Fluorination of Dimethyl Sulphide. Formation of the Fluorodimethylsulphonium Cation, $[Me_2SF]^+$, and Dimethylsulphur Difluoride, Me_2SF_2 †

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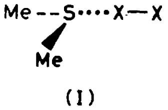
The controlled reaction of dimethyl sulphide with xenon difluoride in a non-acidic medium gives rise *via* CH_2FSMe to a product best formulated as $[Me_2SCH_2SMe]^+[F(HF)_n]^-$. In HF solution at −23 °C, however, the reaction affords the fluorodimethylsulphonium cation, $[Me_2SF]^+$, solid derivatives of which have also been prepared by the reaction of XeF_2 with $Me_2S{\cdot}A$ (A = BF_3 or AsF_5); the species have been characterised by their ^1H and ^{19}F n.m.r. and vibrational spectra. With $CDCl_3$ as a diluent, Me_2S reacts with an excess of AgF_2 at −23 °C to provide the first evidence of the thermally unstable dimethylsulphur difluoride, Me_2SF_2. The ^1H and ^{19}F n.m.r. spectra have served to characterise the new compound and to chart its decomposition (to CH_2FSMe) and other reactions.

Fluorine is unique among the halogens in stabilising sulphur in simple binary molecules of the types SX_4 and SX_6. Of the sulphur(IV) halides, for example, only the fluoride exhibits thermal stability at temperatures above −30 °C,[1] although both the trichlorosulphonium and tribromosulphonium cations have been identified as salts of anions such as $[AsF_6]^-$ and $[SbF_6]^-$.[2] Halogenation of dimethyl sulphide leads to the compounds Me_2SBr_2 and Me_2SI_2 which are almost certainly charge-transfer complexes of the form (I)[3] although the electrical conductivity of sulphur dioxide solutions of the bromine compound invites the formulation $[Me_2SBr]^+Br^-$.[4] A similar structure is indicated for the compound Me_2SCl_2 [5,6] and salts containing the cation $[Me_2SCl]^+$ are well characterised.[7] In these circumstances it is remarkable that neither dimethylsulphur difluoride nor the fluorodimethylsulphonium cation has been identified. By contrast, methyl derivatives of phosphorus pentafluoride, Me_nPF_{5-n} (where n = 1—3), have long been familiar, having attracted much attention, for example, in relation to the effects of the organic substituents on both the stereochemistry and susceptibility to ligand exchange.[8] Evidently the analogous sulphur(IV) compounds are not so easy to prepare, purify, and manipulate, as may be judged by the one report testifying to the formation of methylsulphur trifluoride, $MeSF_3$, by the disproportionation of the sulphenyl fluoride MeSF.[9]

Early attempts to fluorinate dimethyl sulphide led to a mixture of perfluorinated products resulting from the cleavage of the S–C bonds.[10] One of the products of the reaction with mercury(II) fluoride was thought to be Me_2SF_2 or Me_2SF_4 which undergoes a further reaction releasing HF in quartz vessels even at low temperatures.[11] More recently perfluoroalkyl sulphides, $(R_f)_2S$, have been successfully fluorinated to form tetravalent compounds of the type $(R_f)_2SF_2$ but the use of fluorine,[12] chlorine monofluoride,[13] or chlorine trifluoride [14] and of conditions liable to result in further unwanted reaction [12,14,15] holds but little promise as a means of inducing dimethyl sulphide to undergo a similar change. That xenon difluoride has some capacity for selective oxidative fluorination is shown by its reactions with diphenyl sulphide,[16] trifluoromethyl phenyl sulphide,[17] and iodomethane.[18] With methylsulphur compounds, however, it has been reported to fluorinate the CH_3 group in accordance with an equation such as (1) (R = Me, Ph, or CF_3),[16,19,20] a reaction which may evolve *via* an intermediate of the type $R(CH_3)SF_2$.

$$RSCH_3 + XeF_2 \longrightarrow RSCH_2F + HF + Xe \quad (1)$$


(I)
X = Br or I

Here we report a study of the oxidative fluorination of dimethyl sulphide and present spectroscopic evidence for the formation of not only the fluorodimethylsulphonium cation, $[Me_2SF]^+$, but also the parent difluoride Me_2SF_2.

Results and Discussion

The Reaction of Dimethyl Sulphide with Xenon Difluoride under Non-acidic Conditions.—The reaction of an excess of dimethyl sulphide with xenon difluoride in Teflon apparatus occurs explosively at room temperature, but moderation by periodic cooling or by the addition of trichlorofluoromethane as an inert diluent causes the separation of a colourless, viscous liquid which is sparingly volatile and the release of 1 mol of xenon gas for every mol of xenon difluoride taken. The liquid gives rise to a ^1H n.m.r. spectrum which is independent of field strength (60 or 90 MHz), temperature (−70 to +40 °C), and solvent (sulphur dioxide, $[^2H_3]$acetonitrile, or anhydrous hydrogen fluoride), and is, we believe, best formulated as $[Me_2SCH_2SMe]^+[F(HF)_n]^-$.

In support of this conclusion we have prepared the hexachloroantimonate(V) salt of the cation $[Me_2SCH_2SMe]^+$ by the reaction (2) [21] and characterised it by elemental analysis

$$Me_2S + CH_2ClSMe + SbCl_5 \longrightarrow [Me_2SCH_2SMe]^+[SbCl_6]^- \quad (2)$$

and by its vibrational and ^1H n.m.r. spectra. On the evidence of the n.m.r. data listed in Table 1, the cation $[Me_2SCH_2SMe]^+$ is common to the salt and to the liquid product of the reaction between dimethyl sulphide and xenon difluoride.

The formation of the cation $[Me_2SCH_2SMe]^+$ requires the presence of acid.[21] If dimethyl sulphide is caused to react with xenon difluoride in the presence of dry caesium fluoride, which removes any traces of hydrogen fluoride, fluoromethyl methyl sulphide, CH_2FSMe, is the only sulphur-containing product. The fluoromethyl derivative cannot be separated completely from dimethyl sulphide by trap-to-trap distillation *in vacuo*. However, a pure sample has been prepared by the reaction of chloromethyl methyl sulphide with mercury-

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† *Non-S.I. units employed:* mmHg ≈ 133 Pa, atm = 101 325 Pa.

Table 1. ^1H Chemical shifts relating to the dimethyl(methylthiomethyl)sulphonium cation

		δ_H/p.p.m.			
Compound	Solvent	$(CH_3)_2S^+$	CH_2	SCH_3	$[F(HF)_n]^-$
$[(CH_3)_2SCH_2SCH_3]^+Cl^-$	SO_2	3.03	4.50	2.40	
$[(CH_3)_2SCH_2SCH_3]^+[SbCl_6]^-$	SO_2	3.02	4.43	2.43	
$[(CH_3)_2SCH_2SCH_3]^+[SbCl_6]^-$	CD_3CN [a]	2.98	4.50	2.40	
$[(CH_3)_2SCH_2SCH_3]^+[BF_4]^-$	CD_3NO_2 [a]	2.98	4.53	2.38	
$[(CH_3)_2SCH_2SCH_3]^+[BF_4]^-$	CF_3CO_2H [b]	2.99	4.47	2.40	
$(CH_3)_2S + XeF_2$ reaction product	CD_3CN	2.93	4.51	2.37	10.6
	Neat	2.9	4.5	2.4	11.2
	SO_2	3.02	4.48	2.47	11.0
	HF	3.00	4.46	2.46	8.05

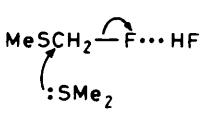
[a] Ref. 21. [b] C. P. Lillya, E. F. Miller, P. Miller, and R. A. Sahatjian, *Int. J. Sulphur Chem., Part A*, 1971, **1**, 79.

$$Me_2S + XeF_2 \xrightarrow[-HF,\ -Xe]{\text{Step 1}} CH_2FSMe \xrightarrow[+Me_2S,\ +HF]{\text{Step 2}} [Me_2SCH_2SMe]^+[F(HF)_n]^-$$

Scheme 1.

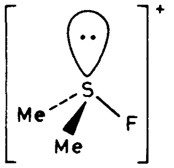
(II) fluoride at room temperature and characterised by elemental analysis and by its vibrational and ^1H and ^{19}F n.m.r. spectra. Hence it has been possible to confirm that this is indeed the product of the dimethyl sulphide–xenon difluoride reaction in strictly acid-free conditions.

These observations can be linked by the reaction sequence given in Scheme 1 in which step 2 involves nucleophilic displacement of fluoride ion by dimethyl sulphide, a reaction catalysed by the acid present. The susceptibility of $MeSCH_2F$ to such a reaction is signalled by what appears to be an unusually low C–F stretching frequency (1 009 cm^{-1}, see Table 4); this suggests a weak C–F bond compatible with an appreciable contribution from the canonical form $[MeS{=}CH_2]^+F^-$. A similar displacement occurs when fluoromethyl methyl sulphide is dissolved in hydrogen fluoride, as revealed by the ^1H and ^{19}F n.m.r. spectra of the solution [equation (3)].



$$2CH_2FSMe \xrightarrow{HF} [Me(CH_2F)SCH_2SMe]^+[F(HF)_n]^- \quad (3)$$

The Fluorodimethylsulphonium Cation, $[Me_2SF]^+$.—Since certain reactions of xenon difluoride appear to be catalysed by traces of acid,[22] we investigated the use of anhydrous hydrogen fluoride as a reaction medium. With an excess of dimethyl sulphide, xenon difluoride reacts at −23 °C to give a new singlet resonance at $\delta_H = 3.7$ in the ^1H n.m.r. spectrum of the hydrogen fluoride solution. This decays swiftly when the solution is allowed to warm up to +35 °C giving place to the spectrum characteristic of the $[Me_2SCH_2SMe]^+$ cation. However, if the reaction is carried out at −23 °C with strictly equimolar proportions of the reagents, the ^1H and ^{19}F n.m.r. spectra of the solution at +35 °C each reveal the development of a single broad resonance; cooling the sample to −30 °C causes the ^1H resonance at $\delta_H = 3.7$ to be resolved into a doublet and the ^{19}F resonance at $\delta_F = -190$ simultaneously to be resolved into a septet ($J_{FH} = 21$ Hz). These results indicate unequivocally the formation of the novel fluorodimethylsulphonium cation, $[Me_2SF]^+$, a conclusion supported by analogy with the ^{19}F n.m.r. spectrum of the isoelectronic species fluorodimethylphosphine, Me_2PF, a liquid at ambient temperatures with $\delta_F = -195.5$.[23] In hydrogen fluoride solution, then, it appears that dimethyl sulphide is converted by xenon difluoride into dimethylsulphur difluoride in the form $[Me_2SF]^+[F(HF)_n]^-$ which is long-lived at ambient temperatures. Attempts to isolate free dimethylsulphur difluoride by evaporation of the solvent *in vacuo* have proved unsuccessful: at −45 °C it was impossible to remove all the hydrogen fluoride whereas the use of higher temperatures resulted in decomposition. In a less acidic medium the reaction of dimethyl sulphide with xenon difluoride does not take place at a temperature low enough to permit the identification of any intermediate along the pathway leading to fluoromethyl methyl sulphide.



(II)

Adducts of the type $Me_2SF_2{\cdot}A$ (A = BF_3 or AsF_5) can be prepared most conveniently by the smooth reaction of the appropriate dimethyl sulphide adduct $Me_2S{\cdot}A$ with xenon difluoride dissolved in anhydrous hydrogen fluoride. At room temperature they are moisture-sensitive white solids with a negligible dissociation pressure which have been characterised by elemental analysis. The presence in hydrogen fluoride solution of the cation $[Me_2SF]^+$, (II), is demonstrated by the ^1H and ^{19}F n.m.r. spectra (see Table 2) which are closely akin to those of a similar solution containing the product of the Me_2S–XeF_2 reaction. One difference between the spectra is that, whereas the Me_2S–XeF_2 reaction product gives well resolved multiplet resonances only with the sample at −30 °C, $Me_2SF_2{\cdot}BF_3$ gives the same results at +35 °C (see Figure 1). This suggests that fluoride exchange involves a reaction such as (4) which is retarded by the ability of BF_3 to reduce the concentration of $[HF_2]^-$ ions, *viz.* equation (5).

$$[Me_2SF]^+ + [HF_2]^- \rightleftharpoons Me_2SF_2 + HF \quad (4)$$

$$[HF_2]^- + BF_3 \rightleftharpoons [BF_4]^- + HF \quad (5)$$

For a fuller characterisation of the adducts $Me_2SF_2{\cdot}A$ in the solid state and in hydrogen fluoride solution, we have examined their vibrational spectra, with the results summarised in Table 3. In practice, the Raman spectra of the

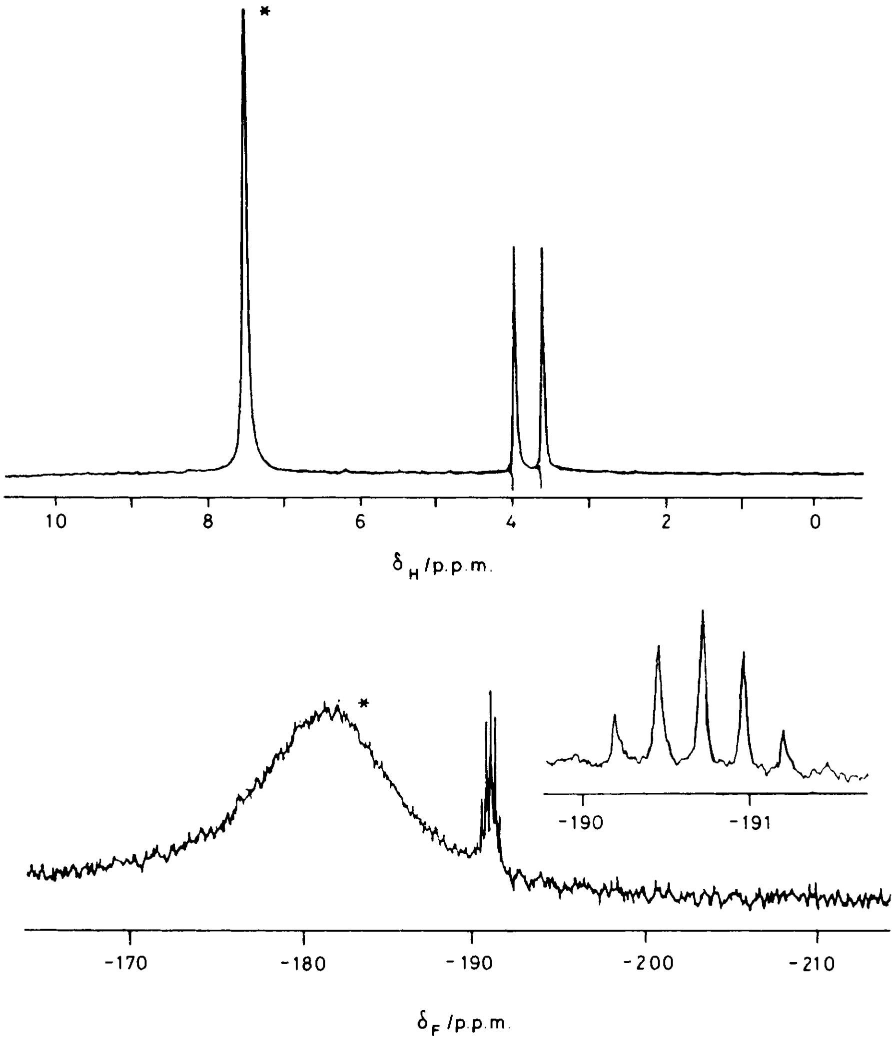


Figure 1. 60-MHz ^1H and 84.6-MHz ^{19}F n.m.r. spectra of $[Me_2SF]^+[BF_4]^-$ in HF solution at 35—40 °C. Solvent resonances are indicated by asterisks

samples provided the more reliable results; for solid samples sandwiched between AgCl windows only was it possible to record any i.r. spectra and these were invariably of relatively poor quality with broad and rather ill defined absorptions. There is no doubt that certain bands in both the Raman and i.r. spectra originate in vibrations of the anions $[BF_4]^-$ [24] and $[AsF_6]^-$ [25] and that the remaining features are more-or-less common to all the samples studied. Several of these features arise from internal vibrations of the methyl group which can be identified by analogy with spectroscopically well characterised compounds like Me_2SO;[26] only the CH_3 torsional modes appear to have escaped detection and these are probably to be found outside the range of the present studies ($\leqslant 250$ cm^{-1}). However, the focus of interest is provided by the vibrational properties of the C_2SF skeleton of the $[Me_2SF]^+$ unit.

In common with the isoelectronic species Me_2SO and Me_2PF, the $[Me_2SF]^+$ ion may be expected to have a trigonal pyramidal framework (II) with C_s symmetry. In these circumstances the C_2SF skeleton has six vibrational fundamentals spanning the representation $4a' + 2a''$. Analogy with the vibrational properties of the molecules Me_2SO and Me_2S [26] suggests that the scattering near 640 and 690 cm^{-1} in the Raman spectra of the Me_2SF_2 adducts corresponds to the symmetric (a') and antisymmetric (a'') S–C stretching modes respectively. Less straightforward is the assignment of the S–F stretching mode (a'). A similar problem exists with the i.r. spectrum of the isoelectronic species Me_2PF,[23] where coupling between the a' stretching fundamentals of the C_2PF unit precludes the assignment of a distinct P–F stretching mode. There is a further complication in that the region 800—1 000 cm^{-1}, where the P–F or S–F stretching mode might be expected to occur, includes also rocking modes of the CH_3 groups.[23,26] Such precedents as exist suggest that the third stretching fundamental of the C_2SF skeleton of the $[Me_2SF]^+$ unit is located between 800 and 900 cm^{-1}, perhaps corresponding to the strong i.r. absorption of the solid BF_3 adduct at 870 cm^{-1} or the Raman scattering of a solution of this adduct at 831 cm^{-1}. The remaining fundamentals involve either symmetric (a') or antisymmetric (a'') deformation of the C_2S–F unit and bending of the C–S–C unit (a'). Tentative assignments of these modes are proposed in Table 3. The most conspicuous feature is the intense band which appears near 435 cm^{-1} in the Raman spectra of the solid adducts but moves to 511 cm^{-1} in the spectrum of the BF_3 adduct in hydrogen fluoride solution. Although we have attributed the band to the symmetric C_2S–F deformation mode, its relatively high intensity and response to change of phase point not only

Table 2. ^{1}H and ^{19}F n.m.r. parameters for $[Me_2SF]^+$ and Me_2SF_2 and related species

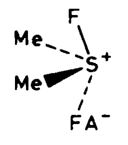
Species	Medium	δ_H/p.p.m.	δ_F/p.p.m.	J(FH)/Hz	Source
Me_2S	$CDCl_3$ solution	2.30	—	—	This work
Me_2SO	$CDCl_3$ solution	2.60	—	—	This work
CH_2FSMe	Pure liquid	CH_3 2.21, CH_2 5.41	−189.6	^2J 54.0, ^4J 2.4	This work
	$CDCl_3$ solution	CH_3 2.29, CH_2 5.43	−189.0	^2J 54.0, ^4J 2.4	This work
	CD_3CN solution	CH_3 2.26, CH_2 5.63	−188.6	^2J 54.0, ^4J 2.6	Ref. 16
$[Me_2SF]^+$	HF solution	3.73	−190.7	^3J 20.7	This work
Me_2PF	Pure liquid	1.45	−195.5	^3J 18.5	Ref. 23
Me_2SF_2	$CDCl_3$ solution	3.27	+0.1	^3J 12.8	This work
Me_3PF_2	$CDCl_3$ solution	1.74	−8.9	^3J 12.7	Ref. 20

Table 3. Vibrational wavenumbers of the adducts $[Me_2SF]^+[BF_4]^-$ and $[Me_2SF]^+[AsF_6]^-$ compared with those of the species Me_2PF, Me_2SO, and Me_2S

I.r.	Raman						
$[Me_2SF]^+[BF_4]^-$ solid	$[Me_2SF]^+[AsF_6]^-$ solid	$[Me_2SF]^+[BF_4]^-$ solid	$[Me_2SF]^+[BF_4]^-$ in HF	Me_2PF I.r. vapour [a]	Me_2SO I.r. + Raman [b]	Me_2S I.r. + Raman [b]	Assignment
		3 065 (sh)					Combination band
3 020w	3 027mw	3 034m	3 035m	2 975s	3 010	2 992, 2 972	Antisym. C–H str.
2 930w	2 945s	2 946s	2 941vs	2 910m	2 933	2 938	Sym. C–H str.
1 440m		1 430 (sh) 1 405m	1 412m	1 430s	1 455, 1 440 1 419, 1 405	1 438	Antisym. CH_3 def.
1 290w				1 290s	1 319, 1 304	1 315	Sym. CH_3 def.
					1 102		S=O str.
1 050vs, br							ν_3 $[BF_4]^-$
			987w	948s	1 016	1 030	CH_3 rock. + S–F or P–F str.
900 (sh)					1 006	973	
870s				883s	953	950	
			831m	878 (sh)	933	902	
770w		770s	771m				ν_1 $[BF_4]^-$
	695 (sh)	701m	681vs	760vs	695	742	Antisym. S–C or P–C str.
	681s						ν_1 $[AsF_6]^-$
645vw	642m	645s		690s	672	694	Sym. S–C or P–C str.
	582m						ν_2 $[AsF_6]^-$
530s		548w	538 (sh)				ν_4 $[BF_4]^-$
	436s	435vs	511vs	460w	382		Sym. C_2X–Y def.[c]
	370w						ν_5 $[AsF_6]^-$
		356w	361w				ν_2 $[BF_4]^-$
		316w	316w		333		Antisym. C_2X–Y def.[c]
		278m			308	282	C–S–C def.

w = Weak, m = medium, s = strong, v = very, br = broad, and sh = shoulder; str. = stretching, def. = deformation, and rock. = rocking

[a] See ref. 23. [b] Vapour or liquid; see ref. 26. [c] X = P or S; Y = F or O.



(III)

A = HF, BF_3, or AsF_5

to vibrational coupling but also to significant fluorine bridging between the $[Me_2SF]^+$ cation and its environment, as represented for example in (III). In these circumstances, the so-called C_2S–F deformation may assume much of the character of a symmetric stretching vibration of the $FMe_2S \cdots F$ unit thus accounting for its relatively high intensity in Raman scattering. Similar arguments involving fluorine bridging have been advanced to explain the Raman spectrum of liquid sulphur tetrafluoride,[27,28] and are likely also to apply to sulphur tetrafluoride complexes like $[SF_3]^+[BF_4]^-$ whose crystal structure reveals significant secondary interactions to produce five-fold co-ordination of the sulphur atom.[27,29] Correlating with the symmetric C_2S–F deformation of $[Me_2SF]^+$ is the symmetric deformation mode ν_2 (a_1) of the C_{3v} cation $[SF_3]^+$ which appears to have a frequency near 530 cm^{-1},[27] in keeping with the assignment we propose here. The interpretation of the other low-wavenumber features listed in Table 3 follows the patterns set by the related species Me_2SO and Me_2S.[26]

Dimethylsulphur Difluoride.—The sluggishness of the reaction of xenon difluoride at low temperatures prompted us to look for a more facile oxidative fluorinating agent. One such agent is silver(II) fluoride which has been successfully used for the preparation of aryl-[30] or perfluoroalkyl-[31]sulphur trifluorides from the corresponding disulphides and of dimethylselenium difluoride from dimethyl selenide.[32] We have found that dimethyl sulphide dissolved in deuteriochloroform reacts with an excess of silver(II) fluoride at −23 °C over a period of 6 h to give a colourless solution shown by its ^{1}H and ^{19}F n.m.r. spectra to contain a single new

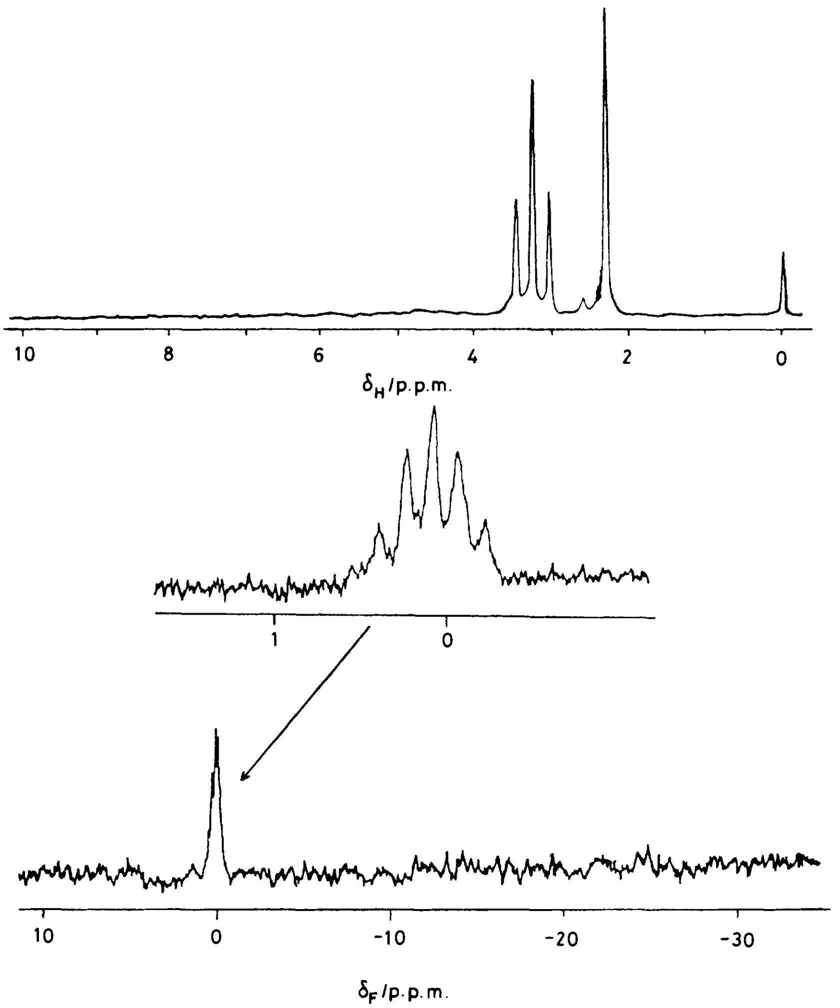
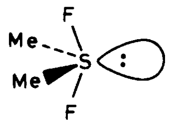


Figure 2. 60-MHz ^1H and 84.6-MHz ^{19}F n.m.r. spectra of Me_2SF_2 in $CDCl_3$ solution at 35—40 °C. The singlet resonance at $\delta_H = 2.30$ p.p.m. is due to unchanged Me_2S



(IV)

species (Figure 2). The appearance of a triplet at $\delta_H = 3.27$ in the ^1H spectrum and of what appears to be a septet at $\delta_F = +0.1$ in the ^{19}F spectrum with an identical coupling constant ($J_{FH} = 12.8$ Hz) argues persuasively that this species is the monomeric molecule dimethylsulphur difluoride which has hitherto eluded characterisation. We presume that the molecule has the structure (IV) analogous to that recently determined by electron diffraction for the gaseous $(CF_3)_2SF_2$ molecule,[33] and also in line with those of the fluorophosphoranes, Me_nPF_{5-n},[34] with the two methyl groups occupying equatorial sites and the two fluorine atoms axial sites of a trigonal bipyramid centred on the sulphur atom.

Dimethylsulphur difluoride decomposes rapidly at ambient temperatures. Thus, in deuteriochloroform solution, we found that decomposition occurred within 5 min at +35 °C, as witnessed by the ^1H and ^{19}F n.m.r. spectra. The ^1H triplet and ^{19}F septet resonances disappeared with the simultaneous development of the features characteristic of fluoromethyl methyl sulphide, CH_2FSMe (see for example Figure 3). A similar decomposition has been described for the compound 'dimethylsulphur dichloride' most plausibly formulated as $[Me_2SCl]^+Cl^-$;[5,6] this decomposes at temperatures above 0 °C with the formation of chloromethyl methyl sulphide, CH_2ClSMe.

Dimethylsulphur difluoride is expected to have a vapour pressure in the order of 10—30 mmHg at ambient temperatures. However, fractionation at low temperatures has so far failed to yield a pure sample of the compound and attempts to record its i.r. spectrum in the vapour phase have been similarly fruitless. On the other hand, deuteriochloroform solutions of the compound have been shown, mainly on the evidence of n.m.r. measurements, to undergo the reactions summarised in Scheme 2. The formation of Me_2SO in conditioned Pyrex apparatus at −23 °C implies that Me_2SF_2, like $MeSF_3$[9] and Me_2SeF_2,[32] attacks glass. Exposure of a cold deuteriochloroform solution of Me_2SF_2 to an atmosphere of BF_3 led to the immediate formation of a white precipitate. Evaporation *in vacuo* of the material volatile at −23 °C left the white solid which dissolved in anhydrous hydrogen fluoride to give a solution whose ^1H and ^{19}F n.m.r. spectra testified to the presence of the cation $[Me_2SF]^+$.

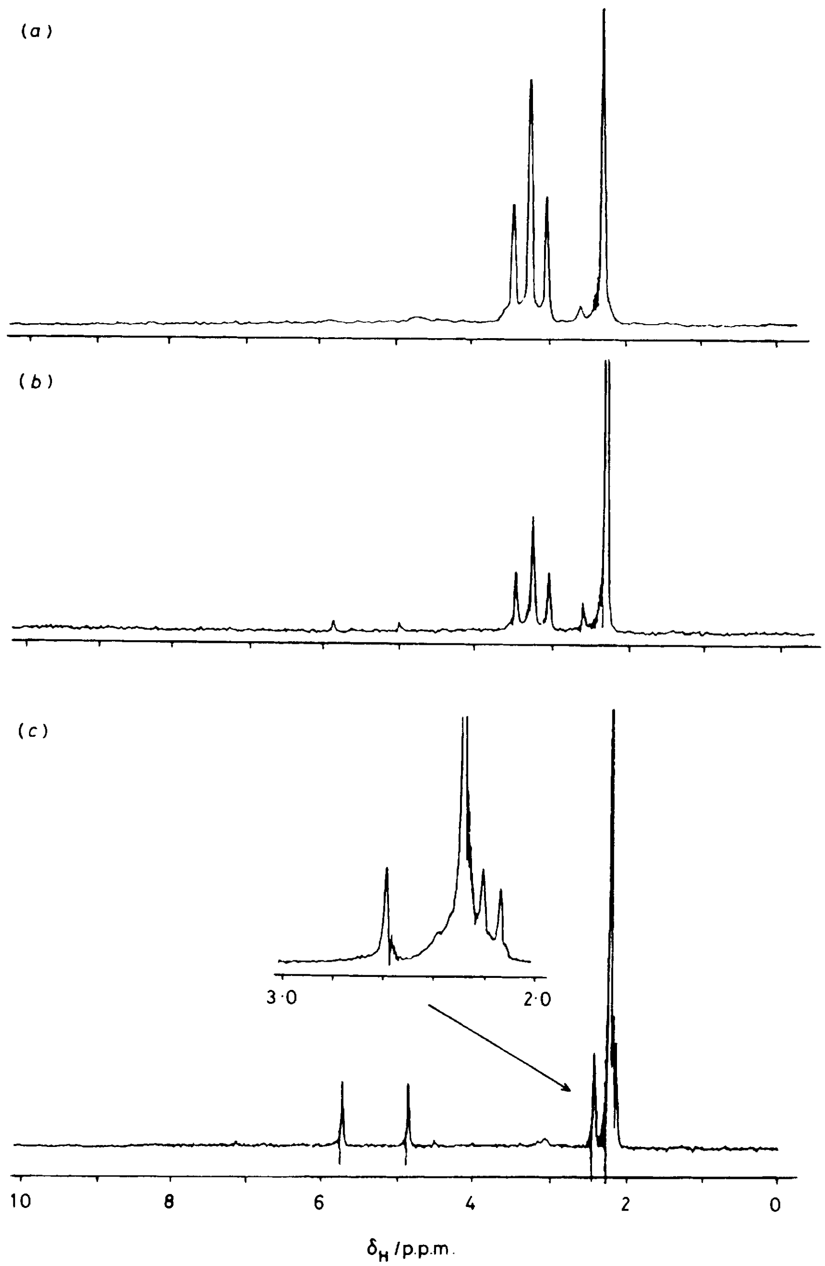


Figure 3. 60-MHz ^1H n.m.r. spectra showing the decomposition of Me_2SF_2 in $CDCl_3$ solution at 35 °C and $t = 0$ (*a*), 1 (*b*), and 5 min (*c*). The weak singlet resonance near $\delta_H = 2.6$ p.p.m. may be due to Me_2SO

Experimental

Apparatus.—Most experiments were carried out with a vacuum system constructed in Teflon-FEP tubing with polytetrafluoroethylene (p.t.f.e.) couplings and needle valves (Production Techniques Ltd.). Apparatus was conditioned before use by exposure overnight to fluorine gas at a pressure of 1 atm. A conventional glass vacuum system was available for the purification of dimethyl sulphide (BDH) and solvents, and a nitrogen-filled glove-box was used for the storage and transfer of solid materials.

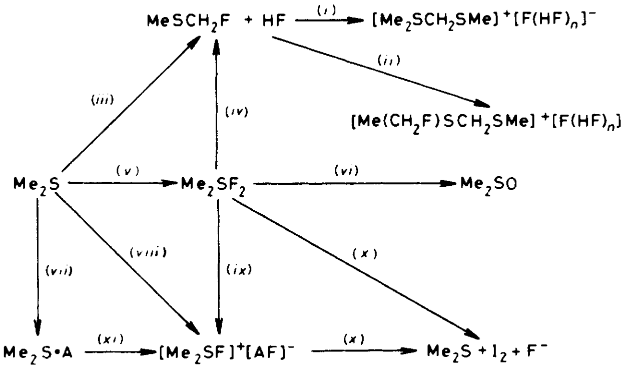
Chemicals.—Xenon difluoride was prepared by exposure to sunlight of a Pyrex bulb containing an equimolar xenon–fluorine mixture, typically for about 1 week.[35] Arsenic pentafluoride was prepared by the action of elemental fluorine on metallic arsenic in a Monel bomb.[36] Boron trifluoride (BDH), silver(II) fluoride (Aldrich), mercury(II) fluoride (Alfa), and caesium fluoride (Alfa, 99.9%) were used as supplied. Hydrogen fluoride (BDH, 99.8%) was purified before use by double distillation from Teflon-FEP traps held at −63 °C.

Spectrometers.—N.m.r. spectra were recorded with the aid of two spectrometers, a JEOL PMX-60 (^1H, 60 MHz) and a Perkin-Elmer R32 (^1H, 90 MHz; ^{19}F, 84.6 MHz), the latter being used for low-temperature measurements. Each sample was normally sealed in a section of FEP tubing 5—10 cm long and 4 mm in external diameter which was inserted into a standard 5-mm precision n.m.r. tube.[37] Chemical shifts were referenced, where possible, to internal $SiMe_4$ or $CFCl_3$; with hydrogen fluoride solutions, ^1H shifts were measured by

Table 4. Vibrational spectra of CH_3SCH_2F and CD_3SCD_2F

CH_3SCH_2F I.r. vapour [a]	CH_3SCH_2F Raman liquid	CD_3SCD_2F I.r. vapour [b]	Assignment
3 010w	2 994m	2 287mw	C–H (C–D) str.
2 940vw	2 935s	2 130mw	
	2 845w		2 × antisym. CH_3 def.
	1 432w		CH_3 (CD_3) def.
	1 384vw	1 177 (sh)	
1 340m		1 169s	
	1 306vw	1 100s	
	1 241vw	1 070m	
1 190m	1 163vw	893 (sh)	CH_2 (CD_2) def.
1 009s		972s	C–F str.
950m	951w, br	880mw, br	CH_3 (CD_3) rock.
810m			
b	761m		C–S str. + C–F def.
710 (sh)	700s	670w	
540w		575w	
	400w		

[a] Sample contained in a stainless-steel cell fitted with AgCl windows.
[b] Region obscured by absorption due to CH_2Cl_2 impurity.



Scheme 2. Formation and chemical reactions of dimethylsulphur difluoride. (*i*) Me_2S; (*ii*) HF; (*iii*) XeF_2–CD_3CN or XeF_2–$CFCl_3$ + CsF; (*iv*) heat; (*v*) AgF_2–$CDCl_3$; (*vi*) Pyrex; (*vii*) A = $(HF)_n$, BF_3, or AsF_5; (*viii*) XeF_2–HF; (*ix*) BF_3; (*x*) I^-(aq); (*xi*) XeF_2

sample interchange using CH_2Cl_2 (δ_H = 5.30 p.p.m.) as a secondary standard.

Infrared spectra of solid samples were measured with a Pye Unicam model SP 2000 spectrophotometer. Raman spectra of solids and liquids, measured with a Spex Ramalog 5 spectrophotometer, were excited at λ = 514.5 nm using the output from a Spectra-Physics model 165 Ar^+ laser. The Raman samples were contained in thin-walled Teflon-FEP tubing, and due allowance was made for the scattering due to the container which was in keeping with that reported elsewhere.[24a]

Elemental analyses were performed by the Analytische Laboratorien Elbach, Engelskirchen, West Germany on samples sealed under vacuum in Teflon-FEP ampoules.

Fluorination of Dimethyl Sulphide.—Experiments were performed with vessels constructed from p.t.f.e. components (Chemcon, Production Techniques Ltd.) and heat-moulded Teflon-FEP tubing. The internal capacity of the vessel was typically 5—10 cm³. With the completion of the reaction, the contents of the reaction chamber could be transferred either by distillation or by decanting into a side-arm which was then sealed for analysis, typically by n.m.r. spectroscopy.

(*a*) *Reactions with* XeF_2. **CAUTION:** Xenon difluoride reacts explosively with dimethyl sulphide in the absence of a diluent. Although no violent reactions occurred with $CFCl_3$, CD_3CN, or HF as the diluent, suitable shielding should be employed at all times.

(*i*) *Preparation of* $[Me_2SCH_2SMe]^+[F(HF)_n]^-$. A mixture of XeF_2 (50—65 mg, 0.3—0.4 mmol) and an excess of Me_2S (*ca.* 0.5 mmol) with $CFCl_3$ (*ca.* 2 cm³) as a diluent was allowed to warm up from 77 K in a closed, passivated reaction vessel. At room temperature there was a mild reaction with the evolution of xenon in >95% yield and the separation of a dense liquid. Apart from xenon, the only volatile materials to be recovered from the mixture at −23 °C were $CFCl_3$ and the excess of Me_2S. The residue was a colourless, viscous liquid with a vapour pressure ⩽ 1 mmHg at ambient temperatures; elemental analysis gave the following results (%):

	C	H	F	S
ound	23.8	6.1	37.7	32.3 *
$C_2H_6F_2S$ requires	24.0	6.0	38.0	32.0
$[Me_2SCH_2SMe]^+[F(HF)_3]^-$ requires	23.8	7.0	37.6	31.7

* Estimated by difference.

The Raman spectrum of the neat liquid exhibited the following features (cm⁻¹): 3 020m, 2 940vs, 1 430m, 760 (sh), 753m, 695s, 640s, 596m, 310m, and 240m (s = strong, m = medium, sh = shoulder, v = very). The liquid $[Me_2SCH_2SMe]^+Cl^-$ and the solid $[Me_2SCH_2SMe]^+[SbCl_6]^-$ showed very similar spectra (with due allowance for features associated with the $[SbCl_6]^-$ anion).[20] The i.r. spectrum of the vapour over the liquid implied decomposition to form Me_2S and an HF adduct $MeSCH_2F \cdots HF$; one of the most prominent features was a strong absorption at 987 cm⁻¹ [940 cm⁻¹ for the product of the reaction between $(CD_3)_2S$ and XeF_2] which is thought to originate mainly in the C–F stretching mode of the co-ordinated $MeSCH_2F$ moiety.[20]

(*ii*) *Preparation of* $[Me_2SF]^+[BF_4]^-$. The adduct $Me_2S{\cdot}BF_3$ was prepared immediately prior to use by direct combination of Me_2S and BF_3 at −77 °C.[38] A portion (*ca.* 170 mg, 1.3 mmol) reacted with XeF_2 (205 mg, 1.2 mmol) in HF solution at 0 °C for 10 min. Evaporation of the materials volatile at 0 °C left a white powder (175 mg) (Found: C, 14.4; H, 3.75; F, 55.9; S, 19.3. $[Me_2SF]^+[BF_4]^-$ requires C, 14.3; H, 3.6; F, 56.5; S, 19.1%). On the basis of the amount of XeF_2 taken, the yield was 81%.

(*iii*) *Preparation of* $[Me_2SF]^+[AsF_6]^-$. The novel adduct $Me_2S{\cdot}AsF_5$ was prepared by direct combination of Me_2S and AsF_5 at −23 °C and isolated at room temperature as an involatile, off-white solid. Xenon difluoride (85 mg, 0.50 mmol) and $Me_2S{\cdot}AsF_5$ (120 mg, 0.52 mmol) dissolved in HF (2 cm³) reacted at 0 °C for 10 min. Evaporation of the volatile products gave a white powder (120 mg) (Found: C, 9.0; H, 2.35; F, 49.25; S, 12.0. $[Me_2SF]^+[AsF_6]^-$ requires C, 8.9; H, 2.25; F, 49.25; S, 11.9%). Based on the amount of XeF_2 taken, the yield was 88%.

(*b*) *Reaction with* AgF_2. In experiments with AgF_2 a disc of sintered p.t.f.e. (60—80 µm porosity, Production Techniques Ltd.) was fitted at the entrance to the reaction chamber. In a typical experiment, AgF_2 (*ca.* 600 mg, 4.1 mmol) and CsF (50 mg) were introduced into the main chamber of the vessel; in addition, CsF (*ca.* 5 mg) was introduced into the n.m.r. side-arm. Deuteriochloroform (3 cm³) and Me_2S (*ca.* 1 mmol) were co-condensed with the AgF_2. The mixture was allowed to thaw and the slurry held at −23 °C for 6 h with occasional shaking. A portion of the cold $CDCl_3$ solution was then filtered through the sinter into the n.m.r. side-arm, frozen, and sealed off for analysis.

Preparation of MeSCH$_2$F.—The compound MeSCH$_2$Cl was prepared by the reaction of Me$_2$SO with SOCl$_2$.[39] Chloromethyl methyl sulphide (0.3 cm^3, 3.6 mmol) and HgF$_2$ (500 mg, 2.1 mmol), contained in a Teflon-FEP vessel, reacted vigorously at room temperature and MeSCH$_2$F was isolated by fractionation *in vacuo*, being retained in an FEP trap held at -63 °C. The product was a mobile, colourless liquid stable in FEP apparatus over a period of weeks (Found: C, 29.9; H, 6.1; S, 39.7. MeSCH$_2$F requires C, 30.0; H, 6.3; S, 40.0%). The ^{1}H and ^{19}F n.m.r. spectra tallied with those reported previously.[16] Details of the vibrational spectra are given in Table 4. Dissolution in HF gave evidence for the formation of [Me(CH$_2$F)SCH$_2$SMe]$^+$[F(HF)$_n$]$^-$ [see equation (3)]. N.m.r.: ^{1}H, $\delta = 2.46$ (3 H), 3.00 (3 H), 4.58 (2 H), and 5.93 (2 H, d); ^{19}F, $\delta = -224$ [t, ^2J(FH) = 48.5 Hz].

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