REACTIONS

OF

SULPHUR FLUORIDES

THESIS

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ABSTRACT

The major aim of the research was the preparation of compounds which could be used as heat-transfer agents. Chemical inertness and high thermal stability were important properties of the materials. Sulphur hexafluoride and many of its derivatives are stable and, initially, research was directed towards the synthesis of substituted S(VI) fluorides.

Substitution into S(VI) fluorides is not a convenient route for the preparation of the desired compounds and in most cases reaction takes place with complete breakdown and formation of unidentified solid products. The chlorofluorination of sulphur tetrafluoride with mixtures of chlorine and caesium fluoride has previously proved successful for the preparation of sulphur chloride pentafluoride and, in the present work, this method is extended to include substituted S(II) and S(IV) fluorides.

When chlorinated in the presence of caesium fluoride dimethylaminosulphur trifluoride produces sulphur chloride pentafluoride, while the straightforward chlorination gives sulphur tetrafluoride. Trifluoromethylsulphur chloride tetrafluoride results from the chlorofluorination of trifluoromethylsulphur trifluoride. This reaction is highly stereospecific, in that only the TRANS isomer is isolated. In contrast to the behaviour of dimethylaminosulphur trifluoride, methyliminosulphur difluoride reacts with chlorine with substitution of chlorine into the methyl group. Both mono and dichloro derivatives, chloromethyliminosulphur difluoride and dichloromethyliminosulphur difluoride, are isolated. Depending on the reaction conditions and the proportion of reactants used, trifluoromethyliminosulphur dichloride is also formed. A mechanism involving isomerisation of C-Cl to C-F bonds is postulated to explain the formation of the trifluoromethyl compound.

Various reactions between sulphur tetrafluoride and sulphur-oxygen compounds were investigated. With dialkylsulphites and sulphates, sulphur tetrafluoride gives alkylfluorosulphites and fluorosulphates respectively. No stable alkoxysulphur fluorides could be prepared from sulphur tetrafluoride and alkoxysilanes and only products resulting from the decomposition of the $(RO)_xSF_{4-x}$ ($x = 1, 2$ or 3) derivatives were observed. There was much greater stability with phenoxy derivatives and the complete series of phenoxysulphur fluorides, $(PhO)_xSF_{4-x}$ ($x = 1, 2, 3$ or 4), were prepared. N.M.R. results are consistent with a trigonal bipyramid geometry for these

compounds with the phenoxy groups in the equatorial plane. Sulphur tetrafluoride reacts in a complex manner with dimethylsulphoxide to produce bis(fluoromethyl)ether as the major product.

Sulphur tetrafluoride behaves as an oxidative fluorinating agent towards trivalent phosphorus compounds of the type L_3P (L = Me_2N, MeO and MeS) to produce fluorophosphoranes, L_3PF_2. With pentavalent phosphorus derivatives, L_3PO or $L_2L'PO$ (L' = Me), there was no evidence for fluorination of the phosphoryl group and the products are best regarded as being formed by a series of competitive exchange reactions.

Reactions between sulphur fluorides and amines were studied. Methyliminosulphur difluoride reacts with dimethylamine to yield bis(dimethylamino)sulphur, tetramethylene diamine and bis(dimethylimino)sulphur. The latter compound is also formed by the action of dimethylaminosulphur trifluoride with monomethylamine. Dimethylaminosulphur trifluoride is the only known dialkylamino derivative of sulphur tetrafluoride. Evidence is presented which suggests the possibility of a series of dialkylaminosulphur fluorides, $(Me_2N)_xSF_{4-x}$.

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INTRODUCTION

Prior to 1940, the known chemistry of sulphur fluorides was very limited and apart from work on sulphur hexafluoride, research in the field had been very sporadic. However, with the advent of World War II, research on sulphur fluorine compounds increased rapidly, primarily due to the interest in fluorine chemistry initiated by the atomic energy programme. Furthermore, the realisation that certain of the compounds had industrial applications, suggested that the possibility of future research in the field would be rewarding. This possibility has become a reality and a renewed impetus in the chemistry of sulphur fluorine compounds has resulted. Indeed, progress has been so rapid that, within the last few years, no less than seven comprehensive review articles covering different aspects of the chemistry have been published.[1-7]

The chemistry outlined in this introduction is not intended to be complete and the specific compounds discussed have been chosen, more or less, through a personal interest. Attention has been focused mainly on the binary fluorides and the different properties and reactions, associated with the valence and co-ordination number of sulphur.

The ability of fluorine, with its high electronegativity and small atomic radius, to stabilise unusual structures and the availability of sulphur to exhibit various valence states have resulted in the preparation of many sulphur fluorine derivatives. Such compounds constitute a uniform group, in that sulphur derivatives are known for co-ordination numbers ranging from 2 to 6.

Co-ordination number 2.

Although the high temperature fluorination of sulphur with silver fluoride was investigated as early as 1923 [8], and has since been re-investigated by other workers [9,10], no pure lower valent sulphur fluorides were isolated until forty years later. Seel and his co-workers [11,12] were successful in producing a sample of disulphur difluoride of sufficient purity to permit characterisation.

Both isomers, disulphur difluoride, FSSF, and thio-thionyl fluoride, SSF_2, have been isolated and studied.[13] Although SSF_2 is four co-ordinate, it is discussed under this heading to complete the chemistry of S_2F_2. The structures of FSSF and SSF_2 have been established by microwave spectroscopy.[14]

Disulphur difluoride readily isomerises to the more stable thio-thionyl fluoride and, in the presence of impurities, the latter compound decomposes below room temperature to sulphur and sulphur tetrafluoride.

$$FSSF \longrightarrow S = SF_2 \longrightarrow S + SF_4$$

Both compounds are hydrolytically unstable [13] and for the preparation of pure compounds rigorous precautions to exclude moisture must be taken.

For a number of years, the existence of sulphur difluoride, SF_2, was in doubt, although the compound had been observed in small quantities from the fluorination of sulphur with silver fluoride.[9] However, the extreme instability of the compound and the inadequate techniques used by early workers hampered the isolation and characterisation of SF_2. Contrary to early suggestions, SF_2 does not result from the decomposition of either FSSF or SSF_2, and only recently has the compound been unequivocally isolated by the action of sulphur dichloride with mercuric fluoride.[15] Sulphur difluoride is very unstable and decomposes to sulphur, sulphur tetrafluoride and disulphur difluoride.

Co-ordination number 3.

The chemistry of thionyl fluoride, SOF_2, appears to have been overshadowed by some of the more reactive sulphur fluorine compounds and, surprisingly, its synthetic uses have been little investigated.

The infra-red [16] and Raman spectra [17] have been interpreted on the basis of a pyramidal configuration at sulphur; these results are consistent with the microwave spectrum.[1]

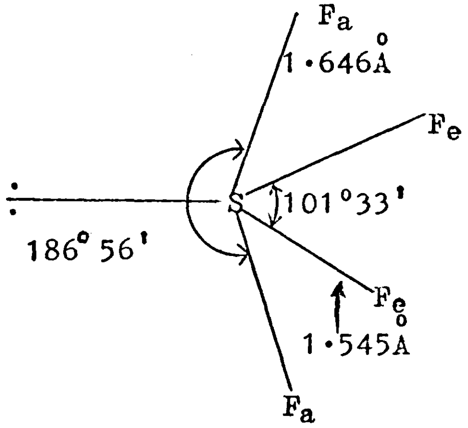
Thionyl fluoride is hydrolysed to sulphur dioxide, but is much more stable to hydrolysis than is sulphur tetrafluoride, or any of the lower sulphur fluorides.

Chemical reactions involving SOF_2 usually involve forcing conditions, although it does react at room temperature with ammonia, diethylamine [18] and fluorine.[19] Recently, the high temperature reaction of thionyl fluoride with dialkylsulphites has been shown to produce alkyl fluorosulphites. The latter compounds can also be prepared by the room temperature reaction of SOF_2 with alkoxytrimethylsilanes.[20]

Co-ordination number 4.

A tetrahedral bond distribution is by far the most common stereochemical arrangement for sulphur, and is the preferred geometry for sulphuryl fluoride, SO_2F_2.[21]

Although sulphur tetrafluoride is four co-ordinate, and was initially thought to have the tetrahedral structure, n.m.r. [22] and vibrational spectra [23] indicated that the structure was a trigonal bipyramid in which it was proposed that the lone pair of electrons occupied one of the equatorial positions. Subsequently, a microwave study proved the trigonal bipyramid structure.[24]



Gillespie has discussed the shape of sulphur tetrafluoride in terms of repulsive interactions between the electron pairs [25], and considered that a trigonal bipyramid arrangement of five electron pairs around the sulphur minimises the repulsive interactions.

The rather gross deviations from the trigonal bipyramid have been explained by the different amounts of s, p and d hybridisation in the axial and equatorial bonds.[24] Alternatively, the deviation can be interpreted on the basis of the Hellmann-Feynman theorem [26], where a displacement of the sulphur nucleus in SF_4 towards the lone pair would make the angle F_eSF_e less than 120° as observed, and would cause the F_aSF_a

angle to depart from 180° in the observed direction. A displacement of the sulphur nucleus by 0·29Å would bring the F_eSF_e angle from 120° to the observed value of 101°33'.[26]

The first unambiguous synthesis and characterisation of sulphur tetrafluoride was due to Brown and Robinson who prepared the compound by the controlled fluorination of sulphur.[27] Nowadays, SF_4 is conveniently prepared by the disproportionation of sulphur dichloride in the presence of sodium fluoride in acetonitrile.[28]

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

The reaction is thought to involve the initial formation of SCl_4, which arises from the equilibrium.

$$3SCl_2 \rightleftharpoons SCl_4 + S_2Cl_2$$

The major impurity in the preparation is SOF_2, which results from the rapid hydrolysis of SF_4. Removal of SOF_2 is best attained by selectively decomposing addition compounds of SF_4.[29]

The high Trouton constant of 27·1 for SF_4 suggests that the molecule is associated. This has been confirmed by low temperature infra-red [30] and n.m.r. studies [31], which support association (in both the liquid and solid phases) through fluorine bridges, but the disposition of the lone pairs is as yet unsettled.

Much of the recent impetus in sulphur fluorine chemistry is due to research involving sulphur tetrafluoride. The compound is a remarkably effective reagent for the selective replacement of a carbonyl oxygen in organic compounds with fluorine.

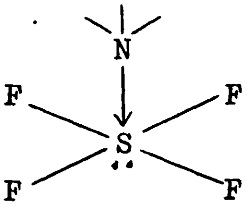
$$>C = O + SF_4 \longrightarrow >CF_2 + SOF_2$$

This reaction has broad scope and is effective with a variety of carbonyl compounds.[32]

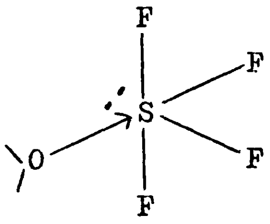
Many hitherto unknown inorganic fluorides have been prepared by fluorination of oxides and sulphides with sulphur tetrafluoride.[33]

Sulphur tetrafluoride forms complexes with Lewis acids e.g. $SF_4.SbF_5$, $SF_4.BF_3$ and $SF_4.PF_5$.[27] Initially, the structures of these adducts were formulated as simple acid-base complexes e.g. $SF_4{:}\longrightarrow BF_3$. However, it is now generally accepted that SF_4 is only a relatively weak donor molecule and Seel and Detmer have suggested an ionic formulation of the adducts, based on the SF_3^+ cation i.e. $SF_3^+BF_4^-$.[34] This is consistent with the observation that all the fluorides which form adducts with SF_4 are strong fluoride ion acceptors and form stable fluoro anions e.g. SbF_5^- and PF_6^-. Association based on fluorine bridge bonds, whereby the salt attains pseudo-octahedral symmetry, is also in keeping with the 1:1 adduct formulation.[31]

Although sulphur tetrafluoride is only a weak electron acceptor, Muetterties has reported the formation of 1:1 adducts with tertiary amines.[35] On the basis of ^{19}F n.m.r. results, the adducts were assigned a square pyramidal structure. However, other weak adducts have been observed between SF_4 and ethers, which show two sets of non-equivalent fluorine atoms in the ^{19}F n.m.r. spectrum, and a trans structure is proposed.[36]



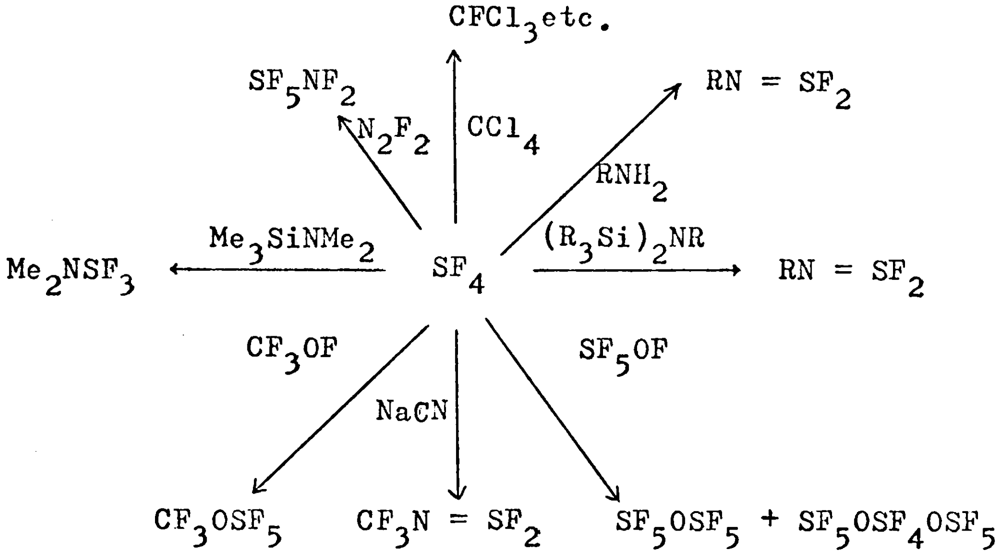
$R_3N \longrightarrow SF_4$



$R_2O \longrightarrow SF_4$

As yet, no convincing argument has been given to explain why the tertiary amines should prefer one structure, and the ethers another.

Some other reactions which demonstrate the versatility of SF_4 as a synthetic reagent are summarised on the following page.



Co-ordination number 5.

Only a few examples of this co-ordination number are known. The adducts produced from the reaction of sulphur tetrafluoride with caesium fluoride [37] or tetramethylammonium fluoride [38], are assumed to contain the SF_5^- ion which is regarded as being square pyramidal. Apart from the adducts already mentioned between sulphur tetrafluoride and tertiary amines, no other examples of sulphur fluorine compounds are known which have the square pyramidal structure.

Thionyl tetrafluoride, SOF_4, is an example of a five co-ordinate compound which has a trigonal bipyramid structure. Infra-red [39] and n.m.r. results are in agreement with the oxygen atom occupying an equatorial position. Though there are two types of fluorine atom, only one signal is observed in the ^{19}F spectrum.[40] Presumably this arises because of fast exchange between the fluorine sites, but no low temperature n.m.r. studies have been reported which confirm this.

SOF_4 can be prepared from SOF_2 using several experimental conditions.[19] The alternative method of preparation involves the oxidation of sulphur tetrafluoride by an oxygen donor.[41] Several inorganic oxides, such as CrO_3 and NO_2, are capable of this reaction.

It is only recently that reactions of SOF_4 have been examined, and the compound takes part in similar reactions to those undergone by SOF_2 and SF_4.

Thionyl tetrafluoride can behave as a weak base and forms addition compounds with several fluoride ion acceptors.[34] These complexes have been formulated as salts ($SF_3O^+MF_x^-$) but the alternative formulation of these materials as complexes $SF_4O \rightarrow MF_x$, has not been eliminated.

The compound reacts with water much more rapidly than either thionyl fluoride or sulphuryl fluoride, which is perhaps a consequence of the unusual co-ordination state of sulphur. In water, it gives sulphuryl fluoride and hydrogen fluoride, while in sodium hydroxide solution, fluoride and fluorosulphate ions are obtained.

With ammonia and primary amines, SOF_4 produces iminosulphur oxydifluorides.[42]

$$NH_3 + SF_4O \xrightarrow{2NaF} HN = SF_2 = 0 + 2NaHF_2$$

The parent compound in this class, $HN = SF_2 = 0$, readily eliminates hydrogen fluoride, using caesium fluoride as a dehydrofluorinating agent, producing a polymer which precipitates as a tough, white rubber.

SOF_4 interacts with $R_2N\text{-}SiMe_3$ compounds ($R = Me, Et$) at room temperature to produce $R_2NS(O)F_3$ derivatives.[43] The proton and ^{19}F n.m.r. spectra suggest that the R_2N group, oxygen and one fluorine atom are in the equatorial plane of a trigonal bipyramid.

Other reactions of thionyl tetrafluoride with various silicon-nitrogen compounds and substituted amines have been reported.[44-46]

Co-ordination number 6.

A co-ordination number of six with valence saturation at sulphur produces stable sulphur fluorine compounds.

Chemically, sulphur hexafluoride, SF_6, is almost totally inert and is unaffected by aqueous or fused alkali. The apparent reluctance of SF_6 to undergo chemical reaction has been explained in kinetic rather than thermodynamic terms.[2] In contrast to the lack of reactivity of SF_6 towards nucleophiles, reactions with electrophiles have been accomplished.[3]

$$SF_6 + AlCl_3 \xrightarrow[24hr.]{200^\circ} AlF_3 + Cl_2 + S_2Cl_2$$

Because of this inherent kinetic stability of SF_6 and lack of reactivity, much of the initial industrial research in the field of sulphur fluorine chemistry was orientated towards the preparation of its derivatives. Accordingly, many perfluoroalkyl derivatives of SF_6 have been prepared [47] and used extensively in industry.[1]

SF_6 is not a convenient starting material for the preparation of substituted S(VI) fluorides, and most derivatives of SF_6 are prepared by oxidative fluorination of organic sulphur compounds [48], although reactions with disulphur decafluoride, S_2F_{10}, and sulphur chloride pentafluoride, SF_5Cl, are preferred for synthesising SF_5 compounds.

Structural studies indicate an octahedral symmetry for the binary fluorides, SF_6 [49] and S_2F_{10} [50], but the monosubstituted derivatives e.g. SF_5Cl, have slightly distorted octahedral structures. Both cis and trans isomers have been observed for disubstituted derivatives of SF_6.[6]

Concluding remarks and possible future developments.

The above brief survey has attempted little more than to bring to light some of the extreme differences in chemical reactivity and stability of several sulphur fluorine compounds. Other aspects of the chemistry are discussed in subsequent chapters.

Although binary fluorides are known for co-ordination numbers of 2, 4 and 6, it is almost certain that future developments in the field will involve the preparation of derivatives of the more stable, higher co-ordinated compounds. The preparation of some of the following unknown compounds appear particularly challenging:-

(1) Compounds containing sulphur in two
different valencies e.g. CF_3SSF_5
and $MeSSF_3$.

(2) Compounds containing hydrogen
e.g. SF_5H and SF_3H.

(3) Mixed chloro-fluorides
e.g. SF_4Cl_2 and SF_3Cl.

Therefore, although the advancement in sulphur fluorine chemistry has been rapid, it is obvious that a number of interesting and thought provoking reactions still await investigation.

GENERAL EXPERIMENTAL METHODS

Standard vacuum techniques using Pyrex-glass apparatus were used throughout. Hygroscopic solids were handled in a nitrogen filled dry box.

Infra-red spectra were measured with a Perkin-Elmer 457 instrument. Normal abbreviations to denote band shapes and intensities were used e.g. (s) = strong; (m.br.) = medium broad; (sh.) = shoulder etc.

N.M.R. spectra were determined on a Perkin-Elmer R.10 spectrometer at 60·0 Mc for proton and 56·4 Mc for fluorine, with a probe temperature of 33°. All fluorine spectra were measured in p.p.m. relative to trichlorofluoromethane, CCl_3F, and proton spectra were recorded in p.p.m. relative to tetramethylsilane (T.M.S.), $(CH_3)_4Si$. Peak multiplicities were 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.9 spectrometer for high resolution mass measurements and an A.E.I. M.S.12 model for normal low resolution spectra. Except where stated to the contrary, a cold inlet system was used.

Elemental analysis were performed by Alfred Bernhardt Microanalytisches Laboratorium.

CHAPTER I

CHLORINATION AND FLUORINATION OF SULPHUR FLUORIDES

INTRODUCTION

In recent years, a large amount of activity has centred on the investigation of per- and poly-fluorinated organic sulphur compounds with the result that much information on the subject is available.[47] Academic interest in fluorocarbon derivatives has been stimulated by the challenge of finding methods of synthesis and by the unique differences that often exist between these compounds and their hydrocarbon counterparts. Industrial interest in fluorocarbon compounds is based mainly on the high chemical and thermal stability of fluorocarbon systems and does much to encourage research in this area of chemistry.

The main object of the research detailed in this chapter was to prepare sulphur fluorine compounds which could be used as heat-transfer agents. The major factors required in any material were chemical stability and inertness. Sulphur hexafluoride and many of its derivatives are chemically inert and have high thermal stability. Attempts have been made to isolate novel perfluoroalkyl derivatives of SF_6 e.g. CF_3SF_4Cl, which should have the required elements of stability and inertness.

Logically, two main synthetic routes appear possible for the preparation of such compounds.

(a) Substitution into S(VI) compounds e.g. SF_5Cl, hoping to introduce other substituents X (X = CF_3S, NMe_2 etc.) by replacement of Cl.

(b) Oxidation of S(II) and S(IV) compounds via chlorofluorination with mixtures of chlorine and caesium fluoride.

SUMMARY OF REACTIONS

A. Substitution into S(VI) compounds.

1. $SF_5Cl + CF_3SCl \longrightarrow$ no reaction.

2. $SF_5Cl + Me_3SiNMe_2 \longrightarrow Me_3SiF$ + solids.

3. $SF_5Cl + (Me_3Si)_2NR \longrightarrow Me_3SiF$ + solids.
R = H or Me

4. $CF_3SF_5 + Me_3SiCl \longrightarrow$ no reaction.

B. Oxidation of S(II) and S(IV) compounds via chlorofluorination.

4. $CF_3SNMe_2 + Cl_2 + CsF \longrightarrow CF_3SCl$ + traces of $CF_3S(O)F$, $(CF_3S)_2$ and SiF_4.

6. $CF_3SSCF_3 + Cl_2 + CsF \longrightarrow CF_3SCl + (CF_3S)_2$(50%) + traces of CF_3Cl, $CF_3S(O)F$ and SiF_4.

7. $Me_2NSF_3 + Cl_2 + CsF \longrightarrow SF_5Cl$.

8. $CF_3SF_3 + Cl_2 + CsF \longrightarrow CF_3SF_4Cl + CF_3Cl$ + traces of $CF_3S(O)F$ and SiF_4.

C. Chlorination of S(IV) compounds.

9. $Me_2NSF_3 + Cl_2 \longrightarrow SF_4 + SCl_2 + Me_2NCl$ (trace).

10. $MeN = SF_2 + Cl_2 \xrightarrow{*} CH_2ClN = SF_2 + CHCl_2N = SF_2 + HCl$.

11. $MeN = SF_2 + \text{excess } Cl_2 \xrightarrow{*} CF_3N = SCl_2 + CHCl_2N = SF_2 \text{ (trace)} + HCl$.

D. Miscellaneous reactions.

12. $SF_4 + CF_3SSCF_3 \xrightarrow{*}$ no reaction.

13. $CH_2ClN = SF_2 + NaF/CH_3CN$ or $CsF \longrightarrow$ no reaction.

14. $CF_3SF_4Cl + Hg + \text{Light} \longrightarrow CF_3Cl + SF_4 + SOF_2 + SiF_4$.

* Reaction conducted both with and without the presence of CsF.

Basic requirements for the stabilisation of substituted S(VI) fluorides.

It is of interest to examine some of the well established S(VI) fluoride derivatives and to attempt to correlate their stability with some basic structural or ligand requirement, which may aid the preparation of further substituted derivatives.

The pentafluorosulphur grouping, SF_5, has been established when attached to perfluoroalkyl groups, R_f, halogens, X, (X = F, Cl or Br) and a variety of other electronegative entities e.g. NF_2, $(CF_3)_2N$ and $N = SF_2$.[5,51] Compounds containing the sulphur tetrafluoride grouping, SF_4, however, are more limited and have only definitely been confirmed for perfluoroalkyl groups, $(R_f)_2SF_4$.[2] As yet, no SF_4X_2 compounds have been prepared.

It is well known that the ability of sulphur to have a co-ordination number greater than four is due to the valence shell of sulphur having available 3d orbitals in addition to 3s and 3p. A study of overlap integrals reveals that, in the free sulphur atom, the 3d orbitals are too weakly bound and diffuse to contribute significantly to the bonding. However, Craig and Magnusson [52] have demonstrated theoretically how the diffuse sulphur 3d orbitals could contract in the presence of small electronegative atoms and for sulphur hexafluoride the bonding can be described in terms of a sp^3d^2 configuration at sulphur, with the hybrids extending towards six octahedral vertices. It was further shown that fluorine had the greatest effect on contracting the 3d orbitals and that other atoms e.g. Cl, C, and H, had much smaller effects.

Although SF_5R compounds are stable when R = Cl or Br (SF_5Cl is thermally stable up to 400°C while SF_5Br begins to decompose at 150°C), it has been observed [6] that, on going from the chloride to the bromide, there is a significant increase in the S-R bond length (SF_5Cl [53], S-Cl = 2·03Å; SF_5Br [54], S-Br = 2·19Å) and suggests that the size and less electronegative nature of I in SF_5I should make this compound unstable. Therefore, as fluorine atoms are replaced by either larger or less electronegative atoms or groups, the possibility of d orbital contraction decreases, causing not only the stability of the bond replaced to fall but the stability of the whole molecule.

Kinetic and thermodynamic effects are important in the preparation of substituted S(VI) fluorides especially when the reactions involve substitution. Although thermodynamically SF_6 should undergo hydrolysis [2], the compound is stable in the presence of water. The lack of hydrolysis has been explained in kinetic terms and various reasons postulated for the high activation energy.

It is concluded that the basic requirements for the preparation of stable S(VI) fluoride derivatives are:-

(1) The presence of small electronegative ligands attached to sulphur which can allow contraction of the 3d orbitals.

(2) A low energy pathway for reaction.

A. Substitution into S(VI) compounds.

(a) Reactions with sulphur chloride pentafluoride.

The ability of sulphur chloride pentafluoride, SF_5Cl, to produce SF_5 radicals on ultra-violet irradiation is an important feature of its chemistry.[6] Addition of SF_5Cl to olefins [55] and cyanides [37] are of considerable preparative value for the introduction of the SF_5 group into organic compounds. Although most reactions involving SF_5Cl have been conducted under u/v conditions, it has been suggested that thermal reactions at $\sim$200°C can produce SF_5 radicals, if materials are present which are reactive towards the chlorine atom.[3]

Reaction of sulphur chloride pentafluoride with trifluoromethylsulphenyl chloride.

Although the possibility of $CF_3S{-}SF_5$ is suggested by the existence of S_2F_{10}, no reaction occurred when a mixture of trifluoromethylsulphenyl chloride, CF_3SCl, and SF_5Cl was heated at temperatures greater than 200°C.

$$SF_5Cl + CF_3SCl \not\longrightarrow CF_3SSF_5 + Cl_2$$

Assuming that the substitution reaction would involve a S_N1 process, where the rate determining step involves a decrease in co-ordination number, the failure to observe a reaction could be due to the lack of a suitable low lying energy pathway for facile S-Cl bond rupture, and tends to indicate that, under these experimental conditions, the chlorine atom is not as reactive as was first thought. An attempt to prepare CF_3SSF_5 by irradiating mixtures of bis(trifluoromethyl) disulphide, $(CF_3S)_2$, and S_2F_{10} has been reported, but only products resulting from the decomposition of the reactants were produced.[56]

Reactions of sulphur chloride pentafluoride with silicon-nitrogen compounds.

Many covalent sulphur halides are known to cause fission of silicon-nitrogen bonds, with the formation of various sulphur-nitrogen compounds.[57] The reactions between SF_5Cl and Si-N containing compounds were investigated in an attempt to prepare SF_5R compounds, where R = NMe_2.

In all cases, SF_5Cl reacted readily with the substituted silylamine, below or at room temperature, to produce trimethylsilylfluoride as the only volatile product.

$$SF_5Cl + Me_3SiNMe_2 \longrightarrow Me_3SiF + \text{solids}$$

$$SF_5Cl + (Me_3Si)_2NR \longrightarrow Me_3SiF + \text{solids}$$

$$R = H \text{ or } Me$$

In addition, yellow intractable viscous solids were produced which, from their appearance, were thought to be polymeric and were not investigated since the prime purpose of the research was to isolate liquid products. Both sulphur dichloride and disulphur dichloride have been shown to react with N-methylhexamethyldisilazane and hexamethyldisilazane, forming high yields of trimethylsilylchloride and yellow polymeric solids.[58]

$$S_nCl_2 + MeN(SiMe_3)_2 \longrightarrow 2Me_3SiCl + (MeNS_n)_x$$

However, in the light of the preparation of dialkylamino derivatives of TeF_6 [59], and recent studies carried out in this laboratory with MoF_6 and Si-N compounds [60], it is now felt that the actual composition of the solid products from the SF_5Cl reactions might prove rewarding and merit further investigation.

It is also interesting to note that the Me_3Si entity scavenges a fluorine and not a chlorine atom from SF_5Cl, forming Me_3SiF. Possibly the thermodynamic preference for very strong Si-F bond formation (Si-F = 135 kcals/mole; Si-Cl = 91 kcals/mole) favours Me_3SiF.

(b) Reaction of trifluoromethylsulphur pentafluoride with trimethylsilylchloride.

By analogy with the reactions of SF_5Cl and Si-N compounds to produce Me_3SiF, it seemed probable that, in the reaction of CF_3SF_5 with Me_3SiCl, the Si-Cl bond could be broken forming Me_3SiF and CF_3SF_4Cl. Furthermore, CF_3SF_4Cl has subsequently been prepared by an alternative route and is capable of existing as a stable compound.

When, however, equimolar quantities of CF_3SF_5 and Me_3SiCl were heated at 120°C, no reaction occurred although the reaction appears to be thermodynamically feasible.

$$CF_3SF_5 + Me_3SiCl \not\longrightarrow CF_3SF_4Cl + Me_3SiF$$

The lack of reaction must be due to kinetic reasons, and accentuates that the main problem in the preparation of stable S(VI) fluorine derivatives via substitution is the need for suitable methods of synthesis, which allow a low activation energy mechanism for reaction.

Chlorofluorination reactions with caesium fluoride and chlorine.

Before discussing the reactions in this section, it is pertinent to examine some aspects of the chlorofluorination technique and to understand the function of alkali metal fluorides in various reactions involving sulphur compounds.

Alkali metal fluorides have been used extensively in reactions as a source of fluoride ions and as catalysts. However, it is often difficult to distinguish between the two different effects and, in many cases, the exact role of the metal fluoride is not fully understood.

The chlorination of sulphur tetrafluoride in the presence of caesium fluoride has produced high yields of sulphur chloride pentafluoride.

$$SF_4 + Cl_2 + CsF \longrightarrow SF_5Cl + CsF$$

The reactive intermediate in this reaction has been postulated to involve the SF_5^- ion.[37]

$$CsF + SF_4 \rightleftharpoons Cs^+SF_5^-$$

Although other workers did not observe compound formation between CsF and SF_4 [38], they did establish that tetramethylammonium fluoride forms a stable adduct with sulphur tetrafluoride. Again the adduct is assumed to contain the SF_5^- ion.

A large number of papers reporting on fluoride ion catalysed reactions have appeared in the literature and a considerable bibliography on the subject can be found in a review article.[61]

The caesium fluoride catalysed reactions between fluorocarbon olefins and sulphur tetrafluoride [62], thionyl fluoride [63] and iminosulphur difluorides [64] have produced structurally interesting fluorocarbon derivatives. Recently, a simplified synthesis of SF_5Cl [65] involving the reaction of SF_4 and ClF in the presence of catalytic quantities of CsF has been reported.

The presence of CsF in a reaction can drastically change the mode of the reaction, while a study of the fluorination of thionyl fluoride has demonstrated the importance of alkali metal fluoride catalysts in controlling the reaction.[4]

The physical state of the alkali metal fluoride can alter the course of the reaction, and the particle size and dryness of the fluoride have a pronounced effect on the yield of the observed products. The physical requirements of the fluoride have been outlined in the preparation of nitrosyl fluoride from the corresponding chloride and CsF.[66] The "state" of the CsF (whether powdered or caked) plays an important part in the F^- catalysed decomposition of N-fluoroformylsulphur difluoride [67], where it has been postulated that, on the surface of the CsF, there are sites which vary in their nucleophilic activity, and that grinding can increase the number of sites of high nucleophilicity and the absorbing power of the fluoride.

Finally, other more subtle effects in addition to the above, can alter the course of the reaction. Shaking the reactor while the reaction is occurring can cause side reactions. During the preparation of SF_2NCl, by the reaction of NSF with CsF and Cl_2, a secondary reaction occurred producing SF_5Cl. The amount of SF_5Cl formed became appreciable if the reactor was shaken during the reaction.[67]

B. Chlorofluorination of S(II) compounds.

(a) N-Dimethyltrifluoromethane sulphenamide.

When a mixture of Me_2NSCF_3 and chlorine were heated at 60°C in the presence of caesium fluoride, trifluoromethylsulphenyl chloride, CF_3SCl, was produced as the major product.

$$Me_2NSCF_3 + Cl_2 + CsF \longrightarrow CF_3SCl + CF_3S(O)F + (CF_3S)_2 + SiF_4$$

Trifluoromethylsulphinyl fluoride, $CF_3S(O)F$, and bis-(trifluoromethyl)disulphide, $(CF_3S)_2$, were isolated in trace quantities.

No evidence was obtained for chlorine substitution into the dimethylamino group, and the products are best visualised as arising from cleavage of the sulphur - nitrogen bond with concomitant chlorination.

$$Me_2N\text{-}SCF_3 + Cl_2 \longrightarrow CF_3SCl + Me_2NCl$$

The fate of the dimethylamino group is not known with any certainty and, since no volatile Me_2N compounds were isolated, it must be assumed that this grouping is incorporated in some manner in the caesium salt c.f. $CsN(SO_2F)_2$.[68]

The formation of $CF_3S(O)F$ is almost certainly due to hydrolysis of CF_3SF_3 [69] which is formed by the fluorination of CF_3SCl.[63]

$$CF_3SF_3 + H_2O \longrightarrow CF_3S(O)F + 2HF$$

$$3CF_3SCl + 3CsF \longrightarrow [3CF_3SF] \longrightarrow CF_3SF_3 + (CF_3S)_2$$

The existence of CF_3SF, as an unstable species [70], is helpful in explaining the formation of $(CF_3S)_2$.

(b) Bis(trifluoromethyl)disulphide.

The products obtained from heating a mixture of $(CF_3S)_2$, chlorine and caesium fluoride were similar to those obtained in the previous reaction.

$$CF_3S\text{-}SCF_3 + Cl_2 + CsF \longrightarrow CF_3SCl + (CF_3S)_2 + CF_3S(O)F + CF_3Cl + SiF_4$$

After 48 hours somewhat over half the $(CF_3S)_2$ was recovered unchanged. It has previously been postulated that the photochemical or thermal chlorination of $(CF_3S)_2$ is a reversible process.[71]

$$CF_3S\text{-}SCF_3 + Cl_2 \rightleftharpoons 2CF_3SCl$$

In both reactions (a) and (b) a trace of an unidentified compound was produced which showed a complex multiplet resonance in the ^{19}F n.m.r. Unfortunately, however, the sample was so small that the substance was not identified, but the chemical shift of the CF_3 group (a) 68·2 p.p.m. (b) 65·4 p.p.m., suggests that this compound was in fact the S(VI) species, CF_3SF_4Cl (see later).

Chlorofluorination of sulphur(IV) compounds.

(a) N-Dimethylaminosulphur trifluoride.

Although sulphur tetrafluoride does not react with chlorine even at high temperatures [72], Me_2NSF_3 reacts readily with chlorine at room temperature. If caesium fluoride were present, then sulphur chloride pentafluoride could be isolated as the major product. When, however, the caesium fluoride was omitted, sulphur tetrafluoride and sulphur dichloride were produced.

$$Me_2NSF_3 + Cl_2 + CsF \xrightarrow{25^\circ C} SF_5Cl$$

$$Me_2NSF_3 + Cl_2 \xrightarrow{25^\circ C} SF_4 + SCl_2$$

The chlorofluorination of Me_2NSF_3 represents an easy synthetic route for preparing SF_5Cl under mild conditions.

The results suggest that the first stage in these reactions involves cleavage of the sulphur-nitrogen bond to form initially SF_3Cl (1).

$$Me_2NSF_3 + Cl_2 \longrightarrow SF_3Cl + Me_2NCl \qquad (1)$$

Many unsuccessful attempts have been made to isolate $SF_{4-x}Cl_x$ (x = 1, 2 or 3) compounds [72], and it is now generally accepted that the failure to isolate such compounds is due to easy disproportionation (2) and (3).

$$2SF_3Cl \longrightarrow SF_4 + SF_2Cl_2 \qquad (2)$$

$$2SF_2Cl_2 \longrightarrow SF_4 + SCl_4 \qquad (3)$$

Certainly the very low energy barrier to fluorine exchange in sulphur tetrafluoride [31] indicates that disproportionation is likely in the chloro-fluoro derivatives.

Although a species of empirical formula SCl_4 exists, the compound has never been fully characterised [6] and is unstable towards dissociation (4).

$$SCl_4 \longrightarrow SCl_2 + Cl_2 \qquad (4)$$

The isolation of SF_4 and SCl_2 from the chlorination of Me_2NSF_3, suggests that the SF_5Cl produced from the chlorination in the presence of CsF, arises from the chlorofluorination of SF_4. Furthermore, SF_4 could be regenerated by the fluorination of SCl_2.[28]

No volatile species containing the dimethylamino group were isolated from the chlorination in the presence of caesium fluoride, and again it must be assumed that this grouping is contained in the solid products. However, in the straightforward chlorination reaction in the absence of caesium fluoride, traces of a compound tentatively assigned to Me_2NCl were isolated. Characterisation of this compound was based on n.m.r. and mass spectral data. Initially, the mass spectrum of the product revealed no chlorine containing species, and only under high sensitivity conditions could such peaks be found. Me_2NCl showed no parent ion but peaks at m/e, 35 and 37; 44; 49 and 51; associated with $^{35,37}Cl$; Me_2N; and $N^{35,37}Cl$ ions, were evident and suggest the presence of such a compound.

Similar difficulties have been encountered in obtaining the mass spectrum of SF_5NCl_2.[73]

It is perhaps not too surprising that Me_2NCl was only present in very small quantities, since it has been shown to be a useful chlorinating agent [74] and could have aided in any one of the chlorination steps cited above.

(b) Trifluoromethylsulphur trifluoride.

CF_3SF_3 reacts with chlorine in the presence of caesium fluoride at room temperature to produce trifluoromethylsulphur chloride tetrafluoride, CF_3SF_4Cl, as the major product.

$$CF_3SF_3 + Cl_2 + CsF \longrightarrow CF_3SF_4Cl + CF_3Cl + CF_3S(O)F + SiF_4$$

Small amounts of CF_3Cl, a normal degradation product from the chlorination of trifluoromethyl groups, and $CF_3S(O)F$, formed by hydrolysis of CF_3SF_3, were isolated. Due to traces of unreacted CF_3SF_3 and $CF_3S(O)F$ impurity, an analytically pure sample of CF_3SF_4Cl could not be obtained by conventional trap to trap distillation. However, partial characterisation of CF_3SF_4Cl was achieved by n.m.r., infra-red and high resolution mass spectrometry.

Properties of CF_3SF_4Cl.

Trifluoromethylsulphur chloride tetrafluoride is a colourless, volatile liquid which is indefinitely stable at room temperature. A n.m.r. spectrum, rerun after several months at room temperature, showed no change in the spectrum. When a sample of CF_3SF_4Cl was exposed to the atmosphere and the mass spectrum recorded, the peaks associated with CF_3SF_4Cl remained unaltered.

After a mixture of CF_3SF_4Cl (containing a very small quantity of $CF_3S(O)F$) and mercury was left in bright sunlight for several hours, no CF_3SF_4Cl was recovered. The reaction products consisted of a mixture of SF_4 (SOF_2 and SiF_4) and CF_3Cl, formed by the decomposition of CF_3SF_4Cl. It was hoped that this reaction would provide a route to $(CF_3SF_4)_2$, which has previously been postulated to arise from the electrochemical fluorination of S-Methylthioglycollic acid chloride, $CH_3SCH_2C(O)Cl$ [75], but has not been fully authenticated.

The apparent mode of decomposition of CF_3SF_4Cl is analogous to that observed in the thermal decomposition of perfluoroalkyl derivatives of sulphur hexafluoride.[47]

$$R_fSF_5 \xrightarrow{\Delta} R_fF + R_f.R_f + SF_4$$

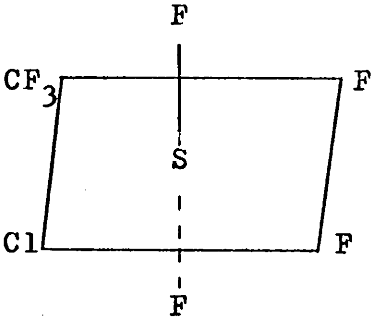
$$(R_f)_2SF_4 \xrightarrow{\Delta} R_f.R_f + SF_4$$

Whether this decomposition of CF_3SF_4Cl is truly genuine, or is perhaps influenced by the $CF_3S(O)F$ impurity, has still to be determined.

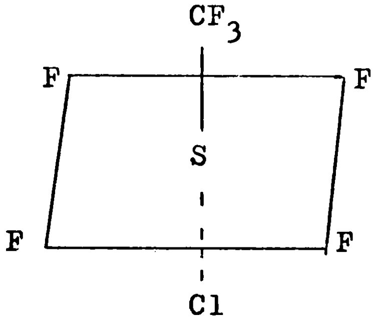
The preparation of CF_3SF_4Cl is important in that it represents the first substituted derivative of SF_5Cl which contains the SF_4Cl grouping, and it is evident that a great deal of interesting chemistry based on CF_3SF_4Cl awaits development. A whole series of reactions similar to those undergone by SF_5Cl [2] seem possible, leading to the preparation of CF_3SF_4R and RSF_4Cl compounds.

The n.m.r. and structure of CF_3SF_4Cl.

Since the compound is a disubstituted derivative of sulphur hexafluoride, the CF_3 and Cl groups could be in either CIS or TRANS configurations



CIS



TRANS

causing the ^{19}F n.m.r. spectrum to be one of the following types:-

(1) $A_2B_2X_3$ (CIS)
(2) A_4X_3 (TRANS)
(3) A mixture of (1) and (2).

The relatively simple nature of the spectrum in the sulphur fluorine region clearly rules out the complex spin system expected for a CIS structure, and it appears that an A_4X_3 system, with TRANS substitution of the CF_3 and Cl groups, exists in CF_3SF_4Cl. The CIS isomer, if present at all, is not present in a substantial proportion.

The ^{19}F n.m.r. spectrum of CF_3SF_4Cl consists of two multiplets integrating as 4:3, associated with the SF_4 and CF_3 groups. The SF_4 resonance is a quartet at -102·1 p.p.m. due to coupling with three fluorine atoms of the CF_3 group. The CF_3 resonance is a quintet centred at +67·3 p.p.m. due to coupling with four equivalent basal fluorine atoms attached to sulphur. The CF_3-SF_4 coupling constant, J_{F-F}, is 24 c/s and a comparison of J_{F-F} in related compounds (Table 1), supports a structure with a CF_3 group attached to an SF_4 entity.

^{19}F N.M.R. SPECTRUM OF TRANS CF_3SF_4Cl

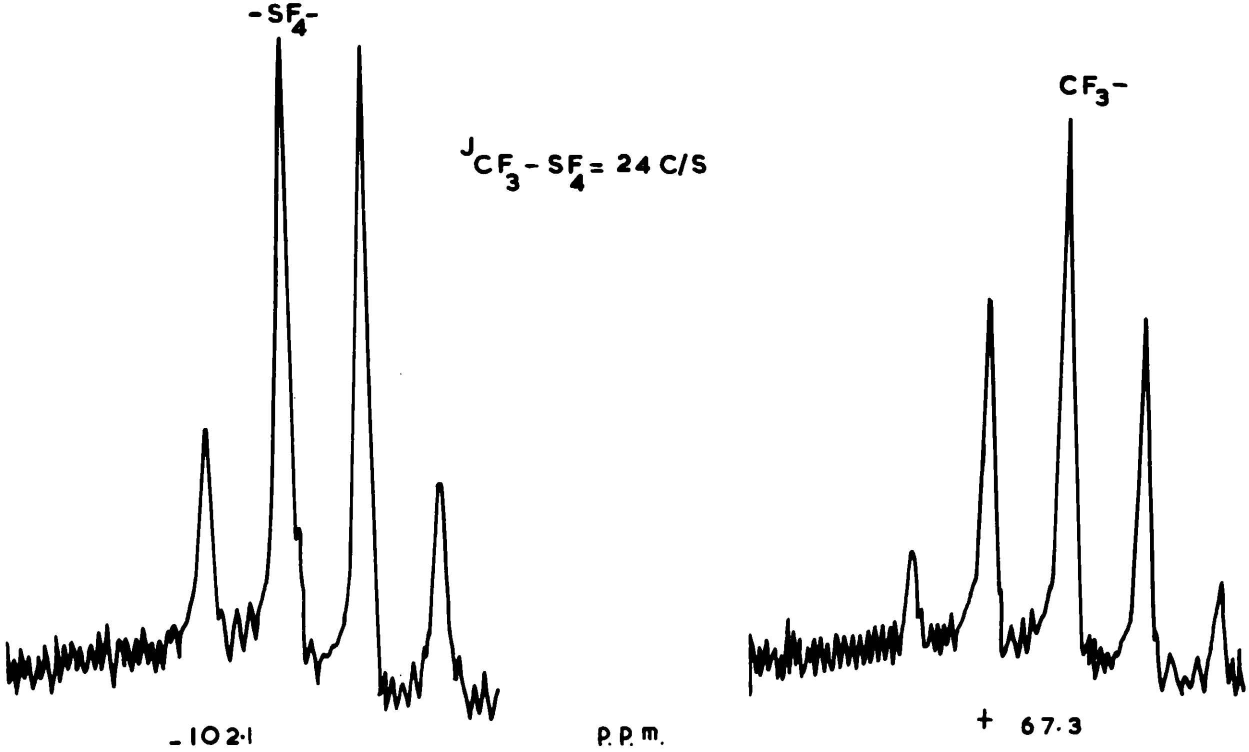


TABLE 1

Compound	$J_{CF_3-SF_4}$ c/s	δ_{SF_4} p.p.m.(a)	δ_{CF_3} axial p.p.m.(a)	Ref.^{n}
CF_3SF_4Cl	24	−101·9	+67·3	
$CF_3SF_4NF_2$	22	−21·9	+66·6	[76]
$CF_3SF_4CF_2CF_3$	24	−21·7	+67·2	[77]
$CF_3SF_4CF_2CO_2CH_3$	23·5	−21·7	+65·9	[77]
CF_3SF_5	22	−30·0	+64·6	[78]
SF_5Cl	—	−116·8	—	[78]

(a) Chemical shift with respect to external CCl_3F.

All of the disubstituted derivatives of SF_6 in (Table 1) show a constancy in the J_{F-F} coupling constant, and a value of between 22 and 24 c/s is taken as characteristic of the CF_3SF_4-group.[79]

The chemical shift of the basal fluorine in bis perfluoroalkyl derivatives, $(R_f)_2SF_4$, occurs in the narrow region of -30 to -20 p.p.m. [77], but the position of the sulphur fluorine resonance in TRANS CF_3SF_4Cl occurs at much lower fields. This is due to the presence of chlorine in the molecule.

In monosubstituted derivatives of sulphur hexafluoride, SF_5X compounds, it has been shown that the order of shielding of the basal fluorine atoms is

$$F > CF_3 > Cl > Br$$

so that, in SF_5Cl, the chlorine atom is less effective in shielding the SF_4 group than the trifluoromethyl group in CF_3SF_5, and consequently, the basal fluorine atoms resonate at much lower fields in SF_5Cl.

As a result, the basal shifts in SF_5Cl and CF_3SF_4Cl are an order of magnitude larger than for any of the other compounds, and are consistent with the presence of chlorine in these molecules.

The position of the axial CF_3 group resonance in the disubstituted derivatives, SF_4AA^1, is approximately constant, and while the basal shifts extend over 80 p.p.m., the apical shifts cover only 1·4 p.p.m. A similar constancy of the axial fluorines has been found in SF_5X compounds.[78]

The infra-red spectrum of TRANS CF_3SF_4Cl.

The infra-red spectrum shows absorption in two distinct regions associated with the CF_3 and SF_4 groups. Recently, a complete vibrational assignment has been carried out on CF_3SF_5 [80] and SF_5Cl [81], and a comparison of the infra-red spectra of these compounds is useful in helping to assign specific vibrations due to the CF_3 and SF_4 groups in CF_3SF_4Cl (Table 2).

The $-SF_4-$ group is a common feature in these molecules, and absorption due to this grouping in CF_3SF_4Cl is attributed to the very strong bands at 860 and 678 cm^{-1}. The absence of any other strong absorptions in this region of the spectrum almost certainly indicates that these bands are due to sulphur-fluorine vibrations.

Absorptions in the (1250-1150 cm^{-1}) region in the spectrum of CF_3SF_4Cl are assigned to the CF_3 stretching modes by analogy with CF_3SF_5. The CF_3 bend is found at 785 cm^{-1}.

The sulphur-chlorine vibration in SF_5Cl has been

TABLE 2

CF_3SF_5	CF_3SF_4Cl	SF_5Cl	Assignment
1256(v.s.)	1250(v.s.)		CF_3 asym. stretch
	1182(m)		
1168(v.s.)	1155(s)		CF_3 sym. stretch
902(v.s.)	860(v.s.)	908(v.s.)	SF_4 square asym. stretch
883(v.s.)		854(v.s.)	S-F axial stretch
755(v.s.)	785(m)		CF_3 asym. bend
692(v.s.)	678(v.s.)	706(v.s.)	SF_4 square sym. stretch

(All values in cm^{-1} recorded on gas samples.)

assigned to a band at 404 cm^{-1}, but no corresponding vibration in the 4000-400 cm^{-1} region can be unambiguously assigned to the S-Cl vibration in the spectrum of CF_3SF_4Cl. It is assumed that this band has perhaps shifted into the far infra-red region of the spectrum.

A medium-weak band, found at 643 cm^{-1} in CF_3SF_4Cl, could be due to the CF_3 asym. bend *c.f.* 558 cm^{-1} in CF_3SF_5.

The mass spectrum of TRANS CF_3SF_4Cl.

The mass spectral cracking pattern of TRANS CF_3SF_4Cl is very similar to that of TRANS $CF_3SF_4NF_2$ [76] (Table 3).

Although no parent ion was observed for CF_3SF_4Cl, the presence of ions due to CF_3 and SF_4Cl is consistent with the proposed structure. As in most other fluorocarbon compounds [83], the CF_3^+ ion is a dominant species in the spectrum of CF_3SF_4Cl, and intensity data reveal that the major fragmentation of the parent ion occurs at the carbon-sulphur bond to give CF_3 and SF_4Cl fragments, either of which may be charged.

$$CF_3^{+} \xleftarrow{-SF_4Cl^{\bullet}} CF_3SF_4Cl^{+\bullet} \xrightarrow{-CF_3^{\bullet}} SF_4Cl^{+}$$

m/e 69. m/e 145, 143.

TABLE 3

TRANS CF_3SF_4Cl (M.W. = 212·5)			TRANS $CF_3SF_4NF_2$ (M.W. = 229)		
m/e	Ion	Intensity	m/e	Ion	Intensity
145*	$SF_4{}^{37}Cl$	—			
143	$SF_4{}^{35}Cl$	—			
139*	CF_5S	16	139	CF_5S	14
			122	SF_4N	4
120	CF_4S	7	120	CF_4S	3
108	SF_4	—	108	SF_4	—
107	$SF_2{}^{37}Cl$	—			
105	$SF_2{}^{35}Cl$	—			
101*	CF_3S	9	103	SF_3N	—
			101	CF_3S	—
89	SF_3	17	89	SF_3	18
82	CF_2S	11	82	CF_2S	—
70	SF_2	27	70	SF_2	32
69	CF_3, $S^{37}Cl$	100	69	CF_3	100
67	$S^{35}Cl$	—			
			52	NF_2	8
51	SF	9	51	SF	8
50	CF_2	4	50	CF_2	3

* accurate mass measurements made on these ions

— intensity of these ions less than 1%

Abundant ions are formed which represent a stepwise removal of fluorine atoms from the basal SF_4 and CF_3 groups.

$$SF_4 \longrightarrow SF_3 \longrightarrow SF_2 \longrightarrow SF$$

$$CF_3 \longrightarrow CF_2 \longrightarrow CF$$

The former is a common process in SF_6 [82] and SF_5X [37] compounds, while the latter occurs in most fluorocarbon compounds.[83,86]

Although extensive re-arrangement occurs during fragmentation in the mass spectra of trifluoromethyl phosphine and arsine compounds [85], with transfer of a fluorine atom from the fluoroalkyl group to P or As, there was no evidence that such a re-arrangement existed in CF_3SF_4Cl to any appreciable extent.

$$CF_3SF_4Cl \not\longrightarrow SF_5Cl + CF_2$$

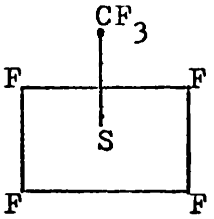
However, the relatively strong ion at m/e 139, due to CF_5S, could be formulated either as CF_3SF_2 or CF_2SF_3, and might suggest some exchange of fluorine atoms between carbon and sulphur. The absence of metastables does not allow certain formulation of the CF_5S ion, although it has been represented as CF_3SF_2 in the mass spectrum of TRANS $CF_3SF_4NF_2$.[76]

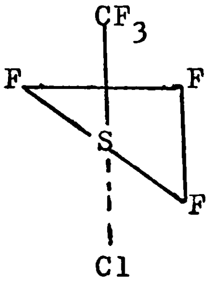
Mechanism for formation of TRANS CF_3SF_4Cl.

Steric factors indicate that in disubstituted derivatives of SF_6, SF_4A_2, TRANS substitution of the A groups is preferred. However, most SF_4A_2 compounds have a CIS octahedral environment [86-88], and hitherto, only perfluoroalkyl derivatives, $(R_f)_2SF_4$ and $CF_3SF_4NF_2$, have been shown to favour trans substitution.[76]

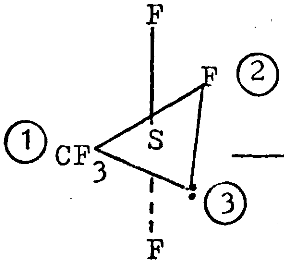
In the chlorofluorination of CF_3SF_3, only the TRANS isomer of CF_3SF_4Cl was obtained, and suggests that this reaction is highly stereospecific.

Although it is unknown whether the fluorine or chlorine atom bonds first to CF_3SF_3, the isolation of the TRANS derivative suggests that ions of the type $(CF_3SF_4)^-$ or $(CF_3SF_3Cl)^+$ are important intermediates.





CF_3SF_3 has a trigonal bipyramidal structure with equatorial substitution of the CF_3 group.[89] The first step in the chlorofluorination is postulated to involve addition of a fluoride ion producing a substituted SF_5^- ion, in which the lone pair may be either CIS or TRANS to the CF_3 group. Subsequent attack by Cl^+ on the $CF_3SF_4^-$ ion produces CF_3SF_4Cl.



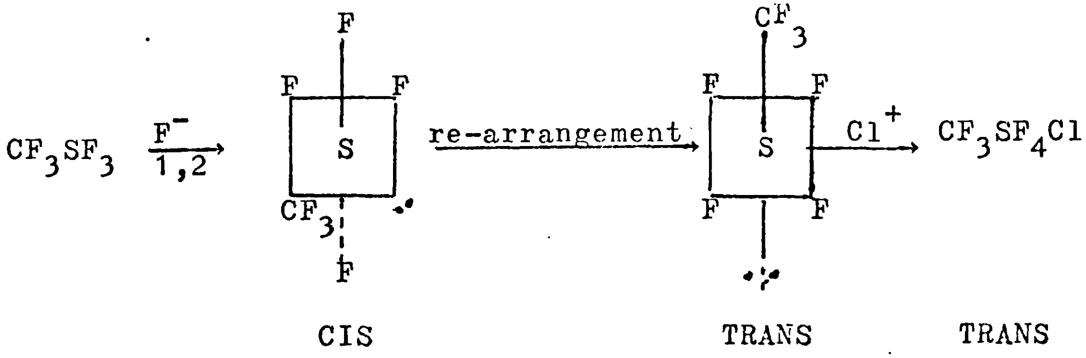
$$\xrightarrow{F^-} \begin{array}{l} 1,2 \text{ or } 2,3 \text{ CIS} \\ 1,3 \text{ TRANS} \end{array} \xrightarrow{Cl^+} \begin{array}{l} 66{\cdot}6\% \text{ CIS} \\ 33{\cdot}3\% \text{ TRANS} \end{array}$$

trigonal bipyramid $\quad CF_3SF_4^-$ octahedron $\quad CF_3SF_4Cl$

Addition of F^- to CF_3SF_3 is assumed to take place in the trigonal plane because the central atom is more accessible at these angles, and a minimum amount of atomic motion is required to generate the octahedron.

Entry of the F^- ion into the 1, 2 or 2, 3 positions leads to an intermediate where the CF_3 and lone pair are CIS to each other, but if the ion comes in between the 1, 3 positions a TRANS configuration should be produced. In the idealised situation, where statistical factors are all that need be considered, the CIS product should be preferentially formed. However, both steric and electrostatic factors must play an important role in the position of entry of the F^- ion, so that the relative amounts of the isomers, calculated on a statistical basis, is probably of very little meaning. To overcome the above factors, the F^- should enter the 1, 2 position preferentially, leading to a CIS compound.

Therefore, to explain the TRANS product, it must be assumed that the initial addition of F^- produces a CIS configuration of the CF_3 group and lone pair in the $CF_3SF_4^-$ ion octahedron, but that, because of the steric requirements of the lone pair, this structure re-arranges to one where a TRANS configuration is preferred.



This tendency for lone pairs to be in positions which give the most space, explains why, when alternative positions are available, they tend to occupy positions which minimise their interactions with other electron pairs.[90] As a result, in ICl_4^- and BrF_4^- [91], the lone pairs occupy the TRANS positions so that the molecule has a square planar shape. By analogy, the ions of the type SF_5^- or $CF_3SF_4^-$ should be isostructural with BrF_5 [37] and consequently prefer the lone pairs in the axial position of the distorted octahedron.

It is concluded that the preference for TRANS CF_3SF_4Cl is due to the structure of the $CF_3SF_4^-$ ion which, in order to minimise steric repulsive effects, has the CF_3 group and the lone pair far apart from each other in axial positions.

C. Reaction of methyliminosulphur difluoride with chlorine.

In contrast to the behaviour of dimethylaminosulphur trifluoride, $(CH_3)_2NSF_3$, methyliminosulphur difluoride, $CH_3N = SF_2$, reacts with chlorine at room temperature, with substitution of chlorine into the methyl group. The products are chloromethyliminosulphur difluoride, $CH_2ClN = SF_2$, dichloromethyliminosulphur difluoride, $CHCl_2N = SF_2$, and hydrogen chloride; the proportion of the products depends upon the relative proportion of starting materials. In the presence of excess chlorine, trifluoromethyliminosulphur dichloride, $CF_3N = SCl_2$, is also formed, but trichloromethyliminosulphur difluoride, $CCl_3N = SF_2$, has not been conclusively identified.

When the reaction between methyliminosulphur difluoride and chlorine is allowed to warm up very slowly to room temperature, the mono- and di-chloro substituted derivatives can be isolated (1).

$$CH_3N = SF_2 + Cl_2 \xrightarrow{slow} CH_2ClN = SF_2 + CHCl_2N = SF_2 + HCl \qquad (1)$$

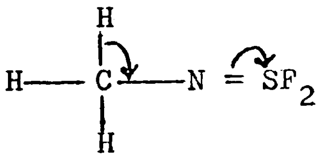
However, when the reactants are allowed to warm quickly to room temperature an extremely exothermic reaction occurs and trifluoromethyliminosulphur dichloride is the major identified product (2).

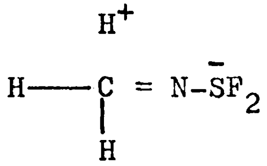
$$CH_3N = SF_2 + Cl_2 \xrightarrow{fast} CF_3N = SCl_2 + HCl \qquad (2)$$

Generally, the chlorination of organic compounds require more forcing conditions than those used for the chlorination of methyliminosulphur difluoride. Mixtures of methane and chlorine, when prepared and kept in the dark, do not react. Exposure to sunlight (photo-chemical induced chlorination) causes substitution of one of the hydrogen atoms by chlorine, and liberation of hydrogen chloride.[92] The reaction does not terminate at this stage, and higher substitution products are found in the mixture, even though considerable methane is still present, which shows that introduction of chlorine renders the molecule more vulnerable than before to the reagent.

$$CH_4 + Cl_2 \xrightarrow{light} HCl + CH_3Cl \longrightarrow CH_2Cl_2 \longrightarrow CHCl_3 \longrightarrow CCl_4$$

The fact that substitution of chlorine into methyliminosulphur difluoride requires only mild conditions, reflects the lability of the methyl protons. The mass spectrum of $CH_3N = SF_2$ shows that the loss of hydrogen from the parent ion is highly favourable (Table 6). Alternatively, when an alkyl group is attached to an unsaturated system hyperconjugation is possible involving structures such as (1), which could allow ionic chlorination, followed by subsequent hydrogen chloride elimination and chlorine re-arrangement. An ionic mechanism has been proposed for the chlorination of organic sulphides.[94]





(1)

A possible reaction mechanism for the chlorination of $CH_3N = SF_2$, which rationalises the observed products might involve:

(a) Stepwise chlorination of the methyl group (where the presence of a chlorine atom in the molecule tends to facilitate further chlorination), with elimination of HCl (a).

$$CH_3- \longrightarrow CH_2Cl- \longrightarrow CHCl_2- \longrightarrow CCl_3- \qquad (a)$$

Although $CCl_3N = SF_2$ has not been positively identified, it is to be expected that such a compound, when formed, could undergo fluorination of the carbon-chlorine bonds by the sulphur-fluorine bonds (b).

$$CCl_3N = SF_2 \longrightarrow CF_2ClN = SCl_2 \qquad (b)$$

This latter stage is similar to that observed in chlorofluoromethylsulphenyl fluorides, $CF_nCl_{3-n}SF$, which rapidly change to the isomeric sulphenyl chlorides, $CF_{n+1}Cl_{2-n}SCl$ (n = 0, 1 or 2), at room temperature.[70]

Initially, the reactions of $CH_3N = SF_2$ with chlorine were carried out in the presence of caesium fluoride, and a similar range of products was observed. This infers that the caesium fluoride has no marked effect on the products produced, although it may help in the isomerisation step (b). Alkali metal fluorides have been shown to catalyse the isomerisation of disulphur difluoride to thio-thionyl fluoride.[12]

$$S_2F_2 \longrightarrow SSF_2$$

To explain the formation of trifluoromethyliminosulphur dichloride, however, it is necessary to postulate intermolecular isomerisation of difluorochloromethyliminosulphur dichloride (c).

$$3CF_2ClN = SCl_2 \longrightarrow 2CF_3N = SCl_2 + CCl_3N = SCl_2 \qquad (c)$$

$CF_3N = SCl_2$ has been previously reported to result from the action of aluminium trichloride on trifluoromethyliminosulphur difluoride, although it was not indicated how the reaction might proceed.[93]

Apparently, the chlorination of $CH_3N = SF_2$ is more complex than the simple chlorination of organic hydrocarbons, and, in addition to the major products, small quantities (less than 5% of the total mixture) of materials were present which could be attributed to $CCl_3N = SF_2$ and $CF_2ClN = SCl_2$. (see discussion of n.m.r.)

Possible isomerisation and fluorination of chloromethyliminosulphur difluoride and dichloromethyliminosulphur difluoride.

Isomerisation of S-F to S-Cl bonds has been postulated in the chlorination of $CH_3N = SF_2$ to account for the formation of C-F bonds, but there was no indication of isomerisation in $CH_2ClN = SF_2$ or $CHCl_2N = SF_2$

$$CHCl_2N = SF_2 \not\longrightarrow CF_2HN = SCl_2$$

$$CH_2ClN = SF_2 \not\longrightarrow CF_2ClN = SH_2$$

Energetically, such isomerisations could be possible because of strong carbon-fluorine bond formation, and the failure to observe this type of reaction must, in part, be due to the ligand configuration around the sulphur.

Generally, the iminosulphur dihalide linkage, $-N = SX_2$, is found only when $X = F$, and only when highly electronegative groups are present e.g. $CF_3N = SCl_2$ does it appear to exist for the dichloride. No compounds are known which contain the $-N = SH_2$ grouping. Perhaps the ineffectiveness of hydrogen and chlorine to contract the sulphur d orbitals, might explain why the iminosulphur dihalide linkage is common only for fluorine.

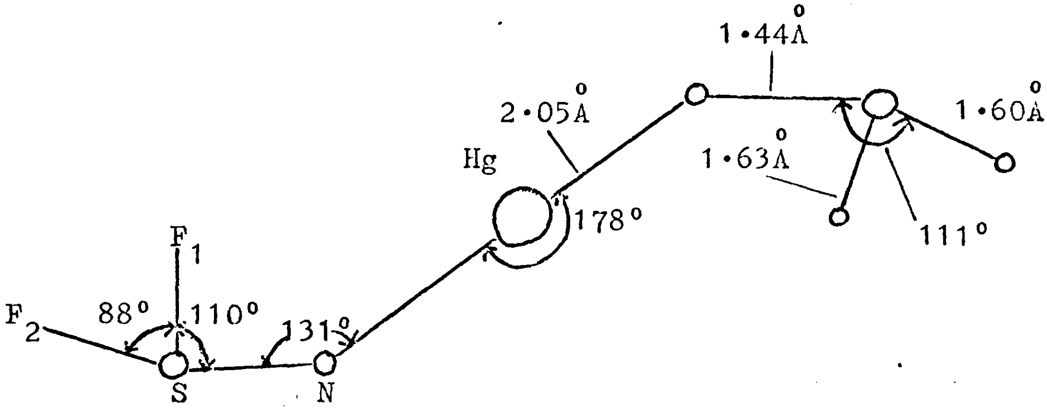
When a mixture of $CH_2ClN = SF_2$ and $CHCl_2N = SF_2$ was treated with either caesium fluoride or a slurry of sodium fluoride in acetonitrile, there was no fluorination of the chlorine atoms. Although these fluorinating conditions are rather mild and a stronger fluorinating system e.g. $SbF_5/SbCl_3$ might have been more successful, it appears that for easy replacement of chlorine by fluorine, three chlorine atoms should be bonded to the carbon.[94] Attempts to replace the chlorine in chlorodimethylsulphides with fluorine have been accomplished in some cases, but in those cases where neither one of the carbon atoms is bonded to three chlorine atoms, no appreciable quantities of fluorodimethylsulphides have been obtained.[94]

<u>Properties and structure of chloromethyliminosulphur difluoride and dichloromethyliminosulphur difluoride.</u>

Both $CH_2ClN = SF_2$ and $CHCl_2N = SF_2$ are colourless volatile liquids which, when hydrolysed by moist air, produce SO_2 and HCl. Although various stoichiometries of reagents were used, the chlorination of $CH_3N = SF_2$ always resulted in a mixture of the chloro- and dichloro- substituted compounds. Conveniently however, the more volatile $CH_2ClN = SF_2$ could be separated from $CHCl_2N = SF_2$ by slow distillation from a -50°C cold bath.

Structurally, the most noticeable feature of the iminosulphur compounds is the non-linearity of the $X\text{-}N = S$ grouping ($X = CH_3$, CH_2Cl etc.).[95] This can be explained by assuming nitrogen uses a set of sp^2 orbitals, two of which are used to form σ bonds to X and S, while the third holds the lone pair. A π bond to S is then formed using the nitrogen p_z orbital.

Although many compounds containing the $-N = SF_2$ grouping are known, X-ray structural data on these compounds are scarce. Recently however, the structure of the novel compound mercury di-iminosulphur difluoride, $Hg(NSF_2)_2$, has been investigated [96] and the bond distances and angles are given below.



Significantly, the $S\hat{N}Hg$ is non-linear, and the very short S-N bond distance is indicative of strong d_π-p_π bonding between S and N. The normal S-N "single bond" distance, obtained from the sum of the covalent radii is 1·74Å.[97]

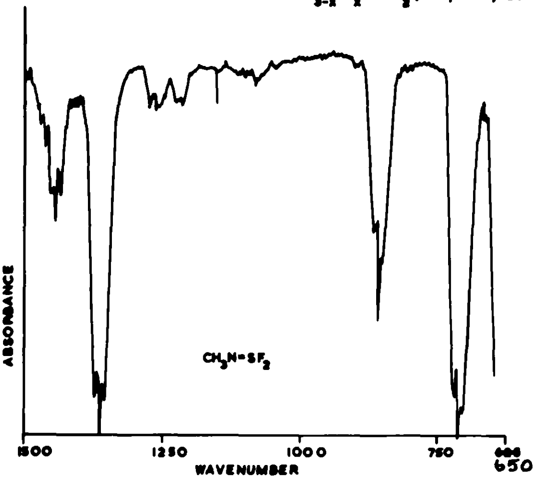
Another feature of the X-N = SF_2 derivatives is the possibility of rotational isomerism. Because of the double bond linking the nitrogen and sulphur atoms, one may have, in addition to the rotational properties of the X group, the rotational characteristics of the X group relative to the SF_2 moiety. In one case, the X group is TRANS to the fluorine atom pair on sulphur and in the other, it is CIS to the fluorine atom pair on sulphur.

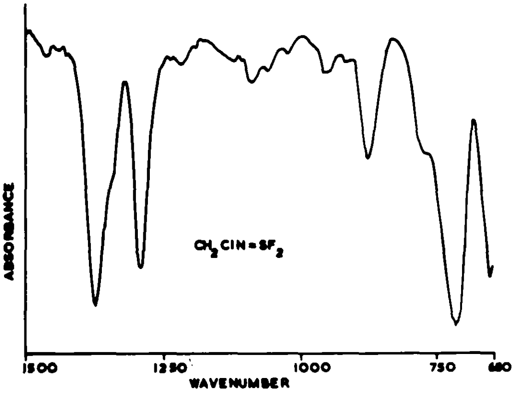
Griffiths has recently examined the possibility of rotational isomerism in $CF_3N = SF_2$ [98], and found no evidence for the presence of two isomeric forms at room temperature. Strictly on a steric basis and on the supposition that molecules prefer a more symmetrical configuration, he concluded that the stable structure of $CF_3N = SF_2$ would involve the TRANS configuration in which the non-bonded electron pairs on nitrogen and sulphur appear on opposite sides of the molecule.

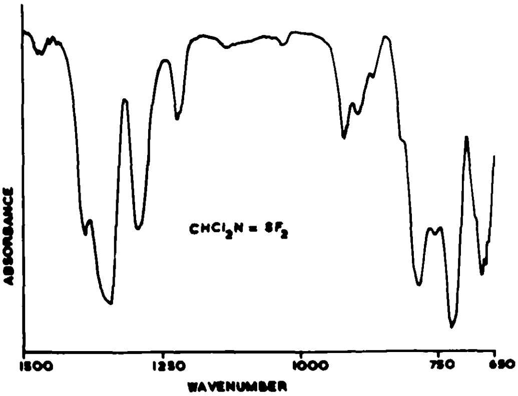
The infra-red spectra of iminosulphur difluorides.

Relatively little data on sulphur-nitrogen stretching frequencies have been reported and, since bond orders of up to three may occur, a considerable range of frequency is observed. Since the nature of the bonding in sulphur-oxygen and sulphur-nitrogen systems is analogous, similar relationships are expected to hold. It has been shown that a linear relationship exists between the bond lengths and the wavelengths of the absorption bands of sulphur-nitrogen bonds.[99]

The position of the infra-red absorption in $CH_2ClN = SF_2$ and $CHCl_2N = SF_2$ are summarised in (Table 4), THE INFRA-RED SPECTRA OF CH$_{3-x}$Cl$_x$N=SF$_2$ (X=0, 1 or 2) COMPOUNDS.







and possible assignments of the bands are made by comparison with other organoiminosulphur difluorides.

Vibrations due to carbon-hydrogen stretching modes were not observed for $CH_2ClN = SF_2$ or $CHCl_2N = SF_2$ under the gas phase conditions used. In the parent compound, $CH_3N = SF_2$, these vibrations are very weak.[100] The very strong absorptions, at 1375 and 1345 cm^{-1} in the chloro- and dichloro- derivatives, are attributed to the N = S stretching vibrations; absorption in the 1400-1350 cm^{-1} region is characteristic of the N = S grouping in organoiminosulphur difluorides.[101]

TABLE 4

$CH_3N = SF_2$	$CH_2ClN = SF_2$	$CHCl_2N = SF_2$	Assignment
1357(v.s.)	1375(v.s.)	1345(v.s.)	N = S stretch
	955(w)	924(m)	
	880(m)	898(w)	C-Cl stretch
	770(m.sh.)	870(w)	
		790(s)	
858(s)	720(v.s.)	729(s)	S-F stretch
708(v.s.)	659(s)	673(s)	

(All values in cm^{-1}, recorded on gas samples; a full list of all the bands is given in the experimental section.)

Although the infra-red spectra of the chloro-compounds contain relatively few bands, the close proximity of the C-Cl and S-F frequencies causes difficulty in the assignment of either. Tentatively, the asymmetric and symmetric vibrations of the SF_2 group are assigned to absorptions at 720 and 659 cm^{-1} ($CH_2ClN = SF_2$), and 729 and 673 cm^{-1} ($CHCl_2N = SF_2$), by analogy with the S-F vibrations at 808 and 748 cm^{-1} (SOF_2 [16]), 759 and 716 cm^{-1} ($CF_3N = SF_2$ [102]) and 744 and 687 cm^{-1} ($ClN = SF_2$ [67]).

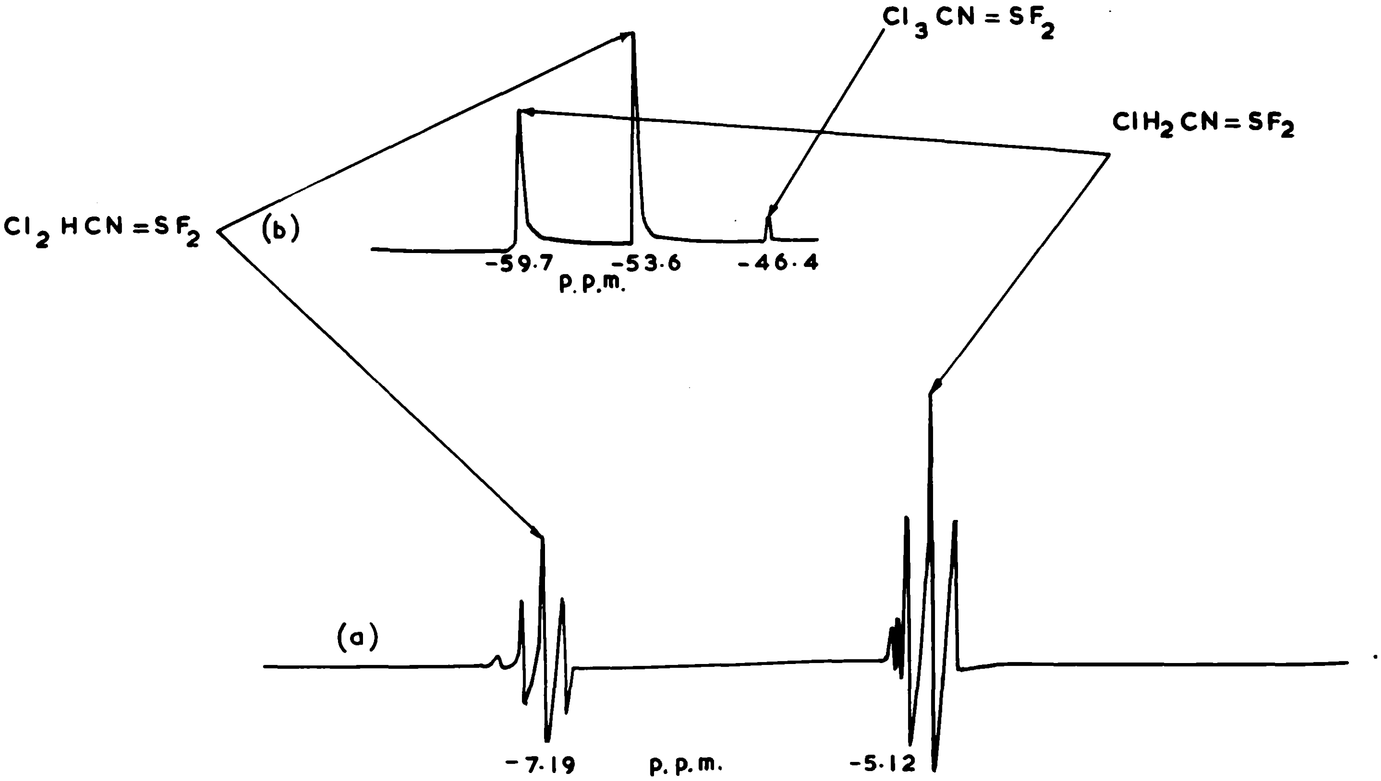
A study of the infra-red spectra of alkyl chlorides [103] revealed that the frequency range of the C-Cl stretching mode is very variable and is a function of the detailed structure in the vicinity of the C-Cl group. The medium to weak absorptions in the 950 to 770 cm^{-1} region are perhaps due to the C-Cl stretching vibrations in the chloro- and dichloro- compounds.

The n.m.r. spectra of iminosulphur difluorides.

The n.m.r. spectra of $CH_2ClN = SF_2$ and $CHCl_2N = SF_2$ (Table 5) are in agreement with the proposed structures.

The proton chemical shift of $ClH_2C\text{-}N = SF_2$ at -5·12 p.p.m. is in a region characteristic of the $\underline{ClH_2C}$- grouping; proton resonances have been found at -5·16 p.p.m. and -4·99 p.p.m. for $ClH_2C\text{-}Br$ and $ClH_2C\text{-}I$

^1H(a) AND ^{19}F(b) N.M.R. SPECTRA OF $Cl_{3-x}CH_xN=SF_2$ (X=0, 1 or 2) COMPOUNDS.



respectively.[77] Similarly, the proton resonance at -7·19 p.p.m. for $Cl_2HC-N = SF_2$ might be compared with -7·20 p.p.m. found for Cl_2HC-Br.[77]

TABLE 5

Compound	δ_{H}(p.p.m.) (a)	δ_{F}(p.p.m.) (b)	J_{H-F} c/s
$H_3CN = SF_2$	-2·3(t)	-67·3(b.s.)	9·5
$ClH_2CN = SF_2$	-5·12(t)	-59·7(b.s.)	8·2
$Cl_2HCN = SF_2$	-7·19(t)	-53·6(b.s.)	6·9

(a) chemical shift with respect to internal $(CH_3)_4Si$

(b) chemical shift with respect to internal CCl_3F

(t) triplet; (b.s.) broad singlet

As expected from simple electronegative inductive effects, replacement of a hydrogen atom by a more electronegative chlorine atom causes the proton resonance to move progressively to lower fields. The hydrogen fluorine coupling constant, J_{H-F}, decreases on substitution of chlorine into the molecule. This decrease might possibly be attributed to the closer spatial proximity of the hydrogen and fluorine atoms in traversing the series CH_3-, CH_2Cl-, $CHCl_2$-, since replacement of a hydrogen atom by the more electronegative chlorine atom should cause the adjacent bonds to receive more s orbital character, and consequently to become shorter.[26]

Although triplet fine structure is observed in the proton spectrum, in all cases the fluorine resonance is a broad unresolved singlet. Small J_{F-H} coupling is usually difficult to detect in the fluorine n.m.r. and attachment to nitrogen could cause excessive broadening of the fluorine resonance. Nuclear quadrupole relaxation is often encountered in the n.m.r. spectra of nitrogen containing compounds [104] and line broadening is a common phenomenon.

Possible n.m.r. evidence for $CCl_3N = SF_2$ and $CF_2ClN = SCl_2$.

In addition to the formation of $CH_2ClN = SF_2$ and $CHCl_2N = SF_2$ by the chlorination of $CH_3N = SF_2$, in one experiment (see page 71) trace quantities of two other compounds were present. Both compounds showed singlet fluorine resonances with no corresponding proton resonance. The singlet at -46·4 p.p.m. might be due to $CCl_3N = SF_2$, while that at +46·2 p.p.m. could possibly originate from $CF_2ClN = SCl_2$.

As the number of chlorine atoms in the CH_3- to $CHCl_2$- series increases, the fluorine chemical shifts move to higher fields in a stepwise fashion.

CH_3 (-67); CH_2Cl (-60); $CHCl_2$ (-54); CCl_3 (-46)

A value of -46·4 p.p.m. for $CCl_3N = SF_2$ is consistent with this trend.

A value of +46·2 p.p.m. for $CF_2ClN = SCl_2$ is in the region characteristic of the CF_2Cl group.[105]

The mass spectra of iminosulphur difluorides.

The mass spectra of the $CCl_xH_{3-x}N = SF_2$ compounds (x = 0, 1 or 2) are characteristic and reveal some distinct similarities (Table 6). It is apparent from the tabulated results that normal fragmentation is the major breakdown pathway. Re-arrangement involving hydrogen migration does not appear to occur to any appreciable extent.

The major fragmentation of the parent compound, $CH_3N = SF_2$, involves rupture of the C-H bond. This indicates that a primary process which takes place is

$$CH_3N = SF_2^{+\bullet} + e^- \longrightarrow \overset{+}{C}H_2-N = SF_2 + H^{\bullet} + 2e^-$$

inferring that the protons on the methyl group are easily removed. This is not unexpected since the resulting ion can be stabilised by positive charge distribution between various resonance forms.

TABLE 6

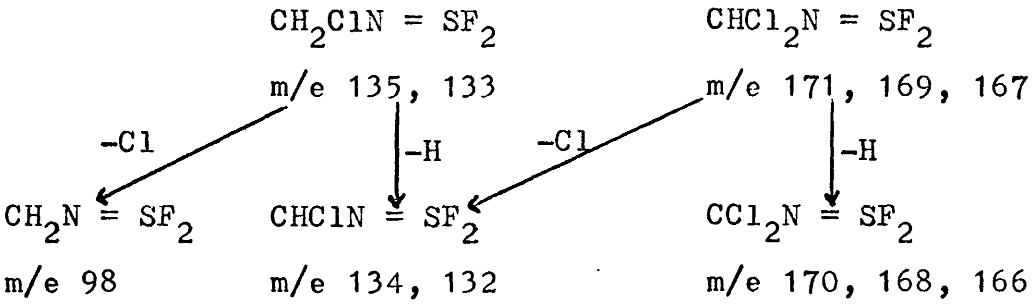
$CH_3N = SF_2$ (M.W. = 99)			$CH_2ClN = SF_2$ (M.W. = 133·5)			$CHCl_2N = SF_2$ (M.W. = 166)		
m/e	Ion	Intensity	m/e	Ion	Intensity	m/e	Ion	Intensity
99	CH_3NSF_2	100·0	134*	$CH^{37}ClNSF_2$	10·4	170	$C^{37}Cl_2NSF_2$	4·4
98	CH_2NSF_2	69·4	133*	$^{13}CH^{35}ClNSF_2$		168*	$C^{35,37}ClNSF_2$	13·5
80	CH_3NSF	32·7	132*	$CH^{35}ClNSF_2$	21·8	166*	$C^{35}Cl_2NSF_2$	22·7
79	CH_2NSF	18·4	98*	CH_2NSF_2	100·0	134	$CH^{37}ClNSF_2$	38·7
77	CNSF	65·3	79	CH_2NSF	9·8	132	$CH^{35}ClNSF_2$	100·0
70	SF_2	28·6	70	SF_2	28·8	78	CHNSF	9·6
61	CH_3NS	20·4	51	$CH_2{}^{37}Cl$,SF	16·4	70	SF_2	43·5
60	CH_2NS	40·8	49	$CH_2{}^{35}Cl$	14·5	51	SF	17·8
51	SF	18·4	46	NS	18·1	46	NS	9·6
46	NS	32·7						

* refers to peaks which were accurately mass measured; the results are found in the experimental section.

$$\overset{+}{C}H_2-N = SF_2 \longleftrightarrow CH_2 = \overset{+}{N} = SF_2 \longleftrightarrow CH_2 = N-\overset{+}{S}F_2$$

Neither of the chlorine containg compounds show a molecular ion, but ions corresponding to the loss of hydrogen and chlorine atoms are abundant. The presence of one and two chlorine atoms is easily detected by the chlorine isotopic ratio pattern.[106]

No metastable ions were detected in the spectra and, for this reason, the route of formation of the ions must remain in doubt. However, possible fragmentation patterns for the chloro- and dichloro- compounds could be represented by the following schemes (omitting positive charges).



The compounds also show strong ion contributions resulting from fragmentation of the iminosulphur difluoride linkage e.g. SF_2, SF and N = S.

Preparation and purification of starting materials.

Compound	Method	Ref.
Me_3SiNMe_2	Me_3SiCl/Me_2NH	[107]
CF_3SNMe_2	CF_3SCl/Me_2NH	[108]
CF_3SCl and $(CF_3S)_2$	CCl_3SCl/NaF	[109]
CF_3SF_3	(a) $(CF_3S)_2/AgF_2$	[69]
	(b) CF_3SCl/KF	[63]
CF_3SF_5	$(CF_3S)_2/AgF_2$ (excess)	[69]
Me_2NSF_3	SF_4/Me_3SiNMe_2	[110]
$MeN = SF_2$	$SF_4/MeNH_2$	[100]

The involatile compounds when prepared were stored over dry activated 4A molecular sieves. The more volatile compounds were purified by the prescribed literature methods and were stored at -196°C in glass weighing vessels until required. The purity of all samples used was confirmed by infra-red, n.m.r. and, in some cases, mass spectrometry. Compounds which hydrolysed easily in glass were kept in evacuated metal containers.

Reaction vessels.

Most of the reactions were carried out in metal vessels, constructed of 3/8" stainless monel tubing, which was crimped and silver soldered at one end and connected through Hoke No. 327 or No. 323 valves to metal 30/40 inner joints on the other end. Alternatively, commercial Hoke metal reactors of 75 ml. capacity were used.

Caesium fluoride.

The caesium fluoride from American Potash Co., or B.D.H. 99%, was dried overnight at 180° under dynamic vacuum. This process resulted in caking of the caesium fluoride, so it was removed to a nitrogen filled dry box and finely ground before being loaded into the metal reactor.

A. Substitution into S(VI) compounds.

1. Reaction of SF_5Cl with CF_3SCl.

No reaction was found between SF_5Cl (2 m.m.) and CF_3SCl (2 m.m.) in a 300 ml. Carius tube at room temperature after 7 days, as was shown by no change in the infra-red spectrum or quantity of the mixture. The reactants were recondensed and the mixture heated at 130°C for 14 hours, 150-200°C for 24 hours and at temperatures greater than 200°C for 2 hours. Fractionation revealed mostly starting materials, with small quantities of SiF_4 and SOF_2 (arising from SF_4 contaminant in the SF_5Cl, $< 5\%$).

2. Reactions of SF_5Cl with Si-N compounds.

(a) Me_3SiNMe_2

SF_5Cl (14·8 m.m.) and Me_3SiNMe_2 (14·8 m.m.) were heated together at 60° in a sealed tube overnight. Fractionation produced Me_3SiF (14·3 m.m.), identified by infra-red [114] and M.W. (Found: M.W. 91·2. Calc: M.W. 92), and small amounts of SiF_4. The reaction vessel contained a red-brown solid which was insoluble in C_6H_6. A similar reaction occurred at room temperature, producing Me_3SiF and a yellow solid.

(b) $(Me_3Si)_2NMe$

SF_5Cl (1·4 m.m.) and $(Me_3Si)_2NMe$ (0·315 g.; 1·8 m.m.) were condensed together at -196°C in a sealed tube. The contents were allowed to warm to room temperature, whereupon a bright yellow solid precipitated out and Me_3SiF was produced.

(c) $(Me_3Si)_2NH$

SF_5Cl (1·27 m.m.) and $(Me_3Si)_2NH$ (0·302 g.; 1·87 m.m.) reacted at room temperature in a sealed tube to produce Me_3SiF and a yellow, sandy coloured solid.

3. Reaction of CF_3SF_5 with Me_3SiCl.

Equimolar quantities of CF_3SF_5 and Me_3SiCl were heated at 126°C overnight in a sealed tube. Fractionation showed that no reaction had occurred, although a trace of CF_3Cl was produced, identified by infra-red.[112]

B. Chloro-fluorination reactions with S(II) and S(IV) compounds.

General procedure.

The metal vessel which had been thoroughly dried was transferred to a dry box and the desired quantity of caesium fluoride added. The vessel was quickly reconnected to the vacuum line and pumped under dynamic vacuum for ~$\frac{1}{2}$ hour. The least volatile reactant was then condensed into the reactor at -196°C and again the system was pumped down. Chlorine, stored over P_2O_5 and freed from HCl by repeated fractionation through a -120°C bath, was distilled into the vessel. The amount of Cl_2 used was determined tensimetrically, using Hg manometers which were protected by a thin film of halocarbon oil. The metal reactor was then removed from the vacuum line and allowed to warm to room temperature, or heated in an oil bath as desired.

Chloro-fluorination of S(II) compounds.

1. CF_3SNMe_2

(1·8 g.; 12·0 m.m.) of SF_4, (1·47 g.; 3·2 m.m.) of CF_3SNMe_2 and (9·7 m.m.) of Cl_2 were heated at 60°C for 2 hours in a 75 ml. metal reactor. Fractionation through -100, -120 and -196°C traps, collected Cl_2 and SiF_4 in the latter bath. The -120°C trap held a mixture of CF_3SCl (major product), $CF_3S(O)F$ (trace) and very small quantities of an unidentified product, the ^{19}F n.m.r. of which showed a complex fluorine resonance at +68·2 p.p.m. Identification of CF_3SCl and $CF_3S(O)F$ was by n.m.r. spectroscopy. [63, 70] The -100° bath contained $(CF_3S)_2$ characterised by infra-red comparison with an authentic sample.

	δ_{CF_3} (p.p.m.)	δ_{SF} (p.p.m.)	J_{F-F} c/s
Compound	85·4(d)	21·6(q)	8·0
$CF_3S(O)F$	84·1(d)	21·6(q)	8·0
Compound	51·2(s)		
CF_3SCl	51·0(s)		

2. $CF_3S-S-CF_3$

Approximately 1 g. of CsF, (0·91 g.; 4·5 m.m.) of $(CF_3S)_2$ and (9·0 m.m.) of Cl_2 were allowed to warm to room temperature in a 75 ml. metal vessel, containing ½ dozen 3/8" metal balls. The reactor was placed on a mechanical shaker for 1 hour at room temperature, then heated at 80-100°C for 48 hours with continual shaking. Room temperature fractionation collected unreacted $(CF_3S)_2$, (0·42 g., ~50%) at -100°C; CF_3SCl and traces of $(CF_3S)_2$, $CF_3S(O)F$ and a compound showing a complex fluorine multiplet at 65·4 p.p.m. were trapped in a -118°C bath. The most volatile components were SiF_4 (trace), Cl_2 and CF_3Cl; the latter compound was identified by infra-red [112] and M.W. (Found: M.W. = 101·2. Calc: M.W. = 104·5). The compounds trapped at -118°C were identified by n.m.r. spectroscopy. [63,70,77]

	Compound	$CF_3S(O)F$	Compound	CF_3SCl	Compound	(CF_3S)
δ_{CF_3}(p.p.m.)	82·2(d)	84·1(d)	49·6(s)	51·0(s)	46·3(s)	46·8(s
δ_{SF}(p.p.m.)	19·4(s)	21·6(s)				

Reaction of SF_4 with $(CF_3S)_2$

A 2:1 ratio of SF_4 and $(CF_3S)_2$ was heated together for 15 hours at 140°C in a sealed tube. Fractionation produced ~90% unreacted $(CF_3S)_2$ together with SF_4, SOF_2 and SiF_4. The reaction was repeated in the presence of CsF in a metal reactor. The vessel was heated at 120°C for 15 hours and at 220°C for 7 hours. Fractionation showed no reaction had occurred.

Chloro-fluorination of S(IV) compounds.

1. Me_2NSF_3

1 g. of CsF, (0·51 g.; 3·7 m.m.) of Me_2NSF_3 and (7·0 m.m.) of Cl_2 were condensed together in a 25 ml. monel vessel and the contents allowed to warm to room temperature overnight. The crude reaction mixture was fractionated through -100 and -196°C cold baths. The -196°C trap contained a small quantity of HCl and SOF_2, the major product being SF_5Cl, identified by comparison with the infra-red spectrum of an authentic sample. No Me_2NSF_3 was recovered, but traces of an unidentified colourless liquid were collected at -100°C, showing infra-red absorption (cm^{-1}) at:

1373(v.s.): 1130(s): 1105(s): 982(m): 750(v.s.): 690(s).

2. CF_3SF_3

Excess CsF, and CF_3SF_3 and Cl_3 in a 1:2 ratio were allowed to warm to room temperature over a 3 hour period in a 75 ml. metal vessel. Fractionation through -120 and -196°C traps, collected excess Cl_2, SiF_4 (trace) and CF_3Cl, identified by infra-red at -196°C.[112] The -120°C bath contained traces of unreacted CF_3SF_3, $CF_3S(O)F$, and TRIFLUOROMETHYLSULPHUR CHLORIDE TETRAFLUORIDE, CF_3SF_4Cl, as the major product. Trap to trap distillation was unsuccessful in separating the products, and CF_3SF_4Cl was never obtained in a completely pure state.

Characterisation of CF_3SF_4Cl.

Infra-red (cm^{-1}). 1250(v.s.): 1182(m): 1155(s): 860(v.s.): 785(m): 678(v.s.): 643(m).

N.M.R. The fluorine n.m.r. showed a quintet at +67·3 p.p.m. due to the trifluoromethyl group, and a quartet at -102·1 p.p.m. due to the sulphur tetrafluoride group, with J_{F-F} = 24 c/s. The integration of the resonances was as 3:4.

Mass spectrum. The low resolution mass spectrum contained the following, given as mass number, probable molecular ion assignment and relative abundance.

N.B. The intensities are not accurate since the mass spectrum indicated impurity due to $CF_3S(O)F$.

145, $SF_4{}^{37}Cl$ (negligible): 143, $SF_4{}^{35}Cl$ (negligible): 139, CF_3SF_2, 16: 120, CF_3SF, 7: 108, SF_4 (negligible):

107, $SF_2{}^{37}Cl$ (negligible): 105, $SF_2{}^{35}Cl$ (negligible): 101, CF_3S, 9: 89, SF_3, 17: 82, CF_2S, 11: 70, SF_2, 27: 69, CF_3, $S^{37}Cl$, <u>100</u>: 67, $S^{35}Cl$ (negligible): 51, SF, 9: 50, CF_2, 4.

High resolution mass measurements on some of the ions diagnostic of CF_3SF_4Cl are given below.

m/e	Ion	Found Mass	Calc. Mass
145	$SF_4{}^{37}Cl$	144·93155	144·93158
139	CF_3SF_2	138·96156	138·96408
101	CF_3S	101·96625	101·96728

<u>Reaction of CF_3SF_4Cl with mercury.</u>

CF_3SF_4Cl (containing a trace of $CF_3S(O)F$ impurity) was condensed into a glass ampoule containing dry Hg. The vessel was then sealed and left for 5 hours on the roof in bright sunlight. On warming, a scum formed on the mercury and there was a slight indication of a reddish tinge on the walls of the glass vessel. An infra-red spectrum of the volatiles showed no CF_3SF_4Cl, but the major products were CF_3Cl, SOF_2, SF_4 (trace) and SiF_4, all identified by infra-red spectroscopy.

C. Chlorination reactions with S(IV) compounds.

1. Me_2NSF_3

(0·23 g.; 1·7 m.m.) of Me_2NSF_3 and (6·0 m.m.) of Cl_2 were allowed to warm to room temperature overnight in a 25 ml. monel reactor. Fractionation through −110, −120 and 196°C baths collected excess chlorine at −196°C, and SF_4 as the major product at -120°C. The least volatile fraction appeared to consist of a mixture of Me_2NCl and SCl_2, the former being identified by n.m.r. [74] and mass spectrometry. SCl_2 was characterised by its cherry red colour and infra-red comparison with an authentic sample.

Compound	δ_H -2·85p.p.m.(s)	Compound	$520cm^{-1}$
Me_2NCl	δ_H -2·85p.p.m.(s)	SCl_2	$514cm^{-1}$ (S-Cl)

2. <u>MeN = SF</u>$_2$

(a) (5·4 m.m.) of $CH_3N = SF_2$ and (13 m.m.) of Cl_2 were condensed into a monel reactor and the vessel allowed to warm slowly to room temperature overnight. Fractionation through -100 and -196°C traps collected excess Cl_2, identified by its colour, and HCl, identified by its infra-red spectrum [114], in the latter bath. The -100°C cold bath contained a mixture of CHLOROMETHYLIMINOSULPHUR DIFLUORIDE, $CH_2ClN = SF_2$, and DICHLOROMETHYLIMINOSULPHUR DIFLUORIDE, $CHCl_2N = SF_2$, in the ratio of 2:3. The more volatile $CH_2ClN = SF_2$ could be separated from $CHCl_2N = SF_2$ by slow distillation from a -50°C trap. The -100°C bath also contained a small amount ($<1\%$ of the total mixture) of two unidentified compounds which showed singlets at +46·2 p.p.m. and -46·4 p.p.m. in the fluorine n.m.r. but no corresponding proton resonance.

Characterisation of $CH_2ClN = SF_2$ and $CHCl_2N = SF_2$

Infra-red (cm^{-1})

$CH_2ClN = SF_2$: 1375(v.s.): 1370(sh.): 1358(sh.): 1292(s): 955(w): 800(m): 770(m.sh.): 720(v.s.): 659(s).

$CHCl_2N = SF_2$: 1390(m): 1345(v.s.): 1295(m): 1124(w): 1118(sh.): 924(m): 898(w): 870(w): 790(s): 729(s): 673(s).

N.M.R.

$CH_2ClN = SF_2$

The proton n.m.r. contained a triplet centred at -5•12 p.p.m., from internal $(CH_3)_4Si$, with $J_{H-F} = 8{\cdot}2$ c/s. The fluorine n.m.r. was a broad singlet, at -59•7 p.p.m. from internal CCl_3F.

$CHCl_2N = SF_2$

The proton n.m.r. contained a triplet centred at -7•19 p.p.m., from internal $(CH_3)_4Si$, with $J_{H-F} = 6{\cdot}9$ c/s. The fluorine n.m.r. was a broad singlet, at -53•6 p.p.m. from internal CCl_3F.

Mass spectrum. The low resolution mass spectra contained the following, given as mass number, probable molecular ion assignment and relative abundance.

$CH_2ClN = SF_2$ (M.W. = 133•5)

134, $CH^{37}ClNSF_2$, 10•4: 132, $CH^{35}ClNSF_2$, 21•8:

98, CH_2NSF_2, 100: 79, CH_2NSF, 9•8: 70, SF_2, 28•8:

51, $CH_2{}^{37}Cl$, 16·9: 49, $CH_2{}^{35}Cl$, 14·5: 46, NS, 18·1.

<u>$CHCl_2N = SF_2$</u> (M.W. = 166)

170, $C^{37}Cl_2NSF_2$, 4·4: 168, $C^{35,37}Cl_2NSF_2$, 13·5: 166, $C^{35}Cl_2NSF_2$, 22·7: 134, $CH^{37}ClNSF_2$, 28·7: 132, $CH^{35}ClNSF_2$, <u>100</u>: 78, CHNSF, 9·6: 70, SF_2, 43·5: 51, SF, 17·8: 46, NS, 9·6.

High resolution mass measurements on some of the more prominent ions identified for:

	m/e	Ion	Found Mass	Calc.Mass
(a) <u>$CH_2ClN = SF_2$</u>	134	$CH^{37}ClNSF_2$	133·94575	133·94569
	133	$^{13}CH^{35}ClNSF_2$	132·95178	131·95198
	132	$CH^{35}ClNSF_2$	131·94878	97·94863
	98	CH_2NSF_2	97·98742	97·98760
(b) <u>$CHCl_2N = SF_2$</u>	168	$C^{35,37}Cl_2NSF_2$	167·90621	167·90675
	166	$C^{35}Cl_2NSF_2$	165·90942	165·90970

(b) $CH_3N = SF_2$ and Cl_2, in approximately 1:3 ratio, were allowed to warm to room temperature slowly overnight. Fractionation produced HCl at -196, and at -100°C trace quantities of an unidentified material, showing infra-red absorption (cm^{-1}.) at:

1375(v.s.): 1132(s): 1105(s): 980(m): 750(s): 690(s).

<u>N.B.</u> The above infra-red was identical to the infra-red of the unidentified product from the Me_2NSF_3/Cl_2 and CsF reaction. The least volatile material trapped at -70°C was a

mixture of $CH_2ClN = SF_2$, $CHCl_2N = SF_2$ and traces of a compound which showed a singlet at -46·6 p.p.m. in the fluorine n.m.r., but no proton resonance. The relative amounts of the compounds collected at -70°C were approximately one part of the unidentified product, five parts $CH_2ClN = SF_2$, and eight parts $CHCl_2N = SF_2$.

(c) (6·6 m.m.) of $CH_3N = SF_2$ and (12·4 m.m.) of Cl_2 were condensed together at -196°C, in a 25 ml. metal pressure vessel. The reaction vessel was allowed to warm freely to room temperature, whereupon a very exothermic reaction occurred, with the monel reactor becoming extremely warm. The reaction time between the vessel being cold and reaching room temperature was less than one hour. Fractionation at room temperature through traps at -30, -95 and -196°C collected HCl in the latter, $CH_2ClN = SF_2$ (trace) and TRIFLUOROMETHYLIMINOSULPHUR DICHLORIDE, $CF_3N = SCl_2$, at -95°C. The -30°C bath contained a yellow-red involatile liquid which was not characterised, but contained no protons or fluorine atoms, as shown by n.m.r. spectroscopy.

Characterisation of $CF_3N = SCl_2$

Infra-red (cm^{-1}). 1425(w): 1309(v.s.): 1215(s): 1190(s): 1138(s): 800(w): 658(w): 620(w): 540(m): 460(sh.): 444(s): 414(s).

N.M.R. The fluorine n.m.r. showed a singlet at

+56·1 p.p.m. from external CCl_3F.

Gas phase hydrolysis. An infra-red sample of $CF_3N = SCl_2$ showed extra peaks associated with SiF_4, HCl, SO_2 and CO_2, when exposed to the atmosphere.

Mass spectrum. The mass spectrum of $CF_3N = SCl_2$ was complex and usually showed peaks at a higher molecular weight than $CF_3N = SCl_2$ e.g. $CF_3N = S = NCF_3$ (Found for m/e, 198, 197·96883: $C_2F_6N_2S$ requires, 197·96801). However, the presence of $CF_3N = SCl_2$ was indicated by peaks at m/e, 46, (NS): 67, ($S^{35}Cl$): 69, (CF_3, $S^{37}Cl$): 115, (CF_3NS): 150, ($CF_3NS^{35}Cl$): 152, ($CF_3NS^{37}Cl$).

Reactions of methyliminosulphur difluoride with chlorine in the presence of caesium fluoride.

(a) (1·14 g.; 7·5 m.m.) of CsF were loaded into a 25 ml. monel vessel. (2·9 m.m.) of $CH_3N = SF_2$ and approximately a 2 fold excess of Cl_2 were added at -196°C. An exothermic reaction occurred on allowing the reactor to warm freely to room temperature. The volatiles were distilled out at room temperature through -95 and -196°C cold baths. The -95°C bath held a yellow-orange liquid, while the -196°C trap contained HCl. The contents of the -95°C trap were consistent with the presence of TRIFLUOROMETHYLIMINOSULPHUR DICHLORIDE, confirmed by infra-red [93] and n.m.r. spectroscopy.[93]

(b) When $CH_3N = SF_2$ and Cl_2, in a 1:2·6 ratio, were reacted overnight at room temperature in a 75 ml. metal reactor containing CsF, the products identified were HCl, $CH_2ClN = SF_2$ and $CHCl_2N = SF_2$.

Attempted fluorination of $CH_2ClN = SF_2$ and $CHCl_2N = SF_2$.

(a) Caesium Fluoride.

A mixture of $CH_2ClN = SF_2$ and $CHCl_2N = SF_2$ was condensed on to dry CsF in a glass reaction vessel, fitted with a Teflon stopcock. The vessel was allowed to warm to room temperature and then held at 40°C for 1 hour. A n.m.r. of the volatile products showed no carbon fluorine products, but consisted essentially of unreacted starting materials.

(b) Sodium fluoride and acetonitrile.

A similar procedure to the above was employed, using a slurry of NaF in CH_3CN at room temperature. An infra-red spectrum of the mixture, after 12 hours at room temperature, revealed that no reaction had occurred.

CHAPTER II

REACTIONS OF SULPHUR TETRAFLUORIDE
WITH
SULPHUR-OXYGEN AND SILICON-OXYGEN COMPOUNDS

SUMMARY OF REACTIONS

A. Reactions of sulphur tetrafluoride with sulphites and sulphates.

1. $SF_4 + (MeO)_2SO \rightarrow MeOS(O)F + MeF + SOF_2$.
2. $SF_4 + (EtO)_2SO \rightarrow EtOS(O)F + EtF + SOF_2$.
3. $SF_4 + (PhO)_2SO \rightarrow PhOS(O)F + \text{solids} + SOF_2$.
4. $SF_4 + (MeO)_2SO_2 \rightarrow MeOSO_2F + MeF + SOF_2$.

B. Reactions of alkylfluorosulphites.

5. $MeOS(O)F + Me_3SiNEt_2 \rightarrow MeOS(O)NEt_2 + Me_3SiF$.
6. $EtOS(O)F + Me_3SiNMe_2 \rightarrow EtOS(O)NMe_2 + Me_3SiF$.
7. $MeOS(O)F + 2Et_2NH \rightarrow MeOS(O)NEt_2 + Et_2NH.HF$.
8. $MeOS(O)F + C_6H_6 \rightarrow MeOS(O)C_6H_5 + HF$.
9. $MeOS(O)F + (MeO)_3P \rightarrow$ no reaction.

C. Reactions of sulphur tetrafluoride with Si-O compounds.

10. $SF_4 + Me_3SiOMe \rightarrow MeF + SOF_2 + Me_3SiF$.
11. $SF_4 + Me_2Si(OMe)_2 \rightarrow MeF + SOF_2 + (MeO)_2SO + Me_2O\ (\text{trace}) + Me_2SiF_2$.
12. $SF_4 + MeSi(OMe)_3 \rightarrow MeF\ (\text{trace}) + SOF_2 + (MeO)_2SO + Me_2O + MeSiF_3$.
13. $SF_4 + Me_3SiOPh \rightarrow PhOSF_3 + Me_3SiF$.
14. $SF_4 + 2Me_3SiOPh \rightarrow (PhO)_2SF_2 + 2Me_3SiF$.
15. $SF_4 + 3Me_3SiOPh \rightarrow (PhO)_4S + 3Me_3SiF$.
16. $SF_4 + 2{\cdot}5Me_3SiOPh \rightarrow (PhO)_2SF_2 + (PhO)_3SF + 2{\cdot}5Me_3SiF$.

D. Reaction of sulphur tetrafluoride with sulphoxides.

17. $SF_4 + Me_2SO \rightarrow CH_2FOCH_2F + SOF_2 + SO_2 + CH_2F_2 + SiF_4$ + traces of involatile liquids.

18. $SF_4 + (CH_2O)_3 \rightarrow CH_2FOCH_2F + SOF_2 + CH_2F_2 + SiF_4$.

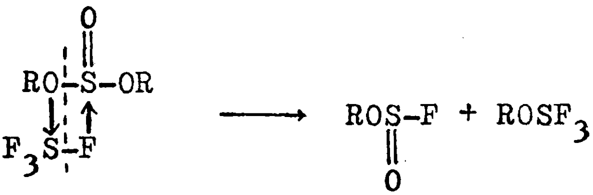
A. Reactions of sulphur tetrafluoride with sulphites and sulphates.

These reactions can be considered together and involve mutual exchange of an alkoxy group for a fluorine atom attached to sulphur.

$SF_4 + (RO)_2SO \rightarrow ROS(O)F + RF + SOF_2$ (R = Me, Et) (1)

$SF_4 + (RO)_2SO_2 \rightarrow ROSO_2F + RF + SOF_2$ (R = Me) (2)

The reactions with dialkyl sulphites might be formulated as involving a four centre transition state, the driving force being mainly the nucleophilic power of the alkoxylic oxygen in co-operation with the electrophilic function of non-metals.



A decrease in the electrophilic nature of the sulphur atom caused by the presence of an extra oxygen atom and effective valency saturation at sulphur, might explain the lower yield of methyl fluorosulphate (~40%) compared to methyl fluorosulphite (>90%).

No alkoxy derivatives of sulphur tetrafluoride, $ROSF_3$, were obtained from any of the above reactions, but stoichiometric quantities of RF and SOF_2, resulting from the thermal decomposition of $ROSF_3$, were produced. The stability of $ROSF_3$ compounds is discussed in a later section.

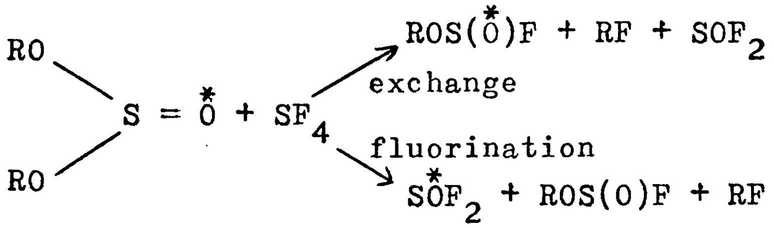
An alternative mechanism which could explain the observed products, involves fluorination of the S = 0 group by SF_4 with abstraction of the oxygen atom as SOF_2;

$$SF_4 + (RO)_2S = 0 \longrightarrow (RO)_2SF_2 + S(0)F_2$$

followed by rapid breakdown of $(RO)_2SF_2$,

$$(RO)_2SF_2 \longrightarrow ROS(0)F + RF$$

Although there is no direct evidence against this mechanism, the initial fluorination step must be thermodynamically suspect, because the energy required to break the desired bonds are of a similar order of magnitude to the energy gained by new bond formation. However, the subsequent decomposition of $(RO)_2SF_2$, with formation of a strong C-F bond, might provide enough energy to allow such a reaction. Unambiguous proof for fluorination could result by isotopic tracer studies involving the double bonded oxygen.



Metal salts of fluorosulphurous acid are well known [115] (MOS(0)F, M = alkali metal), but the corresponding esters, ROS(0)F, have received little attention, apart from work by Zappel involving the fluorination of the corresponding chloro esters with KSO_2F.[116]

$$BuOS(O)Cl + KSO_2F \xrightarrow[\text{2 hrs.}]{100°C} BuOS(O)F$$

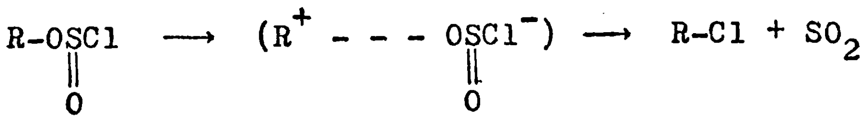
The above high temperature reactions of SF_4 with sulphites have provided an easy, high yield route to the alkyl fluorosulphites, ROS(O)F.

Since this work, alkyl fluorosulphites have been prepared by the reaction of SOF_2 with sulphites, or $\equiv$ Si-OR (R = Me, Et) compounds [20]. An extension [117] of the method used by Zappel has also led to the formation of a complete series of ROS(O)F compounds (R = Me, Et, ^{n}Bu). Where physical measurements overlap, the results obtained in this work are in good agreement with the published values.

The alkyl fluorosulphites are colourless liquids which are easily hydrolysed to SO_2 and RF.

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

Heating causes a similar decomposition and generally precludes the use of the fluorosulphites in high temperature reactions. The observed thermal and hydrolytic instability of ROS(O)F compounds parallels that of the alkyl chlorosulphites, ROS(O)Cl.[118]



$$R\text{-}O\underset{\underset{O}{\|}}{S}Cl \longrightarrow (R^{+} - - - O\underset{\underset{O}{\|}}{S}Cl^{-}) \longrightarrow R\text{-}Cl + SO_2$$

There seems to be quite general agreement that the thermal decomposition of chlorosulphites involves heterolytic fission of the C-O bond in the rate determining step, with the formation of an ion-pair intermediate in which the alkyl group is in effect a carbonium ion.[119]

The infra-red spectra of alkyl fluorosulphites and related compounds.

Structurally, the alkyl fluorosulphites can be regarded as substituted derivatives of thionyl fluoride, SOF_2. In thionyl halides, the XSO bond angle is fairly constant (Table 7) at approximately the tetrahedral angle, but the XSX bond angle covers the range 92·5-114·°.

TABLE 7.

Compound	Bond L°	Bond L°	r_{S-O}(Å)	vS-Ocm^{-1}	Ref.
F_2SO	106·8(FSO)	92·8(FSF)	1·41	1308	[120]
Cl_2SO	106(ClSO)	114(ClSCl)	1·45	1215	[121]
Br_2SO	108(BrSO)	96(BrSBr)	1·45	1121	[122]

The pyramid is chiefly distorted by virtue of the shortness of the S-O bond (1·41-1·45 Å) in comparison with the single bond length of 1·70 Å.[97] For thionyl halides, it is accepted that the short S-O bond is due to interaction between the filled oxygen pπ orbitals and the empty sulphur dπ orbitals. To date, no compound is known in which the S-O bond is as long as the predicted value for the single bond, calculated from the sum of Pauling's covalent radii. The longest reported bonds are 1·66 Å in SF_5OOSF_5 [23] and 1·64 Å in SF_5OF [24], and although the 3d-orbitals normally used for double bonding with oxygen are largely utilised in forming single bonds to other atoms, there is some evidence that, even for these long bonds, some dπ-pπ overlap occurs.[25]

The nature of the sulphur-oxygen bond in thionyl compounds (XYSO) has been discussed in terms of the electronegativity of the groups attached to sulphur.[26] It is considered that two possible extreme forms of the S-O bond may be represented as (i) and (ii).

$$\underset{\text{(i)}}{S = O} \qquad\qquad \underset{\text{(ii)}}{\overset{+}{S}-\overset{-}{O}}$$

Structure (i) represents a situation in which the bonding electrons are shared equally and arises when the atoms attached to sulphur have electronegativities sufficiently great to raise the effective electronegativity of sulphur to that of oxygen. This situation is approached in SOF_2. With decreasing electronegativity of the attached groups, the bond becomes polar and in the limit the π bond electron pair resides essentially on the oxygen atom, structure (ii). Since increasing the electronegativity of the groups attached to sulphur should increase the S-O bond order, the S-O stretching frequency may be used as a measure of the bond order. A similar correlation should exist between the S–O stretching frequency and the length of the S–O bond. These relationships have been verified by Gillespie and Robinson [126] and are illustrated graphically in Figs. 1 and 2.

FIG. 1

Stretching frequency – bond length relationship.

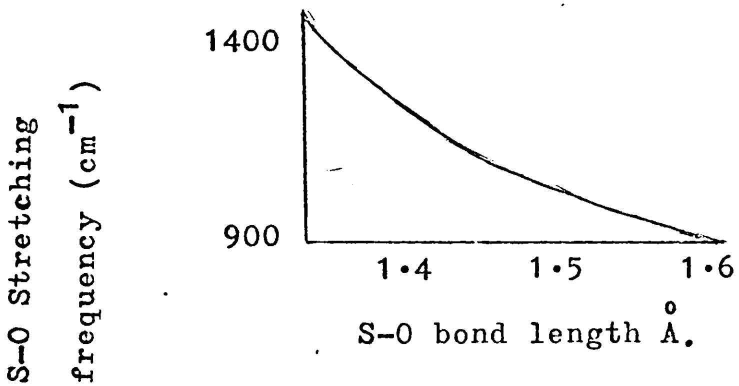
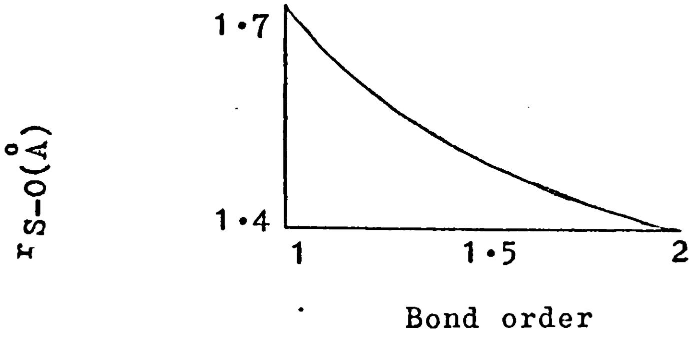


FIG. 2

Bond length – bond order relationship.

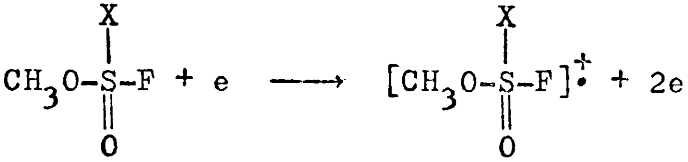


Using the observed S–O stretching frequencies for

Me(1268), Et(1267), and Ph(1262), these plots can be used to predict the approximate bond length, r_{S-O}, and bond order of the S-O bond in the fluorosulphites. The extrapolated r_{S-O} is between 1·43 and 1·44 Å and corresponds to a bond order of 1·7 to 1·8, assuming that the fluorine substituents on the sulphur causes the S-O bond order to achieve its maximum of 2·0 in SOF_2. Since the observed S-O stretching frequencies in the ROS(O)F compounds vary over only a few cm^{-1} in changing the R group, it is to be expected that the bond length and bond order should be approximately constant for such a series. This is in agreement with the conclusions of Moffitt who showed there is a relatively small variation in the bond order in many XSOY compounds.[27]

The mass spectra of fluorosulphites and sulphates.

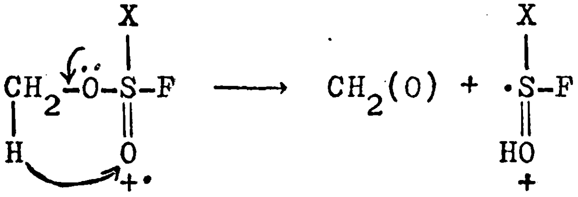
In addition to showing expected decomposition fragments, the mass spectra of methyl fluorosulphite, $CH_3OS(O)F$, and methyl fluorosulphate, CH_3OSO_2F, show evidence of a rearrangement process involving the loss of a species for which m/e = 30. Although no mass measurements were made, the elision species can only be CH_2O, formaldehyde, and results from fragmentation of an alkoxy group followed by hydrogen migration.



$$CH_3O-\overset{\overset{X}{|}}{\underset{\underset{O}{\|}}{S}}-F + e \longrightarrow [CH_3O-\overset{\overset{X}{|}}{\underset{\underset{O}{\|}}{S}}-F]^{+\cdot} + 2e$$

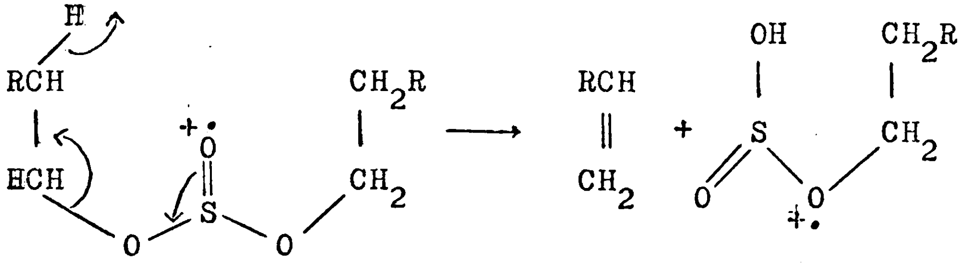
(X = lone pair, or O atom.)

The resultant positive charge must be delocalised to some extent over the whole molecule. However, the abundant ion products can be visualised assuming that the most facile manner in which ionisation can occur, is by removal of an electron from the double bonded oxygen atom. Thus the molecular ion can be represented as (I). This does not mean however, that this is the sole species present in the molecular ion, since the high energy bombarding electrons make many other processes possible.



(I)

Rearrangement of a hydrogen atom to a polar functional group of an odd electron ion leads to major peaks in the spectra of many classes of compounds [128] (McLafferty rearrangement) e.g. in sulphites.



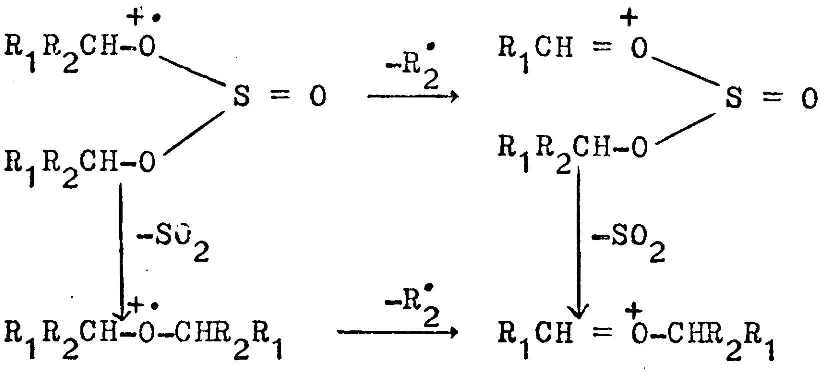
Migration is postulated to oxygen rather than to sulphur, since the main fragments observed originate from ionisation at oxygen in dialkyl sulphites [129] and alkyl sulphones. [130]

The absence of metastable peaks in the spectra of the $CH_3O\overset{X}{\overset{|}{S}}(O)F$ compounds make the fragmentation pathways difficult to postulate. However, since the principal fragment ion peaks should correspond to the most stable ion products of the most favourable reaction paths, possible cracking patterns can be suggested for the abundant ions.

Three major fragmentation pathways are apparent in the mass spectra of dialkyl sulphites. [129] The present work shows that these modes of decomposition occur to some extent in the alkyl fluorosulhpites and sulphates.

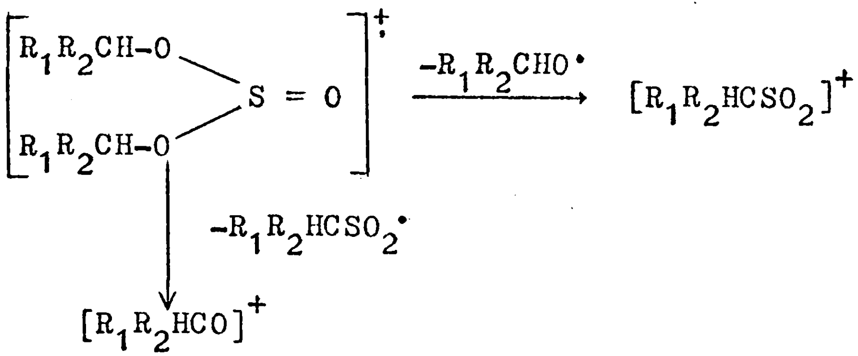
1. Formation of M-R-SO_2 ions (M = molecular ion).

There are two possible routes which involve the loss of an alkyl radical and a neutral sulphur dioxide molecule.



2. S-O bond cleavage.

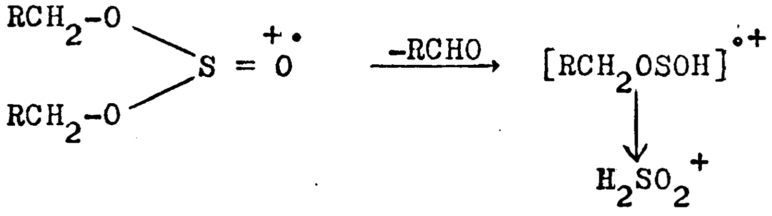
Cleavage of the S-O bond may occur to produce ions of either fragment.



3. McLafferty rearrangement (as outlined previously).

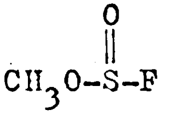
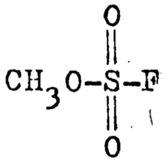
4. S-O bond cleavage and hydrogen migration.

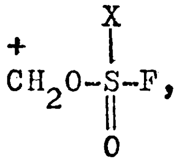
With dimethyl and diethyl sulphites, hydrogen migration is possible after cleavage of the S-O bond.

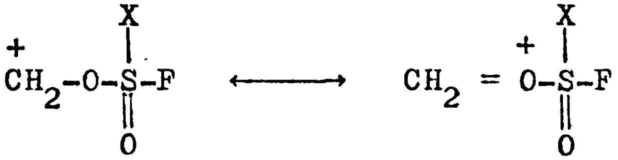


The mass spectra of $CH_3OS(O)F$ and CH_3OSO_2F (Table 8) show molecular ions (M), the abundance of which is reflected in the chemical stability of the molecule.

TABLE 8

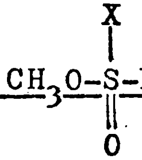
Compound	m/e	Ion	Intensity	Compound	m/e	Ion	Intensity
 $CH_3O-\overset{\overset{O}{\parallel}}{S}-F$ (M.W. 98)	99	$C^{13}H_2SO_2F$	7	 $CH_3O-\underset{\underset{O}{\parallel}}{\overset{\overset{O}{\parallel}}{S}}-F$ (M.W. 114)	115	$C^{13}H_2SO_3F$	5
	98	CH_3SO_2F	26		114	CH_3SO_3F	29
	97	CH_2SO_2F	39		113	CH_2SO_3F	60
	83	SO_2F	42		95	CH_2SO_3	4
	79	CH_3SO_2	39		84	HSO_2F	39
	68	HSOF	70		83	SO_2F	51
	67	SOF	100		79	CH_3SO_2	10
	64	SO_2	60		67	SOF	69
	51	SF	8		65	HSO_2	26
	48	SO	53		64	SO_2	67
	31	CH_3O	62		51	SF	5
	30	CH_2O	54		48	SO	57
					31	CH_3O	38
					30	CH_2O	100

Intensity measurements indicate that the loss of a hydrogen atom from the parent ion (M-H) is a favourable process, producing ions of the type  $\overset{+}{\mathrm{CH}_2}\mathrm{O}-\overset{\overset{X}{|}}{\underset{\underset{O}{\|}}{S}}-F$, which can be stabilised by electron sharing from a neighbouring group.

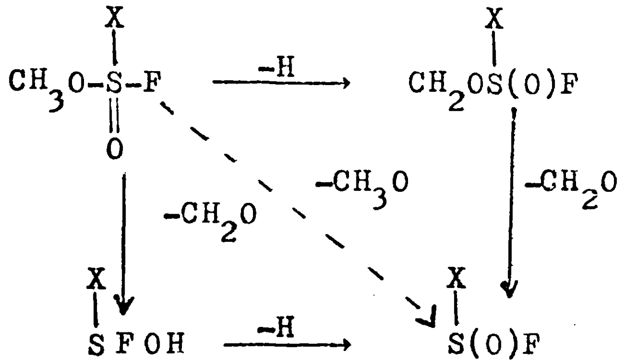


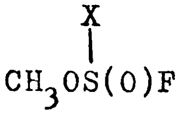
$$\overset{+}{\mathrm{CH}_2}-\mathrm{O}-\overset{\overset{X}{|}}{\underset{\underset{O}{\|}}{S}}-F \longleftrightarrow \mathrm{CH}_2=\overset{+}{\mathrm{O}}-\overset{\overset{X}{|}}{\underset{\underset{O}{\|}}{S}}-F$$

In addition to strong peaks at m/e 68 and m/e 84 for the sulphite and sulphate respectively, corresponding to the loss of CH_2O from the molecular ion ($M-CH_2O$, Scheme 4), high intensity ions are observed for ($M-CH_3O$, Scheme 2). Since such ions can be formed by, at least, three favourable pathways, the contributions from such species are expected to be great.

<u>Suggested cracking pattern for</u>  $\mathrm{CH}_3\mathrm{O}-\overset{\overset{X}{|}}{\underset{\underset{O}{\|}}{S}}-F$ <u>compounds</u>.

(Omitting positive charges.)

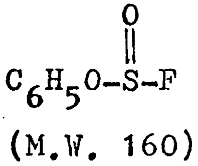


The relatively small intensity ions resulting from (M-F) suggests that such processes are only secondary in the mass spectra of  $CH_3O\overset{X}{\overset{|}{S}}(O)F$ compounds, and that other more favourable decompositions occur.

$C_6H_5OS(O)F$

The mass spectrum of phenyl fluorosulphite, $C_6H_5OS(O)F$, (Table 9) shows a molecular ion (M) of high abundance. Compared with alkyl fluorosulphites and sulphates, the enhanced stability of the phenoxy compound may be explained by possible delocalisation of oxygen electrons into the benzene ring, via pπ-pπ bonding.

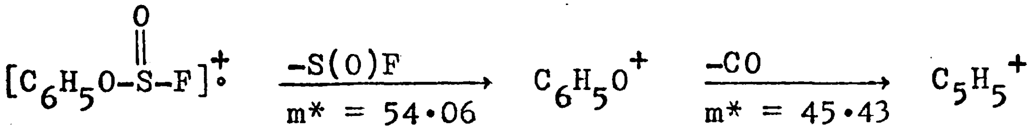
TABLE 9

Compound	m/e	Ion	Intensity
 $C_6H_5O-\overset{\overset{O}{\|}}{S}-F$ (M.W. 160)	160	$C_6H_5SO_2F$	72
	141	$C_6H_5SO_2$	1
	93	C_6H_5O	100
	77	C_6H_5	14
	67	SOF	17
	65	C_5H_5	96
	64	SO_2	9
	51	SF	5
	48	SO	5
	28	CO	91

Metastables:

m*	m_1	m_2
54·06	160	93
45·43	93	65

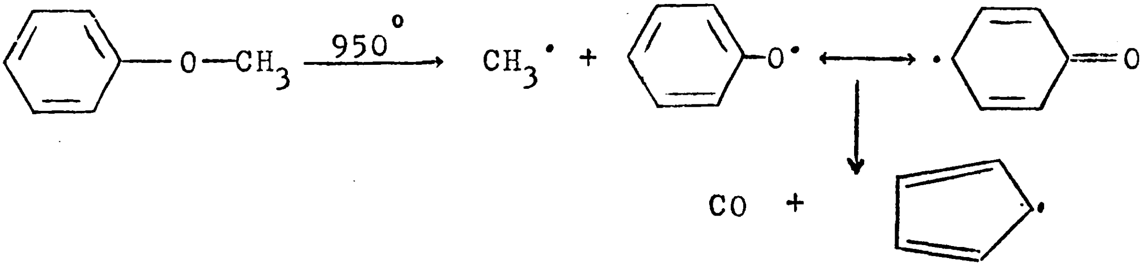
Evidence from metastable peaks established that the following transitions occur.



$$[C_6H_5O-\overset{\overset{O}{\|}}{S}-F]^{+\cdot} \xrightarrow[m^* = 54\cdot06]{-S(O)F} C_6H_5O^+ \xrightarrow[m^* = 45\cdot43]{-CO} C_5H_5^+$$

m/e 160(M)   m/e 93   m/e 65

Loss of CO is characteristic of aryloxy ions [131] and parallels the loss of CO in the thermal decomposition of the phenoxy radical.[132]



A similar production of cyclopentadiene by the pyrolysis of phenol has also been reported.[133] Other noteworthy features in the spectrum of $C_6H_5OS(O)F$ are the loss of a phenoxy group from the molecular ion $(M-C_6H_5O)$ and that, similar to the alkyl derivatives, intensity data show that (M-F) ions are not propitious.

The n.m.r. spectra of fluorosulphites.

The relevant n.m.r. parameters for the fluorosulphites are shown in (Table 10).

TABLE 10

Compound	δ_H p.p.m.$^{(a)}$	δ_F p.p.m.$^{(a)}$	J_{H-F} c/s
FS(O)F [4]		-77·9(s)	
MeOS(O)F	-3·85(d)	-55·6(q)	1·3
EtOS(O)F	-1·35(t)Me	-59·8(t)	1·3
	-4·35(c)CH_2		
PhOS(O)F	-6·88(c)	-62·3(s)	

(a) chemical shifts with respect to Me_4Si and CCl_3F

As the electronegativity of the attached RO group (R = Me, Et and Ph) decreases, there is a progressive decrease in the shielding of the ^{19}F nuclei, and the chemical shifts move to higher fields. The relatively narrow range over which the ^{19}F resonances occur, suggests that "shifts" in the -60 p.p.m. region could be used as diagnostic of the fluorine in the -S(O)F group.

In methyl fluorosulphite, the methyl group is observed as a doublet, due to coupling with a single fluorine atom. The fluorine resonance shows the expected triplet structure.

The methylene protons in ethyl fluorosulphite are complex. In addition to coupling with the methyl and fluorine atoms, further complexity is caused by magnetic non-equivalence of the methylene protons. The origin of magnetic non-equivalence in sulphur compounds is discussed more fully in a later chapter.

No fine structure was detected in either the proton or fluorine spectra of phenyl fluorosulphite, although coupling between the ortho-protons of the aromatic ring and the fluorine atom would be reasonable. Possibly the resolution of the spectrometer was not sufficient to resolve such fine splitting.

B. Reactions of alkyl fluorosulphites.

Being derivatives of thionyl fluoride, it is to be expected that the fluorosulphites should undergo the same type of reactions as those experienced by SOF_2. Thionyl fluoride reacts more as a substrate for substitution rather than a fluorinating reagent, and most of the published reactions of SOF_2 e.g. with amines [18], trialkylsilylamines and Si-O containing compounds [134] involve replacement of the fluorine atoms.

The alkyl fluorosulphites react readily with trialkylsilylamines, below room temperature, to produce trimethylsilylfluoride and high yields of sulphinamides, $ROS(O)NR_2$. Alternatively, the sulphinamides can be prepared by direct reaction with excess secondary amine.

$$ROS(O)F + Me_3SiNR'_2 \longrightarrow ROS(O)NR'_2 + Me_3SiF$$

$$(R = Me, Et) \quad (R' = Me, Et)$$

$$ROS(O)F + 2R'_2NH \longrightarrow ROS(O)NR'_2 + R'_2NH.HF.$$

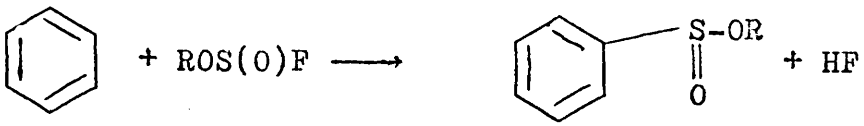
$$(R = Me) \quad (R' = Et)$$

The former method is preferred for the preparation of sulphinamides, because separation of the products is easy, whereas, in the latter method, the presence of the H-F salt tends to make effective separation difficult.

The sulphinamides are colourless, involatile liquids which are stable indefinitely to storage in glass. Previously, sulphinamides have been synthesised by the reaction of alkyl chlorosulphites with secondary amines.[135]

$$ROS(O)Cl + 2R_2NH \longrightarrow ROS(O)NR_2 + R_2NH.HCl$$

With benzene the fluorosulphites react via a substitution reaction, incorporating the ROS(O) - entity into the aromatic system.



There was no evidence of toluene from this reaction [136] and suggests that methyl migration and loss of SO_2 does not occur.

Although SF_4 vigorously fluorinates trimethyl phosphite [137], no reaction was observed under the same conditions with MeOS(O)F. A similar lack of fluorinating properties has been found for methyl fluorosulphate [138] which reacts primarily as an alkylating agent.

C. Reactions of sulphur tetrafluoride with silicon-oxygen containing compounds.

The stability of alkoxy and aryloxy derivatives of non metals.

In general alkoxy derivatives of non metals, which have a tendency to form double bonds to oxygen, are thermally unstable. $MeOPF_4$ [139] has been isolated from the reaction between PF_5 and $(MeO)_3P$, but above -10°C the compound decomposes with the formation of a complex series of reaction products. Reactions of substituted derivatives of PF_5 with trimethylalkoxysilanes, produced no stable fluorophosphoranes containing an alkoxy group. [140]

$$\begin{tikzcd} & R_nPF_{4-n}(OR') + Me_3SiF \\ R_nPF_4 + R'OSiMe_3 \arrow[ur, "\parallel" marking] \arrow[dr] & \\ & R_nP(O)F_{3-n} + R'F + Me_3SiF \end{tikzcd}$$

Similar instability has been found with alkoxyboron derivatives. Alkyl dichloroboronites, $ROBCl_2$ [141], and di-alkyl chloroboronates, $(RO)_2BCl$, [142] decompose readily below room temperature in accordance with the following equations.

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

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

In addition to the above decompositions, the reactions can be further complicated by disproportionation.[141]

$$2ROBCl_2 \longrightarrow (RO)_2BCl + BCl_3$$

With fluoroboronites [143], disproportionation is the major decomposition pathway.

It may therefore be expected that similar thermal instability will prevail with alkoxy derivatives of sulphur tetrafluoride. The two major decomposition mechanisms being:

(1) Breakdown to an alkyl halide, with subsequent formation of a strong S=O bond.

(2) Disproportionation.

Reactions of sulphur tetrafluoride with alkoxysilanes.

In the reactions of SF_4 with dialkyl sulphites and sulphates, alkoxy derivatives of SF_4 were postulated as transient intermediates. Attempts were made to isolate these compounds by the room temperature reaction of SF_4 with Si-O containing compounds, MeO_xSiMe_{4-x}, $(x = 1,2,3)$.

Trimethylmethoxysilane.

SF_4 reacted readily below room temperature with Me_3SiOMe, cleaving the Si-O bond with the production of Me_3SiF. The presence of Me_3SiF suggests that $MeOSF_3$ is formed during an early stage in the reaction. However, due to facile decomposition, only fragments MeF and SOF_2 were detected. The driving force for such a decomposition probably arises from the formation of strong C-F and S=O bonds. The overall reaction between SF_4 and Me_3SiOMe can be represented as:

$$SF_4 + Me_3SiOMe \longrightarrow Me_3SiF + MeOSF_3$$

$$MeOSF_3 \longrightarrow MeF + SOF_2$$

$ROSF_3$ compounds have been previously postulated as being the source of RF and SOF_2 in the reactions of SF_4 and boron esters [144], and are believed to be involved in the fluorination of alcohols [32] with sulphur tetrafluoride. Only recently has the first alkoxysulphur trifluoride compound, 2 fluoro-2, 2-dinitroethoxysulphur trifluoride been isolated.[145]

Dimethyldimethoxysilane.

Although a quantitative yield of Me_2SiF_2 was obtained from the room temperature reaction of SF_4 and $Me_2Si(OMe)_2$, $(MeO)_2SF_2$ was not isolated. Other observed products were MeF, SOF_2, $(MeO)_2SO$ and a trace of Me_2O.

Assuming that $(MeO)_2SF_2$ was formed during the reaction, it might be expected to decompose via two main routes.

$$\begin{array}{lll} (MeO)_2SF_2 & \xrightarrow{(1)} & Me_2O + SOF_2 \quad [146] \\ \quad\;\; \llcorner & \xrightarrow{(2)} & MeF + MeOS(O)F \end{array}$$

Scheme (1) does not appear to be the most favourable decomposition route and may be discounted since only the slightest trace of Me_2O was detected. Route (2) is analogous to the decomposition proposed for $MeOSF_3$. The large amounts of MeF formed could be explained by (2), even though MeOS(O)F was not isolated. Although ROS(O)F compounds are sufficiently stable to permit isolation, there is some evidence for their instability towards disproportionation.[116]

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

The above decomposition might be catalysed by traces of impurities or other products formed in the reaction. Certainly, the formation of $(MeO)_2SO$ suggests that such disproportionation could occur in this reaction.

The overall decomposition of $(MeO)_2SF_2$ can now be represented as:

$$2(MeO)_2SF_2 \longrightarrow 2MeF + 2MeOS(O)F$$
$$2MeOS(O)F \longrightarrow (MeO)_2SO + SOF_2$$

The products of the above reaction can also be rationalised without regard to $(MeO)_2SF_2$, by considering a series of stepwise competitive exchange reactions. The known instability of $MeOSF_3$ should have a pronounced effect on the course of the reaction. For example, ready formation of SOF_2 could lead to a variety of side reactions involving competition for exchange of alkoxy groups.

The first stage might be substituent exchange between the two starting materials, followed by rapid decomposition of methoxysulphur trifluoride (1 and 2).

$$SF_4 + Me_2Si(OMe)_2 \longrightarrow MeOSF_3 + Me_2Si(OMe)F \qquad (1)$$
$$MeOSF_3 \longrightarrow MeF + SOF_2 \qquad (2)$$

Subsequently, it is proposed that SOF_2 undergoes a further exchange reaction with the Si-O starting material (3).

$$SOF_2 + Me_2Si(OMe)_2 \longrightarrow Me_2SiF_2 + (MeO)_2SO \qquad (3)$$

SOF_2 has been shown previously to exchange alkoxy groups for fluorine atoms, [20,134] with eventual formation of dialkyl sulphites.[134]

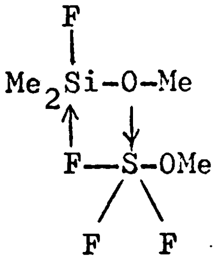
$$SOF_2 + MeOSiMe_3 \longrightarrow Me_3SiF + MeOS(O)F$$

$$MeOS(O)F + MeOSiMe_3 \longrightarrow Me_3SiF + (MeO)_2SO$$

$Me_2Si(OMe)F$ prepared via (1) could be converted into Me_2SiF_2 by reaction with excess SF_4 (4).

$$SF_4 + Me_2Si(OMe)F \longrightarrow Me_2SiF_2 + MeOSF_3 \qquad (4)$$

Furthermore, it is assumed that no exchange takes place between the products formed in (1). Formulating this exchange as involving a four centre transition state, the replacement of an alkoxy group by a halogen atom will be related to the electron density on the oxygen.



Further exchange between the two products should be slow, since the nucleophilic function of the oxygen atom in the fluorosilane will be reduced by the presence of the fluorine. In addition, the electrophilic function of the sulphur will be reduced by the alkoxy group.

<u>Methyltrismethoxysilane</u>.

As the number of alkoxy groups attached to sulphur increases, the mode of reaction becomes more complex, and in addition to $MeSiF_3$, other observed major products from the room temperature reaction were Me_2O, SOF_2, $(MeO)_2SO$ and traces of MeF. Assuming that $(MeO)_3SF$ is formed, the other products, with the exception of $MeSiF_3$, can be explained by the decomposition of the alkoxysulphur compound. The mechanism for decomposition possibly involves the formation of an S=O compound with elimination of dimethyl ether, and subsequent disproportionation of MeOS(O)F.

$$2(MeO)_3SF \longrightarrow 2Me_2O + 2MeOS(O)F$$

$$2MeOS(O)F \longrightarrow (MeO)_2SO + SOF_2$$

It is concluded however, that (under the experimental conditions used) the inherent instability of alkoxy derivatives of sulphur tetrafluoride, prevents any unambiguous reaction mechanism to be drawn from the above reactions. The mechanism of these reactions must await the isolation of the corresponding alkoxysulphur compounds and a detailed study of their modes of decomposition. Perhaps a low temperature n.m.r. study would be fruitful in helping to understand the ultimate mechanism, and might possibly result in the isolation of the unstable intermediates postulated.

Reactions of sulphur tetrafluoride with aryloxysilanes.

Before 1960, organic sulphur trifluorides, RSF_3, were a relatively unknown class of compound and only CF_3SF_3 and $SF_3CF_2SF_3$ had been established. In general, these compounds were only formed when R was a perfluoroalkyl group and were prepared, usually in low yields, by the fluorination of organic sulphur compounds with elemental fluorine, or by electrolytic fluorination in anhydrous hydrogen fluoride.[147,148]

Since 1960, two improved methods have been discovered for the preparation of RSF_3 compounds. The first is the reaction of an organic disulphide with silver difluoride.[84]

$$(C_6H_5S)_2 \xrightarrow{AgF_2} 2C_6H_5SF_3$$

The second method, discovered by Muetterties and Rosenberg, involves the addition of SF_4 to fluoro olefins, in the presence of caesium fluoride as catalyst.[62]

$$SF_4 + CF_3CF = CF_2 \longrightarrow (CF_3)_2CFSF_3$$

More recently, N-dimethylaminosulphur trifluoride, Me_2NSF_3, has been synthesised by the reaction of SF_4 with N,N-dimethyltrimethylsilylamine.[110]

$$SF_4 + Me_3SiNMe_2 \longrightarrow Me_2NSF_3$$

In the present work, aryloxy derivatives of SF_4 have been prepared by the reaction of SF_4 with aryloxysilanes, although no $ROSF_3$ compounds (R = alkyl) could be obtained, either from alkyl sulphites or alkoxysilanes, when reacted with SF_4.

This mode of reaction is similar to that observed in phosphorus chemistry, where no stable alkoxyfluorophosphoranes could be isolated using an alkoxysilane (see page 97). However, this instability was not observed when aryl, or perfluoroaryl groups were present in the molecule.[62]

$$R_nPF_{5-n} + (3-n)ArOSiMe_3 \longrightarrow R_nPF_2OAr_{(3-n)} + (3-n)Me_3SiF$$

Preparation of phenoxysulphur trifluoride.

The reaction between SF_4 and Me_3SiOPh occurs smoothly below room temperature, producing trimethylsilylfluoride (1 mole) and phenoxysulphur trifluoride, $PhOSF_3$.

$$SF_4 + Me_3SiOPh \longrightarrow PhOSF_3 + Me_3SiF$$

During the reaction, small quantities of a white solid were formed in the reaction flask. This solid was not investigated.

Properties of phenoxysulphur trifluoride.

Phenoxysulphur trifluoride is a colourless, involatile liquid, which is stable in dry glass but, in the presence of trace quantities of moisture, becomes pinkish in colour and produces phenyl fluorosulphite in quantitative yield.

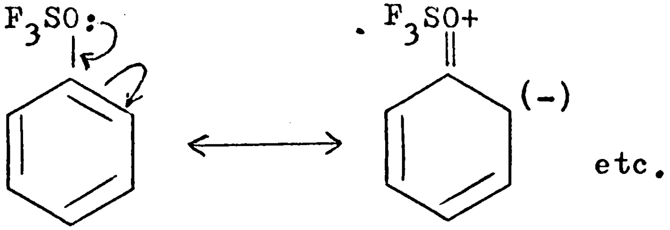
$$PhOSF_3 \xrightarrow{H_2O} PhOS(O)F + HF$$

This ease of hydrolysis, with formation of -S(O)F compounds, is the expected mode of hydrolytic decomposition of RSF_3 compounds.[63, 69] Further hydrolysis of phenyl fluorosulphite produces phenol.[149]

$$PhOS(O)F \xrightarrow{H_2O} PhOH$$

The progress of hydrolysis can be conveniently followed by infra-red and n.m.r. spectroscopy. After only minutes, the infra-red spectrum revealed the presence of a band at 1260 cm^{-1}, characteristic of the S=O stretching frequency in PhOS(O)F.[149] Similarly, a sample of $PhOSF_3$ stored in a n.m.r. tube showed only PhOS(O)F, after having been exposed to the air. Although no toxicity studies were carried out on $PhOSF_3$, it should be stressed that, because of the ease with which it hydrolyses with liberation of hydrogen fluoride, $PhOSF_3$ should be handled with care and should not be allowed in contact with the skin.

Phenoxysulphur trifluoride is thermally stable at room temperature, having been left in a closed n.m.r. tube for several weeks without showing any appreciable change in the spectrum. This enhanced stability of phenoxy, over methoxysulphur trifuloride, possibly involves pπ–pπ overlap between the aromatic ring system and the adjacent oxygen atom.



However, when phenoxysulphur trifluoride is heated in glass to approximately 80°C, it becomes red in colour and at 100°C thionyl fluoride is evolved. Further heating causes the liquid to become a solid purple mass.

$$PhOSF_3 \xrightarrow{\Delta} SOF_2 + \text{solid}$$

There was no indication of fluorobenzene, an expected decomposition product by comparison with $MeOSF_3$. The purple solid was insoluble in water, benzene and acetonitrile and its appearance suggests it may be polymeric in nature.

The thermal instability of $PhOSF_3$ at high temperature, could explain the failure to isolate this compound from the exchange reaction of sulphur tetrafluoride with diphenyl sulphite at 80°C.

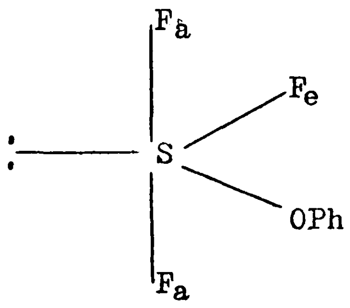
$$SF_4 + (PhO)_2SO \rightarrow PhOS(O)F + PhOSF_3 \xrightarrow{\Delta} SOF_2 + \text{purple solid}$$

The solid obtained from this reaction was insoluble in water and acetonitrile and was similar in appearance to the solid product obtained from the thermal decomposition of phenoxysulphur trifluoride.

Attempts to characterise phenoxysulphur trifluoride by mass spectrometry, using a heated glass inlet system, showed that greater than 90% of the spectrum was due to phenyl fluorosulphite (formed by attack on the glass and hydrolysis in the spectrometer). However, some indication of $PhOSF_3$ was suggested by the presence of weak peaks at m/e 105 (OSF_3^+), m/e 89 (SF_3^+), m/e 86 (OSF_2^+) and m/e 70 (SF_2^+). Other strong peaks at m/e 93 (PhO^+), m/e 77 (Ph^+) and m/e 67 (SOF^+) can be partly attributed to $PhOSF_3$, since peaks at these m/e values also occur in PhOS(O)F.

The infra-red spectrum of phenoxysulphur trifluoride is characteristic of a mono substituted aromatic compound. Although it has been suggested that intense absorption in the infra-red, between 860 and 910 cm^{-1}, is diagnostic for an SF_5 group [150], there are no published spectra of sulphur trifluoride compounds. A very strong, rather broad absorption at 845 cm^{-1} is assigned to the S-F stretching frequency by analogy with S-F bands at 850 cm^{-1} and 807 cm^{-1} found in CF_3SF_3 [63] and $PhSF_3$ [84] respectively.

By comparison with the suggested structures of other RSF_3 compounds [62] and analogous phosphorus compounds [89], substitution of the phenoxy group is expected to occur in the equatorial plane (I).



(I)

This structure is completely consistent with the observed n.m.r. of $PhOSF_3$ (Table 11).

The room temperature ^{19}F n.m.r. consists of a doublet and a triplet, centred at -79 and -30 p.p.m. respectively from external CCl_3F and supports a structure with two different fluorine atom environments in the molecule. The integration of the doublet and triplet is as 2:1 and J_{F-F} is 67·7 c/s (Table 11). As has been observed in alkyl and arylfluorophosphoranes, the axial fluorine atoms resonate at much lower fields than those of the equatorial atoms. Significantly, the doublet resonance of $PhOSF_3$ is 49 p.p.m. to the low field side of the triplet.

The proton n.m.r. consists of a multiplet at -6·55 p.p.m. from external $(CH_3)_4Si$; no H-F coupling was observed.

^{1}H(a) AND ^{19}F (b) N.M.R. SPECTRUM OF PhOSF$_3$

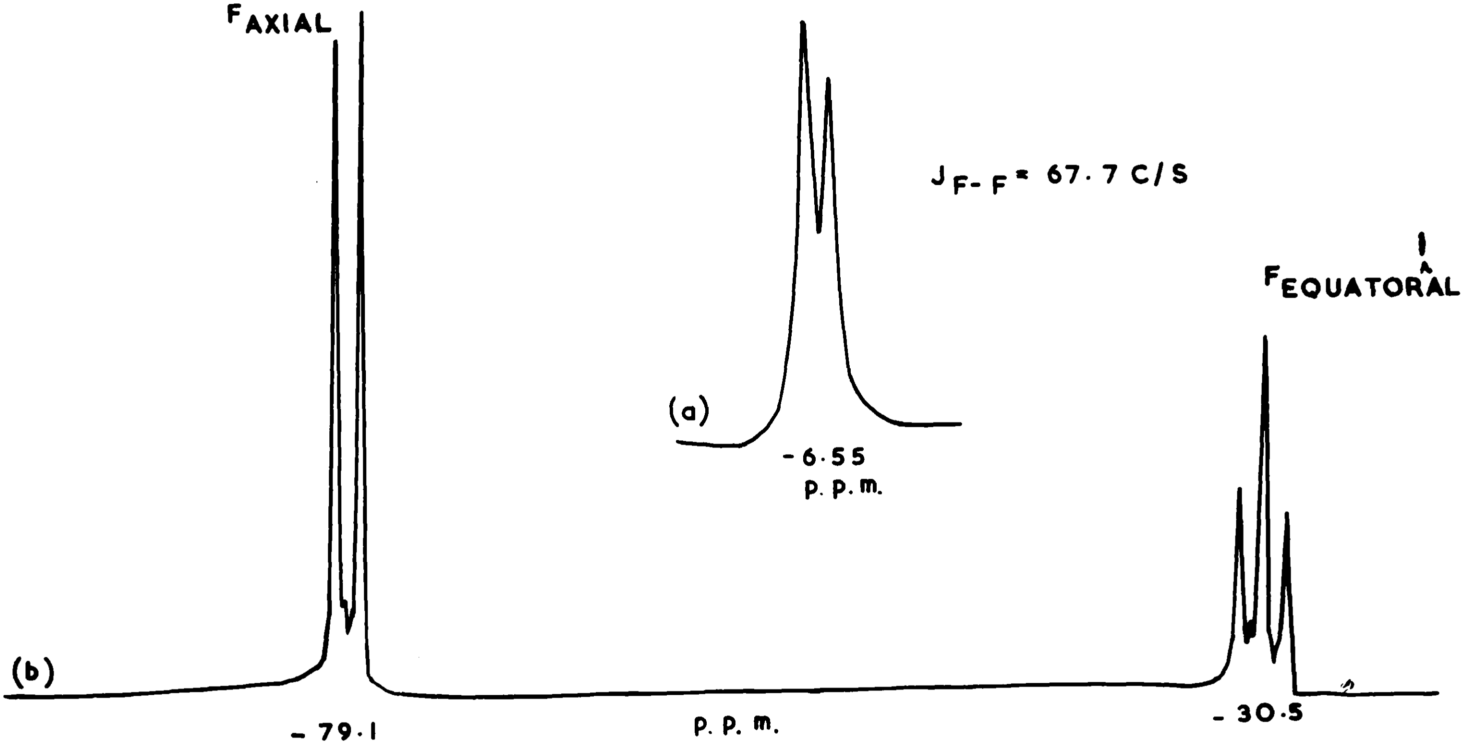


TABLE 11

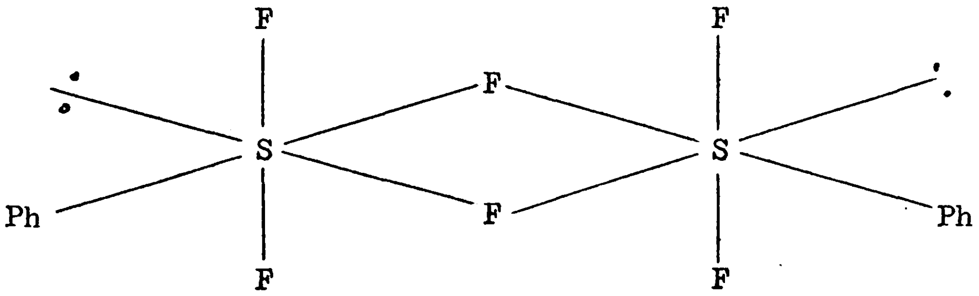
^{19}F n.m.r. data for RSF_3 compounds.

Compound	Temp°C	δ_{F_a}(p.p.m.)	δ_{F_e}(p.p.m.)	$\delta_{F_e-F_a}$(p.p.m.)	J_{F-F}(c/s)
$C_6H_5SF_3$ [84]	R.T.	−13·2(b.s.)			
	−40	−72·2(d)	+25·8(t)	98	53
$C_6H_5OSF_3$	R.T.	−79·1(d)	−30·5(t)	48·6	67·7
Me_2NSF_3 [110]	R.T.	−39·4(b.s.)			
	−100	−57·4(d)	−28·4(t)	29	
CF_3SF_3 [62]	R.T.	−47·4(d. of q.)	+49·6(t)	97	70

(All chemical shifts are measured relative to CCl_3F.)

F_a, axial fluorine shift; F_e, equatorial fluorine shift.

The room temperature ^{19}F n.m.r. of phenylsulphur trifluoride appears as a broad single resonance at low field.[84] On cooling a dilute solution of $PhSF_3$ in chloroform, the spectrum appears as a doublet and triplet of intensity, two to one respectively. Since the rate of exchange is slowed by dilution with an inert solvent, it has been suggested that the exchange process proceeds by a bimolecular (intermolecular) process. An intermediate (II), formed by association of $PhSF_3$ to dimers or polymers, could be effective in producing fluorine exchange.

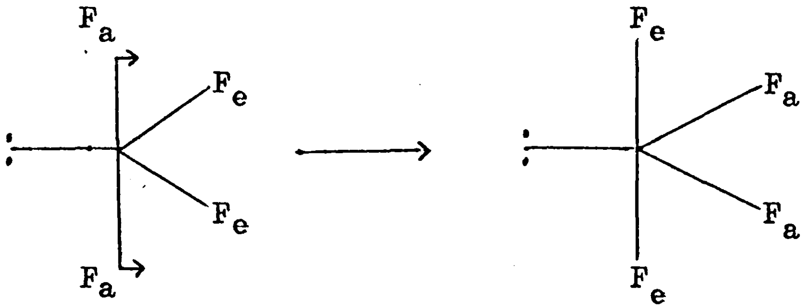


(II)

A similar intermolecular exchange process has been suggested to explain the temperature dependence of the ^{19}F n.m.r. spectrum of SF_4.[31]

Trifluoromethylsulphur trifluoride, CF_3SF_3, and dimethylaminosulphur trifluoride, Me_2NSF_3, also show a temperature dependent fluorine n.m.r. spectrum.[110]

However, no gross structural changes occur at the lower temperatures and it is concluded that the exchange process does not involve association of the molecules and a first order (intramolecular) process is assumed. In this process, an internal vibration in the molecule is thought to cause exchange of equatorial and axial atoms, so that the molecule is rotated, compared to its original state.



This pseudorotation process was first postulated by Berry to rationalise the appearance of equivalent fluorine environments in the ^{19}F n.m.r. spectrum of PF_5.[151]

Phenoxysulphur trifluoride shows no evidence for exchange at room temperature, and any process which could make the fluorine atoms equivalent must be very slow, indicating a high barrier to exchange. Although a variable temperature n.m.r. spectrum was not recorded, it is proposed that at temperatures greater than room temperature any observed exchange might involve an intermolecular process, by comparison with the closely "family" related phenylsulphur trifluoride. The greater rate of exchange in $PhSF_3$ might be related to its greater association and this is reflected in its melting point $\sim 0°C$. Although no accurate melting point was measured for $PhOSF_3$, the compound melts at temperatures below $0° \sim -20°C$. A similar comparison of melting points i.e. molecular association, has been used to explain the rates of fluorine exchange in Group (VI) tetrafluorides[31], the order being:

TeF_4(m.pt. > 200°C) > SeF_4(m.pt.9·5°C) > SF_4(m.pt.-121°C)

Preparation of bisphenoxysulphur difluoride.

The room temperature reaction of sulphur tetrafluoride with a two fold excess of phenoxytrimethylsilane readily produces bisphenoxysulphur difluoride, $(PhO)_2SF_2$.

$$SF_4 + 2Me_3SiOPh \longrightarrow (PhO)_2SF_2 + 2Me_3SiF$$

Except for perfluoroalkyl compounds [62], disubstituted derivatives of sulphur tetrafluoride are generally unknown. Me_2SX_2 species are stable when X is bromide, but are unstable when X is chloride or fluoride.[152]

Properties of $(PhO)_2SF_2$.

Bisphenoxysulphur difluoride is a colourless, involatile liquid which melts at ~25°C. The compound has been characterised by analysis, n.m.r., hydrolytic and thermal modes of decomposition.

Thermally, $(PhO)_2SF_2$ is stable at room temperature. However, heating the compound at temperatures greater than 80°C causes decomposition, forming thionyl fluoride and a purple solid.

$$(PhO)_2SF_2 \xrightarrow{\Delta} SOF_2 + \text{solid}$$

This mode of thermal decomposition is similar to that observed with $PhOSF_3$, and demonstrates the tendency for S=O bond formation.

Although perfluoroalkylsulphur difluorides e.g. $[(CF_3)_2CF]_2SF_2$, are stable towards hydrolysis, $(PhO)_2SF_2$ is quickly hydrolysed to diphenyl sulphite, on exposure to moisture.

$$(PhO)_2SF_2 \xrightarrow{H_2O} (PhO)_2SO + 2HF$$

Steric shielding of the sulphur atom has been proposed to account for the hydrolytic stability of the perfluoro-compounds.[62]

The ^{19}F n.m.r. spectrum of bisphenoxysulphur difluoride consists of a broad singlet at -67·4 p.p.m. from CCl_3F. The ^1H n.m.r. is a broad singlet centred at -6·42 p.p.m. from $(CH_3)_4Si$. The breadth of the resonances might indicate some fast exchange phenomenon (which would be expected to be much faster in $(PhO)_2SF_2$ than in $PhOSF_3$, if the criterion of high melting-greater association holds). A comparison of the fluorine chemical shift of $(PhO)_2SF_2$, with the axial fluorine resonance in $PhOSF_3$ (-79·1), suggests that the fluorine atoms in the bis compound are in axial positions, with both phenoxy groups occupying equatorial positions. It has been suggested that axial substitution of fluorine atoms is preferred in Me_2SeF_2.[153] X-ray structural data on compounds of the type R_2SeX_2 [154] and R_2TeX_2 [155], where R is an alkyl or aryl group and X is chloride or bromide, revealed that the more polar halide groups are invariably in the axial positions, with the organic groups in the equatorial sites.

Preparation of trisphenoxysulphur fluoride.

Unless the stoichiometry of the reaction between sulphur tetrafluoride and phenoxytrimethylsilane is rigorously controlled, higher substitution products are formed.

The action of a 2·5 m.m. excess of the Si-O reagent with SF_4, produces trimethylsilylfluoride and a solid-liquid mixture which is consistent with bisphenoxysulphur difluoride, $(PhO)_2SF_2$ ($\sim$30%), and trisphenoxysulphur fluoride, $(PhO)_3SF$ ($\sim$70%).

$$SF_4 + 2{\cdot}5Me_3SiOPh \longrightarrow (PhO)_2SF_2 + (PhO)_3SF + 2{\cdot}5Me_3SiF$$

Properties of $(PhO)_3SF$.

Trisphenoxysulphur fluoride is a white solid which has not been fully characterised.

The ^{19}F n.m.r. spectrum from the above reaction shows two broad singlets. The first resonance at -67·4 p.p.m. is assigned to $(PhO)_2SF_2$ by comparison with the fluorine resonance of an analytically pure sample. The second resonance at -70·8 p.p.m. is attributed to $(PhO)_3SF$. Interestingly, the position of the fluorine resonance in $(PhO)_3SF$ is very close to that observed for $(PhO)_2SF_2$ and consequently, the fluorine atom is assumed to be in the axial position of a trigonal bipyramid. It appears that addition of phenoxy groups does not drastically alter the position of the fluorine resonance. This is similar to fluorophosphoranes, where the axial chemical shift in R_2PF_3 and $R_3'PF_2$ compounds show very close correlation when $R=R'$.[156]

Preparation of tetrakisphenoxysulphur.

Attempts to prepare trisphenoxysulphur fluoride by using exactly a three fold excess of phenoxytrimethylsilane, produced in addition to trimethylsilylfluoride, traces of a colourless involatile liquid and a white solid. The solid product has been identified as tetrakisphenoxysulphur, $(PhO)_4S$. The liquid product has not been completely characterised, but its involatile properties and the fact that, on many occasions when $(PhO)_4S$ was submitted for analysis, it contained traces of fluorine (less than 1%) and showed low carbon and high sulphur analyses, suggests that the liquid is $(PhO)_2SF_2$.

$$SF_4 + 3Me_3SiOPh \longrightarrow (PhO)_4S + (PhO)_2SF_2 + 3Me_3SiF$$

Thus it appears, assuming that the reaction involves a stepwise replacement of a fluorine atom by a phenoxy group, that $(PhO)_3SF$, when formed, undergoes disproportionation.

$$2(PhO)_3SF \longrightarrow (PhO)_4S + (PhO)_2SF_2$$

Possibly, the proposed ease of disproportionation involves the tendency of the unique axial fluorine atom to regain a symmetrical environment.

Properties of $(PhO)_4S$.

Tetrakisphenoxysulphur is a white solid which is insoluble in benzene, slightly soluble in acetonitrile and very soluble in dimethyl sulphoxide, where it forms a yellow brown solution.

The molecular weight of the solid in dimethylsulphoxide showed that the compound had undergone complete dissociation in the polar solvent. A found molecular weight of 83 is in close agreement with the molecular weight of 81, assuming complete dissociation into five ions. The nature of these ions in solution is unknown and must await conductivity studies.

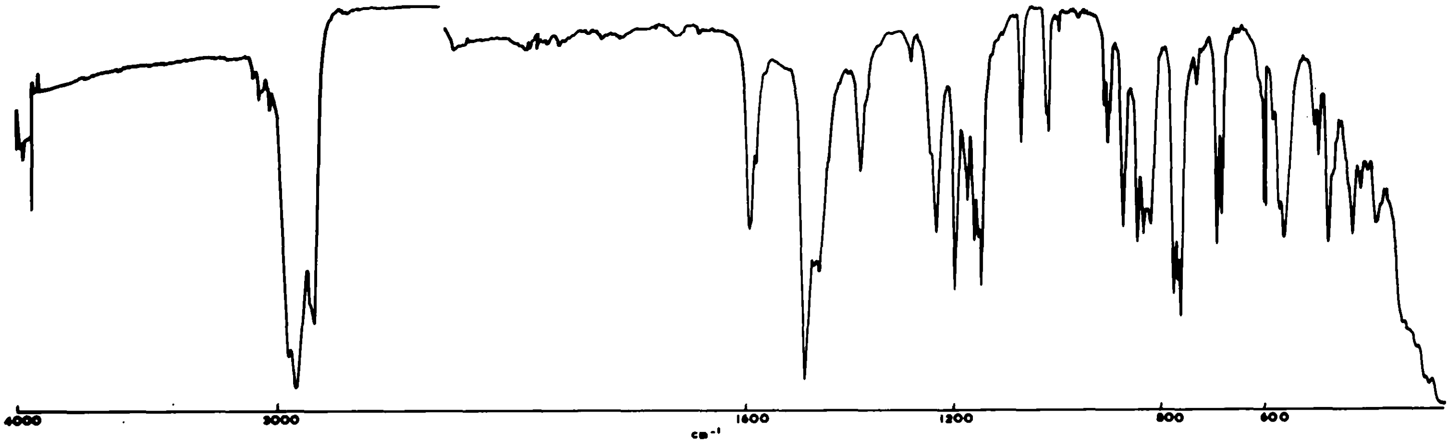
$(PhO)_4S$ is very hygroscopic and is hydrolysed to diphenyl sulphite and phenol, when left in the atmosphere.

$$(PhO)_4S \xrightarrow{H_2O} (PhO)_2SO + 2PhOH$$

The compound, however, is sufficiently stable in the absence of moisture to permit analysis. Possibly this stability involves extensive delocalisation of the π electrons over the whole molecule and apparently overrides any steric factors which are liable to detract from the stability.

The infra-red and n.m.r. spectra are not particularly indicative of $(PhO)_4S$. The infra-red is complex, but shows many bands which can be attributed to phenoxy and sulphur-oxygen vibrations.

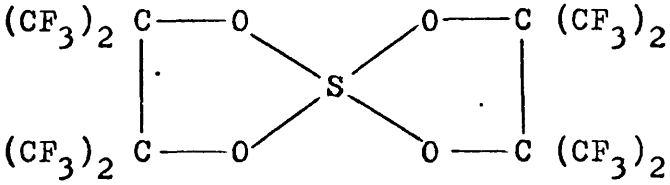
INFRA-RED SPECTRUM OF $(PhO)_4S$



The proton n.m.r. of a dilute solution in deuteroacetonitrile shows a broad complex resonance centred at -6·82 p.p.m. from $(CH_3)_4Si$, and does not allow unambiguous proof of two phenoxy group environments. Intramolecular exchange has been postulated to account for the single methyl resonance in the proton n.m.r. of penta-p-tolyl phosphorane.[157]

Tetrakisphenoxysulphur appears to be the first example of a non chelated ortho-sulphite ester, $(RO)_4S$. The compound is important, in that it contributes a new dimension in the chemistry of sulphur esters, and lends itself very well to the study of structural and stereochemical problems associated with the four valent state of sulphur.

The only other example of a compound in which sulphur (IV) is joined to four oxygens by single bonds, is perfluoropinacol ortho-sulphite (III), prepared by the reaction of sulphur (II) chloride on the disodium alkoxide of perfluoropinacol.[158]



(III)

The stability of this system has been attributed to the bicyclic nature of the compound and the presence of electronegative perfluoroalkyl groups.

Compounds containing five atoms bonded to phosphorus are more abundant and during, the past few years, Ramirez and co-workers have described the preparation and stereochemistry of five membered cyclic oxyphosphoranes.[159] Although pentamethoxyphosphorane [160] has been postulated as a highly reactive species, pentaphenoxy [161] and pentaethoxyphosphorane [162] are well established.

The latter compound decomposes slowly at room temperature in accordance with the following equation.

$$(C_2H_5O)_5P \longrightarrow (C_2H_5O)_3PO + C_2H_5OH + (C_2H_5)_2O$$

Either a trigonal bipyramidal or square pyramidal structure appears possible for tetrakisphenoxysulphur. By analogy with sulphur tetrafluoride and pentaphenoxyphosphorane, both of which have trigonal bipyramidal structures [163], it is suggested that $(PhO)_4S$ could also adopt this structure. However, the possibility of a square pyramidal structure cannot altogether be eliminated and might be the sterically preferred geometry. Furthermore, such a structure could explain the absence of two phenoxy group environments in the proton n.m.r.

of $(PhO)_4S$, without invoking intramolecular exchange.

It is concluded that at present, the available evidence does not allow an unequivocal decision to be made between trigonal bipyramid and square pyramid structures for $(PhO)_4S$, and a crystallographic study is required before the arrangement of the oxygen atoms around the sulphur is known with any certainty.

Bonding and n.m.r. correlations in $(PhO)_xSF_{4-x}$ compounds. (x = 1, 2 or 3)

In the previous section, it was assumed that in aryloxy derivatives of sulphur tetrafluoride, the phenoxy groups were substituted into the equatorial plane of a trigonal bipyramid. A consideration of the bonding in sulphur tetrafluoride tends to support this assumption.

The structure of sulphur tetrafluoride is trigonal bipyramidal and the bonding is based on sp^3d hybridisation of the sulphur atom, with the lone pair of electrons occupying an equatorial position. It has been suggested [24] that the three equatorial bonds are sp^2 in character, while the axial bonds consist of p and d orbitals. It is thus reasonable to assume that alkoxy or aryloxy groups would achieve better overlap with the sp^2 hybrid orbitals in the equatorial plane. Alternatively, better overlap of electronegative groups would be found with the pd hybrid orbitals. Thus, like fluorophosphoranes [89], the preferred structure for substituted derivatives of sulphur tetrafluoride is one which maximises the number of very electronegative fluorine atoms in axial positions in the trigonal bipyramid.

These statements follow Bent's rules [164], saying that atomic p character concentrates in those orbitals directed towards electronegative substituents and atomic s character in those directed towards electropositive groups. Furthermore, electronegative substituents prefer orbitals with large p character and electropositive substituents those with large s character. The result is that, for a number of possible isomers in the $(PhO)_xSF_{4-x}$ compounds, $(x = 1, 2 \text{ or } 3)$, the one with the largest number of axial fluorines is the most stable.

The available n.m.r. data on the aryloxysulphur fluorides (Table 12) are in complete agreement with equatorial substitution of the phenoxy groups.

TABLE 12

Compound	$\delta_{F\ axial}^{(a)}$	$\delta_{F\ equatorial}^{(a)}$	J_{F-F} c/s	δ_H(b)
$PhOSF_3$	-79·1(d)	-30·5(d)	67·7	-6·55(b.m.)
$(PhO)_2SF_2$	-67·4(b.s.)			-6·42(b.m.)
$(PhO)_3SF$	-70·8(b.s.)			

(a) ^{19}F chemical shifts (p.p.m.) from external CCl_3F.

(b) ^{1}H chemical shift (p.p.m.) from external $(CH_3)_4Si$

(b.s.) broad singlet; (b.m.) broad multiplet.

As expected, the protons become less shielded as the number of electronegative fluorine atoms increase and consequently occur at lower fields.

Fluorine chemical shifts have been ascribed to changes in the paramagnetic contribution to the local nuclear screening.[77] The contribution which results in a shift to low fields should be zero for the spherically symmetrical fluoride ion and should increase as the ionic character of the bond to fluorine decreases. Satisfactory agreement with the theory has been observed for the ^{19}F chemical shifts in binary fluorides.[165]

With aryloxysulphur fluoride derivatives, the fluorine chemical shift decreases with decreasing electronegativity of the group bonded to the fluorine atom. Although this trend appears to be at variance with the above theory, other factors besides the electronegativity of the substituents can influence the shielding of the fluorine nuclei.

Partial double bonded species involving π bonding have been suggested to explain the shielding of a fluorine atom in a manner opposite to that expected on normal electronegativity grounds in saturated halofluorocarbons, CCl_xF_{4-x} [166], alkylfluorosilanes [167], and halofluorophosphorus derivatives, PCl_xF_{5-x}.[168] In the latter series, in order to achieve agreement with the theory, it was further assumed that the π contribution increases as the number of fluorine atoms decrease, and that π bonding is greater for axial than for equatorial atoms.[168] Other workers, however, postulated that equatorial bonds are stronger than axial and involve more π bonding.[169]

Alternatively, steric factors, quite unrelated to the electronegativity of the substituents, are of considerable importance in determining trends in ^{19}F chemical shifts.[170] Steric interactions with neighbouring atoms can produce a net displacement of electrons from the fluorine atom, and may play some part in explaining the anomalous chemical shifts in the aryloxy derivatives of sulphur tetrafluoride.

Thus it appears that any conclusions, regarding the ^{19}F chemical shifts in the above compounds, must be drawn with caution since, at the moment, the extent and nature of the fluorine π bonding is somewhat speculative, which, when coupled with the natural tendency to oversimplify the theory of fluorine chemical shifts, leads to a complex problem.

D. Reaction of sulphur tetrafluoride with dimethylsulphoxide (DMSO).

In a recent publication, the reaction of IF_5 with (DMSO) was reported to produce $CH_2FS(O)H$, as the major volatile product.[171] Characterisation of the product was made on the basis of n.m.r., infra-red and low resolution mass spectrometry (Table 13).

TABLE 13

REACTION IF_5 + (DMSO) **PRODUCT** $CH_2FS(O)H$

MASS SPECTRUM	m/e	Ion
	82	$CH_2FS(O)H$
	81	$CH_2FS(O)$
	33	CH_2F

INFRA-RED (cm^{-1})		
3015(m),	2940(m)	C-H
	2810(w)	S-H
	1410(m)	CH_2
	1265(m)	HCF
	1185(s)	S=O
	1050-1100(m.br.)	S-H
	1005(v.s.)	C-F

N.M.R.

δ_H = -5·24p.p.m.(d); -1·99p.p.m.(s).

δ_F = +155·6p.p.m.(t).

J_{H-F} = 55 c/s.

A compound, with similar properties to the alleged $CH_2FS(O)H$, is produced from the room temperature reaction of SF_4 with (DMSO). The compound is a volatile, colourless liquid which attacks glass and deposits white solids on fractionation. It has not been possible to obtain analytical or molecular weight data on this unstable liquid, but for the following reasons, the compound is believed to be bis(fluoromethyl)ether, CH_2FOCH_2F.

(1) Ethers partially fluorinated at the α-carbon atom are known to decompose readily [172] and are sensitive to hydrolysis [173], except when they are protected by a polyfluorinated group such as CH_2F or CF_3 in the β position. Furthermore, CH_2FOCH_2F has been shown to decompose on standing at 4°C.[32]

(2) High resolution mass spectrometry showed that the compound did not contain sulphur. The ions observed are all plausible decomposition products of CH_2FOCH_2F. The relative intensities of the ions are given in brackets (Table 14).

(3) The proton and fluorine n.m.r. spectra are characteristic of the X_2X_2' and AA' parts of an $AA'X_2X_2'$ spin system [174]; the ^1H and ^{19}F chemical shifts are $-5{\cdot}31$ p.p.m. from $(CH_3)_4Si$, and $+158{\cdot}7$ p.p.m from CCl_3F (Table 14). The n.m.r. further indicated that the molecule is symmetrical and $J_{H-F} = 55$ c/s has the value expected for CH_2FOCH_2F by analogy with other hydrofluoro carbon derivatives.[77] The singlet observed in the ^1H spectrum of $CH_2FS(O)H$ at $-1{\cdot}99$ p.p.m., assigned to S-H, seems to be a spurious peak and is

thought to be due to impurity arising from Me_2S (δ_H = -2·00 p.p.m.).[175] This impurity could be removed by slow distillation of the crude mixture from a -60°C cold bath.

(4) The gas infra-red spectrum showed peaks characteristic of the CH_2F group.[176] The peaks at 1181 and 1050-1100 cm^{-1} may best be assigned to the C-O-C stretching modes in ethers.[177]

(5) Bis(fluoromethyl)ether was subsequently prepared from the high temperature reaction of SF_4 with sym-trioxan. A comparison of the spectroscopic properties of the products obtained from the reaction of IF_5 and SF_4 with (DMSO) agrees with the belief that the major product from both these reactions is CH_2FOCH_2F, and not $CH_2FS(O)H$ (Tables 13 and 14).

Other products indentified from the reaction of SF_4 with (DMSO) were SOF_2, SO_2, CH_2F_2 and SiF_4. Traces of involatile liquids were also present, but were not characterised.

The formation of CH_2FOCH_2F is unexpected, but may be explained by analogy with the reactions of (DMSO) with BCl_3, $SiCl_4$ [178] and $Nb(Ta)X_5$, (X = Cl, Br) [152], in which oxygen abstraction occurs to give an oxyhalide complex, or oxide and Me_2SX_2.

^{19}F N.M.R. SPECTRUM OF CH_2FOCH_2F.

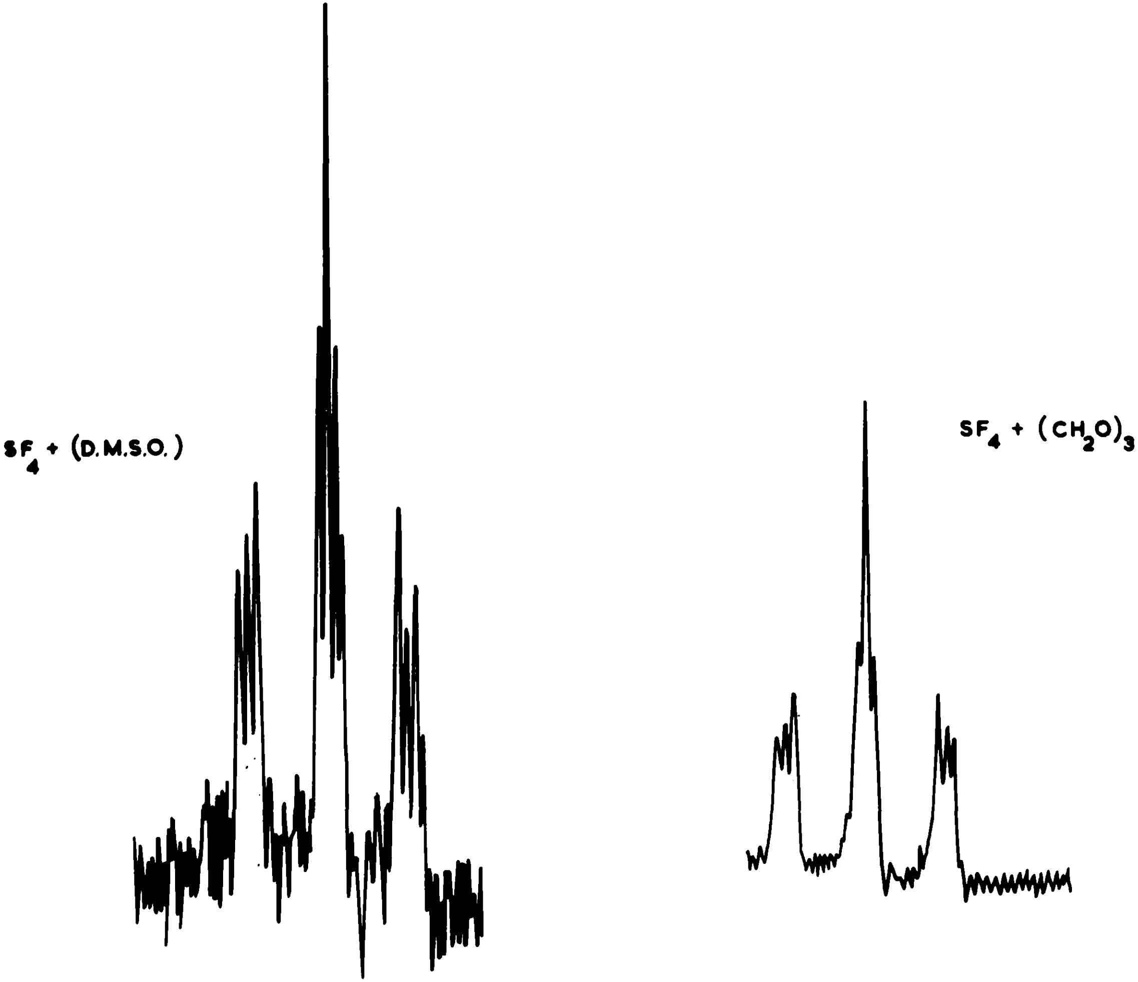


TABLE 14

REACTION	SF_4 + (DMSO)	$SF_4 + (CH_2O)_3$
PRODUCT	CH_2FOCH_2F	CH_2FOCH_2F

MASS SPECTRUM

m/e	Ion	Found Mass	Calc.Mass	m/e	Ion	Found Mass	Calc.Mass
82(6)	$CH_2FO^{13}CHF$	82·01909	82·01855	82	$CH_2FO^{13}CHF$	82·01944	82·01855
81(53)	$C_2H_3F_2O$	81·01472	81·01518	81	CH_2FOCHF	81·01580	81·01518
63(29)	C_2H_4OF	63·02446	63·02460				
33(100)	CH_2F	33·01398	33·01405				

N.M.R.	δ_H = −5·31p.p.m.(d); δ_F = +158·7p.p.m.(t). J_{H-F} = 55 c/s	δ_H = −5·18p.p.m.(d); δ_F = +159·2p.p.m.(t) J_{H-F} = 55 c/s
INFRA-RED (cm^{-1})	3012(m), 2942(m), C–H stretch; 1438(w), CH_2 bend; 1265(m), HCF bend; 1181(s), 1050–1100(m.br.), C–O–C stretch; 1005(v.s.), C–F stretch.	3012(m), 2942(m), C–H stretch; 1415(w), CH_2 bend; 1268(m), HCF bend; 1184(s), 1050–1100(m.br.), C–O–C stretch; 1005(v.s.), C–F stretch.

In (DMSO) the sulphur-oxygen linkage is considerably weakened by the presence of the methyl groups.[179] It is therefore suggested that the reaction with SF_4 involves fluorination of the S=O group to produce Me_2SF_2 and SOF_2.

$$SF_4 + Me_2SO \longrightarrow Me_2SF_2 + SOF_2$$

Although Me_2SeF_2 is a stable molecule [153], the corresponding sulphur analogue Me_2SF_2 is regarded as being extremely unstable.[180] Me_2SBr_2 can be isolated, but Me_2SCl_2 decomposes to give CH_2ClSCH_3 and HCl. Presumably Me_2SF_2 decomposes by a similar process.

$$Me_2SF_2 \longrightarrow CH_2FSCH_3 + HF$$

α Fluorosulphides readily decompose at room temperature [181] and CH_2FOCH_2F could result either from attack on the glass, or from a further complex reaction with (DMSO).

$$CH_2FSCH_3 \xrightarrow{SiO_2} CH_2FOCH_2F + SiF_4 + SO_2 + (CH_3)_2S$$

$$CH_2FSCH_3 \xrightarrow{(DMSO)} CH_2FOCH_2F$$

Such a mechanism appears to be possible, since high resolution mass spectrometry confirmed the presence of CH_2FSCH_3 as a minor product from this complex reaction.

Found for m/e = 80, 80·00953; calculated for $CH_2FSCH_3^+$, m/e = 80·00960. Found for m/e = 65, 64·98675; calculated for CH_2FS^+, m/e = 64·98612

REAGENTS

Commercial sulphur tetrafluoride from Peninsular Chemical Co., was purified by passing the gas through dry sodium fluoride. Sulphur tetrafluoride treated in this manner was practically free from the major hydrolysis impurity, thionyl fluoride ($<5\%$), as shown by infra-red spectroscopy [23].

$(MeO)_2SO$, $(EtO)_2SO$ and $(MeO)_2SO_2$ were obtained from Aldrich Chemical Co., and $Me_2Si(OMe)_2$ and $MeSi(OMe)_3$ from Alfa Inorganics Inc. The remaining starting materials were prepared by well documentated methods and were stored under vacuum over 4A molecular sieves until required.

Compound	Method	Reference
$(PhO)_2SO$	$SOCl_2/PhOH$	[182]
Me_3SiOMe	$Me_3SiCl/MeOH$	[183]
Me_3SiOPh	$Me_3SiCl/PhOH$	[184]
Me_3SiNMe_2	Me_3SiCl/Me_2NH	[107]
Me_3SiNEt_2	Me_3SiCl/Et_2NH	[185]

A. Reaction of sulphur tetrafluoride with sulphites and sulphates.

Generally, the least volatile component was distilled into a large thick walled Carius tube, fitted with a high pressure Teflon stopcock. In the case of involatile liquids e.g. $(PhO)_2SO$, the liquid was poured into the reaction vessel in a dry box, and sufficient SF_4 added to give a slight excess for a 1:1 stoichiometry. After reaching room temperature, the reaction vessel was removed from the vacuum line and heated at the desired temperature in an oil bath.

1. Dimethyl sulphite.

(23·7 m.m.) of SF_4 and (2·2 g.; 20·3 m.m.) of $(MeO)_2SO$ were heated at 140°C for 12 hours. Fractionation of the crude mixture at room temperature through traps held at -110, -130 and -196°C, collected unreacted SF_4 [23] and SOF_2 [16], both identified by infra-red at -130°C, and MeF [114] and traces of SiF_4, again identified by infra-red in the latter bath. Pure METHYL FLUOROSULPHITE, MeOS(O)F, was collected at -110°C in 94% yield (1·83 g.).

Anal. For $CH_3OS(O)F$.

Found: C, 11·96: H, 3·00: F, 19·14: S, 32·75: O, (by difference) 33·15.

Calc: C, 12·24: H, 3·08: F, 19·37: S, 32·69: O, 32·62.

Mol. Wt. Found: M.W. 98 (mass spec.). Calc: M.W. 98.

Infra-red (cm^{-1}). 2960(m): 1460(w): 1268, P.Q.R.(s): 985, P.Q.R.(v.s.): 752(s): 700(v.s.).

N.M.R. $\delta_F = -55{\cdot}6(q)$: $\delta_{CH_3} = -3{\cdot}85(d)$: $J_{H-F} = 1{\cdot}3c/s$.

2. Diethyl sulphite.

(4·5 m.m.) of SF_4 and (0·5 g.; 3·9 m.m.) of $(EtO)_2SO$ failed to react at room temperature. The reactants were recondensed and heated at 120°C for 8 hours; a visible reaction occurred at 100°C. Passage of the volatiles through -100 and -196°C baths separated EtF [114] and SOF_2 [16], identified by their characteristic infra-red spectra, from pure ETHYL FLUOROSULPHITE, EtOS(O)F, collected in the -100°C trap.

Mol. Wt. Found: M.W. 111 (vapour density).

Calc: M.W. 112.

Infra-red (cm^{-1}). 2985(m): 1450(w): 1267, P.Q.R.(s): 1028(v.s.): 917(s): 735(sh.): 699(s).

N.M.R. $\delta_F = -59{\cdot}8(t)$: $\delta_{CH_3} = -1{\cdot}35(t)$:
$\delta_{CH_2} = -4{\cdot}35$ (complex): $J_{H-F} = 1{\cdot}3$ c/s.

3. Diphenyl sulphite.

(7 m.m.) of SF_4 and (1·5 g.; 6·5 m.m.) of $(PhO)_2SO$ were heated together at 80°C for 12 hours in a 75 ml. Hoke pressure vessel. Room temperature fractionation produced SOF_2 and PHENYL FLUOROSULPHITE, PhOS(O)F. Phenyl fluorosulphite could be distilled slowly from the reaction vessel at room temperature, and was identified by infra-red [149] and n.m.r. [149]. The reaction vessel contained a purple solid which was insoluble in water and acetonitrile, and was not investigated further.

COMPOUND. $\delta_F = -62{\cdot}3(s)$: $\delta_H = -6{\cdot}88$ (multiplet)

PhOS(O)F. $\delta_F = -62{\cdot}5$(s): $\delta_H = -6{\cdot}9$ (multiplet).

4. Dimethyl sulphate.

(16·5 m.m.) of SF_4 and (1·56 g.; 12·3 m.m.) of $(MeO)_2SO_2$ were heated at 120°C for 24 hours in a sealed tube. Fractionation collected MeF, SOF_2 and excess SF_4 at -196°C, all identified by infra-red, and METHYL FLUOROSULPHATE, $MeOSO_2F$, collected at -95°C in approximately 40% yield.

Mol. Wt. Found: M.W. 113·97811 (mass spec.).
Calc: M.W. 113·97869.

Infra-red (cm^{-1}). 2970(w): 1468(s): 1236(s):
1020(v.s.): 837(s): 785(m).

N.M.R. COMPOUND: $\delta_F = -30{\cdot}3$(s): $\delta_H = -3{\cdot}86$(s)
[138] CH_3OSO_2F: $\delta_F = -31{\cdot}2$(s): $\delta_H = -4{\cdot}12$(s).

B. Reactions of alkyl fluorosulphites.

5. N, N - diethyltrimethylsilylamine.

A 1:1 mole ratio of MeOS(O)F and Me_3SiNEt_2 reacted at room temperature, producing Me_3SiF (1 mole), identified by infra-red [111] and M. W. (Found: M.W. 93. Calc: M.W. 92), and a colourless involatile liquid, identified as METHOXY DIETHYL SULPHINAMIDE, $MeOS(O)NEt_2$.

Anal. For $CH_3OS(O)N(C_2H_5)_2$.
Found: C, 39·58: H, 8·54: N, 9·32: S, 20·96:
O, (by difference) 21·60.
Calc: C, 39·73: H, 8·60: N, 9·27: S, 21·17: O, 21·23.

N.M.R. $\delta_{CH_3O} = -3\cdot39$(s): $\delta_{CH_3} = -1\cdot10$(t):
$\delta_{CH_2} = -3\cdot16$ (complex): $J_{CH_3-CH_2} = 7$ c/s.

6. N, N - dimethyltrimethylsilylamine

(13·5 m.m.) of EtOS(O)F and (13·5 m.m.) of Me_3SiNMe_2 reacted on warming to room temperature. Fractionation of the volatiles at room temperature separated Me_3SiF and a colourless involatile liquid, identified as ETHOXY DIMETHYL SULPHINAMIDE, $EtOS(O)NMe_2$.

Mol. Wt. Found: M.W. 137 (mass spec.).
Calc: M.W. 137.

N.M.R. $\delta_{CH_3} = -1\cdot81$(t): $\delta_{CH_2} = -3\cdot81$ (complex):
$\delta_{N(CH_3)_2} = -2\cdot57$(s): $J_{CH_3-CH_2} = 7$ c/s.

7. Diethylamine.

A 2:1 mole ratio of Et_2NH and MeOS(O)F was allowed to warm slowly to room temperature. Below room temperature, a vigorous reaction occurred with the formation of a white solid, Et_2NH_2F, and a colourless liquid identified as METHOXY DIETHYL SULPHINAMIDE, $MeOS(O)NEt_2$, by comparison with the n.m.r. of an analytically pure sample prepared as in reaction 5.

8. Benzene.

A 1:1 mole ratio of MeOS(O)F and C_6H_6 was left at room temperature for 3 days. The n.m.r. [175] and liquid film infra-red [186] of the least volatile fraction were consistent with the formation of $MeOS(O)C_6H_5$. The most volatile fraction consisted of SiF_4 and traces of SO_2.

COMPOUND. $\delta_{C_6H_5} = -7\cdot21(s)$: $\delta_{CH_3O} = -3\cdot30(s)$

[175] $CH_3OS(O)C_6H_5$. $\delta_{C_6H_5}$ = —— : $\delta_{CH_3O} = -3\cdot25(s)$.

9. Trimethyl phosphite.

A mixture of MeOS(O)F and $(MeO)_3P$ did not react when left at room temperature for 3 hours. Fractionation produced essentially unreacted starting materials.

C. Reactions of sulphur tetrafluoride with silicon-oxygen compounds.

General procedure.

A weighed quantity of the Si-O reagent was condensed into a 100 ml. glass reaction flask, to which a n.m.r. tube had been attached. SF_4 was then added and the mixture allowed to warm freely into the vacuum line. A visible reaction occurred in all cases. The contents of the flask were refrozen and again allowed to warm up. This operation was repeated several times to ensure complete mixing of the reactants. After removal of the most volatile materials at room temperature, the involatile products were then distilled or, in some cases, tipped into the n.m.r. tube.

10. Methoxytrimethylsilane.

(4·2 m.m.) of SF_4 and (0·42 g.; 4·0 m.m.) of Me_3SiOMe reacted on warming to room temperature.

Fractionation produced Me_3SiF, SOF_2 and MeF, all identified by infra-red spectroscopy.

11. Dimethoxydimethylsilane.

(11·0 m.m.) of SF_4 and (1·01 g.; 8·4 m.m.) of $Me_2Si(OMe)_2$ reacted vigorously on warming to room temperature. Passage of the volatiles through -50, -100 and -196°C baths, collected SOF_2, SF_4 and MeF in the latter, all identified by infra-red spectroscopy; Me_2SiF_2 in the -100°C trap, identified by infra-red [187] and n.m.r. [188] in 92% yield, and $(MeO)_2SO$ identified by comparison with the infra-red and n.m.r. spectra of an authentic sample, in the -50°C bath. Traces of a white viscous solid were left in the reaction vessel and small quantities of Me_2O [114] were collected in the -196° trap.

12. Trismethoxymethylsilane.

(2·7 m.m.) of SF_4 and (0·36 g.; 2·7 m.m.) of $MeSi(OMe)_3$ reacted on warming to room temperature, producing MeF (trace), $MeSiF_3$, identified by infra-red [189] and M.W. (Found: M.W. 100. Calc: M.W. 100), SOF_2, Me_2O and $(MeO)_2SO$, all identified by their characteristic infra-red spectra.

13. Phenoxytrimethylsilane.

(13 m.m.) of SF_4 and (1·8 g.; 11 m.m.) of Me_3SiOPh were allowed to mix at room temperature. Fractionation of the volatiles through traps held at

-100 and -196°C, yielded excess SF_4 in the latter and Me_3SiF (9·4 m.m., 85% yield; Found: M.W. 91. Calc: M.W. 92) in the -100°C cold bath. After removal of the volatiles at room temperature, a warm water bath was placed around the reaction vessel to ensure complete removal of any unreacted Me_3SiOPh. A colourless involatile liquid, melting point ~20°C, identified as PHENOXYSULPHUR TRIFLUORIDE, $PhOSF_3$, remained in the reaction flask.

Anal. For $C_6H_5OSF_3$.

Found: C, 40·09: H, 3·03: F, 29·51: S, 16·59.

Calc: C, 39·56: H, 2·75: F, 31·32: S, 17·58.

Infra-red (cm^{-1}). Liquid film.

3070(m); 1585(s); 1482(v.s.); 1458(m); 1230(w); 1170(s); 1140(s); 1105(m); 1065(m); 1018(m); 905(s); 845(b.s.); 820(sh); 770(s); 740(w); 720(sh); 680(s); 642(m).

N.M.R. δ_{SF_2} = -79·1(d): δ_{SF} = -30·5(t):
δ_{Fa-Fe} = 48·6: J_{F-F} = 67·7 c/s:
δ_H = -6·55 (multiplet).

Hydrolysis of $PhOSF_3$.

$PhOSF_3$ is indefinitely stable in dry glass, but, in the presence of moisture, the colourless liquid becomes pinkish and PHENYL FLUOROSULPHITE, PhOS(O)F, is produced. After only minutes, the infra-red spectrum revealed the presence of a band at 1260 cm^{-1} due to PhOS(O)F; and a n.m.r. sample, when exposed to the air, showed a singlet at -62·8 p.p.m. with respect to external CCl_3F, characteristic of PhOS(O)F.

14. A 2:1 excess of phenoxytrimethylsilane.

(5·0 m.m.) of SF_4 and (1·78 g.; 10·7 m.m.) of Me_3SiOPh were allowed to warm freely to room temperature. Fractionation produced Me_3SiF (9·9 m.m., 93% yield) identified by infra-red [111], and an involatile colourless liquid, melting point ~25°C, identified as BISPHENOXYSULPHUR DIFLUORIDE, $(PhO)_2SF_2$.

Anal. For $(C_6H_5O)_2SF_2$.

Found: C, 56·09: H, 4·05: F, 14·68: S, 12·34.

Calc: C, 56·21: H, 3·90: F, 14·84: S, 12·50.

N.M.R. $\delta_F = -67{\cdot}4$ (b.s.): $\delta_H = -6{\cdot}42$ (broad multiplet).

15. A 3:1 excess of phenoxytrimethylsilane.

(2·7 m.m.) of SF_4 and (1·35 g.; 8·1 m.m.) of Me_3SiOPh were condensed together at -196°C. Reaction occurred below room temperature as shown by effervescence. The reaction vessel was left at room temperature for 15 minutes, then the volatiles were recondensed and, on warming up, a white solid precipitated out. The volatiles were removed at room temperature, and traces of involatile liquid removed from the solid, while pumping. The volatile material consisted of ~3 moles of

Me_3SiF, 96% yield, identified by infra-red [111] and M.W. The white solid was insoluble in C_6F_6, slightly soluble in CH_3CN and very soluble in DMSO. This solid has been identified as TETRAKISPHENOXYSULPHUR, $(PhO)_4S$.

Anal.

Found: C, 71·44: H, 5·07: S, 7·86: O, (by difference) 15·63

C, 71·33: H, 5·11: S, 7·77: O, (by difference) 15·79.

Calc: C, 71·25: H, 4·95: S, 7·92: O, (by difference) 15·88.

Mol. Wt. (Osmometry in (DMSO)).

Found: 83.

Calc: 404. Calc. (for complete dissociation) 81.

Infra-red (cm^{-1}) in Nujol.

2960(s): 2930(v.s.): 2860(s): 1593(s): 1580(m): 1487(v.s.): 1232(s): 1198(s): 1173(m): 1160(m): 1148(s): 1070(m): 1020(m): 905(m): 875(s): 848(s): 835(s): 820(s): 775(s): 764(s): 761(s): 694(s): 683(s): 601(s).

N.M.R. (Dilute solution in CD_3CN).

$\delta_H = -6{\cdot}82$ (complex).

Hydrolysis of $(PhO)_4S$.

A sample of $(PhO)_4S$ was exposed to the atmosphere and the mass spectrum recorded. The spectrum consisted of $(PhO)_2SO$ (m/e found 234, $C_{12}H_{10}SO_3$ requires m/e 234) and PhOH (m/e found 94, C_6H_6O requires m/e 94).

16. A 2·5:1 excess of phenoxytrimethylsilane.

(2·3 m.m.) of SF_4 and (0·9287 g.; 5·6 m.m.) of Me_3SiOPh were allowed to react at room temperature. Fractionation produced Me_3SiF (5·2 m.m., 92% yield) identified by infra-red spectroscopy. The reaction vessel contained a solid-liquid mixture. The ^{19}F n.m.r. spectrum of the mixture showed two singlets, one at -67·4 p.p.m. assigned to BISPHENOXYSULPHUR DIFLUORIDE, $(PhO)_2SF_2$, by comparison with the n.m.r. sample obtained from reaction 14, and another singlet at -70·8 p.p.m. assigned to TRISPHENOXYSULPHUR FLUORIDE, $(PhO)_3SF$. The yields, estimated from n.m.r., were 70% $(PhO)_3SF$ and 30% $(PhO)_2SF_2$.

D. Reaction of sulphur tetrafluoride with sulphoxides.

17. Dimethyl sulphoxide.

(14 m.m.) of SF_4 and (2 mls.; 28·2 m.m.) of Me_2SO, B.D.H. spectroscopic grade, dried over CaH_2, were condensed together in a large Carius tube, fitted with a high pressure Teflon stopcock. The reaction vessel was allowed to warm to -50°C, then left to warm slowly to room temperature overnight. Fractionation through traps cooled to -90°C and -196°C, collected SiF_4, SOF_2,

SO_2 [114] and CH_2F_2 [176] in the latter trap, all identified by infra-red spectroscopy. The -90°C bath contained traces of SO_2 and a colourless volatile liquid, identified as BIS(FLUOROMETHYL) ETHER, CH_2FOCH_2F. SO_2 could be removed from the ether by pumping on the mixture at -90°C, and the ether could be separated from less volatile material by slow distillation from a -60°C bath. The less volatile material consisted of unreacted dimethyl sulphoxide.

CHARACTERISATION OF CH_2FOCH_2F.

Mass spectrum.

The low resolution mass spectrum contained the following, given as mass number, probable molecular ion assignment and relative abundance.

82, $CH_2FO^{13}CHF$, 6: 81, $C_2H_3F_2O$, 53: 63, C_2H_4OF, 29: 33, CH_2F, 100.

High resolution mass measurements identified for CH_2FOCH_2F.

m/e	Ion	Found Mass	Calc. Mass
82	$CH_2FO^{13}CHF$	82·01909	82·01855
81	$C_2H_3F_2O$	81·01472	81·01518
63	C_2H_4OF	63·02446	63·02460
33	CH_2F	33·01398	33·01405

N.M.R. $\delta_F = +158\cdot7$ (basic triplet):
$\delta_H = -5\cdot31$ (basic doublet): $J_{H-F} = 55$ c/s.

Infra-red (cm^{-1}). 3012(m): 2942(m): 1438(w): 1265(m):

1181(s): 1050-1100(m.br.): 1005(v.s.).

When a 1:1 mole ratio of reactants was allowed to warm freely to room temperature, without external cooling, an exothermic reaction occurred. In addition to the above products, involatile viscous liquids were produced which contained CH_2F and CF_2H groups, as shown by n.m.r.

18. Preparation of bis(fluoromethyl)ether from the reaction of sulphur tetrafluoride with sym-trioxan.

(18 m.m.) of SF_4 and (1·5 g.; 17 m.m.) of $(CH_2O)_3$ from B.D.H. were heated together at 140°C for 12 hours in a 75 ml. Hoke pressure vessel. Fractionation produced SiF_4, SOF_2, SO_2 and CH_2F_2 as the most volatile products. The least volatile material, trapped at -95°C, was BIS(FLUOROMETHYL)ETHER, CH_2FOCH_2F.

Mass spectrum.

m/e	Ion	Found Mass	Calc. Mass
82	$CH_2FO^{13}CHF$	82·01944	82·01855
81	CH_2FOCHF	81·01580	81·01519

N.M.R. δ_F = +159·2 (basic triplet):

δ_H = -5·18 (basic doublet): J_{H-F} = 55 c/s.

Infra-red (cm^{-1}). 3012(m): 2942(m): 1415(w): 1268(m): 1184(s): 1100-1050(m.br.): 1005(v.s.).

CHAPTER III

REACTIONS OF SULPHUR TETRAFLUORIDE WITH PHOSPHORUS COMPOUNDS

INTRODUCTION

Although methods of preparing fluorophosphoranes have been extensively investigated in recent years [190], only brief and indirect mention has been made regarding the synthetic uses of sulphur tetrafluoride in these preparations.

With phosphines, sulphur tetrafluoride acts as an oxidative fluorinating agent and can replace the oxygen in phosphoryl compounds with fluorine.[191]

$$2R_3P + SF_4 \longrightarrow 2R_3PF_2 + S$$

$$R_3PO + SF_4 \longrightarrow R_3PF_2 + SOF_2$$

Although it has been considered that the fluorination of the P = 0 group by sulphur tetrafluoride is a general reaction [190], only aromatic phosphorus compounds have been studied in any detail.[191] Usually, high temperatures are required to cause complete reaction, but Mahler [192] has observed that much milder conditions are needed for aliphatic compounds.

The lack of suitable methods for the preparation of alkoxy- and alkylthio- difluorophosphoranes (($(MeO)_3PF_2$ and $(BuS)_3PF_2$ have been isolated as by-products from the reaction of difluorodiazirine with the corresponding phosphites, but characterisation was solely on the basis of n.m.r. evidence [193]) suggested the possible extension of the above reaction methods to include phosphites, phosphates etc. Furthermore, an opportunity to study the scope and generality of these reactions was presented.

SUMMARY OF REACTIONS.

A. Reactions of sulphur tetrafluoride with P(III) compounds.

1. $SF_4 + (Me_2N)_3P \longrightarrow (Me_2N)_3PF_2 + (Me_2N)_2PF_3$ (trace) + $(Me_2N)_3PS$.

2. $SF_4 + (MeO)_3P \longrightarrow (MeO)_3PF_2 + (MeO)_2P(O)F$ + traces of MeOP(O)FMe, Me_2O and MeF.

3. $SF_4 + (MeS)_3P \longrightarrow MeSP(S)F_2 + PSF_3 +$ $Me_2P(S)F$ (trace) + $Me_2S_x + SiF_4$.

4. $SF_4 + (MeO)_2POH \longrightarrow MeOPF_2 + (MeO)_3PF_2 + PF_3 + Me_2O + SOF_2 + SiF_4$ + traces of $HP(O)F_2$, $(MeO)_2P(O)F$ and POF_3.

B. Reactions of sulphur tetrafluoride with P(V) compounds.

5. $SF_4 + (Me_2N)_3PO \longrightarrow$ solids + unreacted starting materials.

6. $SF_4 + (Me_2N)_2P(O)Me \longrightarrow MeP(O)F_2 + Me_2NSF_3$ (trace).

7. $SF_4 + (MeO)_3PO \longrightarrow (MeO)_2P(O)F + MeOP(O)F_2 + Me_2O + SOF_2 + (MeO)_2SO$.

8. $SF_4 + (MeO)_2P(O)Me \longrightarrow MeOP(O)FMe + MeP(O)F_2 + Me_2O + SOF_2 + (MeO)_2SO$.

In all reactions solid products were produced.

A. Reactions of sulphur tetrafluoride with P(III) compounds.

There was no evidence for exchange reactions between sulphur tetrafluoride and trivalent phosphorus derivatives, L_3P, ($L = Me_2N$, MeO or MeS) c.f. the reactions between phosphorus pentafluoride and phosphites or aminophosphines [139, 194] where exchange does occur. The products obtained from the SF_4 reactions involve an oxidative fluorination mechanism yielding fluorophosphoranes and sulphur containing solids. The reduced sulphur species is believed to contain the thiophosphoryl unit.

The general reaction could be considered as occurring in three distinct stages.

$$SF_4 + L_3P \longrightarrow L_3PF_2 + SF_2 \qquad (1)$$

$$2SF_2 \longrightarrow SF_4 + S \qquad (2)$$

$$L_3P + S \longrightarrow L_3P = S \qquad (3)$$

The first stage is visualised as the oxidation-reduction step producing the fluorophosphorane and sulphur difluoride (1). Sulphur difluoride, however, is an extremely unstable compound and undergoes disproportionation to sulphur and sulphur tetrafluoride (2).[15] The high affinity of trivalent phosphorus derivatives for free or bound sulphur [195] makes the formation of P = S compounds highly probable (3). Obviously this general reaction scheme has to be slightly modified to compensate for the possibility of side reactions e.g. Arbuzov re-arrangements, the formation of thermally unstable fluorophosphoranes or exchange reactions between P(V) species and SF_4.

Tris(dimethylamino)phosphine.

The room temperature reaction between SF_4 and $(Me_2N)_3P$ produced high yields of tris(dimethylamino)-difluorophosphorane, $(Me_2N)_3PF_2$, and mixtures of yellow solids which contained predominately tris-(dimethylamino)phosphine sulphide, $(Me_2N)_3PS$. In addition, small quantities of the trifluorophosphorane, $(Me_2N)_2PF_3$, were isolated and possibly resulted by an exchange reaction between SF_4 and $(Me_2N)_3PF_2$.

Trimethyl phosphite.

Tris(methoxy)difluorophosphorane, $(MeO)_3PF_2$, could be produced from the room temperature reaction of SF_4 with $(MeO)_3P$, but the yield of the compound depended very much on the reaction conditions.

When, for example, the reaction was controlled by external cooling, high yields of $(MeO)_3PF_2$ were isolated together with traces of dimethyl phosphorofluoridate, $(MeO)_2P(O)F$, methyl methylphosphonofluoridate, $MeOP(O)MeF$, Me_2O and MeF. Previous evidence has shown that alkoxyfluorophosphoranes are thermally unstable [140] and can readily loose alkyl fluoride, with the formation of phosphoryl compounds, and could account for the formation of $(MeO)_2P(O)F$. Low yields of $(MeO)_2P(O)F$ were also observed in the preparation of $(MeO)_3PF_2$ in the difluorodiazirine reaction.

$$(MeO)_3PF_2 \longrightarrow MeF + (MeO)_2P(O)F$$

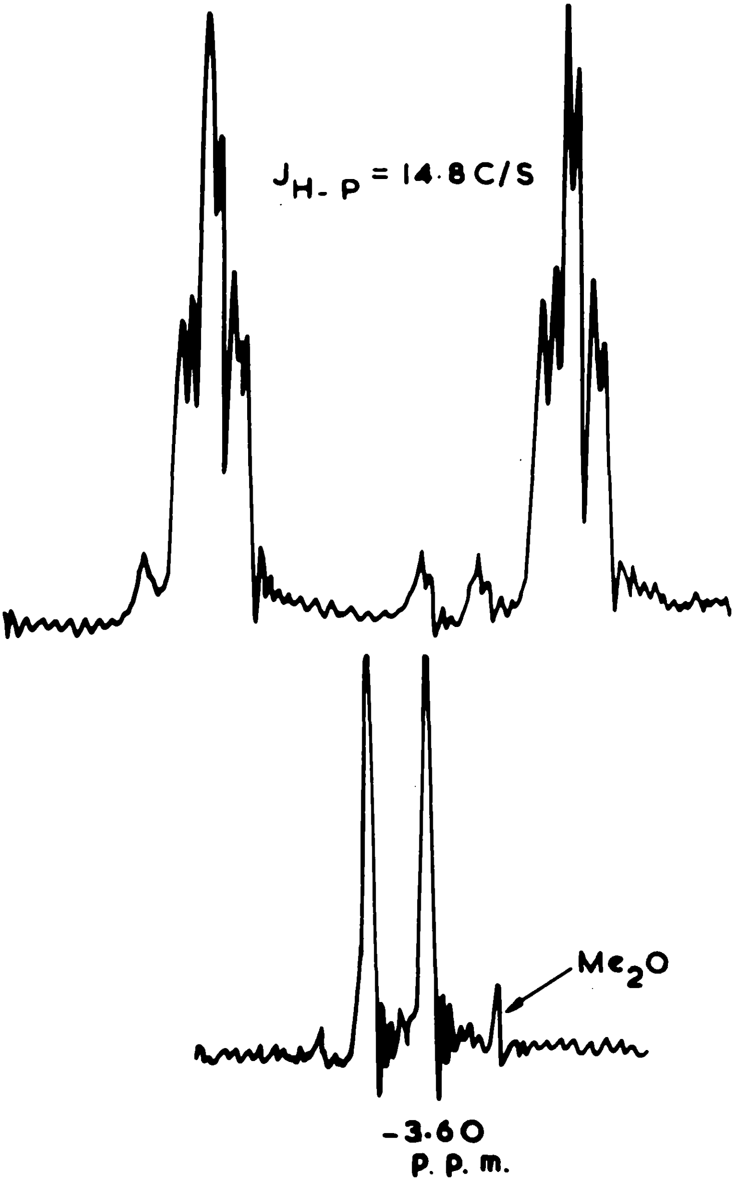
The small amount of $MeOP(O)FMe$ could result by an exchange reaction between SF_4 and $(MeO)_2P(O)Me$, the latter compound being formed by a Michaelis-Arbuzov rearrangement of $(MeO)_3P$. Extensive Arbuzov rearrangements have been observed in the reaction of PF_5 with $(MeO)_3P$.[139]

Only small quantities of $(MeO)_3PF_2$ were produced when the reactants were allowed to warm freely to room temperature. The major products from the reaction were Me_2O and an unidentified phosphorus fluorine compound. The observed n.m.r. parameters of this P-F species were not consistent with any known P-F compound.

$$\delta_F,\ 62{\cdot}9; \quad J_{P-F},\ 732; \quad \delta_H, -3{\cdot}60; \quad J_{H-P},\ 14{\cdot}8.$$

The proton spectrum is best regarded as an initial doublet, which, under high resolution, has the appearance

^{1}H N.M.R. SPECTRUM OF UNIDENTIFIED P–F PRODUCT FROM SF_4 / $(MeO)_3P$ REACTION.



of a symmetrical double doublet of triplets with additional fine structure. The fluorine spectrum consists of a broad doublet. The line spacings are irregular and the spectrum is probably not first order. The observed J_{P-F} is similar to that reported for P(V) fluorides [190], and δ H and J_{H-P} are characteristic of alkoxyphosphorus compounds. [196] The available n.m.r. data are consistent with a symmetrical molecule such as $(MeO)_2PF_2OPF_2(OMe)_2$, which would probably display a second order spectrum c.f. PF_2OPF_2. [197]

The isolation of Me_2O suggests that such a compound could arise by an intermolecular elimination of Me_2O from $(MeO)_3PF_2$.

$$2(MeO)_3PF_2 \longrightarrow Me_2O + (MeO)_2PF_2OPF_2(OMe)_2$$

Obviously, before any definite assignment can be made on this compound, the reaction should be re-investigated. If formed however, $(MeO)_2PF_2OPF_2(OMe)_2$ would represent the first of a new class of P-O-P derivative.

Trimethyl thiophosphite.

SF_4 and $(MeS)_3P$ reacted at room temperature in a complex manner accompanied by abundant solid formation. Many thiophosphoryl compounds were produced and SiF_4 was continually evolved from the products. Observed products were methylphosphorodifluorodithiolate, $MeSP(S)F_2$, dimethylthiophosphoryl fluoride, $Me_2P(S)F$, SPF_3 and a dialkyl polysulphide, Me_2S_x.

Although tris(alkylthio)difluorophosphoranes, $(RS)_3PF_2$ (R = Bu), have been prepared [193], the expected product $(MeS)_3PF_2$ was not observed in this reaction. However, by analogy with the aforementioned reactions of SF_4, it is reasonable to assume that the fluorophosphorane was formed initially but could decompose into the thermodynamically more favoured thiophosphoryl compounds, possibly by MeF or Me_2S elimination. $MeSPF_4$ has been isolated but is considered as being an unstable compound.[200,213]

$$(MeS)_3PF_2 \longrightarrow MeF + (MeS)_2P(S)F$$
$$(MeS)_3PF_2 \longrightarrow Me_2S + MeSP(S)F_2$$

In the reaction with SF_4 however, no MeF was isolated, but dialkyl polysulphides were produced.

SPF_3 could result from exchange reactions between SF_4 and $MeSP(S)F_2$ or $(MeS)_3PS$. The origin of trace quantities of $Me_2P(S)F$ is not clear but possibly involves a complex series of Arbuzov type re-arrangements. Alkylthio derivatives of sulphur tetrafluoride are unknown and under these experimental conditions are presumably unstable, perhaps forming highly reactive and hydrolytically unstable sulphur fluorides e.g. SSF_2 which could account for the formation of SiF_4 and the large amounts of solid products.

$\underline{(MeO)_2POH}$

Dimethyl hydrogen phosphite, $(MeO)_2POH$(I), exists in equilibrium with the more stable phosphonate species $(MeO)_2P(O)H$(II) and, in the room temperature reaction with SF_4, both tri- and penta- valent phosphorus compounds were isolated. The observed major products were methyl difluorophosphite, $MeOPF_2$, $(MeO)_3PF_2$, SOF_2 and SiF_4. Other products were Me_2O, PF_3 and traces of hydrophosphoryl difluoride, $HP(O)F_2$, $(MeO)_2P(O)F$, $P(O)F_3$ and solids. Only when the reaction was controlled, was there any evidence for P-H compounds.

A reaction scheme can be written in which it is considered that SF_4 reacts with both (I) and (II).

With alcohols, SF_4 replaces the OH group with a fluorine atom [32] so that the formation of dimethyl fluorophosphite, $(MeO)_2PF$ (1), is possibly the first stage in the reaction of SF_4 with (I).

$$SF_4 + (MeO)_2POH \longrightarrow (MeO)_2PF + SOF_2 + HF \qquad (1)$$

$(MeO)_2PF$ however, was not observed but had been previously considered to undergo disproportionation (2).[139]

$$2(MeO)_2PF \longrightarrow (MeO)_3P + MeOPF_2 \qquad (2)$$

$(MeO)_3PF_2$ can now be formulated as arising from a subsequent reaction between SF_4 and $(MeO)_3P$ (3).

$$SF_4 + (MeO)_3P \longrightarrow (MeO)_3PF_2 \qquad (3)$$

When the products were quickly fractionated there was evidence for the formation of a P-H compound, perhaps $(MeO)_2PF_2H$, formed by the fluorination of the $P = O$ form of (I) with SF_4 (4).

$$SF_4 + (MeO)_2P(O)H \longrightarrow (MeO)_2PF_2H + SOF_2 \qquad (4)$$

Although $R'PHF_2OR$ compounds ($R' = Me$; $R = Et$) are stable species [198] this P-H compound was very unstable and on warming to room temperature produced HF (5) and Me_2O and $HP(O)F_2$ (6).

$$(MeO)_2PF_2H \longrightarrow HF + (MeO)_2PF \qquad (5)$$

$$(MeO)_2PF_2H \longrightarrow Me_2O + HP(O)F_2 \qquad (6)$$

Small amounts of $HP(O)F_2$ were isolated but, as had been previously shown, the impure compound decomposes quickly at room temperature producing PF_3, $P(O)F_3$ and solids.[199]

It must be stressed however that, although the equations (1-6) rationalise the observed products, the complexity of the reaction with formation of large amounts of HF, precludes a refined mechanistic study.

B. Reactions of sulphur tetrafluoride with P(V) compounds.

Previous studies on the reactions of SF_4 with P(V) oxides have shown SF_4 to be effective in fluorinating the P = O linkage and it has generally been accepted that this is the case with all phosphoryl compounds.[190]

However, in this work, there is evidence that with L_3PO or $L_2L'PO$ phosphorus compounds (L = MeO, Me_2N; L' = Me) that the major reaction path involves exchange of fluorine and alkoxy groups between SF_4 and the phosphorus oxide, and that any fluorination is only a secondary process.

Perhaps the milder conditions used in this investigation and the manner in which the ligands attached to phosphorus affect the strength of the P = O bond could favour an exchange reaction.

Tris(dimethylamino)phosphine oxide.

When SF_4 and $(Me_2N)_3PO$ were heated at 100°C, no products resulting from the fluorination of $(Me_2N)_3PO$ were isolated. Only a brown tar and unreacted starting materials were produced. Lower temperatures produced no solid products but the reactants were recovered unchanged.

This lack of reaction is in contrast to that observed between $(MeO)_3PO$ and SF_4. Since the average bond dissociation energies in $(Me_2N)_3PO$ and $(MeO)_3PO$ are approximately similar in magnitude [201], a satisfactory explanation in simple thermodynamic terms cannot explain the lack of reaction. Possibly kinetic reasons or the failure to obtain the optimum reaction conditions could explain this apparent anomaly.

Tetramethyl methylphosphorodiamidate.

Large amounts of solids were deposited when SF_4 and $(Me_2N)_2P(O)Me$ were reacted at 80°C and only small amounts of volatile products were produced. The main volatile product was methyl phosphoryl difluoride, $MeP(O)F_2$, together with traces of dimethylaminosulphur trifluoride, Me_2NSF_3. Heating the solid material caused the evolution of more $MeP(O)F_2$.

It was hoped that this reaction would produce $(Me_2N)_2PF_2Me$, but the isolation of a phosphoryl compound suggests that fluorination does not occur. The observed products were those expected on the basis of a series of exchange reactions. The failure to isolate $(Me_2N)_2P(O)FMe$ might be due to its rapid reaction with SF_4.

Trimethyl phosphate.

At 110°C the reaction of SF_4 with $(MeO)_3PO$ yielded dimethyl phosphorofluoridate, $(MeO)_2P(O)F$, methyl phosphorodifluoridate, $MeOP(O)F_2$, Me_2O, SOF_2, $(MeO)_2SO$ and solids.

$(MeO)_3PF_2$ is the expected product if the reaction involves a fluorination mechanism. The failure to detect this compound among the products could be due to its decomposition under the relatively high temperature conditions employed in this reaction. Elimination of both MeF and Me_2O could explain the observed phosphorus compounds.

$$MeOP(O)F_2 \xleftarrow{-Me_2O} (MeO)_3PF_2 \xrightarrow{-MeF} (MeO)_2P(O)F$$

However, the failure to observe MeF (since all the volatile products were analysed it must be assumed that any MeF formed would have been isolated) and the fact that $MeOP(O)F_2$ was not observed when $(MeO)_3PF_2$ was prepared in the $SF_4/(MeO)_3P$ reaction suggest an alternative mechanism.

The appearance of a singlet resonance in the proton n.m.r. spectrum of the products, which cannot be due to a phosphorus species, indicates a more complex reaction mechanism than that expected purely on the basis of a fluorination reaction. The singlet resonance has been attributed to $(MeO)_2SO$, and a series of competitive exchange reactions (similar to those postulated for the reaction of SF_4 with Si-O compounds) producing unstable alkoxysulphur compounds is suggested as the alternative reaction path.

Dimethyl methylphosphonate.

Phosphoryl products were produced from the reaction of SF_4 with $(MeO)_2P(O)Me$. The observed phosphorus species were methyl methylphosphonofluoridate, MeOP(O)MeF, and methylphosphoryl difluoride, $MeP(O)F_2$. The non-phosphorus containing products were identical to those obtained in the $(MeO)_3PO$ reaction.

The formation of P = O compounds suggests that exchange reactions are again operative in this reaction.

Some observations on the mass spectra of alkoxyphosphorus compounds.

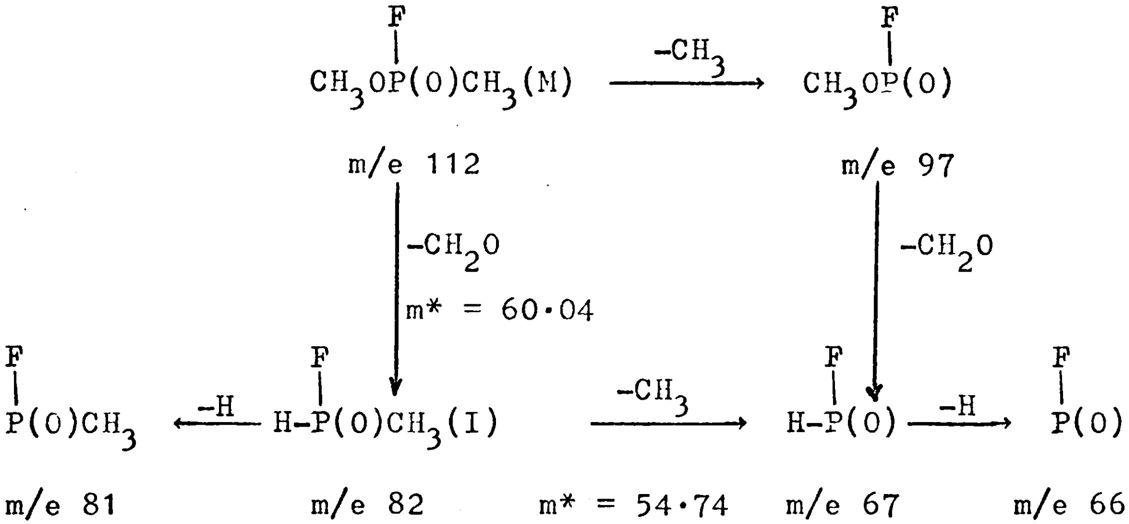
In the previous chapter it was suggested that the loss of formaldehyde was an important re-arrangement process in alkoxysulphur compounds. Further evidence for this suggestion arises from an investigation of the mass spectra of isostructural phosphorus derivatives, $CH_3OP(O)XF$ ($X = CH_3$ or CH_3O) (Table 15). Both compounds show metastable peaks (m*) corresponding to the loss of formaldehyde from the parent ion (M), and thus it can be assumed with reasonable certainty that the fragment of mass m_2 arises in a one step decomposition from the species of mass m_1.

MeOP(O)MeF

The occurrence of P-O bond cleavage accompanied by hydrogen migration was confirmed by detection of a metastable peak, corresponding to the transition ($M-CH_2O$). In addition, a metastable was observed for ($M-CH_2O-CH_3$). Methyl elimination has previously been shown to be a major fragmentation process in methyl phosphines [202] and trimethyl phosphite.[203]

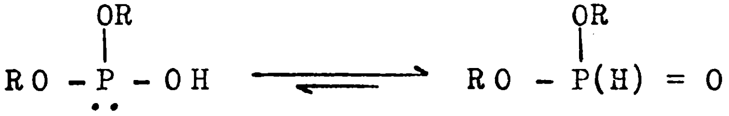
<u>Suggested cracking pattern</u>.

(Omitting positive charges.)



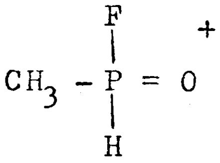
$$\begin{tikzcd}
 & \underset{m/e\ 112}{CH_3O\overset{F}{P}(O)CH_3(M)} \arrow[rr, "-CH_3"] \arrow[d, "-CH_2O", "m^* = 60{\cdot}04"'] & & \underset{m/e\ 97}{CH_3O\overset{F}{P}(O)} \arrow[d, "-CH_2O"] & \\
\underset{m/e\ 81}{\overset{F}{P}(O)CH_3} & \underset{m/e\ 82}{H-\overset{F}{P}(O)CH_3(I)} \arrow[l, "-H"'] \arrow[rr, "-CH_3", "m^* = 54{\cdot}74"'] & & \underset{m/e\ 67}{H-\overset{F}{P}(O)} \arrow[r, "-H"] & \underset{m/e\ 66}{\overset{F}{P}(O)}
\end{tikzcd}$$

Although some workers prefer to visualise hydrogen transfer to oxygen [203], hydrogen transfer to phosphorus is postulated because of the known preference of phosphorus for a four co-ordinate structure [204], which has a primary source in the larger bond strengths of P = O over OH bonds.



$$RO-\underset{\cdot\cdot}{\overset{OR}{P}}-OH \rightleftharpoons RO-\overset{OR}{P}(H)=O$$

Consequently the structure of the ion m/e 82 is best represented as:



$$\mathrm{CH_3-\overset{\overset{F}{|}}{\underset{\underset{H}{|}}{P}}=O}^{+}$$

(I)

If $CH_3-\underset{\cdot\cdot}{P}(F)OH$ were formed it should very rapidly relax into (I).

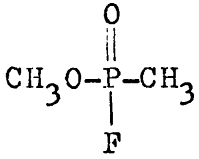
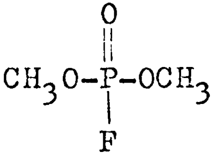
The ion corresponding to (M-31) is regarded as being formed by hydrogen elimination from (I) i.e. $(M-CH_2O-H)$ rather than $(M-CH_3O)$, which is found to be an unfavourable process in dialkyl phosphinates, $R_2P(O)OR'$.[204]

$(MeO)_2P(O)F$

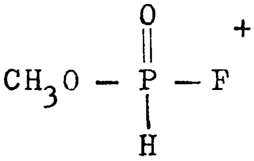
The mass spectrum of $(MeO)_2P(O)F$ (Table 15) is dominated by fragments formed by the loss of CH_2O, a metastable being observed for $(M-CH_2O)$. As with MeOS(O)XF compounds (X = oxygen or lone pair), there is little evidence that (M-F) is a particularly favourable process in the MeOP(O)XF derivatives.

Metastable data indicate that the transition m/e 98 → m/e 80 represents the loss of a water molecule. Because of the greater strength of the P = O bond and the known preference for hydrogen migration to phosphorus in organophosphites [205], the structure of the ion m/e 98 is assigned a four co-ordinate structure (II), although the possibility of a trico-ordinate species (III) cannot altogether be eliminated, since loss of water from this

TABLE 15

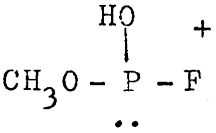
Compound	m/e	Ion	Intensity	Compound	m/e	Ion	Intensity
 $CH_3O-\overset{O}{\overset{\Vert}{\underset{F}{\underset{\vert}{P}}}}-CH_3$	112	$C_2H_6PO_2F$	41	 $CH_3O-\overset{O}{\overset{\Vert}{\underset{F}{\underset{\vert}{P}}}}-OCH_3$	128	$C_2H_6PO_3F$	34
	97	CH_3PO_2F	55		109	$C_2H_6PO_3$	11
	93	$C_2H_6PO_2$	6		98	CH_4PO_2F	100
(M.W. 112)	82	CH_4POF	100	(M.W. 128)	80	CH_2POF	54
	81	CH_3POF	71		79	CH_4PO_2	95
	78	CH_3PO_2	7		68	H_2POF	36
	67	HPOF	80		67	HPOF	86
	66	POF	22		66	POF	25
Metastables:				Metastables:			
	m^*	m_1	m_2		m^*	m_1	m_2
	60·04	112	82		75·03	128	98
	54·74	82	67		65·31	98	80

structure should be a relatively easy process.



$$CH_3O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{|}}{P}}-F\quad +$$

(II)



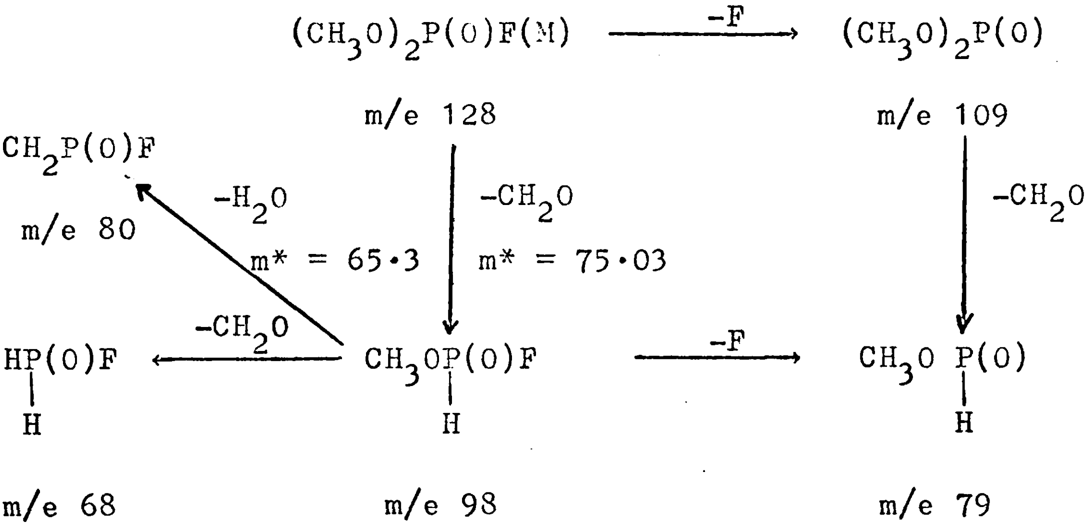
$$CH_3O-\overset{\overset{\displaystyle HO}{|}}{\underset{\cdot\cdot}{P}}-F\quad +$$

(III)

Water elimination is a common process in phosphorus acids and related compounds.[204,203]

Suggested cracking pattern.

(Omitting positive charges.)



Reagents

Most of the phosphorus compounds used in this investigation were commercially available and were purified by distillation before use. $(MeS)_3P$ and and $MeP(O)(NMe_2)_2$ were gifts from Dr. K. Crosbie (Cambridge University). $(Me_2N)_3P$ was prepared by the method of Burg and Slota [206] (Found: P, 19·10; N, 25·66. Calc: for $C_6H_{18}N_3P$, P, 19·02; N, 25·76).

The known toxicity of certain products e.g. phosphorofluoridates required that exposure to these compounds should be kept to a minimum. Consequently, after completion of the reaction, the volatile products were sealed under vacuum into n.m.r. tubes and were characterised by comparing the found n.m.r. parameters with those published in the literature. Approximate percentage yields of the phosphorus fluorine compounds were made on the basis of fluorine line intenstities in the n.m.r. spectra.

A. Reactions of sulphur tetrafluoride with P(III) compounds.

1. Tris(dimethylamino)phosphine.

(8·5 m.m.) of SF_4 and (1·1 g.; 6·8 m.m.) of $(Me_2N)_3P$ were condensed together at -196°C, in a 100 ml. glass reaction vessel. A vigorous reaction occurred on warming to -100°C. After 30 minutes at -100°C the reactants were allowed to warm slowly to room temperature. Fractionation of the volatile products through traps held at -20, -40 and -196°C, collected excess SF_4 at -196°C and a trace of $(Me_2N)_2PF_3$ at -40°C, identified by infra-red [207] and mass spectrometry, including precise mass measurement of the parent ion (Found: m/e 176·06877. Calc: m/e 176·06874). The -20°C bath held $(Me_2N)_3PF_2$, characterised by infra-red and n.m.r. spectroscopy.[203] (Found: δ_F, 53·3; J_{P-F}, 708; δ_H, -2·64; J_{H-P}, 10·8; J_{H-F}, 2·8. Literature: δ_F, 52·4; J_{P-F}, 700; δ_H, -2·60; J_{H-P}, 10·5; J_{H-F}, 2·8.) The reaction vessel contained a yellow hygroscopic solid which analysed for sulphur and showed the following infra-red absorptions (cm^{-1}), in nujol:-

2920(s); 1460(s); 1415(s); 1380(m); 1285(w); 1182(s); 1082(m); 1028(s); 980(s); 863(s); 785(s); 748(s) and 728(s).

The n.m.r. spectrum of the solid, examined in CD_3CN showed that a mixture of compounds was present. The major component was identified as $(Me_2N)_3P(S)$ (Found: δ_H, -2·58; J_{H-P}, 11·3. Literature [196]: δ_H, -2·61; J_{H-P}, 11·3.)

2. Trimethyl phosphite.

(8·4 m.m.) of SF_4 and (0·99 g.; 8·0 m.m.) of $(MeO)_3P$

were condensed together at -196°C. A visible reaction occurred on warming to -100°C. The contents of the reaction vessel were allowed to warm very slowly to room temperature over a 2 hour period. Separation of the volatile products yielded traces of Me_2O and MeF, both identified by infra-red spectroscopy. The least volatile products consisted of $(MeO)_3PF_2$ (major product) together with trace amounts of $(MeO)_2P(O)F$ (20%) and MeOP(O)FMe (<5%). $(MeO)_3PF_2$ was identified by mass spectrometry (no parent ion was observed, but ions corresponding to the loss of a fluorine and a methoxy group from the parent ion were abundant) and n.m.r. [193] $(MeO)_2P(O)F$ was characterised by molecular weight (Found: M.W. 128 (mass spec.). Calc: M.W. 128) and n.m.r. [193] Traces of MeOP(O)FMe were identified by ^1H n.m.r. [139] N.M.R. results are tabulated overleaf. The reaction vessel contained a white viscous solid.

3. Trimethyl thiophosphite.

(7·0 m.m.) of SF_4 and (1·2 g.; 7·1 m.m.) of $(MeS)_3P$ reacted exothermally on warming to room temperature. Removal of the volatile products left a yellow viscous solid in the reaction vessel. The most volatile products, all identified by infra-red spectroscopy [209] were SF_4, SiF_4 and SPF_3. The least volatile products, identified by n.m.r., were in decreasing amounts,

	δ_F	J_{P-F}	δ_H	J_{H-P}	J_{H-F}
$(MeO)_3PF_2$	72·6	705	-3·71	15·2	1·1
Literature	72·8	706	-3·65	15·2	1·0
$(MeO)_2P(O)F$	86·9	970			
Literature	86·1	972			
MeOP(O)FMe			-1·72 (PCH)	18·7 (PCH)	6·0 (FPCH)
			-3·89 (POCH)	11·3 (POCH)	0·7 (FPOCH)
Literature			-1·65 (PCH)	18·7 (PCH)	6·05 (FPCH)
			-3·81 (POCH)	11·3 (POCH)	0·7 (FPOCH)

Me_2S_4 (Found: δ_H, -2·54; Literature [175]: δ_H, -2·55)

$MeSP(S)F_2$ (Found: δ_F, 26·8; J_{P-F}, 1207; δ_H, -2·62;
J_{H-P}, 20·0; J_{H-F}, 1·31.
Literature [210]: δ_F, 26·7; J_{P-F}, 1207; δ_H, -2·59;
J_{H-P}, 20·3; J_{H-F}, 1·3)

$Me_2P(S)F$ (Found: δ_F, 43·7; J_{P-F}, 975·6
Literature [211]: J_{P-F}, 975).

The products produced in this reaction were very reactive and deposited solids on fractionation.

4. Dimethyl hydrogen phosphite.

(a) (11·6 m.m.) of SF_4 and (1·2 g; 10·9 m.m.) of $(MeO)_2POH$ reacted vigorously on warming to room temperature. Fractionation through -70, -110 and -196°C cold baths, collected PF_3, POF_3 (trace) Me_2O, SOF_2 and SiF_4 in the latter bath, all identified by infra-red spectroscopy. The 110°C trap contained $MeOPF_2$ (~40%), characterised by molecular weight (Found: M.W. 100 (mass spec.). Calc: M.W. 100) and n.m.r.[139] The -70°C trap held $(MeO)_3PF_2$ (~50%) and traces of $(MeO)_2P(O)F$ (~15%), both identified by ^{19}F n.m.r.[193]

	δ_F	J_{P-F}	δ_H	J_{H-P}	J_{H-F}
$MeOPF_2$	52•8	1283	-3•66	8•4	
Literature	51•3	1288	-3•66	8•4	0•4
$(MeO)_3PF_2$	72•7	706			
Literature	72•8	706			
$(MeO)_2P(O)F$	87•5	971			
Literature	86•1	972			

The reaction vessel contained traces of a white solid.

(b) In a second experiment (8•0 m.m.) of SF_4 and (0•72 g; 6•5 m.m.) of $(MeO)_2POH$ were allowed to warm to -40°C and material volatile at this temperature quickly fractionated through -100 and -196°C baths. The -100°C trap contained $MeOPF_2$ and a compound which showed infra-red absorption at 2480 cm^{-1}, indicative of a P-H compound. The complexity of the spectrum below 1000 cm^{-1} made assignment of the bands difficult but a very strong absorption band at 880 cm^{-1}, possibly a P-F stretching vibration, was due to the P-H compound. This compound was extremely unstable and, when a sample of the gas was left in an infra-red gas cell for a few minutes, the P-H absorption steadily decreased in intensity and the band at 880 cm^{-1} completely disappeared. New bands appeared in the spectrum due to SiF_4, Me_2O and another P-H compound which showed infra-red absorption and characteristic fine structure due to $HP(O)F_2$.[199]

Found infra-red (cm^{-1}):-

2500(m.w.) P-H; 1375(s) P=O; 932(s); 892(s) P-F.

Literature infra-red of $HP(O)F_2$:-

2500(w); 1377(s); 932(s); 892(s).

When the contents of the -100°C bath were allowed to warm to room temperature an infra-red spectrum showed no peaks due to $HP(O)F_2$, but Me_2O, SiF_4 and PF_3 were produced; peaks due to $MeOPF_2$ were still present but were less intense. The -196°C bath contained $HP(O)F_2$, POF_3, Me_2O, PF_3 and SiF_4 while the least volatile liquid held at -40°C was $(MeO)_3PF_2$.

B. Reactions of sulphur tetrafluoride with P(V) compounds.

5. Tris(dimethylamino)phosphine oxide.

(a) (8·0 m.m.) of SF_4 and (1·37 g; 7·6 m.m.) of $(Me_2N)_3PO$ were heated in a large Carius tube overnight at 100°C. The volatiles consisted of unreacted SF_4, SOF_2 and SiF_4. The major product was a brown tarry solid.

(b) (9·0 m.m.) of SF_4 and (1·55 g; 8·7 m.m.) of $(Me_2N)_3PO$ were heated at 90°C for 6 hours in a sealed tube. No solid formation occurred and the volatiles consisted of unreacted SF_4, SOF_2, SiF_4 and $(Me_2N)_3PO$; the latter compound was characterised by n.m.r. comparison with an authentic sample.

6. Tetramethyl methylphosphonodiamidate.

(7·9 m.m.) of SF_4 and (0·98 g.; 6·6 m.m.) of $MeP(O)(NMe_2)_2$ were heated for 2 hours in a sealed tube at 60°C. Fractionation through baths at -78 and -196°C collected excess SF_4 and small amounts of SOF_2 in the latter trap. The contents of the -78°C trap consisted of a trace of Me_2NSF_3, identified by n.m.r. [110] (Found: δ_F, -39·1, δ_H; -2·87. Literature: δ_F, -39·4; δ_H, -3·15) and $MeP(O)F_2$ characterised by n.m.r. [139] (Found: δ_F, 59·9; J_{P-F}, 1105; δ_H, -1·85; J_{H-P}, 20·0; J_{H-F}, 6·3. Literature: δ_F, 60·3; J_{P-F}, 1105; δ_H, -1·92; J_{H-P}, 20·0; J_{H-F}, 6·3). The reaction vessel contained a brown solid which when heated to 150°C evolved $MeP(O)F_2$.

7. Trimethyl phosphate.

(10·3 m.m.) of SF_4 and (1·6 g.; 11·7 m.m.) of $(MeO)_3PO$ failed to react when left at room temperature overnight in a sealed tube. The reactants were heated for 12 hours at 110°C. Separation of the most volatile products yielded SOF_2, Me_2O and SiF_4, all identified by infra-red spectroscopy. The least volatile products were analysed by n.m.r. [139] and consisted of ~1 part $(MeO)_2P(O)F$ and ~3 parts of $MeOP(O)F_2$.

	δ_F	J_{P-F}	δ_H	J_{H-P}	J_{H-F}
$MeOP(O)F_2$	87·9	1009	-4·09	12·0	0·5
Literature	87·5	1008	-4·05	12·2	0·5
$(MeO)_2P(O)F$	87·1	970			
Literature	86·1	972			

A singlet at -3·61 p.p.m. in the ^1H n.m.r. of the least volatile products was attributed to $(MeO)_2SO$ (Literature [77]: δ_H, -3·58 p.p.m.). The reaction vessel contained a white solid.

8. Dimethyl methylphosphonate.

(9·9 m.m.) of SF_4 and (1·27 g.; 10·2 m.m.) of $MeP(O)(OMe)_2$ were heated at 80°C for 1 hour in a sealed tube. Fractionation through traps held at -40, -78 and -196°C collected SOF_2 and Me_2O in the latter bath, both identified by their characteristic infra-red spectra. The -78°C trap collected $MeP(O)F_2$ ~1 part, identified by n.m.r. [139], while the -40°C bath held MeOP(O)FMe ~3 parts, characterised by molecular weight (Found: M.W. 112 (mass spec.). Calc: M.W. 112) and n.m.r. [139]. A singlet at -3·61 p.p.m. in the proton spectrum of MeOP(O)FMe was due to $(MeO)_2SO$; Literature [77]: δ_H, -3·58 p.p.m.

	δ_F	J_{P-F}	δ_H	J_{H-P}	J_{H-F}
MeOP(O)FMe	62·9	1038	-3·87(POCH)	11·3(POCH)	0·7(FPOCH)
			-1·70(PCH)	18·6(PCH)	6·0(FPCH)
Literature	61·9	1039	-3·81(POCH)	11·3(POCH)	0·7(FPOCH)
			-1·65(PCH)	18·7(PCH)	6·05(FPCH)
$MeP(O)F_2$	60·9	1105			6·0
Literature	60·3	1105			6·0

$MeP(O)F_2$ showed characteristic infra-red absorptions (cm^{-1}) at:- 1370, 1358(s); 933(s); 875(m); 745(m); 470(m); 400(w). (All bands revealed P.Q.R. fine structure.)

MeP(O)FMe showed characteristic infra-red absorptions (cm^{-1}) at:- 1328(m); 1005(s); 925(s); 839(s); 518(m). (All bands revealed P.Q.R. fine structure.)

The reaction vessel contained a white viscous solid.

CHAPTER IV

REACTIONS OF SULPHUR FLUORIDES WITH NITROGEN COMPOUNDS

INTRODUCTION

With primary amines, sulphur tetrafluoride produces iminosulphur difluorides, $RN{=}SF_2$, R = Me or Ph.[100, 212] Further reaction of the difluorides with excess amine is possible, with the formation of bis (imino)sulphur derivatives e.g. $PhN{=}S{=}NPh$.

The reaction of sulphur tetrafluoride with dimethylamine however, is more complex and does not yield the expected product, dimethylaminosulphur trifluoride, Me_2NSF_3.[110] No experimental conditions were given for this reaction and only unidentified oils and solid products were produced.

Me_2NSF_3 was subsequently prepared by the action of sulphur tetrafluoride with dimethylaminotrimethylsilane.[110]

At present, Me_2NSF_3 is the only compound of its type and no further higher substituted products have, as yet, been reported. The isolation of phenoxysulphur fluorides, $(PhO)_xSF_{4-x}$ (prepared in chapter II), suggested the possibility of a similar range of products with dimethylamino groups.

The sulphur atom in methyliminosulphur difluoride is formally isoelectronic with the sulphur atom in thionyl fluoride, and might therefore be expected to behave in an analogous manner. With secondary amines and dialkylaminotrimethylsilanes, SOF_2 produces $R_2NS(O)F$ compounds [13, 213], but no derivatives of the type $MeN{=}S(F)NR_2$ are known.

SUMMARY OF REACTIONS

A. Reactions of sulphur fluorides with amines.

1. $SF_4 + 2Me_2NH \xrightarrow{-78^\circ C}$ complex $\xrightarrow{0^\circ C}$ $(Me_2N)_2S$ (trace) + involatile HF_2^- containing liquid.

2. $MeN = SF_2 + 3Me_2NH \longrightarrow (Me_2N)_2S + (Me_2N)_2CH_2 + (MeN)_2S$ (trace) + red oils and HF_2^- containing solids.

3. $Me_2NSF_3 + 4MeNH_2 \longrightarrow (MeN)_2S + Me_2NH.HF + 2MeNH_2.HF$.

B. Reactions of sulphur fluorides with silicon-nitrogen compounds.

4. $SF_4 + 2Me_3SiNMe_2 \longrightarrow Me_2NSF_3 + Me_3SiNMe_2$ (trace) + Me_3SiF + solids.

5. $Me_2NSF_3 + Me_3SiNMe_2 \longrightarrow Me_2NSF_3 + Me_3SiF$ + solids.

6. $SF_4 + Me_3SiNEt_2 \longrightarrow Et_2NSF_3 + Me_3SiF$.

7. $MeN = SF_2 + Me_3SiNMe_2 \longrightarrow (Me_2N)_2S$ + traces of $(MeN)_2S$ and $(Me_2N)_2CH_2$ + red oils and solids.

8. $SF_4 + Me_3SiN(Et)PPh_2 \longrightarrow Ph_2PF_3 + Ph_2P(O)F$ (trace) + $(EtNS)_x + Me_3SiF$.

A. Reactions of sulphur fluorides with amines.

Reaction of sulphur tetrafluoride with dimethylamine.

MacDiarmid has investigated the reaction of SF_4 with Me_2NH, but only unidentified oily materials were produced. In this work, the reaction was re-investigated.

When a mixture of SF_4 and a large excess of Me_2NH (1:6) was held at -78°C, a white solid was produced. No SF_4 could be distilled from the mixture, although its melting point is -121°C.[27] The products volatile at -78°C were excess Me_2NH and a trace of bis(dimethylamino)sulphur, $(Me_2N)_2S$. The white solid residue consisted of SF_4 and Me_2NH in the ratio of $\sim$1:2.

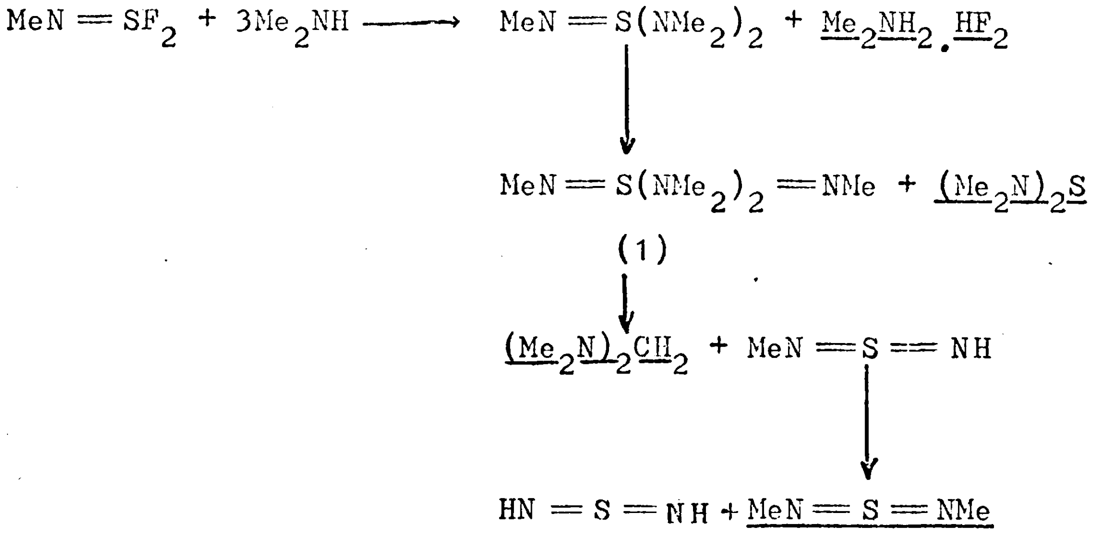
SF_4 is not a strong electron acceptor and it is unlikely that this solid product is a straightforward addition compound. Possibly one Me_2N group is co-ordinated to the sulphur, while the other Me_2N group is merely held in the "octahedral" lattice perhaps, by H---F bonding.

On warming to 0°C, the SF_4 complex melted to an involatile liquid and a further small quantity of $(Me_2N)_2S$ was isolated, but there was no evidence for dissociation of the complex or Me_2NSF_3 formation. As yet, this liquid product has not been identified. The involatile and viscous nature of the liquid, which shows broad n.m.r. resonances in regions characteristic of Me_2NS (-2·9 p.p.m.) and HF (170·6 p.p.m.) groups, suggest association. Broad fluorine resonances in the ~160 p.p.m. region are characteristic of a bifluoride ion [214] containing species.

Reaction of methyliminosulphur difluoride with dimethylamine.

$MeN{=}SF_2$ reacted with excess Me_2NH (1:3) at room temperature to produce orange-red coloured solids and oils, which from n.m.r. appear to contain fluoride or bifluoride ions. The volatile products were bis(dimethylamino)sulphur, $(Me_2N)_2S$, bis(dimethylimino)sulphur, $(MeN)_2S$ and a colourless, volatile liquid, identified as N tetramethylmethylene diamine, $(Me_2N)_2CH_2$.

A speculative mechanism by which the reaction might proceed is illustrated on the following page. The products isolated are underlined.



It is suggested that the first step in the reaction involves complete replacement of the fluorine atoms in $MeN{=}SF_2$ with dimethylamino groups. The isolation of $(Me_2N)_2S$ indicates a disproportionation reaction, perhaps involving the S(IV) species, $MeN{=}S(NMe_2)_2$.

The formation of $(Me_2N)_2CH_2$ is unexpected and is difficult to explain, but possibly arises by further complex re-arrangement and decomposition of (1), although there is no experimental evidence to suggest the mode of decomposition. Recently, compounds containing sulphur surrounded by four nitrogen atoms have been prepared [215], but only compounds which contain electronegative atoms or groups attached to sulphur have been isolated, and compound (1) could possibly be the precursor of $(Me_2N)_2CH_2$.

Sulphur diimide, HN = S = NH, has never been isolated although it has been postulated to be present in the red solution obtained from the action of ammonia with trithiazyl chloride, $N_3S_3Cl_3$ [216], and might be responsible for the red coloured oils produced in this reaction.

Reaction of dimethylaminosulphur trifluoride with monomethylamine.

Bis(dimethylimino)sulphur, $(Me_2N)_2S$, was the only volatile product obtained from the room temperature reaction of Me_2NSF_3 with $MeNH_2$. The other products were involatile solids which presumably were HF salts.

$$Me_2NSF_3 + 4MeNH_2 \longrightarrow MeN = S = NMe + Me_2NH.HF + 2MeNH_2.HF.$$

Methyliminosulphur difluoride, $MeN = SF_2$, has been shown to react with $MeNH_2$ to produce $(MeN)_2S$ [100],

$$MeN = SF_2 + 3MeNH_2 \longrightarrow MeN = S = NMe + 2MeNH_2.HF.$$

and could possibly be an intermediate in the above reaction. Alternatively, the intermediate formation of $Me_2NS(F)NMe$ could explain the formation of $(MeN)_2S$.

When however, less than a 4:1 excess of $MeNH_2$ was used only oils and $(MeN)_2S$ were produced and neither $Me_2NS(F)NMe$ or $MeN = SF_2$ were isolated, inferring that reaction of $MeNH_2$ with the intermediate is a fast reaction.

B. Reactions of sulphur fluorides with silicon-nitrogen compounds.

Reactions of sulphur tetrafluoride and dimethylaminosulphur trifluoride with dimethylaminotrimethylsilane.

Equimolar quantities of SF_4 and Me_3SiNMe_2 react readily below room temperature, to produce Me_2NSF_3 [110] but, as yet, no further higher substituted products e.g. $(Me_2N)_2SF_2$ have been reported.

The products from the room temperature reaction of SF_4 with an excess of Me_3SiNMe_2 (~1:2) were Me_3SiF (~2 moles), Me_2NSF_3, a small amount of unreacted Me_3SiNMe_2 and a white hydroscopic solid which, when heated, yielded $(Me_2N)_2S$.

Me_2NSF_3 could have originated either by a one stage exchange reaction involving a fluorine atom and a dimethylamino group or by a reorganisation reaction of $(MeN)_2SF_2$.

That ~2 moles of Me_3SiF were isolated, indicates the latter route as the source of Me_2NSF_3. Furthermore, Me_2NSF_3 was found to react with Me_3SiNMe_2 forming a similar range of products to those obtained from the reaction of SF_4 with excess Si-N reagent.

$$Me_2NSF_3 + Me_3SiNMe_2 \longrightarrow Me_2NSF_3 + Me_3SiF + \text{solid}$$

Disproportionation of $(Me_2N)_2SF_2$ is therefore postulated as being the source of Me_2NSF_3. Perhaps, the unidentified solid product represents the other "half" of the reorganisation products and is worthy of further investigation.

A n.m.r. spectrum of the solid showed no fluorine resonance, but two singlets (one of which must be an impurity) were present in the proton spectrum in a region characteristic of the Me_2NS grouping. The thermal decomposition of the solid to produce $(Me_2N)_2S$, suggests the possibility of $(Me_2N)_3SF$ or $(Me_2N)_4S$ in the solid (c.f. PhO_xSF_{4-x} compounds).

Reaction of sulphur tetrafluoride with diethylaminotrimethylsilane.

The reaction of SF_4 with Me_3SiNEt_2 to prepare diethylaminosulphur trifluoride, Et_2NSF_3, was carried out in a similar manner and deserves no special comment except that in an initial reaction in addition to Et_2NSF_3, a small amount of ethyliminosulphur difluoride, $EtN = SF_2$, was isolated.

Iminosulphur difluorides decompose thermally to thiazyl and alkyl fluorides [217],

$$RN = SF_2 \longrightarrow RF + NSF$$

and initially, it was considered that Et_2NSF_3 could decompose into $EtN = SF_2$ by a similar loss of EtF. Subsequent reactions however, revealed that $EtN = SF_2$ had arisen from $Me_3SiN(H)Et$ impurity in the Me_3SiNEt_2 starting material [218],

$$SF_4 + Me_3SiN(H)Et \longrightarrow EtN = SF_2 + HF + Me_3SiF$$

and that Et_2NSF_3 is a relatively stable molecule.

Indeed, when a pure sample of Et_2NSF_3 was heated at 100°C, an infra-red spectrum of the volatile products revealed only Et_2NSF_3. Me_2NSF_3 has been reported to decompose at temperatures slightly greater than room temperature [110] but, in the present work, both Et_2NSF_3 and Me_2NSF_3 were found to be stable for days when kept in glass at room temperature and no appreciable decomposition was detected.

Reaction of methyliminosulphur difluoride with dimethylaminotrimethylsilane.

$MeN = SF_2$ reacted at room temperature with Me_3SiNMe_2 in a complex manner to yield Me_3SiF, $(Me_2N)_2S$ and traces of $(MeN)_2S$ and $(Me_2N)_2CH_2$. The products isolated were similar to those obtained from the reaction of $MeN = SF_2$ with Me_2NH, and a similar mechanism is suggested.

The failure to isolate $MeN = S(F)NMe_2$ is perhaps not unexpected since, compared with $Me_2NS(O)F$ which appears to be a stable molecule, the replacement of an oxygen atom by a less electronegative methylimino group should increase the electron density at the sulphur atom, resulting in weaker sulphur fluorine bonding, with resultant instability of the molecule towards disproportionation.

$$2MeN = S(F)NMe_2 \longrightarrow MeN = S(NMe_2)_2 + MeN = SF_2$$

Alternatively, $MeN = S(NMe_2)_2$ could be formed by a further exchange reaction between the Si-N reagent and $MeN = S(F)NMe_2$.

$$MeN = SF_2 \xrightarrow{Me_3SiNMe_2} MeN = S(F)NMe_2 \xrightarrow{Me_3SiNMe_3} MeN = S(NMe)_2$$

<u>Reaction of sulphur tetrafluoride with N-diphenylphosphino N-ethyltrimethylsilane</u>.

The reaction between SF_4 and $Me_3SiN(Et)PPh_2$, $RSiMe_3$ where $R = Ph_2PN(Et)$, was an unsuccessful attempt to prepare the RSF_3 compound. The observed room temperature reaction is represented by the following equation.

$$SF_4 + Me_3SiN(Et)PPh_2 \longrightarrow Ph_2PF_3 + (EtNS)_x + Me_3SiF$$

This single reaction demonstrates the versatility of SF_4 as a synthetic reagent, and exemplifies the general types of reactions investigated in this and the preceding chapter. Namely, that SF_4 readily cleaves

(a) Si-N bonds forming Me_3SiF

and (b) P-N bonds, with simultaneous oxidation of trivalent phosphorus compounds to the pentavalent state.

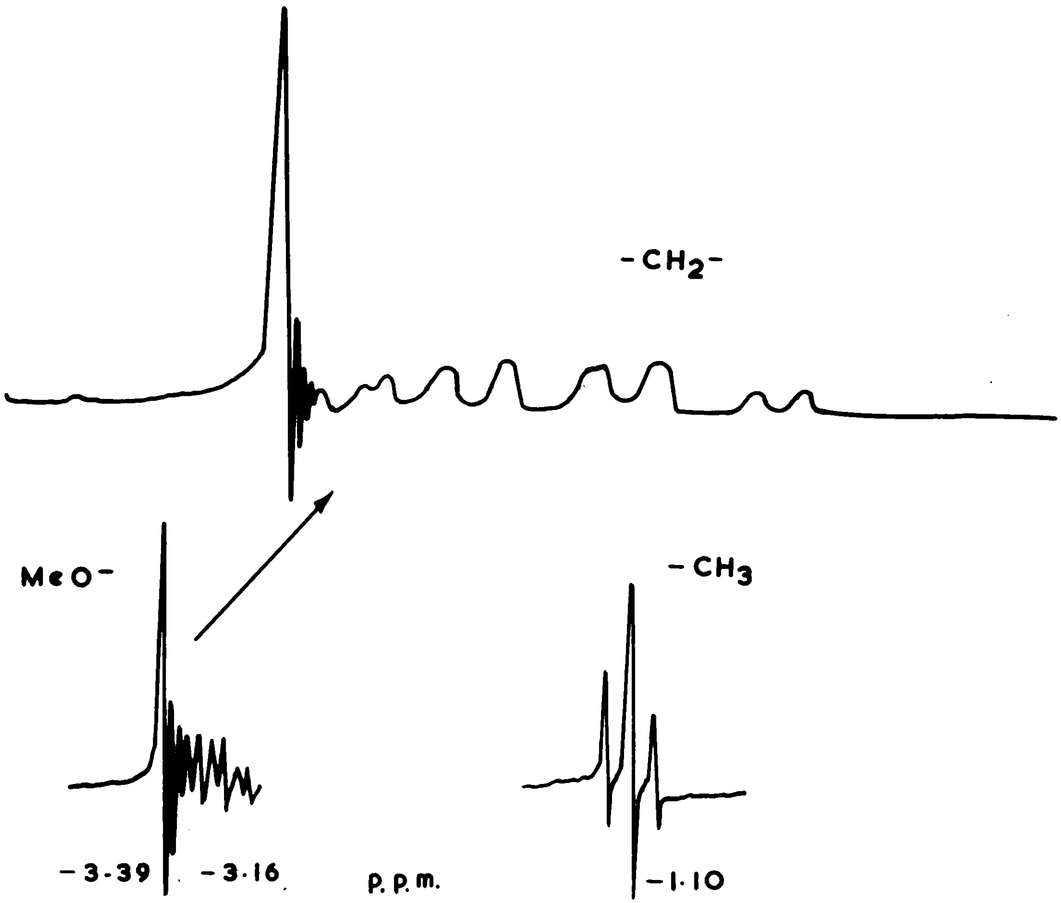
The ethyl compound has not been completely characterised but is perhaps the polymeric chain imide $(EtNS)_x$.[219]

Magnetic non equivalence in the n.m.r. spectra of sulphur-nitrogen compounds.

The n.m.r. spectra of sulphinamides e.g. N-diethylmethoxysulphinamide, $MeOS(O)N(CH_2CH_3)_2$ (I), which were prepared in an earlier chapter, are of particular interest in that the methylene protons exhibit magnetic non equivalence and display an AB, rather than an A_2 spectrum.

Instead of the quartet expected for the splitting of the methylene resonance by the adjacent methyl group, two such quartets are observed, slightly displaced from one another and showing slightly different coupling constants with the methyl group. That is, the two protons of the same methylene group are clearly not

^1H N.M.R. SPECTRUM OF $MeOS(O)NEt_2$



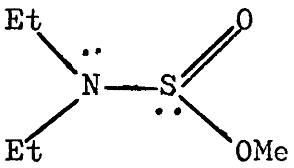
equivalent to each other.

Some of the possible causes of the observed non equivalence of the methylene protons in (I) are considered below.

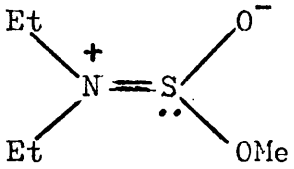
Hindered rotation.

N.M.R. spectroscopy has proven useful for the study of rate processes associated with the barrier to internal rotation about different types of bond.[77]

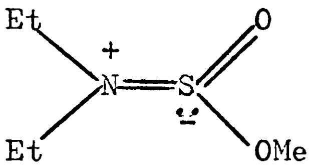
Restricted rotation about the N-S bond in (I), due to delocalisation of the lone pair of electrons on nitrogen into the available d-orbitals of sulphur, can be represented by resonance structures A and B, and could be associated with the observed non equivalence.



(I)



A



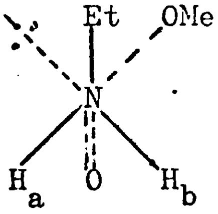
B

Although abundant physical evidence exists for the importance of the $\overset{+}{N} = \overset{-}{S}$ contribution to the bonding e.g. N-S bond lengths are invariably shorter than the length predicted for a true single bond calculated from Paulings covalent radii [97], current thinking attributes little importance to hindered rotation about the N-S bond, as being a major source of magnetic non equivalence in sulphinamides.[220] Even at low temperatures, magnetic non equivalence is not observed for the methyl groups in N-dimethylmethane sulphinamide, $Me_2NS(O)Me$, which indicates essentially free rotation about the N-S bond.[220]

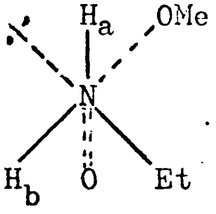
The presence of an asymmetric atom or group.

The presence of an asymmetric atom or group adjacent to a methylene group can confer non equivalence on the protons of the latter [221], and at the present time, asymmetry at sulphur appears to be the most favoured interpretation for the observed magnetic non equivalence of the methylene protons in ethyl sulphinamides.[222]

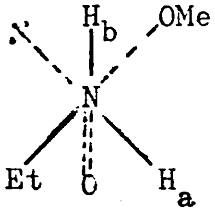
A consideration of the three possible staggered conformations of (I) (a → c), show that the environments of the methylene protons H_a and H_b are not identical, because the spatial distribution of the atoms are different in each of the conformations.



(a)



(b)



(c)

Thus, the observed non equivalence of the methylene protons in (I) is a consequence of the two protons always residing in different magnetic environments, when distributed between the three possible staggered rotamers. At much lower temperatures the three conformations should absorb as separate species and, in principle, a twelve line spectrum corresponding to three different AB systems is possible.

Further evidence for asymmetry at the sulphur atom being a major cause of the non equivalence is found with studies on related sulphonamido compounds [222]; replacement of the S(O)N group by the more symmetrical SO_2N group results in a simple A_2B_3 pattern for the ethyl protons in N diethyl-p toluensulphonamide.

Generally, inversion at nitrogen is very fast at room temperature [77] and is not considered here, as a source of asymmetry in sulphinamides.

In conclusion the interpretation of the n.m.r. spectrum of (I) requires a stable pyramidal structure at sulphur, with probably either a planar sp^2 arrangement about nitrogen or a pyramidal structure which is rapidly undergoing inversion.

A. Reactions of sulphur fluorides with amines.

1. Reaction of SF_4 with Me_2NH.

(4·95 m.m.) of SF_4 and (28·85 m.m.) of Me_2NH were condensed together at -196°C in a 100 ml. glass vessel. On warming to -78°C, a white solid formed and the volatile products were removed over a 2 hour period. The material volatile at -78°C consisted of (19·9 m.m.) of Me_2NH, identified by its infra-red spectrum [114], and a trace of $(Me_2N)_2S$, characterised by infra-red comparison with an authentic sample (prepared by the action of SCl_2 on Me_2NH [223]) and by mass spectrometry, including precise mass measurements of the most prominent ions.

m/e	Ion	Intensity	Found Mass	Calc. Mass
120	$C_4H_{12}N_2S$	62	120·07222	120·07212
77	C_2H_7NS	19	77·03018	77·02992
76	C_2H_6NS	81	76·02085	76·02209
58	C_3H_8N	67	58·06533	58·06567

(The peak at m/e 28(N_2) represents intensity 100).

The white solid formed at -78°C, consisted of SF_4 and Me_2NH in the ratio of 4·95:8·95 or ~1:2. On warming to 0°C, the solid melted to an involatile viscous liquid. Distillation under dynamic vacuum collected a small amount of $(Me_2N)_2S$. The n.m.r. spectrum of the liquid residue consisted of a singlet at $-2{\cdot}9$ p.p.m. in the proton spectrum and a very broad single resonance at $+170{\cdot}6$ p.p.m. in the fluorine spectrum.

2. Reaction of $MeN = SF_2$ with Me_2NH.

A 4:1 ratio of Me_2NH and $MeN = SF_2$ was allowed to warm to room temperature in a sealed tube. At -20°C a vigorous reaction occurred, forming a deep red oil and yellow solids. After 1 hour at room temperature the volatile products were fractionated through traps held at -65, -75 and -196°C. The -196° bath collected 1 mole of unreacted Me_2NH, identified by its infra-red spectrum.[114] The -65°C trap held $(Me_2N)_2S$ and a small amount of $(MeN)_2S$, both identified by infra-red [100] and molecular weight.

(Found: M.W. 120 (mass spec.); Calc: M.W. for $(Me_2N)_2S$ 120;
Found: M.W. 90 (mass spec.); Calc: M.W. for $(MeN)_2S$ 90.)

The -75° trap collected a colourless, volatile liquid, identified as $(Me_2N)_2CH_2$ by n.m.r. and infra-red comparison with a commercial sample obtained from Koch-Light. Unambiguous identification of the compound as $(Me_2N)_2CH_2$ was shown by high resolution mass spectrometry.

m/e	Ion	Found Mass	Calc. Mass
102	$C_5H_{14}N_2$	102·11557	102·11569
101	$C_5H_{13}N_2$	101·10774	101·10786
70	C_4H_8N	70·06560	70·06567
58	C_3H_8N	58·06553	58·06568

A n.m.r. spectrum of the oily-solid residue left in the reaction vessel consisted of a broad proton singlet at -2·93 p.p.m., and a very broad fluorine singlet at +154 p.p.m.

3. Reaction of Me_2NSF_3 with $MeNH_2$.

(0·59 g.; 4·5 m.m.) of Me_2NSF_3 and (21·5 m.m.) of $MeNH_2$ were condensed together at -196°C. On warming to room temperature, orange-red solids were produced. Fractionation through -50 and -196°C cold baths collected (4·3 m.m.) of excess $MeNH_2$ in the latter trap, identified by its infra-red spectrum [114] and $(MeN)_2S$ at -50°C, characterised by infra-red [100] and high resolution mass spectrometry.

m/e	Ion	Intensity	Found Mass	Calc. Mass
90	$C_2H_6N_2S$	53	90·02502	90·02517
76	CS_2		76·94420	76·94414
	C_2H_6NS	6	76·02223	76·02210
	CH_2NOS		76·98587	76·98576

(The peak at m/e 61 (CH_3NS) represents intensity 100.)

B. Reactions of sulphur fluorides with silicon-nitrogen compounds.

4. Reaction of SF_4 with Me_3SiNMe_2.

(2·7 m.m.) of SF_4 and (0·89 g.; 7·6 m.m.) of Me_3SiNMe_2 were allowed to warm to room temperature. The volatile products consisted of (5·5 m.m.) of Me_3SiF, (1·7 m.m.) of Me_3SiNMe_2 and Me_2NSF_3, all identified by infra-red spectroscopy. The reaction vessel contained a white solid which, when heated, produced $(Me_2N)_2S$ (characterised by infra-red spectroscopy).

5. Reaction of Me_2NSF_3 with Me_3SiNMe_2.

(0·33 g.; 2·5 m.m.) of Me_2NSF_3 and (0·27 g.; 2·3 m.m.) of Me_3SiNMe_2 were allowed to warm slowly to room temperature. Repeated warming and freezing of the reactants caused the precipitation of a white solid.

After 1 hour at room temperature the products were fractionated to produce Me_2NSF_3 and (0·202 g.; 2·2 m.m.) of Me_3SiF, both identified by infra-red spectroscopy.[110, 111] A nujol mull of the white hygroscopic solid showed infra-red absorption at (cm^{-1}):-

3010(v.s.); 2860(v.s.); 1450(s); 1375(m); 1225(s); 1192(m); 1158(m); 1100(w); 1050(s); 940(s); 905(s); 710(m); 660(m).

The proton n.m.r. spectrum, recorded in CD_3CN, consisted of two singlet resonances at -2·9 and -2·72 p.p.m. No fluorine resonance was detected. When heated the solid evolved $(Me_2N)_2S$.

6. Reaction of SF_4 with Me_3SiNEt_2.

(11·0 m.m.) of SF_4 and (1·58 g.; 10·9 m.m.) of Me_3SiNEt_2 reacted on warming to room temperature to produce (10·9 m.m., 100%) of Me_3SiF, identified by its infra-red spectrum [111], and a colourless, involatile liquid, identified as DIETHYLAMINOSULPHUR TRIFLUORIDE, Et_2NSF_3.

Anal: For $(CH_3CH_2)_2NSF_3$

Found: C, 29·93; H, 6·31; N, 8·53; S, 19·99; F, 35:13

Calc.: C, 29·81; H, 6·21; N, 8·69; S, 19·88; F, 35·40

Infra-red (cm^{-1})

3000(w); 2970(m); 2940(w); 2915(w); 1465(m.br.)

1390(w); 1355(w); 1230(s); 1190(m); 1060(w); 1030(s); 945(m); 790(sh.); 760(s); 730(sh.); 680(w); 640(s).

N.M.R.

δ_{CH_3} -1·45(t); δ_{CH_2} -3·75(q); δ_F -42·8(b.s.).

$J_{CH_3-CH_2}$ 7 c/s.

In an initial reaction between SF_4 and Me_3SiNEt_2, $EtN = SF_2$ was isolated in addition to Et_2NSF_3.

N.M.R. $CH_3CH_2N = SF_2$

δ_{CH_3} -1·25 (heptuplet); δ_{CH_2} -3·5 (sextet); δ_F -66·5(b.s.). $J_{CH_3-CH_2}$ 7 c/s; J_{CH_3-F} 3·5 c/s; J_{CH_2-F} 7 c/s.

Checking the purity of the Me_3SiNEt_2 starting material revealed the presence of $Me_3SiN(H)Et$ impurity and accounts for the formation of $EtN = SF_2$.

7. Reaction of $MeN = SF_2$ with Me_3SiNMe_2.

(0·52 g.; 5·3 m.m.) of $MeN = SF_2$ and (0·53 g.; 4·5 m.m.) of Me_3SiNMe_2 were condensed together at -196°C in a sealed tube. On warming up, a vigorous reaction took place with the contents of the reaction vessel becoming yellow in colour. After 1 hour at room temperature the volatile products were removed and fractionated. The most volatile products were an inseparable mixture of $MeN = SF_2$ and Me_3SiF, both identified by infra-red scpotroscopy. The least volatile products were identified as $(Me_2N)_2S$, together with traces of $(MeN)_2S$ and $(Me_2N)_2CH_2$; the latter compound was characterised by comparison of its spectroscopic properties with those of $C_5H_{14}N_2$, obtained in the SF_4/Me_2NH reaction. The reaction vessel contained a viscous deep red oil.

8. Reaction of SF_4 with $Me_3SiN(Et)PPh_2$.

$Me_3SiN(Et)PPh_2$ was obtained from Dr. R. Keat (Glasgow University) and was purified by distillation before use.

(4·0 m.m.) of SF_4 and (0·46 g.; 1·5 m.m.) of $Me_3SiN(Et)PPh_2$ reacted on warming to room temperature. The volatile products, identified by infra-red spectroscopy, were excess SF_4 and Me_3SiF. A n.m.r. spectrum of the least volatile products (tipped under vacuum into a n.m.r. tube) revealed Ph_2PF_3 and a very small amount of $Ph_2P(O)F$.[211]

	J_{P-F_a}	J_{P-F_e}	δ_{F_a}	δ_{F_e}
Ph_2PF_3	835	970	34·8	79.2
Literature	838	970	33·5	78.7

$Ph_2P(O)F$ J_{P-F}, 1019; δ_F, 73·8;

Literature J_{P-F}, 1019; δ_F, 74·1;

The liquid residue also contained a compound which showed ethyl protons in the n.m.r. and is regarded as $(EtNS)_x$.

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