

All of the molecules studied here have remarkably small magnetic susceptibility anisotropies compared to the large values reported for ring compounds.³⁻⁵ As the values reported in Table IV are all computed from an estimated bulk susceptibility, they deserve further comment. In Table IV the values of $\langle x^2 \rangle$ in PF₃, OPF₃, and SOF₂ should be within 10% of each other.

The value of $\langle x^2 \rangle$ in SOF₂ is anomalously low which indicates that the Pascal value of χ in SOF₂ is too small. The remaining numbers would fall into approximate order if the magnitude of χ in SOF₂ were larger.

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Silicon-Fluorine Chemistry. VII. The Reaction of Silicon Difluoride with Hydrogen Sulfide

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A study of the reaction of silicon difluoride with hydrogen sulfide by cocondensing the reactants at liquid nitrogen temperature has been made. The resultant low-temperature polymer yielded the following compounds as it warmed to room temperature: SiF₂HSH, SiF₂HSiF₂SH, Si₂F₃H, and small amounts of SiF₂HSSH and Si₂F₄HSSH. These compounds could also be obtained by pyrolysis of the polymer at 120–140°. SiF₂HSH was observed to react with HCl to form SiF₂HCl and H₂S. Compounds were characterized by means of mass spectrometry and, where possible, by ¹H and ¹⁹F nmr and by infrared spectroscopy.

Introduction

The divalent carbene-like molecule silicon difluoride has been shown to possess an extensive reaction chemistry at low temperatures.¹⁻³ SiF₂ is customarily generated at high temperatures then cocondensed at -196° with a particular reactant. Reaction occurs as the condensate is allowed to warm to room temperature. A portion of the reaction products can generally be recovered as volatile products—the rest are bound in an involatile polymer which may often be pyrolyzed as a further source of products.

Much of the reaction chemistry of SiF₂ may be explained on the assumption that the reactive species are diradicals ·SiF₂(SiF₂)_nSiF₂· where $n = 0, 1, 2$, etc. The $n = 0$ species is the most favorable kinetically for addition reactions of the type $AB + (\text{SiF}_2)_{n+2} = \text{SiF}_2\text{A}(\text{SiF}_2)_n\text{SiF}_2\text{B}$, and in such reactions the predominant product often contains two silicon atoms.¹⁻³

Solan and Timms⁴ have recently reported the reaction of SiF₂ with GeH₄. The products obtained correspond to the formula GeH₃(SiF₂)_nH, with $n = 1-3$. The $n = 1$ homolog was the major product and was the only one of the products which was stable at room temperature. The authors suggested that the "usual" diradical dimer mechanism was not operative in this instance and that GeH₄ attacks the SiF₂ polymeric

chain, breaking off units containing one, two, or more silicon atoms.

The H₂S reaction might be expected to follow several different courses. If, for example, reaction occurs exclusively with the SiF₂ dimer, the logical product would be SiF₂HHSiF₂SH. H₂S is known to add across double bonds in the presence of radical initiators.⁵ If the reaction were to proceed in a manner similar to that of the germane reaction, one would expect the products SiF₂HSH, SiF₂HSiF₂SH, and so on. In addition, previous reactions of SiF₂ with dimethyl ether, acetonitrile, and acetone⁶ have indicated that SiF₂ is capable of abstracting a hydrogen atom from such molecules to form eventually SiF₃H, so that such a course would not be surprising for the H₂S reaction.

Few silanethiols, such as the products mentioned above, are known. The literature contains references to SiH₃SH,⁷ SiCl₃SH,⁸ and (C₂H₅)₃SiSH,⁹ and few others. The parent compound silanethiol was synthesized by Emeléus, *et al.*, from the reaction of disilyl sulfide with hydrogen sulfide and was found to be unstable with respect to condensation back into starting materials, even at temperatures as low as -78°. Such compounds as SiF₃SH or SiF₂HSH should be more stable than silanethiol itself because the electron-withdrawing power of the fluorines would make the Si-S bond more polar.

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Experimental Section

SiF_2 was produced as previously described¹⁰ by the reaction of SiF_4 with Si at 1150°. H_2S was obtained from the Matheson Co. and was used without further purification. Amounts of reactants used typically ran in the range 0.01–0.02 mol each. The condensate obtained at liquid nitrogen temperature was light brown to yellow and turned white on warming to room temperature. The volatile products were separated from SiF_4 and unreacted H_2S by trapping the former in a -120° slush bath. Because the silanethiols produced in the reaction proved to be quite unstable, the volatiles were usually not further separated for spectral analysis. Simple trap-to-trap distillation was successful in isolating a sample of pentafluorodisilane which was approximately 80% pure. The $\text{Si}_2\text{F}_5\text{H}$ passed through a -84° bath, but not a -110° bath. None of the volatile products could be recovered from a Kel-F on Teflon Six gas chromatographic column—only SiF_4 , SiF_3H , Si_2F_6 , and H_2S were eluted from the column.

For purposes of obtaining spectra, the compounds were distilled into small sample tubes for mass spectral analysis or into medium-walled Pyrex nmr tubes and sealed under their own vapor pressures at -196° . Nmr spectra were generally taken in the range -40 to 0° . For the ir analyses, a standard 10-cm ir gas cell with KBr windows was utilized. All mass spectra were taken on a Bendix 14-206A time-of-flight instrument; appearance potentials of some of the more important ions were determined utilizing the extrapolated difference method.¹¹ Nmr spectra were taken on a Varian A-56/60A spectrometer and infrared spectra were run on a Beckman IR-9.

Pyrolysis of the Polymer.—The room-temperature polymer is both easily hydrolyzed and quite pyrophoric and must be handled solely in inert atmospheres. A sample of the polymer was removed from the vacuum line under nitrogen and transferred to a glove bag, where it was placed in a sample tube that could be attached to the direct-inlet source of a mass spectrometer. The sample was then carefully heated until volatile species could be detected in the spectrometer.

Results

Mass Spectral Studies.—A typical mass spectrum of the volatile products is presented in Table I. The relative intensities of the peaks (S = small, M = medium, L = large, V = very) are listed for both high- and low-voltage spectra.

Appearance Potentials.—Appearance potentials were determined for those ions believed to be parent ions, and for several ions related to the parent ions as [parent – F]⁺ or [parent – H]⁺. Results are shown in Table II.

Comparison of the high- and low-voltage mass spectra, coupled with appearance potential values, indicates parent ion peaks at masses 100, 132, 166, and 198. These masses correspond, respectively, to $\text{SiF}_2\text{-H}_2\text{S}$ (I), $\text{SiF}_2\text{H}_2\text{S}_2$ (II), $\text{Si}_2\text{F}_4\text{H}_2\text{S}$ (III), and $\text{Si}_2\text{F}_4\text{H}_2\text{S}_2$ (IV). The presence of the compound $\text{Si}_2\text{F}_5\text{H}$ cannot be directly demonstrated from the mass spectra, since it, like Si_2F_6 , does not give rise to a molecular ion but fragments to $\text{Si}_2\text{F}_4\text{H}^-$ instead.

Although fragmentation patterns are not sufficient to determine the structures of compounds II–IV, the fact that peaks at mass numbers 64 and 65, likely due to S_2^+ and S_2H^+ ions, are present and the known tendency for SiF_2 to react as the dimer lead one to postulate the

TABLE I

MASS SPECTRA OF VOLATILE PRODUCTS OF $\text{SiF}_2\text{-H}_2\text{S}$ REACTION

Mass no. ^a	Low voltage (14–17 eV)	High voltage (50 eV)	Identity
61	...	M	SiHS^+
64	S	S	S_2^+
65	S	S	S_2H^+
66	S	L	SiF_2^+
67	S	L	SiF_2H^+
80	L	L	SiFHS^+
81	VL	L	SiFH_2S^+
99	M	L	SiF_2HS^+
100	L	M	$\text{SiF}_2\text{H}_2\text{S}^{+b}$
113	...	S	Si_2F_3^+
114	...	S	$\text{Si}_2\text{F}_3\text{H}^+$
129	...	S	$\text{Si}_2\text{F}_4\text{H}_3\text{S}^+$
132	S	...	Si_2F_4^+ , $\text{SiF}_2\text{H}_2\text{S}_2^{+b}$
133	S	S	$\text{Si}_2\text{F}_4\text{H}^+$
147	M	M	$\text{Si}_2\text{F}_3\text{H}_2\text{S}^+$
151	S	M	Si_2F_5^+
165	M	M	$\text{Si}_2\text{F}_4\text{HS}^+$
166	M	M	$\text{Si}_2\text{F}_4\text{H}_2\text{S}^{+b}$
179	...	S	$\text{Si}_2\text{F}_3\text{H}_2\text{S}_2^+$
180	S	S	$\text{Si}_2\text{F}_3\text{H}_3\text{S}_2^+$
197	S	S	$\text{Si}_2\text{F}_4\text{HS}_2^+$
198	S	...	$\text{Si}_2\text{F}_4\text{H}_2\text{S}_2^{+b}$

^a Mass numbers corresponding to ions derived predominantly from SiF_4 and H_2S , as well as those from background sources, have been omitted. ^b Parent ion peak.

TABLE II

APPEARANCE POTENTIALS FROM $\text{SiF}_2\text{-H}_2\text{S}$ REACTION PRODUCTS

m/e	Ion identity	Appearance potential, eV
166	$\text{Si}_2\text{F}_4\text{H}_3\text{S}^+$	10.6 ^a
100	$\text{SiF}_2\text{H}_2\text{S}^+$	10.7
132	$\text{SiF}_2\text{H}_2\text{S}_2^+$	10.7
133	$\text{Si}_2\text{F}_4\text{H}^+$ (from $\text{Si}_2\text{F}_3\text{H}$)	11.1
147	$\text{Si}_2\text{F}_3\text{H}_2\text{S}^+$	11.3
99	SiF_2HS^+	11.9
81	SiFH_2S^-	12.3
67	SiF_2H^+ (from SiF_3H)	13.4

^a Estimated experimental accuracy ± 0.6 eV; estimated experimental precision ± 0.3 eV.

following structures for compounds II–IV: SiF_2HSSH (II), $\text{SiF}_2\text{HSiF}_2\text{SH}$ (III), $\text{SiF}_2\text{HSiF}_2\text{SSH}$ (IV). Although the mass 198 peak was not sufficiently intense for its appearance potential to be determined, its relative intensity did increase significantly at low voltages.

Nmr Studies.—The samples utilized for nmr studies were liquids under several atmospheres pressure at room temperature. Even when the tubes were not allowed to warm to room temperature and spectra were taken at low temperatures (-30°), the indications were that the compounds which had been observed in the mass spectrometer had largely decomposed to SiF_4 , H_2S , and SiF_3H . Of the reaction products, only SiF_2HSH and $\text{Si}_2\text{F}_5\text{H}$ could be observed without difficulty under nmr conditions. A spectrum of $\text{SiF}_2\text{HSiF}_2\text{SH}$ was obtained only by distilling as much material as possible into an nmr tube and scanning rapidly at -30° . Results of proton and fluorine nmr spectra are summarized in Table III.

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TABLE III
 NMR SPECTRA OF VOLATILE PRODUCTS

Compound	Group structure	δ , ppm	J_{H-H} , Hz	J_{H-F_α} , Hz	J_{H-F_β} , Hz	J_{F-F} , Hz
		1H Spectra				
SiF_2HSiF_3	Triplet of quartets	4.67	...	54.0	13.3	...
SiF_2HSH	Triplet of doublets	4.94	1.2	76.3
SiF_2HSH	Triplet of doublets	0.21	1.2	...	5.8	...
SiF_2HSiF_2SH	Triplet of triplets	4.92	<1	55.0	9.1	...
SiF_2HSiF_2SH	Triplet	0.36	<1	...	7.5	...
^{19}F Spectra						
SiF_2HSiF_3	Doublet of quartets	142.4	...	53.2	...	12.7
SiF_2HSiF_3	Quartet	125.3	12.7	12.7
SiF_2HSH	Doublet of doublets	122.9	...	75.2	5.6	...
SiF_2HSiF_2SH	Doublet of triplets	143.0	...	54.9	...	10.8
SiF_2HSiF_2SH	Unresolved multiplet	118.1	Observed coupling of ~ 10 Hz			

^a TMS external 1H reference; CCl_3F external ^{19}F reference.

The observed spectra can be explained on the basis of first-order coupling between the various nuclei. The absorption of the β -fluorines in Si_2F_5H does not correspond to the expected triplet of doublets because of the similarity of J_{F-F} to J_{H-F_β} ; the situation is confirmed by observing that the quartet splittings for both the proton and F_β resonances are approximately 13 Hz. It is interesting to note that the same phenomenon occurs for pentafluoroethane ($J_{F-F} = 2.79$ Hz, $J_{H-F} = 2.76$ Hz).¹²

The proton spectrum of difluorosilanethiol is first order because of the wide difference in chemical shift (4.7 ppm) between the silicon and sulfur hydrogens. The spectra for 1,1',2,2'-tetrafluorodisilanethiol indicate little or no coupling between the thiol hydrogen and the nuclei bonded to the terminal silicon. The chemical shifts of both the proton and fluorine resonances in the SiF_2H group are nearly identical with those of the corresponding group in Si_2F_5H . The $-SiF_2-$ fluorines would be expected to give rise to a symmetrical 12-line multiplet. The only resonance which could be correlated with these nuclei, however, had the rough appearance of a quintet with a splitting of approximately 10 Hz. Such a group could arise if the fluorines in question are nearly equally coupled with the other four magnetic nuclei in the system.

When the sample tubes used to obtain the above spectra were allowed to stand at room temperature, the spectra associated with SiF_2HSiF_2SH disappeared after a few minutes. After several weeks, the proton spectrum of the sample contained a much larger H_2S peak and a quartet (δ 4.15 ppm, $J_{H-F} = 96.0$ Hz) identified as characteristic of SiF_3H . A small triplet (δ 4.64 ppm, $J_{H-F} = 54.3$ Hz) due to SiF_2H_2 was also observed. These absorptions had appeared at the expense of the pentafluorodisilane and difluorosilanethiol spectra seen in the earlier samples. A large amount of solid material was also formed in the decomposition process.

Infrared Spectra of Volatile Products.—The volatile products were pumped through a series of cold traps at approximately 10 μ pressure in hopes of obtaining samples suitable for infrared analysis. Each fraction was degassed at -120° to remove SiF_4 and then distilled into the ir cell at 10–15 mm. The cell was filled to atmospheric pressure with dry nitrogen before spectra were taken. This procedure was successful for isolating a sample of Si_2F_5H sufficiently pure to yield definitive spectra; however, a spectrum could not be obtained for difluorosilanethiol, since fractions containing a large proportion of this compound generally contained a significant amount of SiF_3H , SiF_4 , H_2S , and Si_2F_5H .

No spectrum of Si_2F_5H completely free from SiF_3H was obtained; the maximum yield of pentafluorodisilane (ca. 80%) was obtained from those volatiles which passed through a -84° bath but not a -110° bath. The infrared spectrum of Si_2F_5H agreed well with that obtained by Baay.¹³ A gaseous sample of composition Si_2F_5H (70%), SiF_3H (20%), and SiF_4 (10%) at 1 cm pressure decomposed to SiF_3H and SiF_4 on standing for 1.5 hr. A window absorption centered at 770 cm^{-1} also appeared as decomposition progressed. Since silicon-fluorine compounds are generally quite moisture sensitive, it is possible that traces of moisture in the infrared cell facilitated decomposition. No evidence for disproportionation of Si_2F_5H to Si_2F_6 and $Si_2F_4H_2$ was obtained.

Reaction of SiF_2HSH with HCl.—A product sample previously shown by its nmr spectrum to consist primarily of difluorosilanethiol and pentafluorodisilane was distilled into a thick-walled Pyrex tube along with an approximately equimolar amount of anhydrous HCl. The tube was sealed and allowed to warm to room temperature. The contents of the tube were then analyzed mass spectrometrically. The mass spectra indicated that the SiF_2HSH had completely reacted and/or decomposed. The volatile products of the reaction were H_2S , SiF_3H , and SiF_2HCl , and a lesser amount of SiF_4 . At least some of the Si_2F_5H apparently remained unchanged. The evidence, including the relative amounts of H_2S and SiF_2HCl in the products, suggested that a portion of the SiF_2HSH underwent reaction with the HCl to produce H_2S and SiF_2HCl , while the remainder suffered thermal decomposition to H_2S and involatile solids (and perhaps to some SiF_3H and SiF_4 as well). It is interesting to note that the reaction of the thiol with HCl is the reverse of a reaction reported by Etienne¹⁴ in which organohalosilanes react with H_2S in the presence of base to form silanethiols and HCl.

Pyrolysis of the Polymer.—The polymer was heated *in vacuo* as described above with the following observations: 80° , SiF_4 , SiF_3H , and Si_2F_6 evolved; 110° , some discoloration of the polymer due to formation of free sulfur; 120 – 140° , Si_2F_5H and SiF_2HSH predominated with smaller amounts of higher molecular weight

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homologs and some Si_2OF_6 was evolved from reaction of the polymer with the Pyrex container; 160° , mostly SiF_4 , higher perfluorosilanes, and Si_2OF_6 evolved.

Discussion

When the $\text{SiF}_2\text{-H}_2\text{S}$ reaction was first investigated, the "diradical" mechanism of SiF_2 reactions seemed well established—with the single exception of the hexafluorobenzene reaction.² In accord with this mechanism, one would expect the predominant product of the reaction to be 1,1',2,2'-tetrafluorodisilanethiol, $\text{SiF}_2\text{-HSiF}_2\text{SH}$. Although this compound is indeed formed in the reaction, it is not the major product— SiF_2HSH and $\text{Si}_2\text{F}_5\text{H}$ are obtained in higher yields. In this regard, the present reaction is analogous to the $\text{SiF}_2\text{-GeH}_4$ reaction.⁴ Moreover, several other reactions recently studied in this laboratory⁶ give rise to major products which contain only one silicon atom. It seems at this point that, among reactions of SiF_2 with inorganic substances, the $\text{SiF}_2\text{-BF}_3$ and the $\text{SiF}_2\text{-benzene}$ reactions in which the products contain at least two silicons should be considered the exception.

The silanethiols produced in this reaction were found to be of limited stability, as have those synthesized in the past. Moreover, as with the fluorosilylgermanes generated in the germane reaction, the stability of the fluorosilanethiols decreases markedly with increasing numbers of silicon atoms. Condensation was evident in the trap-to-trap distillation of the volatiles; each transfer of sample left an intractable viscous liquid or spongy solid on the walls of the trap. It is possible, then, that the compounds $\text{SiF}_2\text{H}(\text{SiF}_2)_n\text{SH}$, where $n > 1$,

are formed in the reaction but decompose very readily to higher molecular weight species of the form $\text{H}(\text{SiF}_2)_n\text{-S}(\text{SiF}_2)_n\text{H}$ or $(\text{SiF}_2)_n$, liberating H_2S . In this respect it is interesting to note that $\text{SiF}_2\text{HSSiF}_2\text{H}$, the product expected from condensation of SiF_2HSH , was not observed.

It is difficult to ascertain whether or not SiF_3H is a product of the reaction or simply a decomposition product of $\text{Si}_2\text{F}_5\text{H}$ and perhaps higher molecular weight homologs. $\text{Si}_2\text{F}_5\text{H}$ does appear to be a legitimate product; it was often obtained in yields as high as 40% (based on total volatiles) and has been reported as a product in the reaction of SiF_2 with HBr .¹³ Consideration of the fact that no compounds such as SiF_3SH or $\text{Si}_2\text{F}_5\text{SH}$ were observed, along with the high yield of pentafluorodisilane, leads to the suggestion that reaction is not a concerted process but that at least two steps are involved. The first is the abstraction of a hydrogen atom from H_2S by an $(\text{SiF}_2)_n$ species. The resultant radical may then either attack the thiol radical produced in the first step or may obtain a fluorine atom from an SiF_4 or $(\text{SiF}_2)_n$ species. A possible explanation of the dithiol functions observed in the products is that they result from attack of SiF_2 (or Si_2F_4) on H_2S_2 , which might in turn be formed from combination of the thiol radicals formed in the first step of the reaction.

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The Melting Curve of Sulfur to 31 kbars

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The melting curve of sulfur has been determined to 31 kbars by the use of the opposed anvil and simple piston-cylinder techniques. Triple points have been found at 9 kbars and 255° , 18 kbars and 344° , and at 20.6 kbars and 375° .

Introduction

The effect of high pressure on the melting temperature of sulfur has been the subject of much inquiry. Tammann,¹ by specific-volume methods, investigated the melting curve of sulfur to a pressure of about 3 kbars. Rose and Mugge,² relying on an optical study of the quenched product, determined the liquidus to about 20 kbars and reported what appears to be a definite slope change at about 9.6 kbars at 205° .

Deaton and Blum,³ using a tetrahedral anvil pressure

apparatus setup for differential thermal conductivity analysis, found the melting curve of sulfur to 45 kbars and 700° to be approximately a straight line with a slope of $15^\circ/\text{kbar}$. Baak,⁴ employing an opposed anvil apparatus, determined the melting curve of sulfur to 60 kbars and found it to be concave toward the pressure axis. Paukov, Tonkov, and Mirinskiy,⁵ employing a thermal analysis method in conjunction with a "cubic" anvil pressure system, located a maximum in the melting curve of sulfur at approximately 16 kbars and 310°

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