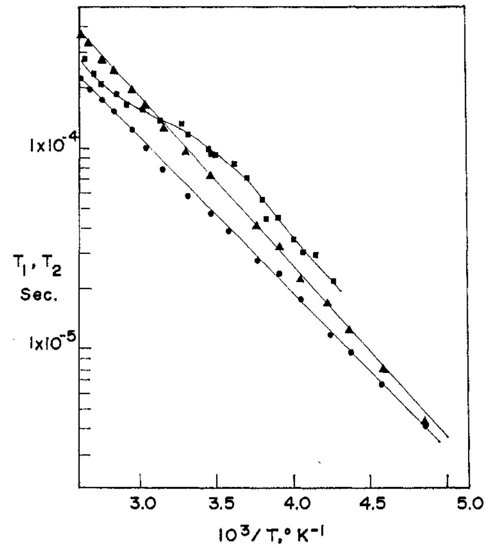

Figure 2.—The temperature dependence of the phosphorus relaxation time T_1 (■) and the proton spin–spin relaxation time T_2 of the methyl (●) and methoxy protons (▲) of $Mn(DMMP)_6^{2+}$.

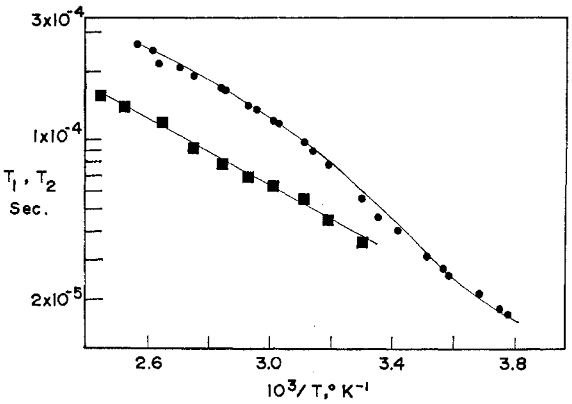

Figure 3.—The temperature dependence of the phosphorus relaxation time T_1 (■) and the proton spin–spin relaxation time T_2 (●) of $Mn(HMPA)_4^{2+}$.

curately measured under rapid exchange conditions. The proton activation energies, Table II, are comparable to $Mn(H_2O)_6^{2+}$.[18] The T_{2H} values show no nonlinearity because T_{2H} is largely due to a contact interaction with $\tau_e = \tau_s$. Considering the temperature range (110 to −66°) the values of T_{2H} give a surprisingly good fit to a simple exponential temperature dependence. The relative values of the proton relaxation times of the methyl and methoxy groups are consistent with coordination through the phosphoryl group.

The phosphorus relaxation times of $Mn(TMP)_6^{2+}$ cannot readily be obtained over an extended temperature range by measuring the separation of the doublet. The data for T_{2H} give a good fit to a simple exponential plot and are comparable to those of $Mn(DMMP)_6^{2+}$, Table II.

The data for $Mn(HMPA)_4^{2+}$ are summarized in Figure 3. The relative values of T_{2H} and T_{1P} clearly show that a dipolar mechanism cannot be operative for both T_{2H} and T_{1P}. Since no reliable estimates have been made for τ_e, one cannot confidently conclude that T_{1P} is dipolar in nature. Since T_{2H} is too small relative to T_{1P}, T_{2H} must contain an appreciable contribution from a contact interaction. The deviation from linearity for T_{2H} is probably due to small differences in the temperature dependence of τ_c and τ_e. The activation energies, Table II, are comparable to those of octahedral systems.

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Pyrolysis of Disilane and Trisilane

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Received December 17, 1968

The preparation of polysilanes from monosilane by an electric discharge in a flow system has been reported by Spanier and MacDiarmid.[1] Fritz[2] has also demonstrated that polysilanes are produced during the pyrolysis of silane. In this note we report our results on the preparation of trisilane and tetrasilane by the flow system pyrolysis of disilane and trisilane, respectively.

Our results on the disilane pyrolysis have demonstrated that the primary decomposition does not produce hydrogen. Also, our data are not in accord with the decomposition of disilane into silyl radicals. Therefore, our results are most consistent with the decomposition of disilane into silane and silene followed by silene insertion into disilane forming trisilane.

Experimental Section

These experiments were carried out in standard high-vacuum systems. Separations were made by trap to trap distillations. The reactants and products were identified by their infrared[1,3-5] and mass spectra (see Table I).

TABLE I

MASS SPECTRUM OF PRODUCTS

	SiH_x^+ *m/e* 28–34	$Si_2H_x^+$ *m/e* 56–64	$Si_3H_x^+$ *m/e* 84–96	$Si_4H_x^+$ *m/e* 112–126	$Si_5H_x^+$ *m/e* 140–156
Si_2H_6	81	248	0	0	0
Si_3H_8	18	146	83	0	0
Si_4H_{10}	22	84	199	57	0

Disilane was prepared by the reduction of hexachlorodisilane with lithium aluminum hydride. The trisilane used was obtained from the pyrolysis of disilane as described herein.

The pyrolysis reactions were carried out in a Pyrex tube with a diameter of 6 mm and an effective volume of 3.8 cm³. The reaction chamber was connected to an automatic Toepler pump for cycling. The inner walls were coated with a silicon mirror from previous pyrolysis reactions. Three runs were made over an uncoated surface by adding Pyrex beads to the reaction chamber.

The chamber was heated with a heating tape which surrounded a thermometer placed between the tape and the chamber. The heating tape was then wrapped with several layers of asbestos. The disilane pressure in the chamber was about 30 Torr which

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(1) E. J. Spanier and A. G. MacDiarmid, *Inorg. Chem.*, **1**, 432 (1962).
(2) G. Fritz, *Z. Naturforsch.*, **7b**, 507 (1952).
(3) J. H. Meal and M. K. Wilson, *J. Chem. Phys.*, **24**, 385 (1956).
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(5) S. D. Gokhale and W. L. Jolly, *Inorg. Chem.*, **3**, 946 (1964).

was set by the −78° bath used to trap the products. For the trisilane pyrolyses, a −36° bath was used to trap the products. This trap maintained a trisilane pressure of about 15 Torr. The trisilane pressure was increased in some runs by a partial closing of the stopcock between the product trap and the reaction chamber.

After each reaction, the noncondensable product, hydrogen, was allowed to pass through a −196° trap and was collected by means of the Toepler pump in a calibrated volume. The monosilane fraction was allowed to pass through a −160° trap and was collected at −196°. The disilane fraction was allowed to pass a −112° trap and was collected at −160°. The trisilane fraction was passed through a −46° trap and stopped at −112°. The tetrasilane fraction was passed through a −23° trap and stopped at −46°.

Results

The results from the pyrolyses of disilane are listed in Table II, while the results from the pyrolyses of trisilane are listed in Table III. In Table IV we list the results from our pyrolyses over added Pyrex beads. The runs listed in Table IV are continuous so that the beads are somewhat coated in the second and third runs.

TABLE II
PYROLYSIS OF DISILANE

Temp, °C	Amt of consumed Si_2H_6, mmol	Amt of products, mmol			Time, hr
		SiH_4	Si_3H_8	H_2	
340	. . .	. . .	. . .	. . .	3
350	. . .	. . .	. . .	. . .	2.75
370	0.32	0.17	0.15	0.018	3.25
370	0.34	0.17	0.16	0.018	3.75
375	1.25	0.64	0.58	0.13	18
380	0.24	0.12	0.11	0.018	2
400	0.97	0.42	0.30	0.11	4.75
410	0.58	0.37	0.14	0.06	3

TABLE III
PYROLYSIS OF TRISILANE

Temp, °C	Amt of consumed Si_3H_8, mmol	Amt of products, mmol				Time, hr	Si_3H_8 pressure, Torr
		SiH_4	Si_2H_6	Si_4H_{10}	H_2		
290	. . .	. . .	. . .	. . .	. . .	3	15
340	0.089	0.018	0.034	0.049	0.01	3	15
340	0.15	0.018	0.036	0.085	0.018	5.5	15
345	0.081	0.01	0.025	0.036	0.01	3.5	20–30
355	0.11	0.015	0.027	0.055	0.013	3	20–30
370	0.11	0.036	0.027	0.01	0.01	3	15
370	0.10	0.036	0.027	0.01	0.01	3	15

TABLE IV
PYROLYSIS OVER PYREX

Temp, °C	Reactant	Amt of reactant consumed, mmol	Amt of products, mmol					Time, hr
			SiH_4	Si_2H_6	Si_3H_8	Si_4H_{10}	H_2	
300	Si_2H_6	0.013	0.005	. . .	0.005	. . .	0.013	1
295	Si_3H_8	0.018	. . .	0.005	. . .	0.005	0.008	2
330	Si_2H_6	0.18	0.09	. . .	0.07	. . .	0.026	3

The infrared spectrum of our tetrasilane was identical with that reported for *n*-tetrasilane by Gokhale and Jolly.[5] The medium-intensity band of isotetrasilane[5] at 915 cm^{-1} was not observed suggesting that our sample was all or at least primarily *n*-tetrasilane. An nmr spectrum of our sample confirmed the above result.[5]

Discussion

We have demonstrated that the pyrolysis of disilane and trisilane follows a distinct route with little hydrogen formation. Since disilane can be easily prepared from commercially available hexachlorodisilane, the pyrolysis of disilane and trisilane are excellent routes to the formation of trisilane and tetrasilane. These results suggest that the pyrolysis of other similar compounds in a flow system should lead to useful syntheses. Such studies are under investigation.

The pyrolysis of disilane can be represented by

$$2Si_2H_6 \longrightarrow SiH_4 + Si_3H_8 \qquad (1)$$

It should be noted that tetrasilane was obtained from trisilane at the temperature at which our disilane pyrolyses were examined. Therefore, the fact that tetrasilane was not detected in the disilane pyrolyses is significant. Since little hydrogen or tetrasilane was formed in the disilane pyrolysis, the mechanism can probably be restricted to: route A

$$Si_2H_6 \longrightarrow SiH_2 + SiH_4 \qquad (2)$$

$$SiH_2 + Si_2H_6 \longrightarrow Si_3H_8 \qquad (3)$$

or route B

$$Si_2H_6 \rightleftarrows 2SiH_3 \qquad (4)$$

$$SiH_3 + Si_2H_6 \xrightarrow{k_1} Si_2H_5 + SiH_4 \qquad (5)$$

$$SiH_3 + Si_2H_5 \xrightarrow{k_2} Si_3H_8 \qquad (6)$$

For route B to fit eq 1, the concentration of silyl radicals must be considerably greater than the concentration of disilanyl radicals.

If one assumes that route B is operative, the concentrations of silyl and disilanyl radicals can be estimated. The disilanyl radical concentration can be estimated as

$$1 = \frac{\text{rate of SiH}_4\text{ formation}}{\text{rate of Si}_3\text{H}_8\text{ formation}} = \frac{k_1(SiH_3)(Si_2H_6)}{k_2(SiH_3)(Si_2H_5)}$$

With the use of *A* factors for similar hydrocarbon reactions[6,7] and an activation energy for methyl abstraction from ethane or butane,[6] one can estimate that the disilanyl concentration in our system was about 10^{-9} *M*. The silyl radical concentration can be estimated as

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(6) A. F. Trotman-Dickinson and G. S. Milne, "Tables of Bimolecular Gas Reactions," National Bureau of Standards Circular No. 9, U. S. Government Printing Office, Washington, D. C., 1967.

(7) S. W. Benson and H. E. O'Neal, "Tables of Unimolecular Gas Reactions," submitted for publication.

$$Si_2H_6 \underset{k_T}{\overset{k_I}{\rightleftharpoons}} 2SiH_3 \qquad (7)$$

$$k_I(Si_2H_6) = k_T(SiH_3)^2$$

With A factors from the ethane[6] pyrolysis and a value for the silicon–silicon bond energy, one can estimate the silyl radical concentration. With $D(H_3Si–SiH_3) = 58$, 67, and 81 kcal/mol, the silyl radical concentrations are 10^{-8}, 10^{-10}, and 10^{-13} M, respectively. The silicon–silicon bond energy in disilane is open to some question. From heats of formation data a value of 46 kcal/mol has been obtained.[8] However, it has been demonstrated that the silicon–hydrogen bonds in disilane are probably weaker than those in silane.[9] This result would somewhat increase the silicon–silicon bond strength calculated by Gunn and Green. A recent kinetic study has set the silicon–silicon bond energy in hexamethyldisilane at 67 kcal/mol.[10] From both steric arguments and predicted changes in hybridization, one would expect $D(SiH_3–SiH_3) > D((CH_3)_3Si–Si(CH_3)_3)$. A direct measurement by electron impact has set $D(H_3Si–SiH_3)$ at 81 ± 4 kcal/mol.[11] This latter value is in agreement with a value for $D(SiH_3–H)$ of 94 kcal/mol obtained both from electron impact studies on silane[12] and from an observation that silyl abstracts hydrogen from toluene at an appreciable rate.[13] Therefore, if $D(H_3Si–SiH_3)$ is at least 67 kcal/mol, which appears to be the case, then the fact that tetrasilane was not obtained in the disilane pyrolysis argues against our route B and therefore is in favor of our route A.

The pyrolysis of trisilane is slightly more complex. Since the trisilane pyrolyses were carried out at temperatures below which disilane did not decompose, it is unlikely that the silane was derived from secondary pyrolysis of disilane.

It would be difficult to calculate with any certainty the relative radical concentrations for this system so it is difficult to determine whether the apparent nonobservation of penta- and hexasilane is significant. If this point is significant, it would also argue against silyl-type radicals. Our results from the pyrolysis of trisilane can be explained by

$$Si_3H_8 \longrightarrow SiH_2 + Si_2H_6 \qquad (8)$$

$$Si_3H_8 \longrightarrow 2SiH_2 + SiH_4 \qquad (9)$$

$$SiH_2 + Si_3H_8 \longrightarrow Si_4H_{10} \qquad (10)$$

The results obtained from the pyrolyses over a Pyrex surface demonstrate that these reactions are catalyzed by Pyrex. Purnell and Walsh have demonstrated[14] that the pyrolysis of silane is catalyzed by Pyrex but is homogeneous over a silicon mirror. It is also of interest that they favor hydrogen elimination as the first step in the pyrolysis of silane

$$SiH_4 \longrightarrow SiH_2 + H_2 \qquad (11)$$

Acknowledgment.—The authors are indebted to Dr. H. E. O'Neal for discussions on kinetics and to the Army Research Office (Durham) for financial support.

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(11) W. C. Steele and F. G. A. Stone, *J. Am. Chem. Soc.*, **84**, 3599 (1962).

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(14) J. H. Purnell and R. Walsh, *Proc. Roy. Soc.*, **A293**, 543 (1966).

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Reactions of Pentafluorosulfanylamine and Pentafluorosulfanyliminosulfur Difluoride[1]

BY ALAN F. CLIFFORD AND GERALD R. ZEILENGA

Received December 26, 1968

In recent years, considerable interest has been shown in nitrogen–sulfur–fluorine compounds. The compounds SF_5NH_2, prepared by the reaction of NSF_3 and HF,[2] and $SF_5N{=}SF_2$, obtained in low yield either from SF_4 and NSF_3 using a BF_3 catalyst[3] or from the fluorination of S_4N_4,[4] have recently been reported. The purpose of this work was to examine some of the reactions of SF_5NH_2 and $SF_5N{=}SF_2$ in an attempt to prepare new pentafluorosulfanyl-nitrogen compounds.

Experimental Section

Apparatus.—Reactions were carried out in 75-ml Hoke stainless steel cylinders equipped with Hoke 300 series needle valves. An all-glass high-vacuum system was used for measurement, handling, and purification of volatile materials. All vacuum stopcocks and other joints were lubricated with Kel-F Brand No. 90 grease. An auxiliary system constructed with copper tubing and a manometer of Kel-F tubing was used for handling HF. Metal-to-glass connections were made with Swagelok (Crawford Fitting Co., Cleveland, Ohio) fittings equipped with Teflon ferrules.

The infrared spectrum of $(SF_5N{=})_2SF_2$ was obtained in the 2–15-μ region using a Perkin-Elmer Model 137 Infracord spectrometer. In the 11–25-μ region a Beckman IR5A spectrometer equipped with CsBr optics was employed. Pyrex 10-cm gas cells were used, fitted with NaCl windows for the 500–700-cm^{-1} region and KBr windows for the 900–400-cm^{-1} region.

Materials.—Sulfur tetrafluoride (Matheson) was used without further purification, since thionyl fluoride was the only impurity observed in the infrared spectrum. Hydrogen fluoride (Blockson Chemical Division of Olin Mathieson), silver(II) fluoride (Harshaw, technical grade), phosphorus pentafluoride (Matheson), and boron trifluoride (Matheson) were also used without purification. Cesium fluoride (American Potash and Chemical Corp.) was treated with fluorine at 110° for 1 hr to remove chloride and carbonate impurities. Fluorine (General Chemical Division of Allied Chemical) was passed over sodium fluoride pellets before use to remove HF. Sodium fluoride pellets (Harshaw) were heated under vacuum to dry them. Fluoroformyliminosulfur difluoride, $F_2S{=}NCOF$, was prepared by the reaction of silicon tetraisocyanate and sulfur tetrafluoride at 120°.[5]

Thiazyl trifluoride, NSF_3, was prepared by the fluorination of SF_2NCOF with AgF_2.[3] Pentafluorosulfanylamine, SF_5NH_2, was prepared by the reaction of NSF_3 and liquid HF.[2]

Reaction of Pentafluorosulfanylamine with Sulfur Tetrafluoride.—A mixture of 9.1 mmol of SF_5NH_2 and 9.2 mmol of SF_4 was allowed to stand for 40 hr at room temperature. The products were placed over NaF pellets for 2 hr to remove HF and

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[1] Taken in part from the thesis submitted to the faculty of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy by Gerald R. Zeilenga.

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