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Silicon–Fluorine Chemistry. III. Infrared Studies of SiF_2 and Its Reactions in Low-Temperature Matrices[1]

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SiF_2(g) has been generated at high temperatures and condensed on a CsI window at 20°K. The infrared spectrum, which has been recorded as SiF_2 molecules polymerize on warm-up, provides evidence for the existence of a reactive species, probably $(SiF_2)_2$. Matrix spectra have also been observed for SiF_2 reacting with BF_3, O_2, CO, NO, and other molecules over the temperature range 20–50°K.

Gaseous, monomeric silicon difluoride is produced as a relatively long-lived species by the action of silicon tetrafluoride on silicon at high temperatures and low pressures. Mass spectroscopic work has indicated that the gaseous species SiF_4 and SiF_2 account for at least 99.5% of the reaction product and that gaseous polymers do not form.[2a] Nevertheless, chemical evidence from the reactions of silicon difluoride[2b] has suggested that the low-temperature, condensed-phase polymerization of the compound might be stepwise, involving interesting intermediates.

Matrix infrared spectroscopy seems an ideal tool for following this low-temperature polymerization. In addition, it was hoped that the method would provide the first infrared data on monomeric silicon difluoride and would enable the reactions of silicon difluoride with other compounds added to the matrix to be studied.

One difficulty, however, with all matrix spectral studies is that splitting and shifting of vibrational bands occurs. As Figure 1 indicates, matrix-isolated silicon tetrafluoride gives a group of strong absorption lines from 1000 to 1030 cm^{-1} instead of the expected single asymmetric stretching vibrational frequency in that region. Although this effect has been found by several researchers,[3] it is not fully understood and it has imposed some limitations on the interpretation of results from the outset of the work.

Experimental Section

Silicon difluoride was produced in a furnace attached directly to a liquid hydrogen cooled cryostat which has been described elsewhere.[4] Its rate of formation was controlled by the amount of silicon tetrafluoride (Matheson Co., nominally 99.6% purity) passed over granular 99.9% pure silicon contained in a quartz tube at 1150°. The off-gas from the furnace, containing a roughly 3:2 molar ratio of $SiF_2:SiF_4$, entered the cryostat along a short curved tube which prevented direct radiation from the hot zone from hitting the cold window.

Argon and krypton (Big Three Welding Co., nominally 99.999% minimum purity, and The Matheson Co., nominally 99.987% minimum purity, respectively) were used as matrix gases without further purification. The molar ratios of matrix gas to reactive species varied from 120:1 for concentrated matrices to 900:1 for very dilute matrices. Approximately 50 μmoles of the reactive species was required to give a clear spectrum. In order to study the matrix reaction of SiF_2 with another compound, the secondary species was mixed with the matrix gas in the desired molar ratio by standard manometric techniques.

When the liquid hydrogen was removed from the cryostat, it took approximately 1 hr for the temperature to rise from 20 to 55°K (the upper limit for a krypton matrix). Spectral changes due to diffusion and reaction of the species trapped in the matrix could be followed over this period.

A Beckman IR-9 instrument was used with the slit width programmed to give a resolution of two wavenumbers.

Polymerization of SiF_2

Results.—The absorption spectrum of the SiF_4–SiF_2 mixture is shown in Figure 2, and the observed frequencies are recorded in Table I. In addition to the asymmetric stretching frequency of SiF_4 at 1020 cm^{-1}, it contains a complex multiplet in the region of 850 cm^{-1}, which, because of its instability at higher temperatures, is assigned to SiF_2. This multiplet exhibits three intense bands, at 855, 843, and 811 cm^{-1}, as well as several bands and shoulders of lesser intensity. In a concentrated matrix this multiplet degenerated into a single broad band with a maximum at 855 cm^{-1} and several low-frequency shoulders.

TABLE I

FREQUENCIES OBSERVED FOR ν_3 OF SiF_4 AND ν_1 OF SiF_2 AT HIGH DILUTION IN A MATRIX

SiF_4[a]		SiF_2	
Band position, cm^{-1}	Rel intensity[b]	Band position, cm^{-1}	Rel intensity[d]
987	0.12	795	0.23
991	0.69	800 sh	
995	0.09	802 sh	
1001	0.15	809 sh	
1006	0.62	811	0.55
1012 sh[c]		823	0.15
1015	0.45	835	0.25
1020 sh		843	0.82
1023	1.00	855	1.00
1029	0.72	858 sh	
1033 sh		864 sh	

[a] In gaseous SiF_4, this fundamental is at 1022 cm^{-1}. [b] Intensities are relative to that of band at 1023 cm^{-1}. [c] Shoulders are designated by "sh." [d] Intensities are relative to that of band at 855 cm^{-1}.

The first changes in this spectrum warm-up experi-

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[1] Abstracted in part from a thesis presented in partial fulfillment of the requirement for the M.S. Degree by Jouette M. Bassler to the Faculty of Rice University, Houston, Texas.

(2) (a) P. L. Timms, R. A. Kent, T. C. Ehlert, and J. L. Margrave, *J. Am. Chem. Soc.*, **87**, 2824 (1965); (b) P. L. Timms, T. C. Ehlert, and J. L. Margrave, *ibid.*, **87**, 3819 (1965).

(3) Private communications with C. V. Berney, Mellon Institute, and S. H. Garnett, Princeton University.

(4) A. Snelson and K. S. Pitzer, *J. Phys. Chem.*, **67**, 882 (1963).

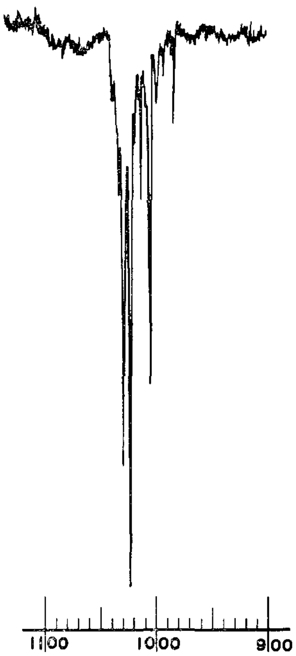

Figure 1.—Infrared spectrum of SiF_4 in argon at 20°K. Only the region of the infrared-active ν_3 fundamental is reproduced; $Ar/SiF_4 = 2000/1$; 9 μmoles SiF_4 deposited.

Figure 2.—Infrared spectrum of SiF_4 and SiF_2 in argon at 20°K. Only the regions of the ν_3 fundamental of SiF_4 and the ν_1 fundamental of SiF_2 are reproduced; $Ar/SiF_2 = 700/1$.

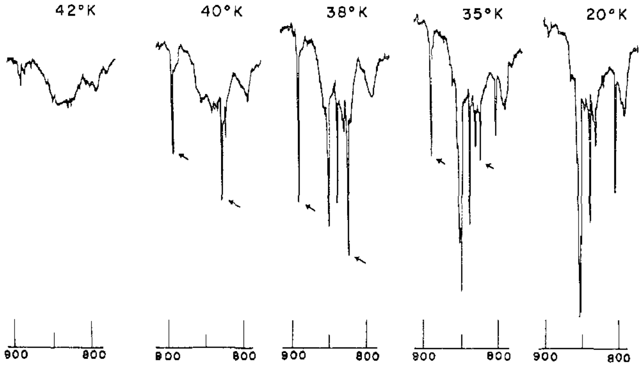

Figure 3.—Infrared spectra of SiF_2 in argon during warm-up procedure. The new bands attributed to Si_2F_4 are indicated by arrows; $Ar/SiF_2 = 700/1$.

ment occur at 35°K in both argon and krypton matrices, at which temperature two sharp new bands appear at 892 and 830 cm^{-1}. As the SiF_2 multiplet decreases in intensity, these new bands grow, reach a maximum intensity, and then disappear (see arrows, Figure 3) by 40°K in argon or 58°K in krypton. As these two bands decrease in intensity, two new, broad bands at 930 and 970 cm^{-1} grow, and the latter remain until the matrix disintegrates. The spectral changes of the concentrated matrix are analogous, although more intense, and a broad band at 840 cm^{-1} also remains until the matrix is destroyed.

Discussion.—Silicon difluoride in its singlet ground state is a bent molecule with C_{2v} symmetry and a bond angle of 101°.[5] Therefore, all three vibrational modes are infrared active. If the single band, or group of bands, at 855 cm^{-1} is assigned to the symmetric stretching frequency of SiF_2, this would represent a matrix shift of -82 cm^{-1} from the gas phase value derived from ultraviolet emission spectra.[6] Although this frequency shift is unusually high, shifts of similar magnitude have been observed by Linevsky,[7] who reports a shift of -70 and -77 cm^{-1} for the spectrum of LiF in krypton and xenon matrices, respectively. The asymmetric stretching frequency is then assumed to be obscured by the intense SiF_4 band at 1020 cm^{-1}. The width of this band (approximately 50 cm^{-1}), as well as its high intensity, facilitates this overlapping. The bending frequency is assumed to occur below 400 cm^{-1}, the low-frequency limit of the instrument used. This assumption is substantiated by the microwave data, which predict a value of 343 ± 1 cm^{-1} for this fundamental.[5]

The multiplicity of the band at 855 cm^{-1} is not well understood. Neither the position nor the relative intensities of the peaks vary significantly when different matrix gases are used, and the phenomenon of associated species is discarded as an explanation since dilution of the matrix does not produce any changes in the relative intensities of the various peaks. The intense band at 811 cm^{-1} is observed to disappear much more rapidly during warm-up experiments than the remainder of the multiplet. Furthermore, this band is absent when the path length from the furnace to the cold window is increased to 10 ft or when nitric oxide is deposited in the same matrix. Because of this be-

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[5] V. M. Rao, R. F. Curl, P. L. Timms, and J. L. Margrave, *J. Chem. Phys.*, **43**, 2557 (1965).

[6] J. W. C. Johns, G. W. Chantry, and R. F. Barrow, *Trans. Faraday Soc.*, **54**, 1589 (1958).

[7] M. J. Linevsky, *J. Chem. Phys.*, **34**, 587 (1961).

havior, this peak and a low-intensity satellite band at 795 cm^{-1} are assigned to a different, more reactive species, perhaps a small amount of triplet SiF_2, or SiF and SiF_3 impurities.

The new, sharp, transient bands which appear at 35°K are assumed primarily due to a reactive dimeric form of SiF_2. They cannot arise from Si_2F_6 since this species would be stable and since the reaction of SiF_2 with SiF_4 has not been observed to occur.[2a] Furthermore, SiF_2 is thought to react with other compounds at higher temperatures in the form of a dimer.[2b] The polymerization of SiF_2 in the matrix is considered to be complete by 50°K because the broad bands then seen in the spectra are essentially identical with those obtained for thin layers of SiF_2 polymer at room temperature.

Heterogeneous Matrix Reactions

The application of matrix isolation methods to the study of reactions has previously been limited to systems in which very reactive species are generated *in situ* by photodecomposition. However, the "free radical" character of silicon difluoride[2a] suggested that its reactions with other compounds should be observable in inert matrices at very low temperatures. It was hoped that these reactions would enable the detection of possible precursors to the products observed with the preparative scale reactions of SiF_2 at liquid nitrogen temperatures.

In practice, reactions were not observed in matrices between SiF_2 and NF_3, PF_3, or C_6H_6, although these were observed to react in preparative experiments at liquid nitrogen temperatures, but BF_3, O_2, CO, and NO reacted in the manner described below.

$SiF_2 + BF_3$.—When boron trifluoride (The Matheson Co., nominally 99.0% minimum purity) and SiF_2 are deposited in the same matrix, the initial spectrum is a superposition of the matrix spectra of the two components. When the matrix is allowed to warm to 35–50°K, in addition to the typical changes in the SiF_2 spectrum, new bands appear at 420, 458, 882, 1242, 1260, and 2282 cm^{-1}. These bands remain until the matrix collapses.

The new bands coincide with those bands of the gas phase spectrum of perfluorodisilanylboron difluoride (Si_2BF_7) which do not overlap the BF_3, SiF_2, or SiF_4 fundamentals. Furthermore, they began to appear when the transient bands assigned to $(SiF_2)_2$ are at their maximum intensity. Thus Si_2BF_7 appears to be formed directly from $(SiF_2)_2$ and BF_3 at temperatures as low as 35°K, and no intermediate complex of the type $(SiF_2)_2BF_3$ has been observed spectroscopically.

$SiF_2 + O_2$.—The spectrum at 20°K of a matrix containing oxygen and SiF_2 is identical in all respects with a typical spectrum of the SiF_2–SiF_4 mixture, even when the matrix contains 50% oxygen. During warm-up, the only spectral changes which occur are the gradual growth at temperatures above 45°K of a very broad band centered at 1200 cm^{-1}, a blue shift of the bands in the 900–1000 cm^{-1} region, and the appearance of a broad new band at 912 cm^{-1}.

The nature and position of the new bands which appear in the spectrum indicate that they arise from a polymeric species which incorporates oxygen. It is surprising that no monomeric reaction product between SiF_2 or $(SiF_2)_2$ and oxygen was detected even in matrices concentrated in oxygen and that the polymerization proceeds so slowly, in view of the extreme reactivity of these two species at room temperature.[2a]

SiF_2 + CO.—Only a single band at 2141 cm^{-1} is observed in addition to the SiF_2–SiF_4 spectrum when carbon monoxide (The Matheson Co., nominally 99.5% minimum purity) is deposited with the matrix gas. The spectra taken during warm-up show the growth of a new band at 1880 cm^{-1} which becomes very intense and which remains until the matrix collapses. Furthermore, SiF_2–polymer bands (930 and 970 cm^{-1}) reach only half of their usual intensity.

The position of the new band at 1880 cm^{-1} is characteristic of bridging carbonyls and could indicate that the reaction product is $(SiF_2)_2(CO)_2$. However, it is more probable that the reaction product is instead a simple compound, SiF_2CO, and that the electron-withdrawing ability of the SiF_2 moiety is sufficient to shift the carbonyl frequency to 1880 cm^{-1}. At high temperatures the SiF_2–CO compound decomposes to yield volatile silicon oxyfluorides and a carbon-rich polymer.

SiF_2 + NO.—The spectrum of nitric oxide (The Matheson Co., nominally 99.0% minimum purity) in a krypton matrix consists of two bands at 1762 and 1863 cm^{-1} with shoulders at 1778 and 1873 cm^{-1}, indicating that a *cis*-dimeric form of nitric oxide is present.[8] No reaction is observed between NO and SiF_4 in a matrix, but when NO and SiF_2 are deposited together in a matrix, even at 20°K, the spectrum contains new bands. During warm-up procedures, these bands disappear and a second series of well-developed bands arises, as indicated in Table II. These bands remain until the matrix disintegrates. The broad bands at 930 and 970 cm^{-1} fail to appear, and the transient bands normally observed for $(SiF_2)_2$ at 830 and 892 cm^{-1} are extremely weak.

TABLE II

NEW BANDS IN NO + SiF_2 MATRIX AT DIFFERENT TEMPERATURES (Kr:NO = 170:1; Kr:SiF_2 = 500:1)

Bands at 20°K, cm^{-1}	Bands at 50°K, cm^{-1}
901 mw, s	587 m, b
1073 mw, s	718 m, b
1098 m, s	1200 m, vb
1495 s, s	1545 m, vb
1511 w, b	1718 m, b
	1830 m, b

The reaction in the matrix is obviously very complex, but some clarifying deductions can be made. First, the disappearance of the band at 811 cm^{-1} from the spectrum of SiF_2 in the presence of nitric oxide has

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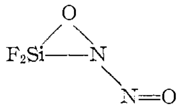
(8) W. G. Fateley, H. A. Bent, and B. L. Crawford, *J. Chem. Phys.*, **31**, 204 (1959).

been taken to indicate the possible presence of some triplet SiF_2 (see above). Second, the initial complex formed between SiF_2 and nitric oxide rapidly converts to a more stable species at 35°K, as all of the sharp new bands initially present are replaced by a different set of bands which persist until the matrix collapses above 55°K. Since very little SiF_2 dimer is formed, the species produced is assumed to be the reaction product of monomeric SiF_2 with the *cis*-dimeric form of nitric oxide which is predominant in the matrix. Mass spectrometric investigations indicate that this reaction product decomposes explosively at −150° to yield silicon oxyfluoride polymer and nitrous oxide. A structure for the reaction product that correlates well with this energetic release of N_2O and the observed frequencies is the heterocycle



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CONTRIBUTION FROM THE GORGAS LABORATORY, ROHM AND HAAS COMPANY,
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The Preparation and Chemistry of N-Chlorimidodisulfuryl Fluoride

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The preparation of $ClN(SO_2F)_2$ is described. It was found to undergo addition with CO, ClCN, and BrCN to produce $ClC(=O)N(SO_2F)_2$, $ClCN \cdot ClN(SO_2F)_2$, and $BrCN \cdot ClN(SO_2F)_2$, respectively. Photodecomposition of $ClN(SO_2F)_2$ produced $N_2(SO_2F)_4$ in high yield. The salt $NON(SO_2F)_2$ was formed by the interaction of NO and $ClN(SO_2F)_2$. Substitution of chlorine by the $N(SO_2F)_2^-$ ion was also found to occur in several metallic and organometallic chlorides. Some of the physical properties of these derivatives are discussed.

Although the preparation of N-fluorimidodisulfuryl fluoride was readily achieved by the action of fluorine on imidodisulfuryl fluoride,[1] the conversion of imidodisulfuryl fluoride to the N-chloro compound could not be accomplished in an analogous manner. However, chlorination of silver imidodisulfuryl fluoride produced N-chlorimidodisulfuryl fluoride in moderate yield. Furthermore the N-chloro compound proved to be a useful intermediate in the preparation of other derivatives containing the $N(SO_2F)_2$ group. For example, it was found to undergo addition reactions with various unsaturated systems as well as to substitute the $N(SO_2F)_2$ group for chlorine in several metallic and organometallic chlorides.

Experimental Section

Preparation of $ClN(SO_2F)_2$.—Chlorine gas, 31.1 mmoles, was condensed into a pressure reactor containing 6.0 g (20.8 mmoles) of $AgN(SO_2F)_2$.[2] The mixture was allowed to stand at ambient temperature for 48 hr before fractionation on the vacuum line through −8, −78, and −196° traps. The product from four runs, which was found in the −78° trap, was distilled through a Holzman[3] column, bp 36° (36 mm) (mp −52.5 to −52.0°). A yield of 62% (2.78 g) was obtained. *Anal.* Calcd for $ClN(SO_2F)_2$: F, 17.6; Cl, 16.5; N, 6.50. Found: F, 17.6; Cl, 16.1; N, 6.66.

Reaction of $ClN(SO_2F)_2$ with Aqueous KI.—A 0.3171-g sample of $ClN(SO_2F)_2$ was added to 1.521 g of KI in 10 ml of 0.1 *N* H_2SO_4 solution which was frozen at −78°. The mixture was allowed to warm to 25° and was then stirred for 0.5 hr. The iodine formed required 12.17 ml of a 0.2428 *M* $Na_2S_2O_3$ solution to reach the end point, suggesting that the reaction followed the equation

$$ClN(SO_2F)_2 + 2I^- \longrightarrow I_2 + Cl^- + N(SO_2F)_2^-$$

Preparation of $NON(SO_2F)_2$.—Nitrogen oxide, 27.9 mmoles, was condensed into a pressure reactor containing 0.917 g (4.25 mmoles) of $ClN(SO_2F)_2$. The reaction mixture was stirred 3 hr at 35–40° before static fractionation through −64, −126, and −196° cold baths. Unreacted nitrogen oxide, 23.6 mmoles, was found in the −196° cold trap. Nitrosyl chloride, 4.11 mmoles, was obtained in the −126° cold bath. It was identified by infrared spectroscopy and by reaction with excess $SbCl_5$ to produce 1.361 g of $NOSbCl_6$. *Anal.* Calcd for $NOSbCl_6$: N, 3.84; Cl, 58.3. Found: N, 3.69; Cl, 58.0. The product, 0.876 g (4.17 mmoles), remained in the reactor as a nonvolatile white solid; mp 43°. *Anal.* Calcd for $NON(SO_2F)_2$: N, 13.35; F, 18.1. Found: N, 13.50; F, 17.7.

Reaction of $NON(SO_2F)_2$ with HCl.—Anhydrous HCl gas, 25.8 mmoles, was condensed into a pressure reactor containing 1.296 g (6.17 mmoles) of $NON(SO_2F)_3$. The mixture was allowed to stand 3 hr at 25° before fractionation through −64, −126, and −196° cold traps. Nitrosyl chloride, 6.05 mmoles, and $HN(SO_2F)_2$, 1.026 g (5.67 mmoles) were formed, and 18.9 mmoles of HCl was recovered.

Preparation of $(FSO_2)_2NCOCl$.—Carbon monoxide, 36.5 mmoles, was added to 3.637 g (16.9 mmoles) of $ClN(SO_2F)_2$ contained in a 1-l. bulb. The reactor was heated to 50° for 3 hr before fractionation. The product was found in a −78° trap. The product from two runs was distilled through a Holzman column; bp 42° (31.5 mm). A yield of 84% was realized.

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[2] J. K. Ruff, *ibid.*, **4**, 1446 (1965).

[3] C. W. Gould, G. Holzman, and C. Nieman, *Anal. Chem.*, **20**, 361 (1948).