REACTIONS
OF
SULPHUR FLUORIDES.

To Heather and Fraser.

THESIS

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ABSTRACT

The work of this thesis is concerned with the reactions of thionyl fluoride, thionyl tetrafluoride and its derivatives, and sulphuryl chloride fluoride.

The reactions of thionyl fluoride have been little investigated, and usually involve forcing conditions. Many of the derivatives have been made before, but little is known of their spectroscopic properties. Particular interest was centred on the effect of attached substituents to sulphur on νSO, in the derivatives of thionyl fluoride. The ^1H n.m.r. of the compounds, $R_2NS(O)X$ (R = Me, Et, i-Pr; X = F, Cl, OR, NR_2), have been investigated over the temperature range +150° to -110°. The halosulphinamides, $R_2NS(O)X$ (R = Me, Et, i-Pr; X = F, Cl), show non-equivalence in the ^1H n.m.r. spectrum at low temperature, and the alkoxysulphinamides, $R_2NS(O)OCH_2CH_3$ (R = Me, Et), show evidence of AB coupling in the methylene signals of the ethoxy group. The possible effects which give rise to these phenomena are discussed.

The reactions of thionyl tetrafluoride with silicon oxygen compounds have been investigated at length. Phenoxysulphur oxytrifluoride, $PhOS(O)F_3$, is obtained in good yield from the one to one reaction of SOF_4 and Me_3SiOPh. The compound, however, is unstable and decomposes on standing. The influence of substitution in the aromatic ring on the stability of the $ArOS(O)F_3$ compounds (Ar = aryl), is discussed. Thus, $m\text{-}FC_6H_4OS(O)F_3$ is very stable, and only partially decomposes on heating at 130°. Higher substituted derivatives of thionyl tetrafluoride have been made, and the stability and spectroscopic properties of these compounds are discussed.

The preparation of derivatives of the aryloxysulphur oxytrifluorides in which single bond formation was maintained, did not meet with success. $PhOS(O)F_3$ and Me_3SiOEt react to form $PhOSO_2F$, which is thought to be given via $PhO(EtO)S(O)F_2$ as an intermediate. The derivatives, $MeN{=}S({=}O)(F)OAr$ (Ar = Ph, m-FC_6H_4), are obtained from $(Me_3Si)_2NMe$ and $ArOS(O)F_3$ as stable compounds which are not air sensitive.

Reactions of sulphuryl chloride fluoride involve preferential cleavage of the sulphur fluorine bond, although sulphur chlorine bonds are more labile. Factors which influence these reactions are discussed. Addition reactions across C=O and C=C bonds did not succeed with sulphuryl chloride fluoride, although other sulphuryl compounds are known to partake in such reactions.

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CONTENTS

Introduction

The main group elements stand out as the most varied in their chemical behaviour in the Periodic Table. Each element is a world on its own, with great differences in behaviour of individual elements within the main group from its immediate neighbours up and down and across that part of the Periodic Table. Not the least of these of great diversity in its chemistry, and a centre of much interest, is the chemistry of sulphur compounds, with the ability of sulphur to exist in a wide range of oxidation states, -II in H_2S to +VI in SF_6. In particular the chemistry of sulphur fluorine compounds has been the subject of numerous reviews in recent years (1-7).

The great difference between the chemistry of the first and second row elements is particularly marked where sulphur is bonded to the halogens. The chemistry of the sulphur fluorides is quite different from that of the other sulphur halides. This introduction will describe some of the known sulphur fluorides, with relevance to the work of this thesis as near as possible.

Divalent Sulphur

SF_2, sulphur difluoride, has evaded proper identification for many years, although SCl_2, sulphur dichloride, is well known, and is very stable. In reacting SCl_2 with mercuric fluoride at low pressure and temperature, Seel managed to characterise SF_2 by mass spectra (8).

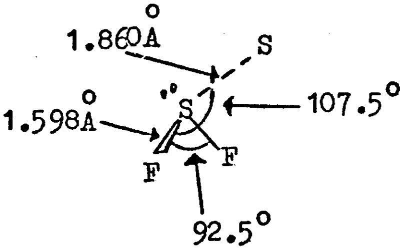
$$SCl_2 + HgF_2 \longrightarrow SF_2 + HgCl_2$$

SF_2 however, is very unstable and decomposes rapidly to sulphur, sulphur tetrafluoride and disulphur difluoride. No molecular parameters for sulphur difluoride are known.

The only known sulphenyl fluoride is i-C_3F_7SF (9), which is obtained from the pyrolysis of the corresponding trifluoride i-$C_3F_7SF_3$ at 200°.

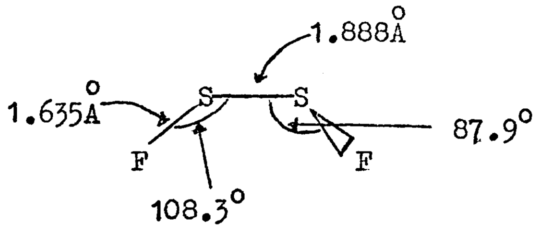
The Disulphur Difluorides

A gas that has been observed to be evolved from the high temperature reaction of sulphur and silver fluoride, has been shown to have the emperical formula S_2F_2. Both isomers FSSF and SSF_2 have been found and studied. Although SSF_2 contains four-valent sulphur, it is discussed here to complete the chemistry of S_2F_2. Kuczkowski and Wilson identified SSF_2, thiothionyl difluoride, by microwave spectroscopy (10), and established the structure as shown below.



SSF_2, thiothionyl difluoride.

Wilson identified the less stable isomer FSSF, disulphur difluoride, and found that it had a hydrogen peroxide-like structure, with a



FSSF, disulphur difluoride.

dihedral angle of 87.9°. FSSF boils at approximately -30° and isomerises at room temperature to SSF_2 (12). SSF_2 is thermally stable up to 200°, where it forms S_8 and SF_4. These compounds have been described over a period of forty years, with a great deal of confusion in establishing their structure. This is not surprising, as in these reactions sulphur tetrafluoride, which so readily hydrolyses, is evolved in isomerisation processes.

Tetravalent Sulphur

Sulphur tetrafluoride: SF_4, sulphur tetrafluoride, was first made by the reaction of fluorine on a thin film of sulphur (13). Now it is prepared more conveniently by the reaction of sulphur dichloride and sodium fluoride in a slurry of acetonitrile (14).

$$3\ SCl_2 + 4\ NaF \longrightarrow SF_4 + S_2Cl_2 + 4\ NaF$$

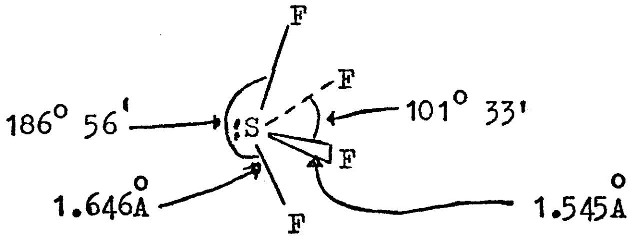
The reaction is best carried out preparing large quantities, as in small apparatus it is difficult to avoid extensive hydrolysis of the product owing to a large surface to volume ratio. SF_4 is readily hydrolysed to SOF_2, thionyl fluoride, which is difficult to separate due to similar boiling points, -38° for SF_4 and -43.7°

for SOF_2. Relatively pure samples of SF_4 can be obtained by adduct formation with BF_3 and pumping away the SOF_2 impurity. The sulphur tetrafluoride may be liberated by other non-volatile reagents which displace it (15,16).

$$BF_3.SF_4 \quad + \quad NaF \longrightarrow SF_4 \quad + \quad Na^+BF_4^-$$

SF_4 forms stable adducts with a number of inorganic fluorides which are thought to have the structure $SF_3^+MF_{n+1}^-$, where MF_n is the Lewis Acid fluoride(15).

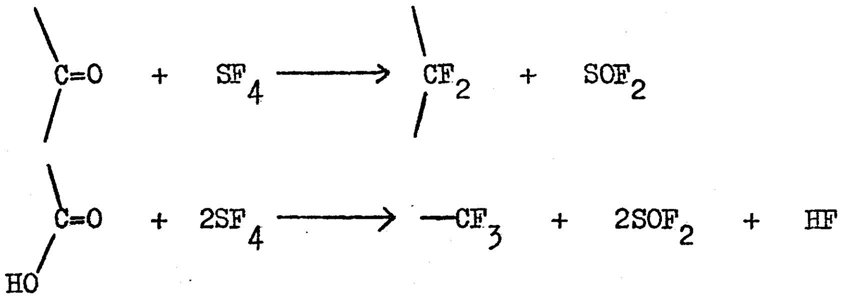
A structure determination by Tolles and Gwinn (17), using microwave spectroscopy, showed two non-equivalent pairs of fluorine atoms.



SF_4, sulphur tetrafluoride.

The structure is trigonal bipyramidal, with two equatorial positions occupied by fluorine atoms and the third equatorial position occupied by a lone pair of electrons. The ^{19}F n.m.r. shows only one signal at room temperature, but at lower temperatures shows two sets of triplets (18), indicative of two pairs of non-equivalent fluorine atoms, in agreement with the trigonal bipyramidal structure.

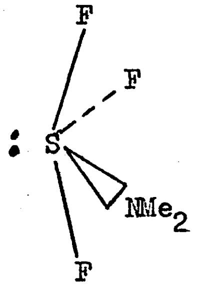
The great spur in the interest of the chemistry of sulphur tetrafluoride, was its ability to fluorinate carbonyl and carboxylic groups (19).



One of the earliest reported monosubstituted derivatives of SF_4 was the dimethylamino compound, made by MacDiarmid (20).

$$SF_4 + Me_3SiNMe_2 \longrightarrow Me_2NSF_3 + Me_3SiF$$

At room temperature, the ^{19}F n.m.r. of Me_2NSF_3 shows a broad singlet which resolves at lower temperatures to give an AX_2 spectrum. This would suggest trigonal bipyramidal symmetry with the dimethylamino group in the equatorial plane.



Me_2NSF_3, dimethylaminosulphur trifluoride.

The disulphides are readily oxidised to the sulphur trifluorides by silver difluoride (21,22).

$$PhSSPh + 6\ AgF_2 \longrightarrow 2PhSF_3 + 6AgF$$

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

These reactions must not be allowed to warm up too quickly, as the oxidative fluorination proceeds to the sulphur VI compounds.

Rosenberg and Muetterties were able to isolate mono and bis-substituted derivatives of sulphur tetrafluoride from the reaction of perfluoropropene and sulphur tetrafluoride in the presence of caesium fluoride (9).

$$CF_3CF{=}CF_2 \quad + \quad SF_4 \xrightarrow{CsF} (CF_3)_2CFSF_3 \quad + \quad [(CF_3)_2CF]_2SF_2$$

$[(CF_3)_2CF]_2SF_2$ is remarkably stable to hydrolysis compared to CF_3SF_3 which hydrolyses with extreme rapidity. The former observation is attributed to steric shielding of the fluorine atoms attached to sulphur by the bulky perfluoroisopropyl groups. More recently, Shreeve (23) has found $(CF_3)_2SF_2$ to be very stable to hydrolysis, which is contrary to the findings of Lawless (24).

Darragh has shown that stepwise substitution of the fluorine atoms of sulphur tetrafluoride by phenoxy groups is readily achieved by reacting sulphur tetrafluoride with controlled amounts of the silyl ether, Me_3SiOPh (25).

$$SF_4 \quad + \quad nMe_3SiOPh \longrightarrow nMe_3SiF \quad + \quad (PhO)_nSF_{4-n}$$

$$n = 1,2,3,4.$$

$(PhO)_4S$, tetrakisphenoxysulphur, is the first example of a non-chelated ortho-sulphite ester, and adds a new dimension to sulphur chemistry.

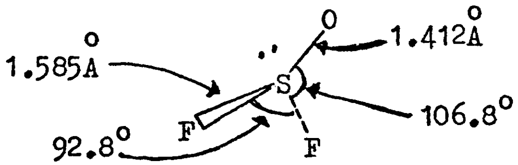
Thionyl fluoride: SOF_2, thionyl fluoride, is the most familiar example of the oxyfluorides of sulphur, and was first reported in 1896 (26). A variety of methods are known for its synthesis, usually involving metathetical exchange of fluoride donours with thionyl chloride. Most commonly dropwise addition of thionyl chloride on to a slurry of sodium fluoride in acetonitrile results in a high yield of thionyl fluoride (27).

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

The intermediate in these metathetical reactions is thionyl chloride fluoride, which can be isolated from the reaction of iodine pentafluoride and thionyl chloride (28). Thionyl chloride fluoride is reactive to mercury and undergoes disproportionation at room temperature to thionyl chloride and thionyl fluoride (6).

$$2SOClF \longrightarrow SOF_2 + SOCl_2$$

Thionyl fluoride like the other thionyl halides, has a pyramidal structure based on the tetrahedral arrangement of four σ-bonding pairs of electrons, one of which is a lone pair (29).



SOF_2, thionyl fluoride.

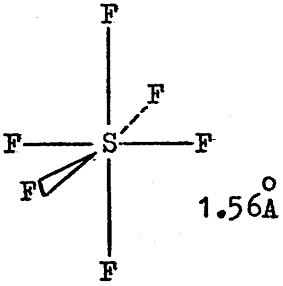
Thionyl fluoride is a colourless gas which boils at -43.8° and hydrolyses in a moist atmosphere, much less readily than thionyl chloride or sulphur tetrafluoride.

$$SOF_2 + H_2O \longrightarrow SO_2 + 2HF$$

The chemistry of thionyl fluoride has received little attention and has been overshadowed to some extent by the more reactive fluorides. Some of the reactions of thionyl fluoride are discussed later.

Hexavalent Sulphur

Sulphur hexafluoride: SF_6, sulphur hexafluoride has long been known for its remarkable inertness and stability. It has the expected octahedral structure for sp^3d^2 hybridisation, as determined by electron diffraction (30,31).



SF_6, sulphur hexafluoride.

Sulphur hexafluoride was first prepared by Moissan and Lebeau, by burning sulphur in an atmosphere of fluorine and removing the lower fluorides by pyrolysis at 400° and washing with aqueous alkali (32).

$$S + 3F_2 \longrightarrow SF_6$$

Sulpur hexafluoride is highly inert and non-toxic. It is of commercial importance as a dielectric in switchgear and transformers. Thermodynamically, the free energy of hydrolysis of sulphur hexafluoride is very favourable, but SF_6 is hydrolytically very stable.

$$SF_6\ (g) + 3H_2O\ (g) \longrightarrow SO_3\ (g) + 6HF\ (g)$$

$$\Delta G = -48\ \text{k.cals./mole.}\ (7)$$

The lack of reactivity of sulphur hexafluoride towards nucleophiles is attributed to kinetic factors, with no ease of access of nucleophiles to the sulphur atom which is covalently saturated. A substantial electronic rearrangement would be required for reaction, which is not favourable. Electrophiles, however, react much more readily, with SF_6 and $AlCl_3$ reacting at 225° giving sulphur chlorides and chlorine (33). SF_6 also reacts with SO_3, giving sulphuryl fluoride (33).

$$SF_6 + 2SO_3 \longrightarrow 3SO_2F_2$$

Many substituted derivatives of sulphur hexafluoride are known, and have been described at length in the reviews mentioned earlier (1-7). For the most part, they lie outwith the interest of this thesis, and will not be discussed further.

Thionyl tetrafluoride: SOF_4, thionyl tetrafluoride is unique among the sulphur VI oxyfluorides in that it is one of the few known examples of pentacoordinated sulphur. Its name may be attributed to it having one oxygen atom bonded to sulphur as in the thionyl halides. Thionyl tetrafluoride was probably first made by Moissan and Lebeau(34) by the oxidative fluorination of thionyl fluoride with elemental fluorine.

$$SOF_2 \quad + \quad F_2 \longrightarrow SOF_4$$

They tentatively established its composition from pressure-volume-temperature measurements, but did not succeed in isolating the product. Its structure was examined by infrared and Raman spectroscopy some time later (35), and was found to be trigonal bipyramidal, with two fluorine atoms and the oxygen atom in the equatorial plane. The structure is discussed more fully later.

The fluorination of thionyl fluoride, to prepare thionyl tetrafluoride, is best done in the absence of active metal fluorides, as the main product of the reaction in that case is pentafluorosulphur hypofluorite, SF_5OF (36). The uncatalysed reaction produces thionyl tetrafluoride exclusively. Thionyl tetrafluoride has been observed to be completely absorbed by an excess of caesium fluoride on heating to 100° to give what is tentatively described as $Cs^+ \, {}^-OSF_5$ (36). Thus with the fluorination of thionyl fluoride by fluorine in the presence of caesium fluoride, the reaction is thought to proceed as below.

$$\begin{tikzcd}
SOF_2 + F_2 \arrow[r] & SOF_4 \arrow[d, "CsF"] & \\
& (Cs^+ \, {}^-OSF_5) \arrow[r, "F_2"] & SF_5OF + CsF
\end{tikzcd}$$

Pentafluorosulphur hypofluorite reacts with thionyl fluoride in the presence of AgF at 190° to give a high yield of very pure thionyl tetrafluoride (37).

$$SF_5OF \quad + \quad SOF_2 \xrightarrow{AgF} 2SOF_4$$

Thionyl tetrafluoride may be made without having recourse to fluorine. It has been prepared by the catalytic oxidation of sulphur tetrafluoride with oxygen in the presence of nitrogen dioxide (38). Oxygen alone reacts with sulphur tetrafluoride very slowly at high temperatures, and with nitrogen dioxide alone to give low yields of thionyl tetrafluoride and large amounts of thionyl fluoride. The catalytic reaction is thought to proceed as below.

$$SF_4 + NO_2 \longrightarrow SOF_4 + NO$$
$$2NO + O_2 \longrightarrow 2NO_2$$

A high yield of thionyl tetrafluoride is obtained from the catalysed reaction. Impurities are removed by selective absorption with dimethyl formamide. Various metal oxides and nitrates are capable of producing thionyl tetrafluoride on reacting with sulphur tetrafluoride, but also give large amounts of sulphuryl fluoride and thionyl fluoride.

Thionyl tetrafluoride is a colourless gas and boils at -49°. It hydrolyses in a moist atmosphere, more readily than thionyl fluoride, but not so quickly as sulphur tetrafluoride.

$$SOF_4 + H_2O \longrightarrow SO_2F_2 + 2HF$$

Thionyl tetrafluoride can behave as a weak base and forms addition compounds with a number of inorganic fluorides, which are formulated as being $(SOF_3^+ MF^-_{x+1})$ (39,40). A weak adduct is formed with BF_3, with a dissociation pressure of 760 mm Hg at -39°, while the arsenic pentafluoride adduct has a dissociation pressure of 7 mm Hg at 20°. Antimony pentafluoride forms a very stable complex with thionyl tetrafluoride, and shows no dissociation pressure at ambient temperature. The observed order of stabilities of these complexes follows the order of increasing Lewis Acidity of the metal fluorides.

Relatively few reactions of thionyl tetrafluoride have been reported, and are discussed later.

Sulphuryl halides:

SO_2F_2, sulphuryl fluoride, is readily obtained by the action of fluorine on sulphur dioxide, and was one of the earliest examples of a sulphur oxyfluoride to be prepared (34).

$$SO_2 + F_2 \longrightarrow SO_2F_2$$

Sulphur dioxide is also oxidised by AgF_2 in a flow reaction at high temperature (41).

$$SO_2 + AgF_2 \longrightarrow SO_2F_2 + AgF$$

More recently it has been prepared by the metathetical reaction of sulphuryl chloride and sodium fluoride in a bomb reaction (27).

$$SO_2Cl_2 + 2NaOH \longrightarrow SO_2F_2 + 2NaF$$

Sulphuryl fluoride is a colourless gas which boils at -54.5°. It is remarkably inert to hydrolysis, and only slowly hydrolyses in alkaline solution giving fluorosulphate ion (7).

$$SO_2F_2 + 2NaF \longrightarrow NaSO_3F + NaF + H_2O$$

The chemistry of sulphuryl fluoride has received little attention. It reacts with ammonia to give sulphamide (42).

$$SO_2F_2 \quad + \quad 4NH_3 \longrightarrow NH_2SO_2NH_2 \quad + \quad 2NH_4F$$

Dropwise addition of sulphuryl chloride on to a slurry of sodium fluoride in acetonitrile gives sulphuryl chloride fluoride, SO_2FCl (27), which is stable at ambient temperature, in contrast to thionyl chloride fluoride. SO_2FCl is a colourless gas at room temperature, and boils at 7.1°. Few reactions of sulphuryl chloride fluoride have been reported.

While sulphuryl bromide has not as yet been properly characterised, sulphuryl bromide fluoride has been made from a mixture of sulphur dioxide, bromine and bromine trifluoride at pressure (28). Sulphuryl bromide fluoride boils at 41°. Its chemistry has been little investigated. No stable sulphuryl iodides are known.

Each year sees an ever increasing volume of activity in the area of sulphur chemistry, but there are some classes of sulphur compounds which thus far have evaded isolation, as listed below.

1. The isolation of stable sulphur iodides.
2. The synthesis of sulphur hydrides, SH_4, SH_6, SF_5H etc..
3. The synthesis of mixed halide sulphur compounds, SF_xCl_{4-x}, SOF_xCl_{4-x}, and SF_xCl_{6-x}.
4. Synthesis of compounds with sulphur atoms of mixed oxidation state bonded to one another.

Techniques are continuously advancing, but working with these types of compounds is fraught with difficulties arising from hydrolysis or thermodynamic instability of the products. Although many of the compounds described are mainly of academic interest, some are of commercial importance as heat exchangers, insulators, dielectrics and fluorinating agents.

General Experimental Methods

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 with Perkin-Elmer 225,257 and 457 spectrophotometers. Infrared spectra of gases were recorded using 5 and 10 cm. gas-cells fitted with KBr windows. Solution spectra were recorded using KBr, semi-permanent cells obtained from R.I.I.C.. Solid spectra were recorded as mulls with nujol, using KBr plates. Normal abbreviations to denote band shapes and intensities are used, e.g. s = strong; m = medium; w = weak; v = very; br = broad; sh = shoulder etc..

n.m.r. spectra were obtained from a Perkin-Elmer R.10 spectrometer at 60.0 M.Hz. for proton, 56.5 M.Hz. for fluorine and 24.3 M.Hz. for phosphorus, with a probe temperature of 33°. Proton spectra were measured in p.p.m. relative to tetramethylsilane (t.m.s.), $(CH_3)_4Si$, fluorine spectra relative to trichlorofluoromethane, CCl_3F, and phosphorus spectra relative to phosphoric acid, H_3PO_4. Peak multiplicities are abbreviated as d = doublet; t = triplet; b.s. = broad singlet etc..

Mass spectra were recorded at 70 e.v. using an A.E.I. M.S.12 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 Beller or Bernhardt.

CHAPTER I

REACTIONS OF THIONYL FLUORIDE AND DERIVATIVES.

INTRODUCTION

The number of known sulphur IV oxyfluorides is quite limited in comparison to the wide variety of known sulphur VI oxyfluorides. This is a consequence of the lower valence state of the sulphur, in that it restricts the number of bonds of oxygen and fluorine to sulphur. Usually the lower oxidation state results in greater reactivity of the sulphur IV derivative in comparison to the sulphur VI derivative, since the sulphur is more accessible to attack by various chemical reagents. SF_4 for example is extremely reactive, whereas SF_6 is highly inert. This is reversed for the oxyfluorides SOF_2 and SOF_4, where the sulphur VI compound, SOF_4, is more reactive. This is probably a consequence of the unusual coordination state in SOF_4, in that it is five-coordinate.

The chemistry of thionyl fluoride has received little attention although it has been known for many years. The more reactive sulphur fluorides have been more fully investigated, and the synthetic uses of SOF_2 have been largely ignored. Reactions with thionyl fluoride usually involve forcing conditions, but some reactions do occur at lower temperatures and pressures.

The main object of the research discussed in this chapter was to investigate some reactions of thionyl fluoride and its derivatives, and closely examine the spectroscopic properties of the products. While many of them are well known, new routes to the thionyl fluoride derivatives are discussed. The spectroscopic properties of a range of sulphinamide derivatives have not been studied to any extent, and have thus formed a major part of the work in this chapter.

SUMMARY OF REACTIONS

A. Reactions of thionyl fluoride with silicon oxygen compounds.

1. $SOF_2 + Me_3SiOMe \longrightarrow MeOS(O)F + (MeO)_2SO + Me_3SiF$
2. $SOF_2 + Me_3SiOEt \longrightarrow EtOS(O)F + (EtO)_2SO + Me_3SiF$
3. $MeOS(O)F + Me_3SiOMe \longrightarrow (MeO)_2SO + Me_3SiF$
4. $SOF_2 + Me_3SiOPh \longrightarrow$ no reaction

B. Reactions of thionyl fluoride with sulphite esters.

5. $SOF_2 + (MeO)_2SO \longrightarrow MeOS(O)F + MeF + SO_2$
6. $SOF_2 + (EtO)_2SO \longrightarrow EtOS(O)F + EtF + SO_2$
7. $SOF_2 + (PhO)_2SO \longrightarrow PhOS(O)F + C_6H_5F + SO_2$

C. Reactions of thionyl fluoride with Si-N, N-H, and P-N compounds.

8. $SOF_2 + Me_3SiNMe_2 \longrightarrow Me_2NS(O)F + Me_3SiF$
9. $SOF_2 + Me_3SiNEt_2 \longrightarrow Et_2NS(O)F + Me_3SiF$
10. $SOF_2 + 2Me_3SiNMe_2 \longrightarrow (Me_2N)_2SO + 2Me_3SiF$
11. $SOF_2 + 2Me_3SiNEt_2 \longrightarrow (Et_2N)_2SO + 2Me_3SiF$
12. $SOF_2 + (Me_3Si)_2NMe \longrightarrow MeNSO + 2Me_3SiF$
13. $SOF_2 + 2Me_2NH \longrightarrow Me_2NS(O)F + Me_2NH.HF$
14. $SOF_2 + P(NMe_2)_3 \longrightarrow Me_2NS(O)F +$ solids
15. $SOF_2 + (Ph_2P)_2NMe \longrightarrow MeNSO +$ oil

16. $SOX_2 + 2Me_3SiNMeP(O)Cl_2 \longrightarrow (Cl_2P(O)NMe)_2SO + 2Me_3SiX$

X = Cl,F.

D. Reactions of fluorosulphinamides with Si-O and Si-N compounds.

17. $Me_2NS(O)F + Me_3SiOMe \longrightarrow Me_2NS(O)OMe + Me_3SiF$

18. $Me_2NS(O)F + Me_3SiOEt \longrightarrow Me_2NS(O)OEt + Me_3SiF$

19. $Et_2NS(O)F + Me_3SiOMe \longrightarrow Et_2NS(O)OMe + Me_3SiF$

20. $Et_2NS(O)F + Me_3SiOEt \longrightarrow Et_2NS(O)OEt + Me_3SiF$

21. $Me_2NS(O)F + Me_3SiNEt_2 \longrightarrow Me_2NS(O)NEt_2 + (Me_2N)_2SO + Me_3SiF$

22. $Et_2NS(O)F + Me_3SiNMe_2 \longrightarrow Me_2NS(O)NEt_2 + (Me_2N)_2SO + Me_3SiF$

E. Reactions of thionyl chloride with N-H and Si-N compounds.

23. $SOCl_2 + 2Me_2NH \longrightarrow Me_2NS(O)Cl + Me_2NH.HCl$

24. $SOCl_2 + 2Et_2NH \longrightarrow Et_2NS(O)Cl + Et_2NH.HCl$

25. $SOCl_2 + 2i\text{-}Pr_2NH \longrightarrow i\text{-}Pr_2NS(O)Cl + i\text{-}Pr_2NH.HCl$

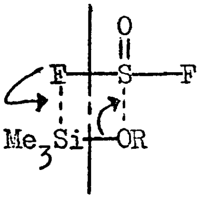
26. $SOCl_2 + Me_3SiNEt_2 \longrightarrow Et_2NS(O)Cl + Me_3SiCl$

A. Reactions of thionyl fluoride with silicon oxygen compounds.

$$\mathrm{SOF_2 + Me_3SiOR \longrightarrow ROS(O)F + (RO)_2SO + Me_3SiF}$$

$$\mathrm{R = Me, Et, \neq Ph}$$

The reactions require forcing conditions, with no reaction taking place at room temperature on prolonged standing. The reaction goes to completion for R = methyl, only partially for R = ethyl, and not at all for R = phenyl. It seems likely that the reactions involve a four-centre transition state, as depicted below.



R = Me, Et, Ph.

The driving force of the reaction is the formation of the strong silicon-fluorine bond (43), coupled with the nucleophilicity of the alkoxylic oxygen of Me_3SiOR. The nucleophilic nature of the oxygen atom in the case of Me_3SiOPh is possibly reduced because of pπ contributions to the aromatic ring. While SF_4 reacts readily with Me_3SiOPh (25), the reaction with SOF_4, as will be discussed later, is slower and does not appear to occur with SOF_2. The reactions of Me_3SiOPh with the sulphur fluorides SF_4, SOF_4 and SOF_2 follow the general trend of the reactivity of these sulphur fluorides towards other reagents, where SF_4 is the most reactive, and SOF_2 the least reactive. There is therefore a very fine distinction for reaction of SOF_2 and

Me_3SiOR between R = alkyl and R = aryl, and probably arises more from electronic rather than steric factors.

The alkylfluorosulphites, ROS(O)F (R = Me, Et), are colourless volatile gases at room temperature. They are indefinitely stable in dry glass containers but decompose on heating.

$$ROS(O)F \xrightarrow{\Delta} RF + SO_2$$

They are moisture sensitive and hydrolyse to give SO_2, HF and ROH. The alkylfluorosulphites can be prepared in better yield from the reaction of sulphur tetrafluoride and the dialkylsulphites (44).

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

SF_3OR is suggested to be the other product of the reaction and is unstable with respect to SOF_2 and RF.

$$SF_3OR \longrightarrow SOF_2 + RF$$

The reactions of Me_3SiOR (R = Me, Et) with SOF_2 include the formation of the dialkylsulphites as well as the alkylfluorosulphites. This is not surprising, as the reaction of methylfluorosulphite with Me_3SiOMe, for example, is fairly vigorous at below room temperature.

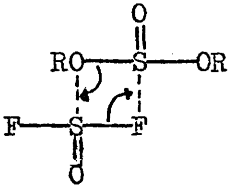
$$MeOS(O)F + Me_3SiOMe \longrightarrow (MeO)_2SO + Me_3SiF$$

Thionyl fluoride has been shown to react with $Me_2Si(OEt)_2$ to give the dialkylsulphite exclusively and is not accompanied by the formation of the alkylfluorosulphite (45).

$$SOF_2 + Me_2Si(OEt)_2 \longrightarrow (EtO)_2SO + Me_2SiF_2$$

B. Reactions of thionyl fluoride with sulphite esters.

The reactions of thionyl fluoride with the dialkylsulphites show a reverse trend to that of the silicon oxygen compounds. Although higher reaction temperatures were employed, the yield of alkylfluorosulphite is very small compared to that of phenylfluorosulphite. Once again, a four-centre transition state seems likely.



R = Me,Et,Ph.

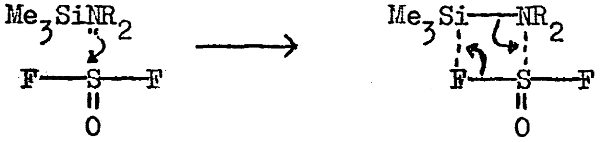
The electrophilic nature of the sulphur atom of the sulphite ester becomes important as to whether or not reaction will occur. This would be greatest in the case of $(PhO)_2SO$, where the phenoxy groups exert a greater electron-withdrawl from the sulphur atom than do the alkoxy groups. The higher reaction temperatures required for reaction of thionyl fluoride with the sulphite esters results in partial decomposition of the fluorosulphites to RF and SO_2.

Phenylfluorosulphite is an involatile, colourless liquid which is moisture sensitve, and hydrolyses to phenol, SO_2 and HF. It was first prepared by the metathetical reaction of phenylchlorosulphite and sodium fluoride in acetonitrile (46).

$$PhOS(O)Cl \quad + \quad NaF \longrightarrow PhOS(O)F \quad + \quad NaCl$$

C. Reactions of thionyl fluoride with Si-N, N-H, and P-N compounds.

Thionyl fluoride reacts with the dialkylaminotrimethylsilanes well below room temperature in contrast to the silicon oxygen and sulphite reactions. The greater reactivity of the silylamines, as opposed to the silyloxy compounds, towards SOF_2, probably arises from the increased basic strength of the nitrogen atom coordinating to the electrophilic sulphur atom of thionyl fluoride. Recently it has been reported that tertiary amines form adducts to the thionyl halides, $SOCl_2$ and $SOBr_2$ (47). This could mean that adduct formation of the silylamines with thionyl fluoride occurs first before reaction and elimination of Me_3SiF.



$$SOF_2 + Me_3SiNR_2 \longrightarrow R_2NS(O)F + Me_3SiF$$

$$R = Me, Et.$$

Dimethylaminofluorosulphinamide, $Me_2NS(O)F$, is an involatile, colourless liquid which moves slowly in vacuo, with a vapour pressure of about 6 mm Hg at 20°. Diethylaminofluorosulphinamide, $Et_2NS(O)F$ is also a colourless involatile liquid which has no observable vapour pressure at room temperature. $Et_2NS(O)F$ has been made previously from the reaction of diethylamine and thionyl fluoride in ethereal solution at low temperature (48).

$$2Et_2NH + SOF_2 \longrightarrow Et_2NS(O)F + Et_2NH.HF$$

Only the synthesis of the compound is described, and no spectroscopic properties are discussed.

The dialkylaminofluorosulphinamides are moisture sensitive materials, decomposing fairly slowly to give SO_2, HF and solids. They are, however, indefinitely stable in dry glass at room temperature and decompose on prolonged heating at 130° to a tarry substance. The infrared spectra of the dialkylaminofluorosulphinamides are given in Table 1, and the ^1H and ^{19}F n.m.r. spectra are given in Table 2 below.

Table 1.

$Me_2NS(O)F$ $\nu\,cm^{-1}$	$Et_2NS(O)F$ $\nu\,cm^{-1}$	Assignment
2935 m	2955 m	C-H stretch
2890 w	2900 w	
1450 w	1450 w	asym C-H deformation
1230 vs	1229 vs	S-O stretch
944 vs	935 s	C-N stretch
702 s	679 m	S-N stretch
629 vs	627 vs	S-F stretch

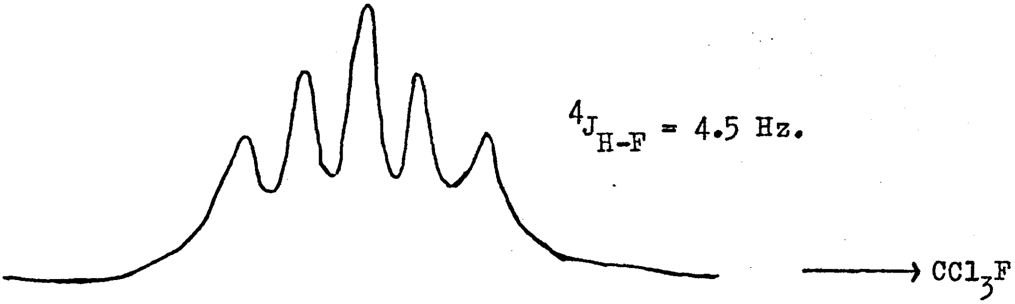
The dominant absorptions arise from νSO and νSF. νSF has moved to much lower wavenumbers with respect to νSF for SOF_2 at 748 cm^{-1} (49). More discussion about the i.r. spectra will be given later.

Table 2.

	δ CH$_3$	δ CH$_2$	δ F	$^4J_{H-C-N-S-F}$ Hz.
$Me_2NS(O)F$	-2.77 d	-	-38.6 bs	4.7
$Et_2NS(O)F$	-1.16 t	-3.33	-55.3	4.5
		(a)	quintet	

(a) = two overlapping quartets

The proton spectrum of $Me_2NS(O)F$ shows evidence of H-F coupling, with the methyl signal appearing as a doublet. The ^{19}F n.m.r., however, shows a broad singlet which did not resolve at -100°. The proton spectrum of $Et_2NS(O)F$ shows a triplet for the methyl signal and two overlapping quartets for the methylene protons. The H-H coupling for the methylene protons is further split by H-F coupling. The ^{19}F n.m.r. spectrum of $Et_2NS(O)F$ shows a well resolved quintet arising from coupling with the four methylene protons.



^{19}F n.m.r. of $Et_2NS(O)F$.

The ^{19}F chemical shift shows a considerable range for the -S(O)F entity, as shown in Table 3.

Table 3.

Compound	^{19}F shift (p.p.m. from CCl_3F)	Reference
FS(O)F	-77.9	(6)
PhOS(O)F	-62.5	(46)
EtOS(O)F	-59.8	(44)
MeOS(O)F	-55.6	(44)
$Et_2NS(O)F$	-55.3	(50)
$Me_2NS(O)F$	-38.6	(50)
$CF_3S(O)F$	21.6	(51)

Progressive deshielding of the fluorine atoms would appear to follow electronegativity trends, moving downfield with respect to the atom attached to sulphur in the order $C<N<O<F$. This is something of an oversimplification, as the CF_3 group is highly electronegative. Further, there is a large difference in chemical shift between $Me_2NS(O)F$ and $Et_2NS(O)F$ and the reason for this is not immediately obvious. A much smaller difference is observed between Me_2NSF_3 at -39p.p.m. (20), and Et_2NSF_3 at -42.8 p.p.m. (52).

The mass spectrum of $Me_2NS(O)F$ is shown in Table 4.

Table 4.

	m/e	Ion	Intensity
$Me_2NS(O)F$	111	$C_2H_6NSOF^+$	35
M.Wt. 111	110	$C_2H_5NSOF^+$	10
	92	$C_2H_6NSO^+$	36
	91	$C_2H_5NSO^+$	5
	76	$C_2H_6NS^+$	8
	67	SOF^+	4
	51	SF^+	2
	48	SO^+	14
	44	$C_2H_6N^+$	3
	43	$C_2H_5N^+$	100
	42	$C_2H_4N^+$	100
	41	$C_2H_3N^+$	100

The mass spectrum is dominated by the breakdown of the dimethylamino ion, which itself is not very intense. The spectrum shows progressive loss of protons from the $C_2H_6N^+$ fragment. The molecular ion is the next most intense along with the $C_2H_6NSO^+$ ion arising from the loss of the fluorine atom from the molecular ion. Both the molecular ion and the $C_2H_6NSO^+$ fragment show loss of only one proton. Other than the molecular ion, ions containing fluorine are of low abundance.

Reactions of SOF_2 and Me_3SiNR_2 in a 1:2 ratio.

The N,N,N',N' tetraalkylaminosulphinamides, $(R_2N)_2SO$, can be made with great ease from thionyl fluoride and the dialkylaminotrimethylsilanes.

$$SOF_2 + 2Me_3SiNR_2 \longrightarrow (R_2N)_2SO + 2Me_3SiF$$

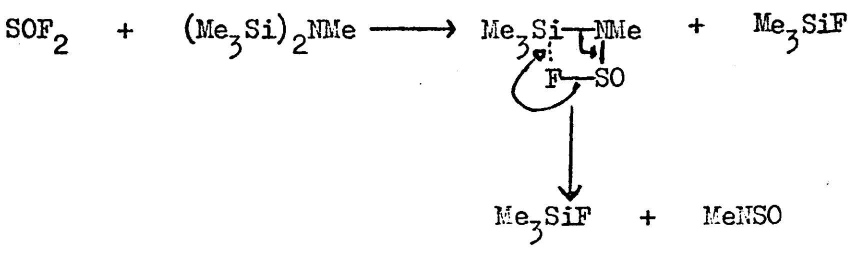
$$R = Me, Et.$$

The reaction proceeds smoothly at room temperature, and on removal of the Me_3SiF, a quantitative yield of the $(R_2N)_2SO$ compounds is obtained. They are involatile liquids at room temperature though $(Me_2N)_2SO$ solidifies not much below room temperature. These compounds have been made previously from the dialkylamines and thionyl chloride in ether, but isolation of the products is more tedious and yields are lower (53,54).

$$SOCl_2 + 4R_2NH \longrightarrow (R_2N)_2SO + 2R_2NH.HCl$$

$SOF_2/(Me_3Si)_2NMe$.

Heptamethyldisilazane reacts with thionyl fluoride fairly slowly at room temperature to produce Me_3SiF and methyl thionylamine, MeNSO. No intermediate compounds were isolated, and a stepwise reaction is thought to occur.



$$SOF_2 + (Me_3Si)_2NMe \longrightarrow \begin{matrix} Me_3Si - NMe \\ F - SO \end{matrix} + Me_3SiF$$

$$\downarrow$$

$$Me_3SiF + MeNSO$$

A similar reaction is observed with thionyl chloride and heptamethyldisilazane (55).

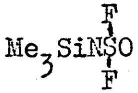
$$SOCl_2 \quad + \quad (Me_3Si)_2NMe \longrightarrow MeNSO \quad + \quad 2Me_3SiCl$$

Methyl thionylamine was first reported from the reaction of thionyl fluoride and methylamine (48).

$$SOF_2 \quad + \quad MeNH_2 \longrightarrow MeNHSOF \quad + \quad HF$$

$$MeNHSOF \longrightarrow MeNSO \quad + \quad HF$$

More recently a stable oxysulphurfluoride with an adjacent silicon-nitrogen bond on the sulphur atom has been prepared (56).



$$(Me_3Si)_3N \quad + \quad SOF_4 \longrightarrow Me_3SiN\overset{F}{\underset{F}{S}}O \quad + \quad 2Me_3SiF$$

Trimethylsilyliminosulphur oxydifluoride, $Me_3SiNMeS(O)F_2$ does however eliminate Me_3SiF on heating.

$$Me_3SiNMeS(O)F_2 \longrightarrow S \quad + \quad SO_2 \quad + \quad SOF_2 \quad + \quad N_2 \quad + \quad Me_3SiF$$

It would appear that a greater degree of double bonding in the sulphur VI compound is stabilising $Me_3SiNMeS(O)F_2$ compared with $Me_3SiNMeS(O)X$ (X = F,Cl) which has not been isolated.

SOF_2/Me_2NH.

A vigorous reaction takes place between thionyl fluoride and dimethylamine at -76^{o} to give colourless solids which turn brown on assuming room temperature. Presumably an adduct was formed at low temperature which was followed by fast reaction at room temperature. $Me_2NS(O)F$ was extracted from the products in lower yield compared to that of the silylamine reaction.

$$SOF_2 \quad + \quad 2Me_2NH \longrightarrow Me_2NS(O)F \quad + \quad Me_2NH.HF$$

$SOF_2/P(NMe_2)_3$.

The reaction of trisdimethylaminophosphine and thionyl fluoride occurs at well below room temperature to give $Me_2NS(O)F$ as the only volatile species. It is surprising that no volatile phosphorus compounds are obtained. The other products are solids which are soluble in acetonitrile. n.m.r. revealed that a complex mixture was present, with many peaks in the proton spectrum. The fluorine spectrum showed a doublet at +73.2 p.p.m. from CCl_3F with J_{P-F} = 715.5 Hz.. Crosbie found that an unidentified solid from the reaction of PF_5 and $MeP(NMe_2)_2$ gave a similar ^{19}F n.m.r. spectrum (57), with a shift of +73.5 p.p.m. from CCl_3F and J_{P-F} = 711.0 Hz..

$SOF_2/(Ph_2P)_2NMe$.

No reaction took place at room temperature with thionyl fluoride and bis(diphenylphosphino)methylamine, and only a partial reaction occurred at elevated temperature. Other than unreacted SOF_2, MeNSO was the only identifiable product. A possible mechanism for reaction is shown below.

$$SOF_2 + (Ph_2P)_2NMe \longrightarrow Ph_2PNMeS(O)F + Ph_2PF$$

$$Ph_2PNMeS(O)F \longrightarrow MeNSO + Ph_2PF$$

Subsequent reaction of Ph_2PF with SOF_2 or $(Ph_2P)_2NMe$ to give a brown tar precluded its isolation.

$SOX_2/Me_3SiNMeP(O)Cl_2$.

The reaction of thionyl fluoride and

dichlorophosphinylmethyl(trimethylsilyl)amine proceeds slowly at room temperature and more vigorously with thionyl chloride to give thionyl bis(dichlorophosphinylmethylamine), $(Cl_2P(O)NMe)_2SO$.

$$\begin{tikzcd} SOX_2 + Me_3SiNMeP(O)Cl_2 \arrow[r] & Cl_2P(O)NMeS(O)X + Me_3SiX \arrow[d, "Me_3SiNMeP(O)Cl_2"] \\ X = F, Cl. & (Cl_2P(O)NMe)_2SO + Me_3SiX \end{tikzcd}$$

$(Cl_2P(O)NMe)_2SO$ is a colourless solid which is soluble in petroleum ether, carbon tetrachloride and acetonitrile. It sublimes unchanged at 90° under dynamic vacuum. It hydrolyses in a moist atmosphere giving SO_2, HCl and a tarry residue. An attempt to fluorinate the compound with NaF in acetonitrile did not succeed. The infrared spectrum shows peaks at 1297 cm^{-1} and 1202 cm^{-1} which are assigned to the P-O and S-O stretching frequencies respectively.

The n.m.r. shows a characeristic spectrum with δCH_3 at -2.57 p.p.m. from t.m.s. appearing as a doublet and $J_{H-C-N-P}$ equal to 14.7 Hz.. The phosphorus spectrum shows a quartet at -7.7 p.p.m. from external H_3PO_4.

C. Reactions of the fluorosulphinamides with Si-O and Si-N compounds.

The dialkylaminofluorosulphinamides react much more readily with the alkoxytrimethylsilanes than does thionyl fluoride.

$$R_2NS(O)F + Me_3SiOR' \longrightarrow R_2NS(O)OR' + Me_3SiF$$

R = R' = Me; R = Me, R' = Et; R = Et, R' = Me; R = R' = Et.

The reactions do not go to completion at room temperature, and gentle heating is required for a short period. $Et_2NS(O)OMe$ has been reported previously as being made from the alkylfluorosulphite (44).

$$MeOS(O)F + Me_3SiNEt_2 \longrightarrow Et_2NS(O)OMe + Me_3SiF$$

The alkoxydialkylaminosulphinamides have been made from the alkylchlorosulphites and secondary amines (58,59).

$$ROS(O)Cl + 2R_2NH \longrightarrow R_2NS(O)OR + R_2NH.HCl$$

They are colourless involatile liquids, which are moderately stable in the atmosphere. While they have been known for some time, the i.r. and n.m.r. spectra have not received attention, and are discussed later.

Dimethylaminodiethylaminosulphinamide, $Me_2NS(O)NEt_2$, has been made in two ways, but is not stable on standing, and the analytical data are not entirely satisfactory.

$$Me_2NS(O)F + Me_3SiNEt_2 \longrightarrow Me_2NS(O)NEt_2 + Me_3SiF$$

$$Et_2NS(O)F + Me_3SiNMe_2 \longrightarrow Me_2NS(O)NEt_2 + Me_3SiF$$

Both reactions give an almost quantitative yield of Me_3SiF and a small amount of $(Me_2N)_2SO$. The latter would suggest that some form of rearrangement has taken place. $Me_2NS(O)NEt_2$ moves slowly in vacuo and decomposes to a black tar on standing after several days.

E. Reactions of thionyl chloride with N-H and Si-N compounds.

The reactions of thionyl chloride and secondary amines have been reported before (54,60), giving the dialkylaminochlorosulphinamides.

$$SOCl_2 \quad + \quad 2R_2NH \longrightarrow R_2NS(O)Cl \quad + \quad R_2NH.HCl$$

$$R = Me, Et, i\text{-}Pr.$$

The yield of $R_2NS(O)Cl$ is low, as isolation of the product is difficult. $Et_2NS(O)Cl$ was prepared in much more satisfactory yield from the silylamine.

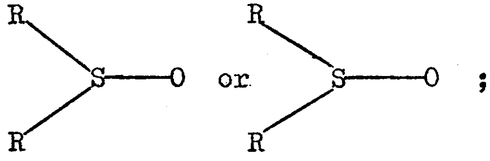
$$SOCl_2 \quad + \quad Me_3SiNEt_2 \longrightarrow Et_2NS(O)Cl \quad + \quad Me_3SiCl$$

$i\text{-}Pr_2NS(O)Cl$ is a low melting solid and $Me_2NS(O)Cl$ and $Et_2NS(O)Cl$ are involatile liquids. They decompose rapidly in a moist atmosphere giving SO_2, HCl and a black tar. The spectroscopic properties of these compounds have not been investigated and are discussed later.

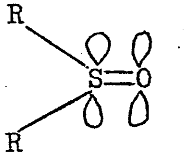
The infrared spectra of sulphinamide derivatives.

The infrared spectra of derivatives containing the S^{IV}=O bond have been fairly extensively investigated (61-63), but the sulphinamides and related compounds have received little attention. The effects of the attached substituents X and Y in the molecules XYSO on νSO will be discussed and νSN and νCN in the sulphinamide derivatives will also be discussed.

The S-O bond. Moffit has considered at length the nature of the sulphur oxygen bond using molecular orbital theory (64). Dissension of opinion had been centred on whether or not the 3d orbitals of sulphur were employed in double bond formation between sulphur and oxygen.



(a)



(b)

Prior to Moffit's work, it was argued by Arndt and Eistert (65) that since argon is an inert gas, the energy of promotion required to produce the requisite sulphur valence state must be too high as to preclude the formulation (b) as above. However, it has been found that the dipole moment associated with the sulphur oxygen link is only about one third of the value required for full transference of charge (66), as in (a) above. Moffit went on to prove that the oxygen sulphur bond is largely double, and the 3d orbitals of sulphur play an important role.

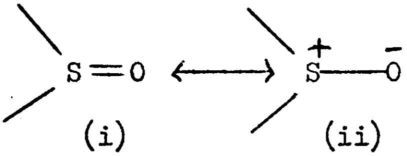
<u>Bond lengths in S-O compounds.</u>

For single S-O bonds, Pauling's covalent radii give a bond length of 1.70Å (67), and the Schomaker Stevenson rule gives 1.69Å (68). For S-O double bonds, the corresponding calculated values are 1.49Å and 1.47Å. From all available data, no compound as yet has been found where the S-O bond is as long as the predicted value for the single bond. The longest reported S-O bonds are 1.66Å in SF_5OOSF_5 (69), 1.64Å in SF_5OF (70), and

1.64Å in $H_2S_2O_7$ (71). In these compounds the 3d orbitals normally used for double bonding with oxygen are largely used in formal single bonds with other atoms (64,72). Despite this, there is some evidence that even for these long bonds some (p-d)π overlap occurs, so that the S-O bond is shorter than the true single bond.

The shortest S-O bond lengths are 1.39Å in $SO_2(NH_2)$ (73), 1.405Å in SO_2F_2 (74), 1.412Å in SOF_2 (29) and 1.40Å in S_3O_9 (75). These bond distances are all much shorter than the predicted value. Abrahams (76) has used Moffit's bond order assignments (64) to predict an S-O double bond length of 1.425Å, which has found fairly wide acceptance. Cruickshank in considering bond length, bond order relationships from a theoretical standpoint (72) found an unsatisfactorily short S-O double bond of 1.30Å.

Gillespie and Robinson (62) have shown correlations between S-O stretching frequencies and molecular parameters and have postulated two possible extreme forms of the S-O bond, as below.



(i) above represents a situation where the attached substituents to sulphur are sufficiently electronegative as to raise the effective electronegativity of sulphur to that of oxygen. The bonding electrons are equally shared thus giving a formal double bond. This is found in thionyl fluoride which has a short S-O bond. Less electronegative substituents will render the d orbitals more diffuse and ineffective for bonding. Thus an inverse relationship exists between the length of the S-O bond and the S-O stretching frequency and thereby the bond order (64) as shown below. The force constant is used in place of the stretching frequency.

Table 5.

Moffit's bond order, force constant relationship.

Compound	p SO (calc.) bond order	k SO (observed) 10^5 dynes/cm
R_2SO	0.82	6.95
Cl_2SO	0.9	9.4
R_2SO_2	0.89	9.6
SO_2	0.93	9.97
SO_2Cl_2	1.0	10.6
SO_3	1.08	10.77
F_2SO	1.12	10.8
SO_2F_2	1.14	-

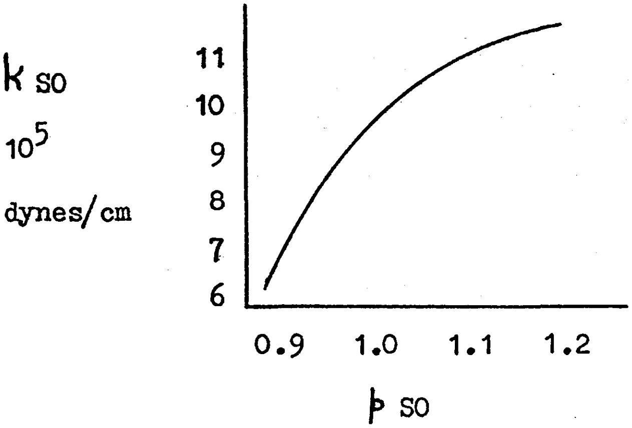
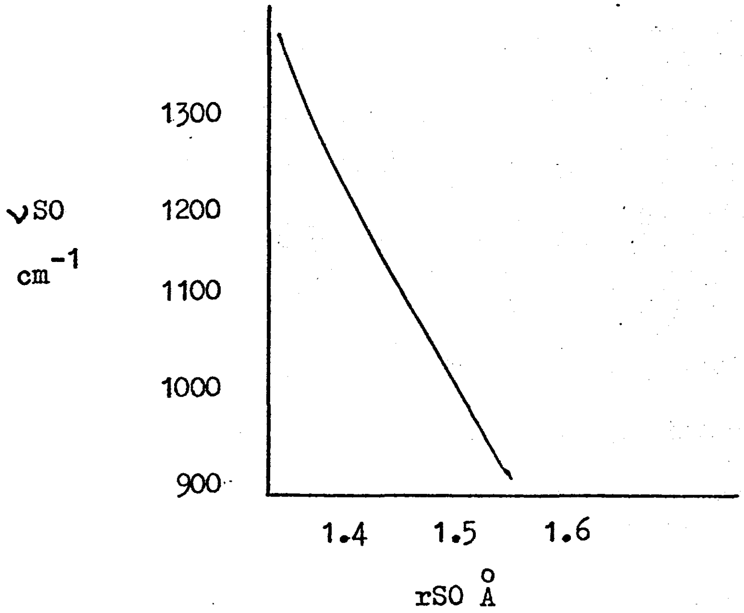


Fig. I

Figure II shows Bannister's inverse relationship between νSO and the S-O bond distance.

Figure II

νSO v. rSO



Solvent effects.

With sulphoxides there is considerable intermolecular interaction, such that (77)

νSO (liquid) < νSO (soln.) < νSO (vapour)

νSO is also very much solvent dependent and shows a great deal of variance from solvent to solvent. See Table 6.

Table 6.

Solvent effects on SO values. (79)

	$(CH_3)_2SO$	$(C_6H_5)SO$	$SOCl_2$
n-hexane	1085	1056	1242
CCl_4	1071	1052	1237
CS_2	1071	1051	1236
C_6H_6	1068	1050	1236
CH_3CN	1061	1041	1235
$CHCl_3$	1055	1040	1234

νSO cm^{-1}

It is essential therefore when making comparisons between νSO values for different compounds that the same phase is employed or the same solvent is used in the case of solution spectra. Ideally gaseous spectra are desireable, but failing this, dilute solutions in solvents such as CCl_4 are equally as good.

νSO of some sulphinamides and related compounds.

Table 7 shows νSO for some sulphinamides and related compounds, along with the results of other workers. The S-O stretching frequency is a highly characteristic feature of thionyl compounds appearing as a strong band near 1200 cm^{-1}. The S-O deformation frequency near 400 cm^{-1} appears as a much weaker band (63). It is obscured by other bands for the complex sulphinamide spectra and will not be discussed further. All solution measurements were made in 0.05M solutions in carbon tetrachloride with a path

Table 7.

S-O stretching vibrations (cm^{-1})

Compound	CCl_4 solution	Other Phase
SOF_2	1310 (78)	1333 (gas) (49)
MeOS(O)F	1253	1266 (gas) (44)
EtOS(O)F	1249	1260 (gas) (44)
$SOCl_2$	1239 (79)	1253, 1251 (gas)
$Me_2NS(O)F$	1218	1230 (gas) (50)
MeOS(O)Cl	1216 (61)	-
EtOS(O)Cl	1215 (61)	-
$Et_2NS(O)F$	1212	1229 (gas) (50)
i-PrOS(O)Cl	1210 (61)	-
$(MeO)_2SO$	1209 (61)	1209 (film)
$(EtO)_2SO$	1210 (81)	1208 (film)
$Me_2NS(O)Cl$	1199, 1202 (79)	1192, 1185 (82) (film)
$Et_2NS(O)Cl$	1198	1192 (film)
$i\text{-}Pr_2NS(O)Cl$	1193	1183 (nujol mull)
$Me_2NS(O)OMe$	1164	1158 (gas), 1157 (film)
$Me_2NS(O)OEt$	1164	-
$Et_2NS(O)OMe$	1156	1152 (film)
$Et_2NS(O)OEt$	1155	-
$(Me_2N)_2SO$	1120	1119 (82), 1125 (83) (melt)
$Me_2NS(O)NEt_2$	1118	-
$(Et_2N)_2SO$	1115	-

length of 0.1 mm or 0.5 mm. Solutions of concentrations greater than 0.05M gave very broad S-O bands and νSO cannot be determined precisely.

Table 7 clearly shows how νSO is dependent on the phase studied. The most noticeable changes are found in the sulphinamides with strongly electronegative substituents. This would be expected on the basis of stronger dipolar interactions. However, for the sulphoxides (see Table 6), νSO shows a greater range of values in different solvents than does νSO for $SOCl_2$

The position of νSO has been shown to have a relationship with the inductive effect of the attached substituents to sulphur (61) as well as the bond order and bond distance of the S-O bond. Using the electronegativity of substituent groups, Steudel (79) predicted stretching modes for νSO at 1218 cm^{-1} for the N-SO-F group and 1167 cm^{-1} for the O-SO-N group which is in remarkable agreement with the values found experimentally. Also on the basis of electronegativity the value for the N-SO-N group was calculated to be at 1120 cm^{-1} as was found for $(C_5H_{10}N)_2SO$ by Steudel and for $(Me_2N)_2SO$ in this work.

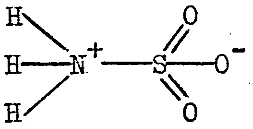
Dialkylamino groups have a greater effect in moving νSO to lower frequencies than do alkoxy groups. As with the alkyl sulphites there is only a small variation in νSO with different alkyl groups attached to the atoms directly bonded to sulphur. The greater electronegativity of oxygen relative to nitrogen results in a smaller change in νSO for the alkoxy compounds compared with the dialkylamino derivatives. The effect is particularly marked where there are two dialkylamino groups attached to sulphur, as opposed to two alkoxy groups. Thus, on going from MeOS(O)Cl to $(MeO)_2SO$, νSO falls by only 3 cm^{-1}, from 1216 cm^{-1} to 1213 cm^{-1}, whereas on going from $Me_2NS(O)Cl$ to $(Me_2N)_2SO$, νSO falls by 79 cm^{-1}, from 1199 cm^{-1} to 1120 cm^{-1}. νSO for $Me_2NS(O)OMe$, at 1164 cm^{-1}, is at an intermediate value between that of νSO for $(MeO)_2SO$ and $(Me_2N)_2SO$.

In both the alkoxy and dialkylamino compounds, a change in the halogen substituent attached to sulphur has a considerable effect on the position of νSO. νSO appears at 1218 cm^{-1} for $Me_2NS(O)F$ and 1199 cm^{-1} for $Me_2NS(O)Cl$. A comparable fall in νSO is observed with the alkoxy compounds, with νSO (solution) at 1249 cm^{-1} for MeOS(O)F, and at 1216 cm^{-1} for MeOS(O)Cl.

Sulphur nitrogen bonds.

Bannister has made a similar study on the infrared stretching frequencies of sulphur nitrogen bonds (84) as did Robinson with sulphur oxygen bonds (62). A linear relationship was established between the bond lengths of the S-N bond and the wavelength frequency of the absorption bands for some sulphur nitrogen compounds. This was with limited data, and there were a number of exceptions.

For $NH_3^+.SO_3^-$, sulphamic acid, the observed bond length for the S-N bond is 1.76Å (85), which is not too different from that of the predicted bond length of 1.74Å (67,68). Sulphamic acid has been shown to have the structure as below (85).



not H_2NSO_2OH

The nitrogen lone pair is unavailable for the sulphur 3d orbitals and the sulphur nitrogen bond is a single bond with νSN coming at 682 cm^{-1} (84).

Methyliminosulphur oxydifluoride, $MeNS(O)F_2$, which would be expected to contain a formal double S-N bond has a particularly high S-N stretching frequency at 1493 cm^{-1} (86). This is higher than νSN for NSF at 1372 cm^{-1} (87), which contains a formal triple S-N bond, and not far from νSN at 1515 cm^{-1} for NSF_3 (87), which has a higher bond order.

With the limited data available, Bannister postulated the relationship between μSN, the wavelength absorption band expressed in microns, and rS-N in Angstrom units.

$$rS\text{-}N = 0.0483\ (\mu SN) + 1.099$$

rS-N has been measured to be 1.693Å for $(Me_2N)_2SO$ (88). Using this value in Bannister's equation νSN should come at 820 cm^{-1}, compared with the observed value of 651 cm^{-1}, and is around 700 cm^{-1} for halosulphinamide compounds, $R_2NS(O)X$ (X=F,Cl).

It is interesting that, for the addition compounds for the tertiary amines and thionyl halides (47), new bands for the adducts appear at around 810 cm^{-1}. They are not present in the free amines or the thionyl halides and have been assigned to νSN. This would infer some degree of double bonding in the S-N bond for these compounds which hardly seems likely. The S-N bond for the adducts must be little different from the S-N bond in sulphamic acid. The relationship between νSN and the S-N bond distance as laid down by Bannister must be of a tenuous nature. Clearly more data is required to establish the true nature of the relationship.

Some bond data of a few dialkylaminosulphur compounds is given below.

Table 8.

	$(Me_2N)_2S$ (88)	$(Me_2N)_2SO$ (88)	$(Me_2N)_2SO_2$ (89)	Me_2NSO_2Cl (90)
rS-N	1.686Å	1.693Å	1.623Å	1.69Å
rS-O	-	1.480	1.441	1.43
∠CNC	116°	113.9°	112.9°	112°
∠SNC	118°	116.1°	117.9°	112°
∠NSN	116°	96.9°	112.6°	-
Σ∠'s at nitrogen	352°	346°	349°	336°

The data obtained for $(Me_2N)_2SO_2$ was from an X-Ray structure determination, while for the other compounds the structures were obtained by electron diffraction in the gaseous phase. Table 8 shows that the angles at nitrogen are very close to 360°, giving a planar nitrogen atom. This permits the lone pair on nitrogen to bond with the sulphur atom in some form of (d-p)π bonding more effectively. All the measurements show that the S-N bond length is shorter than the predicted bond length for the S-N single bond. There is an anomalous difference in bond length for the S-N bond between Me_2NSO_2Cl and $(Me_2N)_2SO_2$ where rS-N is shorter in $(Me_2N)_2SO_2$. Me_2NSO_2Cl would have been expected to have the shorter bond length with the electronegative chlorine atom on sulphur. The d orbitals of sulphur would not be so diffuse and would enable more effective (d-p)π bonding in the S-N bond, giving a shorter S-N bond. The difference could possibly arise by virtue of the different methods employed in determining the structures. The thermal motions of the molecules could have lengthened the S-N bond in Me_2NSO_2Cl which is in the gaseous state as opposed to $(Me_2N)_2SO_2$ which is in a crystalline state. A similar effect has been observed with the P-N bond length in Me_2NPF_2 which has been found to be 1.684Å in the gaseous phase (91) and 1.628Å in the solid state (92).

However, there appears to be little difference in rS-N between $(Me_2N)_2S$ and $(Me_2N)_2SO$, where there would have been expected to be a shorter S-N bond distance in $(Me_2N)_2SO$. In $(Me_2N)_2SO$ the sulphur atom is in a higher oxidation state and thereby a greater positive charge resides on the sulphur atom. This would be expected to increase (d-p)π bonding in the S-N bond which does not manifest itself in a shorter S-N bond. Possible back bonding of the oxygen atom could be operative. A further anomaly arises in potassium sulphamate, KSO_3NH_2, where the S-N bond distance is 1.666Å with an almost pyramidal configuration at nitrogen (88). νSN appears at 805 cm^{-1} for KSO_3NH_2 and does not hold with Bannister's equation.

νSN and νCN for some sulphinamide compounds.

The i.r. spectra of the sulphinamides show characteristic bands between 950 and 900 cm^{-1} (876 cm^{-1} in one case) and between 700 and 645 cm^{-1}. The former is associated with the symmetric NC_2 stretch and the latter with the sulphur nitrogen stretching modes. See Table 9.

Table 9.

C-N and S-N stretching frequencies.

Compound	νNC_2 cm^{-1}	νSN cm^{-1}
$Me_2NS(O)F$	943	702
$Et_2NS(O)F$	939, 930	679
$Me_2NS(O)Cl$	938	691
$Et_2NS(O)Cl$	931, 926	684, 671
$i\text{-}Pr_2NS(O)Cl$	939	not identifiable
$Me_2NS(O)OMe$	930	675, 643
$Me_2NS(O)OEt$	932	659
$Et_2NS(O)OMe$	931, 908	642
$Et_2NS(O)OEt$	932, 908	659
$(Me_2N)_2SO$	929, 909	651
$Me_2NS(O)NEt_2$	922, 907	649
$(Et_2N)_2SO$	924, 894, 876	652

As the electronegativity of the attached groups on sulphur decreases there is a tendency for the NC_2 stretch to move to lower frequencies. Similarly, on replacing a methyl with an ethyl group, the NC_2 stretch falls in frequency. This would be expected on the basis of a mass effect. The same is true for νSN with the highest S-N stretching frequency coming at 702 cm^{-1} for $Me_2NS(O)F$. A bulkier diethylamino group moves νSN for $Et_2NS(O)F$ to 679 cm^{-1} below that of νSN for $Me_2NS(O)Cl$ at 691 cm^{-1}.

Both the bands attributable to νCN_2 and νSN show extensive splitting, especially the diethylamino compounds. This could arise from the presence of conformers in solution.

Nuclear Magnetic Resonanace Spectra of some sulphinamide derivatives.

Stereochemistry at nitrogen and the ways in which it is affected by second row elements such as silicon, phosphorus and sulphur has received a great deal of attention in recent years (93,94). Barriers to inversion for simple amines are small with a free energy of activation usually less than 10 k.cals./mole. However, the inversion barrier at nitrogen is greatly affected by steric effects, effects of angular constriction, effects of conjugation and those due to the proximity of the above mentioned elements. The barriers then fall in the range of 10-20 k.cals./mole and can be confused with other rate processes such as rotation about nitrogen bonds. It is therefore essential to examine more closely the relevant factors which affect the magnitude of the observed barriers. The larger barriers can be examined by nuclear magnetic resonance spectroscopy, or as it is called in this instance, dynamic nuclear magnetic resonance spectroscopy. The theory and application of n.m.r. to the intramolecular exchange processes have been extensively reviewed (95,96).

Two approaches are in common use; one is the use of coalescence phenomena and the other is total line shape analysis. In the former case the rate of exchange k_c at the coalescence temperature T_c is given by the equation:-

$$k_c = \pi/\sqrt{2} \, . \, \Delta\nu AB$$

The two exchanging groups A and B are uncoupled, the signals A and B are of equal intensity and the limiting shift difference $\Delta\nu AB$ is much greater than the line width of the signals in the absence of exchange (97). $\Delta G^{\ddagger}$, the free energy of activation between ground and transition states, is given by the Eyring equation.

$$k_c = \frac{T_c k}{h} \, . \, e^{-\Delta G^{\ddagger}/RT_c}$$

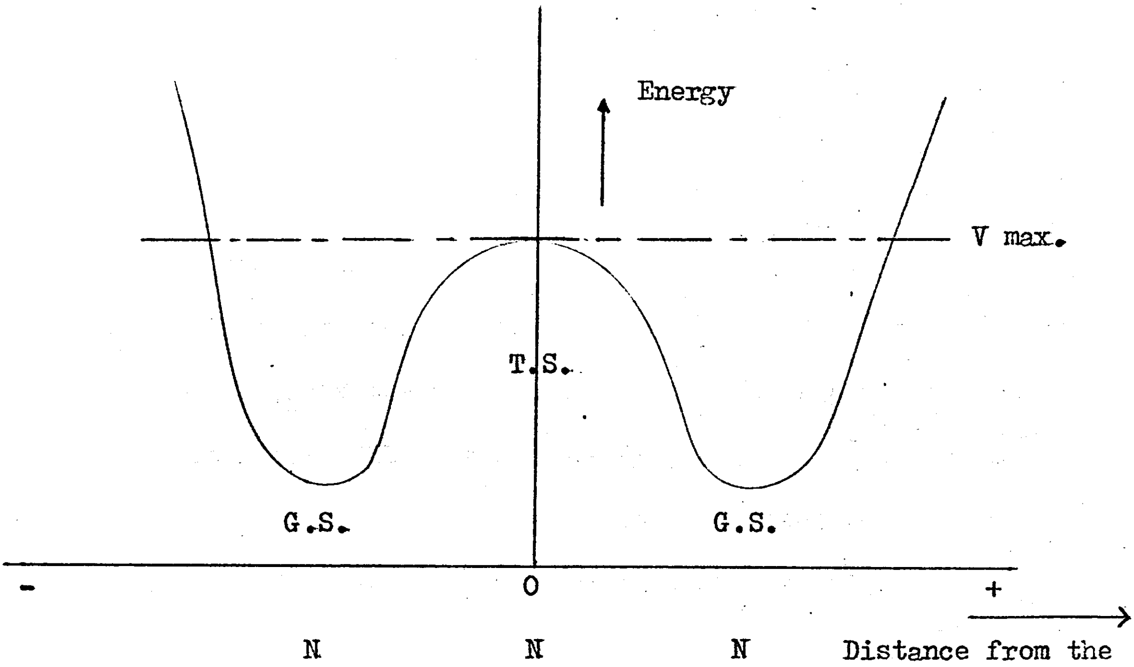
Total line shape analysis gives much more accurate activation parameters and many examples of computer programmes are available (98).

Where only one coalescence phenomenon is observed, and where simultaneous inversion-rotation processes may be present, the identity of the barrier cannot be rigorously established. There have been no reported cases in the inversion-rotation dichotomy where both barriers have been observed.

Inversion at nitrogen.

The potential energy curve for the nitrogen inversion process in NX_3 is a symmetrical double minimum curve with an energy barrier V max..

Potential Energy diagram for inversion at nitrogen.



G.S. = ground state

T.S. = transition state

Figure III

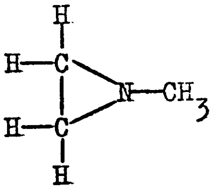
The factors which affect the barriers will be discussed.

Steric Effects.

Steric size manifests itself as an electronic repulsion between non-bonded groups. As the steric requirement of a substituent increases, the pyramidal ground state is destabilised relative to the less crowded planar transition state with a resultant decrease in barrier inversion. The potential energy barrier for the ground state is increased to approximate to the transition state and inversion is then much more rapid. The barrier to inversion for NH_3 has been measured to be 5.8 k.cals./mole (99), 4.8 k.cals./mole for $MeNH_2$ (100) and 4.4 k.cals./mole for Me_2NH (101).

Angular Constraint.

The effect of angular constraint placed on the nitrogen atom within a three membered ring is such that it becomes difficult for the endocyclic angle at nitrogen to open up, thus destabilises the transition state relative to the pyramidal form. The potential well is therefore deepened and inversion is much slower. The activation energy barrier has been found to be 19 k.cals./mole for N-methyl aziridine. See Figure IV.



N-methyl aziridine

N-methyl aziridine.

(102)

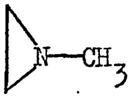
Figure IV.

The barrier to inversion decreases as the ring size increases.

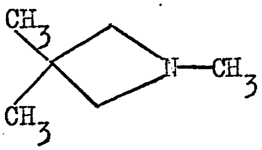
The angular strain is much smaller in the larger rings and will destabilise the ground state. See Table 10.

Table 10.

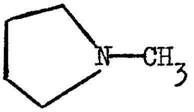
Barrier height as a function of ring size.



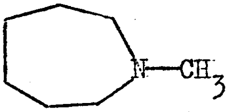
I



II



III



IV

Compound	Ring Size	Energy Barrier to Inversion	Reference
I	3	19.0 k.cals./mole	(102)
II	4	8.8 "	(103)
III	5	8.0 "	(104)
IV	7	7.0. "	(104)

Effects of conjugation.

(p-p)π conjugation: During the inversion process, while changing from the pyramidal ground state to the planar transition state, the hybrid orbitals of nitrogen may be said to be going from an sp^3 to an sp^2 state thereby increasing the "s" character of the orbitals. Thus any system which will increase π delocalisation from nitrogen will induce an sp^2 state and flatten the pyramid. This stabilises the transition state and decreases the inversion barrier. Thus aromatic groups, carbonyl groups, nitrile and nitro groups attached to nitrogen will confer stability on the planar form. See Table 11.

Table 11.

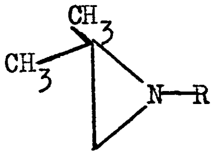
Effects of conjugation.

Compound	Energy Barrier	Reference
NH_3	5.8 k.cals./mole	(99)
NH_2CN	2.0 "	(105)
NH_2CHO	1.1 "	(99)

Groups attached to the aromatic ring linked to the nitrogen atom affect the π acceptor ability of the ring to varying degrees, which is reflected in the energy barriers to inversion. See Table 12.

Table 12.

Effects of the aromatic ring.



(94)

Aryl group, R	$\Delta G^{\ddagger}$, k.cals./mole
4 $CH_3OC_6H_4$	12.5
C_6H_5	11.2
$4ClC_6H_4$	11.0
3 $CF_3C_6H_4$	10.7
4 $CF_3C_6H_4$	10.0
4 $NO_2C_6H_4$	8.2

A methoxy group donates electron density to the ring which decreases conjugation with nitrogen whereas a nitro group increses the conjugative ability of the aromatic ring with nitrogen. The latter stabilises the transition state giving the observed fall in the barrier to inversion.

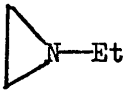
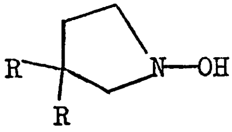
(d-p)π conjugation: Elements with low lying d orbitals directly attached to the nitrogen atom are in a position to conjugate with the lone pair on nitrogen. The effect is more pronounced in the transition state as with (p-p)π conjugation and decreases the barrier to inversion. The configuration at nitrogen for tris-silylamine, $(SiH_3)_3N$ (106), has been found to be planar, and the barrier to inversion for a related compound NH_2SiH_3 has been calculated to be 0.2 k.cals./mole.

Solvent Effects.

As the ground state is more polar than the transition state, increasing solvent polarity should stabilise the ground state and increase the inversion barrier. See Table 13.

Table 13.

Solvent effects on inversion barriers. (93)

Compound	Solvent	Energy Barrier
	neat	19.4 k.cals./mole
	D_2O	21.3 "
	$CDCl_3$	13.0 "
	D_2O	15.0 "

R = H,CH_3

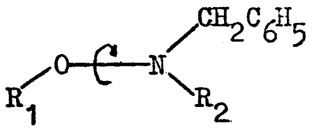
Distinguishing between nitrogen inversion and other rate processes.

In order to differentiate between nitrogen inversion in R_2NX and internal rotation about the N-X bond, three effects need to be considered. Firstly, placing the nitrogen atom within a three membered ring greatly increases the barrier to inversion. In that case, if a large barrier to rotation is expected, the two effects may be difficult to distinguish. Secondly, conjugation at nitrogen with carbonyl groups etc., and thirdly, the attachment of bulky groups to nitrogen will decrease the barrier to nitrogen inversion. It may then be possible in the latter two cases to distinguish slow rotation from inversion at nitrogen if a large barrier to conformational interchange is observed.

Processes involving slow rotation.

Raban (107) has found substantial barriers to rotation about the N-O bond in some trialkylhydroxylamines. See Table 14.

Table 14.

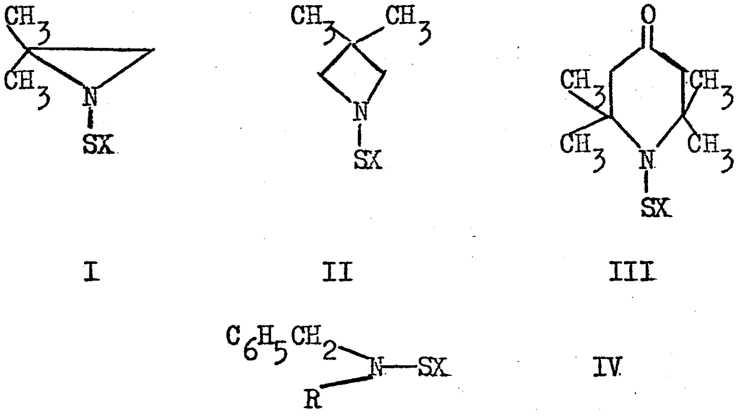


1. $R_1 = R_2 = CH_3$
2. $R_1 = CH_3$, $R_2 = CH(CH_3)_2$
3. $R_1 = CH(CH_3)_2$, $R_2 = CH_3$

Compound	Energy Barrier. k.cals./mole.
1	12.3
2	12.8
3	12.8

As seen from the limited data in Table 14, bulky groups increase the barrier to conformational interchange which cannot be the case for inversion. Of necessity this infers that a torsional barrier at the N-O bond is operative, but the origin of the barrier is not clear.

Lehn and Wagner (108) would appear to have resolved some of the controversy in a series of sulphenamides (sulphur II) where the nitrogen is either cyclic or acyclic. See Figure V.



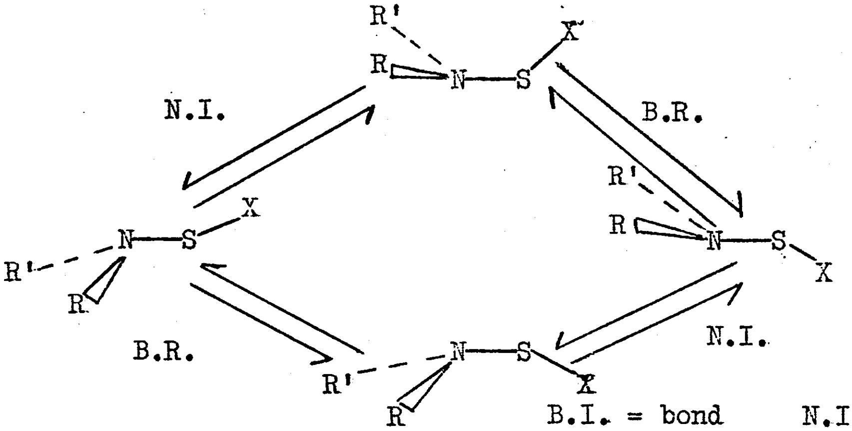
I II III

IV

Figure V

For the ring compounds with the same X substituent on sulphur, the barrier is always lower in I than in II and III. This can only arise from slow rotation about N-S bonds in II and III as the inversion barriers would be much smaller due to the decreased angular constraint at nitrogen. For the aziridine derivative however, it seems likely that slow inversion is the more likely process leading to conformational interchange, rather than slow rotation.

On changing X along the series CCl_3, t-Bu, Ph, Me, the activation energy increases for I, but decreases for II, III and IV, showing that an inverse dependence on the nature of X was operative. Lehn and Wagner considered that for IV at least a simultaneous process of inversion and rotation was taking place. See Figure VI.

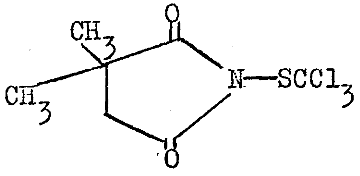


B.I. = bond rotation N.I. = nitrogen inversion

Figure VI

The mechanism would have been resolved should steric acceleration have been observed by increasing the bulkiness of the groups at nitrogen. Inversion in that case would be faster and not of consequence, but larger barriers would definitely indicate slow rotation.

2,2 dimethyl-N-(trichloromethanesulphenyl)succinimide has been found to have a high energy of activation to racemisation (109). See Figure VII. It is safe to assume near planarity at nitrogen which is induced by conjugation by the succinimide linkage. In that case, the barrier to inversion should be extremely small.



2,2 dimethyl-N-(trichloromethanesulphenyl) succinimide

Figure VII

However the barrier to conformational interchange was found to be 11.8 k.cals./mole and could only arise from slow rotation about the sulphur nitrogen bond.

A large barrier to rotation about the N-S bond in dimethylaminotrichloromethanesulphinamide, $Me_2NS(O)CCl_3$, is proposed by Jakobsen and Senning, the free energy of activation for the process being measured to be 11.9 k.cals./mole. The mechanism for the observation is shown in Figure VII (110).

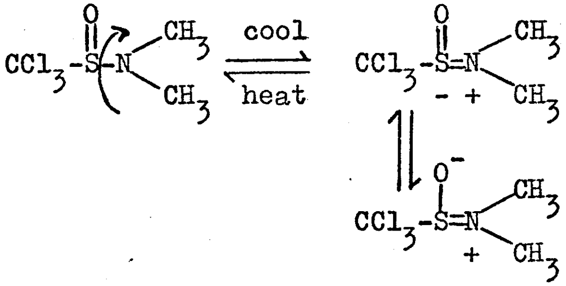


Figure VIII

A negative entropy value was found for the interchange which was thought to imply a greater degree of order at lower temperature with planarity at the nitrogen atom.

While $Me_2NS(O)CCl_3$ shows non-equivalence in the methyl signals at -46° (110), Moriarty has found that the spectrum of dimethylaminomethanesulphinamide, $Me_2NS(O)Me$, is unchanged on cooling down to -60°, with no signs of non-equivalence (111). The conclusion reached was that multiple bonding between sulphur and nitrogen was present even with continuous free rotation and that $(d\text{-}p)\pi$ delocalisation is little affected by small angular increments at all intermediary conformations.

More recently, large barriers to rotation about the N-S bond have been found for some simple sulphonamides, R_2NSO_2X (112). Where X was chlorine, the barriers were around 11 k.cals./mole but if X was much less electronegative, there was little change in the spectrum at lower temperatures. This is somewhat similar to the sulphinamides, $Me_2NS(O)CCl_3$ and $Me_2NS(O)Me$, where the more electronegative CCl_3 group as opposed to a CH_3 group results in a higher barrier to the observed rate process. This could be interpreted in terms of directional dependent $(d\text{-}p)\pi$ bonding which is enhanced by more electronegative substituents.

As outlined in the infrared discussion (see page 45), multiple bonding would appear to be evident in the sulphur II, IV and VI dialkylamino compounds where rN-S is much shorter than the calculated formal single bond. Near planarity conferred at nitrogen is fairly uniform in these compounds as indicated by the sum of the angles at nitrogen approximating to 360°, and so inversion barriers at nitrogen should be very small. The N-S bond length in $(Me_2N)_2SO_2$ is surprisingly short, although the bond distance was established from the crystalline state. This would infer a high degree of (d-p)π bonding and should result in sizeable barriers to rotation about the N-S bond. This is certainly not the case with the related compound $(Et_2N)_2SO_2$, the spectum of which remains unchanged down to -90° (112).

The ^{1}H n.m.r. of the sulphinamide compounds.

The ^{1}H n.m.r. data obtained at 33° for the sulphinamide derivatives in this work are shown in Table 15. The ^{1}H spectra show that replacing a halogen atom in the sulphinyl halides, $R_2NS(O)X$ (R = Me, Et; X = F, Cl), by a dialkylamino group or an alkoxy group, shifts the ^{1}H signals of the original dialkylamino group to higher field. A larger shift is observed with a dialkylamino group than an alkoxy group. This would be expected on the basis of greater shielding of the protons where less electronegative groups are attached to sulphur. However, for a given dialkylamino group, the ^{1}H shifts for the chlorides are to low field of those observed for the fluorides. A similar trend is observed in the ^{1}H signals of some dimethylaminophosphorus halides, $X_{3-n}P(Y)(NMe_2)_n$ (X = F, Cl; Y = nothing or O; n = 1,2), although the trend does not hold where carbon is bonded to phosphorus (113).

Table 15.

${}^1H$ n.m.r. spectra of the dialkylaminosulphinamides at 33°.

Compound	δCH_3*	δCH_2	J_{H-H}	Comments
$Me_2NS(O)F$	-2.77d			${}^4J_{H-C-N-S-F}$ = 3.6 Hz.
$Et_2NS(O)F$	-1.16t	-3.33(a)	7.0 Hz.	${}^4J_{H-C-N-S-F}$ = 4.5 Hz.
$Me_2NS(O)Cl$	-2.83s			
$Et_2NS(O)Cl$	-1.30t	-3.40q	7.4 Hz.	
$i\text{-}Pr_2NS(O)Cl$	-1.44d	-4.09 methine septet	6.0 Hz.	
$Me_2NS(O)OMe$	-2.64s $N\underline{CH_3}$ -3.46s $O\underline{CH_3}$			
$Et_2NS(O)OMe$	-1.10t $NCH_2\underline{CH_3}$ -3.37s $O\underline{CH_3}$	-3.16(a) $N\underline{CH_2}CH_3$	7.1 Hz.	
$Me_2NS(O)OEt$	-2.60s $N\underline{CH_3}$ -1.22t $OCH_2\underline{CH_3}$	-3.80(b) $O\underline{CH_2}CH_3$	7.2 Hz.	$\Delta^{\dagger}$ = 3.2 Hz. at 33°; = 3.0 Hz. at 50°; (and 1.9 Hz. at 150° in PhCl.
$Et_2NS(O)OEt$	-1.11t $NCH_2\underline{CH_3}$ -1.19t $OCH_2\underline{CH_3}$	-3.13(a) $N\underline{CH_2}CH_3$ -3.75(b) $O\underline{CH_2}CH_3$	7.2 Hz. 7.0 Hz.	$\Delta^{\dagger}$ = 2.0 Hz. at 33°; = 2.1 Hz. at 50° and (0.5 Hz. at 150° in PhCl.
$Me_2NS(O)NMe_2$	-2.52s			
$Me_2NS(O)NEt_2$	-1.06t $NCH_2\underline{CH_3}$ -2.47s $N\underline{CH_3}$	-3.05q $N\underline{CH_2}CH_3$	7.5 Hz.	
$Et_2NS(O)NEt_2$	-0.86t	-2.80q	7.0 Hz.	

All measurements were made on neat samples except where indicated.

* From internal t.m.s. $(CH_3)_4Si$.

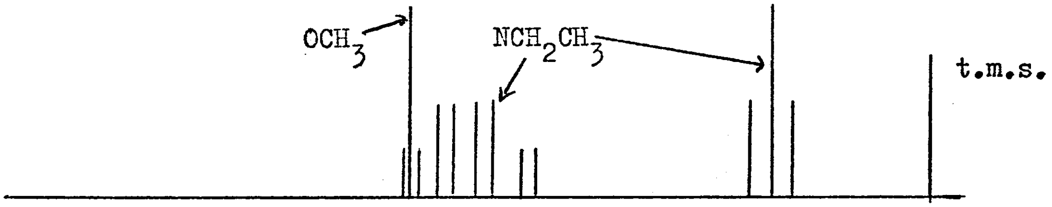
Table 15, continued:

(a) Two overlapping quartets.

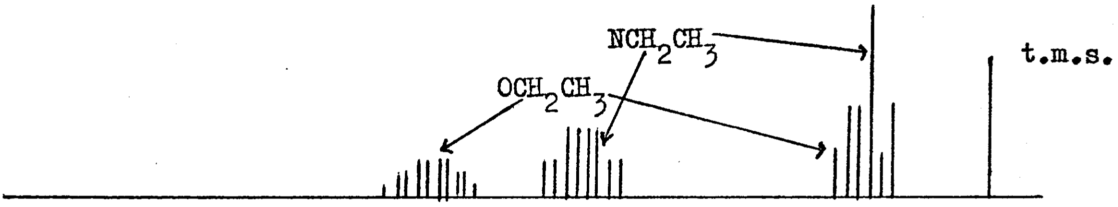
(b) Two overlapping quartets plus outer lines.

= chemical shift between non-equivalent methylene protons at 60 M.Hz..

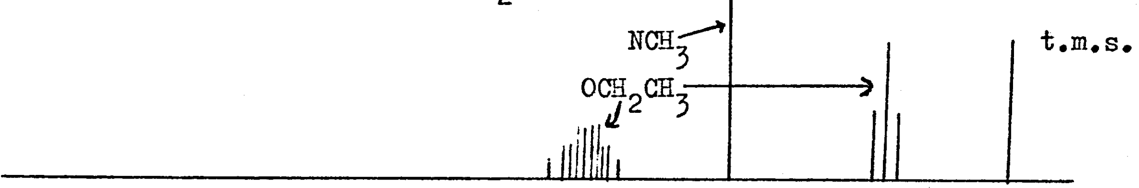
The ^1H spectra of the non-halogen containing derivatives $R_2NS(O)OR'$ (R = Me, R' = Et; R = Et, R' = Me; R = R' = Et), show methylene signals appearing as overlapping quartets. In the ethoxy derivatives, $R_2NS(O)OEt$ (R = Me, Et), these quartets are accompanied by much less intense outer lines, suggesting that AB spin-spin coupling is operative for the methylene protons.



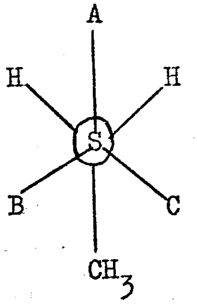
^1H n.m.r. of $Et_2NS(O)OMe$.



^1H n.m.r. of $Et_2NS(O)OEt$.



^1H n.m.r. of $Me_2NS(O)OEt$.



○ = carbon atom in $R_2NS(O)O\underline{C}H_2CH_3$

Figure IX

From Figure IX it can be seen that no matter how fast rotation will be about all bonds, the methylene protons will always be diastereotopic and thereby non-equivalent in the ^1H n.m.r. giving AB type spectra. The magnitude of the chemical shift difference between the overlapping quartets, Δ, is solvent dependent and in the case of the two derivatives $R_2NS(O)OEt$ (R = Me, Et) decreases slightly on raising the temperature.

Magnetic non-equivalence for the dialkylaminosulphinylhalides $R_2NS(O)X$ (R = Me, Et; X = F, Cl) was observed within the range -100° to 0° in both carbon disulphide and trichlorofluoromethane. See Table 16. Exchange broadening is markedly temperature dependent and coalescence signals were observed for the chlorides in the range -30° to -50°, whilst the coalescence temperatures of the fluorides were nearer -100°.

Table 16.

Variable temperature spectra of some dialkylaminosulphur compounds.

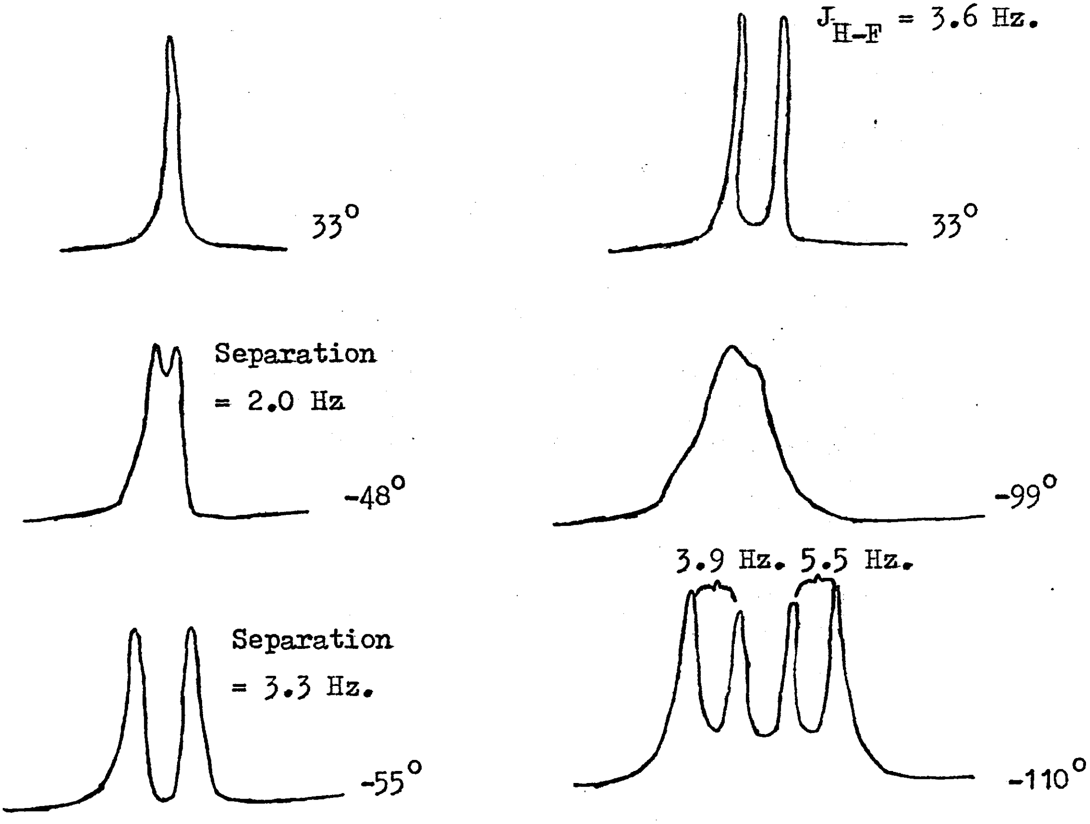
Compound	Coalescence *Temp.(±2°)	Limiting Shift Hz.	Comments
$Me_2NS(O)F$	-99°	7.5	$^4J_{H-C-N-N-S-F}$ = 4.7 Hz at 33° and 3.9 and 5.5 Hz. at -105°.
$Me_2NS(O)Cl$	-48°	3.3	$\Delta G^{\ddagger}$ = -11.4 k.cals./mole.
$Et_2NS(O)F$	~ -110°	†	Coalescence of CH_2 signals. -103° for CH_3 signals.
$Et_2NS(O)Cl$	-33°	5.2 CH_3 7.0 CH_2	Coalescence of CH_2 signals. -39° for CH_3 signals. No AB coupling of CH_2 signal at -80°.
$i-Pr_2NS(O)Cl$	-33°	2.5 CH_3	Two doublets at -75°.
$Me_2NS(O)NMe_2$	<-100°		No signs of broadening.
$Me_2NS(O)Me$	<-60°	-	(111) $CDCl_3$ solution.
$Me_2NS(O)CCl_3$	-46°	-	(110) CS_2 solution.
Et_2NSO_2Cl	-43°	-	(112) $\Delta G^{\ddagger}$ = 11.4 k.cals./mole.
$Et_2NSO_2NEt_2$	<-90°	-	(112) No signs of broadening.

*Spectra ran as CCl_3F solutions at 60 M.Hz.. The use of CS_2 solutions made little or no difference to the coalescence temperatures.

† Beyond range using CCl_3F as solvent.

Only the spectrum of $Me_2NS(O)Cl$ is unambiguous, there being no complications arising from homo or heteronuclear spin coupling as shown in the other spectra. The free energy of activation for conformational interchange can therefore be calculated readily. In the case of $Me_2NS(O)F$, stereospecific spin-spin coupling was well resolved at -100°. See Figure X.

Variable temperature spectrum of $Me_2NS(O)X$ (X = F, Cl).



^1H n.m.r. spectrum of $Me_2NS(O)Cl$

^1H n.m.r. spectrum of $Me_2NS(O)F$

Figure X.

Calculation of free energy of activation for $Me_2NS(O)Cl$;

$$k_c = \; / 2 \,.\, \Delta\nu AB$$

$\Delta\nu$ = 2.0 Hz. at the coalescence temperature.

$$\therefore k_c = 4.44 \text{ sec}^{-1}$$

$$k_c = \frac{T_c K}{h} \,.\, e^{-\Delta G^{\ddagger}/RT_c}$$

K = Bolzmann's constant = $1.3805 \,.\, 10^{-16}$ ergs $^{o}K^{-1}$

h = Planck's constant = $6.6256 \,.\, 10^{-27}$ ergs sec^{-1}

T_c = coalescence temperature
= $-48^{o}C = 225^{o}K$

$$\therefore e^{-\Delta G^{\ddagger}/450} = 4.44 \,.\, 1/46.9 \,.\, 10^{11}$$

$$.\Delta G^{\ddagger} = 11.4 \text{ k.cals./mole}$$

The ^1H n.m.r. of $(Me_2N)_2SO$ shows no signs of broadening of the methyl signals even at -100^{o}, while $Me_2NS(O)Cl$ shows non-equivalence at -48^{o}. This follows the trend observed for $Me_2NS(O)Me$ and $Me_2NS(O)CCl_3$, and Et_2NSO_2Cl and $(Et_2N)_2SO_2$, where an electronegative group at sulphur is necessary before exchange broadening becomes evident. However, the fluorosulphinamides show non-equivalence at much lower temperatures than the chlorosulphinamides, although exchange broadening begins to appear at -80^{o}.

The free energy of activation is shown in Table 16 for the rate process involved in the coalescence of the n.m.r. signals of $Me_2NS(O)Cl$. Because of complications for the other compounds in determining the exact $\Delta G^{\ddagger}$ values arising from spin-coupling, only T_c (coalescence temperature) will be used as a comparison, being directly related to the free energy of activation.

As has been discussed, the appearance of non-equivalence in the n.m.r. signals for the dialkylaminosulphur compounds may arise from slow rotation about the N-S bond or by inversion at nitrogen. Pyramidal inversion barriers at sulphur are far too high to be considered as a possibility, being in the range of 35-42 k.cals./mole for the diaryl sulphoxides (114). The pyramidal stability of sulphur in the non-halogen containing derivatives is very high as magnetic non-equivalence of the methylene proton signals for $R_2NS(O)\underline{CH_2}CH_3$ (R = Me, Et) persists even at 150°. The reasons for the absence of non-equivalence in the methylene protons of $Et_2NS(O)X$ (X = F, Cl) and the methyl proton signals of $i\text{-}Pr_2NS(O)Cl$ at ambient temperature, however, are not clear. It is possible that the chemical shift differences are too small to be observed.

For the chlorosulphinamides, raising the size of the substituents at nitrogen raises the coalescence temperature, which is not a characteristic associated with nitrogen inversion. However, despite the coalescence temperatures (Me, -48°; Et, -39°; i-Pr, -33°) being in the order expected for the rate process to be associated with a rotational barrier, it is not certain that the small differences can be taken to infer an increasing activation energy for the rate process in the series Me $<$ Et $<$ i-Pr.

The lower barriers observed for the fluorosulphinamides could possibly indicate that steric size is also important over and above electronegativity factors. Competitive back-bonding in the order $Cl \leqslant CCl_3 < F < O < N \leqslant CH_3$ may play a considerable part in determining the magnitude of the barriers. Donation of electron density into the N-S bond will make the 3d sulphur orbitals more diffuse and so make double bonding less effective, easing rotation about the N-S bond.

EXPERIMENTAL.

Thionyl fluoride was obtained by the method of Tullock and Coffman (27) by the metathetical reaction of thionyl chloride with sodium fluoride in a slurry of acetonitrile. It was purified in the vacuum line by passing through a trap at -76° to remove SO_2.

$(MeO)_2SO$, $(EtO)_2SO$ and $P(NMe_2)_3$ were obtained from Aldrich Chemical Co., Me_3SiNEt_2 from Alfa Inorganics, Me_3SiCl from Midland Silicones and $SOCl_2$ and NaF from B.D.H.. The remaining compounds were made by standard literature methods and were stored over activated 4A molecular sieves until required. $(Ph_2P)_2NMe$ was kindly donated by Dr. Keat.

Compound	Method	Reference
$(PhO)_2SO$	$SOCl_2/PhOH$	(115)
Me_3SiOMe	$Me_3SiCl/MeOH$	(116)
Me_3SiOEt	$Me_3SiCl/EtOH$	(116)
Me_3SiOPh	$Me_3SiCl/PhOH$	(117)
$(Me_3Si)_2NMe$	$Me_3SiCl/MeNH_2$	(118)
$Me_3SiNMeP(O)Cl_2$	$(Me_3Si)_2NMe/P(O)Cl_3$	(119)
Me_3SiNMe_2	Me_3SiCl/Me_2NH	(120)

In general the least volatile substance was placed in the reaction vessel via the dry-box, or vacuum line if sufficiently volatile. Thionyl fluoride was then added in the required stoichiometry via the vacuum line.

To avoid excessive repetition, SOF_2 was identified by i.r. (49), and Me_3SiF by i.r. (121) and n.m.r. (122).

A. Reactions of SOF_2 with silicon oxygen compounds.

1. SOF_2/Me_3SiOMe.

SOF_2 (10.5 m.moles) and Me_3SiOMe (9.4 m.moles) were condensed together at -196° and allowed to stand at room temperature for 3 hours. Fractionation revealed that no reaction had taken place. The reactants were recondensed and heated to 90° for 12 hours. Fractionation through traps at -76°, -96° and -196° gave $(MeO)_2SO$ in the -76° trap, MeOS(O)F in the -96° trap and Me_3SiF and unreacted SOF_2 in the -196° trap. $(MeO)_2SO$ was identified by comparison with an authentic sample using i.r., n.m.r. and molecular weight: M.Wt.; Found, 110 (mass spec.). Calculated, 110.

MeOS(O)F was identified by i.r. and n.m.r. (44), and molecular weight. Found, 98 (mass spec.). Calculated, 98.

i.r. cm^{-1}. 2960 m, 1460 w, 1268 s, 985 vs, 752 s, 700 vs.

n.m.r.. $\delta F = -55.6q$; $\delta CH_3 = -3.85d$; $J_{H-F} = 1.3$ Hz.

2. SOF_2/Me_3SiOEt.

SOF_2 (11.1 m.moles) and Me_3SiOEt (10.4 m.moles) were heated together for 17 hours at 110°. Fractionation through traps at -76°, -96° and -196° separated unreacted Me_3SiOEt at -76° (approx. 5 m.moles), EtOS(O)F at -96°, and Me_3SiF and unreacted

SOF_2 at -196°. $(EtO)_2SO$ remained in the reaction vessel and was identified by comparison with an authentic sample by i.r. and n.m.r.. EtOS(O)F was identified by i.r. and n.m.r..

i.r. cm^{-1}. 2985 m, 1450 w, 1267 s, 1028 vs, 917 s, 735 sh, 699 s.

n.m.r.. $\delta F = -59.8t$; $\delta CH_3 = -1.35t$; δCH_2 (two overlapping quartets) $= -4.35$; $J_{H-F} = 1.3$ Hz.

3. $MeOS(O)F/Me_3SiOMe$.

MeOS(O)F (8.4 m.moles) and Me_3SiOMe (8.0m.moles) were condensed together at -196° and reacted vigorously well below room temperature. Fractionation through traps at -76° and -196° separated $(MeO)_2SO$ in the -76° trap and Me_3SiF in the -196° trap, both identified by i.r. and n.m.r..

4. SOF_2/Me_3SiOPh.

SOF_2 (12.4m.moles) and Me_3SiOPh (10.5 m.moles) were heated together for three days at 145°. No reaction took place.

B. Reactions of SOF_2 with sulphite esters.

5. $SOF_2/(MeO)_2SO$.

SOF_2 (11.5 m.moles) and $(MeO)_2SO$ (10.5 m.moles) were heated together at 120° for 17 hours. Fractionation through traps at -76°, -96° and -196° separated SO_2, identified by i.r. (123), and unreacted $(MeO)_2SO$, identified by i.r. by comparison with an authentic sample, in the -76°trap, MeOS(O)F, identified by i.r. and n.m.r. (44), in the -96° trap and SOF_2 and CH_3F, identified by n.m.r. (124), in the -196° trap. The yield of MeOS(O)F was about 10 % . For CH_3F $\delta CH_3 = -4.13$; $J_{H-F} = 48.0$ Hz.

6. $SOF_2/(EtO)_2SO$.

SOF_2 (10.4 m.moles) and $(EtO)_2SO$ (9.3 m.moles) were heated together at 125° for 17 hours. Fractionation through traps at -76°, -96° and -196° separated SO_2 in the -76° trap, EtOS(O)F in the -96° trap, identified by i.r. and n.m.r. (44), and unreacted SOF_2 and a small amount of CH_3CH_2F, identified by n.m.r. (124) , in the -196° trap. Unreacted $(EtO)_2SO$ remained in the reaction vessel. For CH_3CH_2F, $\delta CH_3 = -1.21$; $\delta CH_2 = -4.32$; $J_{H-F} = 25.3$ Hz.

7. $SOF_2/(PhO)_2SO$.

SOF_2 (10.6 m.moles) and $(PhO)_2SO$ (9.6 m.moles) were heated together at 130° for 14 hours. Fractionation through traps at -76° and -196° separated C_6H_5F, identified by i.r. (125) and n.m.r. (124), and SO_2 in the -76° trap and unreacted SOF_2 in the -196° trap. An involatile fraction remaining in the flask was shown to contain mostly $C_6H_5OS(O)F$, identified by i.r. and n.m.r. (46).

C_6H_5F. n.m.r.: $\delta F = +114$; $C_6H_5OS(O)F$. n.m.r.: $\delta F = -62.5s$; $\delta H = -6.9$ (complex multiplet)

C. Reactions of SOF_2 with Si-N, N-H and P-N compounds.

8. SOF_2/Me_3SiNMe_2.

SOF_2 (11.2 m.moles) and Me_3SiNMe_2 (10.0 m.moles) reacted vigorously well below room temperature. Fractionation through traps at -65° and -196° gave dimethylaminofluorosulphinamide, $Me_2NS(O)F$ (8.0m.moles) in the -65° trap and Me_3SiF (8.9 m.moles) in the -196° trap. A small amount of brown solid was left in the reaction vessel.

Analysis for $Me_2NS(O)F$: Found. C, 21.4; H, 5.6; F, 17.4; N, 12.6; S, 28.8. Calculated. C, 21.6; H, 5.4; F, 17.1; N, 12.6; S, 28.6.

The vapour pressure at 20° is 6 mm Hg.

Infrared cm^{-1} (gas). 2935 m, 2890 w, 1450 w, 1230 vs, 1065 vs, 935 s, 841 s, 629 s.

n.m.r.: $\delta F = -38.5$bs; $\delta CH_3 = -2.77$d; $J_{H-F} = 4.7$ Hz.

9. SOF_2/Me_3SiNEt_2.

SOF_2 (10.8 m.moles) and Me_3SiNEt_2 (9.5 m.moles) reacted vigorously well below room temperature. $Et_2NS(O)F$ (9.1 m.moles) was trapped at -65° and Me_3SiF (9.3 m.moles) was trapped at -196°. A small amount of brown solid was left in the flask.

Diethylaminofluorosulphinamide, $Et_2NS(O)F$ has no observable vapour pressure at room temperature but moves slowly in vacuo.

Analysis for $Et_2NS(O)F$: Found. C, 33.6; H, 7.0; F, 13.6; N, 9.7; S, 22.6. Calculated: C, 34.5; H, 7.2; F, 13.7; N, 10.1; S, 23.0.

Infrared cm^{-1} (gas). 2995 m, 2900 w, 1450 w, 1229 vs, 1064 m, 935 s, 840 w, 627 s.

n.m.r.: $\delta F = -55.3$ quintet; $\delta CH_3 = -1.16$t; $\delta CH_2 = -3.33$ two overlapping quartets; $J_{H-F} = 4.5$ Hz.

10. $SOF_2/2Me_3SiNMe_2$.

SOF_2 (10.0 m.moles) and Me_3SiNMe_2 (22.2 m.moles) were shaken together for 24 hours at room temperature. Unreacted Me_3SiNMe_2, identified by i.r. by comparison with an authentic sample, and SO_2 (trace) were trapped at -76° and Me_3SiF (21.3 m.moles) was trapped at -196°. $(Me_2N)_2SO$ (9.4 m.moles) was recovered as a colourless solid which melts not much above room temperature. A small amount of brown solid was left in the reaction vessel.

Analysis for $(Me_2N)_2SO$: Found. C, 35.5; H, 9.0; N, 20.6.
Calculated. C, 35.3; H, 8.8; N, 20.6.

Infrared cm^{-1} (gas). 2953 m, 2880 m, 2835 sh, 2794 w, 1250 m, 1198 s, 1167 m, 1117 vs, 1053 m, 930 s, 907 vs, 731 s, 650 s, 638 m.

n.m.r.: δCH_3 = -2.52s.

11. $SOF_2/2Me_3SiNEt_2$.

SOF_2 (8.3 m.moles) and Me_3SiNEt_2 (17.5 m.moles) were shaken together for 24 hours at room temperature. Unreacted Me_3SiNEt_2, identified by i.r. by comparison with an authentic sample, was trapped at -76° and Me_3SiF (16.1 m.moles) was trapped at -196°. $(Et_2N)_2SO$ (7.4 m.moles) was left in the reaction vessel as a colourless liquid which moved slowly in vacuo at room temperature.

Analysis for $(Et_2N)_2SO$: Found. C, 50.2; H, 10.6; N, 14.4; S, 16.6.
Calculated. C, 50.0; H, 10.4; N, 14.6; S, 16.7.

Infrared cm^{-1} CCl_4 solution. 2934 m, 2872 m, 1460 s, 1342 w, 1291 m, 1210 m, 1187 s, 1112 vs, 1065 w, 1000 s, 924 m, 894 s, 876 vs, 652 s, 600 m, 561 w.

n.m.r.: δCH_3 = -0.86t; δCH_2 = -2.80q; J_{H-H} = 7.0 Hz.

12. $SOF_2/(Me_3Si)_2NMe$.

SOF_2 (10.4 m.moles) and $(Me_3Si)_2NMe$ (10.1 m.moles) were shaken together at room temperature for 2 hours during which slow and continuous effervescence occurred. Fractionation through traps at -96°, -126° and -196° separated MeNSO (8.4 m.moles) in the -96° trap, Me_3SiF (17.1 m.moles) in the -126° trap, and unreacted SOF_2 in the -196° trap. Intractable solids were left in the reaction vessel.

MeNSO was identified by i.r. (126), n.m.r. (127) and molecular weight.

n.m.r.: δ CH_3 = -3.51.

M.Wt.: Found, 76.4 (manometrically); 77 (mass spec.). Calculated, 77.

13. $SOF_2/2Me_2NH$.

SOF_2 (14.0 m.moles) and Me_2NH (28.4 m.moles) reacted vigorously at -76°. The reactants were allowed to reach room temperature slowly when colourless solids dissolved to give a brown solution. From this solution $Me_2NS(O)F$ (8.4 m.moles) was extracted, identified by i.r. and n.m.r.. A large amount of brown liquid was left in the reaction vessel which consisted presumably mostly of MeNH.HF.

14. $SOF_2/P(NMe_2)_3$ reacted vigorously well below room temperature. $Me_2NS(O)F$ (3.2 m.moles) was recovered as the only volatile material, and was identified by i.r., n.m.r. and molecular weight. Found, 111 (mass spec.). Calculated, 111.

No volatile P-F compounds were identified and n.m.r. of the solids in acetonitrile showed that a complex mixture was present.

n.m.r. of solids: $F = +73.2d$; $J_{P-F} = 715.5$ Hz. $H = -1.83, -2.32, -2.39, -2.52, -2.57, -2.61, -2.75, -2.78$.

Unidentified solid from reaction of PF_5 and $MeP(NMe_2)_2$ gave a similar ^{19}F n.m.r. spectrum (57). $F = 73.5$; $J_{P-F} = 711.0$ Hz..

15. $SOF_2/(Ph_2P)_2NMe$.

SOF_2 (10.4 m.moles) and $(Ph_2P)_2NMe$ (8.5 m.moles) were heated together for 14 hours at 110°. The volatiles were passed through traps at -96° and -196° to give MeNSO, identified by i.r. (126) and n.m.r. (127), trapped at -96° and unreacted SOF_2 (7.4 m.moles) in the -196° trap. Dark brown solids were left in the reaction flask. n.m.r. failed to reveal the presence of Ph_2PF.

16. $SOF_2/Me_3SiNMeP(O)Cl_2$.

SOF_2 (12.4 m.moles) and $Me_3SiNMeP(O)Cl_2$ (11.4 m.moles) were heated together for 7 hours at 80°. Fractionation through traps at -126° and -196° separated Me_3SiF (10.4 m.moles) in the -126° trap and unreacted SOF_2 in the -196° trap. A small amount of an involatile oil was pumped off under dynamic vacuum over two hours to leave a slightly brown-coloured solid which was identified as thionyl bis(dichlorophosphinylmethylamine), $(Cl_2P(O)NMe)_2SO$, and was purified by recrystallisation from boiling ether under nitrogen. The reaction occurs more slowly at room temperature over a period of three days.

Equimolar quantiities of $SOCl_2$ and $Me_3SiNMeP(O)Cl_2$ shaken together for 12 hours at room temperature produced Me_3SiCl, identified by i.r. (128) and n.m.r. (122), and $(Cl_2P(O)NMe)_2SO$ in high yield without further purification.

Analysis for $(Cl_2P(O)NMe)_2SO$: Found. C, 7.2; H, 2.2; Cl, 41.5; N, 8.2; P, 18.2; S, 9.2. Calculated. C, 7.0; H, 1.8; Cl, 41.6; N, 8.2; P, 18.1; S, 9.4.

Infrared cm^{-1}	2949 m, 2935 w, 1539 m, 1450 w, 1297 vs, 1204 s,
CCl_4 solution.	1174 m, 1085 s, 968 m, 915m, 782 vs, 757 vs,
	630 m, 593 s, 584 s, 550 s.

n.m.r.: δCH_3 = 2.57d; δP^* = -7.7q; J_{H-P} = 14.7 Hz..

* in p.p.m. from H_3PO_4, external.

D. Reactions of fluorosulphinamides with Si-O and Si-N compounds.

17. $Me_2NS(O)F/Me_3SiOMe$.

$Me_2NS(O)F$ and Me_3SiOMe in equimolar quantities did not react to completion at room temperature and heating to 80° for 6 hours was required for complete reaction to give Me_3SiF and $Me_2NS(O)OMe$. The latter is a colourless liquid which moves slowly in vacuo.

Analysis for $Me_2NS(O)OMe$: Found. C, 29.5; H, 7.2; N, 11.5; S, 26.0.
Calculated. C, 29.3; H, 7.3; N, 11.4; S, 26.0.

n.m.r.: $\delta N\underline{CH_3}$ = -2.64s; $\delta O\underline{CH_3}$ = -3.46s.

Infrared cm^{-1}	2982 s, 2959 s, 2910 sh, 2828 s, 2779 s, 1464 w,
CCl_4 solution.	1455 m, 1259 w, 1199 m, 1165 vs, 1115 m, 1057 w,
	999 s, 978 s, 930 vs, 702 m, 675 w, 643 vs, 592 w.

18. $Me_2NS(O)F/Me_3SiOEt$.

$Me_2NS(O)F$ and Me_3SiOEt, in equimolar quantities were heated together for 6 hours at 80° to give Me_3SiF and $Me_2NS(O)OEt$, a colourless involatile liquid which moves slowly in vacuo.

Analysis for $Me_2NS(O)OEt$: Found. C, 35.3; H, 8.2; N, 10.3; S, 23.6.
Calculated. C, 35.1; H, 8.0; N, 10.2; S, 23.4.

n.m.r.: $\delta N\underline{CH_3}$ = -2.60s; $\delta OCH_2\underline{CH_3}$ = -1.22t and $\delta O\underline{CH_2}CH_3$ = -3.80 two overlapping quartets and outer lines. J_{H-H} = 7.2 Hz..

Infrared cm^{-1} 2982 s, 2960 sh, 2825 s, 1473 w, 1453 m, 1256 w,
CCl_4 solution. 1194 m, 1164 vs, 1110 m, 1054 m, 1023 s, 932 s,
881 s, 716 w, 659 s, 613 w, 588 m.

19. $Et_2NS(O)F/Me_3SiOMe$.

$Et_2NS(O)F$ and Me_3SiOMe, in equimolar quantities, were heated together for 6 hours at 80° to give Me_3SiF and $Et_2NS(O)OMe$, a colourless involatile liquid which moves slowly in vacuo.

Analysis for $Et_2NS(O)OMe$: Found. C, 39.7; H, 8.7; N, 9.5; S, 21.0.
Calculated. C, 39.7; H, 8.6; N, 9.3, S, 21.2.

n.m.r. $\delta NCH_2\underline{CH_3}$ = -1.10t; $\delta O\underline{CH_3}$ = -3.37s; $\delta N\underline{CH_2}CH_3$ -3.16 two overlapping quartets. J_{H-H} = 7.1 Hz..

Infrared cm^{-1} 2978 s, 2940 sh, 2872 sh, 2829 s, 2779 s, 1480 w,
CCl_4 solution. 1462 m, 1381 m, 1293 w, 1193 vs, 1156 vs, 1110 m,
1060 m, 990 s, 977 s, 931 m, 908 s, 642 s, 588 w.

20. $Et_2NS(O)F/Me_3SiOEt$.

$Et_2NS(O)F$ and Me_3SiOEt, in equimolar quantities, were heated together for 6 hours at 80° to give Me_3SiF and $Et_2NS(O)OEt$, a colourless involatile liquid which moves slowly in vacuo.

Analysis for $Et_2NS(O)OEt$: Found. C, 43.7; H, 9.2; N, 8.6; S, 19.5.

Calculated. C, 43.7; H, 9.1; N, 8.5; S, 19.4.

n.m.r.: $\delta\ NCH_2\underline{CH_3}$ =-1.11t; $\delta\ OCH_2\underline{CH_3}$ = -1.19t; $\delta\ N\underline{CH_2}CH_3$ = -3.13 two overlapping quartets, J_{H-H} = 7.2 Hz; $\delta\ O\underline{CH_2}CH_3$ = -3.75 two overlapping quartets and outer lines, J_{H-H} = 7.0 Hz..

Infrared cm^{-1} 2978 s, 2939 sh, 2822 s, 2777 m, 1479 w, 1463 m,
CCl_4 solution. 1381 m, 1292 w, 1192 s, 1155 vs, 1110 sh, 1061 w,
1025 w, 10004 m, 932 w, 908 w, 879 s, 702 w, 659 s,
613 w, 590 w.

21. $Me_2NS(O)F/Me_3SiNEt_2$.

$Me_2NS(O)F$ and Me_3SiNEt_2 in equimolar quantities, were shaken together for 12 hours to give Me_3SiF and $Me_2NS(O)NEt_2$ along with a small amount of $(Me_2N)_2SO$. See 22 for data on $Me_2NS(O)NEt_2$

22. $Et_2NS(O)F/Me_3SiNMe_2$.

$Et_2NS(O)F$ and Me_3SiNMe_2, in equimolar quantities were shaken together for 12 hours at room temperature to give Me_3SiF and $Me_2NS(O)NEt_2$ along with a small amount of $(Me_2N)_2SO$, identified by n.m.r.. $Me_2NS(O)NEt_2$ is a colourless involatile liquid which decomposes to a black mass on standing. The analytical data for the compound obtained from Reactions 21 and 22 are given, but are not satisfactory.

Analysis from 21 for $Me_2NS(O)NEt_2$: C, 45.7; H, 9.9; N, 16.4; S, 18.6.

Analysis from 22 for $Me_2NS(O)NEt_2$: C, 42.1; H, 9.2; N, 14.9; S, 22.5.

Calculated: C, 43.9; H, 9.8; N, 17.1; S, 19.7.

n.m.r.: $NCH_2\underline{CH_3}$ = -1.06t; $N\underline{CH_3}$ = -2.47s; $N\underline{CH_2}CH_3$ = - 3.05; J_{H-H} = 7.5Hz.

Infrared cm^{-1} 2973 s, 2868 s, 2827 m, 2779 m, 1454 m, 1377 w,
CCl_4 solution. 1188 m, 1165 m, 1118 vs, 1050 m, 1108 w, 922 sh,
907 s, 649 m, 588 w.

E. Reactions of thionyl chloride with N-H and Si-N compounds.

23. $SOCl_2/2Me_2NH$.

$SOCl_2$ (13.0 m.moles) and Me_2NH (24.5 m.moles) were allowed to stand at -10° for 1 hour after a vigorous reaction had taken place well below that temperature. The volatiles were pumped off to give brown-coloured solids from which was recovered $Me_2NS(O)Cl$ as a colourless involatile liquid which moves slowly in vacuo.

Analysis for $Me_2NS(O)Cl$: Found. C, 18.9; H, 4.6; N, 11.1; S, 24.9.
Calculated. C, 18.8; H, 4.7; N, 11.0; S, 25.0.

n.m.r.: $\delta\, CH_3 = -2.83$s.

Infrared cm^{-1} 2976 s, 2928 s, 2880 sh, 2842 sh, 2794 m, 1452 m,
CCl_4 solution. 1405 w, 1342 w, 1262 m, 1199 vs, 1138 w, 1054 m,
1008 m, 938 s, 691 s, 519 m, 417 s.

24. $SOCl_2/2Et_2NH$

$SOCl_2$ (13.0 m.moles) and Et_2NH (24.8 m.moles) were allowed to stand at -10° for 1 hour after a vigorous reaction had taken place well below that temperature. The volatiles were pumped off to leave brown coloured solids from which was recovered $Et_2NS(O)Cl$ as a colourless involatile liquid which moved slowly in vacuo.

Analysis for $Et_2NS(O)Cl$: Found. C, 30.7; H, 6.3; N, 20.4; S, 9.2.

Calculated. C, 30.9; H, 6.4; N, 20.6; S, 9.0.

n.m.r.: $NCH_2\underline{CH_3}$ = -1.30t; $N\underline{CH_2}CH_3$ = -3.40q.

Infrared cm^{-1} CCl_4 solution. 2997 s, 2944 m, 2878 w, 2823 w, 2779 w, 1462 m, 1455 m, 1385 m, 1369 w, 1342 w, 1291 m, 1237 m, 1198 vs, 1004 m, 926 s, 684 m, 671 m, 538 w.

25. $SOCl_2$/2i-Pr_2NH.

i-Pr_2NH (96 m.moles) was added dropwise with stirring to a solution of $SOCl_2$ in diethyl ether (100 mls) at -76° in an atmosphere of dry nitrogen over a period of 40 minutes. A vigorous reaction took place and solids which formed were filtered off at room temperature. The volatile material was pumped off to give i-$Pr_2NS(O)Cl$ (35 m.moles) as a colourless solid which melts not much above room temperature.

Analysis for i-$Pr_2NS(O)Cl$: Found. C, 39.5; H, 7.4; N, 8.1; S, 16.9.

Calculated. C, 39.3; H, 7.6; N, 7.6; S, 17.4.

n.m.r.: CH_3 = -1.44d; CH = -4.09 methine septet; J_{H-H} = 6.0 Hz..

Infrared cm^{-1} CCl_4 solution. 3278 m, 2990 vs, 2885 s, 2710 s, 2543 m, 2495 s, 2415 m, 2095 m, 1602 m, 1588 m, 1399 s, 1357 m, 1312 m, 1261 w, 1204 m, 1193 s, 1153 s, 1105 s, 1092 m, 939 s, 842 m, 803 m, 721 w, 510 s.

26. $SOCl_2/Me_3SiNEt_2$.

$SOCl_2$ (10.3 m.moles) and Me_3SiNEt_2 (10.1 m.moles) reacted vigorously well below room temperature to give Me_3SiCl (9.7 m.moles), identified by i.r. (128) and n.m.r. (122), and

$Et_2NS(O)Cl$ (9.4 m.moles), identified by n.m.r.. A small amount of a coloured liquid remained in the reaction vessel which n.m.r. would indicate as being $(Et_2N)_2SO$.

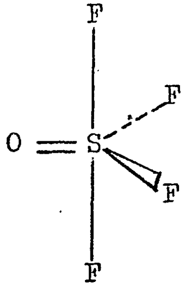
CHAPTER II

REACTIONS OF THIONYL TETRAFLUORIDE

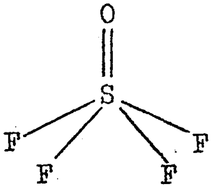
INTRODUCTION

Thionyl tetrafluoride, SOF_4, has been known since the beginning of the century (34), but it is only comparatively recently that the structure has been established. It is unusual in that it is the only pentacoordinated sulphur VI oxyfluoride. With the aid of Raman and infrared spectroscopy (35) and more recently from electron diffraction studies (129,130) it has been found to be trigonal bipyramidal.

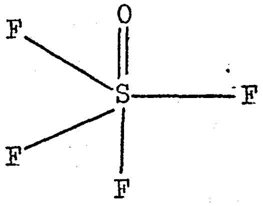
A molecule with the emperical formula F_4SO may adopt two possible structures, F_3SOF and F_4SO. For thionyl tetrafluoride the former structure may be ruled out, as on hydrolysis it decomposes to give SO_2F_2, a hexapositive sulphur compound, while F_3SOF has a formally tetrapositive sulphur atom. F_3SOF may also be excluded on the basis of the ^{19}F n.m.r. spectrum, as two widely separated signals, as given by SF_5OF (131), would be expected and only one signal is observed. Further, the infrared spectrum shows a very strong band at 1379 cm^{-1} (35) which is assigned to the S-O double bond stretching frequency, it being very unlikely that F_3SOF would show any bands as high as 1379 cm^{-1}. Thionyl tetrafluoride therefore does not have the hypofluorite structure. This does establish the structure absolutely, there still being three possibities for the emperical formula F_4SO.



C_{2V}



C_{4V}



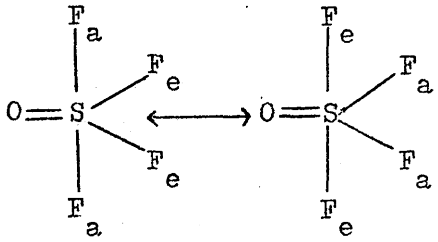
C_{3V}

Goggins, Roberts and Woodward (35) have made a detailed study of the Raman and infrared spectra of thionyl tetrafluoride and found that there were at least 11 Raman active fundamentals and at least 8 infrared active fundamentals, not having looked at lower frequencies in the infrared spectrum. They concluded that the structure was C_{2V} which requires 12 Raman active fundamentals and 11 infrared active fundamentals. The C_{3V} structure requires not more than 8 Raman or infrared active fundamentals and the C_{4V} structure requires only 9 Raman active and 6 infrared active fundamentals.

The ^{19}F n.m.r. spectrum would be expected to show evidence of the two types of fluorine bonded to sulphur, but only one signal is observed at room temperature (131). In this work, no change in the ^{19}F n.m.r. spectrum was observed as low as -115° while sulphur tetrafluoride shows two sets of triplets at -85° (18). It can only be assumed that either fast exchange, or pseudo-rotation as exhibited by IF_5 (132), is taking place.

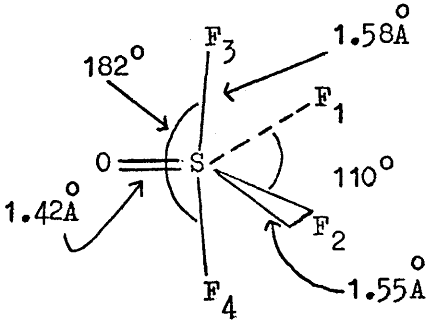
$SOF_4 \rightleftharpoons SOF_3^+ + F^-$

fast exchange



pseudo-rotation

An early electron diffraction study of thionyl tetrafluoride (129) showed that it had the expected trigonal bipyramidal form, with the oxygen atom and the two fluorine atoms in the equatorial plane and the two other fluorine atoms in the axial positions. What was not expected,however, was that the two axial fluorine atoms were distorted towards the oxygen atom, and the F_1SF_2 angle was greater than 120°. The data was later reexamined and refined (130) and gave the structure below.



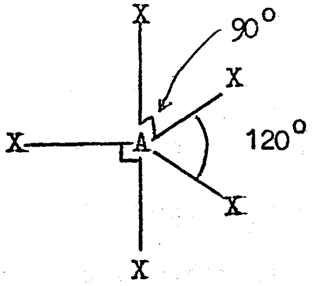
SOF_4, thionyl tetrafluoride.

It is a recurring feature for the trigonal bipyramidal structure that axial bonds are longer than equatorial bonds. See Table 17.

Table 17.

Compound	r_{eq} Å	r_{ax} Å	Reference
PF_5	1.53	1.58	(133)
SF_4	1.55	1.65	(17)
SOF_4	1.55	1.58	(130)

Before discussing the structure of SOF_4, attention must first be drawn to the AX_5 molecule of trigonal bipyramidal symmetry as described by Gillespie (134). All the rA-X distances are the same and the A-X bonds are simple electron pair bonds.



AX_5

Repulsions between electron pairs are negligible when there is not appreciable overlap of the electron pairs. This is the case when angles between bonding electron pairs are greater than or equal to 120°. When the angle between the bonding pairs are of the order of 90°, then repulsion forces increase appreciably. Thus for the simple AX_5 molecule with all the rA-X distances the same, only the repulsions between axial and equatorial electron pairs are of consequence. This being the case, each equatorial pair is interacting with two axial pairs at 90°, while each axial pair is interacting with three equatorial pairs at 90°. There would exist therefore a situation of unstable equilibrium in which repulsion forces were greater in the axial direction than the equatorial direction. This is suitably alleviated by elongation of the axial bond lengths as is observed with all such compounds.

For SOF_4 of C_{2V} symmetry with the oxygen atom in the equatorial plane, the trigonal bipyramid is further modified because of the presence of the doubly bonded oxygen atom. There are two electron pairs in the bond and so the orbital will be larger than a two electron single bond. This results in greater repulsion forces in both axial and equatorial directions. The equatorial fluorine atoms are pushed together and the axial fluorine atoms move away from the oxygen atom. A similar situation is found with SF_4 where non-bonded electrons on sulphur occupy a more diffuse orbital than bonded pairs of electrons resulting in the distorted trigonal bipyramid.

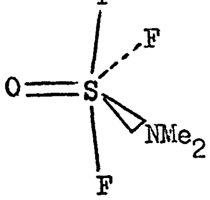
Reactions of thionyl tetrafluoride.

The chemistry of thionyl tetrafluoride has been little investigated, and it was not until 1968 that the first monosubstituted derivative of thionyl tetrafluoride was reported by Glemser (135). This was dimethylaminosulphur oxytrifluoride, made from the silicon amine and thionyl tetrafluoride in an autoclave.

$$SOF_4 + Me_3SiNMe_2 \longrightarrow Me_2NS(O)F_3 + Me_3SiF$$

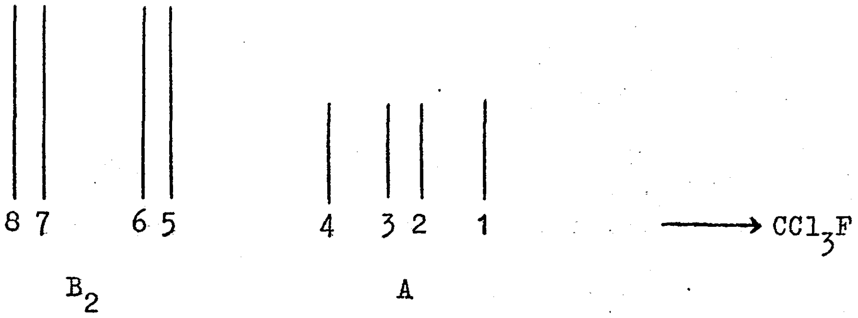
$Me_2NS(O)F_3$ is a colourless viscous liquid which hydrolyses in a moist atmosphere. The ^{19}F n.m.r. shows an AB_2 spectrum unlike Me_2NSF_3 which gives an AX_2 spectrum at low temperatures (20). Before discussing the ^{19}F n.m.r. spectrum of $Me_2NS(O)F_3$ it would be appropriate to discuss the structure.

In the trigonal bipyramidal SOF_4 molecule, the equatorial bonds are sp^2 in character whereas the axial bonds have more pd character. Small electronegative groups have smaller steric requirements, and since steric interactions are greater in the axial directions, the smaller groups will be found in axial positions. Bent's rules predict that atomic p character concentrates on those orbitals directed towards electronegative substituents and atomic s character in those towards more electropositive groups (136). For $Me_2NS(O)F_3$ with a trigonal bipyramidal form, the dimethylamino group is most likely to be found in the equatorial plane.



$Me_2NS(O)F_3$, dimethylaminosulphur oxytrifluoride.

The ^{19}F n.m.r. of $Me_2NS(O)F_3$ shows an AB_2 spectrum of eight lines with the signals of A at higher field with respect to CCl_3F.



^{19}F n.m.r. spectrum of $Me_2NS(O)F_3$.

The theoretical aspects of an AB_2 spectrum are discussed at length in the literature and only the essential features are given below (95,137).

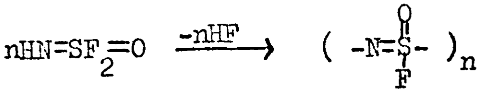
The chemical shift of the equatorial A fluorine atom is given by the position of line 3 relative to CCl_3F and the mean of lines 5 and 7 gives the chemical shift of the axial B_2 fluorine atoms. The coupling constant J_{FeFa} is given by :-

$$3J = (8 - 6) + (4 - 1)$$

Thionyl tetrafluoride reacts with ammonia to give iminosulphur oxydifluoride (138), the hydrogen fluoride evolved from the reaction being scavenged by sodium fluoride.

$$NH_3 + SOF_4 + 2NaF \longrightarrow HN{=}SF_2{=}O + 2Na^+HF_2^-$$

Further elimination of hydrogen fluoride by heating with caesium fluoride produces a rubbery polymer.



$$nHN{=}SF_2{=}O \xrightarrow{-nHF} (\ -N{=}\overset{\overset{O}{\|}}{\underset{\underset{F}{|}}{S}}-\ )_n$$

Methylamine reacts with thionyl tetrafluoride to produce methyliminosulphur oxydifluoride (86).

$$MeNH_2 + SOF_4 + 2NaF \longrightarrow MeNS(O)F_2 + 2Na^+HF_2^-$$

$MeNS(O)F_2$ is remarkably stable towards water and acid conditions, but is slowly hydrolysed by dilute alkali.

Glemser and Sundermeyer (56) have reported independently the reaction of thionyl tetrafluoride with tris(trimethylsilyl)amine to give trimethylsilyliminosulphur oxydifluoride.

$$(Me_3Si)_3N + SOF_4 \longrightarrow Me_3SiN{=}SF_2{=}O + 2Me_3SiF$$

This is one of the few cases in which an Si-N bond and an element halogen bond are resident as immediate neighbours in the same molecule and do not interact with each other either inter- or intramolecularly.

Well after the completion of the work for this thesis, Glemser reported the isolation of the second monosubstituted derivative of thionyl tetrafluoride, $PhOS(O)F_3$ (139).

$$SOF_4 + Me_3SiOPh \longrightarrow PhOS(O)F_3 + Me_3SiF$$

The work in this chapter is concerned with the reactions of thionyl tetrafluoride with silicon oxygen and silicon sulphur compounds, with a view to stepwise substitution of the fluorine atoms of thionyl tetrafluoride and to study the spectroscopic properties of the products.

Summary of Reactions.

1. $SOF_4 + Me_3SiOPh \longrightarrow PhOS(O)F_3 + Me_3SiF$
2. $SOF_4 + 2Me_3SiOPh \longrightarrow (PhO)_2S(O)F_2 + Me_3SiF$
3. $SOF_4 + 3Me_3SiOPh \longrightarrow (PhO)_2S(O)F_2 + (PhO)_3S(O)F + 3Me_3SiF$
4. $SOF_4 + 4Me_3SiOPh \longrightarrow (PhO)_2SO_2 + 4Me_3SiF +$ red oil

5. $SOF_4 + p\text{-}Me_3SiOC_6H_4Me \longrightarrow p\text{-}MeC_6H_4OS(O)F_3 + Me_3SiF$
6. $SOF_4 + 2p\text{-}Me_3SiOC_6H_4Me \xrightarrow[\text{standing}]{\text{on}} (p\text{-}MeC_6H_4O)_2S(O)F_2 + 2Me_3SiF$
7. $SOF_4 + 2p\text{-}Me_3SiOC_6H_4Me \xrightarrow[\text{shaking}]{\text{with}} p\text{-}MeC_6H_4OS(O)F_3 + (p\text{-}MeC_6H_4O)_2S(O)F_2$

   $(p\text{-}MeC_6H_4O)_3S(O)F + 2Me_3SiF$
8. $SOF_4 + 3p\text{-}Me_3SiOC_6H_4Me \longrightarrow (p\text{-}MeC_6H_4O)_2S(O)F_2 + (p\text{-}MeC_6H_4O)S(O)F$

   $+ 3Me_3SiF$
9. $SOF_4 + 4p\text{-}Me_3SiOC_6H_4Me \longrightarrow (p\text{-}MeC_6H_4O)_2SO_2 + 4Me_3SiF +$ red oil
10. $SOF_4 + m\text{-}Me_3SiOC_6H_4Me \longrightarrow m\text{-}MeC_6H_4OS(O)F_3 + (m\text{-}MeC_6H_4O)_4SO$

    $+ Me_3SiF$
11. $SOF_4 + o\text{-}Me_3SiOC_6H_4Me \longrightarrow o\text{-}MeC_6H_4OS(O)F_3 + Me_3SiF$

12. $SOF_4 + p\text{-}Me_3SiOC_6H_4Cl \longrightarrow p\text{-}ClC_6H_4OS(O)F_3 + Me_3SiF$
13. $SOF_4 + 2p\text{-}Me_3SiOC_6H_4Cl \xrightarrow[\text{standing}]{\text{on}} (p\text{-}ClC_6H_4O)_2S(O)F_2 + 2Me_3SiF$
14. $SOF_4 + 2p\text{-}Me_3SiOC_6H_4Cl \xrightarrow[\text{shaking}]{\text{with}} p\text{-}ClC_6H_4OS(O)F_3 + (p\text{-}ClC_6H_4O)_2S(O)F_2$

    $+ (p\text{-}ClC_6H_4O)_3S(O)F + 2Me_3SiF$
15. $SOF_4 + 3p\text{-}Me_3SiOC_6H_4Cl \longrightarrow (p\text{-}ClC_6H_4O)_2S(O)F_2 + (p\text{-}ClC_6H_4O)_3S(O)F$

    $+ 3Me_3SiF$

16. $\mathrm{SOF_4 + 4p\text{-}Me_3SiOC_6H_4Cl \longrightarrow (p\text{-}ClC_6H_4O)_2SO_2 + 4Me_3SiF}$ + red oil

17. $\mathrm{SOF_4 + m\text{-}Me_3SiOC_6H_4Cl \longrightarrow m\text{-}ClC_6H_4OS(O)F_3 + Me_3SiF}$

18. $\mathrm{SOF_4 + o\text{-}Me_3SiOC_6H_4Cl \longrightarrow o\text{-}ClC_6H_4OSO_2F + Me_3SiF + SO_2F_2}$
$\mathrm{+ SiF_4}$ + solids

19. $\mathrm{SOF_4 + p\text{-}Me_3SiOC_6H_4F \longrightarrow p\text{-}FC_6H_4OS(O)F_3 + Me_3SiF}$

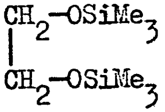
20. $\mathrm{SOF_4 + m\text{-}Me_3SiOC_6H_4F \longrightarrow m\text{-}FC_6H_4OS(O)F_3 + Me_3SiF}$

21. $\mathrm{SOF_4 + o\text{-}Me_3SiOC_6H_4F \longrightarrow o\text{-}FC_6H_4OS(O)F_3 + Me_3SiF}$

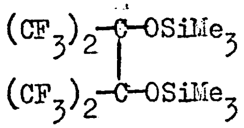
22. $\mathrm{SOF_4 + p\text{-}Me_3SiOC_6H_4NO_2 \longrightarrow (p\text{-}NO_2C_6H_4O)_2S(O)F_2 + Me_3SiF}$

23. $\mathrm{SOF_4 + Me_3SiOC_6F_5 \longrightarrow (C_6F_5O)_3S(O)F + Me_3SiF}$

24. $\mathrm{SOF_4 + 1{,}2(Me_3SiO)_2C_6H_4 \longrightarrow (C_6H_4O_2)_2SO + Me_3SiF}$



25. $\mathrm{SOF_4} + \begin{array}{l}\mathrm{CH_2{-}OSiMe_3}\\ | \\ \mathrm{CH_2{-}OSiMe_3}\end{array} \longrightarrow \mathrm{SO_2F_2 + Me_3SiF + SiF_4}$ + black tar



25. $\mathrm{SOF_4} + \begin{array}{l}\mathrm{(CF_3)_2{-}C{-}OSiMe_3}\\ \quad\quad\ | \\ \mathrm{(CF_3)_2{-}C{-}OSiMe_3}\end{array} \longrightarrow$ no reaction

27. $\mathrm{SOF_4 + Me_3SiOMe \longrightarrow SO_2F_2 + MeF + Me_3SiF}$

28. $\mathrm{SOF_4 + Me_3SiOEt \longrightarrow SO_2F_2 + EtF + Me_3SiF}$

29. $\mathrm{SOF_4 + Me_3SiOCH_2CF_3 \longrightarrow SO_2F_2 + CF_3CH_2F + Me_3SiF}$

30. $\mathrm{SOF_4 + Me_3SiOC_6H_{11} \longrightarrow SO_2F_2 + Me_3SiF + SiF_4}$+ black tar

31. $\mathrm{SOF_4 + (Me_3Si)_2O \longrightarrow SO_2F_2 + 2Me_3SiF}$

32. $SOF_4 + Me_3SiSMe \longrightarrow MeSSMe + Me_3SiF +$ oil

33. $SOF_4 + Me_3SiSPh \longrightarrow PhSSPh + Me_3SiF + SO_2F_2 + SiF_4$
+ black tar

34. $SOF_4 + Me_3SiNCS \longrightarrow {}^*\left[(NCS)_4SO\right]? + Me_3SiF$

*Indeterminate.

Not all the equations are balanced, but give the stoichiometry of the reactants and the products arising from these stoichiometric ratios.

The nature of the reactions and the products resulting from the reactions will be discussed first. The spectroscopic properties of the products, n.m.r., i.r. and mass spectra will be discussed separately.

Reactions 1-4, SOF_4/Me_3SiOPh

The reaction between SOF_4 and Me_3SiOPh in a one to one ratio occurs smoothly at room temperature, taking several hours to go to completion. The main product of the reaction is phenoxysulphur oxytrifluoride, $PhOS(O)F_3$, a colourless viscous liquid which moves slowly in vacuo.

$$SOF_4 + Me_3SiOPh \longrightarrow PhOS(O)F_3 + Me_3SiF$$

$PhOS(O)F_3$ decomposes on standing to give $PhOSO_2F$, SO_2F_2 C_6H_5F and tarry residues. SiF_4 is also formed and presumably arises

C_6H_5F and tarry residues. SiF_4 is also formed and presumably arises

from attack by $PhOS(O)F_3$ on glass containers. It hydrolyses to give the same products. A freshly distilled sample of $PhOS(O)F_3$ when heated to 80° for 30 minutes in an n.m.r. tube, decomposes cleanly to sulphuryl fluoride and fluorobenzene.

$$PhOS(O)F_3 \xrightarrow{\Delta} SO_2F_2 + C_6H_5F$$

Decomposition at temperatures around 0° is much slower. The reaction is also accompanied by the formation of a red oil which can be pumped off over a period of two days to leave a colourless solid, later identified as $(PhO)_2S(O)F_2$.

The reaction of SOF_4 and Me_3SiOPh in a one to two ratio occurs slowly over a period of two days with the production of a stoichiometric amount Me_3SiF and a low yield of bisphenoxysulphur oxydifluoride, $(PhO)_2S(O)F_2$. The reaction always gave a large amount of a red involatile oil which was difficult to pump off. $(PhO)S(O)F_2$ was isolated by recrystallising from CCl_2FCF_2Cl in which it is poorly soluble. It is a colourless solid, soluble in organic solvents such as CCl_4, CH_3CN and C_6H_6. It is indefinitely stable at room temperature in a dry atmosphere or dry solvents, but hydrolyses rapidly in a moist atmosphere to diphenylsulphate.

$$(PhO)_2S(O)F_2 \quad + \quad H_2O \longrightarrow (PhO)_2SO_2 \quad + \quad HF$$

It decomposes on heating to phenylfluorosulphate, diphenylsulphate and sulphuryl fluoride.

$$(PhO)_2S(O)F_2 \xrightarrow{\Delta} PhOSO_2F \quad + \quad (PhO)_2SO_2 \quad + \quad SO_2F_2$$

The reaction of SOF_4 with a three to one molar ratio of silyl ether failed to isolate the trissubstituted derivative, yeilding a large amount of $(PhO)_2S(O)F_2$. $(PhO)_3S(O)F$ was presumed to be present in a mixture, but its identification is based only on n.m.r. evidence. The reaction, in contrast to the two to one reaction of Me_3SiOPh and SOF_4, is over extremely quickly with a quantitative yield of Me_3SiF obtained after 30 minutes. The reaction products decompose to a viscous tar on standing.

Tetraphenyl-ortho-sulphite, $(PhO)_4S$, is readily obtained from a three to one ratio of Me_3SiOPh and SF_4 (25). Unfortunately, the corresponding sulphur VI derivative, tetraphenyl-ortho-sulphate, $(PhO)_4SO$, evaded isolation from the reaction of a four to one ratio of Me_3SiOPh and SOF_4.

$$SOF_4 \quad + \quad 4Me_3SiOPh \longrightarrow (PhO)_2SO_2 \quad + \quad 4Me_3SiF \quad + \quad \text{red oil}$$

Colourless solids precipitated out of solution initially, followed by rapid colour changes from green to red, with a large amount of heat given out during the colour changes. The colourless solids precipitate out of solution more slowly at -22°, but on reaching room temperature, they decompose rapidly in an exothermic reaction. A four molar quantity of Me_3SiF is obtained from the reaction, showing that all the fluorine atoms on sulphur had been substituted. Distillation of the product mixture on removal of Me_3SiF, yielded only diphenylsulphate. A simple decomposition pathway for the formal tetraphenyl-ortho-sulphate could possibly give diphenylsulphate and diphenyl ether, but the latter was not identified from the product mixture.

Reactions of SOF_4 with Me_3SiOAr (Ar = aryl) in which different groups were substituted on the aromatic ring gave products of varying stability.

Reactions 5-11. SOF_4/o,m,p-$Me_3SiOC_6H_4Me$.

SOF_4 reacts with p-$Me_3SiOC_6H_4Me$ in a one to one ratio at room temperature to give p-tolyoxysulphur oxytrifluoride, p-$MeC_6H_4OS(O)F_3$, a colourless, involatile liquid which moves slowly in vacuo.

$$SOF_4 + p\text{-}Me_3SiOC_6H_4Me \longrightarrow p\text{-}MeC_6H_4OS(O)F_3 + Me_3SiF$$

$p\text{-}MeC_6H_4OS(O)F_3$ is indefinitely stable in dry glass, but hydrolyses in a moist atmosphere to give $p\text{-}MeC_6H_4OSO_2F$, HF, SO_2F_2 and solids. It decomposes on heating to give SO_2F_2, $p\text{-}MeC_6H_4F$ and solids.

$$p\text{-}MeC_6H_4OS(O)F_3 \longrightarrow SO_2F_2 + p\text{-}MeC_6H_4F + \text{solids}$$

A solution of $p\text{-}MeC_6H_4OS(O)F_3$ in CCl_4 in an n.m.r. tube was unchanged after two months, as indicated by the ^{19}F n.m.r. spectrum.

A two to one reaction of $p\text{-}Me_3SiOC_6H_4Me$ and SOF_4 gave different products depending on the reaction conditions. If the reactants were left to stand for two days, the only sulphur compound given is the bis-p-tolyloxy-sulphur oxydifluoride, $(p\text{-}MeC_6H_4O)_2S(O)F_2$, while if the reactants are agitated continuously, mono, bis and trissubstituted products are given. Presumably in the latter case a faster reaction took place resulting in a higher degree of substitution. $(p\text{-}MeC_6H_4O)_2S(O)F_2$ is a colourless solid which is indefinitely stable in dry glass and dry solvents at room temperature. It decomposes in a moist atmosphere or on heating to 95° to give the diarylsulphate and hydrogen fluoride.

$$(p\text{-}MeC_6H_4O)_2S(O)F_2 \xrightarrow[\text{heat}]{H_2O} (p\text{-}MeC_6H_4O)_2SO_2 + HF$$

A three to one ratio of $p\text{-}Me_3SiOC_6H_4Me$ and SOF_4 gives both the bis- and trissubstituted products, the latter, $(p\text{-}MeC_6H_4O)_3S(O)F$ being identified only by n.m.r. spectroscopy. Fractional recrystallisation of the solid mixture failed to separate the products.

The four to one reaction of $p\text{-}Me_3SiOC_6H_4Me$ and SOF_4 is extremely vigorous at room temperature with initial precipitation of colourless solids which turn green then red. The solids appear to be more stable at -22°, but decompose vigorously on reaching room temperature. $(p\text{-}MeC_6H_4O)_2SO_2$ was recovered from the product mixture after removal of a four molar ratio of Me_3SiF.

The one to one reaction of $m\text{-}Me_3SiOC_6H_4Me$ and SOF_4 occurs slowly at room temperature to give m-tolyloxysulphur oxytrifluoride, $m\text{-}MeC_6H_4OS(O)F_3$, a colourless, involatile liquid which has the same order of stability of $PhOS(O)F_3$. It decomposes on standing and more quickly on heating to 75° to give $m\text{-}MeC_6H_4OSO_2F$, SO_2F_2, $m\text{-}MeC_6H_4F$ and solids.

$$m\text{-}MeC_6H_4OS(O)F_3 \xrightarrow{\Delta} m\text{-}MeC_6H_4OSO_2F + SO_2F_2 + m\text{-}MeC_6H_4F + \text{solids}$$

It hydrolyses in a moist atmosphere to give the same products along with hydrogen fluoride.

The one to one reaction of $m\text{-}Me_3SiOC_6H_4Me$ and SOF_4 is unusual in that as well as giving the monosubstituted sulphur derivative, a small amount of a colourless solid is given which is believed to be the tetra-m-tolyl-ortho-sulphate, $(m\text{-}MeC_6H_4O)_4SO$. The analysis is not entirely satisfactory, but is nearer in agreement with $(m\text{-}MeC_6H_4O)_4SO$ than any other possibility. For some of the one to one reactions of the Me_3SiOAr and SOF_4, the monosubstituted compound is the main product, but some of the bissubstituted compound is also formed. In the case of the one to one reaction of $m\text{-}Me_3SiOC_6H_4Me$ and SOF_4 the conditions would appear to be such that the formation of the tetrasubstituted derivative is favoured.

SOF_4 and $o\text{-}Me_3SiOC_6H_4Me$ react in a one to one ratio at room temperature to give o-tolyloxysulphur oxytrifluoride, $o\text{-}MeC_6H_4OS(O)F_3$, which is a colourless, involatile liquid and moves slowly in vacuo. It is much less stable than the meta or para derivatives and decomposes after 24 hours to SO_2F_2 and tarry solids. Gentle heating of a freshly prepared sample of $o\text{-}MeC_6H_4OS(O)F_3$ at 75° gives SO_2F_2, $o\text{-}MeC_6H_4F$ and solids.

$$o\text{-}MeC_6H_4OS(O)F_3 \xrightarrow{\Delta} SO_2F_2 + o\text{-}MeC_6H_4F + \text{solids}$$

It hydrolyses in a moist atmosphere to give $o\text{-}MeC_6H_4OSO_2F$, SO_2F_2, HF and solids

Reactions 12-18, $SOF_4/o,m,p\text{-}Me_3SiOC_6H_4Cl$

A one to one ratio of SOF_4 and $p\text{-}Me_3SiOC_6H_4Cl$ react at room temperature to give p-chlorophenoxysulphur oxytrifluoride,

$p\text{-}ClC_6H_4OS(O)F_3$, which is a colourless, involatile liquid and moves slowly in vacuo. It is indefinitely stable in dry glass, but decomposes in a moist atmosphere to give SO_2F_2, $p\text{-}ClC_6H_4OSO_2F$, HF and tarry solids. It decomposes completely on heating at 110° after 10 hours to give SO_2F_2 as the only identifiable product. $p\text{-}ClC_6H_4F$ was not observed as a product of the pyrolysis reaction.

$$p\text{-}ClC_6H_4OS(O)F_3 \xrightarrow{\Delta} SO_2F_2 \quad + \quad \text{solids}$$

On prolonged standing, a solution of $p\text{-}ClC_6H_4OS(O)F_3$ in CCl_4 darkens slightly, but the ^{19}F n.m.r. spectrum would indicate that little decomposition has taken place after two months.

A two to one molar ratio of $p\text{-}Me_3SiOC_6H_4Cl$ and SOF_4 react in a similar manner to the $p\text{-}Me_3SiOC_6H_4Me$ reaction, whereby on standing bis-p-chlorophenoxy-sulphur oxydifluoride, $(p\text{-}ClC_6H_4O)_2S(O)F_2$, is produced, whereas on shaking the reactants, mono, bis and tris-substituted derivatives are formed. This would infer a faster reaction is taking place in the latter case giving a higher degree of substitution.

$(p\text{-}ClC_6H_4O)_2S(O)F_2$ is a colourless solid which is indefinitely stable in dry glass containers or dry solvents, but decomposes on exposure to the atmosphere to give the diarylsulphate and hydrogen fluoride.

$$(p\text{-}ClC_6H_4O)_2S(O)F_2 \quad + \quad H_2O \longrightarrow (p\text{-}ClC_6H_4O)_2SO_2 \quad + \quad HF$$

It decomposes on heating at 95° to give SO_2F_2 and unidentifiable products.

The three to one reaction of p-$Me_3SiOC_6H_4Cl$ and SOF_4 gave both the bis and trissubstituted products. (p-$ClC_6H_4O)_3S(O)F$ was identified only by the ^{19}F n.m.r. spectrum. An attempt to isolate the compound by fractional recrystallisation did not succeed.

A four molar ratio of p-$Me_3SiOC_6H_4Cl$ and SOF_4 reacted fairly vigorously, giving initially colourless solids which turned red accompanied by an exothermic reaction. On removal of a four molar ratio of Me_3SiF from the product mixture, (p-$ClC_6H_4O)_2SO_2$ was recovered from the red mass by distillation at low pressure as the only other identifiable product. Presumably the tetrasubstituted compound was formed, but ~~that~~ it is unstable with respect to (p-$ClC_6H_4O)_2SO_2$ and possibly (p-$ClC_6H_4)_2O$ ~~which~~ was not identified.

A one to one ratio of m-$Me_3SiOC_6H_4Cl$ and SOF_4 react smoothly at room temperature to give m-chlorophenoxysulphur oxytrifluoride, m-$ClC_6H_4OS(O)F_3$, which is a colourless, involatile liquid and moves slowly in vacuo. It is stable in dry glass but hydrolyses in a moist atmosphere to give HF, SO_2F_2, m-$ClC_6H_4OSO_2F$ and solids. It would appear to be much more stable than p-$ClC_6H_4OS(O)F_3$, as on prolonged heating at 130° the compound failed to decompose completely, although some SO_2F_2 and m-$ClC_6H_4OSO_2F$ was formed.

$$\text{m-}ClC_6H_4OS(O)F_3 \xrightarrow{\Delta} SO_2F_2 \quad + \quad \text{m-}ClC\ H\ OSO\ F$$

An attempt to prepare higher substituted m-chlorophenoxysulphur derivatives did not succeed.

The reaction of SOF_4 and o-$Me_3SiOC_6H_4Cl$ in a one to one ratio failed to give o-chlorophenoxysulphur oxytrifluoride, o-$ClC_6H_4OS(O)F_3$. The reaction was fairly vigorous giving colourless products initially followed by a darkening of the solution and precipitation of tarry solids. SO_2F_2 and o-$ClC_6H_4OSO_2F$ were identified as the only sulphur products of the reaction. A large amount of SiF_4 was formed, presumably arising from formation of hydrogen fluoride and subsequent attack on the glass reaction vessel.

Reactions 19-21, o,m,p-$Me_3SiOC_6H_4F/SOF_4$.

The reaction of p-$Me_3SiOC_6H_4F$ and SOF_4 in a one to one ratio gave p-fluorophenoxysulphur oxytrifluoride, p-$FC_6H_4OS(O)F_3$, a colourless, involatile liquid which moves slowly in vacuo. It hydrolyses in a moist atmosphere to give HF, SO_2F_2, p-$FC_6H_4OSO_2F$ and solids. It decomposes slowly on standing, turning to a red colour with precipitation of solids. The decomposition at 120° in an n.m.r. tube was rapid to give SO_2F_2, p-$FC_6H_4OSO_2F$ and solids.

$$\text{p-}FC_6H_4OS(O)F_3 \xrightarrow{\Delta} SO_2F_2 + \text{p-}FC_6H_4OSO_2F + \text{solids}$$

A one to one reaction of m-$Me_3SiOC_6H_4F$ and SOF_4 gave m-fluorophenoxysulphur oxytrifluoride, m-$FC_6H_4OS(O)F_3$, a colourless, involatile liquid which moves slowly in vacuo. It is indefinitely stable in dry glass, but hydrolyses in a moist atmosphere to give HF, SO_2F_2, m-$FC_6H_4OSO_2F$ and solids. It is more stable than p-$FC_6H_4OS(O)F_3$ and m-$ClC_6H_4OS(O)F_3$, and was only partially decomposed on prolonged heating at 130° to give SO_2F_2, m-$FC_6H_4OSO_2F$ and solids.

$$\text{m-}FC_6H_4OS(O)F_3 \longrightarrow SO_2F_2 + \text{m-}FC_6H_4OSO_2F + \text{solids}$$

The reaction of o-$Me_3SiOC_6H_4F$ and SOF_4 in a one to one ratio gives o-fluorophenoxysulphur oxytrifluoride, o-$FC_6H_4OS(O)F_3$, a colourless, involatile liquid which moves slowly in vacuo. It is the least stable of the fluorophenoxysulphur derivatives and decomposes on standing or in a moist atmosphere to give HF, SO_2F_2, o-$FC_6H_4OSO_2F$ and a black viscous mass.

Reaction 22, SOF_4/p-$Me_3SiOC_6H_4NO_2$.

With a large excess of SOF_4 to p-$Me_3SiOC_6H_4NO_2$, the reaction gives only the bissubstituted derivative, bis-p-nitrophenoxy-sulphur oxydifluoride, $(NO_2C_6H_4O)_2S(O)F_2$, a colourless solid which is moderately stable in the atmosphere. The mass spectrum, however, showed the hydrolysed product, the diarylsulphate.

$$(\text{p-}NO_2C_6H_4O)_2S(O)F_2 + H_2O \longrightarrow (\text{p-}NO_2C_6H_4O)_2SO_2 + 2HF$$

The n.m.r. spectrum of the compound was not obtained as it proved to be insoluble in a range of boiling solvents such as CCl_4, CH_3CN, CH_3NO_2 and $(CH_3)_2SO$. It dissolved slowly in ethanol or water, but hydrolysed on dissolving in these solvents. The compound is possibly ionic, $(\text{p-}NO_2C_6H_4O)_2S(O)^{2+}.2F^-$, or has a polymeric structure.

An attempt to form higher substituted products did not succeed.

Reaction 23, $SOF_4/Me_3SiOC_6F_5$

SOF_4 and $Me_3SiOC_6F_5$ failed to react at room temperature, but at 110° gave trispentafluorophenoxysulphur oxyfluoride, $(C_6F_5O)_3S(O)F$. Large amounts of unreacted SOF_4 and $Me_3SiOC_6F_5$ were recovered from the products. $(C_6F_5O)_3S(O)F$ is a colourless solid, and is the only trissubstituted derivative of SOF_4 for which satisfactory analysis has been obtained. It hydrolyses in a moist atmosphere to give a clear liquid which was not identified. It sublimes readily on heating at 80°, but the mass spectrum obtained via the heated inlet did not show a molecular ion.

Reactions 24-26, SOF_4/bis(silyloxy) compounds.

SOF_4 and 1,2 bis(trimethylsilyloxy) benzene react slowly at room temperature over a period of a week to give the totally substituted sulphur compound, bis-phenylene-ortho-sulphate, $(C_6H_4O_2)_2SO$, and no intermediate sulphur fluorine compound was obtained. The reaction probably proceeds as below.

$$SOF_4 + 1,2(Me_3SiO)_2C_6H_4 \longrightarrow (C_6H_4O_2)S(O)F_2 + 2Me_3SiF$$

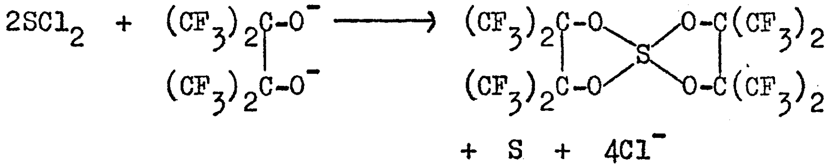
$$(C_6H_4O_2)S(O)F_2 + 1,2(Me_3SiO)_2C_6H_4 \longrightarrow (C_6H_4O_2)_2SO + 2Me_3SiF$$

$(C_6H_4O_2)_2SO$ is stable in a dry atmosphere, but hydrolyses on standing in a moist atmosphere to a black mass from which cathecol can be identified. It is soluble in most organic solvents and recrystallises from n-pentane to give large platelet crystals.

SOF_4 reacts with 1,2 bis(trimethylsilyloxy) ethane to give SO_2F_2, Me_3SiF, SiF_4 and a black intractable tar. The reaction occurs much more quickly than the previous reaction and is possibly accompanied by the elimination of hydrogen fluoride by interaction of the fluorine atoms on sulphur and the protons of the ethane fragment.

No reaction between SOF_4 and 1,1',2,2'-tetratrifluoromethyl; 1,2 bis(trimethylsilyloxy) ethane was observed, even on prolonged heating. It was hoped that the perfluoropinacol-ortho-sulphate would be formed, as the corresponding ortho-sulphite is known.

(140)



Reactions 27-31, SOF_4/Me_3SiOR, (R = alkyl).

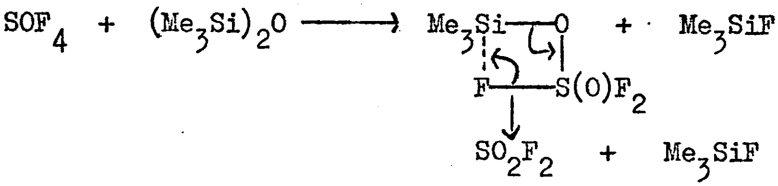
The reactions of SOF_4 with alkoxy trimethylsilanes failed to give the alkoxysulphur oxytrifluorides. The reaction between Me_3SiOMe and SOF_4 is extremely vigorous well below room temperature, but the other reactions proceed more slowly. With the cyclohexanol derivative, only SO_2F_2 and Me_3SiF were identified among the products which consisted mostly of tarry solids. It seems likely that the alkoxysulphur oxytrifluorides are formed, but are unstable with respect to the fluoroalkanes and sulphuryl fluoride.

$$ROS(O)F_3 \longrightarrow RF + SO_2F_2$$

$$(R = Me, Et, CF_3CH_2)$$

Reaction 31, $SOF_4/(Me_3Si)_2O$

The reaction between SOF_4 and hexamethyldisiloxane occurs slowly at room temperature and much more quickly at 80° to give SO_2F_2 and Me_3SiF. No intermediate compounds were given and possibly the reaction occurs stepwise.



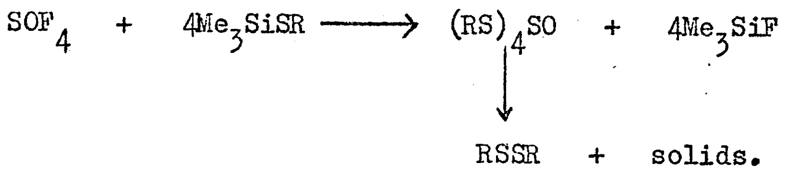
$$SOF_4 + (Me_3Si)_2O \longrightarrow Me_3Si{-}O{-}S(O)F_2 \cdots F + Me_3SiF \longrightarrow SO_2F_2 + Me_3SiF$$

Reactions 32 and 33, SOF_4/Me_3SiSR, R = Me, Ph.

SOF_4 reacts with Me_3SiSMe very vigorously at room temperature and more slowly at lower temperatures to give Me_3SiF and MeSSMe as the only identifiable products. A large amount of unreacted SOF_4 was recovered from the reaction.

SOF_4 and Me_3SiSPh react more slowly at room temperature than the above reaction. The products of the reaction are Me_3SiF, SO_2F_2, SiF_4 and tarry solids from which PhSSPh was recovered.

These reactions proceed possibly with two-valent and six-valent sulphur atoms linked together initially followed by rapid decomposition.



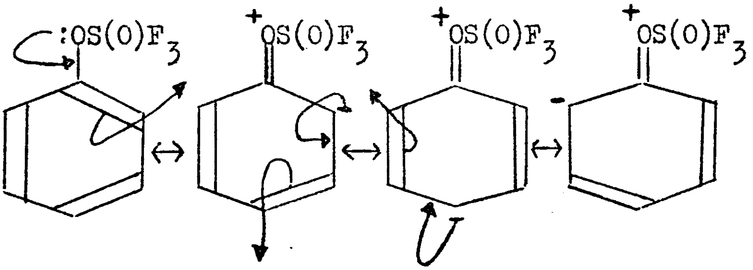
$$\begin{tikzcd} \mathrm{SOF_4} + \mathrm{4Me_3SiSR} \arrow[r] & \mathrm{(RS)_4SO} \arrow[d] & + \mathrm{4Me_3SiF} \\ & \mathrm{RSSR} + \text{solids.} & \end{tikzcd}$$

Reaction 34, SOF_4/Me_3SiNCS

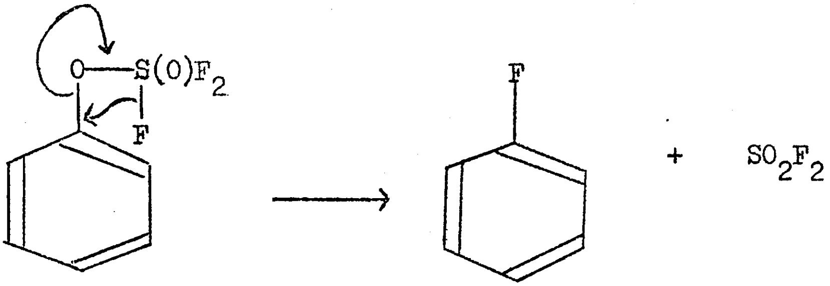
SOF_4 and Me_3SiNCS react slowly at room temperature to give initially colourless crystals which turn red on standing. A large amount of unreacted SOF_4 is recovered from the reaction. The analysis of the red compound, which is air stable would approximate to thionyl tetrathiocyanate, $(NCS)_4SO$, but this is by no means certain and conclusive. The compound decomposes on heating at 100° to a black mass. The mass spectrum is complex and does not show a molecular ion corresponding to $(NCS)_4SO^+$. The red compound is insoluble in a range of solvents such as CH_3CN, EtOH, water and decomposes in dilute H_2SO_4. The infrared spectrum shows a very strong, broad band around 1220 cm^{-1}. The compound is possibly polymeric. The reaction gives well defined crystals at lower temperatures and a structural analysis might be fruitful to elucidate the nature of this compound.

Stability of the substituted derivatives of thionyl tetrafluoride.

It has been observed that alkoxy derivatives of non-metals which have a tendency to double bond formation are thermally unstable. $MeOPF_4$ is unstable above -10° (141) and the reactions of SF_4 and alkoxysilanes have failed to isolate alkoxysulphur trifluorides (52). This is also the case with the alkoxysulphur oxytrifluorides which appear to break down as soon as they are formed. The stability of the aryloxysuphur oxytrifluorides presumably arises from the formation of resonance hybrids.



$PhOS(O)F_3$ is stable for only a relatively short period at room temperature and decomposes on standing or on heating to give SO_2F_2 and C_6H_5F among other products. $PhOSF_3$ is stable on standing and when heated does not give C_6H_5F (52), although SOF_2 is observed to form. It would appear that the oxygen atom attached to sulphur in the sulphur VI derivative has a definite effect on the aromatic ring. The difference may also arise from the higher valence state of sulphur in $PhOS(O)F_3$ where, because of the greater pull of charge on the aromatic ring, the C-O bond is activated to attack by a fluorine atom on sulphur.



The observed thermal stability of p-$MeC_6H_4OS(O)F_3$ could possibly arise from the electron release of the methyl group mesomerically to the C-O bond which impedes the attack of a fluorine atom on sulphur. The same effect, however, could possibly offset the stability of the compound arising from the formation of the resonance hybrids. Electron release by the methyl group in m-$MeC_6H_4OS(O)F_3$ is possible by only inductive effects and is insufficient to counteract attack of fluorine on the C-O bond. Both m-$MeC_6H_4OS(O)F_3$ and o-$MeC_6H_4OS(O)F_3$ do not decompose so cleanly as the para derivative at high temperatures. They form large amounts of tarry solids which could possibly indicate the coupling of aromatic groups. It is possible that steric effects are important in the ortho derivative.

The thermal decomposition of the halophenoxysulphur oxytrifluorides is quite different from that of the other aryloxysulphur oxytrifluorides in that the haloaromatic is not observed to form. Cramer and Coffman (142), in reacting various phenols with SOF_4, found that with m-ClC_6H_4OH and SOF_4 a high yield of m-ClC_6H_4F was obtained among other products, though they did not identify m-$ClC_6H_4OS(O)F_3$. The elimination of HF in the reaction with the phenol reaction possibly catalyses the formation of m-ClC_6H_4F, though the mechanism is not immediately obvious.

While p-$XC_6H_4OS(O)F_3$ (X = F, Cl) is fairly stable, the meta derivatives have greatly enhanced stability, especially the fluoro derivative. The reason for this is difficult to establish as the thermal breakdown of these compounds is complex, resulting in the formation of tarry solids and the formation of SO_2F_2.

All of the ortho-substituted aryloxysulphur oxytrifluorides are very unstable, particularly the chloro derivative which was not isolated, as it decomposed as the reaction of the aryloxy silyl ether and SOF_4 proceeded. It seems possible that ring coupling reactions are occurring in these reactions and a chromatographic study of the tarry, decomposition products may be informative.

The bissubstituted compounds $(ArO)_2S(O)F_2$ (Ar = Ph, p-MeC_6H_4, p-ClC_6H_4, p-$NO_2C_6H_4$) are more stable than the corresponding monosubstituted derivatives, notably $(PhO)_2S(O)F_2$ which is indefinitely stable at room temperature, while $PhOS(O)F_3$ decomposes on standing. The greater stability possibly arises from the lattice energy of the solid $(ArO)_2S(O)F_2$ compounds, as they decompose readily on melting. Further, the ease of formation of SO_2F_2 for the monosubstituted derivatives is not possible to the same extent for the bissustituted compounds.

The trissubstituted derivatives $(ArO)_3S(O)F$ have been only partially characterised, with analytical data only for $(C_6F_5O)_3S(O)F$. For both the tris and tetrasubstituted derivatives, steric crowding at sulphur possibly leads to the decomposition of these compounds, although $(m\text{-}MeC_6H_4O)_4SO$ would appear to be stable. This could indicate that the nature of the reactions has an important bearing on the stability of the higher substituted derivatives, where the medium of the reactants and products has considerable influence.

The preference which sulphur has for double bond formation does not avail itself in the case of the chelated derivative, $(C_6H_4O_2)_2SO$, which possibly gives rise to the stability of the compound.

The instability of the S(II)S(VI) compounds probably arises from the lower valence state of the S(II) entity which has a tendency to dimerise. This could be offset possibly by placing sufficiently electronegative groups on the S(II) grouping, such as CF_3 or C_6F_5.

n.m.r. spectra of thionyl tetrafluoride derivatives.

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

The dominant contribution to the shielding, or local molecular screening, of fluorine nuclei arises from paramagnetic effects (95,124). The magnitude of the effect is dependent on the degree of the ionic character of the bond. Electronegative atoms attached to fluorine decrease the ionic character of the bond between fluorine and the atom concerned which increases the paramagnetic contribution to the shielding. For elemental fluorine, the fluorine-fluorine bond is largely covalent and the ^{19}F shift is at low field. For binary fluorides, a decrease in electronegativity of the atom attached to fluorine moves the ^{19}F shift to higher fields. See Table 17.

Table 17.

^{19}F shifts of some binary fluorides.

Compound	δ CF_3CO_2H ext. p.p.m. (143)	δ F_2 ext. p.p.m. (144)
NF_3	-219.0	+285.0
ClF_3	-193.0, -81.0	+343.3
BrF_3	-54.3	+461.1
PF_3	-42.3	+463.7
CF_4	-11.9	+491.0
BF_4^-	+71.0	-
MoF_6	-355.0	-
WF_6	-242.0	-
F_2	-	0.0
HF	-	+625.0

Factors other than electronegativity can influence ^{19}F chemical shifts. The ^{19}F chemical shift of nitrosyl fluoride, O=N-F, is one of the lowest recorded at -420.0 p.p.m. from external fluorine (145). This has been attributed to the fluorine atom experiencing a large paramagnetic deshielding effect due to the presence of a low-lying electronic energy level of suitable symmetry in the molecule. The orbitals of nitrogen and fluorine are positioned such that transfer of electron density from fluorine to nitrogen is strongly favoured. This deshields the fluorine nucleus and moves the chemical shift to very low field.

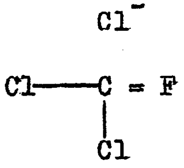
A further effect which contributes to the deshielding of fluorine nuclei is the occurrence of partial double bonding in the halofluorocarbon derivatives. See Table 18.

Table 18.

^{19}F chemical shifts of the fluoromethanes and the halofluoromethanes.

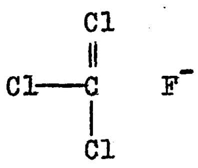
Compound	δ CF_4 ext. p.p.m.	
CH_3F	+210.0	(146)
CH_2F_2	+80.9	
CHF_3	+18.2	
CF_4	0.0	
$CFCl_3$	-76.7	
CF_2Cl_2	-60.4	
CF_3Cl	-36.8	
CF_4	0.0	

The ^{19}F shifts of the fluoromethanes follow the trend expected from electronegativity considerations, where successive replacement of protons by fluorine atoms moves the ^{19}F shift to lower field because of increased deshielding of the fluorine nuclei. The chlorofluoromethanes show the reverse trend where successive replacement of chlorine atoms by fluorine atoms moves the ^{19}F shift to higher field. These anomalous shifts have been explained by postulating the presence of contributions to the molecular structures of the halofluoromethanes of double bonded structures and ionic species of the type as shown.



Cl^{-} / $Cl-C(Cl)=F$

I



$Cl-C(=Cl)-Cl \quad F^{-}$

II

It was assumed that fluorine was more able to form double bonds, and thus type I structures are more important leading to greater deshielding of the fluorine nucleus which moves the shift to lower field than would otherwise be expected.

Changing the oxidation state of the atom attached to fluorine usually results in more shielding of the fluorine nuclei. See Table 19.

Table 19.

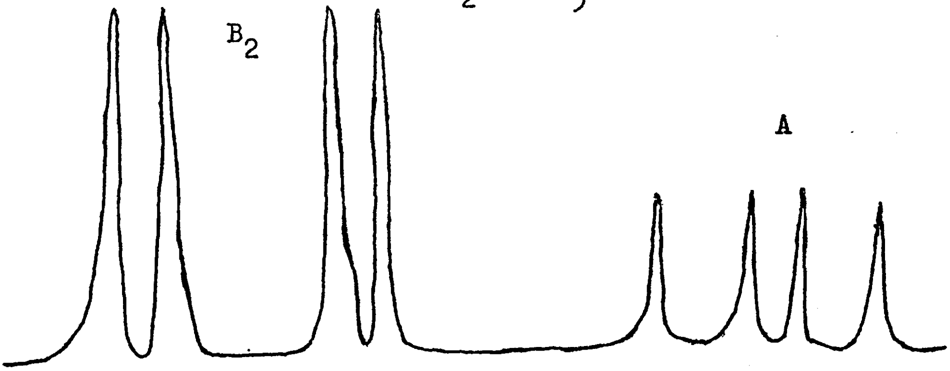
Compound	^{19}F shift from CCl_3F	
PF_3	+26.7	
PF_5	+78.3	
SF_4	-62.0	(143,144)
SF_6	-48.0	
SOF_2	-76.0	(this work)
SOF_4	-81.0	(")

This has been attributed to the need for the use of higher energy d orbitals in the higher valence state. The oxygen atom attached to sulphur would appear to reverse the trend for thionyl fluoride and thionyl tetrafluoride, where there is more shielding of the fluorine nuclei in the lower valence state. The reason for this is not immediately obvious.

From these few considerations, it can be seen that it is unwise to come to hasty conclusions regarding trends in ^{19}F chemical shifts.

^{19}F n.m.r. spectra of the derivatives of thionyl tetrafluoride.

The ^{19}F n.m.r. spectra of the aryloxysulphur oxytrifluorides give an AB_2 spectrum, which has been discussed earlier with reference to the spectrum of $Me_2NS(O)F_3$. This would suggest trigonal bipyramidal symmetry, with the ArO group in an equatorial position, with a structure similar to that of $Me_2NS(O)F_3$ (135).



^{19}F n.m.r. spectrum of $PhOS(O)F_3$

The ^1H and ^{19}F n.m.r. spectral data of the derivatives of thionyl tetrafluoride are summarised in Table 20.

Table 20.

^1H and ^{19}F n.m.r. spectra of derivatives of thionyl tetrafluoride.

Compound	δH p.p.m. from t.m.s.	δFe p.p.m.	δFa from CCl_3F	$\lvert J_{FeFa}\rvert$ Hz.
$PhOS(O)F_3$	-7.24	-67.6	-89.1	213.2
$p\text{-}MeC_6H_4OS(O)F_3$	-7.19, -2.32(CH_3)	-67.2	-88.4	217.5
$m\text{-}MeC_6H_4OS(O)F_3$	-7.08, -2.22(CH_3)	-67.0	-88.2	213.4
$o\text{-}MeC_6H_4OS(O)F_3$	-7.17, -2.18(CH_3)	-67.4	-86.4	209.4
$p\text{-}ClC_6H_4OS(O)F_3$	-7.20	-68.1	-89.7	222.2
$m\text{-}ClC_6H_4OS(O)F_3$	-7.28	-68.4	-89.5	219.8
$p\text{-}FC_6H_4OS(O)F_3$	-7.08($\delta C\underline{F}$ at 112.3)	-67.4	-88.2	215.4
$m\text{-}FC_6H_4OS(O)F$	-7.12($\delta C\underline{F}$ at 108.2)	-67.6	-88.9	218.0
$o\text{-}FC_6H_4OS(O)F_3$	-7.24($\delta C\underline{F}$ at 129.4)	-69.8	-86.1	218.0
$(PhO)_2S(O)F_2$	-7.13	-89.0		
$(p\text{-}MeC_6H_4O)_2S(O)F_2$	-7.14, -2.32(CH_3)	-86.0		
$(p\text{-}ClC_6H_4O)_2S(O)F_2$	-7.34	-89.0		
$(PhO)_3S(O)F$	-	-68.4		
$(p\text{-}MeC_6H_4O)_3S(O)F$	-	-67.0		
$(p\text{-}ClC_6H_4O)_3S(O)F$	-	-69.9		
$(C_6F_5O)_3S(O)F$	$\delta C\underline{F}$ at 154.0 (o), 157.2(p), 164.2(m)	-68.1		
$(m\text{-}MeC_6H_4O)_4SO$	-7.12, -2.31(CH_3)			
$(C_6H_4O_2)_2SO$	-6.92			

Table 20 shows that δFa and δFe are not very sensitive to changes in the aromatic ring for the aryloxysulphur oxytrifluorides. The chemical shift difference between δFa and δFe is also invariant at around 20 p.p.m., whereas it reduces from 10 p.p.m. for $Me_2NS(O)F_3$ to 4 p.p.m. for $Et_2NS(O)F_3$ (147). The axial fluorines ^{19}F chemical shifts are at lower field for the aryloxysulphur oxytrifluorides with respect to the shifts of the axial fluorines of the dialkylaminosulphur oxytrifluorides. See Table 21. This would be expected on the basis of electronegativity differences between oxygen and nitrogen. This is also observed in the AX_2 spectra of the sulphur IV trifluorides.

Table 21.

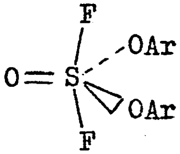
^{19}F n.m.r. spectra of sulphur IV and VI trifluorides.

Compound	Temperature	δFa	δFe	$\lvert\delta Fa - \delta Fe\rvert$	$\lvert J_{FeFa}\rvert$
		p.p.m.	from CCl_3F	p.p.m.	Hz.
$PhOS(O)F_3$	R.T.	-89.1	-67.6	22.5	213.2
$Me_2NS(O)F_3$(135)	R.T.	-76.8	-66.5	10.3	163.1
$PhOSF_3$(25)	R.T.	-79.1	-30.5	48.6	67.7
Me_2NSF_3(20)	-100°	-57.4	-28.4	29.0	-

For the aryloxysulphur oxytrifluorides $\lvert J_{FeFa}\rvert$ shows a small variation, ranging from 209.4 Hz. for $o\text{-}MeC_6H_4OS(O)F_3$ to 222.2 Hz. for

$p\text{-}ClC_6H_4OS(O)F_3$. $|J_{FeFa}|$ is smaller for the dialkylaminosulphur oxytrifluorides at around 163 Hz.

The bis-aryloxy-sulphur oxydifluorides are the first bis-substituted derivatives of SOF_4, which makes comparison of the n.m.r. spectra impossible. It is striking, however, that the ^{19}F n.m.r. spectra of the bissubstituted derivatives give a signal as a singlet at very close proximity to the δFa chemical shifts of the corresponding monosubstituted compounds. It would be reasonable to assume that both the fluorine atoms of the $(ArO)_2S(O)F_2$ compounds are in axial positions and the aryloxy groups are in equatorial positions, as depicted below.

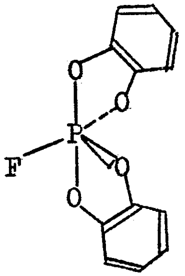


Ar = Ph, $p\text{-}MeC_6H_4$, $p\text{-}ClC_6H_4$, $p\text{-}NO_2C_6H_4$?.

Probable structure of $(ArO)_2S(O)F_2$

The ^{19}F shifts are at marginally higher field with respect to the δFa values of the sulphur oxytrifluorides which would suggest that there is little departure from the trigonal bipyramidal structure.

$(C_6F_5O)_3S(O)F$ is the only properly characterised trissubstituted derivative, but the ^{19}F n.m.r. of the other supposed trissubstituted compounds show a resonance at the same position as $(C_6F_5O)_3S(O)F$ at around -68.0 p.p.m. from CCl_3F. This would suggest by comparison with the bis and monosubstituted compounds, that the remaining fluorine attached to sulphur is in an equatorial position for a trigonal bipyramidal structure. This has been found to be the case for the single fluorine atom attached to phosphorus for the compound shown below.



2-fluoro-2,2'-spiro-1,3,2-benzodioxaphosphole.

The phenylene groups can only bridge the axial-equatorial distances, which of neccessity forces the remaining fluorine into the equatorial position. This need not be the case for the non-chelated trisaryloxysulphur oxyfluorides, and it seems probable that there has been an alteration in structure departing from the trigonal bipyramid.

C-F chemical shifts:

Substitution of a benzene molecule influences the ortho, meta and para positions to the substituent in different ways. The ortho position is influenced by a combination of inductive, resonance and steric effects, the meta position mainly by inductive effects and the para position mainly by resonance effects. Several workers have examined ^{19}F resonance spectra of fluorobenzene derivatives in an attempt to obtain information about the electron distribution in aromatic systems (124). In most cases, the ortho substituted fluorine is the most shielded followed by the para and meta substituted fluorine atoms. This is not the case with the polyfluoro benzenes, where increased conjugation disturbs that order. The shielding of the ^{19}F nucleus in the halogen ortho-substituted fluorobenzenes decreases with decrease in the electronegativity of the halogen substituent in the series F, Cl, Br and I. This deshielding is said to arise from van der Waals interactions of the more bulky halogen atom with the adjacent fluorine atom inducing intramolecular electric fields. See Table 22.

Table 22.

^{19}F shifts of monosubstituted fluorobenzenes. (124)

Substituent	Ortho	Meta	Para	
	^{19}F shifts from CCl_3F			
I	90.7	111.4	115.2	
Br	108.5	111.6	116.3	
Cl	116.7	111.9	116.4	
F	139.9	110.9	120.4	
OH	139.9	113.1	124.6	
OMe	136.4	-	125.4	
OEt	135.7	112.7	125.5	
$OS(O)F_3$	129.4	108.2	112.3	(this work)

For the fluorophenoxysulphur oxytrifluorides, the $OS(O)F_3$ group shields the ortho substituted fluorine most, followed by the para and meta fluoro atoms. This would be expected from resonance and inductive effects which are greatest at the ortho position. The resonance effect of the para substituted fluorine atom is greater than the inductive effect for the meta fluorine atom in shielding the fluorine nucleus.

For $(C_6F_5O)_3S(O)F$ the resonance of the para substituted fluorine is readily assigned as being intermediate in shift between that of the ortho and meta fluorines, simply on the basis of integration of the heights of the signals with only one fluorine atom in the para position. The convention used by Boden and co-workers has been used to assign the ortho and meta signals. See Table 23.

Table 23.

^{19}F shifts of monosubstituted polyfluorobenzenes (149)

C_6F_5X Substituent X	Ortho	Para	Meta	
	^{19}F shift from CCl_3F			
F	162.3	162.3	162.3	
Cl	140.6	156.1	161.5	
Br	132.5	154.7	160.6	
H	138.9	153.5	162.1	
OS(O)F	154.0	157.2	164.2	(this work)

The ^{19}F shifts are not consistent with predictions from π electron densities, and these anomalous effects have been attributed to van der Waals interactions and increased conjugation of the ring.

^{1}H n.m.r. of the thionyl tetrafluoride derivatives. (See Table 20, P117)

The ^{1}H n.m.r. spectra of the phenoxy compounds show a singlet which moves to lower field as the number of fluorines attached to sulphur increases, as would be expected from electronegativity arguments. The ^{1}H shifts are to lower field with respect to the corresponding sulphur IV compounds (52). See Table 24.

Table 24.

^{1}H shifts of phenoxysulphur fluorides.

Compound	^{1}H shift w.r.t. t.m.s.
$PhOS(O)F_3$	-7.24
$(PhO)_2S(O)F_2$	-7.13
$PhOSF_3$ (52)	-6.55
$(PhO)_2SF_2$ (52)	-6.42

The shift to lower field for the sulphur VI derivatives may arise from the increased valence state of sulphur which is more electronegative and thus deshields the protons more effectively.

The ^{1}H n.m.r. in the aromatic region of the compounds with substituents on the aromatic ring is more complex, showing multiplets which have not been analysed. The methyl signals of the tolyloxysulphur compounds show a singlet, and are not complicated by coupling. The shielding of the methyl protons decreases with distance from the $OS(O)F_3$ group, which would imply that the $OS(O)F_3$ group is electron releasing. This is hardly likely, and the reason behind the observation is not immediately obvious.

The protons of $(p\text{-}ClC_6H_4O)_2S(O)F_2$ move downfield with respect to $p\text{-}ClC_6H_4OS(O)F_3$, while the aromatic protons of the other bis-substituted compounds move upfield with respect to the monosubstituted derivatives as expected. The ^1H shift of the protons of $(m\text{-}MeC_6H_4O)_4SO$ also move to lower field with respect to the monosubstituted compound.

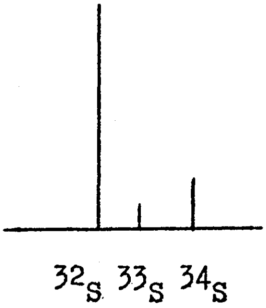
The ^1H n.m.r. of bis-phenylene-ortho-sulphate, $(C_6H_4O_2)_2SO$, shows a moderately broad singlet, which would imply chemical equivalence of the protons of both aromatic rings. A more complex spectrum would have been expected because of ortho substitution of the rings.

Mass spectra of the thionyl tetrafluoride derivatives.

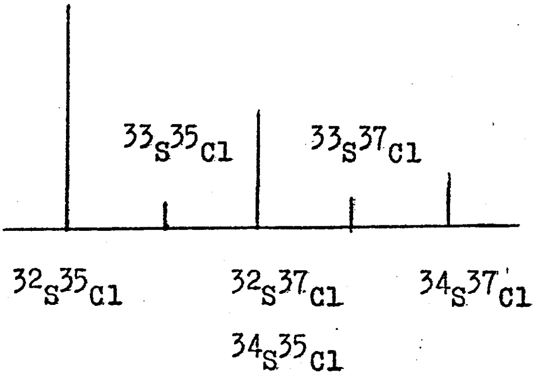
The aryloxysulphur oxytrifluorides were the only derivatives to give meaningful spectra. The compounds, while none too volatile, had sufficient vapour pressure to be observed in the mass spectrometer via the cold inlet. The bisaryloxysulphur oxydifluorides decomposed in the heated inlet or in the atmosphere when applied to the probe directly. The spectra in the latter case showed only the diarylsulphate resulting from hydrolysis.

$$(ArO)_2S(O)F_2 \quad + \quad H_2O \longrightarrow (ArO)_2SO_2 \quad + \quad HF$$

The very high energies used in mass spectrometers (70 e.V. as against 15 e.V. for ionising an atom) would be expected to lead to the indiscriminate cleavage of bonds, and possibly the use of lower voltages in some cases would give more informative spectra. Despite this, major fragments in mass spectra arise from the most stable ion products which are formed by the most favourable reaction pathways of the ground-state reactions (150). The fragmentation pattern of a particular molecule is usually dependent on the stability of the ionic rather than the radical species. Ionization of organic species proceeds via the loss of an electron from a heteroatom with non-bonded electrons. Where no heteroatom is present, the electron is removed from a particular bond (151). Organic compounds break down to form fragments with positive charges almost exclusively, but with more electronegative entities, such as fluorine atoms, there is a possibility of forming stable negatively charged species in the mass spectrometer. However, only positive ion spectra have been studied. Mass measurements have not been made, but the spectra are highly characteristic, as they give the standard sulphur isotopic ratio patterns. For elemental sulphur, the distribution of sulphur isotopes is 95.1 % ^{32}S, 0.74 % ^{33}S, 4.2 % ^{34}S and 0.016 % ^{36}S. The latter isotope ^{36}S is not usually observed, but the others are readily identified. The spectra of the chlorophenoxysulphur oxytrifluorides are further complicated by chlorine isotopic abundances of approximately 75 % ^{35}Cl and 25 % ^{37}S. In these cases, the abundances quoted for fragments containing sulphur and chlorine refer to the $^{32}S^{35}Cl$ contribution, and those containing chlorine refer to the ^{35}Cl contribution.



Isotopic pattern of sulphur.



Isotopic pattern of fragments with sulphur and chlorine.

The mass spectra of the aryloxysulphur trifluorides are summarised in Table 25. The relative abundance of the molecular ion is masked by the very high abundance of other fragments. The molecular ion, however, is in moderate abundance, in contrast to the mass spectrum of SOF_4 where the parent ion is in very small abundance (152). The parent ion for $Me_2NS(O)F_3$ is also in small abundance (135), and is not observed at all for $Et_2NS(O)F_3$ (147). The increased stabilisation of the parent ion of the aryloxysulphur oxytrifluorides probably arises from the ease of withdrawl of the positive charge by the mesomeric effect of the aromatic ring. This is particularly evident in the tolyl derivatives, where inductive release of charge by the methyl group stabilises the positive charge on the ion.

Table 25.

Mass spectra of the $ArOS(O)F_3$ compounds.

Compound/Ion	$ArOS(O)F_3^+$	$ArOS(O)F^+$	SOF_3^+	ArO^+	SOF_2^+	Ar^+	SOF^+	SO^+
	Relative abundances of the ions (%).							
$PhOS(O)F_3$	5	11	100	63	25	54	36	7
$p\text{-}MeC_6H_4OS(O)F_3$	10	6	44	100	16	3	29	11
$m\text{-}MeC_6H_4OS(O)F_3$	18	21	100	100	12	30	27	9
$o\text{-}MeC_6H_4OS(O)F_3$	19	11	49	100	50	25	3	59
$p\text{-}ClC_6H_4OS(O)F_3$	1	7	100	66	32	15	11	41
$m\text{-}ClC_6H_4OS(O)F_3$	15	7	100	18	4	10	13	59
$p\text{-}FC_6H_4OS(O)F_3$	8	7	100	78	25	31	60	22
$m\text{-}FC_6H_4OS(O)F_3$	7	5	100	19	8	16	17	6
$o\text{-}FC_6H_4OS(O)F_3$	11	6	100	46	19	21	35	9

(The columns of figures refer to the percentage abundance of the various ions listed at the top of the table arising from the breakdown of the compounds listed in the left hand column.)

The principal fragmentation pattern of the aryloxysulphur oxytrifluorides arises from cleavage at the sulphur oxygen single bond rather than at the carbon oxygen bond.

$$ArOS(O)F_3 \xrightarrow{-e^-} Ar^+ + OS(O)F_3^{\bullet} \quad \text{or} \quad Ar^{\bullet} + OS(O)F_3^{+} \qquad 1.$$

$$ArOS(O)F_3 \xrightarrow{-e^-} ArO^+ + S(O)F_3^{\bullet} \quad \text{or} \quad ArO^{\bullet} + S(O)F_3^{+} \qquad 2.$$

For all of the spectra, an ion corresponding to SO_2F_3 was not observed. Although Ar^+ fragments were observed, they are believed to arise from the breakdown of $ArO^\bullet$ and ArO^+ fragments. Fragmentation via the second pathway is believed therefore to be the more favourable. This does, however, leave the possibility of the two breakdown pathways. For the tolyl derivatives, inductive and mesomeric release of electrons from the methyl groups to the aromatic ring would appear to stabilise the ArO^+ fragment by neutralising the charge. The favoured mechanism in that case is shown below.

$$\text{o,m,p-MeC}_6\text{H}_4\text{OS(O)F}_3 \xrightarrow{-e^-} \text{o,m,p-MeC}_6\text{H}_4\text{O}^+ + \text{S(O)F}_3{}^\bullet$$

With electronegative substituents attached to the aromatic ring, electron release is reduced. This destabilises the ArO^+ fragment and the formation of the $S(O)F_3{}^+$ fragment is favoured.

$$\text{ArOS(O)F}_3 \xrightarrow{-e^-} \text{ArO}^\bullet + \text{S(O)F}_3{}^+$$

$$\text{Ar} = \text{o,m,p-FC}_6\text{H}_4\text{; m,p-ClC}_6\text{H}_4.$$

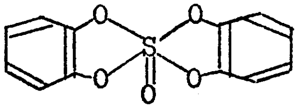
This is especially evident where the halogen on the aromatic ring is in the meta position. The relative abundance of the ArO^+ fragment increases greatly for ortho and moreso para substitution of the halogens. This possibly arises from π donation to the ring by mesomeric effects and is greater for fluorine as expected.

The Ar^+ fragment is much less abundant than the ArO^+ fragment which favours the argument that breakdown of the parent takes place at the S-O bond rather than the C-O bond.

While the parent ion does not show evidence of progressive loss of fluorine atoms, the $SOF_3{}^+$ fragment shows relatively high abundances of SOF_2^+, SOF^+ and SO^+ ions.

Mass spectra of other compounds:

$(C_6H_4O_2)_2SO$. The compound obtained from the reaction of $C_6H_4(OSiMe_3)_2$ and SOF_4 has the emperical formula $C_{12}H_{18}O_5S$ as obtained from analysis, which does not establish the structure. Two possibilities are given below, either of which need not be correct.



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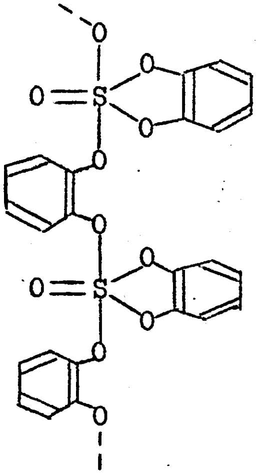


II

Structure I should give a parent ion at m/e 264, whereas the highest m/e value observed is at 248, which could possibly arise from the loss of an oxygen atom from the parent structure I. Structure II has the same emperical formula as I, and although polymeric, facets of structure appear in the spectrum, such as $C_6H_4O_2^+$, $C_6H_4O_2SO_2^+$ etc., which would agree with II. See Table 26.

Table 26.

Breakdown pattern of $(C_6H_4O_2)_2SO$

Ion	m/e
$C_6H_4O_2^+$	108
$C_6H_4O_2S^+$	140
$C_6H_4O_2SO^+$	156
$C_6H_4O_2SO^+$	172

It must be mentioned, however, that the spectrum was measured by placing the sample directly on the probe, and the compound is both thermally and hydrolytically unstable. Other peaks appear in the spectrum at m/e 160, 190 and 212 which have not been assigned. Relative abundances are not given as the precise nature of the fragmentation pattern is not known. Peaks above m/e 108 show the characteristic sulphur isotopic pattern.

$(C_6F_5O)_3S(O)F$. The spectrum was measured via the heated inlet as the compound sublimes readily. The spectrum is complex, showing peaks at almost every mass number up to m/e 300. There is no parent ion and the highest mass number appears very weakly at m/e 414. This possibly arises from $(C_6F_5O)_2SO^+$ with loss of a fluorine atom and a pentafluorophenoxy group from the parent.

Compound from SOF_4/Me_3SiNCS. While the compound is suggested tentatively to be $(NCS)_4SO$, the mass spectrum would not agree with that formulation. The spectrum is dominated by the breakdown of S_8 showing progressive loss of sulphur atoms. m/e values appear 256,224,192,160,128,96,64 and 32 corresponding to S_8^+, S_7^+, S_6^+, S_5^+, S_4^+, S_3^+, S_2^+ and S^+. Other spurious peaks appear in the spectrum, but there is no molecular ion corresponding to $(NCS)_4SO$ and no ion corresponding to an $(NCS)^+$ fragment.

Infrared spectra of the thionyl tetrafluoride derivatives.

The infrared spectrum of the aryloxysulphur compounds are complex as would be expected for molecules of low symmetry and the aromatic ring giving rise to a number of bands. Assignment is then difficult, but an attempt has been made to assign some of the more important bands. Full details of all the spectra are given in the experimental section.

The infrared spectra were measured as solution spectra in carbon tetrachloride using KBr plates with a path length of 0.1 mm. Solution concentrations were approximately 0.05M and were prepared in the dry-box. In some cases, dilution was necessary. Spectra were measured using a Perkin Elmer 457 spectrophotometer.

While the infrared spectra of the thionyl halides and their derivatives have received much attention, little is known of the infrared spectra of derivatives of thionyl tetrafluoride. Some of the bands appearing in the spectra of thionyl tetrafluoride and its derivatives are shown in Table 27.

For the aryloxysulphur compounds, ring absorptions of variable intensity appear at around 1600 cm^{-1}, 1500 cm^{-1} and 1000 cm^{-1}. The ring absorptions for both the mono and bissubstituted compounds appear at approximately the same frequencies. The C-F stretching frequency appears as an intense, broad band centred at 1513 cm^{-1} for $(C_6F_5O)_3S(O)F$, and another strong band at 1005 cm^{-1} is assigned as the C-F bending frequency.

Table 27.

Infrared spectra of thionyl tetrafluoride and derivatives (cm^{-1}).

Compound	νring	νSO	νCOS	νSF
SOF_4(35)	-	1379	-	927,820,750
$Me_2NS(O)F_3$ (135)	-	1296	-	821,709
$Et_2NS(O)F_3$ (147)	-	1277	-	815,710
$PhOS(O)F_3$	1589	1323	1235	924,835,721
p-$MeC_6H_4OS(O)F_3$	1604	1324	1220	928,829,721
m-$MeC_6H_4OS(O)F_3$	1619,1586	1323	1220	923,875,719
p-$ClC_6H_4OS(O)F_3$	1590	1327	1211	924,848,709
m-$ClC_6H_4OS(O)F_3$	1602,1584	1327	1262	946,864,718
p-$FC_6H_4OS(O)F_3$	1606	1331	1208	928,854
m-$FC_6H_4OS(O)F_3$	1611	1334	1231	949,863
$(PhO)_2S(O)F_2$	1589	1288	1231,1219	910,688
(p-$MeC_6H_4O)_2S(O)F_2$	1598	1284	1230,1209	895,680
(p-$ClC_6H_4O)_2S(O)F_2$	1590	1294,1287	1220	910,698
(p-$NO_2C_6H_4O)_2S(O)F_2^*$	1612,1589	1284?	1232,1214	918,751
$(C_6F_5O)_3S(O)F$	1513,1005	1297	1250,1220	694

* KBr pressed disc/nujol mull.

One of the strongest absorptions in these spectra arises from νSO at around 1300 cm^{-1}. νSO for thionyl tetrafluoride appears at 1379 cm^{-1}, higher than νSO for thionyl fluoride at 1333 cm^{-1} (49). The increase in the wavenumber frequency is due to the effect of the two additional fluorine atoms attached to sulphur. This puts a higher formal positive charge on sulphur and increases the degree of (p-d)π bonding in the sulphur oxygen bond which increases the force constant and moves νSO to higher frequency.

There is a large difference in νSO between $Me_2NS(O)F_3$ and $Et_2NS(O)F_3$ with νSO falling by 23 cm^{-1}, while for the sulphur IV compounds, νSO falls by only 6 cm^{-1} from $Me_2NS(O)F$ to $Et_2NS(O)F$. See Page 41. νSO is at lower frequency for the dialkylaminosulphur oxytrifluorides than the aryloxysulphur oxytrifluorides as would be expected from electronegativity differences between nitrogen and oxygen as well as the influence of the aromatic ring. The highest frequency for νSO appears at 1334 cm^{-1} for m-$FC_6H_4OS(O)F_3$, and νSO is usually at higher frequency with an electronegative substituent on the aromatic ring. νSO falls below 1300 cm^{-1} for the bissubstituted compounds because of the additional, less electronegative oxygen atom on sulphur. For $(NO_2C_6H_4O)_2S(O)F_2$, νSO is 1284 cm^{-1} but is somewhat obscured by absorptions from the aromatic ring. Comparison of the spectrum with that of p-$NO_2C_6H_4OH$ showed a similar absorption at 1280 cm^{-1}, with the sulphur compound showing a band at 1280 cm^{-1} and shoulders at 1291 cm^{-1} and 1272 cm^{-1}. A very strong absorption at 1342 cm^{-1} is attributable to νs NO_2, appearing at 1328 cm^{-1} for the phenol. νSO is tentatively assigned at 1297 cm^{-1} for $(C_6F_5O)_3S(O)F$, appearing as a weaker band which is not observed in the spectra of C_6F_5OH or $Me_3SiOC_6F_5$.

COS appears as a weak absorption at 1138 cm^{-1} for PhOS(O)Cl and 1183 cm^{-1} for PhOS(O)F (46). νCOS can be assigned at 1230 cm^{-1} for $PhOSF_3$ (52) and so would appear to move to higher frequency with greater electron withdrawl from sulphur.

For the aryloxysulphur VI compounds, νCOS appears as a band of variable intensity which is sometimes split, especially for the higher substituted compounds. An absorption at 1235 cm^{-1} for $PhOS(O)F_3$ would appear to be too intense for νCOS, but bands at 1231 cm^{-1} and 1219 cm^{-1} for $(PhO)_2S(O)F_2$ are of the same order of intensity and it seems probable that they are due to νCOS. Bands appearing above 1250 cm^{-1} which have been assigned as νCOS are possibly at frequencies which are too high to be due to νCOS, but for $m\text{-}ClC_6H_4OS(O)F_3$, for example, there is no other band in that region lower than 1250 cm^{-1}. Weak absorption at 1250 cm^{-1} and 1220 cm^{-1} for $(C_6F_5O)_3S(O)F$ do not appear in the spectrum of C_6F_5OH and $Me_3SiOC_6F_5$ and are supposedly due to νCOS.

S-F stretching frequencies appear as strong absorptions below 1000 cm^{-1}. For the $R_2NS(O)F_3$ compounds, νSF comes at around 820 cm^{-1} and 710 cm^{-1}, while for the aryloxysulphur compounds they appear at higher frequency, as high as 949 cm^{-1} for $m\text{-}ClC_6H_4OS(O)F_3$.

However, they are in a region which is obscured by absorptions due to the aromatic ring, and it is only their intensity which would differentiate them as being probable S-F stretching frequencies. Strong absorptions at around 850 cm^{-1}, and as low as 680 cm^{-1} for $(p\text{-}MeC_6H_4O)_2S(O)F_2$, are also assigned as S-F stretching frequencies.

The infrared spectra of the ortho-sulphates $(m\text{-}MeC_6H_4O)_4SO$ and $(C_6H_4O_2)_2SO$, are relatively simple, but show close resemblance to the corresponding hydroxy compounds, with the absorptions having shifted to lower frequencies for the sulphates. The peaks are sharp in contrast to the hydroxy compounds.

EXPERIMENTAL.

Reagents: Me_3SiCl was obtained from Midland Silicones; $(Me_3Si)_2NH$, PhSH, all alcohols and non-fluorine cotaining phenols were obtained from B.D.H.; p-FC_6H_4OH, m-FC_6H_4OH, o-FC_6H_4OH and C_6F_5OH were obtained from Pierce Chemical Co.; SF_4 and $(CF_3)_2CO$ were obtained from Peninsular Chemresearch, and NO_2 and MeSH were obtained from Cambrian Chemicals. The silyl compounds were prepared by standard methods outlined in Table 28. Many of the silyl ethers have not been reported in the literature. All liquid samples were stored over 4A sieves until required.

Preparation of thionyl tetrafluoride:

SOF_4 was made by the method of Engelhardt and Smith (38), from SF_4, NO_2 and oxygen in a bomb reaction. The introduction of oxygen in large amounts into a bomb by safe means posed a problem which is not answered in the literature. The following method was found to be satisfactory.

An oxygen cylinder (22 cu.ft.) was pressurised to 500 p.s.i. with oxygen and connected by a hose with suitable adaptors to a 300 ml, stainless steel, Hoke-bomb. The oxygen cylinder was opened at full pressure with the Hoke-valve fully open. After about 15 seconds, both Hoke-valve and the oxygen cylinder were closed. This gave a sufficient quantity of oxygen to proceed with the preparation of SOF_4, as observed from the conversion of the amount of SF_4 used for reaction.

SF_4 (54 gms, 0.5 m.moles) and NO_2 (4 gms, 0.09 m.moles) were condensed into a 400 ml, monel, Hoke-bomb at -196°. While the bomb was at -196°, it was connected by tygon tubing to the bomb with the oxygen. Both valves were opened and the oxygen was condensed into the reaction bomb over a period of about 20 seconds. The bomb was allowed to reach room temperature and heated to 200° for 8 hours in an oven. The bomb was allowed to cool and the contents were bled to a bath at -78° at atmospheric pressure. The crude product was scrubbed with dimethylformamide in a Hoke-bomb to give approximately 45 gms (70 %) of SOF_4, contaminated with small amounts of SO_2F_2, SF_6 and SOF_2.

It cannot be overemphasised that all these operations require extreme caution , as explosions of extreme violence have been reported in reactions of this kind.

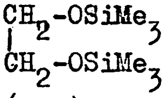
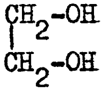
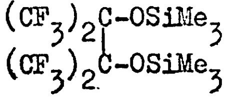
The ^{19}F shift of SOF_4 is reported as being at -91p.p.m. from CCl_3F after conversion from C_4F_8 as reference (131). In this work, the ^{19}F shift for SOF_4 from internal CCl_3F has been found to be -80.3 p.p.m..

To avoid excessive repetition, reference can be made to the following table for spectra which are encountered frequently.

Compound	n.m.r.	i.r.
SOF_4	as above	(35)
SO_2F_2	(6)	(153)
Me_3SiF	(122)	(121)
SiF_4	(124)	(154)

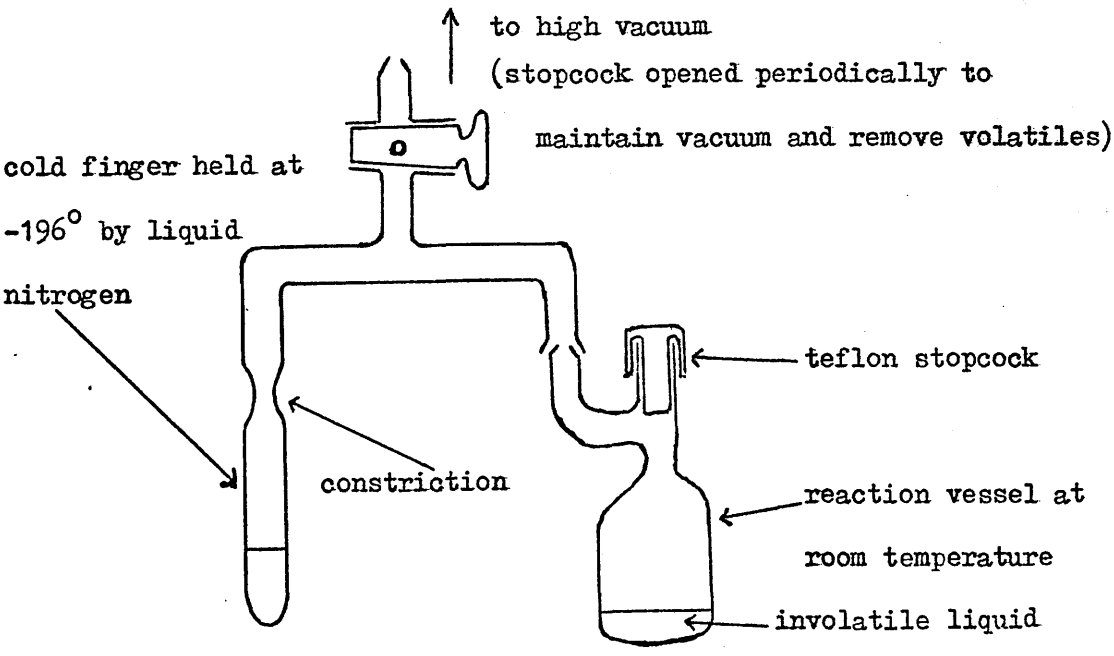
Table 28.

Preparation of silicon compounds.

Compound	Method	Reference	B.Pt.
Me_3SiOPh	$Me_3SiCl/PhOH$	(117)	182-3°/760 mm
$p-Me_3SiOC_6H_4Me$	$Me_3SiCl/p-HOC_6H_4Me$	-	196-8°/758 mm
$m-Me_3SiOC_6H_4Me$	$Me_3SiCl/m-HOC_6H_4Me$	-	195-7°/742 mm
$o-Me_3SiOC_6H_4Me$	$Me_3SiCl/o-HOC_6H_4Me$	-	194-6°/755 mm
$p-Me_3SiOC_6H_4Cl$	$Me_3SiCl/p-HOC_6H_4Cl$	-	204-5°/761 mm
$m-Me_3SiOC_6H_4Cl$	$Me_3SiCl/m-HOC_6H_4Cl$	-	212-3°/750 mm
$o-Me_3SiOC_6H_4Cl$	$Me_3SiCl/o-HOC_6H_4Cl$	-	198-9°/748 mm
$p-Me_3SiOC_6H_4F$	$Me_3SiCl/p-HOC_6H_4F$	-	175-6°/741 mm
$m-Me_3SiOC_6H_4F$	$Me_3SiCl/m-HOC_6H_4F$	-	178-9°/750 mm
$o-Me_3SiOC_6H_4F$	$Me_3SiCl/o-HOC_6H_4F$	-	179-180°/760 mm
$p-Me_3SiOC_6H_4NO_2$	$(Me_3Si)_2NH/p-HOC_6H_4NO_2$	-	89-90°/0.2 mm
$Me_3SiOC_6F_5$	Me_3SiCl/C_6F_5OH	(155)	176-8°/763 mm
$Me_3SiOCH_2CF_3$	$(Me_3Si)_2NH/CF_3CH_2OH$	-	86-7°/754 mm
$Me_3SiOC_6H_{11}$	$Me_3SiCl/C_6H_{11}OH$	-	164-6°/743 mm
$1,2(Me_3SiO)_2C_6H_4$	$Me_3SiCl/1,2(HO)_2C_6H_4$	-	234-6°/743 mm
 $\begin{array}{l} CH_2-OSiMe_3 \\ \vert \\ CH_2-OSiMe_3 \end{array}$	$(Me_3Si)_2NH/$  $\begin{array}{l} CH_2-OH \\ \vert \\ CH_2-OH \end{array}$	(117)	170-2°/734 mm
 $\begin{array}{l} (CF_3)_2C-OSiMe_3 \\ \vert \\ (CF_3)_2C-OSiMe_3 \end{array}$	$(CF_3)_2CO/Li/Me_3SiCl$	(140)	99-102°/ 30 mm
Me_3SiSMe	$Pb(SMe)_2/Me_3SiCl$	(156)	110-1°/760 mm
Me_3SiSPh	$Pb(SPh)_2/Me_3SiCl$	(157)	40-2°/0.3 mm
$Pb(SR)_2$	$PbAc_2/RSH$, R = Me, Ph		
Me_3SiNCS	$AgNCS/Me_3SiCl$	(158)	143-4°/760 mm

The silicon ethers which have not been given a reference in Table 28, have not been described in the literature, but their method of preparation differs little from other preparations described in reference (117).

Reactions: The reactions 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, or distilled in via the vacuum line if sufficiently volatile. The reaction vessel was then cooled to -196° and the stoichiometric amount of SOF_4 required for reaction was weighed in via the vacuum line. Liquid products were distilled from the reaction vessel as shown below, and solids were transferred in the dry-box.



Apparatus for distilling involatile liquids at room temperature.

Reaction 1. SOF_4/Me_3SiOPh.

Me_3SiOPh (10.2 m.moles) and SOF_4 (11.4 m.moles) were allowed to stand at room temperature for 3 hours, during which slow effervescence occurred and the solution turned red. The volatile products were Me_3SiF and small amounts of SOF_4 and SO_2F_2. Phenoxysulphur oxytrifluoride, $PhOS(O)F_3$ (8.4 m.moles), was recovered from the product mixture by slow distillation. Bisphenoxysulphur oxydifluoride, $(PhO)_2S(O)F_2$ (1.1 m.moles) (identified by n.m.r.-see later) remained in the reaction vessel after removal of a red involatile liquid, which moved only under dynamic vacuum.

$PhOS(O)F_3$: Molecular Weight. Found, 198 (mass spec.). Calc., 198.

Infrared. cm^{-1}. CCl_4 soln.	3066 m, 3045 w, 2975 sh, 1972 w, 1949 w, 1872 w, 1782 w, 1589 s, 1486 vs, 1452 s, 1323 vs, 1284 sh, 1267 s, 1235 s, 1172 s, 1143 vs, 1070 m, 1022 s, 1006 w, 972 m, 924 vs, 910 s, 903 s, 854s, 835 vs, 720 m, 684 s.

n.m.r.: $\delta Fe = -67.6$ and $\delta Fa = -89.1$. $J_{FeFa} = 213.2$ Hz.

$\delta C_6H_5 = -7.24s$.

Heating $PhOS(O)F_3$ gave SO_2F_2 and C_6H_5F, both identified by n.m.r.; for C_6H_5F, $\delta F = +113.5$ (124).

Hydrolysis of $PhOS(O)F_3$: on exposure to the atmosphere in a glass vessel, $PhOS(O)F_3$ was found to give SO_2F_2, SiF_4, C_6H_5F (all identified by n.m.r.) and $PhOSO_2F$, also identified by n.m.r., $\delta F = -36.6$.

M.Wt. for $PhOSO_2F$; Found, 166 (mass spec.). Calc., 166.

2. $SOF_4/2Me_3SiOPh$

Me_3SiOPh (14.0 m.moles) and SOF_4 (7.1 m.moles) were allowed to stand at room temperature for 48 hours. The products were Me_3SiF (13.8 m.moles) and a small amount of SO_2F_2. Removal of the volatiles left bisphenoxysulphur oxydifluoride, $(PhO)_2S(O)F_2$, contaminated with a red liquid. $(PhO)_2S(O)F_2$ was recrystallised from Cl_2FCCF_2Cl at 0°, to give a colourless solid which melted at 80° with decomposition.

Analysis for $(PhO)_2S(O)F_2$: Found. C, 53.1; H, 3.8; F, 14.1; S, 11.9.
Calculated. C, 52.9; H, 3.7; F, 14.0; S, 11.8.

Infrared cm^{-1}. 3065 m, 3044 w, 2970 sh, 1942 w, 1834 w, 1780 w,
CCl_4 soln. 1458 m, 1424 w, 1407 w, 1288 vs, 1231 m, 1219 m,
1173 s, 1146 vs, 1069 m, 1022 s, 953 s, 910 vs,
851 m, 712 m, 688 m.

n.m.r.: $\delta F = -89.0s$. $\delta C_6H_5 = -7.31s$.

$(PhO)_2S(O)F_2$, on heating to 80°, gave $PhOSO_2F$ and $(PhO)_2S(O)F_2$, identified by mass spectrum and n.m.r., and SO_2F_2, identified by i.r.. Exposure of $(PhO)_2S(O)F_2$ to moisture in a glass vessel gave SiF_4, identified by i.r., and $(PhO)_2SO_2$, identified by mass spectrum.

3. $SOF_4/3Me_3SiOPh$.

Me_3SiOPh (12.0 m.moles) and SOF_4 (4.1 m.moles) were allowed to react at room temperature for 30 minutes. The products were Me_3SiF (11.8 m.moles), $(PhO)_2S(O)F_2$, identified by n.m.r., and trisphenoxysulphur oxyfluoride, $(PhO)_3S(O)F$, which is unstable and was not isolated from the mixture.

n.m.r.: The mixture showed two singlets in the ^{19}F n.m.r. at -88.2 ($(PhO)_2S(O)F_2$), and at -68.4 which is presumed to be due to $(PhO)_3S(O)F$.

4. $SOF_4/4Me_3SiOPh$.

Me_3SiOPh (12.0 m.moles) and SOF_4 (3.0 m.moles) were allowed to react at room temperature for 20 minutes. The products were Me_3SiF (11.9 m.moles) and a dark red liquid from which was distilled diphenylsulphate $(PhO)_2SO_2$, as the only identifiable product.

Mass spectrum. m/e found, 250. Calc for parent ion of $(PhO)_2SO_2$, 250.

5. $SOF_4/p\text{-}Me_3SiOC_6H_4Me$.

$p\text{-}Me_3SiOC_6H_4Me$ (10.5 m.moles) and SOF_4 (11.2 m.moles) were allowed to stand at room temperature for 3 hours. The products were Me_3SiF (10.4 m.moles), p-tolyoxysulphur oxytrifluoride, $p\text{-}MeC_6H_4OS(O)F_3$ (9.9 m.moles) and bis-p-tolyloxysulphur oxydifluoride, $(p\text{-}MeC_6H_4O)_2S(O)F_2$ (1.1 m.moles), identified by n.m.r., see later.

$p\text{-}MeC_6H_4OS(O)F_3$. M. Wt., found, 212 (mass spec.). Calc., 212.

Analysis: Found. C, 39.8; H, 3.5; F, 26.8; S, 14.9.

Calculated. C, 39.6; H, 3.3; F, 26.9; S, 15.1.

Infrared cm^{-1}	3108 sh, 3044 w, 2992 sh, 2958 w, 2929 m, 1892 m,
CCl_4 soln.	1643 w, 1604 s, 1500 vs, 1451 w, 1382 w, 1324 vs,

Infrared cm^{-1} cont. 1314 w, 1287 m, 1220 m, 1179 m, 1149 s, 1019 m, 938 s, 928 vs, 862 m, 850 s, 829 s, 721 m, 692 w, 631 w, 549 s, 501 m.

n.m.r.: $\delta Fe = -67.2$, $\delta Fa = -88.4$, and $J_{FeFa} = 221.5$ Hz..

$\delta C_6H_4 = -7.19$ multiplet, and $\delta CH_3 = -2.32$s.

Heating p-$MeC_6H_4OS(O)F_3$ at 90° gave p-MeC_6H_4F and SO_2F_2, both identified by n.m.r., and solids. For p-MeC_6H_4F, $\delta F = 120.2$ (124).

Hydrolysis of p-$MeC_6H_4OS(O)F_3$: Exposure of p-$MeC_6H_4OS(O)F_3$ to the atmosphere in a glass vessel gave SO_2F_2, SiF_4, p-$MeC_6H_4OSO_2F$ and solids. For p-$MeC_6H_4OSO_2F$, M. Wt. found, 190 (mass spec.). Calc., 190. $\delta F = -37.1$s.

6. SOF_4/2p-$Me_3SiOC_6H_4Me$ (on standing)

p-$Me_3SiOC_6H_4Me$ (12.2 m.moles) and SOF_4 (6.1 m.moles) were allowed to stand for 48 hours. The products were Me_3SiF (11.9 m.moles) and bis-p-tolyloxysulphur oxydifluoride, (p-$MeC_6H_4O)_2S(O)F_2$ (4.9 m.moles).

Analysis for (p-$MeC_6H_4O)_2S(O)F_2$: Found. C, 56.3; H, 4.9; F, 12.9; S, 10.9.
Calculated. C, 56.0; H, 4.7; F, 12.7; S, 10.7.

Infrared cm^{-1}. CCl_4 soln. 3105 sh, 3039 m, 2991 w, 2958 w, 2928 m, 2868 w, 1893 m, 1598 s, 1501 vs, 1450 m, 1380 m, 1321 m, 1303 w, 1284 vs, 1230 m, 1209 s, 1183 vs, 1151 vs, 1106 s, 1039 m, 1019 vs, 955 m, 892 s, 858 vs, 825 vs, 713 s, 680 vs.

n.m.r.: $\delta F = -86.0$s, $\delta C_6H_4 = -7.14$ multiplet, δCH_3 -2.32s.

Thermal and hydrolytic decomposition of $(p\text{-MeC}_6H_4O)_2S(O)F_2$ gave $(p\text{-MeC}_6H_4O)_2SO_2$. M.Wt. found, 278 (mass spec.). Calc., 278.

7. $SOF_4/2$ $p\text{-Me}_3SiOC_6H_4Me$ (with shaking).

$p\text{-Me}_3SiOC_6H_4Me$ (12.3 m.moles) and SOF_4 (6.2 m.moles) were agitated continuously at room temperature for 12 hours, when all the SOF_4 had reacted. The volatiles contained only Me_3SiF (12.1 m.moles). $p\text{-MeC}_6H_4OS(O)F_3$ (2.8 m.moles), identified by n.m.r., was distilled from the product mixture, to give a solid mixture of $(p\text{-MeC}_6H_4O)_2S(O)F_2$, and tris-p-tolyloxysulphur oxyfluoride which was not isolated and was partially characterised by n.m.r., giving a singlet at -67.0 in the ^{19}F spectrum.

8. $SOF_4/3$ $p\text{-Me}_3SiOC_6H_4Me$.

$p\text{-Me}_3SiOC_6H_4Me$ (12.6 m.moles) and SOF_4 (4.3 m.moles) were allowed to stand for 30 minutes at room temperature. The products were Me_3SiF (12.5 m.moles) and a mixture of $(p\text{-MeC}_6H_4O)_2S(O)F_2$ and $(p\text{-MeC}_6H_4O)_3S(O)F$ in approximately equal amounts, as indicated by ^{19}F n.m.r. spectrum. The mixture decomposed to an intractable mass on standing.

9. $SOF_4/4$ $p\text{-Me}_3SiOC_6H_4Me$.

$p\text{-Me}_3SiOC_6H_4Me$ (13.2 m.moles) and SOF_4 (3.4 m.moles) were

Me_3SiF (13.2 m.moles) and a red viscous oil from which was distilled $(p\text{-}MeC_6H_4O)_2SO_2$, identified by mass spectroscopy. M.Wt. found, 278 (mass spec.). Calc., 278.

10. $SOF_4/m\text{-}Me_3SiOC_6H_4Me$.

$m\text{-}Me_3SiOC_6H_4Me$ (12.5 m.moles) and SOF_4 (13.0 m.moles) were allowed to stand at room temperature for 3 hours. The products were Me_3SiF (12.5 m.moles), SO_2F_2 (trace), m-tolyloxysulphur oxytrifluoride, $m\text{-}MeC_6H_4OS(O)F_3$ (8.9 m.moles) and tetra-m-tolyl-orthosulphate, $(m\text{-}MeC_6H_4O)_4SO$ (1.4 m.moles).

$m\text{-}MeC_6H_4OS(O)F_3$: M.Wt. found, 212 (mass spec.). Calc., 212.

Infrared cm^{-1}. 3070 sh, 3035 w, 2957 w, 2925 m, 2862 w, 1941 w,
CCl_4 soln. 1838 w, 1619 s, 1488 s, 1453 vs, 1380 w, 1323 vs,
1281 sh, 1268 m, 1220 s, 1122 vs, 1083 w, 1008 m,
996 w, 948 vs, 923 s, 902 m, 875 vs, 719 s, 684 s,
634 w.

n.m.r.: $\delta Fe = -67.0$, $\delta Fa = -88.2$. $J_{FeFa} = 213.4$ Hz..
$\delta C_6H_4 = -7.08$ multiplet, $\delta CH_3 = -2.22$.

$m\text{-}MeC_6H_4OS(O)F_3$ decomposes slowly on standing and quickly on heating to 75° to give $m\text{-}MeC_6H_4F$, SO_2F_2 and $m\text{-}MeC_6H_4OSO_2F$, all identified by n.m.r.. For $m\text{-}MeC_6H_4F$, $\delta F = +115.2$ (124). For $m\text{-}MeC_6H_4OSO_2F$, $\delta F = -36.9$s, M.Wt. found, 190 (mass spec.). Calc., 190.

$(m\text{-}MeC_6H_4O)_4SO$: Analysis: Found. C, 69.4; H, 5.7; S, 7.3.
Calculated. C, 70.6; H, 5.7; S, 6.9.

n.m.r.: $\delta\ C_6H_4$ = -7.12 multiplet, $\delta\ CH_3$ = -2.31s.

11. SOF_4/o-$Me_3SiOC_6H_4Me$.

o-$Me_3SiOC_6H_4Me$ (13.9 m.moles) and SOF_4 (14.0 m.moles) were allowed to stand at room temperature for 3 hours. The products were Me_3SiF (13.8 m.moles), o-tolyloxysulphur oxytrifluoride, o-$MeC_6H_4OS(O)F_3$ (8.1 m.moles) and a yellow viscous liquid.

o-$MeC_6H_4OS(O)F_3$: M.Wt. found, 212 (mass spec.). Calc., 212.

Several attempts to obtain i.r. spectra were unsuccessful.

n.m.r.: δ Fe = -67.4, δ Fa = -86.4. J_{FeFa} = 209.4 Hz.

$\delta\ C_6H_4$ = -7.17 multiplet, $\delta\ CH_3$ = -2.18s.

o-$MeC_6H_4OS(O)F_3$ decomposes on standing to a tar and SO_2F_2. Heating to 75° gives o-MeC_6H_4F, SO_2F_2 and solids. For o-MeC_6H_4F, δF = 119.0 (124). Hydrolysis gave SO_2F_2, and o-$MeC_6H_4OSO_2F$, δF = -38.5s.

12. SOF_4/p-$Me_3SiC_6H_4Cl$.

p-$Me_3SiOC_6H_4Cl$ (10.5 m.moles) and SOF_4 (11.0 m.moles) were allowed to stand at room temperature for 3 hours. The products were Me_3SiF (10.4 m.moles) and p-chlorophenoxysulphur oxytrifluoride p-$ClC_6H_4OS(O)F_3$ (8.9 m.moles).

p-$ClC_6H_4OS(O)F_3$: M.Wt. found, 232 (mass spec. $^{35}ClC_6H_4OS(O)F_3$).

Calc., 232.

Analysis: Found. C, 31.1; H, 1.9; F, 25.3; Cl, 15.4; S, 13.5.

Calculated. C, 31.0; H, 1.7; F, 24.5; Cl, 15.3; S, 13.8.

Infrared cm^{-1}. CCl_4 soln.	3104 m, 3075 w, 1891 m, 1590 m, 1484 vs, 1434 w, 1409 m, 1327 vs, 1273 m, 1211 w, 1173 s, 1151 s, 1092 vs, 1017 s, 924 vs, 848 vs, 837 vs, 730 w, 709 m, 684 m.

n.m.r.: $\delta Fe = -68.1$, $\delta Fa = -89.7$. $J_{FeFa} = 221.2$ Hz.

$\delta C_6H_4 = -7.20$ multiplet.

Heating p-$ClC_6H_4OS(O)F_3$ at 110° for 12 hours gave SO_2F_2 and a dark tarry substance. p-ClC_6H_4F was not identified. Hydrolysis gave SO_2F_2, SiF_4 and p-$ClC_6H_4OSO_2F$. For $^{35}ClC_6H_4OSO_2F$, M.Wt. found, 210 (mass spec.). Calc., 210. $\delta F = -36.8$.

13. SOF_4/2 p-$Me_3SiOC_6H_4Cl$ (on standing).

p-$Me_3SiOC_6H_4Cl$ (12.1 m.moles) and SOF_4 (6.1 m.moles) were allowed to stand at room temperature for 48 hours. The products were Me_3SiF (12.1 m.moles) and bis-p-chlorophenoxysulphur oxydifluoride, $(p\text{-}ClC_6H_4O)_2S(O)F_2$ (5.2 m.moles).

Analysis: Found. C, 42.4; H, 2.6; F, 11.3; Cl, 21.0; S, 9.2.

Calculated. C, 42.0; H, 2.4; F, 11.1; Cl, 20.8; S, 9.4.

Infrared cm^{-1}. CCl_4 soln.	3095 w, 3070 w, 1887 w, 1590 m, 1483 vs, 1403 w, 1325 w, 1294 s, 1287 s, 1172 m, 1220 w, 1174 s, 1149 s, 1098 vs, 1012 s, 910 vs, 838 vs, 723 m, 698 s, 664 w.

n.m.r.:δF = -89.0s; δC_6H_4 = -7.34 multiplet.

$(p\text{-}ClC_6H_4O)_2S(O)F_2$ decomposes on heating to give SO_2F_2 and a tar, at 95°. Hydrolysis gives $(p\text{-}ClC_6H_4O)_2SO_2$ and HF. M.Wt for $(^{35}ClC_6H_4O)_2SO_2$, found, 318 (mass spec.). Calc., 318.

14. SOF_4/2 p-$Me_3SiOC_6H_4Cl$ (with shaking).

p-$Me_3SiOC_6H_4Cl$ (11.5 m.moles) and SOF_4 (5.8 m.moles) were agitated continuously for 12 hours at room temperature. The products were Me_3SiF (11.4 m.moles), p-$ClC_6H_4OS(O)F_3$, identified by n.m.r., and a solid mixture of $(p\text{-}ClC_6H_4O)_2S(O)F_2$, identified by n.m.r., and tris-p-chlorophenoxysulphur oxyfluoride, $(p\text{-}ClC_6H_4O)_3S(O)F$. The latter was partially characterised by n.m.r., showing a singlet at -69.9 in the ^{19}F n.m.r. spectrum. The mixture decomposed on standing.

15. SOF_4/3 p-$Me_3SiOC_6H_4Cl$.

p-$Me_3SiOC_6H_4Cl$ (12.4 m.moles) and SOF_4 (m.moles) were left standing for 30 minutes. The products were Me_3SiF and a solid mixture of $(p\text{-}ClC_6H_4O)_2S(O)F_2$ and $(p\text{-}ClC_6H_4O)_3S(O)F$, both identified by n.m.r.. The mixture decomposed on standing to a black tar.

16. SOF_4/4 p-$Me_3SiOC_6H_4Cl$. See over.

p-$Me_3SiOC_6H_4Cl$ (10.5 m.moles) and SOF_4 (2.6 m.moles) were allowed to stand at room temperature for 30 minutes. The products were Me_3SiF (10.5 m.moles) and a dark red liquid from which was distilled (p-$ClC_6H_4O)_2SO_2$, identified by mass spectroscopy.

For $(^{35}ClC_6H_4O)_2SO_2$, M.Wt found, 318 (mass spec.). Calc., 318.

17. SOF_4/m-$Me_3SiOC_6H_4Cl$.

m-$Me_3SiOC_6H_4Cl$ (11.5 m.moles) and SOF_4 (12.9 m.moles) were allowed to stand at room temperature for 3 hours. The products were Me_3SiF (11.4 m.moles) and m-chlorophenoxysulphur oxytrifluoride, m-$ClC_6H_4OS(O)F_3$ (9.5 m.moles).

m-$ClC_6H_4OS(O)F_3$: M.Wt, $^{35}ClC_6H_4OS(O)F_3$, found, 232 (mass spec.). Calc., 232.

Analysis: Found. C, 31.1; H, 1.7; F, 24.8; Cl, 15.2; S, 13.9.

Calculated. C, 31.0; H, 1.7; F, 24.5; Cl, 15.3; S, 13.8.

Infrared cm^{-1}. CCl_4 soln.	3085 w, 3065 m, 1938 w, 1705 w, 1602 s, 1584 vs, 1530 s, 1519 s, 1468 vs, 1433 s, 1327 vs, 1295 m, 1262 m, 1163 s, 1156 m, 1088 m, 1070 m, 1004 s, 941 vs, 898 s, 864 vs, 814 s, 718 m, 703 s, 675 s, 653 w, 618 w.

n.m.r.: $\delta Fe = -68.4$, $\delta Fa = -89.5$. $J_{FeFa} = 219.8$ Hz..

Heating m-$ClC_6H_4OS(O)F_3$ to 130° gave SO_2F_2, m-$ClC_6H_4OSO_2F$ and solids. Hydrolysis gave the same products along with HF. For m-$ClC_6H_4OSO_2F$, mass spec. shows m/e at 210 and 212; $^{35}ClC_6H_4OSO_2F$ and $^{37}ClC_6H_4OSO_2F$

require m/e 210 and 212. F = -38.8s.

18. SOF_4/o-$Me_3SiOC_6H_4Cl$.

o-$Me_3SiOC_6H_4Cl$ (9.4 m.moles) and SOF_4 (10.6 m.moles) were allowed to stand at room temperature for 3 hours. The products were Me_3SiF (7.1 m.moles), SO_2F_2, SiF_4 and o-$ClC_6H_4OSO_2F$ along with an intractable tar.

For o-$ClC_6H_4OSO_2F$, mass spec. showed m/e 210 and 212. $^{35}ClC_6H_4OSO_2F$ and $^{37}ClC_6H_4OSO_2F$ require m/e 210 and 212.

n.m.r.: $\delta F = -40.6$s; $\delta C_6H_4 = -7.18$ multiplet.

19. SOF_4/p-$Me_3SiOC_6H_4F$

p-$Me_3SiOC_6H_4F$ (11.1 m.moles) and SOF_4 (11.9 m.moles) were allowed to stand at room temperature for 3 hours. The products were Me_3SiF (11.0 m.moles) and p-fluorophenoxysulphur oxytrifluoride, p-$FC_6H_4OS(O)F_3$ (9.8 m.moles).

p-$FC_6H_4OS(O)F_3$. M.Wt. found, 216 (mass spec.). Calc., 216.

Analysis: Found. C, 33.7; H, 2.0; F; 34.8; S, 15.1.

Calculated. C, 33.4; H, 1.8; F; 35.2; S, 14.8.

Infrared cm^{-1}. CCl_4 soln. 3087 w, 1885 w, 1606 m, 1553 m, 1508 vs, 1462 s, 1441 w, 1331 s, 1239 vs, 1208 m, 1092 m, 1012 m, 1003 m, 978 m, 936 m, 928 s, 911 s, 854 s, 847 s, 799 m, 685 w, 624 m.

n.m.r.: δFe = -67.4, δFa = -88.2. J_{FeFa} = 215.4 Hz.. δC-$\underline{F}$ = 112.3.

δC_6H_4 = -7.08 multiplet.

Heating p-$FC_6H_4OS(O)F_3$ at 120° gave SO_2F_2 as the only identifiable product. p-FC_6H_4F was not identified from the pyrolysis.

Hydrolysis of p-$FC_6H_4OS(O)F_3$ gave HF, SO_2F_2 and p-$FC_6H_4OSO_2F$.

For p-$FC_6H_4OSO_2F$, M.Wt. found, 194 (mass spec.). Calc., 194. δF = -36.2.

20. SOF_4/m-$Me_3SiOC_6H_4F$.

m-$Me_3SiOC_6H_4F$ (10.8 m.moles) and SOF_4 (11.5 m.moles) were allowed to stand for 3 hours at room temperature. The products were Me_3SiF (10.4 m.moles) and m-fluorophenoxysulphur oxytrifluoride, m-$FC_6H_4OS(O)F_3$ (9.5 m.moles).

m-$FC_6H_4OS(O)F_3$: M.Wt. found, 216 (mass spec.). Calc., 216.

Analysis. Found. C, 33.5; H, 1.9; F, 35.0; S, 14.6.

Calculated. C, 33.4; H, 1.8; F, 35.2; S, 14.8.

Infrared cm^{-1}.	3096 w, 1611 vs, 1546 m, 1484 s, 1453 m, 1334 vs,
CCl_4 soln.	1302 m, 1272 s, 1246 s, 1231 m, 1157 m, 1112 vs,
	1076 m, 1012 m, 968 vs, 949 s, 882 vs, 863 s,
	818 s, 751 vs, 684 s, 634 m.

n.m.r.: δFe = -67.6, δFa = -88.9. J_{FeFa} = 218.0 Hz.. δC-$\underline{F}$ = 108.2.

Heating m-$FC_6H_4OS(O)F_3$ at 130° gave partial decomposition to SO_2F_2, m-$FC_6H_4OSO_2F$ and solids. Hydrolysis gave the same products along with HF. For m-$FC_6H_4OSO_2F$, mass spec gave m/e 194. Calc. for molecular ion, 194. δS-$\underline{F}$ = -37.6s, δC-F = 110.3.

21. SOF_4/o-$Me_3SiOC_6H_4F$.

o-$Me_3SiOC_6H_4F$ (8.5 m.moles) and SOF_4 (9.7 m.moles) were allowed to stand at room temperature for three hours. The products were Me_3SiF (8.1 m.moles), SO_2F_2 (trace) and o-fluorophenoxysulphur oxytrifluoride, o-$FC_6H_4OS(O)F_3$ (6.5 m.moles).

o-$FC_6H_4OS(O)F_3$ proved too unstable to give a satisfactory analysis or an i.r. spectrum.

M.Wt. found, 216 (mass spec). Calc., 216.

n.m.r.: δFe = -69.8, δFa = -86.1. J_{FeFa} = 218.0 Hz.. δC-$\underline{F}$ = 129.4.

o-$FC_6H_4OS(O)F_3$ decomposes slowly on standing and quickly on heating at 70° to give SO_2F_2, o-$FC_6H_4OSO_2F$ and a black mass. Hydrolysis gave the same products along with HF.

For o-$FC_6H_4OSO_2F$, mass spec. gave m/e 194. Parent ion requires 194. δS-$\underline{F}$ = -38.8. δC-$\underline{F}$ = 127.1.

22. SOF_4/p-$Me_3SiOC_6H_4NO_2$.

p-$Me_3SiOC_6H_4NO_2$ (7.4 m.moles) and SOF_4 (8.9 m.moles) were left to stand at room temperature for 3 hours. The products were Me_3SiF (7.3 m.moles) and unreacted SOF_4 (3.9 m.moles), leaving a solid which analysed for bis-p-nitrophenoxysulphur oxydifluoride, (p-$NO_2C_6H_4O)_2S(O)F_2$ (3.1 m.moles).

(p-$NO_2C_6H_4O)_2S(O)F_2$: Analysis. Found. C, 40.2; H, 2.6; F, 10.5; N, 8.0; S, 8.9. Calculated. C, 40.0; H, 2.2; F, 10.7; N, 7.9; S, 9.4.

The infrared spectrum was measured using a KBr disc and a nujol mull.

The disc and mull spectrum are closely analagous, but the disc spectrum has fewer bands.

Infrared cm^{-1}. KBr disc. 3115 w, 3080 w, 1612 m, 1589 s, 1532 s, 1498 m, 1482 s, 1451 m, 1419 w, 1342 vs, 1283 m, 1232 m, 1214 w, 1170 s, 1142 s, 1109 s, 1008 w, 918 m, 863 s, 782 m, 751 s, 717 m, 686 m, 622w.

Attempts to obtain n.m.r. spectrum were unsuccessful as the compound is insoluble in a range of boiling solvents, such as CH_3CN, CCl_4, CH_3NO_2, $(CH_3)_2SO$, and dissolved slowly in EtOH and water with decomposition.

Mass spectrum showed the diarylsulphate, $(p\text{-}NO_2C_6H_4O)_2SO_2$, m/e 328, as required for the parent ion.

23. $SOF_4/Me_3SiOC_6F_5$

$Me_3SiOC_6F_5$ (7.1 m.moles) and SOF_4 (10.0 m.moles) were heated at 110°for 17 hours. The products were Me_3SiF (3.1 m.moles), unreacted SOF_4 (6.0 m.moles), SO_2F_2 (trace), unreacted $Me_3SiOC_6F_5$ (3.9 m.moles) and trispentafluorophenoxysulphur oxyfluoride, $(C_6F_5O)_3S(O)F$ (2.1 m.moles).

$(C_6F_5O)_3S(O)F$. Analysis. Found. C, 35.2; F, 49.8; S, 5.4.

Calculated. C, 35.0; F, 49.4; S, 5.2.

Infrared cm^{-1}. CCl_4 soln. 2675 w, 2458 w, 1718 m, 1705 m, 1651 w, 1513 vs, 1496 s, 1403 w, 1375 w, 1318 s, 1250 w, 1220 w, 1148 w, 1137 m, 1005 vs, 943 w, 839 m, 718 m, 694 s, 664 s.

n.m.r.: δS-$\underline{F}$ = -68.1s. δC-$\underline{F}$ = 154.0 (o), 157.2 (p), 164.2 (m).
$(C_6F_5O)_3S(O)F$ decomposes on heating above 150° and on exposure to the atmosphere to unidentifiable products.

24. $SOF_4/C_6H_4(OSiMe_3)_2$.

$C_6H_4(OSiMe_3)_2$ (11.9 m.moles) and SOF_4 (14.3 m.moles) were left to stand at room temperature for 8 days. The products were Me_3SiF (22.2 m.moles), unreacted SOF_4 (6.8 m.moles) and bis-phenylene-ortho-sulphate, $(C_6H_4O_2)_2SO$, a colourless solid, recrystallised from n-pentane.

$(C_6H_4O_2)_2SO$. Analysis: Found. C, 54.6; H, 3.2; S, 11.9.
Calculated. C, 54.6; H, 3.0; S, 12.1.

Infrared cm^{-1}. CCl_4 soln. 3099 w, 3078 m, 3056 w, 1621 m, 1485 vs, 1467 m, 1410 w, 1349 w, 1334 m, 1278 s, 1258 vs, 1249 vs, 1177 s, 1152 w, 1102 s, 1013 s, 980 w, 921 m, 874 s, 856 m, 818 vs, 756 vvs, 720 vvs, 630 m.

n.m.r.: δC_6H_4 = -6.92s.
$(C_6H_4O_2)_2SO$ decomposes to a tar on exposure to the atmosphere, from which can be identified $C_6H_4(OH)_2$ by i.r. on comparison with an authentic sample.

25. $SOF_4/Me_3SiOCH_2CH_2OSiMe_3$

$Me_3SiOCH_2CH_2OSiMe_3$ (7.4 m.moles) and SOF_4 (8.4 m.moles) were allowed to stand for 2 hours at room temperature. The products were a complex mixture of SO_2F_2, SOF_4, SiF_4 and a tarry residue, which was not further investigated.

26. $SOF_4/Me_3SiOC(CF_3)_2C(CF_3)_2OSiMe_3$.

$Me_3SiOC(CF_3)_2C(CF_3)_2OSiMe_3$ (5.4 m.moles) and SOF_4 (8.3 m.moles) were heated at 130° for 3 days with no reaction occurring.

27. SOF_4/Me_3SiOMe.

Me_3SiOMe (10.4 m.moles) and SOF_4 (11.0 m.moles) reacted immediately at -76°. The products were Me_3SiF (10.3 m.moles), SO_2F_2 (10.2 m.moles) and MeF (10.2 m.moles), identified by n.m.r. (124). For MeF, δCH_3 = -4.13d, J_{H-F} = 48.0 Hz..

28. SOF_4/Me_3SiOEt.

Me_3SiOEt (10.8 m.moles) and SOF_4 (11.0 m.moles) were allowed to stand at room temperature for 2 hours. The products were Me_3SiF (10.4 m.moles), SO_2F_2 (10.1 m.moles) and EtF (10.1 m.moles), identified by n.m.r.(124). For CH_3CH_2F, δCH_3 = -1.21 two triplets, and δCH_2 = -4.32 two quartets. J_{H-F} = 25.3 Hz..

29. $SOF_4/Me_3SiOCH_2CF_3$. See over.

$Me_3SiOCH_2CF_3$ (10.3 m.moles) and SOF_4 (11.1 m.moles) were left to stand for 3 hours at room temperature. The products were Me_3SiF (10.1 m.moles), SO_2F_2 (10.1 m.moles) and CF_3CH_2F (10.4 m.moles), identified by n.m.r. (124). For CF_3CH_2F, CF_3 = 77.9 multiplet, $CH_2\underline{F}$ = 239.4 multiplet. CH_2 = -3.95 two quartets, J_{H-F} = 46.0 Hz..

30. $SOF_4/Me_3SiOC_6H_{11}$.

$Me_3SiOC_6H_{11}$ (8.9 m.moles) and SOF_4 (9.8 m.moles) were allowed to stand for 4 hours at room temperature. The products were a complex mixture of SO_2F_2, SOF_4, SiF_4, Me_3SiF and a black tar, which was not investigated further.

31. $SOF_4/(Me_3Si)_2O$.

$(Me_3Si)_2O$ (9.6 m.moles) and SOF_4 (10.4 m.moles) were left to stand at room temperature for 2 hours, during which slow effervescence occurred. The products were SO_2F_2 (9.3 m.moles) and Me_3SiF (9.2 m.moles).

32. SOF_4/Me_3SiSMe.

Me_3SiSMe (8.3 m.moles) and SOF_4 (9.6 m.moles) reacted slowly at -76° and more quickly when raised to room temperature. The products were Me_3SiF (8.1 m.moles) and unreacted SOF_4 (6.4 m.moles).

A viscous oil remained in the reaction vessel, which was shown to contain MeSSMe by n.m.r. and mass spectrometry. The oil went black on standing. For MeSSMe, ^{1}H n.m.r. showed a singlet at -2.44, in agreement with an authentic sample. Mass spec. showed m/e at 47 and 94, corresponding to CH_3S^+ and $C_2H_6S_2^+$.

33. SOF_4/Me_3SiSPh.

Me_3SiSPh (9.1 m.moles) and SOF_4 (10.4 m.moles) were allowed to stand at room temperature for 5 hours. The products were a complex mixture of SO_2F_2, SiF_4, SOF_4 and Me_3SiF. A black mass remained from which was extracted PhSSPh by CCl_4 and identified by n.m.r. and i.r. by comparison with an authentic sample.

34. SOF_4/Me_3SiNCS.

Me_3SiNCS (8.4 m.moles) and SOF_4 (9.3 m.moles) were left standing for 3 hours. Initially, colourless solids were deposited which turned red on standing. The products were Me_3SiF (8.2 m.moles) and unreacted SOF_4 (5.1 m.moles), leaving a red crystalline solid which was air stable. The exact nature of this solid is indeterminate, but the analysis compares with that of $(NCS)_4SO$.

Analysis for red solid. Found. C, 17.6; F, 0.2; N, 20.3; S, 61.4.

Calculated for $(NCS)_4SO$. C, 17.2; F, 0.0; N, 20.0; S, 57.2.

The infrared spectrum obtained from a pressed disc and nujol mull were comparable, but the disc spectrum showed fewer bands.

Infrared cm^{-1}. KBr disc. 3430 m, 2155 w, 2045 w, 1618 w, 1437 m, 1220 vvs (vbr), 1162 sh, 1063 w, 995 w. There were no bands in the far infrared.

CHAPTER III

REACTIONS OF THE ARYLOXYSULPHUR OXYTRIFLUORIDES AND RELATED REACTIONS.

INTRODUCTION

Few reactions of SOF_4 have been reported where single bond formation to sulphur is maintained when fluorine atoms are replaced by less electronegative substituents. The dialkylaminosulphur oxytrifluorides, $R_2NS(O)F_3$ (R = Me (135), R = Et (147)), are quite stable possibly because there is not a ready reaction pathway for their decomposition. The aryloxysulphur oxytrifluorides are stable to varying degrees, but decompose readily with the elimination of SO_2F_2 on standing or with heating.

This chapter is concerned with the attempted formation of derivatives of thionyl tetrafluoride in which single bonds to sulphur were maintained, but has not succeeded for three main reasons.

1. The ease with which SOF_4 assumes double bonding pervades its chemistry.

$$SOF_4 + 2RNH_2 \longrightarrow RN{=}S(O)F_2 + RNH_2.HF \quad (86)$$

$$SOF_4 + (Me_3Si)_3N \longrightarrow Me_3SiN{=}S(O)F_2 + Me_3SiF \quad (56)$$

$$SOF_4 + Me_3SiOMe \longrightarrow SO_2F_2 + MeF + Me_3SiF$$

(this work)

2. Inertness of SOF_4.

Sulphur VI compounds are the most stable among the family of sulphur fluorides, notably SF_6 and SO_2F_2. Reactions of the lower valent sulphur fluorides, such as SF_4, require controlled conditions, while many of the reactions of SOF_4 have required forcing conditions or at least longer reaction times.

3. Ease of decomposition.

The unusual stereochemistry at sulphur in SOF_4, of trigonal bipyramidal symmetry, is likely to be found in derivatives of SOF_4 where fluorine atoms have been replaced by other groups or atoms which form single bonds. This possibly gives rise to the low stability of such compounds. The $(ArO)_4SO$ compounds, which are assumed to form in the reactions $SOF_4/4Me_3SiOAr$, readily eliminate the diarylsulphates, $(ArO)_2SO_2$, which have a more stable tetrahedral configuration at sulphur. Increased double bonding is probably a contributory factor as well.

Summary of Reactions.

1. $PhOS(O)F_3 + Me_3SiOC_6F_5 \longrightarrow Me_3SiF + \text{oil}$
2. $PhOS(O)F_3 + Me_3SiNMe_2 \longrightarrow (PhO)_2S(O)F_2 + Me_3SiF + \text{oil}$
3. $p\text{-}MeC_6H_4OS(O)F_3 + Me_3SiNMe_2 \longrightarrow (p\text{-}MeC_6H_4O)_2S(O)F_2 + Me_3SiF$
   $+ \text{oil}$
4. $PhOS(O)F_3 + Me_3SiOEt \longrightarrow PhOSO_2F + EtF + Me_3SiF$
5. $PhOS(O)F_3 + (Me_3Si)_2NH \longrightarrow 2Me_3SiF + \text{tar}$
6. $PhOS(O)F_3 + (Me_3Si)_2NMe \longrightarrow 2Me_3SiF + MeN{=}S({=}O)(F)OPh$
7. $m\text{-}FC_6H_4OS(O)F_3 + (Me_3Si)_2NMe \longrightarrow 2Me_3SiF +$
   $MeN{=}S({=}O)(F)OC_6H_4m\text{-}F$
8. $Me_2NS(O)F_3 + HCl \longrightarrow SOF_2 + Cl_2 + \text{solids}$
9. $SOF_2 + Cl_2 + CsF \longrightarrow$ no reaction
10. $Me_2NS(O)F + Cl_2 + CsF \longrightarrow$ solids
11. $CF_3SF_3 + NO_2 + O_2 \longrightarrow$ no reaction
12. $(CF_3)_2CFSF_3 + NO_2 + O_2 \longrightarrow$ no reaction
13. $CF_3CF{=}CF_2 + SOF_4 + CsF \longrightarrow$ no reaction
14. $CF_3S(O)F + AgF_2 \longrightarrow CF_4 + CF_3SF_3 + SO_2F_2$

1. $PhOS(O)F_3/Me_3SiOC_6F_5$.

The reaction was hoped to yield the mixed aryloxy derivative, $PhOS(=O)(OC_6F_5)F_2$, but it was not isolated.

$$PhOS(O)F_3 + Me_3SiOC_6F_5 \not\longrightarrow PhOS(=O)(OC_6F_5)F_2 + Me_3SiF$$

SOF_4 and $Me_3SiOC_6F_5$ react together only under forcing conditions, but the reaction between $PhOS(O)F_3$ and $Me_3SiOC_6F_5$ occurs at as low as -22°, and slightly quicker at room temperature. Although a quantitative yield of Me_3SiF was obtained from the reaction, large amounts of unreacted $PhOS(O)F_3$ remained. This would indicate that either disproportionation had occurred, or continuous substitution of fluorine atoms on sulphur had taken place.

$$PhOS(O)F_3 + 3Me_3SiOC_6F_5 \longrightarrow \underset{\substack{\downarrow \\ \text{oil}}}{PhOS(=O)(OC_6F_5)_3} + 3Me_3SiF$$

Removal of unreacted $PhOS(O)F_3$ in total proved difficult but most of it was recovered. A viscous oil remained which showed no S-$\underline{F}$ signals in the ^{19}F n.m.r. but a number of resonances in the C-$\underline{F}$ region were observed, indicative of a mixture of some kind. This could possibly contain $(C_6F_5O)_2SO_2$ and $C_6F_5OSO_2(OPh)$.

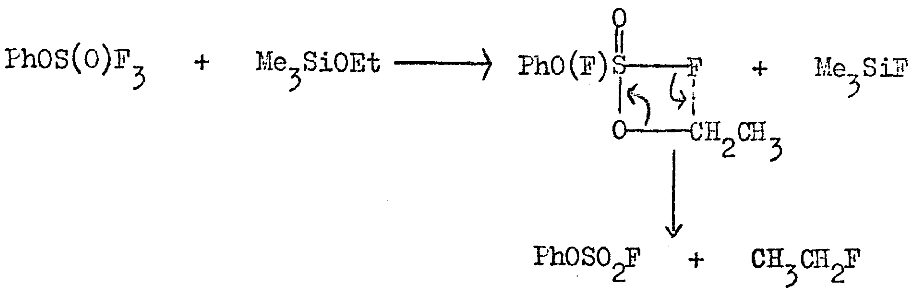
2 and 3. $ArOS(O)F_3/Me_3SiNMe_2$.

The aryoxysulphur oxytrifluorides reacted with Me_3SiNMe_2 at low temperature, with complete reaction occurring, but not giving $Me_2N(ArO)S(O)F_2$ exclusively as expected. Disproportionation would appear to have occurred, as on removal of a molar quantity of Me_3SiF, solids precipitated out of the oil remaining in the flask, and these solids proved to be $(ArO)_2S(O)F_2$. The ^1H n.m.r. of the oil both in the aromatic region and at higher field, where the N methyl signals appear, is complex, and would indicate the presence of a mixture. The ^{19}F n.m.r. shows only one resonance at -78 p.p.m. from CCl_3F.

If disproportionation is the main mechanism in reactions 2 and 3, then both $(ArO)_2S(O)F_2$ and $(Me_2N)_2S(O)F_2$ would be expected to form. $(Me_2N)_2S(O)F_2$ is, however, as yet unknown. An attempt to synthesise $(Me_2N)_2S(O)F_2$ from a two to one ratio of Me_3SiNMe_2 and SOF_4 did not succeed, and yielded only $Me_2NS(O)F_3$ and a viscous mass, the latter which gave no signal in the ^{19}F n.m.r.spectrum. However it is worthy of note, that the oil which is obtained from reactions 2 and 3, showing a resonance at -78 p.p.m. from CCl_3F in the ^{19}F n.m.r., gives the signal in close proximity to that of the resonance of the axial fluorines of $Me_2NS(O)F_3$ at -76.8 p.p.m.(135). This could well indicate the presence of $(Me_2N)_2S(O)F_2$ or $Me_2N(ArO)S(O)F_2$ in the oily mixture.

4. $PhOS(O)F_3/Me_3SiOEt$.

The reaction occurs smoothly at room temperature, giving quantitative yields of $PhOSO_2F$, EtF and Me_3SiF. It seems likely that the products were derived from the breakdown of the alkoxyphenoxysulphur oxydifluoride, $EtO(PhO)S(O)F_2$.

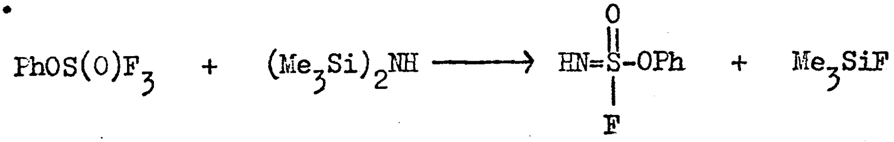


$$PhOS(O)F_3 + Me_3SiOEt \longrightarrow PhO(F)\overset{O}{\overset{\|}{S}}(F)(OCH_2CH_3) + Me_3SiF \longrightarrow PhOSO_2F + CH_3CH_2F$$

The reaction bears close resemblance to the reactions SOF_4/Me_3SiOR (R = Me, Et, CF_3CH_2) and shows further the preference which sulphur has for double bonding. The spectroscopic properties of $PhOSO_2F$ are discussed later.

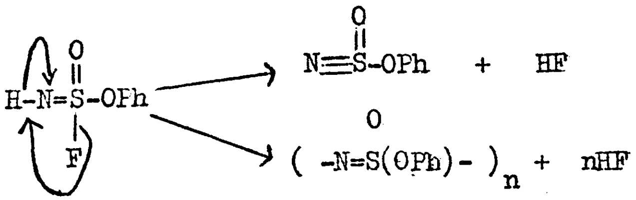
5. $PhOS(O)F_3/(Me_3Si)_2NH$.

The reaction occurred smoothly at low temperature with continuous darkening of the solution on reaching room temperature. The reaction afforded a two molar ratio of Me_3SiF along with a viscous tar. The reaction is presumed to proceed initially as below.



$$PhOS(O)F_3 + (Me_3Si)_2NH \longrightarrow HN{=}\overset{O}{\overset{\|}{\underset{F}{\underset{|}{S}}}}{-}OPh + Me_3SiF$$

It is probable that this is followed by the elimination of HF, followed subsequently by polymerisation or attack by HF on the products.



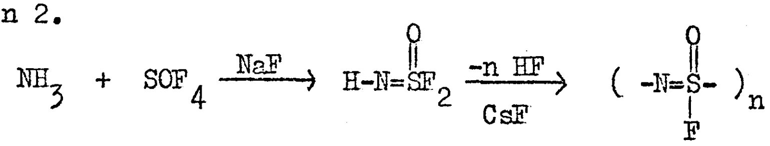
$$H{-}N{=}\overset{O}{\overset{\|}{\underset{F}{\underset{|}{S}}}}{-}OPh \longrightarrow N{\equiv}\overset{O}{\overset{\|}{S}}{-}OPh + HF \qquad 1.$$

$$H{-}N{=}\overset{O}{\overset{\|}{\underset{F}{\underset{|}{S}}}}{-}OPh \longrightarrow (\,{-}N{=}\overset{O}{S}(OPh){-}\,)_n + nHF \qquad 2.$$

The compound proposed from 1., bears close resemblance to a derivative of thiazyl trifluoride reported by Glemser (5).

$$N{\equiv}SF_3 \quad + \quad PhOH \longrightarrow N{\equiv}SF_2OPh \quad + \quad HF$$

Ammonia reacts with SOF_4 to give a polymer (138) as is possibly the case in 2.



$$NH_3 + SOF_4 \xrightarrow{NaF} H\text{-}N{=}\overset{\overset{O}{\|}}{S}F_2 \xrightarrow[CsF]{-n\ HF} (\ \text{-}N{=}\overset{\overset{O}{\|}}{\underset{\underset{F}{|}}{S}}\text{-}\ )_n$$

It is possible therefore, for either reaction to take place as proposed in 1. and 2. for reaction 5. It may prove useful to reinvestigate the reaction by carrying it out in the presence of a hydrogen fluoride acceptor.

6. $PhOS(O)F_3/(Me_3Si)_2NMe$

The reaction occurs slowly at 0°, giving a two molar ratio of Me_3SiF and methyliminosulphurphenoxy oxyfluoride, $Me{=}NS({=}O)(F)OPh$, which is a colourless liquid and appears to be insensitive to moisture. This is possibly a consequence of increased double bonding at sulphur. It is the first derivative of $MeNS(O)F_2$, which is also very stable to moisture, and which hydrolyses readily only in alkaline solution (86). $Me{=}NS({=}O)(F)OPh$ was stable enough in the atmosphere to have the mass spectrum measured by placing the sample directly on the probe, in contrast to the $(ArO)_2S(O)F_2$ compounds, which hydrolysed instantly. The spectroscopic properties are discussed later. The reaction has also been reported by Glemser (139).

7. m-$FC_6H_4OS(O)F_3$/$(Me_3Si)_2NMe$.

The reaction occurred slowly at 0° to give a two molar ratio of Me_3SiF and methyliminosulphur(m-fluorophenoxy) oxyfluoride, $MeN{=}S({=}O)(F)OC_6H_4$m-F, which is a colourless liquid, and is stable in the atmosphere.

These oxyfluorides isolated from reactions 6 and 7 have increased stability over the proposed intermediate N-H compound from reaction 5, as the methyl group on nitrogen blocks any possible reaction in which the fluorine attached to sulphur can be eliminated.

The n.m.r. spectral data of the oxyfluorides and related compounds are given in Table 29.

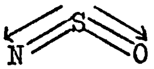
Table 29.

Compound	δF p.p.m. from CCl_3F	δH p.p.m. from t.m.s.	J_{H-F} Hz.
$PhOSO_2F$	-36.6s	-7.27s	-
$MeN{=}S({=}O)(F)OPh$	-45.4q	-7.23s C_6H_5	
		-2.87d CH_3	4.2
$MeN{=}S({=}O)(F)OC_6H_4$m-F	-44.1q S-F	-7.08 complex C_6H_4	
	109.1s C-F	-2.95d	5.3
$NCN{=}S({=}O)(F)(NMe_2)$	-49.8 (147)		
$MeSO_2N{=}S({=}O)F_2$	-47.6 (159)		
$Me_3SiN{=}S({=}O)F_2$	-55.9 (56)		

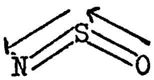
The ^{1}H n.m.r. of the methyliminosulphuraryloxy oxyfluorides give a doublet for the N methyl protons arising from coupling to fluorine. The S-F resonance appears as a quartet in the ^{19}F n.m.r., the fluorine coupling with the three protons on the N-CH_3 group. The C-F resonance for the m-fluorophenoxy compound, appears at much the same position as the C-F resonance in m-$FC_6H_4OS(O)F_3$. The ^{19}F shifts for the fluorine atoms attached to sulphur in the compounds listed in Table 29 show a considerable range moving to lower field where doubly bonded oxygen attached to sulphur is replaced by doubly bonded nitrogen. Other than $Me_3SiN{=}S({=}O)F_2$, the $N{=}S({=}O)\underline{F}$ resonance is in a narrower range, between -44 and -50 p.p.m. from CCl_3F.

The infrared spectra of the methyliminosulphuraryloxy oxyfluorides were recorded as films on KBr plates. They show a number of bands and some of the more important absorptions are assigned in Table 30.

The bands at 1378 cm^{-1}, 1381 cm^{-1} and 1239 cm^{-1}, 1254 cm^{-1} are described as the NSO asymmetric and NSO symmetric stretches respectively.



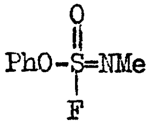
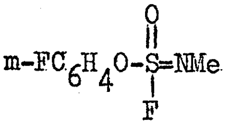
ν_s NSO



ν_{as} NSO

Table 30.

Infrared spectra of the methyliminosulphuraryloxy oxyfluorides.

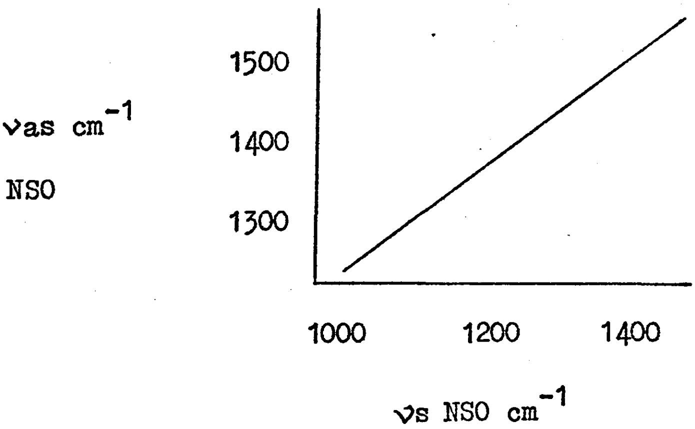
 $\mathrm{PhO{-}S(=O)(F){=}NMe}$	 $\mathrm{m{-}FC_6H_4O{-}S(=O)(F){=}NMe}$	Assignment
cm^{-1}	cm^{-1}	
3070	3085	C-H stretch N-$\underline{\mathrm{CH}}_3$
2945	2930	C-H stretch $\mathrm{C_6H_4}$
1602	1605	C-H ring
1583	1489	vibrations
1485	-	
1378	1381	NSO as stretch
1239	1254	NSO s stretch
-	1102	C-F stretch
908	912	S-F stretch

The NSO fragment has been assumed to be non-linear (84), as the relative intensities of the NSO vibrations for the aliphatic N-sulphinyl compounds are similar to those observed for $\mathrm{SO_2}$, which is angular. The NSO symmetric and asymmetric stretches have been shown to have a linear relationship for a number of compounds containing the NSO grouping. See Table 31. The values found for the methyliminosulphuraryloxy oxyfluorides for νs NSO and νas NSO, are in close proximity to the values for $\mathrm{(NS(O)F)_n}$ at 1250 cm^{-1} and 1351 cm^{-1} respectively.

Table 31.

Symmetric (νs) and asymmetric (νas) stretching frequencies of -NSO compounds (84 and references therein).

Compound type	νs cm^{-1}	νas cm^{-1}
RNSO	1120-1135	1238-1252
ArNSO	1137-1179	1272-1300
ArSO(NH)OPh	1160	1295
$(NSOF)_n$	1250	1351
MeNSO(F)OAr	1239-1254	1378-1381 (this work)



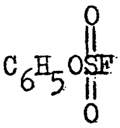
Correlation of νs(NSO) and νas (NSO) stretching frequencies.

The S-F stretching frequencies for the methyliminosulphuraryloxy oxyfluorides at around 910 cm^{-1} are very close to the values of the S-F stretching frequencies of the $ArOS(O)F_3$ compounds.

The mass spectra of the methyliminosulphuraryloxy oxyfluorides and phenylfluorosulphonate are shown in Tables 32-34, and were obtained by placing the samples directly on to the probe. They give a strong parent ion, but the spectra are dominated by the ArO^+ fragment.

Table 32.

Compound



$C_6H_5OS(=O)_2F$

M.Wt. 176.

m/e	Ion	Intensity %
176	$C_6H_5OSO_2F^+$	55
160	$C_6H_5OSOF^+$	12
157	$C_6H_5OSO_2^+$	1
125	$C_6H_5OSO^+$	3
93	$C_6H_5O^+$	100
83	SO_2F^+	17
77	$C_6H_5^+$	31
65	$C_5H_5^+$	100
64	SO_2^+	28
51	SF^+	8
48	SO^+	15
28	CO^+	91

Metastable Transition

m^*	m_1	m_2
45.4	93	65

The metastable transition establishes that the following took place:-

$$\underset{m/e\ 176(M)}{C_6H_5OSO_2F^+} \longrightarrow \underset{m/e\ 93}{C_6H_5O^+} \xrightarrow{-CO\quad m^*=45.4} \underset{m/e\ 65}{C_5H_5^+}$$

Loss of CO is characteristic of aryloxy ions (160) and is also observed in the pyrolysis of phenoxy radical (161).

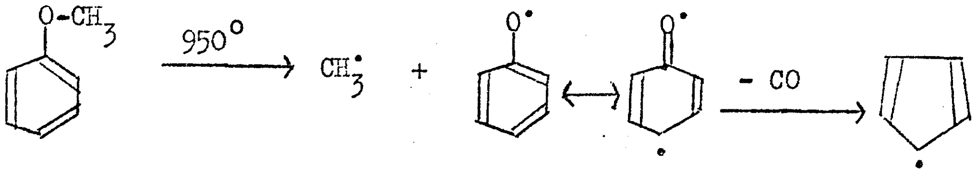
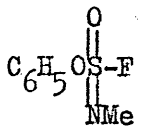


Table 33.

Compound	m/e	Ion	Intensity %
 $C_6H_5OS(O)(NMe)F$	189	$C_6H_5OS(O)(NMe)F^+$	12
	160	$C_6H_5OS(O)F^+$	24
	141	$C_6H_5OS^+$	11
M.Wt. 189	96	$MeNS(O)F^+$	6
	93	$C_6H_5O^+$	100
	77	$C_6H_5^+$	42
	67	$S(O)F^+$	7
	65	$C_5H_5^+$	100
	64	SO_2^+	5
	48	SO^+	11
	28	CO^+	100

Metastable Transition

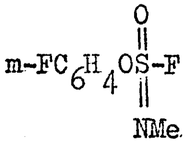
m^*	m_1	m_2
45.4	93	65

The mass spectra of phenylfluorosulphonate and methyliminosulphurphenoxy oxyfluoride are very similar, the only difference being that the parent ion of phenylfluorosulphonate is much more intense.

Loss of carbon monoxide in the spectrum of methyliminosulphur-m-fluorophenoxy oxyfluoride is also observed, but by a different mechanism, and would appear to come from the parent ion.

Table 34.

Compound



$m\text{-}FC_6H_4O\overset{O}{\underset{NMe}{S}}\text{-}F$

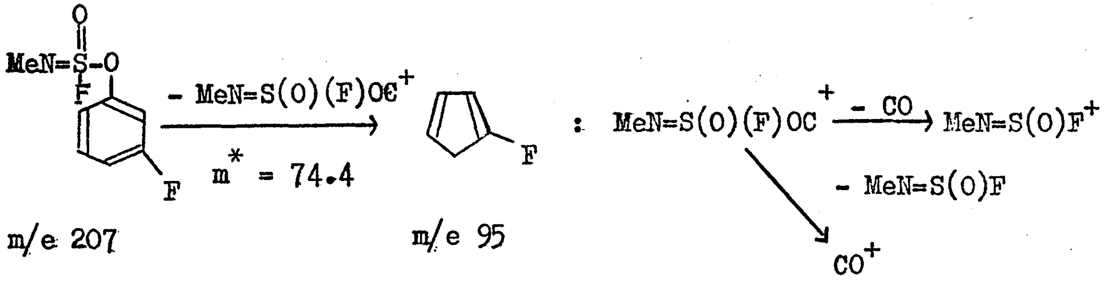
M.Wt. 207

m/e	Ion	Intensity %
207	$FC_6H_4OS(O)(NMe)F$	11
178	$FC_6H_4OS(O)F^+$	9
159	$FC_6H_4OS(O)^+$	7
124	$OCS(O)(NMe)F^+$	100
111	$FC_6H_4O^+$	100
96	$MeNS(O)F^+$	12
95	$FC_6H_4{}^+$	25
83	$FC_5H_4{}^+$	100
81	$NS(O)F^+$	6
67	$S(O)F^+$	15
48	SO^+	18
28	CO^+	95

Metastable transition

m*	m_1	m_2
74.4	207	124

The metastable originates from the parent ion with the initial loss of $MeNS(O)(F)CO^+$ and subsequent breakdown to $MeNS(O)F^+$ and CO.



Reactions 8-10.

From these reactions, it was hoped that the mixed chlorofluoride derivative of thionyl tetrafluoride, SOF_3Cl, would be formed. The reaction between chlorine monofluoride and SOF_2 gives SOF_4, and it is thought that SOF_3Cl was an intermediate (162).

$$SOF_2 + ClF \longrightarrow SOF_3Cl \xrightarrow{ClF} SOF_4 + Cl_2$$

It is equally likely that disproportionation took place.

$$\begin{tikzcd}
2SOF_3Cl \arrow[r] & SOF_4 + & SOF_2Cl_2 \arrow[d] \\
 & & SOF_2 + Cl_2
\end{tikzcd}$$

Chlorofluorides of phosphorus can be made readily from exchange reactions with HCl and the corresponding dimethylaminofluorophosphorus compound (163).

$$Me_2NP(O)F_2 + 2HCl \longrightarrow P(O)F_2Cl + Me_2NH.HCl$$

A parallel reaction was attempted with $Me_2NS(O)F_3$ and HCl, but did not succeed in isolating SOF_3Cl. The products of the reaction were SOF_2, Cl_2 and solids, and it seems some form of disproportionation has occurred as mentioned earlier.

$$\begin{tikzcd}
Me_2NS(O)F_3 + 2HCl \arrow[r] & SOF_3Cl \arrow[d] & + Me_2NH.HCl \\
Cl_2 + SOF_2 & SOF_2Cl_2 \arrow[l] & + SOF_4
\end{tikzcd}$$

SOF_4 was not identified in the products and possibly reaction with the solids precluded its isolation.

SF_5Cl can be obtained from the reaction with SF_4 and chlorine in the presence of caesium fluoride at high temperature. The reactive intermediate in the reaction is postulated to be the SF_5^- ion.

$$SF_4 + CsF \longrightarrow Cs^+SF_5^- \xrightarrow{Cl_2} CsCl + SF_5Cl$$

The reaction between SOF_2 and chlorine in the presence of caesium fluoride failed to occur probably because SOF_2 is not absorbed sufficiently by caesium fluoride.

$$SOF_2 + Cl_2 + CsF \longrightarrow \text{no reaction}$$

Me_2NSF_3 and chlorine, in the presence of caesium fluoride, react to give SF_5Cl as the major product (165). It is thought to be given by SF_4 as an intermediate.

$$\begin{tikzcd}
Me_2NSF_3 + Cl_2 \arrow[r] & SF_3Cl \arrow[d] & + Me_2NCl \\
SF_5Cl & SF_4 \arrow[l, "CsF"', "Cl_2"] & + (SF_2Cl_2)
\end{tikzcd}$$

$Me_2NS(O)F$ and chlorine in the presence of caesium fluoride gave only solid products which were not identified. It is surprising that no volatile material was formed.

Reactions 11-14.

The purpose of these reactions was to form the $R_fS(O)F_3$ derivatives, which ought to be very stable.

SF_4 can be readily oxidised to SOF_4 with oxygen in the presence of nitrogen dioxide (38). The corresponding reactions with the perfluoroalkylsulphur trifluorides failed to give the oxytrifluorides.

$$R_fSF_3 + O_2 + NO_2 \longrightarrow \text{no reaction}$$

$R_f = CF_3, (CF_3)_2CF$

CF_3SF_3 can be oxidised to CF_3SF_4Cl by chlorine in the presence of caesium fluoride (165).

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

CF_3SF_4Cl has octahedral symmetry with all the fluorine atoms on sulphur in trans positions, which possibly eases the reaction.

$(CF_3)_2CFSF_3$ also undergoes chlorofluoronation but gives SF_5Cl (166).

$$(CF_3)_2CFSF_3 + Cl_2 + CsF \longrightarrow [(CF_3)_2CF]_2SF_2 + SF_5Cl$$

The R_fSF_3 compounds, therefore, can be oxidised, but it seems likely that to form the oxytrifluorides, extremely forcing conditions are required.

SF_4 has been reported to add across the double bond of perfluoropropene (9).

$$CF_3CF{=}CF_2 + SF_4 \xrightarrow{CsF} (CF_3)_2CFSF_3 + [(CF_3)_2CF]_2SF$$

SOF_4 and perfluoropropene failed to react in the presence of CsF, even on prolonged heating.

$$CF_3CF{=}CF_2 + SOF_4 \xrightarrow{CsF} \text{no reaction}$$

It is probable that very high pressures and temperatures are required for reaction, beyond the scope of the apparatus at hand.

$CF_3S(O)F$ reacts with fluorine in the presence of silver fluoride, to give CF_4 and SF_6 , and not $CF_3S(O)F_3$ as expected (51).

$$CF_3S(O)F \quad + \quad F_2 \xrightarrow{AgF} CF_4 \quad + \quad SF_6$$

It was hoped that a milder fluorinating agent, such as AgF_2, on reaction with $CF_3S(O)F$ would give $CF_3S(O)F_3$. However, the products of the reaction were CF_4, SO_2F_2 and CF_3SF_3.

$$CF_3S(O)F \quad + \quad AgF_2 \longrightarrow CF_4 \; + \; SO_2F_2 \; + \; CF_3SF_3$$

EXPERIMENTAL

Standard vacuum procedures were used throughout. The aryloxysulphur oxytrifluorides were made as described in Chapter II, and other materials were made by well documented methods.

Compound	Method	Reference
$Me_2NS(O)F_3$	Me_3SiNMe_2/SOF_4	(135)
Me_3SiNMe_2	Me_3SiCl/Me_2NH	(120)
Me_3SiOEt	$Me_3SiCl/EtOH$	(116)
$(Me_3Si)_2NMe$	$Me_3SiCl/MeNH_2$	(118)
CF_3SF_3	CF_3SSCF_3/AgF_2	(22)
$CF_3S(O)F$	$CF_3S(O)F/H_2O$	(51)
$(CF_3)_2CFSF_3$	$CF_3CF{=}CF_2/SF_4/CsF$	(9)

CF_3SSCF_3 and $CF_3CF{=}CF_2$ were obtained from Peninsular Chemresearch, and AgF_2 and CsF were obtained from Ozark Mahoning.

For reactions 11 and 12, oxygen was condensed into the reaction bombs as outlined in the preparation of SOF_4 in the experimental section of Chapter II.

1. $PhOS(O)F_3/Me_3SiOC_6F_5$. See over.

$PhOS(O)F_3$ (8.2 m.moles) and $Me_3SiOC_6F_5$ (8.3 m.moles) were left at -22° for 2 hours, at -10° for 2 hours, and at room temperature for 1 hour. The products were Me_3SiF (8.1 m.moles) and a viscous liquid, which contained $PhOS(O)F_3$ and a small amount of $PhOSO_2F$, as indicated by n.m.r. as the only identifiable products. The n.m.r. in the C-F region was complex, and showed a number of resonances, indicative of a mixture.

n.m.r.: C-F = 125.8, 133.3, 144.7, 150.5, 157.6, 165.2.

2. $PhOS(O)F_3/Me_3SiNMe_2$.

$PhOS(O)F_3$ (8.4 m.moles) and Me_3SiNMe_2 (8.2 m.moles) were left to stand at -22° for 2 hours, and at room temperature for 2 hours. The volatiles consisted only of Me_3SiF (8.1 m.moles). Solids precipitated from the viscous oil on removal of Me_3SiF. The solids were recovered by washing the oil with CCl_3F, and proved to be $(PhO)_2S(O)F_2$ by n.m.r. and i.r.. $\delta F = -89.1$.

The oil showed one resonance at -78.0 p.p.m. from CCl_3F in the ^{19}F n.m.r. The proton n.m.r. was more complex, showing signals -7.25 bs, and singlets at -3.36, -3.16, -3.01, -2.94, -2.74 and -2.41 p.p.m. from t.m.s..

3. $p\text{-}MeC_6H_4OS(O)F_3/Me_3SiNMe_2$.

$p\text{-}MeC_6H_4OS(O)F_3$ (7.1 m.moles) and Me_3SiNMe_2 (7.3 m.moles) were left at -22° for 2 hours and at room temperature for 2 hours. Me_3SiF (6.9 m.moles) were pumped off, giving a viscous liquid and solids. The solids proved to be $(p\text{-}MeC_6H_4O)_2S(O)F_2$ as indicated by i.r. and n.m.r.; $\delta F = -87.1$. The oil gave a resonance at -78.7 p.p.m. from CCl_3F in the ^{19}F n.m.r.. The ^1H n.m.r. showed singlets at -7.55, -7.16, -7.10, -3.60, -3.33, -3.07, -2.83, -2.68, -2.42 and -2.19 p.p.m. from t.m.s..

4. $PhOS(O)F_3/Me_3SiOEt$.

$PhOS(O)F_3$ (8.5 m.moles) and Me_3SiOEt (8.7 m.moles) were left at -22° for 3 hours and at room temperature for 1 hour. The products were Me_3SiF (8.2 m.moles), SO_2F_2 (trace), EtF (7.7 m.moles), identidied by n.m.r. (124), and $PhOSO_2F$ (7.9 m.moles).

$C_6H_5OSO_2F$: Analysis. Found. C, 41.1; H, 3.0; F, 10.7; S, 18.1.
Calculated. C, 40.9; H, 2.8; F, 10.8; S, 18.2.

n.m.r.: $\delta F = -36.6$; $\delta C_6H_5 = -7.27$.

5. $PhOS(O)F_3/(Me_3Si)_2NH$.

$PhOS(O)F_3$ (6.4 m.moles) and $(Me_3Si)_2NH$ (6.1 m.moles) were left at -10° for 2 hours and at room temperature for 1 hour. The products were Me_3SiF (11.8 m.moles), and a brown intractable mass.

6. $PhOS(O)F_3/(Me_3Si)_2NMe$.

$PhOS(O)F_3$ (7.1 m.moles) and $(Me_3Si)_2NMe$ (6.9 m.moles) were left at -10° for 2 hours, and at room temperature for 1 hour, to give Me_3SiF (13.1 m.moles), and a lightly coloured, involatile liquid, which proved to be methyliminosulphurphenoxy oxyfluoride, MeN=S(=O)(F)OPh.

MeNS(O)(F)OPh: Analysis. Found. C, 44.7; H, 4.1; F, 10.5; N, 7.2; S, 16.7.
Calculated. C, 44.4; H, 4.2; F, 10.1; N, 7.4; S, 16.9.

Infrared cm^{-1}. 3070 w, 2945 w, 1602 m, 1583 s, 1378 s, 1239 s,
(film) 1173 w, 1141 m, 1070 w, 1023 m, 908 s, 852 m,
772 m, 683 m, 539 m, 489 w.

n.m.r.: $\delta F = -45.4q$; $\delta C_6H_5 = -7.23$, $\delta CH_3 = -2.87d$; $^4J_{H-C-N-S-F} = 4.2$ Hz..

7. $m\text{-}FC_6H_4OS(O)F_3/(Me_3Si)_2NMe$.

$m\text{-}FC_6H_4OS(O)F_3$ (6.1 m.moles) and $(Me_3Si)_2NMe$ (5.9 m.moles), were left to stand at -10° for 2 hours and at room temperature for 1 hour. The products were Me_3SiF (11.9 m.moles), and a colourless, viscous liquid identified as being methyliminosulphur-m-fluorophenoxy oxyfluoride, $MeN{=}S({=}O)(F)OC_6H_4m\text{-}F$.

$MeNS(O)(F)OC_6H_4m\text{-}F$: Analysis. Found. C, 40.9; H, 3.4; F, 18.3; N, 6.6, S, 15.2.
Calculated. C, 40.6; H, 3.4; F, 18.4; N, 6.8, S, 15.5.

n.m.r.: $\delta S\text{-}\underline{F} = -44.1q$, $\delta C\text{-}\underline{F} = 109.1$; $\delta C_6H_4 = -7.08$ multiplet, n.m.r.: (contd.) $CH_3 = -2.95d$; $^4J_{H-C-N-S-F} = 5.3$ Hz..

Infrared cm^{-1}. 3085 w, 2930 m, 1605 s, 1489 s, 1381 s, 1254 s,
(film) 1153 w, 1102 s, 1070 w, 950 s, 908 s, 862 m,
804 m, 673 m, 519 m, 495 w.

8. $Me_2NS(O)F_3/HCl$.

HCl (4.5 m.moles) was dried by passing through two traps at -76°, and condensed together with $Me_2NS(O)F_3$ (7.4 m.moles) at -196°, and held at -22° for 30 minutes. The volatiles were passed through traps at -124° and -196°, trapping chlorine and SOF_2 respectively. Chlorine was identified by its greenish-yellow colour, its action on mercury, and KI, displacing iodine. The molecular weight was found to be 75 (calculated for Cl_2, 71), using a mercury manometer with the mercury protected by fluorlube. SOF_2 was identified by i.r. (49) and mass spectrum, showing peaks at m/e 86, SOF_2^+; m/e 67, SOF^+; m/e 48, SO^+ and m/e 33.5, SOF^{2+}. All of the HCl was consumed in the reaction, leaving unreacted $Me_2NS(O)F_3$ and solids.

9. $SOF_2/Cl_2/CsF$.

SOF_2 (3.1 m.moles), Cl_2 (2.9 m.moles) and CsF (4.2 m.moles) were condensed into a 75 ml Hoke-bomb at -196°, and allowed to reach room temperature. No reaction was observed on standing at room temperature for 3 hours, or on heating at 150° in an oven for 12 hours, with almost complete recovery of the starting materials.

10. $Me_2NS(O)F/CsF/Cl_2$.

$Me_2NS(O)F$ (5.4 m.moles), Cl_2 (4.9 m.moles) and CsF (5.1 m.moles) were condensed together into a 75 ml Hoke-bomb at -196°. The reactants were allowed to reach room temperature and heated to 130° for 4 hours. This resulted in complete consumption of the gases, and heating the bomb while under dynamic vacuum failed to give any volatile material.

11. $CF_3SF_3/NO_2/O_2$.

CF_3SF_3 (22 m.moles), NO_2 (5.1 m.moles) and oxygen (at approximately 500 p.s.i.) were condensed into a 400 ml, monel, Hoke-bomb, and heated to 180° for 17 hours. The bomb was bled to a trap at -196°, and the oxygen pumped away. The volatiles contained a complex mixture of NO_2 (identified by i.r. on comparison with an authentic sample), CF_3SF_3 and $CF_3S(O)F$, identified by i.r. and n.m.r (51).

12. $(CF_3)_2CFSF_3/NO_2/O_2$.

$(CF_3)_2CFSF_3$ (17.8 m.moles), NO_2 (4.3 m.moles) and oxygen (at approximately 500 p.s.i.) were condensed into a 400 ml, monel, Hoke-bomb, and heated to 180° for 17 hours. The bomb was bled to a trap at -196°, and the oxygen pumped away. The volatiles consisted of unreacted starting materials, $(CF_3)_2CFSF_3$ (identified by i.r. and n.m.r. (9)), and NO_2, identified by comparison with an authentic sample (i.r.). Storing $(CF_3)_2CFSF_3$ and NO_2 in a pyrex-glass vessel resulted in the precipitation of unidentified solids, consumption of NO_2 and the formation of a large amount of SiF_4

13. $CF_3CF{=}CF_2/SOF_4/CsF$.

$CF_3CF{=}CF_2$ (14.5 m.moles), SOF_4 (21.2 m.moles) and CsF (5.3 m.moles) were heated together at 150° for 3 days in a 25 ml, stainless-steel bomb, fitted with a Hoke-valve. This resulted in almost complete recovery of the reactants.

14. $CF_3S(O)F/AgF_2$.

$CF_3S(O)F$ (4.2 m.moles) and AgF_2 (12.5 m.moles) were heated together at 120° for 5 hours in a 15 ml stainless-steel bomb, fitted with a Hoke-valve. The volatiles consisted of CF_4, identified by i.r. (167) and n.m.r. (124) , CF_3SF_3, identified by i.r. (51) and SO_2F_2, identified by i.r. (6), and n.m.r. (153).

CHAPTER IV

REACTIONS OF SULPHURYL CHLORIDE FLUORIDE

INTRODUCTION

The chemistry of sulphuryl chloride fluoride has received little attention although it has been known for a number of years (168). It can be prepared most conveniently , and in high yield, by the mild fluorination of sulphuryl chloride with sodium fluoride in a slurry of acetonitrile (27).

$$SO_2Cl \quad + \quad NaF \xrightarrow{CH_3CN} SO_2ClF \quad + \quad NaCl$$

The reaction also gives small amounts of sulphuryl fluoride which is removed readily because of its lower boiling point. Complete conversion of sulphuryl chloride fluoride to sulphuryl fluoride can be effected by heating with sodium fluoride in tetramethylenesulphone in a bomb (27).

The sulphuryl halide fluorides show anomalous ^{19}F chemical shift differences (6). See Table 35.

Table 35.

Compound	B.Pt. °C	δ F p.p.m. from CCl_3F
FSO_2F	-55.4	-33.7
FSO_2Cl	7.1	-100.6
FSO_2Br	40.0	-120.9

The ^{19}F shift moves to lower field as less electronegative atoms replace fluorine. It would have been expected to result in more shielding of the fluorine nuclei and so move the shifts to higher field. This has been observed as well for the chlorofluorides of phosphorus (169). See Table 36.

Table 36.

Compound	δF p.p.m. from CCl_3F
POF_3	15.8
POF_2Cl	-30.4
$POFCl_2$	-69.0

No satisfactory explanation of this effect has been suggested.

The infrared spectrum of SO_2FCl has been interpreted on the basis of a tetrahedral structure (153).

Unlike SO_2F_2, SO_2FCl is readily hydrolysed and more reactive.

$$SO_2FCl + 2H_2O \longrightarrow H_2SO_4 + HCl + HF$$

This parallels the behaviour of SF_6 and SF_5Cl. For the former, this has been explained by the reluctance of combined fluorine atoms to interact with nucleophiles, as when one fluorine is replaced by chlorine, hydrolysis by base is rapid (7).

SO_2FCl can be stored in a bomb indefinitely, at ambient temperature without decomposition, unlike SOFCl which undergoes disproportionation at room temperature to SOF_2 and $SOCl_2$ (6).

Summary of reactions.

1. $SO_2FCl + Me_3SiNMe_2 \longrightarrow Me_2NSO_2Cl + Me_3SiF$
2. $SO_2FCl + Me_3SiOMe \longrightarrow (MeO)_2SO_2 + Me_3SiF + Me_3SiCl$
3. $SO_2FCl + Me_3SiOPh \longrightarrow$ no reaction
4. $SO_2FCl + (Me_3Si)_2NH \longrightarrow (Me_3SiNH)_2SO_2 + Me_3SiF + Me_3SiCl$
5. $SO_2FCl + (Me_3Si)_2NMe \longrightarrow (Me_3SiNMe)_2SO_2 + Me_3SiF$
   $+ Me_3SiCl$
6. $SO_2FCl + (Me_3Si)_2O \longrightarrow (Me_3SiO)_2SO_2 + Me_3SiF + Me_3SiCl$
7. $SO_2FCl + (CF_3)_2C{=}O \xrightarrow[\text{or heat}]{h\nu}$ no reaction
8. $SO_2FCl + CH_2{=}CH_2 \xrightarrow{h\nu} (CH_2{-}CH_2)_n + SO_2FCl$
9. $SO_2FCl + CF_3CF{=}CF_2 \xrightarrow[\text{or heat}]{h\nu}$ no reaction

1. SO_2FCl/Me_3SiNMe_2

The reaction occurs smoothly at room temperature, to give Me_3SiF and Me_2NSO_2Cl as the only products. A similar reaction was observed by Emeleus (168) with diethylamine, but the reaction gave small amounts of the fluorosulphonamide, as well as the

the chlorosulphinamide.

$$2Et_2NH + SO_2FCl \longrightarrow Et_2NSO_2Cl + Et_2NSO_2F + Et_2NH.HF + Et_2NH.HCl$$

The fluorosulphonamide would have been expected exclusively on the basis of sulphur chlorine bonds being more labile than sulphur fluorine bonds. This factor must be outweighed by the strength of the Si-F and H-F bonds as opposed to the weaker Si-Cl and H-Cl bonds (43).

Bond Combination	S-Cl + Si-F	S-F + Si-Cl
Bond Energies	65 + 143 → 208 k.cals.	79 + 96 → 175 k.cals.

Bond Combination	S-Cl + H-F	S-F + H-Cl
Bond Energies	65 + 136 → 201 k.cals.	79 + 103 → 202 k.cals.

While the bond energy values must be an approximation for these systems, it is evident that the silicon nitrogen reaction would favour the formation of the chlorosulphonamide, while the amine reaction would give an even distribution of products, though experimentally, the chlorosulphonamide is formed in higher yield.

Me_2NSO_2Cl is a colourless liquid and was first made from $Me_2NH.HCl$ and SO_2Cl_2 (170). It can be fluorinated to the fluorosulphonamide by SbF_3 (171).

2 and 3. SO_2FCl/Me_3SiOR (R = Me, Ph). See over.

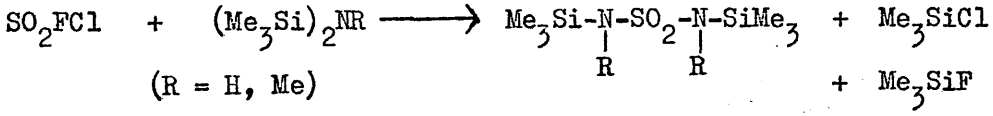
Sulphuryl chloride fluoride reacts vigorously with methoxy trimethylsilane to give dimethylsulphate and no intermediate products ($MeOSO_2X$, $X = F, Cl$?), in contrast to thionyl fluoride which gave both the halosulphite and the sulphite (See Chapter I).

Sulphuryl chloride fluoride failed to react with phenoxy trimethylsilane, even on prolonged heating, but has been observed to react with phenol to give phenylfluorosulphonate (142), although Emeléus reported earlier that the latter reaction failed to occur (168).

$$PhOH + SO_2FCl \longrightarrow PhOSO_2F + HCl$$

4 and 5. $SO_2FCl/(Me_3Si)_2NR$ (R = H, Me).

Sulphuryl chloride fluoride reacts with the silazanes to give the bis(aminotrimethylsilyl)sulphonyl derivatives.



$$\begin{array}{l} SO_2FCl + (Me_3Si)_2NR \longrightarrow Me_3Si\text{-}\underset{\displaystyle R}{\underset{|}{N}}\text{-}SO_2\text{-}\underset{\displaystyle R}{\underset{|}{N}}\text{-}SiMe_3 + Me_3SiCl \\ \qquad (R = H, Me) \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad + Me_3SiF \end{array}$$

These aminosilylsulphonyl derivatives have been prepared previously from sulphamide and the silazanes.

$$NH_2SO_2NH_2 + (Me_3Si)_2NR \longrightarrow (Me_3SiNR)_2SO_2 + 2Me_3SiNH_2$$

(R = H (172); R = Me (173))

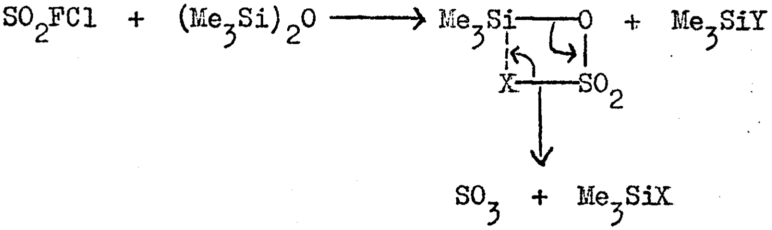
6. $SO_2FCl/(Me_3Si)_2O$.

Hexamethyldisiloxane reacts with the thionyl halides to give sulphur dioxide (45), and with SOF_4 to give SO_2F_2 (this work).

Only a partial reaction was observed with sulphuryl chloride fluoride, giving small amounts of Me_3SiF and Me_3SiCl and $(Me_3SiO)_2SO_2$. Two possible modes of reaction are suggested below.

1a. $SO_2FCl + (Me_3Si)_2O \longrightarrow Me_3SiOSO_2X + Me_3SiY$ (X or Y = F, Cl ?)

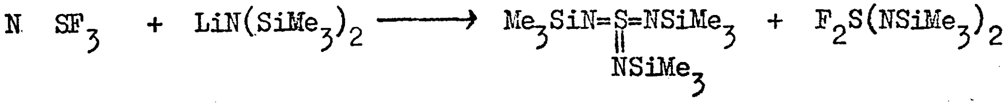
b. $Me_3SiOSO_2X + (Me_3Si)_2O \longrightarrow (Me_3SiO)_2SO_2 + Me_3SiX$

2a. 

$SO_2FCl + (Me_3Si)_2O \longrightarrow [Me_3Si{-}O{-}SO_2{-}X] + Me_3SiY \longrightarrow SO_3 + Me_3SiX$

2b. $SO_3 + (Me_3Si)_2O \longrightarrow (Me_3SiO)_2SO_2$

The first reaction pathway seems the more likely, involving fewer steps, and is similar to the silazane reactions. The second reaction involves the formation of three double bonds to sulphur, and few reactions of this kind are known. Glemser has reported the formation of a sulphur triimide from thiazyl trifluoride (174).



$NSF_3 + LiN(SiMe_3)_2 \longrightarrow Me_3SiN{=}\underset{\underset{NSiMe_3}{\|}}{S}{=}NSiMe_3 + F_2S(NSiMe_3)_2$

The high temperature reaction of sulphur trioxide and hexamethyldisiloxane has been reported (175), but it is doubtful if this is occurring as an intermediate reaction as in 2b for the sulphuryl chloride fluoride reaction.

Reactions with double bonds.

A number of addition reactions across the carbon oxygen double bond in hexafluoroacetone have been reported (176).

$$PF_2X \quad + \quad (CF_3)_2C{=}O \longrightarrow (CF_3)_2C(OPF_2)X$$

$$X = Br,\ I;\ \neq H,\ F,\ Cl.$$

A reaction between SO_2FCl and $(CF_3)_2C{=}O$ failed to occur, either on heating or with U.V. irradiation. This has also been found to be the case with SF_5Cl (177). It is probable that the more reactive corresponding bromides, SO_2FBr and SF_5Br, will succeed in adding across the carbon oxygen double bond.

Ethylene and SO_2FCl on irradiation together, at below one atmosphere pressure, yielded a coating on the walls of the vessel which proved to be polyethylene, with complete recovery of the SO_2FCl. Sulphuryl chloroisocyanate has been reported to add across the double bond in ethylene (178).

$$OCNSO_2Cl \quad + \quad CH_2{=}CH_2 \longrightarrow OCNSO_2CH_2CH_2Cl$$

No reaction was observed between hexafluoropropene and SO_2FCl either on heating or with U.V. irradiation, although a reaction with SO_2F_2 has been reported (179).

$$SO_2F_2 \quad + \quad CF_3CF{=}CF_2 \longrightarrow (CF_3)_2CFSO_2F$$

The reaction is catalysed by CsF, which cannot be employed in the reaction with SO_2FCl, as this would result in the conversion of SO_2FCl to SO_2F_2.

EXPERIMENTAL

Sulphuryl chloride fluoride was prepared by the method of Tullock and Coffman, by adding sulphuryl chloride dropwise to a stirred suspension of sodium fluoride in acetonitrile (27).

Ethylene was purchased from Peninsular Chemresearch and the other materials were obtained from sources described earlier in the text.

Ultraviolet photolysis reactions were carried out using a Hanovia U.V. lamp employing a 100 watt medium pressure arc tube.

1. SO_2FCl/Me_3SiNMe_2

SO_2FCl (11.4 m.moles) and Me_3SiNMe_2 (10.9 m.moles) reacted vigorously at -10°. The reactants were left standing at room temperature for 30 minutes and the products passed through traps at -45° and -196° to give Me_3SiF (8.8 m.moles) with a small amount of Me_3SiCl and unreacted SO_2FCl in the -196° trap and Me_2NSO_2Cl in the -45° trap. Me_2NSO_2Cl was identified by n.m.r. and analysis.

Me_2NSO_2Cl. Analysis: Found.	C, 16.9; H, 4.3; Cl, 24.6; N, 9.6; S, 22.4.
Calculated.	C, 16.7; H, 4.2; Cl, 24.7; N, 9.8; S, 22.3.

n.m.r.: CH_3 = -2.95s.

2. SO_2FCl/Me_3SiOMe. See over.

SO_2FCl (9.4 m.moles) and Me_3SiOMe (9.1 m.moles) reacted at well below room temperature and were left to stand at room temperature for 2 hours. The volatiles were passed through traps at -66° and -196°. Me_3SiF, Me_3SiCl and SO_2FCl were trapped in the -196° trap and $(MeO)_2SO_2$ in the -66° trap and was identified by comparison with an authentic sample by i.r. and n.m.r..

n.m.r.: $(MeO)_2SO_2$, $\delta CH_3 = -3.51$

3. SO_2FCl/Me_3SiOPh.

SO_2FCl (12.3 m.moles) and Me_3SiOPh (10.8 m.moles) were heated together at 145° for 2 days with no reaction taking place.

4. $SO_2FCl/(Me_3Si)_2NH$.

SO_2FCl (10.9 m.moles) and $(Me_3Si)_2NH$ (10.4 m.moles) reacted slowly over a period of 1 hour at room temperature. Fine, colourless, needle-like crystals precipitated out of solution. The volatiles contained Me_3SiF, Me_3SiCl and SO_2FCl, as indicated by n.m.r. and i.r.. The solid was shown to be bis(trimethylsilyl)-sulphamide, $(Me_3SiNH)_2SO_2$.

$(Me_3SiNH)_2SO_2$. M.Wt.; found, 240 (mass spec.). Calc., 240.

Analysis: Found. C, 29.4; H, 8.1; N, 11.9; S, 13.6.

Calculated. C, 30.1; H, 8.4; N, 11.8; S, 13.4.

n.m.r.: $\delta Si\underline{CH_3} = -0.23s$, $\delta N\underline{H} = -4.75s$.

5. $SO_2FCl/(Me_3Si)_2NMe$.

SO_2FCl (10.9 m.moles) and $(Me_3Si)_2NMe$ (10.5 m.moles) reacted slowly on reaching room temperature to give colourless, platelet crystals. The volatiles contained Me_3SiF, Me_3SiCl and SO_2FCl, as indicated by i.r. and n.m.r.. The solid was identified as bis(trimethylsilyl)-dimethylsulphamide, $(Me_3SiNMe)_2SO_2$.

$(Me_3SiNMe)_2SO_2$. M.Wt.; found, 268 (mass spec.). Calc., 268.

Analysis: Found. C, 35.1; H, 8.5; N, 10.3; S, 12.3.

Calculated. C, 35.8; H, 7.9; N, 10.5; S, 12.0.

n.m.r.: $\delta Si\underline{CH_3} = -0.12s$, $\delta N\underline{CH_3} = -2.35$.

6. $SO_2FCl/(Me_3Si)_2O$.

SO_2FCl (10.4 m.moles) and $(Me_3Si)_2O$ (9.7 m.moles) were heated together at 150° for 17 hours. Most of the starting materials were recovered along with small amounts of Me_3SiF and Me_3SiCl, as indicated by i.r. and n.m.r., leaving a viscous liquid which was shown to contain bis(trimethylsilyl)sulphate, $(Me_3SiO)_2SO_2$, as indicated by i.r. and n.m.r. on comparison with an authentic sample. (The latter was kindly donated by D. Walker.)

7. $SO_2FCl/(CF_3)_2CO$.

SO_2FCl (2.5 m.moles) and $(CF_3)_2CO$ (2.6 m.moles) were irradiated with U.V. light in a quartz vessel for 48 hours with an internal pressure of approximately 450 mm Hg. No reaction was observed. The contents were condensed into a metal bomb of 17 ml capacity and heated to 150° for 3 days with no reaction taking place.

8. $SO_2FCl/CH_2=CH_2$.

SO_2FCl (2.7 m.moles) and $CH_2=CH_2$ (2.8 m.moles) were irradiated by U.V. light in a quartz vessel for 12 hours with an internal pressure of approximately 520 mm Hg. A coating formed on the walls of the reaction vessel which was presumed to be polyethylene, as there was complete recovery of SO_2FCl, and no $CH_2=CH_2$ left after reaction.

9. $SO_2FCl/CF_3CF=CF_2$.

SO_2FCl (3.1 m.moles) and $CF_3CF=CF_2$ (3.2 m.moles) were irradiated by U.V. light at an internal pressure of approximately 640 mm Hg in a quartz vessel with no reaction after 25 hours. The contents were recondensed into a 17 ml metal bomb and heated for 4 days at 150° with no reaction taking place.

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