

Short Communication

The isolation and characterization of pentafluorodisilane

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Very few members of the class of compounds corresponding to the formulas $\text{Si}_2\text{H}_n\text{F}_{6-n}$ have been characterized. Disilanylfluoride, the first fluorodisilane to be reported, can be obtained from the reaction of tris(disilanyl)amine with boron trifluoride¹. $\text{Si}_2\text{H}_5\text{F}$ is stable at 0° if trace amounts of acids and bases are excluded. More recently, the species 1,1-difluoro- and 1,1,1-trifluoro-disilane have been reported to arise from the interaction of 1,1-dichlorodisilane with antimony(III) fluoride². $\text{SiH}_3\text{SiF}_2\text{H}$ and SiH_3SiF_3 were characterized by means of their ¹H and ¹⁹F NMR spectra; no other physical or chemical properties of the compounds were described except for selected bands in the Raman spectrum of the difluoro-disilane.

Two references to pentafluorodisilane, $\text{Si}_2\text{F}_5\text{H}$ (I), exist; both concern reactions of the high-temperature molecule silicon difluoride. The reactions of SiF_2 with hydrogen halides, HX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), are reported³ to yield (I), but no details of characterization have been supplied. The reaction of SiF_2 with hydrogen sulfide has been shown to generate (I)⁴. In the latter system, however, (I) could not be separated from the other reaction products and was characterized (chiefly *via* ¹H and ¹⁹F NMR) as a component of a complex mixture. We now wish to report the isolation of (I) and to substantially extend its known properties.

In the course of re-investigating the reaction of SiF_2 with HBr , we have determined that $\text{Si}_2\text{F}_5\text{H}$ is not a major primary product of the reaction, as previously supposed. The compound results, instead, from the decomposition of 1-bromo-1,1,2,2-tetrafluorodisilane, $\text{SiF}_2\text{HSiF}_2\text{Br}$ (II), which is itself the preponderant product of the reaction. Physical separation of (II) from (I) is difficult due to a surprising similarity in the volatilities of the two compounds. Isolation of (I) can

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nevertheless be effected by multiple runs on a low-temperature distillation column. A much more efficient process for the production of (I), however, involves fluorination of the Si-Br bond in (II) with antimony(III) fluoride. If excess SbF_3 is employed, the bromotetrafluorodisilane is completely consumed to give high yields of pentafluorodisilane. The latter can then conveniently be separated from the by-products of fluorination (chiefly SiF_4 and SiF_3H) *via* conventional low-temperature fractionation techniques.

Pure $\text{Si}_2\text{F}_5\text{H}$ [mol. wt., calcd. 152.2, found 153.6; analysis: calcd., F, 62.4%; found, F, 61.5%] melts at -13.7° and conforms to the relationship $\log p(\text{mmHg}) = -2387.00/T + 11.6315$ in the range -66° to -22° , giving an extrapolated hypothetical sublimation temperature of -0.4° .

The infrared spectrum of $\text{Si}_2\text{F}_5\text{H}$ has been determined between 4000 and 200 cm^{-1} . The major bands, with approximate relative intensities, are as follows: 2233 (m), 973 (vs), 918 (w), 848 (m), 812 (s), 807 (s), 515 (m), 369 (m), 334 (m), 306 (w). On the basis of known spectra of other Si-F and Si-H compounds, the following assignments are indicated: Si-H stretch, 2233 cm^{-1} ; Si-H bend, 848 cm^{-1} ; Si-F symmetric stretch, 812 and 807 cm^{-1} ; Si-F antisymmetric stretch, 973 cm^{-1} .

The NMR spectra of pentafluorodisilane have been reported⁴. We present here new parameters for the ^1H spectrum which represent a refinement of the previous values in that we have utilized a purer sample and coupling constants have been determined to a precision of 0.03 Hz with the use of audio sidebands. The new values are as follows: $\delta(\text{H}) = 5.02\text{ ppm}^*$; $J(\text{H-Si-F}) = 53.44\text{ Hz}$; $J(\text{H-Si-Si-F}) = 13.23\text{ Hz}$. The following ^{19}F NMR data are taken from ref. 4: $\delta(\text{SiF}_3) = 125.3\text{ ppm}^{**}$; $\delta(\text{SiF}_2\text{H}) = 142.4\text{ ppm}$; $J(\text{H-Si-F}) = 53.2\text{ Hz}$; $J(\text{H-Si-Si-F}) = 12.7\text{ Hz}$; $J(\text{F-F}) = 12.7\text{ Hz}$. As noted previously⁴, the most interesting feature of the fluorine spectrum is the collapse of the expected triplet of doublets for the SiF_3 fluorines to a quartet, due to the close similarity between the F-F and H-Si-Si-F coupling constants. A similar phenomenon is observed in the ^{19}F NMR spectrum of pentafluoroethane, $\text{C}_2\text{F}_5\text{H}$ ⁵.

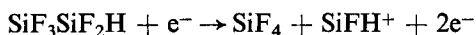
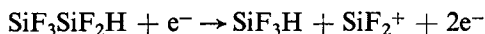
The mass spectrum of $\text{Si}_2\text{F}_5\text{H}$ has been determined on a single-focusing 180° sector magnetic instrument (A.E.I. MS10)[†] at 70 and 15 eV. The molecular ion is of low intensity at the higher electron voltages and remains one of the less intense ions even at 15 eV. Ionic species observed, with relative abundances at 70 eV [$\text{SiF}^+ = 100.0$] are as follows: SiF^+ (100.0), SiFH^+ (9.1), SiF_2^+ (73.6), SiF_2H^+ (77.0), SiF_3^+ (74.3), $\text{Si}_2\text{F}_4\text{H}^+$ (78.7), Si_2F_5^+ (70.1), $\text{Si}_2\text{F}_5\text{H}^+$ (10.0).

* From TMS (cyclohexane used as internal reference and corrected to external TMS using $\delta(\text{C}_6\text{H}_{12}) = 1.42\text{ ppm}$). Positive shifts are downfield.

** CCl_3F external reference. Positive shifts upfield.

† Certain commercial instruments are identified in this paper in order to adequately specify the experimental procedure. This does not imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the equipment identified is necessarily the best available for the purpose.

The two most important low-voltage (15 eV) fragmentation processes for pentafluorodisilane presumably involve formation of SiF_3H and SiF_4 :



The mass spectral observations are consistent with known spectra of other highly fluorinated silanes. Thus, Si_2F_6 does not give rise to a molecular ion of significant intensity even at low (< 15 eV) voltages, and several fluoropolysilanes such as Si_3F_8 ⁶ or $\text{Si}_2\text{F}_5\text{OSiF}_3$ ⁷ exhibit low-voltage fragmentation patterns which favor formation of stable neutrals such as SiF_4 .

The thermal stability of $\text{Si}_2\text{F}_5\text{H}$ is of interest in view of the tendency of Si-H and Si-X bonds to randomize in many of the known halosilanes. Si_2F_6 demonstrates remarkable resistance to pyrolytic decomposition; only at temperatures near 700° does thermolysis (to SiF_4 and SiF_2)⁸ occur. We find that pentafluorodisilane will withstand a temperature of 145° for 16 h with < 5% decomposition. Pyrolysis does take place at 225° (> 95% in 20 h), with SiF_4 and HSiF_3 the resultant volatile products. Some polymeric material was also present and an air-stable, gray-brown mirror, presumably elemental silicon, was observed on the walls of the vessel.

$\text{Si}_2\text{F}_5\text{H}$ is stable in the presence of substantial amounts of HBr. Base-catalyzed decomposition, however, is observed with both water and trimethylamine. Gas-phase hydrolysis proceeds under homogeneous conditions but is accelerated by condensation and revaporization cycles. Products of hydrolysis are SiF_4 , SiF_3H and a pyrophoric white polymer. In a sealed tube containing (I) and H_2O in a ratio of 40:1, decomposition of (I) occurred to the extent of 45% in 30 h. Much the same behavior is observed in the system $\text{Si}_2\text{F}_5\text{H}/\text{NMe}_3$. Here decomposition is more rapid — a 1% concentration of the amine causes complete decomposition of the silane in less than 60 min — but the products of decomposition are the same, *i.e.* SiF_4 , SiF_3H and an involatile polymer. More SiF_3H than SiF_4 is generated in both reactions. No detectable amounts of disiloxanes were formed in any of the hydrolytic systems, even when equimolar amounts of reactants were used.

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