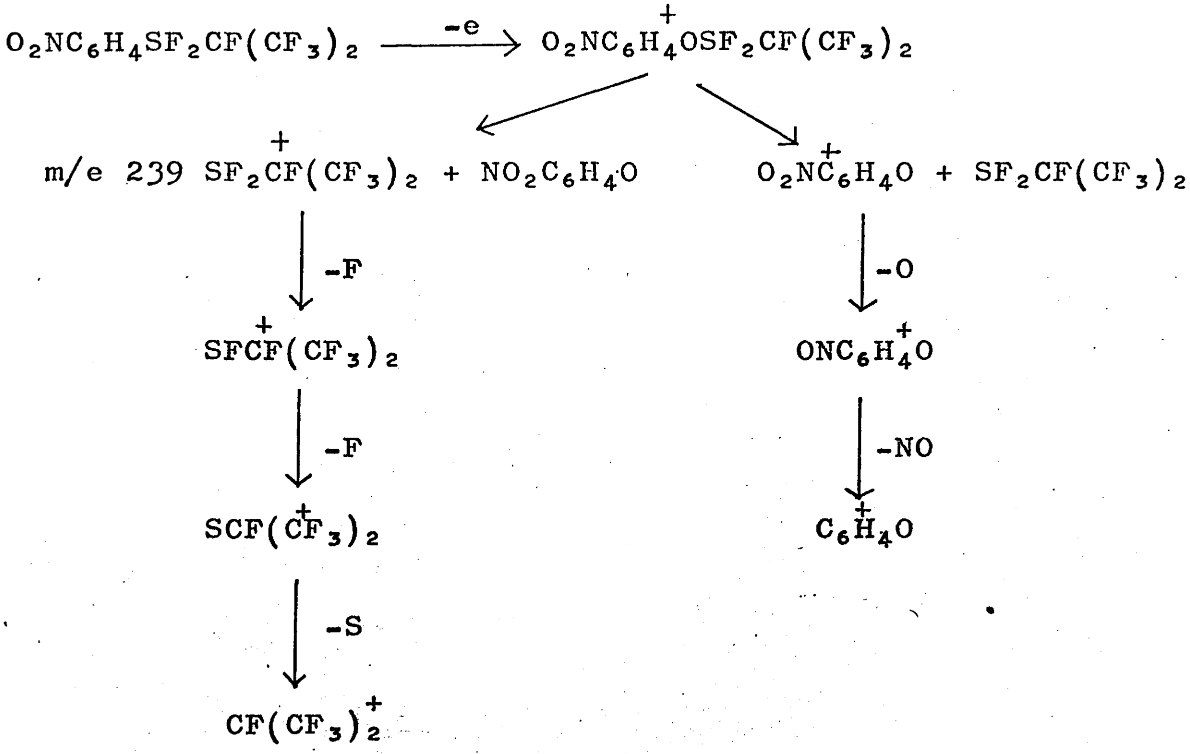
The mass spectra were obtained by means of a heated inlet system for $\underline{p}CF_3C_6H_4OSF_2CF(CF_3)_2$ and by applying the sample directly to the probe in the case of $\underline{p}NO_2C_6H_4OSF_2CF(CF_3)_2$. In both cases the parent ion peak are obtained in reasonably high relative intensities. They are confirmed by running the spectra at 7 ev when the intensities of the molecular ion peaks increase while the intensities of the other peaks lessen.

3. $CF_3C_6H_4OSF_2CF(CF_3)_2$:

The spectrum contains comparatively high abundances of the molecular ion peak. From the fragmentation pattern it is difficult to predict a possible major pathway for breakdown. From m/e 239 to m/e 119, the spectrum is dominated by the fluoroalkyl groups. The absence of $CF_3C_6H_4^+O$ is noticeable and may be explained by the ease of the removal of any one of the substituents from the benzene ring [134].

4. p$O_2NC_6H_4OSF_2CF(CF_3)_2$:

This compound is highly involatile so a cold inlet or a heated inlet system could not be used to obtain its spectrum and the spectrum was obtained by direct probe. The $O_2NC_6H_4SO_2^+$ ion detected probably arises from hydrolysis of the compound. The hydrolysis may occur while inserting the compound into the mass spectrometer. Ions such as $\overset{+}{M}-F$ and $\overset{+}{M}-2XF$ are present in relatively high abundance. This is not observed in other SF_4 derivatives [Chapter I and II] but is observed in $(CF_3)_2CFSF_2NR_2$ [124]. The high abundances of the ions $(CF_3)_2CFSF_2^+$, $O_2NC_6H_4^+O$ and $ONC_6H_4^+O$ suggest that the major reaction pathways involve the breakdown of the S-O bond rather than C-S bond. On the basis of the most intense peaks, a possible mechanis of breakdown is:


$O_2NC_6H_4SF_2CF(CF_3)_2$
-e
$O_2NC_6H_4^{+}OSF_2CF(CF_3)_2$
m/e 239 $\overset{+}{S}F_2CF(CF_3)_2$ + $NO_2C_6H_4O$
$O_2N\overset{+}{C}_6H_4O$ + $SF_2CF(CF_3)_2$
-F
$SF\overset{+}{C}F(CF_3)_2$
-F
$SCF(\overset{+}{C}F_3)_2$
-S
$CF(CF_3)_2^{+}$
-O
$ONC_6H_4^{+}O$
-NO
$C_6\overset{+}{H}_4O$

and so on.

EXPERIMENTAL

Reagents:

$CF_3CF_2=CF_2$ hexafluoropropene was obtained from Pierce Chemical Co. Ltd. $(CF_3)_2CFSF_3$ was prepared as described by Muetterties <u>et al</u> [16]. $(CF_3)_2CFSF_3$ was dried over dry NaF and was stored in a steel bomb. silylethers were obtained as described previously.

<u>Reactions:</u>

1. $Me_3SiOCH_3/(CF_3)_2CFSF_3$ 1:1 molar ratio.

9.6 mmole of Me_3SiOCH_3 and 13 mmole of $(CF_3)_2CFSF_3$ were allowed to react for twelve hours. On fractionation the volatile products were CH_3F (4.1 mmole), Me_3SiF (8 mmole) (-126°C trap), excess $(CF_3)_2CFSF_3$ (-78° trap) and a little volatile colourless liquid (-45°C trap). The involatile liquid was confirmed as $(CF_3)_2CFS(O)OMe$

Mol wt. cal. 248 Found 248 (by mass spec.)

^1H nmr $\delta OCH_3 = -3.66$ ppm TMS ext.

^{19}F nmr $\delta CF_3 = +73.3$ ppm (doublet)

$\delta CF = +184.1$ ppm (septet)

$J_{CF_3-CF} = 8\ H_z$

MeF [75] $\delta CH_3 = -4.13$ d $J_{H-F} = 48\ H_z$

2. $Me_3SiOC_2H_5/(CF_3)_2CFSF_3$ 1:1 molar ratio

10.2 mmole of $Me_3SiOC_2H_5$ and 12.6 mmole of $(CF_3)_2SF_3$ were condensed in a glass vessel. The mixture was then allowed to react at room temperature for a day. The volatile products were Me_3SiF (9.6 mmole) -126°C), C_2H_5F (4 mmole) and $(CF_3)_2CFSF_3$ (-82°C) and a little volatile colourless liquid (-45°C). The liquid in the -45°C trap was confirmed as $(CF_3)_2CFS(O)OEt$.

Mol. Wt. Cal 262 Found 262 (by mass spec)

^1H nmr δCH_3 = -1.1 ppm (triplet
δCH_2 = -4.15 (quartet) TMS (ext)

^{19}F nmr δCF_3 = +71.3 ppm (multiplet)
δCF = +180.5 ppm (septet) CCl_3F(int)
J_{CF_3-CF} = 8 H_z

CH_3CH_2F [75]

δCH_3 = -1.21 two triplet
δCH_2 = -4.32 two quartet
J_{H-F} = 25.3 H_z

3. $PhOSiMe_3/(CF_3)_2CFSF_3$ 1:1 molar ratio

12.2 mmole of $PhOSiMe_3$ and 12.6 mmole of $(CF_3)_2CFSF_3$ were allowed to react at room temperature. After about ten to twelve hours the reaction appeared complete. The volatile products were Me_3SiF (6.2 mmole), $(CF_3)_2CFSFO$ (7 mmole). The residue was an unidentified coloured polymeric solid.

$(CF_3)_2CFSFO$ was identified by ^{19}F nmr spectroscopy [97]

δSF = + 10.2 ppm
δCF = + 180·4 ppm
δCF_3 = 70.4 ppm relative to CCl_3F

4. $\underline{p}CH_3C_6H_4OSiMe_3/(CF_3)_2CFSF_3$ 1:1 molar ratio

11.2 mmole of $pCH_3C_6H_4OSiMe_3$ and 14 mmole of $(CF_3)_2CFSF_3$ were allowed to react at 20°C. The reaction completed in one hour. The volatile products were Me_3SiF (5.1 mmole) and $(CF_3)_2CFSFO$ (6 mmole) and traces of unreacted $(CF_3)_2CFSF_3$. The residue was an unidentified black mass.

5. $\underline{m}FC_6H_4OSiMe_3/(CF_3)_2CFSF_3$ 1:1 molar ratio

12.6 mmole of $mFC_6H_4OSiMe_3$ and 15 mmole of $(CF_3)_2CFSF_3$ were condensed in a vessel. The mixture was then allowed to react at room temperature for several hours. The volatile products wer Me_3SiF (8 mmole) $C_6H_4F_2$ (4 mmol) and $(CF_3)_2CFSFO$ (6 mmole).

$C_6H_4F_2$ was confirmed by ^{19}F nmr [75]

$\delta F = -108.2$ ppm CCl_3F (int)

Mol wt. Cal. 114 Found 114 (by mass spec.)

6. $\underline{p}CF_3C_6H_4OSiMe_3/(CF_3)_2CFSF_3$ 1:1 molar ratio

10 mmole of $\underline{p}CF_3C_6H_4OSiMe_3$ and 15 mmole of $(CF_3)_2CFSF_3$ were allowed to react at 70°C for 18 hours. The volatile products were Me_3SiF (4 mmole) and excess $(CF_3)_2CFSF_3$. The involatile yellow coloured liquid was confirmed as $(CF_3)_2CFSF_2OC_6H_4CF_3$ and unreacted $Me_3SiOC_6H_4CF_3$.

Mol. wt. Cal 400 Found 400 (by mass spec.).

^1H nmr $\delta C_6H_4 = -7.56$ ppm (A_2B_2 quartet) TMS ext

^{19}F nmr $\delta SF_2 = -44.4$ ppm (multiplet)

$\delta CF_3 = +68.8$ ppm (triplet of doublet)

$\delta CF = +152.1$ ppm (triplet of septet) CCl_3F

$\delta CCF_3 = +61.8$ ppm

$J_{SF_2-CF} = 28H_z$ $J_{SF_2-CF_3} = 12\ H_z$ $J_{CF_3-CF} = 6H_z$

7. $Me_3SiOC_6H_4NO_2p/(CF_3)_2CFSF_3$ 1:1 molar ratio

12 mmole of $Me_3SiOC_6H_4NO_2p$ and 14 mmole of $(CF_3)_2CFSF_3$ reacted at 90°C in 30 hours to produce Me_3SiF (11.2 mmole) and an involatile red liquid, confirmed as $(CF_3)_2CFSF_2OC_6H_4NO_2p$.

Mol wt Cal 377 Found 377 (mass spec)

Elemental Analysis.

Carbon Cal.	28.64	Found	28.82
Nitrogen Cal.	3.74	Found	3.62
Fluorine Cal.	45.35	Found	45.13
Hydrogen Cal.	1.06	Found	1.13
Sulfur Cal.	8.48	Found	8.41
Oxygen Cal.	12.73	Found	11.89

^{1}H nmr δC_6H_4 = -7.93 ppm (A_2B_2 quartet) TMS ext

^{19}F nmr δSF_2 = -42.4 ppm (multiplet)

δCF_3 = $+69.2$ ppm (triplet of doublet) CCl_3F(int)

δCF = $+151.8$ ppm (triplet of septet)

$J_{SF_2-CF} = 28\ H_z$ $J_{SF_2-CF_3} = 12\ H_z$ $J_{CF_3-CF} = 6\ H_z$

Infrared:

liquid film: 3128(m), 2991(m), 1622(m), 1591(s) 1529(v.s) 1486(s), 1348(s), 1285(br.s), 1170(s), 1153(v.s), 1112(m), 1014(m), 969(s), 924(m), 867(v.s) 764(w), 754(m), 740(w), 716(s), 686(m), 658(s), 633(s) 612(m).

CHAPTER IV

Preparation and Properties of $ROS(O)F$ compounds

ARYLOXYFLUOROSULFITES - Preparation and Properties :

Zappel [129] reported the preparation of a number of alkoxyfluorosulfites by the fluorination of alkoxychlorosulfites synthesised by the reaction of alcohol with thionyl chloride.

$$SOCl_2 + ROH \longrightarrow ROS(O)Cl + HCl$$

$$ROS(O)Cl + KSO_2F \longrightarrow ROS(O)F + KSO_2Cl$$

When dialkylsulfites [115] were treated with SF_4 alkoxyfluorosulfites were one of the products.

$$SF_4 + (RO)_2SO \longrightarrow ROS(O)F + SOF_2 + RF$$

Thionylfluoride [132] cleaved the Si-O bond of Me_3SiOR [where R is an alkyl group] to produce alkoxyfluorosulfites and Me_3SiF

$$SOF_2 + Me_3SiOR \longrightarrow FS(O)OR + Me_3SiF$$

Although a number of alkoxyfluorosulfites are [130] known, very few aryloxyfluorosulfites have been reported. In the reaction of SF_3ORX [Chapter I], it is observed that on controlled hydrolysis, SF_3ORX produces XROSOF [where XR = substituted phenyl group]. Some of the aryloxyfluorosulfites have been prepared by already reported methods. The ^{19}F nmr spectra and mass spectra of these compounds are discussed here.

An attempt [92] to prepare PhOS(O)F (phenylfluorosulfite) from the reaction of $PhOSiMe_3$ with SOF_2 was not successful; the reaction did not proceed. A similar observation was made in the reaction of SOFCl with $PhOSiMe_3$ [82].

$$SOF_2 + PhOSiMe_3 \longrightarrow \text{No reaction}$$

$$SOFCl + PhOSiMe_3 \longrightarrow \text{No reaction}$$

Phenylfluorosulfinate [82] was prepared by the fluorination of phenylchlorosulfinate with NaF in acetonitrile solution. Phenylchlorosulfinate [131] was prepared by the reaction of phenol and $SOCl_2$ using CCl_4 or CH_3CN as a solvent. The earlier attempts to prepare phenylchlorosulfinate from phenol and thionylchloride were not successful. HCl being one of the products complicated the reaction by producing a number of side products. However a solvent in which HCl was insoluble was used, phenylchlorosulfinate was produced in high yield.

$$SOCl_2 + PhOH \xrightarrow{CCl_4} S(O)ClOPh + HCl$$

$$S(O)ClOPh + F^- \xrightarrow[\text{in } CH_3CN]{NaF} S(O)FOPh + NaCl$$

In this work, compounds such as $CH_3C_6H_4OS(O)F$ (meta and para) and $FC_6H_4OS(O)F$ are prepared by the above mentioned method. The properties of these compounds are identical with the compounds prepared by the hydrolysis of SF_3ORX. A number of aryloxyfluorosulfinates have been prepared by the controlled hydrolysis of SF_3ORX which are prepared by the action of SF_4 on $XROSiMe_3$ [Chapter I].

$XROS(O)F$ disproportionates to give $(XRO)_2SO$ and $S(O)F_2$. It is observed that HF catalyses the disproportionation

$$2XROS(O)F \longrightarrow (XRO)_2SO + S(O)F_2$$

Zappel [129] observed a similar disproportionation in the case of alkoxyfluorosulfites.

$$2ROS(O)F \longrightarrow SOF_2 + (RO)_2SO$$

Since HF catalysis the disproportionation, an ionic mechanism of the following type may be suggested.

$$XROS(O)F \longrightarrow XROSO^+ + F^-$$
$$F^- + XROS(O)F \longrightarrow SOF_2 + XRO^-$$
$$XRO^- + XROSO^+ \longrightarrow (XRO)_2SO$$

where XR = $CH_3C_6H_4$
ClC_6H_4
FC_6H_4
(meta and para)

XROS(O)F hydrolysis in moist air to give phenol, SO_2 and HF.

$$XROS(O)F + H_2O \longrightarrow HF + ROH + SO_2$$

On heating they decompose to SO_2 and RF.

$$ROS(O)F \longrightarrow SO_2 + RF$$

XROS(O)F compounds are unstable at room temperature. On standing in glass, they decompose in about 24 hours, to give a number of products including SOF_2 and $(XRO)_2SO$ (confirmed by mass spectroscopy).

^{19}F nmr Chemical Shifts of Fluorosulfites

Table 1 related to CCl_3F

Compounds	δ SF	References
1. FS(O)F	-77.9 ppm	
2. PhOS(O)F	-62.5	[82]
3. EtOS(O)F	-59.5	[115]
4. MeOS(O)F	-55.6	[115]
5. $Et_2NS(O)F$	-55.3	[132]
6. $Me_2NS(O)F$	-38.6	[132]

The ^{19}F chemical shifts of alkoxy, dialkylamines and phenoxy substituted thionyl fluoride are shown in the table 1. The change in shielding of the fluorine nuclei with the decrease of the electronegativity of the group attached to sulfur atom is consistent with the behaviour expected. The difference in the chemical shifts between (5) and (6) is relatively large and cannot be explained by electronegativity alone and indicates that other factors influence the shielding of the fluorine nuclei. These factors are not understood at the moment.

^{19}F Chemical Shifts of the Compounds $XC_6H_4OS(O)F$ prepared in this work.

Table 2 CCl_3F (int reference)

Compounds	δSF	δCF	Reference
$PhOS(o)F$	-62.5	-	[82]
$\underline{p}CH_3C_6H_4OS(O)F$	-66.0	-	this work
$\underline{m}CH_3C_6H_4OS(O)F$	-64.1	-	this work
$\underline{p}FC_6H_4OS(O)F$	-62.4	+108.8	this work
$\underline{m}FC_6H_4OS(O)F$	-65.8	+104	this work
$\underline{o}FC_6H_4OS(O)F$	-59.7	+129.5	this work
$\underline{p}ClC_6H_4OS(O)F$	-64.5	-	this work
$\underline{m}ClC_6H_4OS(O)F$	-64.1	-	this work

The chemical shifts of the products of controlled hydrolysis of SF_3ORX and the compounds prepared otherwise are identical. Considering the trend in Table I, it is expected that the groups will deshield the S-F fluorine atom. Accordingly it can be assumed that the downfield shift of the S-F fluorine atom in aryloxyfluorosulfites relative to $PhOS(O)F$ will be because of the electron withdrawing effect of the aryloxy groups. One of the powerful tools for investigating the electron withdrawing or donating power of a substituent which acts by resonance with the π-orbital of the aromatic system is the measurement of σR (where R is the Hammet substituent constant separated into one of their components e.g. resonance contribution). Since in the <u>para</u> position of a benzene ring, the resonance contribution is pronounced σR should be related to shift for para substituted derivatives. σR for the three parasubstituted aryloxyfluorosulfites are given below with the ^{19}F shift.

	σR [75]	SF
$\underline{p}CH_3C_6H_4OS(O)F$	-0.13	-66.00
$\underline{p}ClC_6H_4OS(O)F$	-0.24	-64.15
$\underline{p}FC_6H_4OS(O)F$	-0.44	-62.4

The negative value of σR indicates electron donation to the ring. The ^{19}F nmr chemical shifts of the above three compounds are consistent with an electron withdrawing effect of the three substituents. For a <u>meta</u> substituted aryloxy group, an inductive effect is the main contributing factor for electron withdrawl at the sulfur atom. From the observation that an electron withdrawing aryloxy group deshields the S-F fluorine atom, a $\underline{m}FC_6H_4O$-group appears to act as a better electron withdrawing group than $mClC_6H_4O$ or $mCH_3C_6H_4O$. For the oFC_6H_4O-, the change of the chemical shifts is anomalous and its is possible that steric effects are important. The C-F chemical shifts of the three fluorobenzoylluorosulfites are very close to the expected region [Chapter I]. A discussion of the chemical shifts of C-F fluorine atom has been given in the first chapter.

Mass Spectra of XROS(O)F (XR = $CH_3C_6H_4$, ClC_6H_4, FC_6H_4) <u>meta</u> and <u>para</u>

Mass Spectra Data:

1. $\underline{p}CH_3C_6H_4OS(O)F$: 174$M^+$ 21.9, 155 $CH_3C_6H_4OSO^+$ 0.14, 107 $CH_3C_6H_4{}^+O$ $\underline{100}$, 91 $CH_3C_6H_4^+$ 7.01, 79 $CH_3C_5H_4{}^+$ 70.0, 77 $C_6H_5{}^+$ 75.4, 67 SO^+F 9.47, 64 SO_2^+ 1.92, 51 $\overset{+}{S}F$ 8.94, 48 SO^+ 7.01.

2. $\underline{m}CH_3C_6H_4OS(O)F$: 174 M^+ 38.46, 155 $CH_3C_6H_5OSO^+$ 0.76, 107 $CH_3\overset{+}{C}_6H_4O$ $\underline{100}$, 91 $CH_3C_6H_4{}^+$ 12.3, 79 $CH_3\overset{+}{C}_5H_4$ 81.0, 77 $C_6\overset{+}{H}_5$ 95, 67 SO^+F 19.2, 64 SO_2^+ 2.0, 51 SF^+ 34.61.

3. $\underline{p}FC_6H_4OS(O)F$: 178 M^+15, 159 $FC_6H_4OSO^+$ 8.42, 111 $C_6\overset{+}{H}_4O$ $\underline{100}$, 95 $F\overset{+}{C}_6H_4$ 73.68, 83 $FC_5\overset{+}{H}_4$ 80.1, 67, SO^+F 26.31, 64 $SO_2{}^+$ 12.1, 51 SF^+ 7.1, 48 SO^+ 18.42.

4. $\underline{m}FC_6H_4OS(O)F$: 178$M^+$16.6, 159 $FC_6H_4OSO^+$ 59.92, 143 $FC_6\overset{+}{H}_4OS$ 1.42, 111 $FC_6H_4\overset{+}{O}$ 85, 95 $FC_6H_4{}^+$$\underline{100}$, 83 $FC_5H_4{}^+$ 74.42, 67 $S\overset{+}{O}F$ 8.57, 67 $SO_2{}^+$ 26.19, 51 $\overset{+}{S}F$ 18, 48 SO^+ 14.28.

5. $\underline{o}FC_6H_4OS(O)F$: 178$M^+$ 13.4, 159 $FC_6H_4O\overset{+}{S}O$ 79.2, 111 $FC_6H_4\overset{+}{O}$ $\underline{100}$, 95 $FC_6H_4^+$ 72, 83 $FC_5H_4^+$ 74.1, 67 SO^+F 2.0, 64 SO_2^+ 59.2, 51 $\overset{+}{S}F$ 6.1, 48 $S\overset{+}{O}$ 10.2

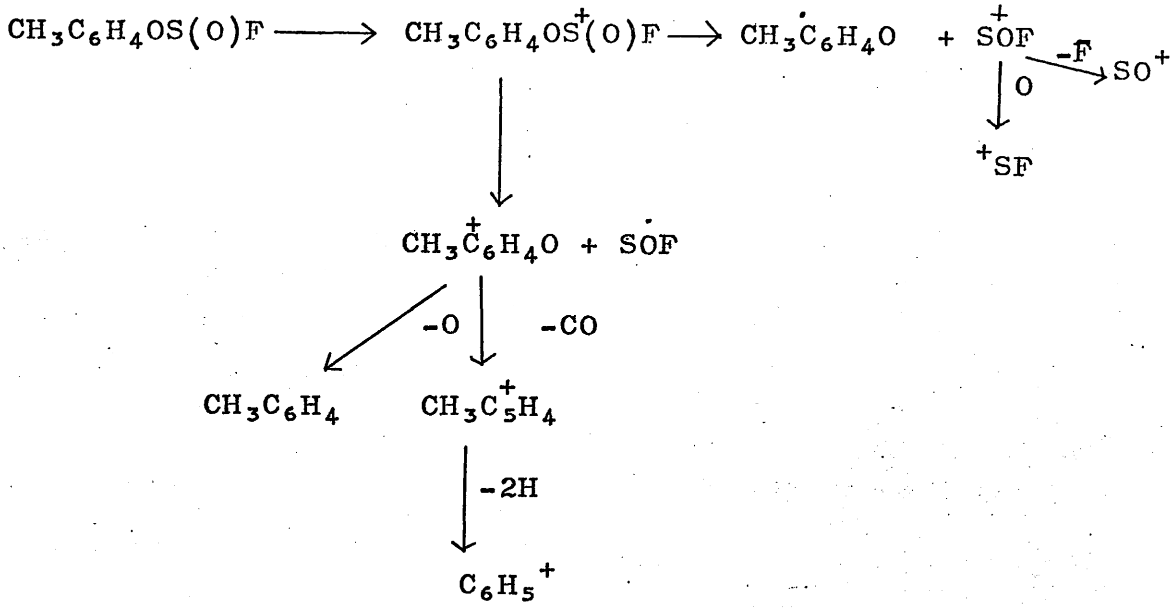
6. $\underline{p}ClC_6H_4OS(O)F$ 194 M^+ 14.5, 175 $ClC_6H_4O\overset{+}{S}O$ 8.9, 127 $ClC_6H_4^+O$ $\underline{100}$, 111 Cl $C_6H_4^+$ 95, 99 $ClC_5\overset{+}{H}_4$ 84, 67 SO^+F 7.5, 64 $\overset{+}{S}O_2$ 18, 51 S^+F 16.1 48 $\overset{+}{S}O$ 18.4.

7. $m\mathrm{ClC_6H_4OS(O)F}$: 194M^+ 17, 175 $\mathrm{ClC_6H_4O\overset{+}{S}O}$ 39.4, 127 $\mathrm{ClC_6H_4\overset{+}{O}}$ 60.1, 111 $\mathrm{ClC_6H_4}$ <u>100</u>, 99 $\mathrm{ClC_5H_4}$ 58, 67 $\mathrm{\overset{+}{S}OF}$ 9.3, 64 $\mathrm{SO_2^+}$ 30.0, 51 $\mathrm{S\overset{+}{F}}$ 17, 48 $\mathrm{S\overset{+}{O}}$ 15.

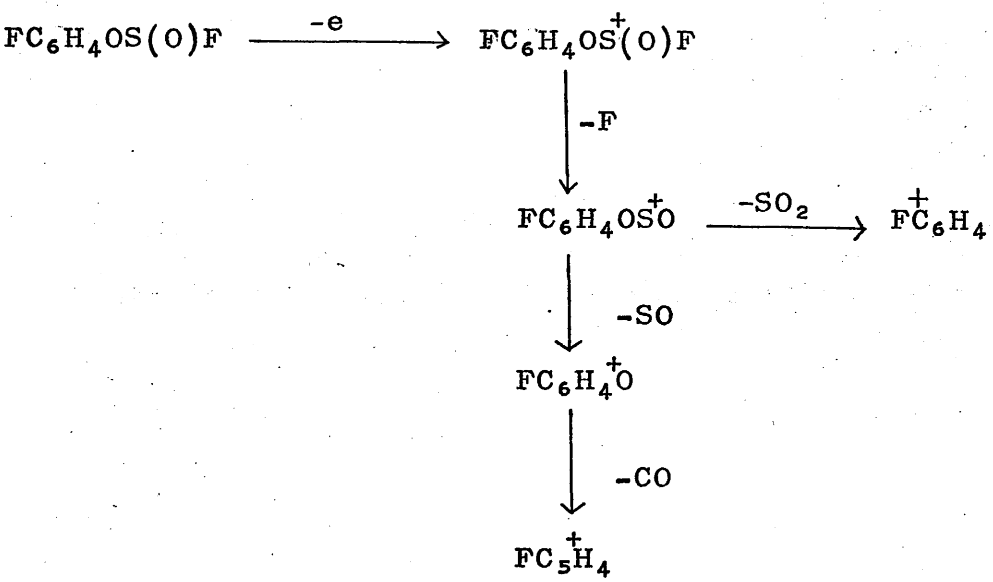
<u>Discussion of mass spectral data</u>

The mass spectra of all aryloxyfluorosulfites show parent ions in high relative intensities. The parent ions and ions such as $\mathrm{XROSO^+}$, $\mathrm{XRO^+}$, $\mathrm{SO^+F}$, $\mathrm{XR^+}$ and $\mathrm{SO^+}$ confirm the proposed structures of the compounds. The spectra show a difference of the fragmentation patterns in the case of (1) and (2) as compared with (3), (4), (5), (6) and (7). While in (1) and (2), the ion $\mathrm{XRO\overset{+}{S}O}$ m/e 155 is almost negligible, in the other cases the ion $\mathrm{XROS\overset{+}{O}}$ is present in high relative abundance. In (4), (5) and (7) the high relative abundance of the ion $\mathrm{XROS\overset{+}{O}}$ probably demonstrates the stability of this ion which is due to a high inductive effect on the oxygen atom from the <u>meta</u> or <u>ortho</u> fluorine or chlorine. In (1) and (2), the intensities of these ions indicate that major fragmentation probably involves the breakdown of the S-O bond, whereas in (4), (5) and (7) the major fragmentation probably occurs with elimination of the fluorine atom from the parent ion and thereafter the breakdown involves the C-O bond with the elimination of the $\mathrm{SO_2^+}$ ion. However, in (5) the high abundance of the $\mathrm{XRO^+}$ ion suggest that breakdown involving an S-O bond is also probable. In (3), (4), (5), (6) and (7), the intensities of the ions $\mathrm{XR\overset{+}{O}}$, $\mathrm{XR^+}$ and $\mathrm{SO_2^+}$ suggest equal possibility as for the two mechanisms for breakdown of the parent ion ion or ion $\mathrm{XRO\overset{+}{S}O}$ involving the breakage of C-O or S-O bond.

Compound (1) and (2):



Compound (4) and (5):



In the cases of (3), (6) and (7), no single pathway for the mechanism of breakdown of ions can be predicted. The mechanism possibly involves both the ways described above.

Reactions of SeF_4

PREPARATION:

Selenium reacted with dilute fluorine at 0°C to give selenium tetrafluoride and a small proportion of hexafluoride [139].

$$Se + F_2 \xrightarrow{0°C} SeF_4$$

Selenium was also formed by the action of ClF_3 on selenium and selenium dioxide [140].

In the present work [141] selenium tetrafluoride was prepared by the reaction of SF_4 with SeO_2 (selenium dioxide was dried in vacuum at 150°C). Sulfurtetra fluoride was condensed in a steel bomb containing dried selenium dioxide in a molar ratio of 4:1. The mixture was allowed to react at 150°C for a period of thirty hours. On fractionation selenium tetrafluoride was obtained as a colourless liquid, m.p. 0°C and was confirmed by the ^{19}F n.m.r. [55] and infrared spectrum [146].

$$SeO_2 + 2SF_4 \longrightarrow SeF_4 + 2SOF_2$$

Properties:

Electron diffraction studies of SeF_4 [142] described the molecule as a distorted tetrahedral with Se-F distances 1.765 ± 0.025Å, but mathematical correction of this work showed the molecular shape to be a trigonal bipyramid [143].

A further electron diffraction study supported the later structure [144]. A Raman spectroscopic examination of the liquid indicated C_{2v} symmetry and confirmed trigonal bipyramid model [145]. As in SF_4, there is unshared electron pair in the equatorial plane of SeF_4. The fluorine n.m.r. spectrum also supported this structure [55]. Infrared studies of both solid and vapour showed association by a fluorine bond between fluorine atom of one molecule and the central atom of the next [61].

Reactions of SeF_4

1. $SeF_4 + MeSiOPh \longrightarrow Se(red) + Me_3SiF$ + unidentified products
2. $SeF_4 + Me_3SiNMe_2 \longrightarrow Se(red) + Me_3SiF$ + unidentified products
3. $SeF_4 + Me_3SiOC_6F_5 \rightarrow Se + Me_3SiF$ + unidentified products.

The reaction of SeF_4 with Si-O compounds and with Si-N compound do not produce substituted derivative of SeF_4. The production of Me_3SiF indicates a possibility of intermediate formation of a derivative of SeF_4 which decomposes to elemental selenium and unidentified products. In the reaction of $Me_3SiOC_6F_5$ and SeF_4, a white solid was produced but before being separated, the solid decomposed to red selenium and other unidentified products.

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