

Low Temperature Infrared Spectrometric Studies of Difluorodisulfane, Thiothionylfluoride and Difluorotrisulfane*

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The low temperature IR stretching vibrations of difluorodisulfane (FSSF) and thiothionylfluoride (SSF₂), in the solid phase and in a cyclohexane matrix, of the mixtures FSSF–SSF₂, FSSF–OSF₂ and SSF₂–OSF₂, and of solid difluorotrisulfane (FS₃F) have been investigated.

While SSF₂ forms no distinct oligomers, a dimer with absorption bands at 635 and 682 cm⁻¹ has been detected in the case of FSSF. These differences between FSSF and SSF₂ are rationalized by the different S–F bond lengths. A structure of the FSSF dimer similar to that of the sulfur tetrafluoride dimer is proposed. The low temperature spectrum of FS₃F shows 3 bands in the frequency range between 460 and 1000 cm⁻¹: 590, 605 and 680 cm⁻¹, due to associated molecules. FS₃F decomposes on warming. The main decomposition products containing fluorine are FSSF and SSF₂. Mechanisms for the rearrangement and decomposition of the three compounds studied are discussed.

Introduction

During the last decade interest in the lower sulfur fluorides has increased¹. The first identification of the isomers of disulfur difluoride, difluorodisulfane (FSSF) and thiothionylfluoride (SSF₂), carried out independently by Kuczkowski^{2,3}, Seel^{4,5} and their coworkers, has called for a detailed investigation of the chemical and physical properties of these two compounds. In 1965, Seel and Budenz⁶ suggested an FSSF·SSF₂ intermediate, stable in the gas phase, as being formed during rearrangement of FSSF to SSF₂, from vapor pressure measurements. However, this molecular compound could neither be detected by IR or UV spectroscopy nor by mass or NMR spectroscopy.

If there exists a cryoscopically stable molecular compound FSSF·SSF₂, it should be detectable by low temperature IR matrix spectrometry. In this work an IR matrix spectrometric study of FSSF, SSF₂, of mixtures of these compounds and of their mixtures with thionylfluoride (OSF₂) is presented along with an investigation of the solid phase low temperature IR spectrum and the decomposition of difluorotrisulfane (FSSSF) which gives further insight into the decomposition mechanisms of lower sulfur fluorides.

* Dedicated to Professor F. Seel on the occasion of his 60th birthday.

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Experimental

Commercially available thionylfluoride and sulfur tetrafluoride (lecture bottles, Baker Chemikalien, 608 Groß-Gerau) were purified before use by trap-to-trap condensation.

FSSF, SSF₂ and FSSSF were prepared by reaction in a vacuum apparatus described elsewhere⁷. After separation of the volatile products by trap-to-trap condensation, a mixture of difluorotrisulfane with higher difluoropolysulfanes remains in the trap, in which the various products of the silverfluoride-sulfur reaction have been collected. The volatile products, thionylfluoride, formed as an impurity by hydrolysis of the sulfur fluorides, difluorodisulfane and thiothionylfluoride were separated by codistillation⁸. Raising the temperature in the codistillation column, the three compounds appear in the order OSF₂, SSF₂ and FSSF. The differences in the appearance temperatures are: OSF₂–SSF₂: +8 K, SSF₂–FSSF: +22 K. Small transportable IR low temperature cells have already been described elsewhere in the literature^{9–11}. The cell utilised in this work has been designed for use with liquid nitrogen as coolant and equipped with silver chloride windows. The samples were deposited on a silver-chloride plate, which was fixed directly to a hollow ring, the latter being connected to the liquid nitrogen reservoir of the dewar vessel.

Before deposition of a pure sample (10⁻⁴ to 10⁻⁵ mols), its purity was controlled, with the exception of difluorotrisulfane, by recording a gas phase IR spectrum. The deposition rate was about 10⁻⁶ mols per minute. Difluorotrisulfane was deposited directly from a trap on the silver chloride plate, until an IR spectrum of sufficient intensity



could be recorded. Difluorotrisulfane is stable only at low temperatures¹² and reacts with traces of water and glass. Therefore the absence of the intense absorption band due to OSF_2 at 810 cm^{-1} was used as a purity control. Difluorotrisulfane always contains a small proportion of higher difluoropolysulfanes. However, the vapor pressure of difluorotetrasulfane is much smaller than that of difluorotrisulfane. Therefore the deposit would contain, if at all, only traces of the higher difluoropolysulfanes.

Thereafter IR spectra of the solid samples were recorded with a Beckman IR spectrometer IR 10 under conditions of highest possible spectral resolution (about 5 cm^{-1}).

With liquid nitrogen as coolant, the lowest temperatures, measured directly at the cooled silver chloride window by a resistance thermometer, were 95 to 100 K. Therefore, it was problematic finding a suitable matrix compound¹³. Preliminary experiments showed cyclohexane, which for this purpose has already been utilised by Baker and Pimentel¹⁴, to be suited. Cyclohexane has no IR absorption bands in the region of the strong bands of the disulfur difluorides; its melting point of 279.7 K is high enough to obtain a matrix of sufficient rigidity, as estimated from Tammann's rule. Cyclohexane exists in a cubic and a monoclinic modification with a transformation point of 186.4 K¹⁵. It tends to solidify in a glaseous form and is a plastic crystal like the solid noble gases Kr and Xe¹⁶. The intermolecular forces in solid cyclohexane are mainly van der Waals and dispersion forces¹⁷. Cyclohexane does not induce rearrangement of difluorodisulfane to thiotionylfluoride. However, with cyclohexane only matrix to solute ratios smaller than 300:1 could be employed. At higher ratios the matrix became impermeable or the absorption bands of the solute became too weak to be observed.

Unless otherwise stated, the matrix spectra were recorded at a matrix to solute ratio of 100:1.

To obtain matrix IR spectra, suitable mixtures of the sulfur fluoride under study and cyclohexane (uvasol grade, Merck AG, Darmstadt) were prepared manometrically, their composition and purity were controlled by recording a gas phase IR spectrum. Thereafter the procedure described above for pure samples was carried out.

Temperature recycling was initiated by reducing the amount of liquid nitrogen in the low temperature dewar. When the deposition window had reached the appropriate temperature, it was cooled down again. The annealing cycles were repeated until a sufficient effect was observed in the IR spectrum.

Results

Thiotionylfluoride, Solid Phase and in Cyclohexane Matrix

The results for SSF_2 in the spectral region from 850 to 550 cm^{-1} are summarised in Table 1a and depicted in Figs. 1a – 1d. The IR spectrum of SSF_2 in the gas phase in the region of the stretching vibrations is relatively simple. Three bands are observed. The assignment of the vibrations $\nu_2(\text{a}')$ to the sulfur-sulfur stretching vibration, $\nu_1(\text{a}')$ to the symmetric sulfur-fluorine stretching vibration and of $\nu_5(\text{a}'')$ to the antisymmetric sulfur-fluorine stretching vibration has previously been carried out by IR^{6,18} and Raman spectroscopic¹⁹ measurements. The molecule belongs to the point group C_s . The other vibrations of SSF_2 in the region of longer wavelengths could not be observed because the silver chloride windows are impermeable in this spectral region. These bands are furthermore of low intensity. Therefore a relatively thick matrix layer would be necessary to achieve sufficient absorption intensity. Cyclohexane matrices become impermeable at relatively thin layers. For this reason, observation of the bands ν_3 , ν_4 and ν_6 would not be possible even with other window materials, using the same coolant and matrix compound.

The displacements $\Delta\nu^1$ of the IR bands to longer wave lengths of the isolated molecules in the cyclohexane matrix compared with the gas phase spectrum are relatively large, indicating interaction between matrix and solute. Temperature recycling, as shown in Fig. 1b and 1c cause broad bands to appear at slightly lower frequencies, the original monomer bands becoming unsymmetric. After several temperature cycles the monomer bands are displaced by broad absorptions, which are only slightly shifted to longer wavelengths with the exception of the antisymmetric S–F stretching vibration, which is shifted -8 cm^{-1} . The spectrum in Fig. 1c resembles the spectrum of pure solid SSF_2 , shown in Figure 1d. As can be expected, the bands in the spectrum of solid SSF_2 are shifted again to longer wavelengths ($\Delta\nu^4$). The same is true for the comparison of the spectrum of the tempered SSF_2 in the matrix with the Raman absorptions of liquid SSF_2 obtained by Brown et al.¹⁹, ($\Delta\nu^3$). The shifts observed in the liquid phase are significantly smaller than those in the solid phase, they are, however, of the same magnitude as for the annealed matrix.

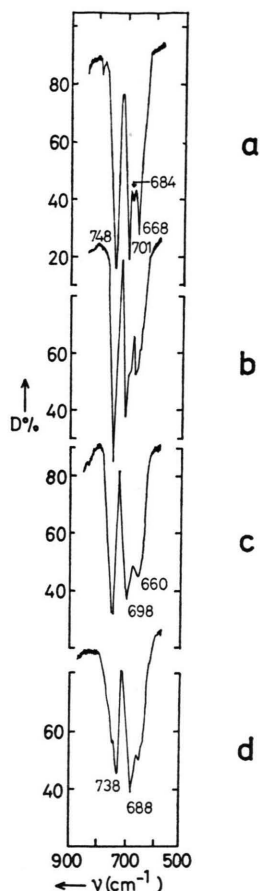


Fig. 1. Thiothionylfluoride in cyclohexane matrix, a) spectrum recorded at 95 K; b) and c) spectra recorded at 95 K after temperature recycling through $T = 158$ K. d) Pure solid SSF_2 at 100 K.

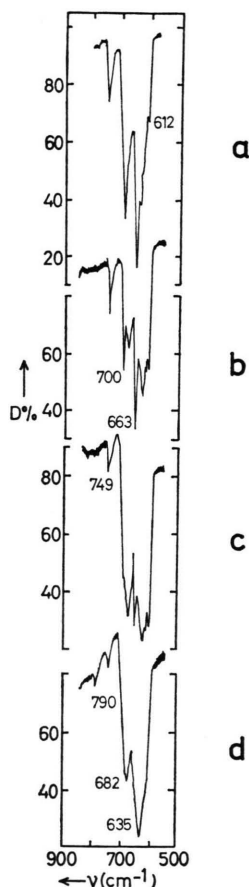


Fig. 2. Difluorodisulfane in cyclohexane matrix, a) spectrum at $T = 106$ K; b), c) and d) spectra recorded at 106 K after successive temperature recycling through 158 K.

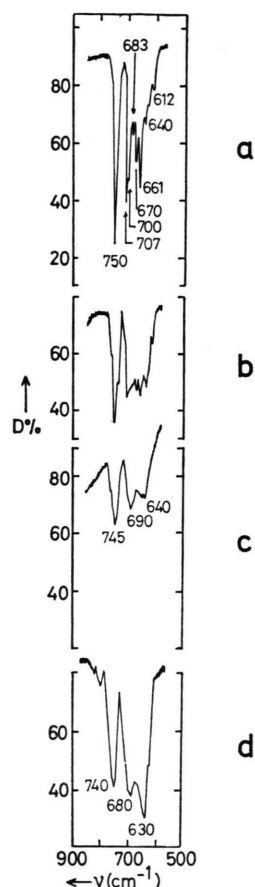


Fig. 3. a) 1:1 mixture of FSSF and SSF_2 in a cyclohexane matrix at $T = 103$ K; b) and c) spectra recorded at 103 K after successive temperature recycling through 173 K. d) Mixture of FSSF and SSF_2 in a molar ratio of 3:2 without matrix at $T = 103$ K.

Difluorodisulfane, Solid Phase and in Cyclohexane Matrix

The results for FSSF are summarised in Table 1b and depicted in Fig. 2 a–d. The IR absorption spectrum of FSSF, which is well known^{6, 19} and like that of SSF_2 relatively simple in the region of the stretching vibrations, is assigned as follows: ν_1 (a) sulfursulfur stretching vibration, ν_2 (a) and ν_5 (b) symmetric and antisymmetric sulfurfluorine stretching vibrations. The assignments of these vibrations have been well established by IR and Raman¹⁹ spectroscopic measurements and force constant calculations¹⁹. FSSF belongs to the point group C_2 . The other normal vibrations ν_3 , ν_4 and ν_6 were not

be observed. The reasons for this are the same as already stated for the case of SSF_2 .

On temperature recycling FSSF behaves differently to SSF_2 . Bands of a dimer (or an oligomer), which only appear as small shoulders in the spectrum of the monomer (Fig. 2 a), grow rapidly and become broader after repeated annealing cycles (Figs. 2 b and 2 c). After a few annealing cycles the monomer bands disappeared completely, the spectrum resembles that of solid FSSF, which is not shown, because the bands have the same contours as in the spectrum of annealed FSSF (Figure 2 d).

The shifts $\Delta\nu^1$ of the IR bands to longer wave lengths of the isolated molecules in the matrix com-

Table 1. Comparison of the S-S and S-F vibrations of the two disulfurdifluoride isomers.

a) SSF ₂	gas phase	matrix, isol.	$\Delta\nu^1$	matrix, ass.	$\Delta\nu^2$	Raman, liq. ¹⁹	$\Delta\nu^3$	pure solid	$\Delta\nu^4$
ν_2 SS(a')	721	701	-20	698	-23	710	-11	688	-33
ν_1 SF(a')	760	748	-12	745	-15	745	-15	738	-22
ν_5 SF(a'')	700	668	-32	660	-40	650-700	-	660	-40
b) FSSF									
ν_2 SS(a)	612	612	0	-	-	623	+11	610?	- 2
ν_1 SF(a)	715	700	-15	682	-33	-	-	681	-34
ν_5 SF(b)	679	663	-16	635	-44	683	+ 4	620	-59

All the frequencies are given in wave numbers. $\Delta\nu_i$ ($i = 1, 2, 3, 4$) shows the differences between the wave numbers of a vibration in the state, noted in the preceding column and the gaseous state.

pared with the gas phase spectrum are surprisingly small. They are given in Table 1 b: ν_2 (a) is at the same position, ν_1 (a) and ν_5 (b) are shifted by -15 and -16 cm⁻¹ respectively. ν_1 and ν_5 of the dimer are shifted again to longer wave lengths ($\Delta\nu^2$). In solid FSSF the ν_5 band is shifted once again to longer wave lengths, while the ν_2 band remains in the same position. However, the results for this band are uncertain, because it is, if at all, only observed as a shoulder. There is a remarkable difference between the values of ν_2 and ν_5 of the Raman spectrum of the liquid, recorded by Brown and Pez¹⁹ and the solid state IR values.

The wavenumber shifts of the individual bands of SSF₂ and FSSF are also different. While the S-S stretching vibration of FSSF remains nearly unaffected, the corresponding vibration of SSF₂ is shifted. The shifts of the antisymmetric S-F stretching vibrations are greater than those of the symmetric vibrations. However, to a greater extent the shift of the SSF₂ bands is caused by the matrix environment. In the case of the other isomer interaction of the solute molecules is the main reason for the band shift.

Mixtures

Difluorodisulfane - Thiothionylfluoride

The spectra of 1:1 mixtures of FSSF and SSF₂ are shown in Fig. 3 a - 3 c. They represent a superimposition of the spectra obtained with one single disulfurdifluoride isomer in the matrix, not only for the isolated molecules (Fig. 3 a), but also after temperature recycling (Fig. 3 b and 3 c). The absorp-

tions of isolated FSSF disappear after warming up and recooling and are replaced by bands with the same positions and contours, already assigned to FSSF dimers in the matrix spectrum of the pure compound. In the case of SSF₂ once again only broadening is observed. The low temperature spectrum of a mixture of FSSF and SSF₂ in the molar ratio of 3:2, shown in Fig. 3 d, is also a superimposition of the corresponding spectra of the single compounds. Therefore it can be concluded, that FSSF forms cryoscopically stable dimers (or oligomers) only with other FSSF molecules even in the presence of SSF₂.

Disulfurdifluorides - Thionylfluoride

Mixtures of the two disulfurdifluoride isomers with OSF₂ in the molar ratio 1:1 in cyclohexane matrices show no additional bands after temperature recycling. The spectra always represent superimpositions of the spectra of the pure compounds in cyclohexane matrices. This is shown for a 1:1 mixture of FSSF and OSF₂ in Fig. 4 a and 4 b. Figure 4 a depicts the spectrum of the isolated molecules, Fig. 4 b that after temperature recycling, indicating the absorptions of FSSF dimers. OSF₂ has partially condensed from the matrix to the walls of the liquid nitrogen dewar vessel. However, the remainder shows a band shift to slightly longer wave lengths indicating an interaction, which resembles that in solid OSF₂. Contrary, the ν_5 (a'') antisymmetric S-F stretching frequency of OSF₂ is shifted to higher frequencies in the case of interactions of SF₄ and OSF₂²².

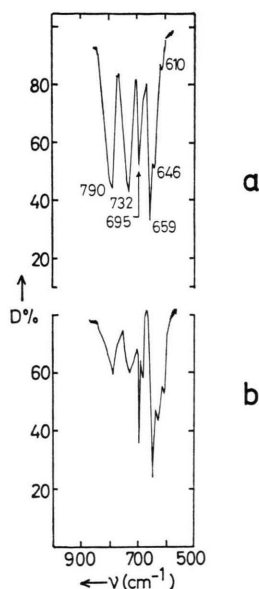


Fig. 4. a) 1:1 mixture of FSSF and OSF_2 in cyclohexane matrix at $T = 105 \text{ K}$; b) spectrum recorded at 100 K after temperature recycling through 150 K .

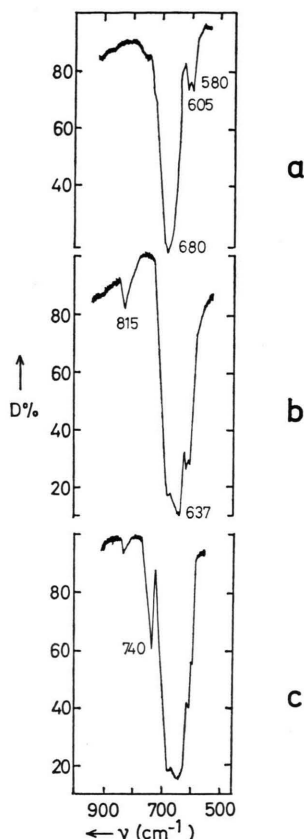


Fig. 5. IR low temperature spectra a) of pure solid difluorotrisulfane, b) of solid difluorotrisulfane, which contains FSSF and FSSF_3 and c) of partially decomposed FS_3F after annealing.

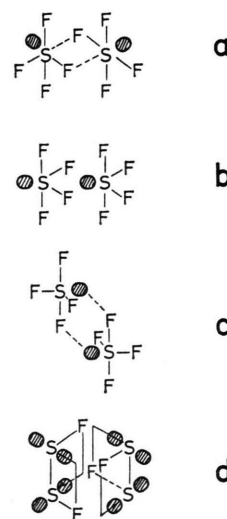


Fig. 6. a), b) and c) Structures proposed in the literature for the SF_4 dimer (see text); d) structure suggested for the FSSF dimer.

Difluorotrisulfane, Solid Phase

The spectrum in Fig. 5 a shows a low temperature IR spectrum of FS_3F in the spectral range from 460 to 1000 cm^{-1} . It consists of three bands at 590 , 605 and 680 cm^{-1} . The spectrum of another sample is shown in Fig. 5 b. However, this sample is impure, it contains a small proportion of 1,2-difluorodisulfane-1,1-difluoride, identified by the appearance of the band at 815 cm^{-1} ; ^{7, 20}. This absorption cannot be assigned to OSF_2 , because it shows two bands of almost equal intensity at 718 and 790 cm^{-1} ; ²¹ in the solid state. Moreover, the most intense band in the spectrum shown in Fig. 5 b at 637 cm^{-1} is due to FSSF. The contour of this band, however, is quite different from those, observed in a spectrum of pure solid FSSF, shown in Figure 2 d.

The shoulder at 680 cm^{-1} is therefore identifiable as an absorption due to FS_3F .

Figure 5 c shows a spectrum recorded after temperature recycling. FS_3F decomposes on warming, the proportion of FSSF increasing. A new absorption at 740 cm^{-1} appears and is assigned to SSF_2 . The intensity of this new band increases rapidly with duration of the warming up period. S_2F_4 also decomposes, the intensity of the band at 815 cm^{-1} decreases on warming. However, the proportion of S_2F_4 is too small to generate all the SSF_2 .

Discussion

Applicability of the Cyclohexane Matrix

The use of a noble gas matrix at liquid helium temperature is undoubtedly one of the most useful

Table 2. IR spectra of sulfur tetrafluoride.

assignment	gas phase	cyclohexane matrix	solid phase	Ar matrix isol.	²² ass.	solid phase form ²³	Raman spectr. liquid ²⁴
$\nu_1(a_1)$ symm. eq. stretch.	982		890	884	891	885	898
$\nu_6(b_1)$ as. ax. stretch.	730	700 682 667 660		706	689, dimer 669, polymer		620–760
			635			640	
$\nu_8(b_2)$ as. eq. stretch.	870	—	861	858	858	856	858

All the frequencies are given in wave numbers (cm^{-1}).

methods for isolating stable and unstable molecules and studying their absorption spectra, decomposition and association phenomena. Although the technique of IR low temperature dewars, using liquid helium as coolant has been improved in the last decade, its application has continued to be restricted to use in relatively few specialised laboratories. The use of more simple IR dewars with liquid nitrogen as coolant involves the problem of finding a suitable matrix compound, which in most cases must be different, for samples with differing absorption bands. Therefore, the matrix should be tested with compounds, having vibration frequencies in the same region as the compound under study.

The low temperature IR spectrum of the lower sulfur fluoride SF_4 has been investigated in detail in rare gas matrices²² as well as in the solid phase²³. Therefore the $\nu_6(b_1)$ axial antisymmetric S–F stretching vibration of SF_4 has been used as a test for the cyclohexane matrix. Solute to matrix ratios of about 1:100 proved to be sufficient in isolating approximately half of the trapped molecules. Such a ratio has also been used by Redington and Berney²² to obtain partially isolated molecules in their above-mentioned Ar matrix study of SF_4 . Lowering the concentration of the solute SF_4 to get a more complete isolation leads to absorption bands, which are too weak, because only thin matrix layers are transparent. On warming up and recooling the deposit, the band, which was assigned by Redington and Berney to various SF_4 oligomers, becomes more intense. The quantitative results are listed and compared with the literature values in Table 2.

Association of Disulfur difluorides

The matrix compound cyclohexane was selected to enable us to observe the three most intense absorption bands of the disulfur difluorides. The matrix shifts ($\Delta\nu^1$ in Table 1) are not unexpected. The ν_6 band of SF_4 is shifted -22.5 cm^{-1} ; ²² compared with the gas phase even in an Ar matrix.

Within experimental limits, only shoulders at low frequencies can be observed after temperature recycling with matrix isolated SSF_2 . The absorptions mainly become broader and are only partially shifted to greater wave lengths. The $\nu_5\text{SF}(a'')$ shows the greatest shift of -8 cm^{-1} compared with the matrix isolated molecule. Therefore, SSF_2 is thought to form no cryoscopically stable oligomers, especially no dimer, provided that the formation of oligomers causes a band shift large enough to be observed with the utilised spectrometric equipment. Such a band shift should be expected from the other results discussed above in the case of oligomer formation. The shoulders at low frequencies, which appear after temperature recycling and lead to band broadenings and displacement of the band maxima may be due to interactions of SSF_2 molecules in the solid state without formation of isolated stable dimers or other oligomers.

Contrary to this, new absorptions appear after temperature recycling in the spectrum of FSSF , which are too large to be produced by site effects. Site effects are also excluded by concentration studies. In the course of temperature recycling with matrix isolated FSSF , the $\nu_5\text{SF}$ band is shifted

–28 and the ν_1 SF band –18 cm⁻¹. The shifts of these two bands indicate formation of a cryoscopically stable dimer. The frequencies of the S–F vibrations show a greater shift than those of the S–S vibration. Therefore, the dimers are thought to be formed via interaction of the S–F bonds of one FSSF molecule with the sulfur lone pair electrons of another, analogous to the oligomer formation of SF₄^{22, 23, 25}, leaving the S–S bonds unaffected.

Since 1959 when Muetterties and Phillips²⁶ proposed, from NMR experiments, a SF₄ dimer as a fluorine exchange intermediate with bridged equatorial fluorine atoms (Fig. 6a), numerous investigations of the structure of SF₄ oligomers and fluorine exchange mechanisms have been published. Based on the assignments of the SF₄ vibrations, accepted at the time, Redington and Berney²² proposed the SF₄ dimer, shown in Fig. 6b from matrix IR spectrometric measurements. However, studies of the matrix IR spectra of ClF₃ and BrF₃ lead to a reassignment of the antisymmetric axial and equatorial stretching vibrations of SF₄²⁵ and a proposal of a dimeric structure (Fig. 6c) in which axial S–F bonds are used, was made. A great deal of support exists for structure 6c based on IR and Raman spectra of solid SF₄²³ and from NMR spectrometric measurements^{27, 28}.

The bond lengths of the axial and equatorial S–F bonds in SF₄ are different [axial: $d(\text{S–F}) = 1.646 \text{ \AA}$, equatorial: $d(\text{S–F}) = 1.545 \text{ \AA}$ ²⁹], association occurs via the long S–F bonds. SSF₂ and FSSF have different S–F bond lengths [SSF₂: $d(\text{S–F}) = 1.598 \text{ \AA}$ ², FSSF: $d(\text{S–F}) = 1.635 \text{ \AA}$ ³⁰]. The role of the two distinct S–F bonds of the disulfur difluoride isomers in the formation of stable dimers during matrix annealing appears to be similar to the role which play the equatorial and axial S–F bonds of SF₄. In both cases stable dimers are formed employing the long S–F bonds.

Figure 6d shows a possible structure of a FSSF dimer. As in the SF₄ dimer, each sulfur atom is bonded to one fluorine atom. Such a dimer is not possible in the case of SSF₂, which can form a structure where each fluorine interacts with one sulfur atom only in a polymer but not in a dimer.

Both SSF₂ and OSF₂ show the same matrix shifts whether FSSF is present or not. Similarly the presence of SSF₂ or OSF₂ does not alter the shifts of FSSF. Because it seems unlikely that the matrix

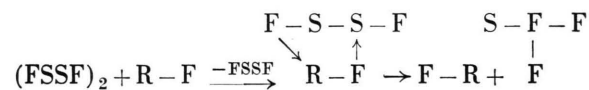
shifts are not altered by the formation of different adducts, it is thought, that the FSSF dimer is formed also in the presence of the other two sulfur fluorine compounds.

Rearrangement and Decomposition of FSSF, SSF₂ and FSSSF

SSF₂ is the thermodynamically more stable disulfur difluoride isomer, however, the stability difference between SSF₂ and FSSF is small¹. The spontaneous rearrangement of FSSF to SSF₂ is prevented by an energy barrier of approximately 1 eV, as estimated by a CNDO/2 calculation³¹.

The low temperature matrix results discussed above do not support the existence of an FSSSF·SSF₂ adduct, postulated by Seel and Budenz⁶. Rearrangement of FSSF to SSF₂ seems to be a bimolecular process, however an intermediate FSSSF·SSF₂ adduct is not formed. In the gas phase FSSF is stable even in the presence of large amounts of HF²¹, which is known to catalyze rearrangement in the liquid phase¹, FSSF is also stable at pressures of about 600 torr and for extended periods of time (300 hours)²¹. FSSF forms, as SSF₂, no adducts in the gas phase at pressures lower than 10 torr, no deviation from linearity have been observed for Bouguer-Lambert-Beer plots²¹.

In the condensed state, only FSSF dimers are to be found. Regarding such dimers, a catalytic rearrangement must be induced by a displacement of one FSSF molecule by the catalysing reagent, which only attacks at one S–F bond and therefore has a destabilising effect. If the catalysing compound contains a fluorine atom, the rearrangement can proceed via fluorine exchange.



The single fluorine containing product, observed NMR spectroscopically¹², in the decomposition of FS₃F is FSSF. This result is not in accordance with our observation that SSF₂ and FSSF are the only fluorine containing decomposition products. Because rearrangement of FSSF into SSF₂ has never been observed on recording low temperature spectra these different results may be rationalised by the different compositions of the samples investigated by Seel and coworkers¹² compared to our samples.

Seel et al. have investigated liquid mixtures of FS_3F with FS_4F . Some of our FS_3F samples contained the other lower sulfur fluorides S_2F_4 and FSSF , but never FS_4F (and never HF).

It seems possible to suggest formation of adducts of FS_3F molecules similar to those of FSSF . That

means, the spontaneous decomposition of FS_3F proceeds via a dimer (or an oligomer) and may be autocatalytic above a certain temperature. From this point of view the formation of SSF_2 seems to be probable, because its formation from the dimer is possible as well as the formation of FSSF .

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