LOWER SULFUR FLUORIDES

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I. Introduction

Five binary sulfur–fluorine compounds, S_2F_2, SF_2, SF_4, SF_6, and S_2F_{10}, are reported in the literature up to 1960. The compound S_2F_2, disulfur difluoride, which is sometimes called "sulfur monofluoride" on the basis of its stoichiometric composition, and SF_2, sulfur difluoride, are designated as "lower" sulfur fluorides because of the low fluorine contents or low oxidation state of sulfur. Frequently the tetrafluoride, SF_4, is also included in this group. In view of recent detailed reviews (*5*, *80*) it will not be dealt with in this article. On the other hand, difluoropolysulfanes, S_nF_2, which are not mentioned in the earlier literature, and the sulfenic acid fluorides, RSF, which are closely related to SF_2, will be considered, since they also contain bivalent sulfur.

Earlier references to SF_2 are questionable. Until recently, too, no exact data about S_2F_2 were available although we must conclude that it was prepared one hundred and sixty years ago. H. Davy wrote in 1813 in his report on "Some Experiments and Observations on the Substances Produced in Different Chemical Processes on Fluor Spar" as follows: "I distilled the fluates of lead and mercury with phosphorus and sulphur. In all experiments of this kind a decomposition took place, and the glass tubes employed were violently acted upon, and sulphurets and phosphorets were formed" (*19*). In fact, disulfur difluoride together with the tetrafluoride results when Hg_2F_2 or HgF_2 is heated with sulfur, although PbF_2 does not react with the elements. Though no analytical data were given, the existence of S_2F_2 was no longer in doubt, when Gore first described a hundred years ago some properties of the product which he obtained on melting a mixture of sulfur and silver fluoride (*28*): "Fluoride of sulphur was found to be a heavy colourless vapour, uncondensable at the temperature of melting ice and at the ordinary atmospheric pressure. It corrodes glass, fumes strongly in the air, and has a characteristic and very powerful dusty odour, not very unlike that of a mixture of chloride of sulphur and sulphurous anhydride." What was actually published until 10 years ago contains only contradictions (*27*). Thus, there are divergences even in the values for the boiling point of S_2F_2 given by different authors (cf. Table I). Clearly, both Centnerszwer and Strenk (*16*) and Trautz and Ehrmann (*85*) were dealing mainly with SiF_4, whereas Ruff (*54*) and Jaenckner (*36*) must have isolated SF_4. An IR spectrum, attributed to S_2F_2, was first published in 1955 (*3*), but it turned out to be the spectrum of thionyl fluoride (*49, 67*).

TABLE I

EARLIER VALUES FOR THE BOILING POINTS OF DISULFUR DIFLUORIDE COMPARED WITH SILICON TETRAFLUORIDE AND SULFUR TETRAFLUORIDE

Compound	Boiling point (°C)	Reference
S_2F_2	−99	Centnerszwer and Strenk (*16*)
	−95 to −85	Trautz and Ehrmann (*85*)
	−38	Ruff (*54*), Jaenckner (*36*)
	−30	Dubnikov and Zorin (*20*)
SiF_4	−96	Handbook value
SF_4	−38	Brown and Robinson (*8*)

Even more obscure is the early history of sulfur difluoride. According to Ruff (*54*), Luchsinger (*48*), Trautz and Ehrmann (*85*), and Dubnikov and Zorin (*20*), it should be formed in very small amounts (4–6%) from the reaction of sulfur with silver fluoride and have a boiling point of −40° to −35° (*48, 54, 85*). It was not possible, however, to isolate the compound in a pure state. Based on a report of Fischer and Jaenckner (*22*), Dubnikov and Sorin believed that they could analyze a mixture of SF_2, S_2F_2, and SF_4 by removing SF_4 with mercury. In fact, however, SF_4 does not react with mercury. Just a few years ago some authors thought

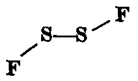
SF_2 to be a blue gas (*50*). It was also repeatedly assumed that S_2F_2 decomposes to sulfur and SF_2 either spontaneously (*26*) or between 200° and 350° (*85*). Cady wrote in Volume 2 of *Advances in Inorganic Chemistry and Radiochemistry*: "If the reader is now confused about S_2F_2 and SF_2, he is in the same position as the writer" (*14*).

Highly developed experimental techniques for handling sensitive and reactive substances, and particularly the use of modern electronic equipment in instrumental analysis during the last 10 years, have finally provided a clearer picture of the compounds S_2F_2 and SF_2, the last problem of volatile binary compounds to be solved. The most surprising results of this recent research have been that SF_2 dimerizes to S_2F_4 (*62*) and that there are two isomers of S_2F_2, the existence of which was established independently by microwave spectroscopy in Harvard University (*41–43*) and in the author's laboratories (*58–60*, *66*, *67*).

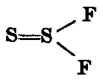
II. The Isomers of Disulfur Difluoride

A. MOLECULAR STRUCTURE AND PHYSICAL DATA

The existence of branch bonding in disulfur dihalides, $S{=}S\genfrac{}{}{0pt}{}{\diagup X}{\diagdown X}$, has long been discussed (*45*, *47*, *81*). Electron diffraction (*51*), IR, and Raman studies (*82*), however, have proved that S_2Cl_2 and S_2Br_2 consist of molecules which have a staggered chain configuration similar to hydrogen peroxide (*2*). There is no definitive proof of a small amount of branch-bonded isomers in S_2Cl_2 and S_2Br_2. Yet fluorine chemistry offered the possibility of two isomers in the series of disulfur dihalides. One of the two isomeric forms of disulfur difluoride (I) has the C_2 structure of disulfane or dichlorodisulfane (disulfur dichloride) (III), while the other (II) has the C_s structure of thionyl fluoride (IV).



(I)



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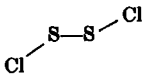

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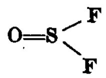


(IV)

They may therefore be named difluorodisulfane and thiothionyl (or thionothionyl) fluoride, respectively. Experimental work with the disulfur difluorides leads to the conclusion that thiothionyl fluoride is the more stable isomer at room temperature; stability for the chainlike and branched arrangement of atoms is exactly the reverse of that for the possible isomers of disulfur dichloride and dibromide.

Detailed information on molecular data for FSSF and SSF_2 is provided by molecular spectroscopy (cf. Table II). It can be seen that bond distances in FSSF are somewhat greater than in SSF_2. This is in accord with the lower stability of FSSF. Moreover, it is interesting to compare molecular dimensions of FSSF with those of HSSH and ClSSCl (cf. Table III) and also those of SSF_2 with OSF_2 and SSO (Table IV). The short distance between the sulfur atoms in FSSF compared with that in HSSH and the long sulfur–fluorine bonds are notable. The distance between the two sulfur atoms of FSSF coincides with that in the

TABLE II

MOLECULAR DATA AND PHYSICAL PROPERTIES OF THE TWO ISOMERS OF DISULFUR DIFLUORIDE

Property		Unit	FSSF	SSF_2	Δ	Refs.
d(SS)		Å	1.888	1.860	0.028	*42, 43*
d(SF)		Å	1.635	1.598	0.037	
$\sphericalangle$(SSF)		deg	108.3	107.5	—	
$\sphericalangle$(FS_2F)		deg	87.9	—	—	
$\sphericalangle$(FSF)		deg	—	92.5	—	
I_A	$FS^{32}S^{32}F$ and $S^{32}S^{32}F_2$	Amu·Å²	44.843	61.808	—	
I_B			181.720	127.397	—	
I_C			196.703	166.668	—	
μ		D	1.45	1.03	—	
f(SS)		dyn/cm	3.72	5.0	−1.28	*12*
f(SF)		dyn/cm	3.21	4.5	−1.29	
b.p.		°C	15	−10.6	25.6	*9, 67*
m.p.		°C	−133	−164.6	31.6	
ΔH_S		kcal/mole	5.97	5.45	—	
ΔS_S		e.u.	20.7	20.8	—	
C_P(298°K)		kcal/deg mole	15.78	14.55	1.23	*12, 13*
$S°$(298°K)		e.u.	70.26	69.97	0.29	
$(H°_{298}-H°_0)$		kcal/mole	3.488	3.175	$1.05-\Delta H°_0$	
$-(F_{298} - H°_0)$		kcal/mole	17.460	17.302	$0.53-\Delta H°_0$	
IE^v_1		eV	10.84	10.68	0.16	*87*
IE^v_2		eV	11.25	11.33	−0.08	
IE^v_3		eV	12.94	12.81	0.13	

TABLE III

Comparative Data for Molecules with Sulfur–Sulfur and Sulfur–Fluorine Bonds

Property	Unit	S_2	HSSH	FSSF	ClSSCl	SF_4	SF_6	Refs.
d(SS)	Å	1.889	2.05	1.888	1.97	—	—	*32, 83, 42, 34*
d(SF)	Å	—	—	1.635	—	1.545 1.646	1.58	*42, 84, 7*
ν(SS)	cm^{-1}	—	5.09	610	538	—	—	*90, 60, 84*
f(SS)	dyn/cm	4.96	2.58	3.72	2.46	—	—	*32, 83, 12, 34*

S_2 molecule. On the other hand, the distance between sulfur and fluorine is even greater than in sulfur hexafluoride and almost as large as the longer S–F bond distance in sulfur tetrafluoride. A particularly strong bond between the sulfur atoms in difluorodisulfane is also indicated by the displacement to higher wave numbers of the IR absorption band associated with the S–S valency vibration. The shortness of the S–S bond and the high-field force may be explained in terms of the formation of a "double bond" which is possible because of the electron-withdrawing action of the fluorine atoms.

TABLE IV

Comparative Data for Thiothionyl Fluoride and Related Compounds

Property	Unit	SSF_2	OSF_2	SSO	S_2	Refs.
d(SS)	Å	1.860	—	1.884	1.89	*43, 36, 32*
d(SF)	Å	1.598	1.585	—	—	*43, 46*
∢ (FSF)	deg	92.5	92.8	—	—	*43, 46*
∢ (FSS)	deg	107.5	—	—	—	*43*
∢ (FSO)	deg	—	106.8	—	—	*46*
f(SS)	dyn/cm	5.0	—	—	—	*12*
f(SF)	dyn/cm	4.5	4.5	4.7	—	*12, 13*

$$\mathrm{F{-}S{-}S{-}F} \leftrightarrow \overset{\ominus}{\mathrm{F}}\ \mathrm{S{=}\overset{\oplus}{S}{-}F}$$

It is of some interest that a similar hypothesis is necessary for dioxygen difluoride (*38*). The molecular data for thiothionyl fluoride are extraordinarily similar to those for thionyl fluoride. The S–S distance again indicates a multiple bond and corresponds with that in disulfur oxide.

Ionization energies of FSSF and SSF_2 have been determined from photoelectron spectra (*87*). The lower first ionization energy (IE) of the more stable isomer and the greater difference between IE_2 and IE_1 of SSF_2 are remarkable.

EHMO and CNDO/2 calculations with or without *d* orbitals give a larger energy of formation for the more stable isomer, and for both isomers comparable orbital sequences (*87*). The value for the heat of atomization of "S_2F_2" (=FSSF?) given by Sanderson (*55*) seems to be erroneous for both isomers, because the bond energy of the sulfur–sulfur bond does not equal the energy of a weak single bond. From the data for the bond energies postulated for the sulfur–fluorine bonds in S_2F_2 and the sulfur–sulfur bond in S_2O, one obtains for the heat of atomization of SSF_2 251.2 kcal/mole corresponding to a heat of formation of −80.2 kcal/mole.

The melting and boiling points of thiothionyl fluoride may be determined without particular difficulty. The melting point of S_2F_2, which has been repeatedly checked (*25*, *67*, *73*), is strikingly low. The extrapolated boiling point of difluorodisulfane appears to be abnormally high for a sulfur–fluorine compound, but that of disulfur dichloride is also very high. The measured vapor pressures (in Torr) are given by the following equations:

$$\text{FSSF } (9): \quad \log_{10} p = 7.44 - 1310/T$$

$$\text{SSF}_2 \ (67): \quad \log_{10} p = 7.415 - 1190/T$$

The heats and entropies of vaporization of difluorodisulfane and thiothionyl fluoride may be determined from the vapor pressure curves. Mixtures of FSSF and SSF_2 solidify to a glass on cooling.

B. PREPARATION AND CHEMICAL BEHAVIOR

As a mixture of the two isomers, mostly contaminated with SF_4, disulfur difluoride may be prepared in various ways. The action of sulfur vapor on silver, mercury(I), or mercury(II) fluorides at 120° to 165° at low pressure (<10 Torr) is a rational route to difluorodisulfane which is formed as a primary product. Minor quantities of sulfur tetrafluoride and thiothionyl fluoride may be separated by partial vaporization. (SF_4 may result from decomposition of a further primary product, sulfur difluoride, and SSF_2 from the isomerization of FSSF.) At extremely low pressures and toward the end of the reaction only slightly volatile difluoropolysulfanes also result in small amounts (cf. Section IV). If the very hygroscopic metallic fluorides are not entirely free of water or oxides, the condensate obtained on cooling with liquid air is colored carmine red by a decomposition product of disulfur monoxide, possibly S_4, and then becomes bright yellow on warming as the result of more stable forms of sulfur. In this case the gaseous mixture also contains thionyl fluoride as a product of the hydrolysis of sulfur tetrafluoride. Disulfur dichloride vapors react with AgF, Hg_2F_2, HgF_2, or active potassium fluoride [which may be prepared by thermal decomposition of potassium fluorosulfite, KSO_2F (*67*)] at 140° to 150°, preferably at low pressures (<10 Torr), to yield a mixture of FSSF and SSF_2. At higher temperatures predominantly SSF_2 is obtained. Lead fluoride does not react with S_2Cl_2. Undecomposed KSO_2F reacts with S_2Cl_2 vapor to yield a mixture of thiothionyl fluoride and sulfur dioxide which cannot be separated by distillation. Toward the end of the reaction fluorochlorodisulfane, FSSCl (m.p. −96.0°, b.p. 96°), is obtained. SSF_2, FSSF, and FSSCl differ so greatly in volatility that they may be separated relatively easily by trap-to-trap distillation.

Another method of forming thiothionyl fluoride is based on the reaction of sulfur with nitrogen trifluoride (*25*).

$$NF_3 + 3S \rightarrow S_2F_2 + NSF$$

In the reaction of sulfur with uranium hexafluoride about 15% S_2F_2 was found in addition to SF_4, which is the main product (*1*).

The fact that both isomers result in the reactions of AgF, Hg_2F_2, and HgF_2 with sulfur and of S_2Cl_2 with KF (although FSSF is often present only in small amounts) indicates that the free enthalpy of the transition FSSF → SSF_2, which is dependent on temperature only to a small extent, amounts to only a few kilocalories per mole. From the infrared spectrum it can be shown that gas samples consisting of pure FSSF or containing a high percentage of it rapidly change in the presence of traces of hydrogen fluoride or boron trifluoride to mixtures which contain a high percentage of SSF_2. (Small amounts of FSSF are difficult to detect in the presence of SSF_2 by IR spectroscopy.) In vessels made of pure nickel which are absolutely free of hydrogen fluoride, FSSF is stable for days at normal temperatures.

Experiments with FSSF can be made only at low temperatures and in the gas phase at low pressures. The more stable isomer SSF_2 which may be heated to at least 250°, has been more fully investigated. In spite of its thermal stability in the pure state, SSF_2 is a thermodynamically unstable compound: it is instantly transformed to sulfur tetrafluoride by catalysts such as HF or BF_3. This reaction is noteworthy, first, because it would be expected that thiothionyl fluoride, like thiosulfuric acid, would decompose to sulfur and sulfur difluoride (*26*).

$$SSF_2 \rightarrow S + SF_2$$

It is also striking that if only traces of HF are present, the sulfur deposits as beautiful crystals. It is surprising that a reaction involving very large numbers of molecules occurs so unequivocally.

$$12S_2F_2 \rightarrow 3S_8 + 8SF_4$$

Finally, it may be mentioned that the conversion of S_2F_2 to SF_4 provides a very advantageous preparation of sulfur tetrafluoride. With the given heat of atomization of SSF_2, the decomposition of two moles of S_2F_2 into one mole of SF_4 and sulfur yields $\Delta H° = 2(251.2) - 327.4 - 3(66.6) = -24.8$ kcal/mole.

In spite of their different structures the chemical behavior of thiothionyl fluoride and difluorodisulfane is very similar. Thus, hydrolysis with pure water gives tetra-, penta-, and hexa-thionic acid and sulfur, in addition to hydrogen fluoride. With alkali hydroxide solutions the main products are thiosulfate and sulfur, in addition to fluoride. Trithionate is the chief sulfur-containing product from the reaction of S_2F_2 with a hydrogen sulfite solution. It can be shown by UV spectroscopy that the primary product in the hydrolysis of both FSSF and SSF_2 in the vapor phase is disulfur monoxide, S_2O, which rapidly decomposes into sulfur

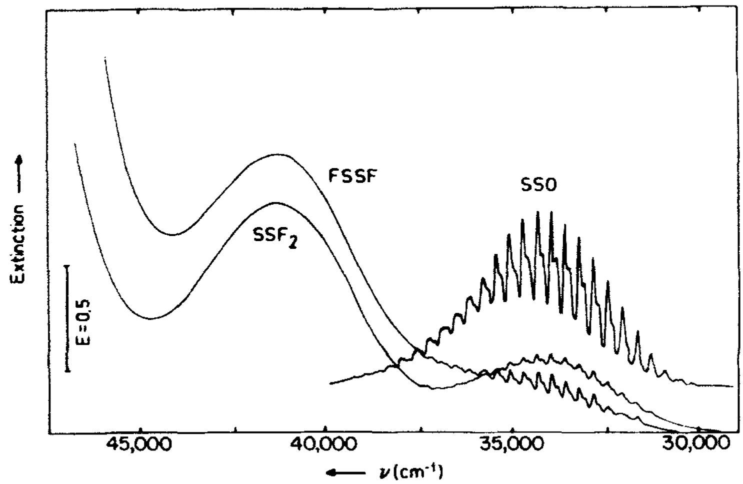


FIG. 1. UV spectra of gas mixtures resulting from the hydrolysis of FSSF ($p = 5$ Torr) and SSF_2 ($p = 3$ Torr). The spectra are recorded 2 min after the commencement of reaction. For comparison the UV spectrum of S_2O is shown. From Ref. (*88*).

and sulfur dioxide (cf. Fig. 1). It seems very likely that the hydrolysis in solution proceeds with S_2O as the first intermediate via the following routes.

$$\begin{aligned} S_2F_2 + H_2O &\rightarrow S_2O + 2HF \\ 2S_2O &\rightarrow SO_2 + 3S \\ S_2O + 2H_2SO_3 &\rightarrow H_2S_4O_6 + H_2O \\ H_2S_4O_6 + S &\rightarrow H_2S_5O_6 \\ H_2S_4O_6 + H_2SO_3 &\rightarrow H_2S_3O_6 + H_2S_2O_3 \end{aligned}$$

SSF_2 and ClSSCl are also very similar in their behavior toward ammonia. The deep dark coloration of the reaction mixture and obvious multiplicity of reaction products are indicative of a very complicated mechanism. From the resulting mixture it is possible to isolate N_4S_4 and heptasulfur imide, S_7NH. The isomers form unstable adducts with trimethylamine (*11*).

At low temperature and pressure FSSF and SSF_2 react with the glass surface only to a limited extent, but at room temperature the glass is vigorously corroded. There are also very significant differences in the reactivity toward normal glass, Pyrex, and quartz glass. The higher the alkali content, i.e., the smaller the degree of cross-linking in the glass, the quicker and more strongly is it attacked. Water and hydrogen fluoride act as catalysts. Two reaction mechanisms may operate which will explain this.

Reaction (*a*)

$$\begin{aligned} 2S_2F_2 + H_2O &\rightarrow 4HF + S_2O \rightarrow S + SO_2 \\ SiO_2 + 4HF &\rightarrow SiF_4 + H_2O \end{aligned}$$

Reaction (*b*)

$$\begin{aligned} 2S_2F_2 &\rightarrow 3S + SF_4 \\ 2SF_4 + 2H_2O &\rightarrow 2SOF_2 + 4HF \\ SiO_2 + 4HF &\rightarrow SiF_4 + 2H_2O \end{aligned}$$

The second series of reactions occurs in the condensed phase in particular. At partial pressures under 10 Torr and temperatures under –50°, S_2F_2 must be handled throughout in Pyrex apparatus. If these conditions are not satisfied, it becomes necessary to work with apparatus made of nickel, special steels, polytetrafluoroethylene, or polytrifluorochloroethylene.

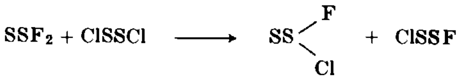
Thiothionyl fluoride burns with a pale blue flame when ignited to yield SO_2, SOF_2, and SO_2F_2. It is also oxidized at higher temperatures by nitrogen dioxide. Surprisingly, a liquid mixture of SSF_2 and N_2O_4 reacts only slowly, being decomposed in the course of days to nitrosyl fluorosulfonate, $NOSO_3F$. This reaction gave the first indication that an equilibrium would exist with a second isomer FSSF.

$$(SSF_2 \rightarrow FSSF) + 6NO_2 \rightarrow 2NO^+SO_3F + 4NO$$

The action of nitrogen dioxide on difluorodisulfane is a characteristic reaction which distinguishes the two isomers. It is also interesting that FSSF and SSF_2 react very rapidly with a clean copper surface to give a black amorphous product. (Disulfur difluoride cannot therefore be prepared in copper apparatus.)

With hydrogen chloride, bromide, and iodide, or with their tetramethylammonium salts, a solution of SSF_2 in liquid sulfur dioxide is decomposed to S_2Cl_2, S_2Br_2, or sulfur and iodine. There is no evidence for the formation of the S_2Cl_2 isomer, thiothionyl chloride, $SSCl_2$, in this reaction. It is of interest that $SOCl_2$ is converted by liquid hydrogen fluoride to SOF_2, whereas S_2Cl_2 does not yield S_2F_2.

In the liquid phase thiothionyl fluoride and dichlorodisulfane react with partial exchange of the halogen atoms. The two isomers of disulfur chlorofluoride which would be expected,



$$SSF_2 + ClSSCl \longrightarrow SS\begin{smallmatrix}F\\Cl\end{smallmatrix} + ClSSF$$

however, are not formed in this case. Instead, in addition to difluorodisulfane, only one new compound is formed, which on the basis of the position of its ^{19}F resonance signal must be fluorochlorodisulfane, FSSCl. In a hypothetical equilibrium between the six compounds FSSF, FSSCl, ClSSCl, SSF_2, SSFCl, and $SSCl_2$ the last two must therefore participate only in very small concentrations.

The compound FSSF reacts with anhydrous methanol even at −100°, whereas SSF_2 remains unchanged up to −30° (*88*). In each case the main products are methyl fluorosulfite, CH_3OSOF, and sulfur. (SF_4 gives CH_3F and SOF_2 with methanol.) The two isomers also differ in their reactivity toward acetone; FSSF reacts in presence of cesium fluoride at 20° to give 2,2-difluoropropane, with SOF_2 and sulfur as by-products, whereas SSF_2 is unchanged in 12 hours at 25°. Both isomers react with benzoic acid at room temperature to give benzoyl fluoride, thionyl fluoride, hydrogen fluoride, and sulfur (*11*).

FSSF and SSF_2 dissolve in fluorosulfonic acid and anhydride-containing sulfuric acid (30% oleum) at low temperatures to give a deep blue color, which is unchanged on prolonged storage at −80° (*70*). On warming, the solution first becomes green, then deep blue, and finally red-brown. UV and ESR spectra indicate that both the blue and the brown solutions contain all sulfur cations, which have been found when sulfur is oxidized with $S_2O_6F_2$ in fluorosulfonic acid (*4*, *24*). Moreover, it was found that in the reaction of S_2F_2 with HSO_3F, disulfuryl fluoride and thionyl fluoride are formed, both of which are also produced in the reaction of SF_4 with HSO_3F.

$$2HSO_3F + SF_4 \rightarrow S_2O_5F_2 + SOF_2$$

When a gaseous mixture of SSF_2 and FSSF is condensed with BF_3 onto an AgCl plate cooled by liquid nitrogen, a compound is formed which is stable only at low temperatures. It shows the infrared bands of the tetrafluoroborate ion at 1040 and 1080 cm^{-1} and a characteristic band at 830 cm^{-1}. Arsenic pentafluoride reacts with S_2F_2 even below $-100°$ in a 1:1 molar ratio to form a compound which also shows a new infrared band at 850 cm^{-1} together with the characteristic bands of AsF_6^-. Clearly, the compounds formed are $S_2F^+BF_4^-$ and $S_2F^+AsF_6^-$. In keeping with this interpretation is the fact that BF_3 catalyzes the conversion of FSSF to SSF_2.

$$FSSF + BF_3 \rightarrow S_2F^+ + BF_4^- \rightarrow SSF_2 + BF_3$$

It is noteworthy that the $\nu_3(F_{1u})$ band of the AsF_6^- ion is split into two components at 691 and 662 cm^{-1}, denoting a lowering of the symmetry of the ion due to the formation of fluorine bridges. This is also shown by the width of the band at 850 cm^{-1}, which is clearly assigned to the S–F valency vibration of the S_2F^+ ion. This broad and intense band probably masks the absorption attributable to S–S vibration. (The maxima of the SF and SS valency bands of SSF_2 are separated by only 8 cm^{-1}.)

The color of $S_2F_2 \cdot AsF_5$ changes on warming to yellow ochre; when heated to 100° or in presence of AsF_5 at room temperature, it becomes deep blue. Finally, with strong heating, it goes to deep red. The blue ($\nu_{max} = 17{,}000$ cm^{-1}) and red products resemble in appearance the compounds $S_8[AsF_6]$ and $S_{16}[AsF_6]$, which Gillespie, Passmore, and Ummat (*24*) have prepared by the reaction of sulfur with AsF_5. The products obtained from S_2F_2 are, however, mixtures in which $SF_4 \cdot AsF_5$ ($=SF_3^+AsF_6^-$) can be also detected by IR and NMR spectra [$\nu_{SF} = \nu_3(E) = 926$ cm^{-1}; $\delta_{FS} = -30$ ppm with respect to $CFCl_3$ in SO_2 solutions]. Moreover, radical cations of sulfur can be detected by the ESR spectrum. Decomposition of $S_2F_2 \cdot AsF_5$ ($=S_2F^+AsF_6^-$) thus differs from the disproportionation of disulfur difluoride to sulfur and SF_4 in that, instead of molecular sulfur, complex sulfur cations are formed since the initially formed negative charge carrier AsF_6^- cannot be decomposed.

It may be concluded from the observations that no free AsF_5 is formed in the decomposition of $S_2F_2 \cdot AsF_5$ that $S_4[AsF_6]_2$ is produced as a main product as well as $SF_3[AsF_6]_2$. The overall equation may be

$$12S_2F[AsF_6] \rightarrow 4SF_3[AsF_6] + 3S_4[AsF_6]_2 + S_8[AsF_6]_2$$

In liquid sulfur dioxide reaction of S_2F_2 with AsF_5 proceeds just as fast as the reaction with fluorosulfonic acid; after initial red coloration a deep blue solution is formed. ^{19}F NMR signals indicate unstable intermediates, which rapidly exchange fluorine, and the presence of two end products which contain fluorine, SF_3^+ and AsF_6^-.

C. Analysis and Spectroscopy

The presence of disulfur difluoride in a mixture of sulfur–fluorine compounds is easily recognized by the separation of sulfur on hydrolysis and also by its decomposition from the gas or liquid phase on the inner wall of glass vessels used for storage. The decomposition of S_2F_2 by glass or quartz powder at higher temperatures (>300°C) also provides a possible method for its quantitative analysis:

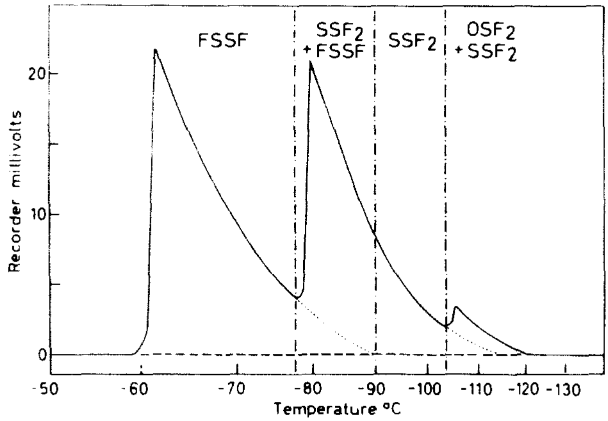


FIG. 2. Separation of a mixture of sulfur fluorides by codistillation.

$$2S_2F_2 + SiO_2 \rightarrow 3S + SO_2 + SiF_4$$

The Cady method of codistillation (*15*) enables the separation of small quantities of pure SSF_2 and FSSF and the quantitative determination of their amount by measuring the areas under the curve of the recorder (cf. Fig. 2).

TABLE V

MASS SPECTRUM OF THE ISOMERS OF S_2F_2[a,b] *(60)*

	Relative abundance	
Particle	FSSF	SSF_2
$S_2F_2^+$	53	71
S_2F^+	23	15
SF_2	0	1
S_2	12	5.5
SF^+	6.5	1
S^+	4.5	6.5
$n_{SF^+}/n_{S_2F_2^+}$	1/8	1/70

[a] At 70 eV. From Ref. *(60)*.

[b] Obtained with a spectrometer Model MS 10 from AEI Sunvic Regler GmbH. The data relate to the portion of the particles containing sulfur.

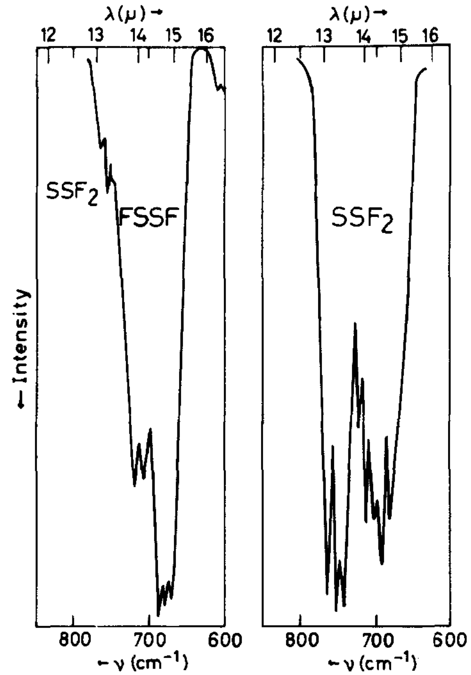


FIG. 3. IR spectra of difluorodisulfane and thiothionyl fluoride.

TABLE VI

INFRARED AND RAMAN FREQUENCIES AND VIBRATIONAL ASSIGNMENTS OF FSSF AND SSF_2 (*12*)

Raman (liquid)		Infrared (gas)		Vibrational assignment	
Frequency (cm^{-1})	Depolarization ratio	Frequency (cm^{-1})	Band contour	Normal mode	Expected band type
FSSF					
193 ± 1.5	0.67 ± 0.05	182.5 ± 0.5	PR	ν_4FSSF (a)	B
297 ± 1.5	0.84 ± 0.05	301 ± 2	PQR	ν_6FSS (b)	A + C
322 ± 1.5	0.60 ± 0.05	319.8 ± 0.3	PR	ν_3FSS (a)	B
623 ± 1.5	0.12 ± 0.01	614.6 ± 0.4	PQR	ν_2SS (a)	B
				[$\nu_3 + \nu_6$ (B)]	A + C
683 ± 1	0.4 ± 0.2	680.8 ± 0.3	PQR	ν_5SF (b)	A + C
		717.0 ± 0.5	PR	ν_1SF (a)	B
		941 ± 2	PR	$\nu_2 + \nu_3$ (A)	B
		1389 ± 1		$\nu_1 + \nu_5$ (B)	A + C
SSF_2					
274 ± 1.5	0.87 ± 0.05	Not observed	—	ν_6SSF (a″)	B
339 ± 1.5	0.60 ± 0.05	330	PQR	ν_4SSF (a′)	A + C
413 ± 1.5	0.45 ± 0.03	411.2	PQR	ν_3FSF (a′)	A + C
650–700	?	692.3	PR	ν_5SF (a″)	B
710 ± 2	0.30 ± 0.02	718.5	PQR	ν_2SS (a′)	A + C
745 ± 2	0.26 ± 0.02	760.5	PQQR	ν_1SF (a′)	A + C

TABLE VII

^{19}F NMR SPECTRA OF SULFUR–FLUORINE COMPOUNDS[a]

Compound	Chemical shift δ (ppm)
FSSF	+122.5
ClSSF	+172
SSF_2	−79.5
OSF_2	−74.5
SF_4	−48 −102

[a] $CFCl_3$ as internal standard. From Ref. (*58*).

The mass spectra of FSSF and SSF_2 (*42*, *60*) differ in the abundance of specific ions produced on fragmentation (cf. Table V). A rapid qualitative estimate of the composition of gaseous mixtures of the S_2F_2 isomers may be based on the infrared spectrum (*60*) which shows characteristic differences for the two compounds in the sodium chloride region (cf. Fig. 3 and Table VI). The UV spectra of the two forms of disulfur

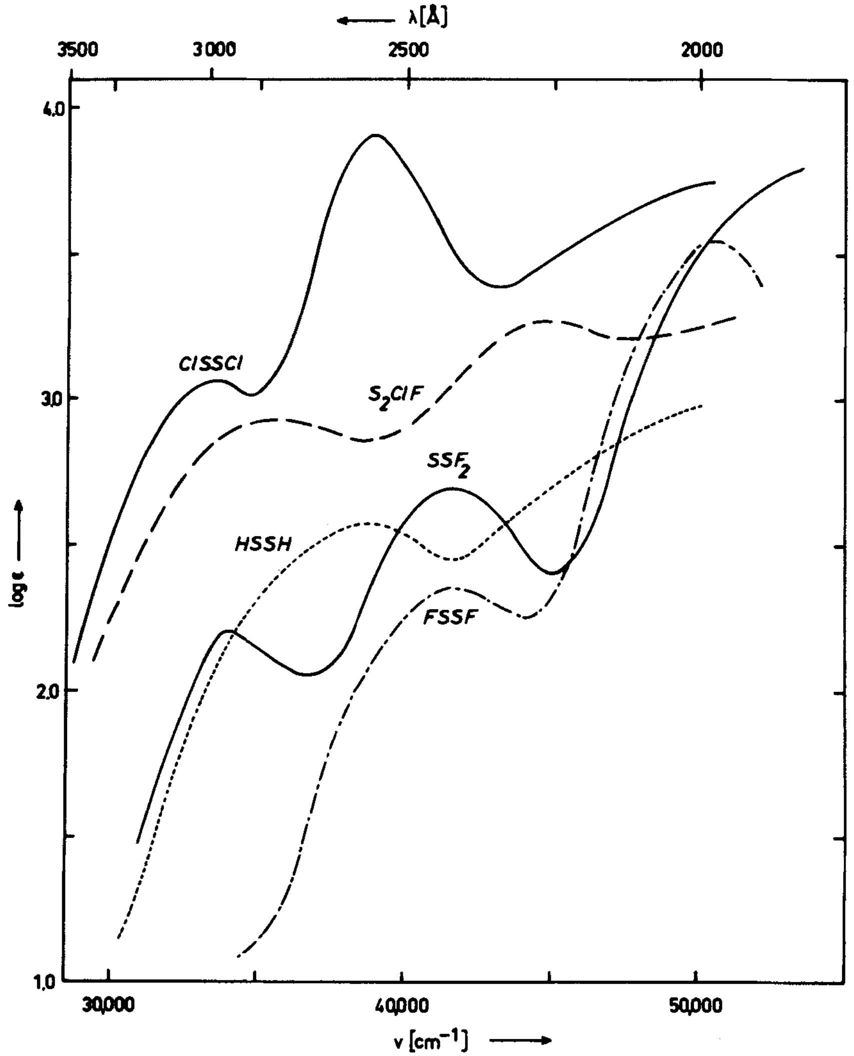


FIG. 4. UV spectra of disulfane, difluoro-, fluorochloro-, and dichlorodisulfane, and thiothionyl fluoride.

difluoride (cf. Fig. 4) also characterize them as different compounds (*77*). The quantitative composition of liquid mixtures of the isomers may be preferably determined by ^{19}F NMR spectroscopy, even in the presence of other fluorine compounds (*65*). Signals for the two isomers are clearly separated from one another; that for thiothionyl fluoride lies close to the signal for thionyl fluoride (cf. Fig. 4 and Table VII). Reactions of FSSF and SSF_2 or their isomerization may be followed very satisfactorily by infrared or NMR spectroscopy (cf. Fig. 5).

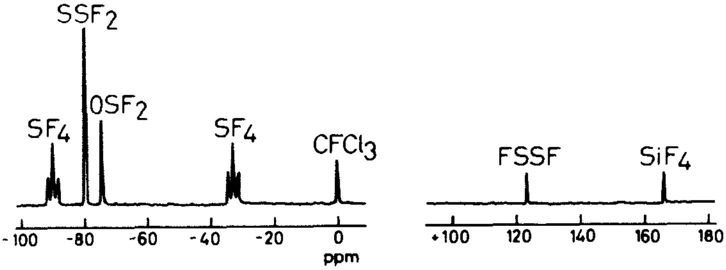


FIG. 5. ^{19}F NMR spectra of difluorodisulfane after 3 hr storage in a glass tube at 20° (temperature at time of measurement −50°).

The photoelectron spectra of the two isomers (*87*) exhibit only small differences (cf. Fig. 6).

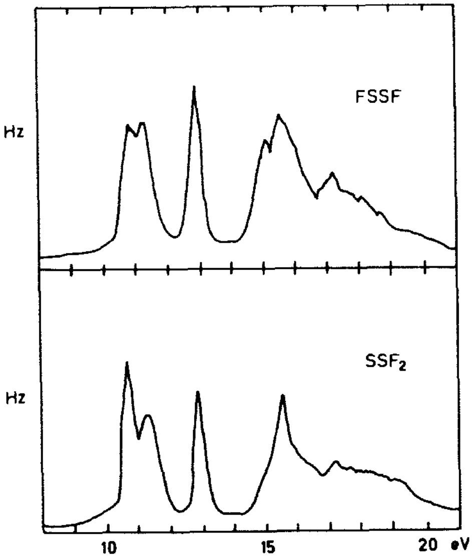


FIG. 6. Photoelectron spectra of difluorosulfane and thiothionyl fluoride.

III. Sulfur Difluoride and Difluorodisulfane Difluoride

A. CAUSE OF INSTABILITY

It is very surprising that sulfur difluoride was for so long not included in the series SiF_4, PF_3, ClF, whereas, in the series of hydrides SiH_4, PH_3, SH_2, HCl, sulfur presents no anomaly. In the series SF_2, SF_4, SF_6, sulfur difluoride is a laboratory curiosity whereas the tetra- and the hexa-fluorides are commercial substances. The method of Mendelejeff, of studying missing compounds by considering the properties of their neighbours, suggests that the reason for the instability of SF_2 could be found by studying the behavior of ClF and PF_3. Chlorine monofluoride is clearly a stable compound which is formed in an almost quantitative yield on mixing the trifluoride and chlorine (*57*). Phosphorus trifluoride is a well-known compound which appears to be very stable and shows no tendency to disproportionate to the pentafluoride and elementary phosphorus. However, both methylphosphorus difluoride and dimethylphosphorus fluoride, which may be considered as model compounds for SF_2, decompose at normal temperature to give fluorine compounds of pentavalent phosphorus together with methylphosphorus compounds which, like elemental phosphorus, contain P–P bonds (*75*, *76*).

$$10CH_3PF_2 \rightarrow 5CH_3PF_4 + (CH_3P)_5$$
$$3(CH_3)_2PF \rightarrow (CH_3)_2PF_3 + (CH_3)_2P{-}P(CH_3)_2$$

It can therefore be expected that SF_2 will decompose into SF_4 and S_8, or some other oligomer or polymer of sulfur, or into SF_4 and FSSF.

$$2SF_2 \rightarrow SF_4 + \frac{1}{n}S_n$$
$$3SF_2 \rightarrow SF_4 + S_2F_2$$

More insight into the problem of the stability of SF_2 is obtained from thermodynamic considerations. From an estimated value for the atomization energy of SF_2 (*55*) one can calculate that the enthalpy change for the decomposition of two moles of SF_2 to yield SF_4 and S_8(gas) is -75.7 kcal/mole (corresponding to -78.8 kcal/mole if solid sulfur is formed). An interpretation for this high enthalpy change is governed by bond energies and the change in the number of bonds. If the reactants are gaseous, we get for

$$2SF_2 \rightarrow SF_4 + \tfrac{1}{8}S_8$$

$\Delta H^\circ = 2(2\cdot78.8) - 4(81.85) - 63.5 = -75.7$ kcal/mole from previously given energies of atomization (*55*). There are two reasons for the decomposition of sulfur difluoride: The polymerization of sulfur atoms produces new bonds, and the sulfur–fluorine bonds in SF_2 and SF_4 are nearly of equal strength. Likewise it can be shown that SF_4 is thermodynamically unstable with respect to SF_6 and sulfur. For

$$3SF_4 \rightarrow 2SF_6 + \tfrac{1}{8}S_8$$

we obtain $\Delta H^\circ = 3(4\cdot81.85) - 2(6\cdot81.35) - 53.5 = -62.9$ kcal/mole. It can be shown that the temperature dependence of the ΔH° value and the decrease in entropy for the two reactions do not affect these predictions. SF_2 and SF_4 are no exceptions to the rule that the majority of compounds having elements in their intermediate oxidation states are thermodynamically unstable. The question of preparing and isolating sulfur difluoride then becomes a question of kinetic stability, i.e., the rate of its decomposition and the way in which this is influenced by catalysts.

The disproportionation of PF_3 into PF_5 and P_4 does not seem to be as favored thermodynamically as is the decomposition of SF_2. $\Delta H^\circ = 2.5(2\cdot121.9) - 1.5(5\cdot110.9) - 76.2 = -0.6$ kcal/mole relates to

$$2.5PF_3 \rightarrow 1.5PF_5 + \tfrac{1}{4}P$$

and $\Delta H^\circ = 3(62.8) - 124.7 - 58.2 = 3.5$ kcal to

$$3ClF \rightarrow ClF_3 + Cl_2$$

In the case of these two reactions the decrease in entropy will be decisive. It is interesting that the conversion of SF_2 into SF_4 produces stronger bonds, whereas weaker bonds are formed if PF_3 is converted into PF_5 and ClF into ClF_3. Actually, the relative stability of SF_4 is the cause of the instability of SF_2, and the relative instability of PF_5 and ClF_3 the cause for the stability of PF_3 and ClF compared with SF_2. The stability break in the series PF_3, SF_2, ClF originates from stability changes in the series PF_5, SF_4, ClF_3 owing to changes in bond type. Calculations by the VESCF molecular orbital method also show that the electronic structure of the static as opposed to the reacting sulfur difluoride molecule exhibits no special abnormality (*10*).

Finally it is interesting to compare the enthalpies of formation for the fluorine and oxygen compounds of sulfur (cf. Table VIII). The close relationship between sulfur difluoride and sulfur monoxide is at once apparent.

TABLE VIII

ENTHALPIES OF FORMATION OF FLUORINE AND OXYGEN COMPOUNDS OF SULFUR[a]

Compound	$\Delta H_f°$	Compound	$\Delta H_f°$
SF_2	−21.6	SO	1.5
SF_4	−46.3	SO_2	−35.4
SF_6	−48.6	SO_3	−31.5

[a] In kilocalories per gm-atom of F or O. All data taken from Ref. (*55*).

B. MOLECULAR STRUCTURE

Sulfur difluoride consists of angular triatomic molecules with C_{2v} symmetry, as would be expected for a derivative of H_2S. Its molecular geometry can be determined with the greatest precision from its microwave spectrum (*37*). The almost constant value for the sulfur–fluorine distance in compounds with SF_2 groups, including SF_6, is noteworthy (cf. Table IX). This may indicate that the mean bond dissociation energies of the SF_2 group are approximately the same in all compounds with this group.

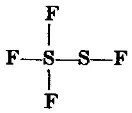
TABLE IX

MOLECULAR DATA OF SULFUR DIFLUORIDE (*37*) COMPARED WITH SF_4 (*84*), SF_6 (*32*), OSF_2 (*46*), AND SSF_2 (*43*)

Property	Unit	$^{32}SF_2$	SF_4	SF_6	OSF_2	SSF_2
d(SF)	Å	1.589	1.545 1.646	1.58	1.585	1.598
∡ (FSF)	deg	98°16′	—	—	—	—
I_A	Amu·Å²	18.7725	—	—	—	—
I_B		54.8813	—	—	—	—
I_C		73.8442	—	—	—	—
μ	D	1.05	—	—	—	—

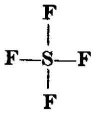
It is quite clear from the NMR spectrum of the dimer (cf. Section III, D) that it has an unsymmetrical molecular structure (*62*); i.e., three fluorine atoms are bonded to one of the two sulfur atoms and only one fluorine to the other sulfur atom. The relationship of S_2F_4 to FSSF is like that of SF_4 to SF_2.

F—S—S—F



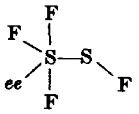
$$F\text{—}\overset{F}{\underset{F}{S}}\text{—}S\text{—}F$$

F—S—F



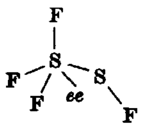
$$F\text{—}\overset{F}{\underset{F}{S}}\text{—}F$$

Consequently, it can be designated as 1,2-difluoro-disulfane 1,1′-difluoride. The NMR spectrum shows further that the SF_3 group of S_2F_4 is not an equilateral pyramid, i.e., the compound cannot be compared structurally with CF_3SF. The infrared spectrum of S_2F_4 (*61*) can be interpreted on the hypothesis that the molecule is a trigonal bipyramid with one sulfur atom at the centre, a second sulfur atom together with one atom of fluorine and a lone pair of electrons (*ee*) in the equatorial plane, and two fluorine atoms in axial positions (V).



(V)

The fact that the three fluorine atoms of the SF_3 group can be differentiated by NMR spectroscopy may be explained on the basis of this model, but only on the assumption that, at low temperatures, the fourth fluorine atom does not lie in the equatorial plane and that free rotation about the sulfur–sulfur bond is hindered. Nonequivalence of the axial fluorine atoms is also found in the alkyl- and arylmercaptotetrafluorophosphoranes, $F_2\overset{F}{\underset{F}{P}}\text{–}SR$, and has been explained by assuming that free rotation about the phosphor–sulfur bond becomes "frozen" at low temperatures (*52*). This hypothesis is not absolutely necessary in the case of S_2F_4 if it is assumed that the molecule has a simple tetragonal structure (VI).

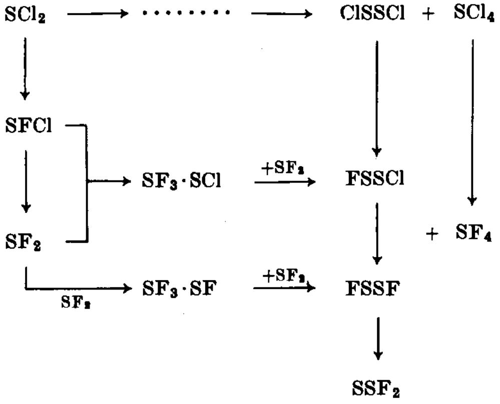


(VI)

It is quite possible that the actual structure corresponds with a transition between (V) and (VI). The same structural problem is also encountered in the compound SF_3SCl, which is formed as a by-product in the preparation of S_2F_4 from SCl_2.

C. Preparation and Chemical Properties

The compounds SF_2 and S_2F_4 are best prepared by reaction of sulfur dichloride vapor with active potassium fluoride, obtained from KSO_2F, or with mercury(II) fluoride at temperatures of 150° to 160° (*62*, *74*). If the reaction is carried out under preparative conditions one obtains mainly SF_4 and FSSF together with SSF_2 and sulfur, which separates. The reaction leads to SF_2 if the vapor over a sample of SCl_2 that is cooled with solid carbon dioxide is drawn through a bed of HgF_2 which is heated to 150° (*74*). At pressures up to 10 mm, difluorodisulfane difluoride is produced and, in addition, FSSF, SSF_2, SF_4, and the fluoro–chloro compounds S_2F_3Cl and FSSCl. Bearing in mind that SCl_2 can also disproportionate, the overall reaction may be represented by the following scheme.



The reaction may be carried out in a closed glass vacuum apparatus which has been pretreated with SF_4 for a long period at a higher temperature and then strongly heated. The products may be separated from one another by trap-to-trap distillation at low temperature. Cady codistillation in a nickel U-tube packed with nickel turnings proves that the volatilities of $F_3S \cdot SF$ and FSSF are very similar. A mixture of these two compounds may be separated from SSF_2 and SF_4 by codistillation.

It can be shown by codistillation and infrared spectroscopy that S_2F_4 is formed in small amounts from the reaction of silver fluoride with sulfur (*64*). S_2F_4 is also a product of the photolysis of FSSF and SSF_2, although SF_2 is not formed in the spontaneous breakdown of SSF_2. From our estimated values for the energies of atomization of SSF_2 and SF_2 we obtain for the reaction

$$SSF_2 \rightarrow SF_2 + \tfrac{1}{8}S_8$$

$\Delta H^\circ = 251.2 - 157.6 - 66.6 = 27.0$ kcal/mole. The sulfur–sulfur double bond prevents S_2F_2 from decomposing.

The gaseous, in fact, impure and highly diluted, sample of SF_2 which was investigated by Johnson and Powell by microwave spectroscopy, was prepared by passing SF_6 through a radio frequency discharge and reacting the products with COS in a rather obscure way.

The compound SF_2 is stable only as a highly dilute gas, whereas S_2F_4 exists in the solid or liquid state or as a solution in other sulfur fluorides up to about −75°. Both these compounds are more reactive than all other sulfur–fluorine compounds, especially toward glass. S_2F_4 is certainly the first intermediate in the disproportionation of SF_2. Like FSSF and SSF_2, it is very sensitive to hydrogen fluoride. Decomposition of SF_2 to FSSF and SF_4 (through S_2F_4 as an intermediate) probably occurs by the following steps.

$$\begin{aligned} 2SF_2 &\rightarrow SF_3SF \\ SF_3SF + HF &\rightarrow SF_4 + HSF \\ SF_2 + HSF &\rightarrow FSSF + HF \end{aligned}$$

It is almost unnecessary to mention that SF_2 and S_2F_4 are extremely sensitive to hydrolysis. At high temperatures they react with metals, including the noble metals, e.g., copper, to form sulfides and fluorides. At low temperatures, on the other hand, metals are passive if they are covered with a fluoride layer which is free of hydrogen fluoride. Apart from the greater reactivity, the behavior of SF_2 and S_2F_4 lacks specificity in relation to that of their disproportionation products S_2F_2 and SF_4. The chloro compound may be removed from a mixture of S_2F_4 and S_2F_3Cl by reaction with mercury.

When dry oxygen is admitted into an infrared cell containing difluorodisulfane difluoride all the bands of the latter disappear and are replaced by those of thionyl fluoride (*61*). No other sulfur–fluorine compound reacts spontaneously with oxygen. It may be noted in this connection that phosphorus trifluoride is oxidized by molecular oxygen in the presence of nitric oxide as catalyst to form phosphorus oxide trifluoride.

D. SPECTROSCOPY

The infrared and NMR spectra of both S_2F_4 and S_2F_3Cl show clearly that they may be regarded as derivatives of SF_4 (cf. Fig. 7). The five strong bands of difluorodisulfane difluoride in the region above 500 cm^{-1} may be assigned to the five valence vibrations which are required by structure (V) shown in Section III, C (cf. Table X). In place of the two bands at higher wave numbers owing to the valence vibrations of the equatorial

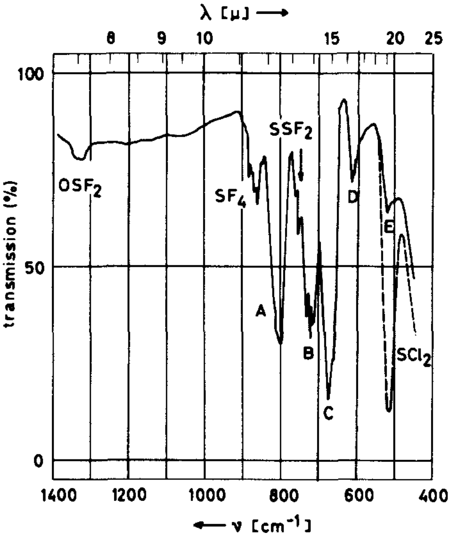


FIG. 7. Infrared spectrum of S_2F_4.

TABLE X

VALENCE VIBRATION BANDS OF DIFLUORODISULFANE (*12*), DIFLUORODISULFANE DIFLUORIDE (*61*), AND SULFUR TETRAFLUORIDE (*23*, *44*)

Compound	ν(SF, eq)	ν(SF, ax)	ν(SF)	ν(SS)
FSSF	—	—	717.0 680.8	614.6
$F_3S\cdot SF$	810	678 530	725	618
SF_4	891.5 867	728 558.4	—	—

fluorine atoms of SF_4, there is a single band in the case of SF_3SF. The band at 725 cm^{-1}, which varies in height in mixtures of SF_3SF and SF_3SCl relative to the other bands, corresponds with the band of sulfenyl fluorides at 790 cm^{-1} which likewise has a PQR structure. It also lies very close to the two SF valence bands of FSSF. The weak sulfur–sulfur vibrational frequency occurs almost in the same position as in difluorodisulfane.

Using the geometrical data obtained from the microwave spectrum of SF_2 and estimated force constants it has been possible to calculate theoretically the vibrational frequencies with the aid of the FG-matrix method (*6*). The values found were $\nu_1 = 795 \pm 10$ cm^{-1}, $\nu_2 = 430 \pm 5$ cm^{-1}, $\nu_3 = 830 \pm 10$ cm^{-1}. This serves to confirm the suggestion that a band at 830 cm^{-1} observed as a shoulder to the 810 cm^{-1} band in mixtures of sulfur–fluorine compounds containing S_2F_4 and S_2F_3Cl is associated with the monomer SF_2. It can be seen that at low gas concentrations only this band is produced. Its rounded maximum coincides with the P branch of the ν_2 band of SOF_2. The maximum of the relatively broad S_2F_4 band at 830 cm^{-1} first appears at higher concentrations and has almost the same position as the very narrow Q branch of the SOF_2 band. The separation of S_2F_4 and S_2F_3Cl by fractional vaporization may be monitored by means of their infrared spectra (cf. Fig. 8).

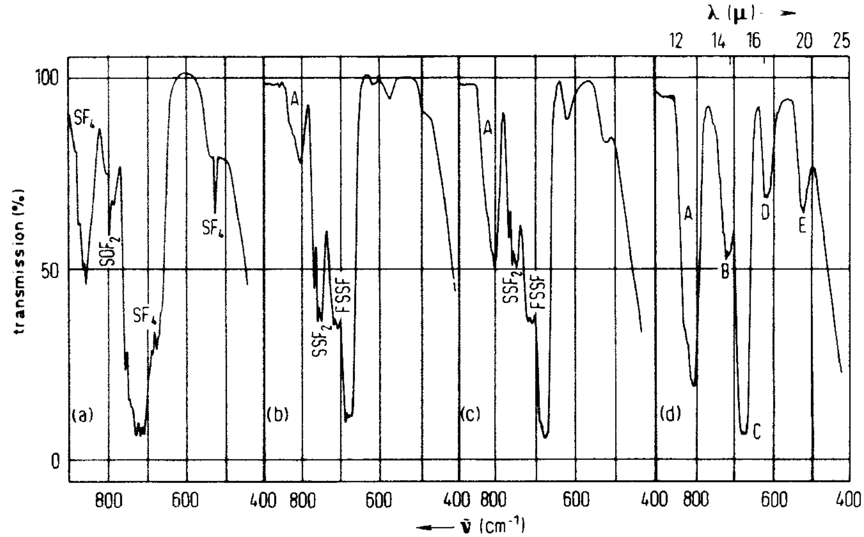


FIG. 8. IR spectra of the vapor over a mixture of SOF_2, SF_4, SSF_2, FSSF, SF_2, S_2F_4, and S_2F_3Cl on progressive fractionation. [From Seel *et al.* (*62*). Reproduced by permission of Verlag Chemie.]

The NMR spectra of S_2F_4 and S_2F_3Cl provide impressive examples of a first-order spin system and an ABX system (cf. Table XI and Fig. 9). Clearly, the four fluorine atoms in S_2F_4 have very different environments.

TABLE XI

^{19}F RESONANCE DATA FOR SULFUR–FLUORINE COMPOUNDS AT −100°.[a]

F_3S–SF	F_3S–SCl	SF_4	CF_3SF_3	$CF_3SF_2SCF_3$
δ_1 −53.2	δ_A −70.8	δ_{ax} −90	−46.7	−10.5
δ_2 −5.7	δ_B −67.6	δ_{aq} −35	+48.8	—
δ_3 +26.3	δ_X +22.4	—	—	—
δ_4 +204.1	—	—	—	—
J_{12} 86.3	J_{AB} 149	79.9	63.0	—
J_{13} 32.8	J_{AX} 14.9	—	—	—
J_{23} 32.2	J_{BX} 5.1	—	—	—
J_{13} 40.2	—	—	—	—
J_{24} 156.0	—	—	—	—
J_{34} 63.5	—	—	—	—

[a] δ Values are in ppm relative to an external $CFCl_3$ standard and coupling constants are in Hz. From Ref. (*62*).

The fluorine atom of the SF group (F_4) may be recognized by the extremely high chemical shift characteristic of sulfenyl fluorides. Its strong coupling with the fluorine atoms of the SF_3 group is characteristic of groups of atoms which are joined by a sulfur bridge. Overall, the position of the signals for the fluorine atoms in S_2F_4, S_2F_3Cl, SF_4, and FSSF and the coupling constants for S_2F_4 and S_2F_3Cl do not show the interrelationships as clearly as the infrared spectra. As would be expected, the chemical shifts of both the fluorine atoms which are arranged axially in mercaptotetrafluorophosphoranes (*64*) are almost equal ($\delta = 14$–15 or 17–22 ppm referred to $CFCl_3$), as in the case of S_2F_3Cl. Coupling of the equatorial ($\delta = 65$–66 ppm) with the axial fluorine atoms is strong (102–114 Hz), while that of the axial fluorine atoms with one another is weak (18–20 Hz) in accordance with the rule. In the case of S_2F_4 and S_2F_3Cl, on the other hand, coupling of fluorine atoms F_1 and F_2 is very strong and on the basis of their chemical shift they may be considered as being situated axially. This is contrary to the concept of an ideal bipyramidal structure. Examination of the NMR data in Table XI shows that NMR spectra are far more sensitive to structural changes than are IR spectra. Indeed, the differences in NMR data of structurally related compounds are astonishing.

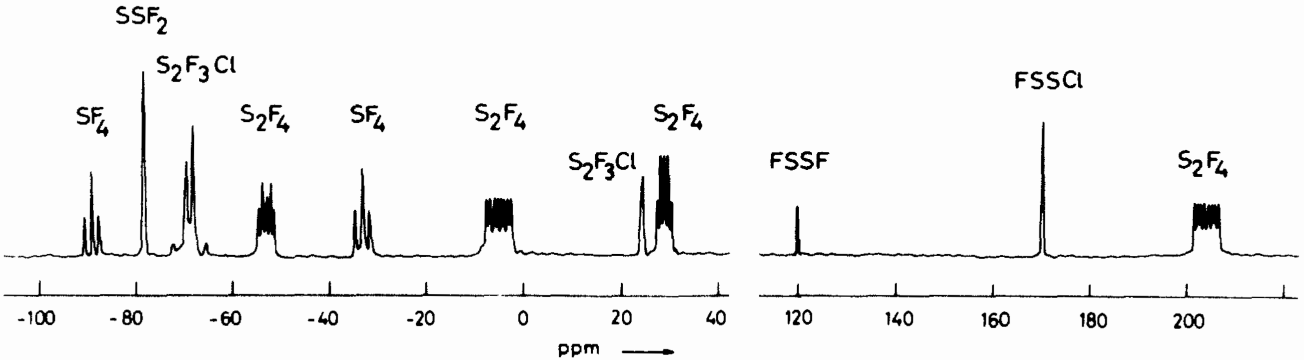


FIG. 9. ^{19}F NMR spectrum of the mixture of sulfur–fluorine and sulfur–fluorine–chlorine compounds resulting from the reaction of sulfur dichloride vapor with potassium fluoride. (δ relative to external $CFCl_3$, temperature −100°.) [From Seel *et al.* (*62*). Reproduced with permission of Verlag Chemie].

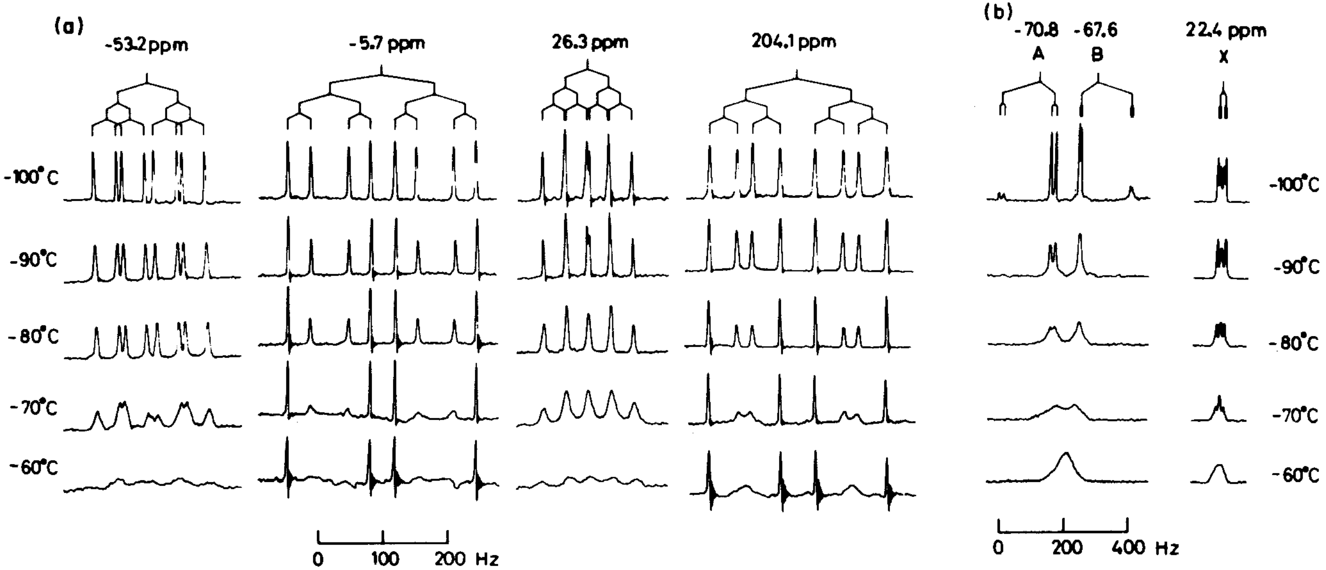


FIG. 10. Temperature dependence of the NMR spectra of S_2F_4 (a) and S_2F_3Cl (b). [From Seel *et al.* (*62*). Reproduced with permission of Verlag Chemie.]

In conclusion, the temperature dependence of the NMR spectra of S_2F_4 and S_2F_3Cl should be considered (cf. Fig. 10 a and b). The striking change in the spectrum of S_2F_4 in the range between −100° and −60° can be explained by supposing that two fluorine atoms of the SF_3 group change either their position or their environment on warming. This may be related to a rotation of the SF group. S_2F_3Cl clearly shows the transition from an ABX to an A_2X spectrum, which may be explained by rotation of the S–Cl group.

In the high vacuum of the mass spectrograph the equilibrium $2SF_2 \rightleftarrows S_2F_4$ lies far on the side of the monomer and apparently this

TABLE XII

MASS SPECTRUM OF THE REACTION PRODUCTS OF SULFUR DICHLORIDE AND POTASSIUM FLUORIDE[a]

m/e	Relative abundance		Ion	Source
64	100		S_2^+	$S_2F_2 + S_2Cl_2$
67	142	95.8	SOF^+	SOF_2
		46.2	$S^{35}Cl^+$	S_2Cl_2, SCl_2
69	15		$S^{37}Cl^+$	
70	19.5	12.7	SF_2^+	SF_2
		6.8	SF_2^+	SF_4
83	54.4		S_2F^+	S_2F_2
86	67.6	55.2	SOF_2^+	SOF_2
		12.4	$SF^{35}Cl^+$	SFCl
88	4.0		$SF^{37}Cl^+$	
89	13.5		SF_3^+	SF_4
99	86		$S_2{}^{35}Cl^+$	S_2Cl_2
101	28		$S_2{}^{37}Cl^+$	
102	190	153	$S_2F_2^+$	S_2F_2
		37	$S^{35}Cl_2^+$	SCl_2
104	17.5		$S^{35}Cl^{37}Cl^+$	
106	3		$S^{37}Cl_2^+$	
119	2.55		$S_2F^{35}Cl^+$	S_2FCl
121	8.35	0.82	$S_2F^{37}Cl^+$	
		7.53	$S_2F_3^+$	$S_2F_4 + S_2F_3Cl$
134	11.5		$S_2Cl_2^+$	S_2Cl_2
136	8.5			
138	1.9			
140	0.6	0.1		
		0.5	$S_2F_4^+$	S_2F_4
156	0.45		$S_2F_3{}^{35}Cl^+$	S_2F_3Cl
158	0.15		$S_2F_3{}^{37}Cl^+$	

[a] At 70 eV. From Ref. *(62)*.

serves to establish the equilibrium between sulfur difluoride or difluorodisulfane difluoride, on the one hand, and difluorodisulfane together with sulfur tetrafluoride, on the other.

$$3SF_2 \rightarrow (S_2F_4 + SF_2 \rightarrow)\ FSSF + SF_4$$

It has not proved possible to obtain the mass spectrum of SF_2 and S_2F_4 entirely free of S_2F_2 and SF_4. It is possible, however, to recognize SF_2 from the fact that the intensity of the signal of SF_2^+ is greater than that for SF_3^+ derived from SF_4 (cf. Table XII). The fragments shown with mass numbers 140 and 156/158 serve to establish the molecular size of S_2F_4 and S_2F_3Cl, in the mass spectrum of which the $S_2F_3^+$ ion, which is isoelectronic with SPF_3, is the most abundant.

IV. Difluoropolysulfanes

Many years ago Centnerszwer and Strenk (*16*) and Trautz and Ehrmann (*85*) observed that, when liquid sulfur reacted with silver fluoride, drops of a volatile liquid separated in the upper end of the reaction vessel. These drops became cloudy when the apparatus was opened. When sulfur vapor reacts with AgF a bright yellow oil is formed, mainly toward the end of the reaction (*63*, *65*). Liquids containing only sulfur and fluorine also result in the reaction of hydrogen sulfide with excess disulfur difluoride (*67*). These products are all mixtures of difluoropolysulfanes.

Analysis of samples of the yellow oil showed F:S atomic ratios between 2:3.5 and 2:3.9. From the NMR spectrum it is quite clear that

TABLE XIII

CHEMICAL SHIFTS FOR FLUORINE ATOMS IN COMPOUNDS WITH THE F–S GROUP

Compound	δ (ppm)	Temp. (°C)	Solvent	Standard	Ref.
FSSF	123.2	–50	—	$CFCl_3$, ext.	*65*
FSSSF	200.5	–50	$CFCl_3$	$CFCl_3$, int.	*63*
FSSSSF	204.1	–50			
SF_3SF	204.1	–100	—	$CFCl_3$, ext.	*62*
CCl_3SF	249	–50	—	—	*70*
CF_3SF	351.5	–50	—	—	*70*

the oil contains only two fluorosulfanes. The two signals lie close together and show the shift to high δ values characteristic of the F–S group, so that there can be no doubt that the compounds are difluorotrisulfane, FSSSF, and difluorotetrasulfane, FSSSSF (cf. Table XIII).

From the signal intensities the $S_2F_2{:}S_4F_2$ molar ratio lies between 1:0.37 and 1:0.49, corresponding with an F:S atomic ratio of 2:3.27 to 2:3.33. In no experiment were predominantly S_4F_2 (to which the weaker signal with the higher δ value relative to FSSF is attributed) or other difficultly volatile sulfur–fluorine compounds formed. It must therefore be assumed, from the analytical data, that the bright yellow oil always contains dissolved sulfur. The temperature dependence of the chemical shift of the two signals shows clearly that the fluorine compounds in the bright yellow oil constitute an homologous series which includes FSSF (cf. Fig. 11). It is notable that the temperature coefficient of the chemical shift increases greatly in the series FS_2F, FS_3F, FS_4F. This can be explained on the assumption that a mixture of conformers is present in the case of the tri- and tetrasulfanes and that the stretched forms are favored at higher temperature and the crumpled forms occur at lower temperatures.

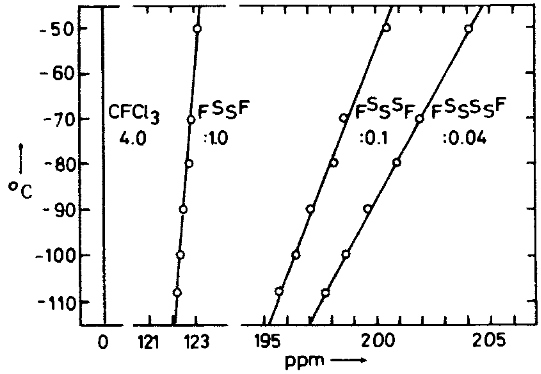


FIG. 11. Temperature dependence of the chemical shift of fluorine atoms in S_2F_2, S_3F_2, and S_4F_2 ($CFCl_3$ as solvent).

The positions of the S_3F_2 and S_4F_2 signals depend on concentration ratios as well as on temperature. For mixtures containing only the two substances the two signals lie close together at −110°, but at still lower temperature the signal for S_4F_2, which is always weaker, shifts to the other side of S_3F_2. In this connection it may be mentioned that the proton signals for S_3H_2 and S_4H_2 in the series of polysulfanes are also close together (*56*).

It is not yet possible to separate the two fluoropolysulfanes; even in high vacuum they cannot be distilled without decomposition. They decompose in glass tubes below 0°C, even when the vessels have been previously boiled with hydrochloric acid and etched with hydrofluoric acid. The only fluorine-containing decomposition product that can be detected by NMR spectroscopy is FSSF. Evidently the S–S bond is cleaved on thermolysis. It is quite possible that S_4F_2 dissociates homolytically into S_2F, just as O_4F_2 decomposes to O_2F (*39*).

Introduction of difluoropolysulfanes into the mass spectrometer is very difficult because of their instability and low volatility. It was possible, however, to detect S_3F_2 in presence of a 600-fold quantity of its decomposition product S_2F_2 by the abundance ratio of ions of mass 134 ($={}^{32}S_3F_2{}^+$) and 136 ($={}^{32}S_2{}^{34}SF_2{}^+$), which was equal to 100:11.7 in accordance with theoretical prediction.

The polyfluorosulfanes are strikingly similar in their chemical behavior to the corresponding chlorine–sulfur compounds. For example, in their hydrolysis, sulfur and polythionic acids are formed in addition to halide. Difluoropolysulfanes dissolve in fluorosulfonic acid and immediately produce a deep blue color, attributed to the $S_8{}^{2+}$ cation. A deep blue solid reaction product is produced with boron trifluoride and arsenic pentafluoride.

V. Sulfenyl Fluorides

As in the case of SF_2, all attempts to synthesize the sulfenyl fluorides, RSF, were fruitless for many years (*17*, *18*, *21*, *31*). In 1950 a product cited as $C_8H_{17}SF$ was reported in a patent (*79*), but no data supporting the structure of the compound were given. The preparation of the two sulfenyl fluorides, CCl_3SF and n-C_3F_7SF, from the corresponding sulfur–chlorine compounds by reaction with mercury(II) fluoride was reported in 1955 (*40*), although 1 year later the synthesis of trichloromethylsulfenyl fluoride by the prescribed method could not be repeated in another laboratory. The isomeric compound $CFCl_2SCl$ was obtained instead of CCl_3SF (*78*). The first sulfenyl fluoride to be unambiguously identified by NMR spectroscopy was the perfluoroisopropyl compound $(CF_3)_2CFSF$, which was discovered as a decomposition product from the pyrolysis of perfluorobisisopropylsulfur difluoride, $[(CF_3)_2CF]_2SF_2$ (*53*).

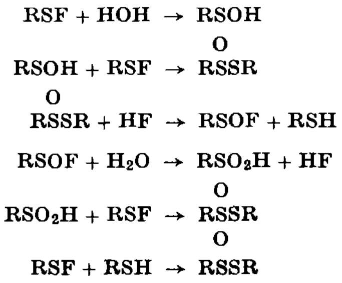
In fact, by working carefully, sulfenyl fluorides can be obtained as relatively stable compounds from the corresponding sulfenyl chlorides by simple chlorine–fluorine substitution using active potassium fluoride or mercury(II) fluoride, especially if the alkyl group is perhalogenated

(*68*, *70*). With trichloromethylsulfenyl chloride ("perchloromethylmercaptan"), reaction with KF or HgF_2 in the gas phase at 150° gives, in succession, the compounds CCl_3SF, $CFCl_2SCl$, $CFCl_2SF$, CF_2ClSCl, CF_2ClSF, CF_3ClSF, and CF_3SF, in addition to $CFCl_3$, CF_2Cl_2, and CF_3Cl (*70*). The sulfenyl fluorides $CF_nCl_{3-n}SF$ ($n = 0$ to 2) can clearly change to the isomeric sulfenyl chlorides, although the reaction mechanism has not yet been clarified. Recently, NF_2CCl_2SF and $NF_2CCl_2SF_3$ have been obtained by reaction of NF_2CCl_2SCl with silver(II) fluoride (*89*). Finally, by reaction of the vapors of chlorosulfenyl dimethylamide and diethylamide with silver fluoride the corresponding fluorosulfenyl amides, $FSNR_2$ ($R = CH_3$ or C_2H_5) may be produced (*71*). Treatment of chlorosulfenyl amide with mercury(II) fluoride gives an alkyliminosulfur difluoride, $RNSF_2$, as the chief product (*71*).

The sulfenyl fluorides are very reactive compounds which can be stored for long periods without decomposition only in the frozen state. Like sulfur difluoride and the alkylfluorophosphines, RPF_2 and R_2PF, they are thermodynamically unstable. Their spontaneous disproportionation to alkylsulfur trifluorides and dialkyl disulfides appear to be catalyzed by hydrogen fluoride.

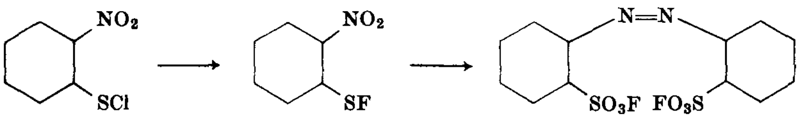
$$3RSF \rightarrow RSF_3 + RS\text{–}SR$$

Sulfenyl fluorides react rapidly with less noble metals (e.g., magnesium) and also with noble metals such as copper and mercury to give metallic fluorides and dialkyl disulfides (*68*). The compound CCl_3SF is particularly unstable, but $CF_2Cl{\cdot}SF$ decomposes in a matter of days at 20° in nickel vessels to $CF_2Cl{\cdot}SS{\cdot}CF_2Cl$, $CF_2Cl{\cdot}SS{\cdot}CF_3$, and CF_3Cl. The sulfenyl fluorides also react with the walls of glass vessels which have not been baked and pretreated with SF_4. Trifluoromethylsulfenyl fluoride reacts with glass and moist potassium fluoride to yield CF_3SSCF_3, CF_3SOF, and $CF_3SO_2SCF_3$. 1,2-Bis(trifluoromethyl)disulfane 1,1′-dioxide (*S*-trifluoromethyltrifluoromethanethiol sulfonate) has already been detected as a hydrolysis product of CF_3SCl (*30*). The course of the reaction is given by the following equations.



$$\begin{aligned}
RSF + HOH &\rightarrow RSOH \\
RSOH + RSF &\rightarrow R\overset{O}{S}SR \\
R\overset{O}{S}SR + HF &\rightarrow RSOF + RSH \\
RSOF + H_2O &\rightarrow RSO_2H + HF \\
RSO_2H + RSF &\rightarrow R\overset{O}{\underset{O}{S}}SR \\
RSF + RSH &\rightarrow RSSR
\end{aligned}$$

The sulfenyl fluorides are strong reducing agents. It has been reported that NF_2CCl_2SF reacts at normal temperature with oxygen to form SO_2, $FN{=}CCl_2$, and NF_2CCl_2SOF (*89*). The formation of *p*-nitrobenzenesulfonyl fluoride and bis(2,2′-fluorosulfenyl)azobenzene in the reactions of *p*- or *o*-nitrobenzenesulfenyl chloride with liquid hydrogen fluoride (*18*, *21*) also depends on the ready oxidizability or reducing action of the SF group of the sulfenyl fluorides formed initially.



Identification of sulfenyl fluorides is very much facilitated by the fact that the ^{19}F NMR resonance of the SF group is displaced to very high fields. In the case of perhalogenated compounds it occurs in the range of 255–360 ppm relative to $CFCl_3$. This shift is unusually high bearing in mind that fluorine resonances, in general, lie within the value for fluorine (–430 ppm) and hydrogen fluoride (194.5 ppm). It has been assumed that there is a paramagnetic shift attributable to triplet states which arise from excitation of the nonbonding electrons of sulfur (*53*). Table XIV summarizes the ^{19}F NMR data for sulfenyl fluorides known at present.

TABLE XIV

CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR THE ^{19}F NMR SPECTRA OF SULFENYL FLUORIDES[a]

Compound	$\delta(F_{C,\,N})$	$\delta(F_S)$	J(F–F)	Ref.
$Cl_3C–SF$	—	249	—	*70*
$FCl_2C–SF$	31 (doublet)	265 (doublet)	4.85	*70*
$F_2ClC–SF$	45 (doublet)	297 (triplet)	6.85	*70*
$F_3C–SF$	57 (doublet)	351 (quartet)	24.4	*70*
$(CF_3)_2CF–SF$	68 158 (multiplets)	361 (multiplet)	22 10	*53*
$NF_2CCl_2–SF$	–53 (broad)	270 (triplet)	7.5	*89*
$(CH_3)_2N–SF$	—	163 (septet)	—	*71*
$(C_2H_5)_2N–SF$	—	162 (quintet)	—	*71*

[a] δ(ppm); J(Hz). $CFCl_3$ as external standard.

The gaseous compound CF_3SF is unequivocally characterized by its mass spectrum and its very simple IR spectrum, which shows the independence of the CF valency vibrations (1190 and 1152 cm^{-1}) and the SF vibration (808 cm^{-1}). Surprisingly, the NMR spectrum of the liquid compound is much more complicated than would be expected (cf. Fig. 12). It contains not only a signal characteristic of sulfenyl fluorides at extremely high δ values (with a 1,3,3,1 quadruplet splitting owing to spin coupling with the CF_3 group and an associated doublet that is to be assigned to the CF_3 group) but also very intense signals (two triplets having a quartet fine structure, four superposed quadruplets) due to a more complicated compound. The position of the signals and their fine structure (cf. Table XV) indicate the compound to be an unsymmetrical dimer of CF_3SF, 1,2-bis(trifluoromethyl)disulfane 1,1′-difluoride:

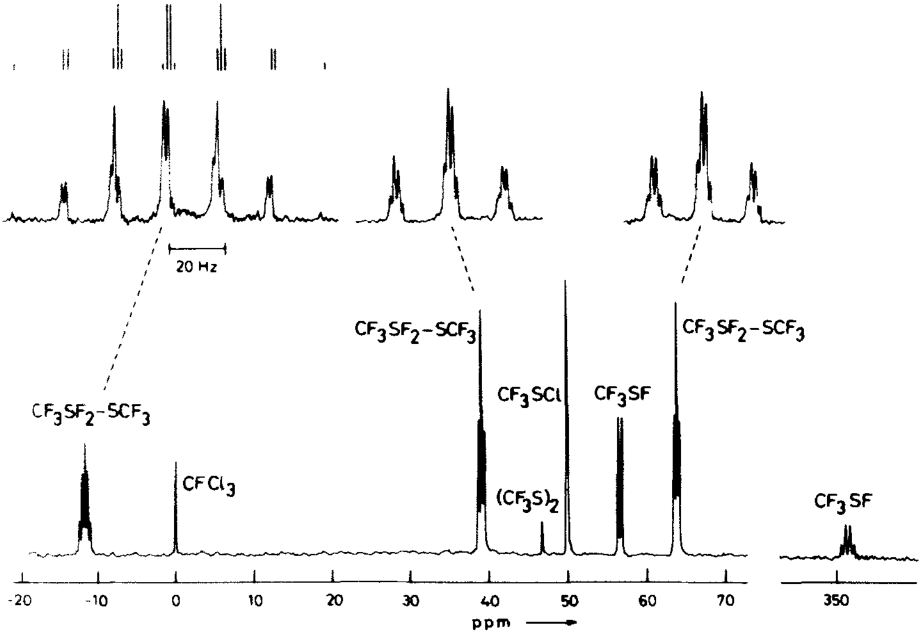
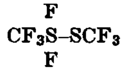


FIG. 12. ^{19}F NMR spectrum of a mixture of CF_3SCl, CF_3SF, $CF_3SF_2SCF_3$, and $CF_3SS{\cdot}CF_3$. [From Seel and Gombler (*68*). Reproduced by permission of Verlag Chemie.]



$$\overset{F}{\underset{F}{CF_3S}}\text{–}SCF_3$$

The approximately equally strong coupling for the fluorine atoms of both CF_3 groups with that of fluorine atoms bonded to sulfur is not in any way

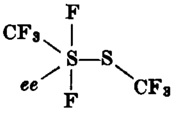
TABLE XV

^{19}F NMR DATA OF 1,2-BIS(TRIFLUOROMETHYL)DISULFANE 1,1′-DIFLUORIDE AND 1,2-BIS(TRIFLUOROMETHYL)DISULFANE 1,1′-DIOXIDE[a]

Compound	δ_{F_a}	δ_{F_b}	δ_{F_c}	$J_{F_aF_b}$	$J_{F_aF_c}$	$J_{F_bF_c}$
$CF_3SF_2SCF_3$	−12.6	+39.1	+63.7	19.4	17.9	1.5
$CF_3SO_2SCF_3$	—	+34.8	+70.2	—	—	—

[a] F_a, fluorine atoms bonded to sulfur; F_b, fluorine atom of the SCF_3 group; F_c, fluorine atom of the other CF_3 group. From Ref. (*68*).

inconsistent with an unsymmetrical structure; it may be explained by the presence of a sulfur bridge. It is interesting that the two fluorine atoms bonded to sulfur are not differentiated. If the molecule is assigned a trigonal-bipyramidal structure,



it has to be assumed that both CF_3 groups lie in the equatorial plane. It is clear from steric considerations that a structure analogous to that of S_2F_4 cannot be formed. The readily observed doublet splitting of the multiplets of $CF_3SF_2SCF_3$ shows that the planar or almost planar group CF_3–S–S–CF_3 can occur in either a cis or trans configuration.

Codistillation and NMR spectroscopic investigations show that below 0°C the equilibrium between CF_3SF and its dimer is established very slowly. In the liquid phase it lies largely on the side of the dimer. The chlorine compound boils at −1°C (*29*), whereas the dimer of CF_3SF has a vapor pressure of about 300 mm Hg at 0°C. Interestingly, $CF_2Cl\cdot SF$ does not dimerize. Its vapor pressure equation

$$\log_{10} p(\text{mm}) = -1236/T + 4.458$$

yields the normal entropy of vaporization, 20.4 eu, a boiling point of 4.5°C and an enthalpy of vaporization equal to 5.66 kcal/mole (*69*).

REFERENCES

1. Aubert, J., Cochet-Muchy, B., and Cuer, J. P., French Patent 1,586,833 (1968).
2. Bain, O., and Giguere, P. A., *Can. J. Chem.* **33**, 527 (1955).
3. Barceló, J. R., and Otero, C., *An. Real Soc. Espan. Fis Quim., Ser. B.* **51**, 223 (1955); *Chem. Abstr.* **49**, 14586h (1955).

4. Barr, J., Gillespie, R. J., and Unmat, P. K., *Chem. Commun.* 264 (1970).
5. Bell, C. F., "Synthesis and Physical Studies of Inorganic Compounds," p. 113. Pergamon, Oxford, 1972.
6. Bliefert, C., and Wanczek, K. P., *Z. Naturforsch., A* **25**, 1770 (1970).
7. Braune, H., and Knoke, S., *Z. Phys. Chem., Abt. B* **21**, 297 (1933).
8. Brown, F., and Robinson, P. L., *J. Chem. Soc.* 3147 (1955).
9. Brown, R. D., Burden, F. R., and Pez, G. P., *Chem. Commun.* 277 (1965).
10. Brown, R. D., and Peel, J. B., *Aust. J. Chem.* **21**, 2605 (1968).
11. Brown, R. D., and Pez, G. P., *Aust. J. Chem.* **20**, 2305 (1967).
12. Brown, R. D., and Pez, G. P., *Spectrochim. Acta, Part A* **26**, 1375 (1970).
13. Brown, R. D., Pez, G. P., and O'Dwyer, M. F., *Aust. J. Chem.* **18**, 627 (1965).
14. Cady, G. H., *Advan. Inorg. Radiochem.* **2**, 115 (1960).
15. Cady, G. H., and Siegwarth, D. P., *Anal. Chem.* **31**, 619 (1959).
16. Centnerszwer, M., and Strenk, C., *Ber. Deut. Chem. Ges.* **56**, 2249 (1923).
17. Chamberlain, D. L., and Kharasch, N., *J. Amer. Chem. Soc.* **77**, 1041 (1955).
18. Chamberlain, D. L., Peters, D., and Kharasch, N., *J. Org. Chem.* **23**, 381 (1958).
19. Davy, H., *Phils. Trans. Roy. Soc.*, London, *Ser. A* **103**, 277 (1813).
20. Dubnikov, L. M., and Zorin, N. I., *Z. Allgem. Chem.* **17**, 185 (1947); *Chem. Abstr.* **42**, 51 (1948).
21. Emeléus, H. J., and Heal, H. G., *J. Chem. Soc.* 1126 (1946).
22. Fischer, J., and Jaenckner, W., *Z. Angew. Chem.* **42**, 810 (1939).
23. Frey, R. A., Redington, R. L., and Aljibury, A. L. K., *J. Chem. Phys.* **54**, 344 (1971).
24. Gillespie, R. J., and Passmore, J., *Chem. Commun.* 1333 (1969); Gillespie, R. J., Passmore, J., Unmat, P. K., and Vaidya, O. C., *Inorg. Chem.* **10**, 1327 (1971).
25. Glemser, O., Biermann, U., Knaak, J., and Haas, A., *Chem. Ber.* **98**, 446 (1965).
26. Glemser, O., Heussner, W. D., and Haas, A., *Naturwissenschaften* **50**, 402 (1963).
27. "Gmelin's Handbuch der anorganischen Chemie," Verlag Chemie, Vol. 9, Part B 3, pp. 1699–705. 1963.
28. Gore, G., *Chem. News* **24**, 291 (1871).
29. Haszeldine, R. N., and Kidd, J. M., *J. Chem. Soc.* 2901 (1955).
30. Haszeldine, R. N., and Kidd, J. M., *J. Chem. Soc.* 3225 (1953).
31. Helfrich, O. B., and Reid, E. E., *J. Amer. Chem. Soc.* **43**, 592 (1921).
32. Herzberg, G., "Diatomic Molecules." Prentice-Hall, Englewood Cliffs, New Jersey, 1939.
33. Hirota, E., *J. Chem. Phys.* **28**, 839 (1958).
34. Hirota, E., *Bull. Chem. Soc. Jap.* **31**, 130 (1958).
35. Jackson, R. H., *J. Chem. Soc.* 4585 (1962).
36. Jaenckner, W., Dissertation, Technische Hochschule Breslau (1933).
37. Johnson, D. R., and Powell, F. X., *Science* **164**, 950 (1969).
38. Kirshenbaum, A. D., Grosse, A. V., and Aston, J. G., *J. Amer. Chem. Soc.* **81**, 6398 (1959).
39. Kirshenbaum, A. D., and Streng, A. G., *J. Amer. Chem. Soc.* **88**, 2434 (1966).
40. Kober, E., *J. Amer. Chem. Soc.* **81**, 4810 (1959).
41. Kuczkowski, R. L., *J. Amer. Chem. Soc.* **85**, 3047 (1963).
42. Kuczkowski, R. L., *J. Amer. Chem. Soc.* **86**, 3617 (1964).
43. Kuczkowski, R. L., and Wilson, E. B., Jr., *J. Amer. Chem. Soc.* **85**, 2028 (1963).
44. Levin, I. W., and Berney, C. V., *J. Chem. Phys.* **44**, 2557 (1966).

45. Matossi, F., and Aderhold, H., *Z. Phys.* **68**, 683 (1931).
46. Meschi, D. J., and Myers, R. J., *J. Mol. Spectrosc.* **3**, 405 (1959).
47. Meyer, J., *Z. Anorg. Allgem. Chem.* **203**, 146 (1931).
48. Luchsinger, W., Dissertation, Technische Hochschule Breslau (1935).
49. Otero, C., and Barceló, J. R., *An. Real Soc. Espan. Fis. Quim., Ser. B* **53**, 195 (1957); *Chem. Abstr.* **53**, 11079 (1959).
50. Padma, D. K., and Satyanarayana, S. R., *J. Inorg. Nucl. Chem.* **28**, 2432 (1966).
51. Palmer, K. J., *J. Amer. Chem. Soc.* **60**, 2360 (1938).
52. Peake, S. C., and Schmutzler, R., *Chem. Commun.* 1662 (1968).
53. Rosenberg, R. M., and Muetterties, E. L., *Inorg. Chem.* **1**, 756 (1962).
54. Ruff, O., *Angew. Chem.* **46**, 739 (1933).
55. Sanderson, R. T., "Chemical Bonds and Bond Energy," pp. 101, 193, 195. Academic Press, New York, 1971.
56. Schmidbaur, H., Schmidt, M., and Siebert, W., *Chem. Ber.* **97**, 3374 (1964).
57. Schmitz, H., and Schumacher, H. J., *Z. Naturforsch., A* **2**, 362 (1947).
58. Seel, F., *Chimia* **22**, 79 (1968).
59. Seel, F., and Budenz, R., *Chimia* **17**, 335 (1963).
60. Seel, F., and Budenz, R., *Chem. Ber.* **98**, 251 (1965).
61. Seel, F., and Budenz, R., *J. Fluorine Chem.* **1**, 117 (1971/72).
62. Seel, F., Budenz, R., and Gombler, W., *Chem. Ber.* **103**, 1701 (1970).
63. Seel, F., Budenz, R., Gombler, W., and Seitter, H., *Z. Anorg. allgem. Chem.* **380**, 262 (1971).
64. Seel, F., Budenz, R., and Wanczek, K. P., *Ber.* **103**, 3946 (1970).
65. Seel, F., Budenz, R., and Werner, D., *Ber.* **97**, 1369 (1964).
66. Seel, F., and Gölitz, D., *Chimia* **17**, 207 (1963).
67. Seel, F., and Gölitz, D., *Z. Anorg. Allgem. Chem.* **327**, 32 (1964).
68. Seel, F., and Gombler, W., *Angew. Chem.* **81**, 789 (1969).
69. Seel, F., and Gombler, W., unpublished data (1972).
70. Seel, F., Gombler, W., and Budenz, R., *Angew. Chem.* **79**, 686 (1967).
71. Seel, F., Gombler, W., and Budenz, R., *Z. Naturforsch., B* **27**, 78 (1972).
72. Seel, F., Hartmann, V., Molnar, I., Budenz, R., and Gombler, W., *Angew. Chem.* **83**, 173 (1971).
73. Seel, F., and Heinrich, E., (1971) unpublished data.
74. Seel, F., Heinrich, E., Gombler, W., and Budenz, R., *Chimia* **23**, 73 (1969).
75. Seel, F., and Rudolph, K., *Z. Anorg. Allgem. Chem.* **363**, 233 (1968).
76. Seel, F., Rudolph, K., and Budenz, R., *Z. Anorg. Allgem. Chem.* **341**, 196 (1965).
77. Seel, F., and Wanczek, K. P., *Z. Phys. Chem.* [NF] **72**, 109 (1970).
78. Sheppard, W. A., and Harris, J. F., Jr., *J. Amer. Chem. Soc.* **82**, 5106 (1960).
79. Simons, J. H., U.S. Patent 2,519,983 (1950).
80. Smith, W. C., *Angew. Chem.* **74**, 742 (1962).
81. Spong, A. H., *J. Chem. Soc.* 485 (1934).
82. Stammreich, H., *Spectrochim. Acta* **8**, 46 (1956).
83. Stevenson, D. P., and Beach, J. Y., *J. Amer. Chem. Soc.* **60**, 2872 (1938).
84. Tolles, W. M., and Gwinn, W. D., *J. Chem. Phys.* **36**, 1119 (1962).
85. Trautz, M., and Ehrmann, K., *J. Prakt. Chem.* [2]**142**, 79 (1935).
86. Vaugham, J. D., and Muetterties, E. L., *J. Phys. Chem.* **64**, 1787 (1960).
87. Wagner, G., and Bock, H., *Chem. Ber.* **106**, 1285 (1973).
88. Wanczek, K. P., Dissertation, Saarbrücken (1970).
89. Zaborowski, L. M., and Shreeve, J. M., *Inorg. Chim. Acta* **5**, 311 (1971).
90. Zengin, N., and Giguere, P. A., *Can. J. Chem.* **37**, 632 (1959).