parison in Table VIII. For $(CH_3)_2NPCF_3Cl$ the instrument was the Perkin-Elmer Infracord (KKJ), but for the nine others the Beckman IR7 was employed with NaCl or CsI optics (ABB). Calibrations based upon known fine-structure peaks brought the uncertainty down to 0.5 cm.$^{-1}$ in the range below 800 cm.$^{-1}$ or to 1 cm.$^{-1}$ at higher frequencies, for all sufficiently well-defined peaks. However, some absorption maxima were broader than that (usually multiplets lacking resolution) and some P and R branches for the simpler compounds appeared as shoulders for which the significant frequencies could not be closely defined. The relative intensity of absorption, defined as $k = (100/PL) \log I_0/I$ for pressure of vapor P at 25° and path L (both in cm.) is shown in parentheses after each frequency. The k value represents the actual chart record of absorption at the indicated frequency, implying overestimation of the intrinsic intensity of any weak band superposed upon a branch of a stronger band; but the method does offer empirical reproducibility.

The "Group mode" column of Table VIII describes the vibrational modes to be expected in each frequency range, but the listed frequencies may often include unassigned minor peaks, or overtones enhanced by Fermi resonance. This effect makes specific identification difficult in some ranges; for example, sometimes the C–H stretching in the CH_3CF_3P unit has such low intensity that overtones and combinations are not to be sorted out. However, greater intensity does not necessarily identify C–H stretching in the N–CH_3 unit.

Methyl group rocking and wagging are fairly clear for the simpler compounds, but asymmetric P–N–P stretching can appear in the same region, and even symmetric P–N–P stretching might intrude if the P–N–P bond angle is sufficiently narrow. Or a peak at 527.5 (1.9) for $HN(PCH_3CF_3)_2$ and another at 585 (0.2) for $CH_3N(PCH_3CF_3)$ might be assigned to that mode. Rocking and wagging of the NH_2 group in $H_2NPCH_3CF_3$ were not clearly recognized, but could be confused with the similar CH_3 motions.

The N–CH_3 stretching mode might be expected in the range 1000–1100 cm.$^{-1}$ but was not to be found in that range for $CH_3NHPCH_3CF_3$. One might be tempted to assign it to a peak at 1080 (3.4) for $CH_3N(PCH_3CF_3)_2$, one at 1067 (0.7) for $(CH_3)_2NPCH_3CF_3$, and one at 1063 (m) for $(CH_3)_2NPCF_3Cl$, except that a Fermi-resonating overtone of CF_3 asymmetric deformation often is seen as just such a peak or shoulder, riding on the P branch of a C–F stretching band. Thus for CH_3CF_3PCl we find 1030 (0.06); or for CH_3CF_3PI, 1080 sh (1.4), 1074 (1.1), and 1013 (0.16); or for $(CH_3CF_3P)_2$, 1081 sh (1.1).

The five N-PCH_3CF_3 compounds have a common feature which is not immediately explained: peaks near 390 and 490 cm.$^{-1}$. These might represent some kind of coupled N–P–CH_3 vibration. Even less intelligible are the sigmoid absorptions shown by $CH_3NHPCH_3CF_3$, located roughly at 626 (0.32) and 593 (0.42). These may be related to the unassigned peaks 656 (0.80) for $(CH_3)_2NPCH_3CF_3$, 607 (0.24) and 585 (0.20) for $CH_3N(PCH_3CF_3)_2$, and 623 (0.83) and 648 sh (0.63) for $H_2NPCH_3CF_3$.

Still other peaks not included in Table VIII, and mostly assignable to overtones and combinations, are listed with intensities as follows (cm.$^{-1}$).

CH_3CF_3PH: 2267 (0.14), 1984 (0.07), 1923R (0.030), 1917Q (0.033), 1912P (0.030), 1871 (0.09).

CH_3CF_3PCl: 2343 (0.07), 2314 (0.12), 2240 (0.10), 2175–99 (0.27).

CH_3CF_3PI: 2328 (0.7), 2322 (0.5), 2216 (0.14), 1229 (0.2), 1213 (0.2), 841 (0.15), 794 (0.27), 776 (0.16).

$(CH_3CF_3P)_2$: 2335–2260 (sh, 0.18), 2243 (0.34), 2205 (0.14), 1017 (0.11).

$H_2NPCH_3CF_3$: 2440–20 (0.03), 2320–05 (0.12), 2279 (0.19), 2250 (0.11), 2225 (0.07).

$HN(PCH_3CF_3)_2$: 2355–2220 with maximum at 2260 (0.15), 960 (0.24).

$CH_3NHPCH_3CF_3$: 3344 (0.02), 2775 (0.17), 2758 (0.12), 2300 (0.13), 2244 (0.13), 2178 (0.09), 1995 (0.05), 1912 (0.05), 1850 (0.06).

$(CH_3)_2NPCH_3CF_3$: 2475 (0.07), 2383 (0.04), 2327 (0.04), 2293 (0.04), 2229 (0.04).

Some of the peaks of Table VIII were seen as closely spaced doublets or unresolved multiplets, and accordingly are marked d or m. Other abbreviations, such as sh for shoulder or parenthetical intensity estimates such as vw, w, m, ms, s, or vs, have the usual meanings.

Studies of Silicon–Nitrogen Compounds. The Base-Catalyzed Elimination of Silane from Trisilylamine[1,2]

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Abstract: The reactions of bases with trisilylamine have been studied, and it has been found that a reaction takes place in the liquid phase. Silane is always formed in these reactions, and under certain conditions N,N′,N″-trisilylcyclotrisilazane can be prepared. Kinetic studies and reactions utilizing labeled compounds have been carried out, and it has been shown that the elimination of silane from trisilylamine is base catalyzed and probably an intermolecular reaction.

Trisilylamine, $(SiH_3)_3N$, the only silylamine isolated from the reaction of excess silyl chloride with ammonia,[4,5] is a planar molecule[6] and exhibits very weakly basic properties.[5,7–9] These properties have been attributed to the partial double bond character of the silicon–nitrogen bond which results from the interaction between the electron pair of the nitrogen and the empty d orbitals of the silicon.[10–12]

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(1) Part of this work was presented at the 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1961.

(2) This paper represents part of the work submitted by R. L. Wells in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Indiana University.

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Although trisilylamine is readily prepared from silyl chloride and ammonia, it has been reported that under certain conditions secondary products are formed. Thus, Burg reported high yields of trisilylamine when gaseous ammonia is introduced slowly into gaseous silyl chloride, whereas Stock reported that the reaction of *excess* ammonia with silyl chloride resulted in the formation of trisilylamine, silane, and the nonvolatile polysilazane, $(H_2SiNH)_x$.[4,5,7,8] It was postulated that in the latter reaction the secondary products resulted from the decomposition of mono- and disilylamine; however, the primary and secondary amines were not isolated and there is no direct evidence to support their existence.

Considerable attention has been given to the study of the weakly basic properties of trisilylamine and the electron-accepting ability of the silyl group in general; however, no report has been made on the possible further interaction of the silyl groups in trisilylamine with suitable electron donors. Recently it has been shown that disilyl sulfide and disiloxane react with bases, and in the course of these reactions of compounds containing silyl groups, silane is produced.[13,14,14a] On the other hand, it has been reported that the weak base tetrasilylhydrazine gives no indication of compound formation with trimethylamine and it was concluded that tetrasilylhydrazine possessed neglible donor and acceptor properties.[15] In the course of other studies of trisilylamine, a slightly volatile substance was isolated that appeared to warrant further study. In connection with this study we chose to investigate the reactions of trisilylamine with strong bases to determine if it had electron-accepting properties and also to re-examine the reaction of silyl chloride with ammonia in an attempt to isolate volatile silylamines other than trisilylamine.

Experimental Section

Apparatus and Equipment. Conventional high-vacuum apparatus and techniques were employed throughout the course of this investigation.[16] The fractionating system incorporated mercury float valves, but vacuum stopcocks lubricated with Apiezon N or T grease were used throughout the system as required. Gases that were not condensed by liquid nitrogen were moved by an automatic Toepler pump, manufactured by Delmar Scientific Laboratories.

The apparatus for the kinetic studies consisted of a null manometer connected to a reaction tube. The reaction tube contained a vertical magnetic stirrer which could be activated by a circular electromagnet placed around the reaction tube. The entire apparatus was connected to the main vacuum line by a vacuum stopcock and a mercury float valve.

Vapor pressure data were obtained by the use of an all-glass immersible tensimeter with a calibrated volume. The constant temperature bath for temperatures above 25° was controlled to ±0.5° by a Yellow Springs Instrument Co. Thermistemp Model 71 temperature control. All pressures in the mercury manometer were read with a cathetometer to ±0.01 mm.

Infrared spectra were obtained with a Perkin-Elmer Infracord spectrophotometer Model 137, or a Perkin-Elmer Model 21 recording spectrophotometer. The samples were confined in a 5-cm. gas cell with sodium chloride windows. Proton n.m.r. spectra were obtained at 60 Mc./sec. with a Varian DP60 high resolution spectrometer. A Consolidated Engineering Corporation Model 21-620 mass spectrometer was used to record mass spectra.

Preparation and Purification of Chemicals. The preparations and infrared spectra for the compounds silane, silane-d_1, silane-d_2, silane-d_3, and silane-d_4 have been previously reported.[17-20] In this work, the suitable chlorosilane was reduced in diethyl ether with either lithium aluminum hydride or lithium aluminum deuteride to give the desired silane.[21,22] The infrared spectra of the silanes prepared in this manner were identical with those reported in the literature. The deuterated silanes always had a trace of impurity in each one due to the species with one less deuterium atom.

Silyl chloride was prepared from silane and hydrogen chloride with aluminum chloride as a catalyst in a manner similar to that described by Stock[23] and later by Emeléus.[24] Dichlorosilane was recovered as a secondary product in the silyl chloride preparation. Silicon tetrachloride was obtained from the Stauffer Chemical Co. Deuterated chlorosilanes were synthesized from silane-d_4 and deuterium chloride, the latter being generated from silicon tetrachloride and deuterium oxide (99.4% purity).

Ammonia-d_3 (98% D) from the Volk Radiochemical Co., Chicago, Ill., was used without further purification. Lithium aluminum deuteride (99.9% D) was obtained from Metal Hydrides Inc., Beverly, Mass.

Reaction of Silyl Chloride with Ammonia. The preparation of trisilylamine by the reaction of silyl chloride with ammonia has been previously described.[4,8] The yields of trisilylamine varied depending on the method of mixing and the purity of the reactants. In this work, trisilylamine was prepared by using the method of Burg.[8] The reactants were allowed to mix in the gas phase by introducing the ammonia from below into a 1-l. bulb containing silyl chloride. After introducing the gaseous ammonia very slowly, the reaction bulb and contents were allowed to remain at room temperature for 15 min. Copious amounts of white solid were precipitated on the walls of the bulb as soon as mixing occurred. The bulb was opened to the vacuum line and the volatile materials were passed into a trap at −112°. Most of the trisilylamine was condensed in the −112° trap. The −112° fraction was distilled through a trap at −45° and the trisilylamine was collected in a U-tube at −196°. When 17.90 mmoles of ammonia and 14.20 mmoles of silyl chloride were allowed to react in the above matter, 3.66 mmoles of trisilylamine were formed. Also isolated were 1.61 mmoles of excess silyl chloride and a trace of silane. The purified trisilylamine had a vapor pressure of 110 mm. at 0° (lit. 109[4] and 110 mm.[9]), and the infrared spectrum of this compound was identical with the reported spectrum.[25]

When silyl chloride and ammonia were condensed in a reaction bulb and warmed from −196° to room temperature, secondary products were formed. Careful separation of the resulting mixture allowed the isolation of volatile products other then trisilylamine. Nonvolatile solids, presumably ammonium chloride and the polysilazane, $(SiH_2NH)_x$, were also formed. Table I shows the results of two such experiments. All products were identified by characteristic vapor pressures and/or infrared and mass spectra.

Trisilylamine-d_9 was prepared from ammonia and monochlorosilane-d_3 in the manner described for the preparation of trisilylamine. As Woodward has mentioned, ammonia and monochlorosilane-d_3 do not exchange hydrogens in this reaction.[25] When these reactants are condensed together and allowed to warm from −196° to room temperature, as was done in the case of the prepara-

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tion of trisilylamine, secondary products were formed. The silane present was identified as silane-d_4.

Preparation and Properties of N,N′,N′′-Trisilylcyclotrisilazane. (a) **Reaction of Trisilylamine with Ammonia.** In a typical reaction, 2.7 mmoles of trisilylamine and 1.3 mmoles of ammonia were condensed into one of four U-tubes connected by 2-mm. vacuum stopcocks. The reactants were allowed to warm slowly and mix in the liquid phase. When the reactants were in the liquid phase, the stopcock to the second U-tube was opened. As the mixture vaporized, it passed into the second U-tube which was cooled with a −45° bath, and then into a third U-tube at −196°. The less volatile product, N,N′,N′′-trisilylcyclotrisilazane (I), which stopped in the −45° trap, was then transferred to the fourth U-tube to avoid further contact with the reaction mixture. The fraction that passed through the U-tube at −45° was fractionated under vacuum through a −157° bath in which the unreacted ammonia and trisilylamine stopped, whereas silane passed through as identified by its characteristic infrared spectrum and mass spectrum. The procedure was repeated 14 times; the total amount of silane thus liberated was 3.73 mmoles. The total material from all runs which condensed at −45° was distilled through a U-tube at −22.8°, and into a U-tube at −45°. The larger part of the material passed through the trap at −22.8° and stopped in the second U-tube. The total amount of I prepared was 0.29 mmole. In the U-tubes where the reactions had taken place, comparatively large amounts of a nonvolatile, oily material and solid were deposited.

Table I. Reaction of Silyl Chloride with Ammonia

Reactants, mmoles		Products, mmoles			
SiH_3Cl	NH_3	SiH_4	NH_3	$(SiH_3)_3N$	$(SiH_3NSiH_2)_3$
3.37	4.30	0.37	0.86	0.27	Trace
3.22	3.98	0.14	0.34	0.86	Trace

In other typical experiments all reactants and products were isolated after allowing them to mix one time in the liquid phase. Again, small quantities of nonvolatile materials were deposited on the surface of the reaction vessel. Table II shows the results of two such experiments.

Table II. Reaction of Trisilylamine with Ammonia

Reactants, mmoles		Products, mmoles			
$(SiH_3)_3N$	NH_3	$(SiH_3)_3N$	NH_3	SiH_4	(SiH_3NSiH_2)
1.07	0.56	0.86	0.52	0.22	Trace
0.86	0.52	0.66	0.55	0.24	Trace

When trisilylamine and ammonia were allowed to mix in the gas phase, no silane was eliminated in 16 hr. Even after heating the mixture for 1 hr. at 100°, no reaction took place. The reactants were subsequently condensed with liquid nitrogen, then allowed to warm to room temperature and thus mix in the liquid phase; silane was now eliminated.

(b) **Analysis.** Separate samples of I were hydrolyzed with 35% sodium hydroxide and with standard hydrochloric acid solution. Because of the air sensitivity and the small samples of the compound available, considerable difficulty was encountered. The acid hydrolysis was incomplete after 3 weeks at 90°, whereas the base hydrolysis was complete in 3 days at room temperature. Hydrogen was measured in the vacuum line, silicon was determined gravimetrically as silicon dioxide, and nitrogen was determined by titrating the ammonia liberated with standard acid. *Anal.* Calcd. for $(SiH_3NSiH_2)_3$: Si, 74.7; N, 18.6; H, 6.70. Found: Si, 68.8; N, 17.8; H, 6.39. Base hydrolysis of a sample where only hydrogen was determined gave 6.63% H. All of the experimental values for the analyses were low as compared to theoretical values; however, the empirical formula from these data is $Si_{1.93}N_{1.00}H_{5.03}$, in good agreement with the formula Si_2NH_5.

Attempts were made to decompose I with hydrogen chloride to give a group analysis by the reaction

$$(SiH_3NSiH_2)_3 + 12HCl \longrightarrow 3NH_4Cl + 3SiH_2Cl_2 + 3SiH_3Cl \quad (1)$$

For this reaction, 0.124 mmole of I and 1.90 mmole of hydrogen chloride gas were sealed in a 100-ml. glass flask. The reactants were allowed to warm from liquid nitrogen temperature to room temperature, and as the mixture warmed a white film formed on the walls of the flask. After allowing the mixture to stand at room temperature for 1 hr., the reaction flask was opened to the vacuum line. Separation of the volatile components led to the recovery of 1.32 mmoles of hydrogen chloride, 0.07 mmole of dichlorosilane, and 0.40 mmole of monochlorosilane. The recovered monochlorisilane was in fair agreement with the amount expected from eq. 1. A small trace of less volatile material was present, which indicated that the decomposition reaction was incomplete or that other products were formed. This reaction was repeated a number of times, and in each case the yield of monochlorosilane was good, but the yield of dichlorosilane was always low.

(c) **Vapor Pressure Data.** Vapor pressures of I in the range −22.8–50.0° were measured and agreed after a heating and cooling cycle, indicating that decomposition of the sample did not occur. Vapor pressures in the range −22.8–50.0° are well reproduced by the equation

$$\log p\ (\text{mm.}) = \frac{-2057.3}{T} + 7.9456 \quad (2)$$

The extrapolated normal boiling point is 133.0°. The molar heat of vaporization is calculated as 9414 cal. mole^{-1} and Trouton's constant as 23.2 cal. deg.$^{-1}$ mole^{-1}. An experimental molecular weight of 220 was obtained as compared to the calculated molecular weight of 225.7 for $(SiH_3NSiH_2)_3$.

(d) **Infrared, N.m.r., and Mass Spectra.** Infrared measurements were made on gaseous samples at pressures between 5 and 10 mm. in a 5-cm. gas cell (Table III).

Table III. Infrared Spectrum of $(SiH_3NSiH_2)_3$

Infrared, cm.$^{-1}$	Intensity	Designation
745	m	SiH_3 rocking
881	vs, broad	SiH_2 deformation
885		
940		
945	vs, sh	SiH_3, SiH_2, Si–N–Si, deformation
992	vs, sh	N–Si stretch
1018	s, sh	N–Si stretch
1096	w	
1184	m	
2170	vs	Si–H stretch

The mass spectrum of I was complicated and not well resolved with our instrument so that specific peak assignments were not made, but there was a series of strong peaks in the *m/e* region of 220–230. This limiting value gives further support for the molecular formula.

The proton n.m.r. spectrum was found to consist of a sharp singlet and a small spike at −4.44 and −4.72 p.p.m. referred to internal tetramethylsilane standard. A sample with accurately known amounts of I and tetramethylsilane was used to obtain the integrated areas under the resonance peaks. By comparing the area of the standard tetramethylsilane peak to the total area of the peaks from the compound, it was shown that there are 14.2 hydrogen atoms per molecule compared to an expected 15.0. Even though the spectrum is not readily interpreted on the basis of the cyclotrisilazane structure proposed for I, it does afford a further check on the analysis for total hydrogen content.

(*e*) **Reaction with Ammonia.** A sample of 0.07 mmole (16.2 mg.) of I and 0.21 mmole of ammonia were condensed in a glass bulb and then allowed to warm from −196° to room temperature. During this warming period, the reactants mixed in the liquid phase and effervesced. Small droplets of a viscous liquid deposited on the walls of the reaction bulb. After two more coolings and warmings, more of the viscous material formed in addition to what appeared to be a solid deposited on the walls of the bulb. After all of the volatile materials had been removed from the reaction bulb, a nonvolatile liquid and a small amount of solid remained. From the volatile fraction, 0.12 mmole of silane and 0.14 mmole of excess ammonia were recovered.

Reactions of Bases with Trisilylamine. Various bases were allowed to react with trisilylamine and trisilylamine-d_9 to ascertain whether silane formed. In a typical experiment a mixture of 1.10 mmoles of trisilylamine and 0.30 mmole of ammonia-d_3 was condensed into a 50-ml. bulb and then allowed to warm from −196° to room temperature and to mix in the liquid phase. Silane was eliminated in this reaction and was identified as isotopically normal silane; *i.e.*, no deuterium atoms were present in the silane formed by elimination.

In a typical experiment using solvent, a sample of 100 mg. of lithium deuteride was placed in a reaction tube equipped with a vertical magnetic stirrer, the tube was evacuated, and 0.35 mmole of trisilylamine and 2.0 ml. of tetrahydrofuran were condensed into it at −196°. The reaction mixture was allowed to warm to −45° and maintained at this temperature for 1.5 hr. During this time there was a very slow increase in pressure, but at the end of 1 hr. the total pressure change was negligible. The volatile products were separated and 0.49 mmole of silane was isolated. No partially deuterated silanes were formed in this reaction. The same procedure was used to follow the reaction of 0.38 mmole of trisilylamine and 50 mg. of lithium deuteride in 1.0 ml. of diethyl ether. No silane was eliminated at −45° but reaction did take place when the mixture was allowed to warm to room temperature. The reaction was also found to proceed at 0°. A total of 0.18 mmole of silane was recovered from this reaction.

Table IV summarizes the results of the silane elimination reactions.

Table IV. Silanes Eliminated from Trisilylamine

Reactants	Silane eliminated
$(SiH_3)_3N + NH_3$	SiH_4
$(SiH_3)_3N + ND_3$	SiH_4
$(SiH_3)_3N + LiH$	SiH_4
$(SiH_3)_3N + LiD$	SiH_4
$(SiH_3)_3N + CH_3NH_2$	SiH_4
$(SiH_3)_3N + (CH_3)_3N$	SiH_4
$(SiD_3)_3N + NH_3$	SiD_4
$(SiD_3)_3N + LiH$	SiD_4
$(SiD_3)_3N + CH_3NH_2$	SiD_4
$(SiD_3)_3N + (CH_3)_3N$	SiD_4
$(SiH_3)_3N, (SiD_3)_3N + NH_3$	$SiH_4, SiH_3D, SiHD_3, SiD_4$

Reaction of Ammonia with an Equimolar Mixture of Trisilylamine and Trisilylamine-d_9. For a typical experiment, 0.30 mmole of each of the amines and 0.15 mmole of ammonia were allowed to react in the liquid phase until the silane produced was sufficient for infrared and mass spectral analyses, *i.e.*, about 0.16 mmole. The infrared spectrum of the silane eliminated indicated that it was a mixture of silane, silane-d_4, and partially deuterated silanes.

Mass Spectral Analysis of the Silane Mixture from Trisilylamine and Trisilylamine-d_9. The silane mixture was analyzed by employing standard mass spectral method.[26] Standard spectra with an internal standard of argon were obtained. The infrared spectrum of the mixture and other chemical evidence indicated that only trace quantities of silane-d_2 were present in the unknown mixture. The four simultaneous equations required for each *m/e* peak were set up using the standard spectral data. Data were not sufficiently reliable to permit direct calculation of all components by solution of simultaneous equations. The number of unknown quantities to be calculated was therefore reduced at the outset by setting up the requirements that the sum of the components in the mixture must equal one, the fraction of silane equals silane-d_4, and silane-d_1 equals silane-d_3. Thus, the problem was initially reduced to two equations with two unknowns and solutions were readily calculated. Average values for these unknowns were then used to calculate intensities and compare them to the corresponding *m/e* peaks in the unknown mixture. It was now possible to vary the fraction of each component in the calculated mixture in an attempt to obtain better agreement with the unknown mixture. The unknown mixture was calculated to consist of 0.30 silane, 0.22 silane-d_1, 0.20 silane-d_3, and 0.28 silane-d_4.

Kinetic Studies of the Ammonia Trisilylamine Reaction. Considering previously cited information, the elimination of silane from trisilylamine can be represented to the first isolated product by the equation

$$xNH_3 + 3(SiH_3)_3N \longrightarrow 3SiH_4 + (SiH_3NSiH_2)_3 + xNH_3 \quad (3)$$

From the above equation, a general rate equation assuming no other components would be

$$\frac{-d[N(SiH_3)_3]}{dt} = \frac{d[SiH_4]}{dt} = k[N(SiH_3)_3]^m[NH_3]^n \quad (4)$$

Since ammonia is not consumed (see above) the equation can be simplified to

$$\frac{-d[N(SiH_3)_3]}{dt} = k'[N(SiH_3)_3]^m \quad (5)$$

From the total amount of silane eliminated at t_f and the known amount of trisilylamine at t_0, the pressures at intermediate times were converted to concentrations of trisilylamine. That is

$$\frac{(p_t - p_0)[SiH_4]_f}{(p_f - p_0)} = [SiH_4]_t \quad (6)$$

Then

$$[(SiH_3)_3N]_t = [(SiH_3)_3N]_{t=0} - [SiH_4]_t \quad (7)$$

where p_t = pressure at time t, p_0 = pressure at time t equals zero, p_f = pressure at final time, $[SiH_4]_f$ = concentration of silane at final time, $[SiH_4]_t$ = concentration of silane at time t, and $[(SiH_3)N]_t$ = concentration of trisilylamine at time t.

The experimental procedure used for rate studies was first to condense with liquid nitrogen the ammonia, trisilylamine, and tetrahydrofuran as solvent into the reaction tube of the null manometer apparatus. Tetrahydrofuran has been shown previously not to react with trisilylamine, and 1.3 ml. was used in each experiment. Next, an appropriate temperature bath was placed around the reaction tube and the magnetic stirrer activated. Depending somewhat on the temperature to be maintained throughout an experiment, temperature equilibrium was reached in approximately 2 to 4 min. Pressure *vs.* time data were recorded over long periods of time, usually until 70 to 80% of the total silane available was eliminated according to eq. 3. These data were then converted to corresponding trisilylamine concentrations (eq. 6 and 7). The total amount of silane eliminated in each experiment was determined by separating the silane from the reaction mixture at the conclusion of each run. This separation was accomplished by quickly removing the bulk of the silane while the reaction mixture was at a low temperature, and then allowing the reaction mixture to warm rapidly to separate completely the remainder of the silane. The amount of silane collected during the warming procedure was relatively very small as compared to the amount collected in the initial separation.

The rate data obtained resulted in a straight line when log $[(SiH_3)_3N]$ was plotted *vs.* time and the slope of the straight line was calculated to obtain the rate constant k'. A series of values of k' were obtained at constant temperature and constant concentration of trisilylamine, but with varying concentration of ammonia. Now k was calculated by substituting various integers for n in the expression $k' = k[NH_3]^n$. The results of these calculations are tabulated in Table V. The most constant value for k, in the ammonia concentration range given, is for $n = 3$. A plot of log k' *vs.* log (NH_3) resulted in a straight line with a slope of 3.1.

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[26] Mass Spectra Computing Manual, Consolidated Engineering Corporation, 3:02.

Table V. Determination of the Order of Ammonia Rate Constants Measured at $-77°$

$(SiH_3)_3N$, mmole	NH_3, mmole	$k' \times 10^4$, sec.$^{-1}$	Various values of $k \times 10^4$ sec.$^{-1}$ $n = 1$	$n = 2$	$n = 3$
0.353	0.540	0.77	1.42	2.64	3.99
0.352	0.707	1.70	2.41	3.40	4.81
0.352	0.736	1.68	2.28	3.10	4.19
0.353	0.972	4.42	4.55	4.69	4.79

The apparent rate constants k' for this reaction were determined in the temperature range -105 to $-64°$. Assuming the reaction is third order in ammonia, the rate constants k were then calculated at various temperatures. These results are contained in Table VI. From the Arrhenius plot of these data a value of 4.31 kcal. mole^{-1} was calculated for the activation energy.

Table VI. Temperature Dependence of the Rate Constant

Temp., °C.	$(SiH_3)_3N$, mmole	NH_3, mmole	$k \times 10^4$, sec.$^{-1}$
−64	0.352	0.670	8.06
−77	0.353	0.540	3.99
−77	0.352	0.707	4.81
−77	0.352	0.736	4.19
−77	0.353	0.972	4.79
−86	0.352	0.737	2.53
−95	0.352	0.740	1.37
−105	0.352	0.743	0.41

Discussion

The above studies show that ammonia and a number of other bases will react with trisilylamine, provided that the reactants are allowed to come in contact in the liquid phase. There is no evidence for a reaction if trisilylamine and ammonia are mixed in the gas phase; but if this mixture is condensed and allowed to stand in the liquid phase, reaction takes place. Silane is always produced in these reactions, and depending upon the length of time that the reactants are maintained in the liquid phase, one also obtains the volatile compound N,N′,N′′-trisilylcyclotrisilazane (I), as well as a nonvolatile liquid and solid. Limited reaction times allowed the formation of I and silane, and the recovery of most of the ammonia (see Table II and eq. 3), but extended liquid phase contact of the reactants resulted in the formation of only silane and nonvolatile products. In the latter case all of the ammonia could not be recovered, but this was understandable after it was observed that I and ammonia undergo a reaction in the liquid phase. Apparently I is one intermediate in the conversion of trisilylamine to silane and polymeric materials.

The isolation and purification of I was difficult because of its reactivity in the presence of bases, but careful separation of many reaction mixtures gave enough material to allow its characterization. Elemental analysis and molecular weight determinations indicated I to be a trimer with the formula $(SiH_3\text{-}NSiH_2)_3$. The presence of SiH_3– and $-SiH_2$– groups was confirmed by the reaction of this compound with hydrogen chloride.

Infrared data also indicated the presence of SiH_3– and $-SiH_2$– groups in the molecule, and there was no evidence in the infrared spectra for any hydrogens bonded to the nitrogen. Thus, the infrared data support the structure proposed for I. The mass spectrum of I shows a series of strong peaks in the m/e region of 220–230. This limiting value gives further support for the molecular formula.

Considering the fact that ammonia reacts in the liquid phase with trisilylamine, it is now quite apparent why trisilylamine forms in better yield from a gas phase reaction between silyl chloride and ammonia. In this work, trisilylamine was obtained in approximately 90% yields by using a gas phase reaction; however, when silyl chloride and ammonia were condensed into a reaction bulb with liquid nitrogen and allowed to warm to room temperature, the yields of trisilylamine were low and traces of I and silane were in evidence. When silyl chloride-d_3 and ammonia are allowed to react in the latter manner, silane-d_4 is formed in addition to the main product, trisilylamine-d_9.

These observations do not preclude the existence of mono- and disilylamines, but their formation and immediate decomposition do not have to be postulated to account for the traces of silane and other impurities that have been previously reported when trisilylamine is prepared from silyl chloride and ammonia.

As a result of the observation that ammonia acted as a catalyst in the silane elimination from trisilylamine, other bases were allowed to react with trisilylamine. It was found that monomethylamine and trimethylamine reacted in a similar manner forming I and silane. The elimination of silane was quite slow in the reaction utilizing the tertiary amine, but the primary amine appeared to react at about the same rate as ammonia. If the base attack is initiated through a pentacovalent intermediate of the silicon atoms in the trisilylamine, the tertiary amine would be less favored because of steric effects.

Studies were carried out to investigate the origin of the hydrogen incorporated in the silane eliminated in the base-catalyzed reactions. The reactions of ammonia-d_3 with trisilylamine and ammonia with trisilylamine-d_9 showed that the hydrogens from the ammonia are not incorporated in the silane eliminated. Only light silane was produced in the first reaction and only silane-d_4 was produced in the second reaction. Likewise, in the reactions of trisilylamine-d_9 with monomethylamine and trimethylamine, only silane-d_4 was eliminated. Silane and silane-d_4, respectively, were eliminated in the reactions of lithium deuteride with trisilylamine and lithium hydride with trisilylamine-d_9.

The results of the silane elimination experiments did allow the conclusion to be made that the reaction is base catalyzed with no exchange of base hydrogens, but the question remained whether it is an intermolecular or intramolecular reaction. For the intramolecular elimination, the base attack could be initiated through a pentacovalent silicon intermediate. The subsequent elimination of silane from this intermediate would result in a second intermediate containing a formal double bond between silicon and nitrogen. If the intermediate formed is $H_2Si{=}N{-}SiH_3$, it would have a basic nitrogen site that could in turn attack a molecule of trisilylamine and again an intramolecular elimination of silane could occur. It is also possible that a molecule of trisilylamine and the intermediate containing the double bond could undergo an intermolecular rearrangement, resulting in the elimination of silane. The intermediate containing the double bond could conceivably eliminate another molecule of silane, but this would result in a highly unlikely intermediate containing a silicon–nitrogen triple bond. Base-catalyzed intermolecular reactions between molecules of trisilylamine also could result in the formation of silane. In this case, the eliminated silane would contain a silyl group from one molecule of trisilylamine and a hydrogen from another trisilylamine molecule. If the reaction is intramolecular, an equimolar mixture of trisilylamine and trisilylamine-d_9 with ammonia should result in the formation of only silane and silane-d_4. On the other hand, an intermolecular reaction would result in a mixture of silanes with zero, one, three, or four deuteriums in each molecule. The mass spectrum of the silane mixture from this type of experiment was analyzed, and it was found to consist of a mixture of the possible silanes. The experimental data were best interpreted on the basis of a mixture containing 0.30 silane, 0.22 silane-d_1, 0.20 silane-d_3, and 0.28 silane-d_4. Although small variations in the fractions of each of the components in the mixture still give fairly good agreement with the experimental data, the data do not correspond to a mixture from a predominantly intramolecular reaction. It is concluded that the eliminated silane results from an intermolecular reaction, or from a combination of intermolecular and intramolecular reactions.

The ammonia-catalyzed elimination of silane from trisilylamine at temperatures between -105 and $-64°$ has been studied kinetically. The reaction was found to be first order in trisilylamine and approximately third order in ammonia for the concentration range given in Table V. The heat of activation for this reaction was calculated as 4.31 kcal. mole^{-1}. The results of the kinetic studies are best interpreted on the basis of the following scheme.

$$3NH_3 + N(SiH_3)_3 \overset{K}{\rightleftharpoons} N(SiH_3)_3\cdot 3NH_3$$

$$N(SiH_3)_3\cdot 3NH_3 \xrightarrow{k} \text{products}$$

Previously discussed results of the elimination reactions involving deuterated compounds showed that the silicon d orbitals are apparently available to accept additional electrons from a suitable donor, making it possible for the weak base trisilylamine to undergo a reaction with a base. It is therefore likely that at relatively high concentrations of ammonia, a weak complex is formed with one ammonia being associated with each silyl group in the trisilylamine molecule. In support of this idea, MacDiarmid has cited evidence to indicate that in the reaction of ammonia with disilyl sulfide, the initial step is the formation of the adduct $(SiH_3)_2S\cdot 2NH_3$.[13]

It is possible that at high concentrations of ammonia, the apparent rate constant is a sum of the rate constants for third-order and lower-order reactions. Attempts were made to verify the change in order at very low concentrations of ammonia, but reproducible results were not obtained. If the order with respect to ammonia does decrease, it is unlikely that at very low concentrations it would eventually be zero. The elimination reactions with labeled compounds rule out some mechanisms where the reaction is zero order with respect to ammonia. For example, a mechanism compatible with zero-order ammonia could be

$$N(SiH_3)_3 \overset{K}{\rightleftharpoons} {}^{+}N(SiH_3)_2 + SiH_3^-$$

$${}^{+}N(SiH_3)_2 + NH_3 \longrightarrow SiH_3{-}N{=}SiH_2 + NH_4^+$$

$$SiH_3^- + NH_4^+ \longrightarrow SiH_4 + NH_3$$

This scheme would result in a mixture of silane and silane-d_1 if the reactants were trisilylamine and ammonia-d_3, and a mixture of silane-d_4 and silane-d_3 if the reactants were trisilylamine-d_9 and ammonia. These two reactions resulted in only silane being formed in the first case and silane-d_4 in the second; thus, the above mechanism does not fit the experimental results.

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