

Infrared spectra of other base adduct complexes also were observed. No uncoordinated carbonyl frequencies were noticed for any of these complexes.

Discussion

Spectra of $\text{Ni}(\text{AA})_2\text{bipy}$ and $\text{Ni}(\text{AA})_2(\text{py})_2$ (with excess pyridine to prevent disproportionation⁹ to $[\text{Ni}(\text{AA})_2]\text{py}$ and py) suggested that the intensity of the d-d absorption bands in $\text{Ni}(\text{AA})_2(\text{py})_2$ might be lower than in the $\text{Ni}(\text{AA})_2\text{bipy}$ species (Figure 1) owing to a centrosymmetric (*trans*) configuration for the former compound while, of course, the bipyridine adduct must have a *cis* (noncentrosymmetric) configuration. Removing the center of symmetry in a complex allows mixing of functions which cannot mix in the centrosymmetric field, thereby supposedly increasing the intensity of d-d transitions. Unfortunately, the extent to which the intensity will increase cannot be estimated reliably since the intensity mechanism for the bands in centrosymmetric complexes is not yet well understood.²⁰ Presumably d-d transitions in centrosymmetric complexes are observed in the first place only because of vibrational or magnetic dipole interaction effects which are not readily calculated in molecules as complex as the ones studied here. Thus while the ${}^3\text{T}_{2g} \leftarrow {}^3\text{A}_{2g}$ (in O_h), $\sim 10,000 \text{ cm}^{-1}$, and ${}^3\text{T}_{1g}(\text{F}) \leftarrow {}^3\text{A}_{2g}$, $\sim 16,500 \text{ cm}^{-1}$, transitions apparently have a higher intensity in $\text{Ni}(\text{AA})_2\text{bipy}$ than in $\text{Ni}(\text{AA})_2(\text{py})_2$, the data are consistent with but do not require a *trans* arrangement in the latter complex. Since the position of the d-d bands in these complexes is the same in solution as in the diffuse reflectance spectra, it is reasonable to suggest, however, that the arrangement of the pyridines in $\text{Ni}(\text{AA})_2(\text{py})_2$ is for the most part the same in benzene as in the solid.

Single crystal X-ray data for $\text{Ni}(\text{AA})_2(\text{py})_2$ definitely show the complex²¹ to have a *trans* arrangement of pyridines. A similar configuration is required for the isomorphous crystalline $\text{Co}(\text{AA})_2(\text{py})_2$ and is likely for

(20) T. M. Dunn in "Modern Coordination Chemistry," J. Lewis and R. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960.

(21) It is noted that H. Montgomery and E. C. Lingafelter, *Acta Cryst.*, **7**, 1481 (1964), recently reported $\text{Ni}(\text{AA})_2(\text{H}_2\text{O})_2$ to have a *trans* configuration.

$\text{Fe}(\text{AA})_2(\text{py})_2$ from the similarity of the infrared spectra and the X-ray powder patterns, even though the latter compound is not strictly isomorphous with the others.

The solution spectra of all base adducts of the nickel(II) complexes studied in this work show a lower intensity (Table III) for the principal d-d transitions than is found in $\text{Ni}(\text{AA})_2\text{bipy}$. While a noncentrosymmetric arrangement of the six ligand atoms surrounding the nickel(II) is not definitely excluded, it is consistent to formulate these complexes also as being *trans*.

All attempts to cause the primary amine adducts of the nickel(II) β -ketoenolates studied to undergo a Schiff base rearrangement in nonpolar solvents were unsuccessful. Since a Schiff base rearrangement readily occurs in carbon tetrachloride between a metal salicylaldehyde and a primary amine, the possibility was considered that β -ketoenolato complexes do not react owing to steric protection of the ketonic carbon²² by the methyl groups. However, the inability of the adducts of $\text{Ni}(\phi\text{-Ac})_2$ to undergo a Schiff base rearrangement, even after 24 hr. of reflux, precludes steric inhibition as the cause for failure.

Since valence bond "resonance" structures are possible with metal salicylaldehydato complexes which are not permissible with β -ketoenolates, electronic differences may explain why base adducts of the latter compounds are stable to Schiff base "rearrangement" while adducts with the former materials are not. Studies currently in progress are designed to test this possibility with suitably substituted β -ketoenolato complexes.

Acknowledgments. This work was generously supported by the Public Health Service through a grant from the Division of Arthritic and Metabolic Diseases. We also wish to thank Professor Kerro Knox for his assistance in the X-ray studies.

(22) W. P. Jenks, *J. Am. Chem. Soc.*, **81**, 475 (1959), has presented evidence which indicates Schiff base formation in systems not involving a metal ion proceeds through base attack on the carbonyl. Recently, E. L. Muettterties and C. M. Wright, *ibid.*, **87**, 21 (1965), showed that $\text{Si}(\text{AA})_3^+$ hydrolysis by base occurs by attack on the chelate rather than the metal.

Silicon-Fluorine Chemistry. I. Silicon Difluoride and the Perfluorosilanes¹

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Silicon difluoride gas has been formed from silicon tetrafluoride and silicon at 1150° and low pressures. It has a lifetime at least 100 times greater than that of most carbenes. Condensation of the gas at low temperatures gives a plastic polymer $(\text{SiF}_2)_n$ which on heating generates all perfluorosilanes from SiF_4 through $\text{Si}_{14}\text{F}_{30}$. The new compounds Si_3F_8 and Si_4F_{10} have been isolated from the

distillate and characterized. The $(\text{SiF}_2)_n$ polymer reacts with aqueous HF to give 25–40% yields of silanes from SiH_4 through Si_8H_{14} .

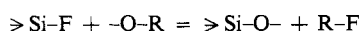
Relatively little is known about silicon-fluorine compounds compared with other silicon halides or the silicon hydrides, probably because of the lack of convenient routes to the fluoro compounds. For ex-

(1) Presented in part before the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

ample, the silanes and perchlorosilanes are known in detail up to Si_6X_{14} , whereas only SiF_4 , Si_2F_6 , and $\text{Si}_{10}\text{F}_{22}$ have been previously reported among analogous fluoro compounds.

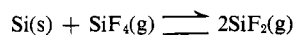
In 1954 Schmeisser^{2a} prepared $(\text{SiF}_2)_x$ from magnesium and dibromofluorosilane, but few properties of this polymer were determined. In 1958 Pease^{2b} showed that silicon difluoride gas could be formed in 50% yield from silicon tetrafluoride and silicon at high temperatures and low pressures, and that the gas, after condensing at temperatures below -80° , formed a plastic polymer $(\text{SiF}_2)_x$. These results made it possible to begin the present approach to silicon-fluorine chemistry.

The chemistry of silicon-fluorine compounds is influenced by two main properties of the Si-F bond. First, the bond energy is very high [$D(\text{Si-F})_{\text{av}} = 142 \pm 2$ kcal. in SiF_4 and SiF_2],³ so that the bond is rarely broken thermally, and compounds of type $>\text{SiF-XF}$ may decompose spontaneously or on pyrolysis to $>\text{SiF}_2 + \text{-X-}$. Second, the bond is often broken in reactions of the type



since the reaction is usually exothermic by about 10–15 kcal./mole. Thus, most Si-F compounds will react with water and with many oxygen-containing organic molecules. The Si-F bond is shorter than predicted (see, for example, Ebsworth⁴) and this has been ascribed to $(p \rightarrow d)\pi$ -bonding. This, however, does not seem to reduce the electron-acceptor properties of the silicon or general reactivity of silicon-fluorine compounds.

In this work, silicon difluoride, made from silicon and silicon tetrafluoride according to the equation



has been used as the raw material for the synthesis of a number of new silicon compounds either directly or *via* its polymer $(\text{SiF}_2)_x$. This paper will discuss the reactions of the polymer, the stability of silicon difluoride gas, and the properties of the perfluorosilanes $\text{Si}_n\text{F}_{2n+2}$, while subsequent papers will be concerned with the reactions of silicon difluoride with other compounds.

Experimental

Commercial silicon tetrafluoride (nominally 98.5% pure from the Matheson Co.) was passed over iron powder at 800° to remove sulfur dioxide and oxygen and was admitted to a vacuum system through a needle control valve at a rate of about 20 ml./min. The gas was passed through a vertically mounted 18-mm. bore quartz tube which was packed with 3–8-mm. pieces of 99.9% pure silicon in a 15-cm. section contained within the hot zone of a furnace at 1150° . The gases emerging from the quartz tube were vacuum pumped directly to a trap cooled in liquid nitrogen. This pumping enabled the pressure at the

top of the quartz tube to be maintained at 0.1–0.2 mm.

The emerging gas mixture condensed to form a red-yellow deposit at low temperatures. When 5–15 g. of silicon tetrafluoride had been passed over the silicon, the condensate was allowed to warm up and excess silicon tetrafluoride was pumped off. At room temperature the residue of polymer $(\text{SiF}_2)_x$ was a white or slightly yellow rubbery solid, moulded to the sides of the trap. The trap was removed from the apparatus under argon and placed in a glove box filled with dry nitrogen. The polymer was handled only in inert atmospheres because it was spontaneously inflammable in air.

For experiments on the stability of SiF_2 gas, the cold trap was omitted from the system described above. The SiF_2 – SiF_4 gas mixture was then pumped through flasks or tubes as desired; the maximum pressure of SiF_2 that could be attained was about 0.2 mm., together with at least 0.1 mm. of silicon tetrafluoride.

A conventional all-glass vacuum line employing greaseless valves (made by Springhams of Harlow, Essex, England) or mercury cutoffs was used to handle the volatile perfluorosilanes. The system frequently required cleaning because of the ready polymerization of impure samples of the compounds on the glass surfaces.

All mass spectral data were obtained with a Model 14-206A Bendix time-of-flight mass spectrometer (Bendix Corp., Cincinnati, Ohio). For work involving the higher perfluorosilanes, an optical path was arranged between the source of the compounds, *e.g.*, heated $(\text{SiF}_2)_n$, and the ion source. For work with the perfluorosilanes and silicon difluoride gas, the sample at 0.1–2.0 mm. pressure was leaked through a 0.5-mm. glass orifice into the optical path to the ion source.

Results

Reactions of $(\text{SiF}_2)_x$. The rubbery solid $(\text{SiF}_2)_x$ catches fire in moist air but reacts incompletely with water forming a voluminous white mass which slowly evolves hydrogen and silanes. It dissolves rapidly in concentrated alkali liberating hydrogen.

With 20% aqueous hydrofluoric acid the polymer forms silanes from SiH_4 to at least Si_6H_{14} plus much hydrogen. The formation of the silanes can be represented by equations of the type

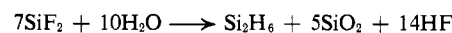
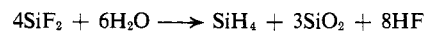


Table I. Analysis of Silanes Formed from $(\text{SiF}_2)_n$ and 20% HF

Species	% of total	Species	% of total
SiH_4	~4	<i>i</i> - Si_4H_{10}	2.4
Si_2H_6	40.0	<i>i</i> - Si_5H_{12}	3.9
Si_3H_8	17.0	<i>i</i> - Si_6H_{14}	2.4
<i>n</i> - Si_4H_{10}	15.0	$(\text{SiH}_3)_2\text{SiH}_8$	~0.1 ^a
<i>n</i> - Si_5H_{12}	8.6		
<i>n</i> - Si_6H_{14}	2.5		

^a See ref. 5.

(2) (a) M. Schmeisser, *Angew. Chem.*, **66**, 713 (1954); "Silicium, Schwefel, Phosphate," IUPAC Colloquium, Münster, 1955; p. 28; (b) D. C. Pease, U. S. Patents 2,840,588 and 3,026,173, assigned to the Du Pont Co., Wilmington, Del.

(3) (a) S. S. Wise, W. N. Hubbard, H. M. Feder, and J. L. Margrave, *J. Phys. Chem.*, **66**, 381 (1962); **67**, 815 (1963); (b) T. C. Ehlert and J. L. Margrave, *J. Chem. Phys.*, **41**, 1066 (1964).

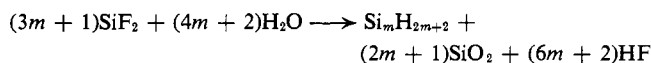
(4) E. A. V. Ebsworth, "Volatile Silicon Compounds," Pergamon Press, New York, N. Y., 1963.

Table II. Relative Abundances ($\text{Si}_2\text{F}_5^+ = 100$) of Ions from the Mass Spectrum of Pyrolyzed $(\text{SiF}_2)_n$ at 70, 20, and 16 E.v.

Ion type	Mass numbers and abundance ^a															
	No. of Si atoms															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
$\text{Si}_n\text{F}_{2n+2}$	104 ^b	170	236	302	368	434	500	566	632	698	764	830	896	962	1028	1094
	9.8 ^c	v.s.	8.2	1.0	2.3	2.0	1.6	1.2	0.6	0.3	0.2	0.1	0.07	0.1
	v.s. ^d	v.s.	22	5.5	22	25	19	15	10	5.5	1.0
	v.s. ^e	v.s.	48	17	103	117	107	100	86
$\text{Si}_n\text{F}_{2n+1}$	85	151	217	283	349	415	481	547	613	679	745	811	877	943	1009	1075
	202	100	22	18	6.0	5.2	3.2	3.0	2.4	1.3	1.0	0.7	0.4	0.2
	0.6	100	12	23	18	23	18	14	8.1	5.8	2.9
	16	100	26	129	129	138	112	60	17
Si_nF_{2n}	66	132	198	264	330	396	462	528	594	660	726	792	858	924	990	1056
	96	37	24	13	30	2.5	2.6	1.2	0.6	0.3	0.4	0.2	0.3	0.2	0.08	...
	94	274	48	42	8.1	5.5	3.4	2.3	1.1	1.9	1.3
	167	603	638	258	72	45	52	38	26
$\text{Si}_n\text{F}_{2n-1}$	47	113	179	245	311	377	443	509	575	641	707	773	839	905	971	1035
	515	83	3.3	5.3	1.2	1.1	0.6	0.6	0.6	0.9	0.3	0.6	0.4	0.3	0.3	...
	284	28	3.2	v.s.	v.s.	v.s.	v.s.	v.s.	v.s.	v.s.	v.s.
	638	62	v.s.	v.s.	31	31	16	8.6	16
$\text{Si}_n\text{F}_{2n-2}$	28	94	160	226	292	358	424	490	556	622	688	754	820	886	952	1016
	...	21	4.6	1.8	1.1	0.6	0.8	0.6	0.7	0.6	0.5	0.3	0.5	0.4	0.1	...
	...	1.3	v.s.	v.s.	v.s.	v.s.	v.s.	v.s.	v.s.	v.s.	v.s.
	...	v.s.	v.s.	v.s.	v.s.	v.s.	8.6	4.9	v.s.
$\text{Si}_n\text{F}_{2n-3}$	75	141	207	273	339	405	471	537	603	669	735	801	867	933	997	...
	4.4	2.1	1.4	1.0	1.1	0.6	0.6	0.5	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.1
	v.s.	v.s.	v.s.	v.s.	v.s.	v.s.	v.s.	v.s.	v.s.	v.s.	v.s.
	v.s.	v.s.	v.s.	v.s.	v.s.	v.s.	v.s.	v.s.
$\text{Si}_n\text{F}_{2n-4}$	56	122	188	254	320	386	452	518	584	650	716	782	848	914	978	...
	1.3	1.0	0.6	0.4	0.2	0.2	0.2	0.1	0.2	0.1	0.1	0.04	0.07	0.04	0.04	0.04
	v.s.	v.s.	v.s.	v.s.	v.s.	v.s.	v.s.	v.s.	v.s.	v.s.	v.s.
	v.s.	v.s.	v.s.	v.s.	v.s.	v.s.	v.s.	v.s.

^a v.s., very small (<0.04); ..., not measured; relative intensities of Si_2F_5^+ at 70, 20, and 16 e.v. are 100:1:0.1, respectively. ^b Mass number. ^c Relative abundance at 70 e.v. ^d Relative abundance at 20 e.v. ^e Relative abundance at 16 e.v.

or

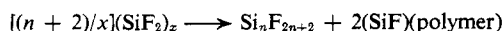


Over-all yields of silanes are only 25–40% of the theoretical. The silanes were separated by fractional condensation and by gas-liquid chromatography. The yields of the different species were determined either by direct weighing or, less accurately, from peak area measurements on the chromatogram. Table I shows the approximate percentage yields of the various silanes obtained in a typical run.

This reaction is in many ways comparable with the formation of silanes from silicon monoxide and hydrofluoric acid.⁵ Both SiO and $(\text{SiF}_2)_x$ probably contain long silicon chains which may be hydrogenated and fragmented during the hydrolysis.

Silicon difluoride polymer seems insoluble in most organic or inorganic solvents except the perfluorosilanes. It is unchanged by many hydrocarbons or halogenated hydrocarbons but reacts with alcohols, ketones, ethers, and amines. The reaction with diethyl ether or diethylamine is smooth and gives highly reactive but complex adducts. With diethylamine the reaction may involve loss of HF and formation of Si–N bonds. A white crystalline compound is formed which dissolves in aqueous hydrofluoric acid generating small amounts of silanes, suggesting that the Si–Si skeleton has not been destroyed.

When $(\text{SiF}_2)_x$ is heated under vacuum to 200–350° it melts and slowly decomposes to give perfluorosilanes, $\text{Si}_n\text{F}_{2n+2}$, and leaves a solid, silicon-rich polymer.



(5) P. L. Timms and C. S. G. Phillips, *Inorg. Chem.*, **3**, 606 (1964).

At $400 \pm 10^\circ$ the decomposition suddenly becomes very fast, even explosive, and mainly SiF_4 and silicon are formed.

By passing the volatile products from the heated polymer directly into a Bendix time-of-flight mass spectrometer, spectra were obtained with peaks corresponding to the mass numbers of the ions in the series $(\text{Si}_n\text{F}_{2n+2-y})^+$ for n values from 1 to at least 14, and y values from 0 to 6. The heaviest ion observed, mass 997, was assigned to $\text{Si}_{16}\text{F}_{31}^+$. Heavier species were undoubtedly present in detectable amounts, but the mass spectrometer would not scan beyond mass 1000. The molecular ions corresponding to the perfluorosilanes containing 3–14 silicon atoms were clearly distinguished by their abundance relative to possible fragment ions at low electron voltages, *i.e.*, ≥ 15 e.v.

The relative abundances of the ions in the mass spectrum of a sample of polymer heated under high vacuum at 200° are shown at 70 and 15 e.v. in Table II. There is no evidence that cyclic or unsaturated silicon fluorides were generated by the heating. However, unless stringent precautions were taken to exclude oxygen and moisture from the polymer both during its formation and in subsequent handling, appreciable amounts of silicon oxyfluorides were also observed with the perfluorosilanes.

The behavior of Teflon, $(\text{CF}_2)_x$, on heating under high vacuum is quite different from that of $(\text{SiF}_2)_x$, as tetrafluoroethylene is formed in high yield.⁶ Nevertheless, Kuriakose and Margrave⁷ have recently shown

(6) R. E. Florin, L. A. Wall, D. W. Brown, L. A. Hymo, and J. D. Michaelson, *J. Res. Natl. Bur. Std.*, **53**, 121 (1954).

(7) A. K. Kuriakose and J. L. Margrave, unpublished work, Rice University, 1964.

Table III. Properties of Perfluorosilanes and Silanes

Compd.	M.p., °C.	B.p., °C.	Liquid range, °C.	ΔH_{vap} , kcal./mole	ΔH_{sub} , kcal./mole	ΔH_{fus} , kcal./mole	Trouton's constant
Si ₂ F ₆ ^a	-18.6	-18.9	~0	6.5 ± 0.5	10.4 ± 0.5	3.9 ± 0.8	25.6
Si ₂ H ₆ ^b	-132.5	-14.5	118	4.6	17.2
Si ₃ F ₈	-1.2	+42.0	43.2	8.8 ± 0.5	14.1 ± 0.5	5.3 ± 0.8	27.8
Si ₃ H ₈ ^b	-117.6	+52.9	170.3	6.7	20.5
Si ₄ F ₁₀	+66-68	+85.1	~18	10.8 ± 0.5	17.8 ± 0.5	7.0 ± 0.8	30.2
Si ₄ H ₁₀ ^{b,c}	-88.0	+107.4	195.4	8.7	23.0
(n-isomer)							

^a Values taken from W. C. Schumb and E. L. Gamble, *J. Am. Chem. Soc.*, **53**, 3191 (1931). ^b Values taken from A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933. ^c Values taken from P. L. Timms, C. C. Simpson, and C. S. G. Phillips, *J. Chem. Soc.*, 1467 (1964).

that pyrolysis of (CF)_x polymers (made by fluorinating graphite) yields a complex mixture of CF compounds.

Properties of the Perfluorosilanes. By destructive distillation of 10-g. batches of silicon difluoride polymer at 250–350° followed by vacuum fractionation of the products, samples of a few hundred milligrams of the known perfluorodisilane (hexafluorodisilane), Si₂F₆, and the compounds perfluorotrisilane, Si₃F₈, and perfluorotetrasilane, Si₄F₁₀, which have not been previously reported, were isolated. Attempts to purify these compounds further by gas-liquid chromatography failed because no stationary phase could be found in which they exhibited appreciable solubility. However, by mass spectrometry it was estimated that the Si₃F₈ and Si₄F₁₀ were more than 98 and 95% pure, respectively, the main impurity in Si₃F₈ being Si₃OF₈, and in Si₄F₁₀, the higher homolog Si₅F₁₂.

The lower perfluorosilanes are colorless liquids or white crystalline solids at room temperature. The very high melting, white, powdery Si₁₀F₂₂ reported by Schmeisser^{2a} is probably typical of the higher members of the series. The melting and boiling points of the perfluorosilanes are given in Table III alongside the properties of equivalent silanes. The boiling points in the two types of compounds are similar but the melting points of the silanes are much lower than those of the perfluorosilanes. With the alkanes and perfluoroalkanes both melting and boiling points are alike. This difference in behavior may reflect the greater ionic character of the Si-F bond, compared with the C-F bond, which causes stronger short-range forces in the perfluorosilanes than in the perfluoroalkanes.

Liquid perfluorosilanes are readily supercooled. A small sample of liquid Si₄F₁₀ has been repeatedly cooled 60–100° below its freezing point (its eventual crystallization was quite violent).

The structures of the first two perfluorosilanes, Si₂F₆ and Si₃F₈, were conveniently proved from their ¹⁹F nuclear magnetic resonance spectra. Perfluorodisilane shows the expected singlet (chemical shift $\delta = 126.0 \pm 0.6$ p.p.m. [CCl₃F = 0]), arising from six equivalent fluorine atoms in F₃²⁹Si²⁹SiF₃, with a complex satellite structure arising from F₃²⁹Si²⁹SiF₃ molecules in which the six fluorine atoms are no longer equivalent. The spectrum of Si₃F₈ shows two main resonances, a triplet ($\delta = 126.0 \pm 0.6$ p.p.m.) due to the splitting of the resonances of the SiF₃ groups by the SiF₂ group and a septet ($\delta = 139.0 \pm 0.7$ p.p.m.) due to the splitting of the resonance of the SiF₂ group by the two SiF₃ groups. The ratio of the area of the

triplet to that of the septet was found to be close to 3:1. The coupling constants $J_{\text{Si}^{29}\text{F}}$ and $J_{\text{Si}^{29}\text{SiF}}$ were measured as 345 ± 3 and 66 ± 1 Hz., respectively, for the SiF₃ groups of Si₃F₈, while J_{FF} was 11.0 ± 0.3 Hz. for both the SiF₃ and SiF₂ groups. The spectrum of Si₄F₁₀ has not yet been determined because of the difficulty of obtaining an adequate amount of pure material, but it is thought that the chemical shifts in *n*-Si₄F₁₀ will be very similar to those in Si₃F₈.

Table IV shows the mass spectra of the first four perfluorosilanes at 70 and 18 e.v. Among the perfluorosilanes the spectrum of Si₂F₆ may be unique in that no parent ion is observed at any electron voltage. This is in contrast to the series of the perfluoroalkanes in which C₂F₆⁺ is observed from perfluoroethane while few other perfluoroalkanes give a parent ion.⁸

The gas phase infrared spectra of the perfluorosilanes, which closely resemble those of the corresponding perfluoroalkanes, are being analyzed in detail. The absorption bands for Si₂F₆, Si₃F₈, and Si₄F₁₀, are listed in Table V.

Chemically the perfluorosilanes are very reactive. Perfluorotetrasilane and higher perfluorosilanes catch fire spontaneously in air. If the compounds are exposed to limited amounts of air and water, polymers are formed which, in contrast to the pure perfluorosilanes, evolve silanes with HF. The compounds have only very limited solubility in organic solvents.

Traces of secondary or tertiary amines catalyze the formation of polymers from the perfluorosilanes. This reaction is similar to that observed for hexachlorodisilane which gives Si₅Cl₁₂ and Si₆Cl₁₄ with tertiary amines,⁹ but the products in the case of the perfluorosilanes seem less well defined.

Silicon Difluoride Gas. The composition of the gases emerging from the furnace after treating silicon with silicon tetrafluoride was monitored mass spectrometrically, and it was found that SiF₂ and SiF₄ accounted for at least 99.5% of the gaseous species present. The silicon difluoride gas had the same ionization potential as that previously observed for the molecule formed by heating silicon and calcium fluoride together at high temperatures.^{3b} Silicon difluoride was first detected in the Si-SiF₄ reaction at 1030°, and its concentration increased to a constant maximum

(8) F. L. Mohler, V. H. Dibeler, and R. M. Reese, *J. Res. Natl. Bur. Std.*, **49**, 343 (1952).

(9) A. Kaczmarczyk, M. Millard, and G. Urry, *J. Inorg. Nucl. Chem.*, **17**, 186 (1961).

Table IV. Mass Spectrometric Ion Abundances for SiF₄, Si₂F₆, Si₃F₈, and Si₄F₁₀

<i>m/e</i>	Peak identity	Relative ion abundances $\pm 5\%$							
		SiF ₄ 70 e.v.	Si ₂ F ₆		Si ₃ F ₈		Si ₄ F ₁₀		
			70 e.v.	18 e.v.	70 e.v.	18 e.v.	70 e.v.	18 e.v.	
47	SiF ⁺	4	260	~50	650	940	5000	...	
66	SiF ₂ ⁺	2	170	~1600	191	582	409	...	
85	SiF ₃ ⁺	100 ^a	97.0	~50	194	88.0	1230	25.0	
104	SiF ₄ ⁺	2	<1	<1	<1	<1	18.0	<1	
132	Si ₂ F ₄ ⁺		<1	...	6.0	88.0	155	1210	
151	Si ₂ F ₆ ⁺		100 ^a	100 ^a	100 ^a	100 ^a	100 ^a	100 ^a	
170	Si ₂ F ₆ ⁺		<0.01	<0.01	
198	Si ₃ F ₈ ⁺		<1	11.7	30.0	74.0	
217	Si ₃ F ₈ ⁺		28.8	35.3	23.0	83.0	
236	Si ₃ F ₈ ⁺		10.9	194	<1	<1	
264	Si ₄ F ₁₀ ⁺		18.0	8.3	
283	Si ₄ F ₁₀ ⁺		41.0	16.7	
302	Si ₄ F ₁₀ ⁺		4.0	31.0	

^a Reference ion.**Table V.** Infrared Spectra of Si₂F₆, Si₃F₈, and Si₄F₁₀^{a, b}

Si ₂ F ₆		Si ₃ F ₈		Si ₄ F ₁₀	
418	s	412	s	420	m
438	m	497	m	429	w
515	m	525	w	481	w
653	w	697	w	507	m
704	w	710	m	697	m
831	vs	750	w	739	m
848	s	791	w	820	m
861	s	822	s	822	s
878	m	828	vs	828	m
921	w	849	s	844	w
975	vs	855	s	847	m
980-1005	vvs	860	s	852	m
1080	m	875	m	857	m
1185	m	909	w	859	s
		950	m	862	w
		990	vs	975	m
		1005	s	990	vs
		1030	s	1004	s
		1035	s	1020	vs
		1084	w	1027	vvs
		1166	m	1034	vs
				1100	m
				1188	m
				1190	m

^a 10-cm. gas cell, 1-cm. pressure KBr windows; spectra in cm.⁻¹.^b s, strong; m, medium; w, weak; v, very.

of about 65% of the total pressure of 0.1–0.2 mm. at temperatures above 1120°.

Silicon difluoride monomer is isoelectronic with carbenes. Estimates of the "half-life" of gaseous carbenes range from a few hundredths of a second for CH₂ to about 1 sec. for CF₂. The half-life of silicon difluoride gas was estimated by following its decay in a flask with a mass spectrometric detector. The mixture of silicon difluoride and silicon tetrafluoride produced by the reaction of silicon tetrafluoride on silicon at 1150° and 0.1 mm. was pumped through a 5-l. Pyrex flask. A portion of the gas passing through the flask was bled into the mass spectrometer through a glass orifice. When a steady concentration of silicon difluoride was being measured in the flask, *i.e.*, constant current for the ion SiF₂⁺, the flask was isolated from the furnace and pumping system and the decrease in the silicon difluoride ion intensity followed on the mass spectrometer. Under these conditions at room temperature, the concentration of SiF₂ fell to half its original value in 150 sec. No gaseous

polymers were formed during its decay, but a very thin film of solid polymer appeared on the walls of the flask. It is interesting that the reaction SiF₂(g) + SiF₄(g) = Si₂F₆(g) has not been observed under these or other conditions. Reactions of this type are known for germanium and silicon hydrides¹⁰ and probably the silicon chlorides,¹¹ and should be energetically favored since the average M–X bond energies in the reactants and products are similar.

The half-life of the silicon difluoride was only slightly affected by nitrogen at pressures up to 2 mm., and even boron trifluoride, carbon monoxide, and oxygen, which have been found to give new compounds with silicon difluoride,¹² showed no signs of reaction in the gas phase. With oxygen, however, there was a very rapid reaction on the walls of the flask, and 1 mm. pressure of oxygen reduced the half-life of silicon difluoride from 150 to 6 sec. In contrast the lifetime of CF₂ is reported to be scarcely changed by the presence of oxygen.¹³

When pumped through a U-trap at a pressure of 0.1 mm., silicon difluoride first began to condense out in the trap at temperatures between –40 and –50°, and condensation was almost complete by –70°. As with the experiments at room temperature, no gaseous polymers were observed to be formed during the condensation process. If the silicon difluoride was condensed at liquid nitrogen temperature, traces of perfluorodi-, tri-, and tetrasilane were evolved from the polymer along with excess silicon tetrafluoride, on warming it to room temperature.

Acknowledgments. This work was supported by a grant from the Advanced Research Projects Agency, administered through the Army Research Office, Durham, by Dr. George Wyman. We are pleased to recognize the help of Dr. S. Slaymaker of the Shell Refinery, Houston, Texas, in carrying out preliminary n.m.r. studies and of Drs. F. Brinckman, T. Farrar, and T. Coyle of the National Bureau of Standards, Washington, D. C., who performed the more refined n.m.r. measurements. Also, Mr. Decherd Stump has assisted in sample preparations and mass spectrometric analyses.

(10) See footnote c, Table III.

(11) H. Schäfer, "Silicium, Schwefel, Phosphate," ref. 2a, p. 28.

(12) P. L. Timms, R. A. Kent, T. C. Ehlert, and J. L. Margrave, *Nature*, to be published.(13) F. W. Dalby, *J. Chem. Phys.*, **41**, 2297 (1964).