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# STUDIES OF LIGHT WEIGHT ELEMENTS

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# PART I

## INTRODUCTION

Previous work has shown that the only volatile silicon-nitrogen compound formed in the reaction between ammonia and excess silyl chloride is trisilyamine.[1,2,3]

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1. A. Stock and C. Somieski, Ber., 54, 740 (1921).
2. A. Stock, Hydrides of Boron and Silicon, Cornell U. Press, Ithaca, New York (1933).
3. A. B. Burg and E. S. Kuljian, J. Am. Chem. Soc., 72, 3103 (1950).

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Stock and Somieski[1] reported that the mono- and di-silyl amines, $SiH_3NH_2$ and $(SiH_3)_2NH$, are formed when excess ammonia and silyl chloride are allowed to react; however, such compounds have not been isolated since they rapidly condense to form trisilylamine and ammonia. Disilylamine was reported to decompose with the formation of silane and the non-volatile polysilazane, $(SiH_2NH)_x$.[1,2,4]

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4. A. G. MacDiarmid, Quart. Rev. 10, 224 (1956).

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Also, Burg noted that for a good yield of trisilylamine, gaseous ammonia must be introduced slowly into gaseous silyl chloride; otherwise, silane and $(SiH_2NH)_x$ are obtained in large proportions.[3]

In this paper, results will be given to show that a volatile silicon-nitrogen compound, $(SiH_3NSiH_2)_3$, other than trisilylamine can be isolated from the reaction between silyl chloride and ammonia. Also, it has been shown that trisilylamine and ammonia in the liquid phase produce this volatile compound plus silane and non-volatiles. This leads to another explanation for the formation of silane in the preparation of trisilylamine from excess ammonia and silyl chloride. The mechanism and kinetics of the trisilylamine-ammonia reaction will be discussed. Also, experimental results and data will be given to show that the compound $(SiH_3NSiH_2)_3$ is N,N',N"-trisilylcyclotrisilazane.

## RESULTS AND DISCUSSION

Stock and Somieski[1] first observed the absence of base forming properties of trisilylamine. Subsequent investigations have shown this compound to have quite weak basic properties, and this has been cited as evidence for double-bond character in the Si-N bond.[3-9]

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5. A. B. Burg, XVII$^{th}$ International Congress of Pure and Applied Chemistry, Butterworths, London, Vol. I, 40 (1959).
6. B. J. Aylett, H. J. Emeleus and A. G. Maddock, J. Inorg. Nucl. Chem. Vol. I, 187 (1955).
7. S. Sujishi and S. Witz, J. Am. Chem. Soc. 76, 4631 (1954).
8. K. Hedburg, J. Am. Chem. Soc. 77, 6491 (1955).
9. D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel and L. E. Sutton, J. Chem. Soc., 332 (1954).

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Even though considerable attention has been given to the reactions of trisilylamine with Lewis acids, there has been very little said about its reactions with bases. Since silicon can attain a maximum covalency of six, and the partially substituted silanes are liable to attack by nucleophilic reagents, one would expect trisilylamine to undergo some type of reaction with basic compounds. Trisilylamine reacts with ammonia in the liquid phase but there is no evidence for reaction in the gas phase even at 100°. In this reaction silane is formed as well as a nonvolatile liquid, a solid, and the cyclotrisilazane, $(SiH_3NSiH_2)_3$. If trisilylamine is prepared from silyl chloride and ammonia in the ratio of 3:4 by warming the reactants from -196° to ambient temperatures, secondary products are formed. Careful separation of the products allowed the isolation of silane and the cyclotrisilazane. One may now conclude that high yields of trisilylamine are obtained when silyl chloride and ammonia are mixed in the gas phase since secondary decomposition is unimportant because ammonia and trisilylamine do not react in the gas phase. Since a reaction takes place in the liquid phase, the presence of silane and other secondary products in the preparation of trisilylamine can now be explained on a basis other than the condensation of the hypothetical lower amines. This evidence does not preclude the existence of the lower amines. However, other workers[10] have questioned the

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10. S. D. Brewer and C. P. Haber, J. Am. Chem. Soc., 70, 3888 (1948).

formation of aminosilane in the reaction mixtures of Stock and Somieski.[1] In the reaction between trisilylamine and ammonia with the elimination of silane, an analysis of the reactants and products indicated that the ammonia could be recovered if the reaction was stopped after a short time. If the reaction was allowed to take place for an extended period of time the ammonia could not be recovered, and nonvolatiles were formed. This indicates that the ammonia acts as a catalyst in the first stages of the reaction. When the reaction was terminated after a short time and $(SiH_3NSiH_2)_3$ isolated and allowed to react with ammonia, silane and nonvolatiles were formed. The molar relationships observed for the trisilylamine and ammonia reaction in the initial step are summarized by equation 1.

(1) $xNH_3 + 3N(SiH_3)_3 \rightarrow 3SiH_4 + (SiH_3NSiH_2)_3 + xNH_3$

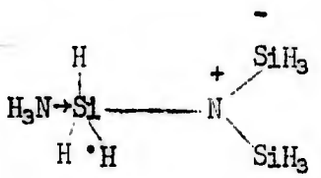
Other bases such as trimethylamine, monomethylamine and lithium hydride could be substituted for ammonia and also eliminate silane from trisilylamine.

The reactions of ammonia-$d_3$ with trisilylamine and ammonia with trisilylamine-$d_9$ show that the hydrogens from the ammonia are not incorporated in the silane eliminated. Only silane was produced in the first reaction and only silane-$d_4$ was produced in the second reaction. In the reaction of trisilylamine with lithium deuteride only pure $SiH_4$ was eliminated. Also, in the reaction between excess ammonia and silyl chloride-$d_3$, only silane-$d_4$ was formed.

Preliminary kinetic studies show that the reaction is first order

in trisilylamine. Thus, either inter or intramolecular elimination of silane could occur.

When a 1:1 mixture of trisilylamine and trisilylamine-$d_9$ was allowed to react with ammonia, the resulting silane was a mixture of silane, silane-$d_4$ and partially deuterated silanes. A preliminary analysis of the mass spectrum of this silane mixture indicated that it contains approximately twenty-five per cent each of $SiH_4$, $SiHD_3$, $SiH_3D$, and $SiD_4$. Thus, although base attack could be initiated through a pentacovalent silicon intermediate as in equation 2, with subsequent

(2) $H_3N + N(SiH_3)_3 \rightarrow$ 

elimination of silane, resulting in an intermediate containing a formal double bond between silicon and nitrogen, the experimental evidence indicates a definitely intermolecular reaction.

## EXPERIMENTAL PART

### 1. Preparation of Trisilylamine

The preparation of trisilylamine from silyl chloride and ammonia has been previously described.[1,3]

When silyl chloride and ammonia were allowed to react in the approximate ratio of 3:4 by warming the reactants from -196° to room temperature secondary products were formed. Table I-1 shows the results of two such experiments.

TABLE I-1

Reaction of Silyl Chloride with Ammonia

| Mmoles Reactants | | Mmoles Products | | | |
|---|---|---|---|---|---|
| $SiH_3Cl$ | $NH_3$ | $SiH_4$ | $NH_3$ | $N(SiH_3)_3$ | $(SiH_3NSiH_2)_3$ |
| 3.37 | 4.30 | 0.37 | 0.86 | 0.27 | (trace) |
| 3.22 | 3.98 | 0.14 | 0.34 | 0.86 | (trace) |

All products were identified by characteristic vapor pressures and/or infrared spectra.

2. Preparation of N,N',N"-trisilylcyclotrisilazane, $(SiH_3NSiH_2)_3$

a. Ammonia and Trisilylamine

An apparatus was built consisting of a small manifold with four U-tubes and vacuum stopcocks, all connected to a standard high vacuum line.[11]

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11. R. T. Sanderson, Vacuum Manipulation of Volatile Compounds, John Wiley and Sons, Inc., New York, N.Y., 1948.

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In a typical reaction 2.7 millimoles of trisilylamine and 1.3 millimoles of ammonia were condensed into one of the four U-tubes. 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

cooled to -195°. The less volatile product, $(SiH_3NSiH_2)_3$, which stopped in the -45° bath 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 then fractionated in vacuum through a -157° bath. The unreacted ammonia and trisilylamine stopped whereas the silane prepared passed through the trap at -157°. The most volatile fraction was identified as silane by its characteristic infrared spectrum and mass spectrum. The procedure was repeated fourteen times and the total amount of silane thus liberated was 3.73 mmoles. The entire fraction 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 $(SiH_3NSiH_2)_3$ prepared was 0.29 mmole.

In another typical experiment, the reactants and products were separated after a short reaction time and the data obtained are given in Table I-2.

TABLE I-2

Reaction of Trisilylamine with Ammonia

| | Mmoles Reactants | | Mmoles Products | | | |
|---|---|---|---|---|---|---|
| | $N(SiH_3)_3$ | $NH_3$ | $N(SiH_3)_3$ | $NH_3$ | $SiH_4$ | $(SiH_3NSiH_2)_3$ |
| (a) | 1.07 | 0.56 | 0.86 | 0.52 | 0.22 | (trace) |
| (b) | 0.86 | 0.52 | 0.66 | 0.55 | 0.24 | (trace) |

Thus, the ammonia is apparently involved in the reaction essentially as a catalyst.

When trisilylamine and ammonia were allowed to mix in the gas phase and stand sixteen hours no silane was eliminated. Even after heating the mixture for one hour at 100° there was no indication of a reaction having taken 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. Since the reaction was subsequently shown to be first order in trisilylamine the reaction may only have been very slow owing to the low concentration of reactants. From a practical point of view, however, no reaction occurs in the gas phase.

3. Analysis of $(SiH_3NSiH_2)_3$

Separate samples of $(SiH_3NSiH_2)_3$ were hydrolyzed with 35% sodium hydroxide and with standard acid. The base hydrolysis was continued for four days at room temperature and the acid hydrolysis continued for three weeks at 90°. Hydrogen was measured in the vacuum line, silicon was determined gravimetrically as $SiO_2$ and the nitrogen was determined by titrating the ammonia liberated with standard acid. Calculated for $(SiH_3NSiH_2)_3$: Si, 74.7%; N, 18.6%; H, 6.7%. Found: Si, 68.8%; N, 17.8%; H, 6.4%. All of the experimental values for the analyses were low as compared to the theoretical values; however, the emperical formula from these data is $Si_{2.00}N_{1.04}H_{5.18}$ in good agreement with the formula $Si_2NH_5$.

4. Vapor Pressure Data for $(SiH_3NSiH_2)_3$

Table I-3 gives vapor pressure data for $(SiH_3NSiH_2)_3$. The

apparatus used was an all glass immersible tensimeter with a calibrated volume. The constant temperature bath was controlled to $\pm 0.1°$ by a Yellow Springs Instrument Co. Thermistemp Model 71 Temperature Control. All pressures in the mercury manometer were read with a cathetometer to $\pm .01$ mm.

The observed vapor pressures on heating and cooling do not indicate decomposition of the sample in the temperature range given. Vapor pressures in the range -22.8° to 50.0° are well reproduced by the following equation.

$$(3) \qquad \log p(\text{mm}) = -\frac{2057.3}{T} + 7.9456$$

The extrapolated boiling point is 133.0°. The molar heat of vaporization is calculated as 9414 cal. $\text{mole}^{-1}$ and Trouton's constant as 23.2 cal. $\text{deg.}^{-1}$ $\text{mole}^{-1}$. From the known volume of the vapor pressure apparatus and the weight of the sample, an experimental molecular weight of 220 was obtained when the sample was entirely in the vapor state.

TABLE I-3 [a]

Vapor Pressure Data for $(SiH_3NSiH_2)_3$

| t °C | Vapor Pressure (mm) On heating | | t °C | Vapor Pressure (mm) On cooling | |
|---|---|---|---|---|---|
| | Obs. | Calc. | | Obs. | Calc. |
| -22.8 | 0.55 | 0.54 | -22.8 | 0.10 | 0.54 |
| -18.0 | 0.70 | 0.77 | -18.0 | 0.95 | 0.77 |
| - 6.0 | 1.55 | 1.76 | -12.0 | 1.20 | 1.18 |
| 0.0 | 2.45 | 2.61 | 0.0 | 2.88 | 2.61 |
| 8.5 | 4.00 | 4.39 | 8.5 | 4.80 | 4.39 |
| 16.6 | 5.45 | 7.01 | 16.6 | 6.90 | 7.01 |

TABLE I-3[a] (continued)

| | | | | | |
|---|---|---|---|---|---|
| 22.5 | 9.55 | 9.72 | 22.5 | 10.15 | 9.72 |
| 25.0 | 11.25 | 11.16 | 25.0 | 11.65 | 11.16 |
| 30.0 | 15.12 | 14.58 | 30.0 | 15.47 | 14.58 |
| 35.0 | 19.18 | 18.61 | 35.0 | 19.87 | 18.61 |
| 40.0 | 23.73 | 23.81 | 40.0 | 24.42 | 23.81 |
| 45.0 | 29.86 | 30.17 | 45.0 | 30.90 | 30.17 |
| 50.0 | 36.47 | 38.05 | 50.0 | 37.11 | 38.05 |

(a) All observed data corrected to mercury density at 0°. Duration of experiment twelve hours. Observed data treated by Method of Least Squares.

5. Infrared, NMR and Mass Spectra for $(SiH_3NSiH_2)_3$

Infrared data for $(SiH_3NSiH_2)_3$ are recorded in Table I-4. The data were obtained with a Perking-Elmer Model 21 recording sphectrophotometer. The sample was confined in a 5 cm gas cell with sodium chloride windows. Sample pressures between 5 and 10 mm were used to give good spectra.

TABLE I-4

Infrared Spectrum of $(SiH_3NSiH_2)_3$

| $\nu cm^{-1}$ | Intensity |
|---|---|
| 745 | m |
| 881<br>885 | vs, broad |
| 940<br>945 | vs, broad |
| 992 | vs, shoulder |
| 1018 | s, shoulder |
| 1096 | w |
| 1184 | m |
| 2170 | vs |

Comparing these data with the infrared data for trisilylamine given by Woodward, the bands at 940-945 $cm^{-1}$ and 745 $cm^{-1}$ are indicative of a $SiH_3$-group[12].

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12. E. A. V. Ebsworth, J. R. Hall, M. J. MacKillop, D. C. McKean, N. Sheppard and L. A. Woodward; Spectrochimica Acta, 13, 202 (1958).

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Also, Fassel has shown that mono, di, and tri substituted silanes can be distinguished by observing the bands in the 950 to 750 $cm^{-1}$ region.[13]

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13. R. N. Kniseley, V. A. Fassel and E. E. Conrad; Spectrochimica Acta, 15, 651 (1959).

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For a mono substituted silane ($SiH_3$-), there are two bands in the 950-900 $cm^{-1}$ region, and for a di substituted silane (-$SiH_2$-), there are two bands, one in the 950-900 $cm^{-1}$ region and one in the 890-825 $cm^{-1}$ region of the spectrum. Hence, infrared evidence suggests that both $SiH_3$ and $SiH_2$ groups are present in the molecule.

The mass spectrum of $(SiH_3NSiH_2)_3$ shows 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 of the compound in carbon disulfide solution was obtained at 60Mc/s with a Varian DP60 High Resolution Spectrometer and was found to consist of a sharp singlet and a small spike. Other evidence had indicated the presence of $SiH_3$- and $SiH_2$-

groups in the molecule and thus the spectrum obtained was not expected. A sample with accurately known amounts of $(SiH_3NSiH_2)_3$ 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. Even though the spectrum is not readily interpreted on the basis of the cyclotrisilazane structure proposed for $(SiH_3NSiH_2)_3$, it does afford a further check on the analysis for total hydrogen content.

6. Reaction Between Ammonia and $(SiH_3NSiH_2)_3$

In the preparation of $(SiH_3NSiH_2)_3$ from ammonia and trisilylamine there are nonvolatile products formed which could result from the reaction of $(SiH_3NSiH_2)_3$ and ammonia. In an effort to investigate this reaction $(SiH_3NSiH_2)_3$ was allowed to react in the liquid phase with ammonia. A sample of 0.07 mmole (16.2 mg) of $(SiH_3NSiH_2)_3$ and 0.21 mmole of $NH_3$ were condensed in a glass bulb and then allowed to warm from -195° to room temperature. During this warming period, the reactants mixed in the liquid phase and effervesced. There were small droplets of a viscous liquid deposited on the walls of the reaction bulb. After two more coolings and warmings there was more of the viscous material formed plus what appeared to be a solid deposited on the walls of the bulb. The bulb was opened to the vacuum line and all volatile components transferred to the fractionating system. After all of the volatile materials had been removed from the reaction bulb, there remained a

non-volatile viscous liquid and a small amount of solid on the walls. From the volatile fraction 0.12 mmole of $SiH_4$ and 0.14 mmole of excess ammonia were recovered. There was a trace of a slightly volatile material recovered; however, there was not enough of this material to identify it as unreacted $(SiH_3NSiH_2)_3$. The reaction bulb containing the nonvolatiles were opened to the air and after thirty minutes there was no indication of a reaction, and the appearance of the viscous liquid and solid had not changed. There was no visual evidence for a reaction when pure water was added to the materials, but the addition of sodium hydroxide solution caused vigorous effervescence.

7. Reaction Between Excess Hydrogen Chloride and $(SiH_3NSiH_2)_3$

Stock reported that trisilylamine is quantitatively decomposed by hydrogen chloride to silyl chloride and ammonium chloride, but the solid polymer $(SiH_2NH)_x$ liberated $SiH_2Cl_2$ less readily when allowed to react with hydrogen chloride. An attempt was made to decompose the compound $(SiH_3NSiH_2)_3$ with hydrogen chloride to give a group analysis by the reaction

$$(4)\quad (SiH_3NSiH_2)_3 + 12HCl \rightarrow 3NH_4Cl + 3SiH_2Cl_2 + 3SiH_3Cl$$

For this reaction 0.124 mmole of $(SiH_3NSiH_2)_3$ and 1.90 mmoles 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 one hour, 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 mmoles of $SiH_2Cl_2$, and 0.40 mmoles of $SiH_3Cl$. Silyl chloride was in fair agreement with the amount expected from equation 4. There was a very small trace of less volatile material, which indicated that the decomposition reaction was incomplete or that other products were formed. Repeated reactions with excess hydrogen chloride and $(SiH_3NSiH_2)_3$ allowed nearly quantitative amounts of $SiH_3Cl$ but the yield of $SiH_2Cl_2$ was always low.

A later section of this report will further discuss the $(SiH_3NSiH_2)_3$ and hydrogen chloride reactions.

8. Reactions of Bases with Trisilylamine

When trisilylamine and ammonia react to form $(SiH_3NSiH_3)_3$ and silane, the ammonia can be recovered if the reaction is stopped after a very short time. Thus, the ammonia apparently catalyzes the elimination of silane from trisilylamine in the first stages of the reaction. With this in mind reactions of other bases with trisilylamine were investigated.

a. Trimethylamine and Trisilylamine

A mixture of 1.10 mmoles of trisilylamine and 0.33 mmole of trimethylamine were allowed to react in a glass bulb for twelve hours; after this time there was very little silane produced. After allowing the mixture to stand at room temperature for seven days, 0.09 mmole of silane had been produced. Careful separation of the mixture allowed the isolation of a very small amount of material that gave an infrared spectrum identical to $(SiH_3NSiH_2)_3$ prepared from trisilylamine and ammonia.

b. Monomethylamine and Trisilylamine

A mixture of 0.31 mmole of trisilylamine and 0.06 mmole of monomethylamine were condensed into a U-tube of the vacuum line. The mixture was allowed to warm from -195° to room temperature and remain at this temperature for one hour and then condensed with liquid nitrogen. It was immediately warmed to room temperature again so that the mixture was in the liquid phase for a short time. This procedure was repeated ten times over a period of twelve hours. At the end of this time there was 0.07 mmoles of silane produced and a small quantity of material that could be identified as $(SiH_3NSiH_2)_3$.

It is of interest to note that in this case there was no evidence for the presence of a viscous liquid and a solid such as formed in the reactions using ammonia.

c. Lithium Aluminum Hydride and Trisilylamine

A slurry of lithium aluminum hydride (250 mg) and diethyl ether (4 cc.) was made and then 1.62 mmoles of trisilylamine were condensed into the same reaction bulb. The mixture was allowed to warm from -195° to room temperature and at approximately -20° some effervescence observed. After allowing the mixture to stand at room temperature for five minutes the effervescence subsided. The mixture from the reaction bulb was then separated by fractional condensation. There were 2.24 mmoles of silane and a small amount of $(SiH_3NSiH_2)_3$ produced in this reaction. No ammonia was recovered from the reaction products.

d. Lithium Hydride and Trisilylamine

For this reaction 95 mg of lithium hydride, and 2 ml of diethyl ether were introduced into a reaction tube that contained a glass spring stirrer with a metal in glass end which could be moved vertically by a magnet. After condensing 2.21 mmoles of trisilylamine into the reaction tube the mixture was allowed to warm to 0° and then maintained at this temperature with an ice bath for two hours. Constant stirring was maintained during the course of the reaction. After this time 0.45 mmole of silane had been formed. In a second experiment at a lower temperature, a similar mixture was cooled with a -22.8° bath and allowed to react for one hour. No silane was detected after this time. The 0° bath was again placed around the reaction tube and after six more hours the total silane produced was 2.53 mmoles. At this time the $(SiH_3NSiH_2)_3$ prepared was separated from the reaction mixture. There was trisilylamine that was unreacted and this was returned to the reaction tube and the reaction continued for two and one half hours. More silane was produced and the total was now 3.07 mmoles. The total amount of $(SiH_3NSiH_2)_3$ prepared in this experiment was 0.12 mmoles.

9. Kinetic Studies of the Ammonia Trisilylamine Reaction

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.

The procedure was to first condense the ammonia, trisilylamine and tetrahydrofuran as solvent into the reaction tube of the apparatus. (Tetrahydrofuran did not react with trisilylamine.) Next the 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 one minute. The first pressure reading was usually taken within three minutes from the time the constant temperature bath was put into place. The data recorded for each experiment was the increase in pressure versus time.

Various experiments have been done and the concentrations of reactants and temperatures maintained are given in Table I-5.

TABLE I-5

Conditions of Kinetic Studies of Silane Elimination

| Expt. No. | Reactants (mmoles) $N(SiH_3)_3$ | $NH_3$ | Temperature t °C |
|---|---|---|---|
| 1 | 0.67 | 0.20 | -45 |
| 2 | 0.35 | 0.20 | -45 |
| 3 | 0.35 | 0.20 | -77 |
| 4 | 0.35 | 0.20 | -23 and -31 |

The best data were obtained from experiments 1,2 and 3. For experiment 4 the elimination of silane was very slow and the pressure increase thus very small. Complete data are given in Table I-6.

TABLE I-6

Kinetics Data

| Expt. 1 | | Expt. 2 | | Expt. 3 | | Expt. 4 | |
|---|---|---|---|---|---|---|---|
| $tx10^{-3}$ sec. | p(mm) | $tx10^{-3}$ sec. | p(mm) | $tx10^{-3}$ sec. | p(mm) | $tx10^{-3}$ sec. | p(mm) |
| 0.600 | 17.5 | 0.131 | 29.5 | 0.195 | 7.5 | 0.154 | 42.5 |
| 1.371 | 23.4 | 0.712 | 32.0 | 0.567 | 10.8 | 0.280 | 59.0 |
| 2.178 | 25.2 | 1.306 | 34.2 | 1.023 | 15.2 | 0.762 | 61.7 |
| 2.770 | 26.9 | 2.055 | 37.5 | 1.414 | 18.8 | 1.320 | 64.5 |
| 3.396 | 28.0 | 2.787 | 41.8 | 2.073 | 23.5 | 2.242 | 65.5 |
| 4.015 | 30.5 | 3.368 | 45.5 | 2.861 | 29.7 | 3.330 | 66.5 |
| 4.821 | 34.1 | 4.037 | 49.8 | 3.839 | 36.8 | 4.985 | 67.5 |
| 6.017 | 40.9 | 4.959 | 55.2 | 4.765 | 43.8 | 6.825 | 68.2 |
| 7.670 | 51.1 | 6.253 | 65.0 | 5.955 | 52.5 | 8.637 | 68.7 |
| 9.080 | 61.9 | 7.378 | 73.5 | 7.011 | 59.5 | 11.305 | 69.5 |
| 10.850 | 75.5 | 9.052 | 83.0 | 8.505 | 69.5 | Now at -31° | |
| 13.297 | 94.0 | 10.500 | 90.0 | 10.200 | 79.0 | 12.036 | 61.5 |
| 15.180 | 107.2 | 12.154 | 97.5 | 12.705 | 91.5 | 13.000 | 62.5 |
| 16.987 | 118.8 | 13.669 | 105.5 | 14.755 | 102.5 | 14.745 | 65.0 |
| 19.054 | 131.5 | 15.434 | 112.2 | 17.010 | 111.0 | 16.802 | 68.0 |
| 20.410 | 140.9 | 17.640 | 120.0 | 19.015 | 120.5 | 18.325 | 70.5 |
| 22.953 | 152.0 | 19.920 | 127.5 | 21.377 | 131.5 | | |
| 25.107 | 161.9 | 22.320 | 133.0 | 23.766 | 139.0 | | |
| 28.528 | 176.2 | 24.480 | 137.8 | 27.876 | 148.0 | | |
| 31.886 | 185.3 | 26.580 | 142.5 | | | | |
| 34.817 | 193.9 | | | | | | |
| 38.067 | 201.4 | | | | | | |
| 41.325 | 210.2 | | | | | | |

Previously cited information indicated that the elimination of silane from trisilylamine could be represented in the first step by the equation

(5) $xNH_3 + 3N(SiH_3)_3 \rightarrow 3SiH_4 + (SiH_3NSiH_2)_3 + xNH_3$

Assuming the above equation is correct:

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

And: $k' = k[NH_3]^m$ for first step

(6) Then if ammonia is not consumed:

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

From the total amount of silane eliminated at $t_f$ and the known amount of trisilylamine at $t_o$, the pressures at the times listed were converted to concentrations of trisilylamine.

That is:

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

Then: $[N(SiH_3)_3]_t = [N(SiH_3)_3]_{t=o} - [SiH_4]_t$

The graphs of log $[N(SiH_3)_3]$ vs. t for the -77° and -45° data resulted in straight lines. The -77° data followed a straight line for about four hours and then tailed off whereas the -45° data followed a straight line for only two hours. Since straight lines are obtained for these data for the first few hours, the assumptions made in equations 5 and 6 appear to be valid and the reaction is initially first order in trisilylamine. The rate constants k' were obtained from the slopes of the graphs and then corrected with their corresponding constant ammonia concentrations which resulted in the rate constants k. Table I-7 contains these data.

TABLE I-7

Rate Constants for Silane Elimination

| Temperature | $k'$ | $[NH_3]$ Soln. | $k$ |
|---|---|---|---|
| -77° | $1.10 \times 10^{-5} sec^{-1}$ | 0.185 mmoles | $5.95 \times 10^{-5} sec.$ |
| -45° | $6.31 \times 10^{-6} sec^{-1}$ | 0.141 mmoles | $4.48 \times 10^{-5} sec.$ |

From the values of k an apparent heat of activation of -795 cal. $mole^{-1}$ was calculated.

The apparent negative activation energy indicates that the initial stages of the reaction are complex. In all probability the explanation lies in a temperature dependent acid-base equilibrium between ammonia and trisilylamine prior to the rate controlling step of the reaction. Further data at lower temperatures will be obtained in the near future.

10. Preparations of Deuterated Silanes and Derivatives

The preparations and infrared spectra for the compounds $SiH_4$, $SiH_3D$, $SiH_2D_2$, $SiHD_3$ and $SiD_4$ have been previously reported.[14-17]

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14. Tindal, Straley, and Nielsen, Phys. Rev., 47, 828 (1935).
15. S. R. Polo and M. K. Wilson, J. Chem. Phys., 22, 1559 (1954).
16. D. R. J. Boyd, J. Chem. Phys., 23, 922, (1955).
17. J. H. Heal and M. Kent Wilson, J. Chem. Phys., 24, 385 (1956).

In this work suitable silyl chlorides were reduced with the appropriate hydride to give the desired silane.

(7) $SiCl_4 \xrightarrow{LiAlH_4} SiH_4$

(8) $SiH_3Cl \xrightarrow{LiAlD_4} SiH_3D$

(9) $SiH_2Cl_2 \xrightarrow{LiAlD_4} SiH_2D_2$

(10) $SiD_3Cl \xrightarrow{LiAlH_4} SiHD_3$

(11) $SiCl_4 \xrightarrow{LiAlD_4} SiD_4$

The general procedure was to freeze with liquid nitrogen an ethereal solution of the hydride in a flask and then condense the chloride into this flask. The flask was then allowed to warm to room temperature. The silane formed was separated by passing through a trap at -157°. The infrared spectra of the silanes prepared in this matter were identical to those reported in the literature. In the case of the deuterated silanes there was always a slight trace of impurity in each one due to the species with one less deuterium atom.

Woodward et al. have described the preparation of $N(SiD_3)_3$ from DCl and $SiD_3Cl$ in their paper on the infrared spectrum of $N(SiD_3)_3$.[12] Since most of the experimental details were not described completely the procedures used are the following.

a. Preparation of Deuterium Chloride

(12) $SiCl_4 + 4D_2O \rightarrow 4DCl + Si(OD)_4$

20 mmoles of silicon tetrachloride were condensed into a one liter

reaction bulb which contained approximately 80 mmoles of $D_2O$ (96%). The reaction bulb was sealed off and allowed to warm to room temperature. The reaction appeared to be quite smooth with the formation of a gelatinous material, presumably hydrated silica. The reaction bulb was cooled to -195° and opened to the vacuum line. The volatile material was fractionally distilled three times through a -112° bath. The vapor pressure of the DCl prepared was 121 mm at -112°. The DCl prepared in this preparation was 17.5 mmoles.

b. Preparation of Silyl Chloride-$d_3$

$$(13) \qquad SiD_4 + DCl \xrightarrow{AlCl_3} SiD_3Cl + D_2$$

Both 8.5 mmoles of silane-$d_4$ and 5.5 mmoles of deuterium chloride were condensed into a one liter bulb which contained aluminum chloride sublimied onto the walls. The mixture was heated to 100° for 3 hours, then cooled with liquid nitrogen and the hydrogen pumped off. The condensables were transferred to the vacuum line and the excess reactants were separated by passing the mixture through a -142° trap. The -142° fraction was mostly silyl chloride-$d_3$ which could be purified by repeated passes through a trap cooled with a -112° bath. By using an excess of silane-$d_4$ there were only trace quantities of higher chlorinated silanes produced in this preparation. The yield was 3.1 mmoles of silyl chloride-$d_3$.

c. Preparation of Trisilylamine-$d_9$

$$(14) \qquad 3SiD_3Cl + 4NH_3 \rightarrow N(SiD_3)_3 + 3NH_4Cl$$

Trisilylamine-$d_9$ was prepared in the same manner as the trisilylamine discussed before. Just as Woodward[12] has mentioned, ammonia and silyl chloride-$d_3$ do not exchange hydrogens in this reaction. When these reactants are mixed in the approximate ratio of 4:3 and allowed to warm from -195° to room temperature as was done in the case of the preparation of trisilylamine, there were secondary products formed. The silane present was $SiD_4$, whereas in the similar reaction between silyl chloride and ammonia the silane was $SiH_4$. Thus no hydrogens in the trisilylamine arise from N-H bonds of the reactant ammonia.

11. Reaction of Trisilylamine and Ammonia-$d_3$

A mixture of 1.10 mmoles of trisilylamine and 0.3 mmole of ammonia-$d_3$ were condensed into a 50 ml bulb, and then allowed to warm from -195° to room temperature and mix in the liquid phase. There was silane eliminated in this reaction and it was identified as $SiH_4$.

12. Reaction of Trisilylamine-$d_9$ and Ammonia

Both 0.56 mmole of trisilylamine-$d_9$ and 0.21 mmole of ammonia were condensed into a 50 ml bulb, and allowed to react in the liquid phase. The silane eliminated in this reaction was identified to be $SiD_4$.

13. Reaction of Trisilylamine and Lithium Deuteride

a. In Tetrahydrofuran as Solvent

A sample of 100 mg of lithium deuteride was placed in a reaction tube equipped with a vertical magnetic stirrer, and 0.35 mmoles of trisilylamine and 2 ml of tetrahydrofuran were then condensed into the

tube. The reaction mixture was allowed to warm from -195° to -45° and then maintained at this temperature for 1.5 hours. During this period of time there was a slow increase in pressure and at the end of 1.0 hour the pressure rise was negligible. The volatile products were separated and there was 0.49 mmole of silane present. The silane was identified as only $SiH_4$. No partially deuterated silanes were present.

b. In Diethyl Ether as Solvent

Same procedure was used as above, but with 1 ml of diethyl ether as solvent and 0.38 mmole of trisilylamine and 50 mg of lithium deuteride. There was no silane eliminated at -45°, but a reaction did take place when the mixture was allowed to warm to room temperature. The reaction was found to proceed also at 0°. There was 0.18 mmole of $SiH_4$ recovered from this reaction.

14. 1:1 Mixture Trisilylamine and Trisilylamine-$d_9$ with Ammonia

Equal quantities of trisilylamine and trisilylamine-$d_9$ were allowed to react in the liquid phase with ammonia. For a typical experiment 0.30 mmole of each of the amines and 0.15 mmole of ammonia were allowed to react until the silane produced was sufficient for infrared and mass spectral analysis, i.e. about 0.16 mmole. The infrared spectrum of the silane eliminated from the mixture indicated that $SiH_4$ and $SiD_4$ were the predominant components, but there were bands from partially deuterated silanes. A known mixture of $SiH_4$ and $SiD_4$ was made and an infrared spectrum of this mixture verified the presence of partially deuterated silanes in the mixture obtained from the elimination reaction.

15. 1:1 Mixture Trisilylamine and Trisilylamine-$d_9$ with Lithium Deuteride in Diethyl Ether

Equal quantities of trisilylamine and trisilylamine-$d_9$ were allowed to react with lithium deuteride in diethyl ether at 0°. The procedure was the same as that described earlier for the reaction of trisilylamine and lithium deuteride. The silane eliminated in this reaction was also a mixture of silanes; however, the infrared spectrum was not identical to that for the silane mixture in the ammonia reaction. There appeared to be less $SiH_4$ and $SiD_4$ in this mixture.

16. Analysis of the Silane Mixture from Trisilylamine and Trisilylamine-$d_9$

The analyses of the silane mixtures described above have been initiated. The technique being used is a mass spectral analysis. Standard spectra with an internal standard of argon were obtained for the compounds $SiH_4$, $SiH_3D$, $SiH_2D_2$, $SiHD_3$ and $SiD_4$. Also, mass spectra of the unknown mixtures with an argon internal standard have been obtained. The data were obtained on a Consolidated Engineering Corporation Model 21-620 Mass Spectrometer. The raw data are given in Table I-8. In the absence of a micromanometer to accurately measure sample pressures, a procedure was developed where aliquots of known pressures of samples were expanded into the sample chamber of the spectrometer. For each silane, a pressure of 50 mm as read on the inlet manometer was admitted to the small aliquot volume. The aliquot volume was isolated and the sample allowed to expand into the sample chamber. The argon internal standard was introduced in the same manner.

TABLE I-8

Mass Spectra Data for Standard Silanes and Silane Mixtures with Argon Standard

| m/e | Scale Divisions | | | | | | |
|---|---|---|---|---|---|---|---|
| | $SiH_4$ | $SiH_3D$ | $SiH_2D_2$ | $SiHD_3$ | $SiD_4$ | Silanes from $NH_3$ | Silanes from LiD |
| 14 | 36.3 | 36.0 | 40.5 | 36.6 | 33.0 | 39.0 | 41.4 |
| 14.5 | 78.9 | 48.0 | 30.3 | 13.5 | 3.0 | 40.5 | 33.9 |
| 15 | 52.5 | 49.8 | 69.0 | 70.8 | 71.1 | 65.4 | 69.9 |
| 15.5 | 7.2 | 33.9 | 31.5 | 19.5 | 4.8 | 15.0 | 27.0 |
| 16 | | 6.0 | 21.0 | 31.8 | 43.5 | 21.9 | 24.0 |
| 16.5 | | | 3.9 | 3.0 | | | 3.0 |
| 20[a] | 1032.0 | 1041.0 | 1023.0 | 1020.0 | 1023.0 | 1032.0 | 1110.0 |
| 28 | 948.0 | 827.0 | 793.0 | 750.0 | 670.0 | 846.0 | 910.0 |
| 29 | 1023.0 | 583.0 | 336.0 | 170.4 | 49.5 | 502.0 | 413.0 |
| 30 | 4160.0 | 2274.0 | 1149.0 | 783.0 | 723.0 | 2110.0 | 1680.0 |
| 31 | 3370.0 | 2865.0 | 2730.0 | 1770.0 | 183.9 | 2175.0 | 2550.0 |
| 32 | 296.0 | 2475.0 | 2280.0 | 2430.0 | 3550.0 | 2244.0 | 2760.0 |
| 33 | 99.3 | 276.0 | 1845.0 | 2040.0 | 348.0 | 606.0 | 1350.0 |
| 34 | | 78.0 | 189.0 | 993.0 | 2580.0 | 978.0 | 720.0 |
| 35 | | | 57.0 | 102.0 | 132.0 | 55.8 | 68.4 |
| 36[a] | 19.8 | 18.0 | 18.9 | 45.0 | 106.8 | 43.5 | 39.0 |
| 38[a] | 3.3 | 3.9 | 3.6 | 3.6 | 3.9 | 3.3 | 4.5 |
| 40[a] | 5500.0 | 5500.0 | 5350.0 | 5400.0 | 5350.0 | 5460.0 | 5810.0 |

a. Peaks from argon standard. For m/e = 36 no contribution from $SiH_4$, $SiH_3D$ and $SiH_2D_2$.

A preliminary analysis of the mixture from the ammonia reaction has shown that it consists approximately of twenty-five per cent each of the species $SiH_4$, $SiH_3D$, $SiHD_3$ and $SiD_4$. A more rigorous calculation will be made in the very near future fitting all the data by a Least Squares Method.

Table I-9 shows the comparison between the observed data and that to be expected for an equimolar mixture of $SiH_4$, $SiH_3D$, $SiD_3H$ and $SiD_4$.

TABLE I-9

Preliminary Analysis of Silane Mixture

| m/e | Silane Mixture from $NH_3$ Reaction | Equimolar Mixture $SiH_4$, $SiH_3D$, $SiHD_3$, $SiD_4$ |
|---|---|---|
| 28 | 852 | 807 |
| 29 | 506 | 458 |
| 30 | 2125 | 1994 |
| 31 | 2191 | 2057 |
| 32 | 2256 | 2224 |
| 33 | 610 | 703 |
| 34 | 985 | 935 |
| 35 | 56 | 60 |
| 36 | 44 | 29 |

17. Reaction of Excess $(SiH_3NSiH_2)_3$ and Hydrogen Chloride

In the reaction of $(SiH_3NSiH_2)_3$ with excess hydrogen chloride it was observed that the $SiH_3^-$ groups were quite readily removed from the molecule as silyl chloride; however, the formation of dichlorosilane was very slow and incomplete. It was then considered feasible to attempt to prepare an unsubstituted cyclotrisilazane by cleaving the silyl groups from $(SiH_3NSiH_2)_3$.

Reactions were carried out in the gas phase with an excess of $(SiH_3NSiH_2)_3$ to reduce the possibilities of completely destroying the parent molecule. For a typical reaction 40.5 mg of $(SiH_3NSiH_2)_3$ was condensed into a 1 liter bulb and 0.15 mmole of hydrogen chloride was condensed into a 50 ml bulb that was connected to the 1 liter bulb with a vacuum stopcock. When the reactants were at room temperature in their respective bulbs, the hydrogen chloride was slowly introduced from below into the $(SiH_3NSiH_2)_3$. A very small amount of white solid appeared

as the gases mixed. The volatile materials were then transferred to the vacuum line and fractionally distilled with pumping through a trap at -126°. The material passing through this trap was silyl chloride (0.122 mmole). The -126° fraction was passed through a trap at -95° and a small amount of dichlorosilane was isolated (0.026 mmole). The 95° fraction was then distilled into a trap at -63.5° and there was a substance that passed through this trap. There was also a fraction that stopped in the -63.5° trap, which was identified as $(SiH_3NSiH_2)_3$. The fraction that stopped in a -95° trap and passed through a -63.5° trap was carefully purified by successive fractionations through a -63.5° trap. There was 0.07 mmole of this substance collected. The infrared spectrum of this fraction was considerably different from the spectrum of $(SiH_3NSiH_2)_3$. A mass spectrum of the substance contained peaks up to the region of 160 m/e. The molecular weight by vapor-density was determined to be approximately 132. From this information it was suspected that perhaps the substance was the cyclotrisilazane $(SiH_2NH)_3$. More reactions were carried out to prepare large quantities of the compound and eventually a large enough sample (18.3 mg) was collected for determination of vapor pressure data. It would seem wise to point out at this time that 18.3 mg is a large quantity considering the difficulty in obtaining the starting material $(SiH_3NSiH_2)_3$.

Table I-9 gives vapor pressure data for the compound tentatively assigned the formula $(SiH_2NH)_3$. The same apparatus was used as previously described for the determination of the vapor pressures of $(SiH_3NSiH_2)_3$. The vapor pressures in the range -45° to +15° are well

reproduced by the following equation.

$$(15) \qquad \log p(mm) = -\frac{1789.3}{T} + 7.8226$$

The extrapolated boiling point is 89.0°. The molar heat of vaporization is calculated as 8187.9 cl. mole$^{-1}$ and Trouton's constant as 22.6 cal. deg.$^{-1}$ mole$^{-1}$.

TABLE I-10 [a]

Vapor Pressure Data for $(SiH_2NH)_3$

| t °C | Obs. Vapor Pressure (mm) Heating | Cooling | Calc. Vapor Pressure (mm) |
|---|---|---|---|
| - 45 | 0.98 | 2.05 | 0.96 |
| - 30.6 | 2.58 | 3.35 | 2.80 |
| - 22.8 | 5.15 | 6.05 | 4.75 |
| - 14.0 | 8.05 | 8.95 | 8.31 |
| - 8.0 | 12.10 | | 11.90 |
| 0.0 | 18.75 | 19.65 | 18.76 |
| + 8.5 | 29.80 | 30.50 | 29.52 |
| + 15.0 | 40.20 | | 41.12 |

(a) All observed data treated by Method of Least Squares.

The compound which was presumed to be $(SiH_2NH)_3$ was tried in reactions with diborane, trimethyl boron and boron trichloride. There was no indication of a complex being formed or a reaction taking place with the first two boron compounds. The compound with boron trichloride did undergo a reaction at room temperature. When a three-fold excess of boron trichloride was used there was a small quantity of silyl chloride formed. No other products were identified, but there was a small amount of a less volatile substance formed.

# PART II

## NUCLEAR MAGNETIC RESONANCE STUDIES OF SILICON-HYDROGEN COMPOUNDS

As a result of earlier work in these laboratories, largely reported in TR 1, some substituted silicon-hydrogen compounds were available.

The proton nuclear magnetic resonance spectra of $C_2H_5I$, $CH_3SiH_3$, and $CH_3SiH_2I$ were obtained in carbon disulfide solution with tetramethylsilane added as an internal standard. That of disilanyl iodide, $Si_2H_5I$, was observed in the "neat" state and with $Me_4Si$ and as a solution with $CCl_4$. The following data were obtained.

TABLE II-1

NMR Spectra of Some Silicon Hydride Derivatives

| Compound | δ (cps) relative to $Me_4Si$ | | $\delta MH_2$ - $\delta MH_3$ (cps) | J (cps) | $\frac{\Delta\delta}{J}$ |
|---|---|---|---|---|---|
| | $\delta MH_3$ | $\delta MH_2$ | | | |
| $SiH_3SiH_2I$ | -171 | -148 | - 23.3 | 2.16 | 10.8 |
| $CH_3CH_2I$ | -109.5 | -194.4 | 84.9 | 7.2 | 11.8 |
| $CH_3SiH_2I$ | - 62.0 | -252 | 190 | 3.9 | 49.0 |
| $CH_3SiH_3$ | ($CH_3$) - 10.2 | ($SiH_3$) -214 | 204 | 4.2 | 48.2 |

It should be noted that any interpretation using δ values (in reference to tetramethylsilane) should take into account the possibility that δ is dependent on concentration (due to bulk diamagnetic susceptibility effects). In the future, it will be necessary to

make measurements to extrapolate these δ to infinite dilution. The Δδ and J values should be quite independent of concentration. Some trends are evident, however.

1) The methyl groups in the last three compounds fall downfield in relation to $Me_4Si$ and in the order one might expect.

2) When one compares the relative shifts of the methylene versus the silylene protons on going from $SiH_3CH_3$ to the compounds, $CH_3CH_2I$ and $CH_3SiH_2I$, it is seen that the silylene group drops downfield by 38 cps while the methylene protons shift downfield about 184 cps. The downfield shift is, probably in both cases, due to the inductive effect of the electron-withdrawing iodine atom. That it is less pronounced in the case of the silylene group can be interpreted as evidence for "feed-back" of electrons through dative $\pi$-bonding between the filled p orbitals of iodine and the empty, available silicon d orbitals.

A further indication of such an effect is found in comparing the spectra of disilanyl iodide and ethyl iodide. In $C_2H_5I$, the methylene group quartet occurs downfield from the methyl group triplet. The decrease in electron density between the methylene carbon and hydrogen atoms via electron withdrawal by the electronegative iodine atom causes proton resonance at a lower field strength. That the positions of the triplet and quartet in $Si_2H_5I$ are reversed is again evidence of intramolecular $\pi$-bonding, although intermolecular association (again, via $\pi$-bonding) could conceivably cause the same effect. This latter possibility should be dependent on concentration and will be investigated further.

3) The ratio $\Delta\delta/J$, which has no theoretical basis, seem to fall into two types with values approximately equal to ten or fifty depending whether the two atoms having protons attached to them are identical or different, respectively.

Further study of NMR shifts will continue as compounds are available.

# PART III

## EXCHANGE REACTIONS OF SILICON-HYDROGEN COMPOUNDS

Considerable valuable information can be obtained about the fundamental properties of silicon compounds by study of exchange processes. The presence of available d orbitals considerably alters the chemistry of these substances. In unsubstituted silanes the d orbitals are too far above the ground state to sensibly affect their behavior. Even here, however, activated states may cause quite different behavior from that observed for corresponding carbon compounds. In substituted derivatives substantial effects are possible. Certain exchange reactions bear particularly close relation to other problems being studied in these laboratories and closer examination of some of these has been undertaken.

Thus, direct interchange of hydrogen between $N(SiH_3)_3$ and $N(SiD_3)_3$ would substantially alter the conclusions reached in Part I. Such exchange could occur either by $\cdot SiR_3$ interchange or direct hydrogen interchange.

### 1. Exchange Between $N(SiH_3)_3$ and $N(SiD_3)_3$

The possibility of silyl group exchange in trisilylamine can be readily followed with a mass spectrometer. Mass spectra of pure $(SiH_3)_3N$ and $(SiD_3)_3N$ were obtained. It was observed that the fragmentation patterns of the two species were much the same. Then an equimolar mixture of the two was studied under varying conditions:

1. Warm to remove some sample, liquid phase
2. -45° for 5 minutes, liquid phase
3. -45° for 52 minutes, liquid phase
4. Room temperature for 20 minutes, gas phase
5. Room temperature for 10 hours, gas phase

Since the mass spectrum of the peaks from 98-116 did not change and appeared to be only a mixture of $(SiH_3)_3N$ and $(SiD_3)_3N$, it may be concluded that no exchange occurred. Thus, the conclusions drawn in Part I are valid; no interference occurs by reason of direct exchange.

The material was then transferred to a smaller bulb and allowed to remain at room temperature for another 7.5 hours. Again there was no exchange observable in the mass spectrum. When warmed to 100° for three hours, it appeared that some exchange had taken place (the ratio of the intensities of the 116 peak to that of the 110 peak was diminished). Since the peaks in the range m/e = 28--34 remained much the same, it is believed that silyl groups were exchanging. (If hydrogen exchange were significant, one would expect different features in that range). A rough calculation showed exchange was about 6% complete.

Another one to one mixture of $(SiH_3)_3N$ and $(SiD_3)_3N$ was heated to 100° (gas phase) in an oil bath for 14 hours. On opening the flask a slight amount of non-condensable gas was noticeable but no peaks owing to impurities were visible in the mass spectrum. The spectrum in the 98-116 region was grossly changed (see Table III-2). The entire

region had taken on a symmetrical shape with resolvable peaks at every mass unit with the exception of peaks 114--116. Examination of the 28--34 region indicates hydrogen exchange. There appeared little change in the 28--31 peaks, but the 34 peak was diminished and the 32 and 33 peaks increased.

Mass spectral data are given in Table III-1. It should be observed that the data for trisilylamine given in TR 1 substantially changed in the present series.

TABLE III-1

Mass Spectra of $N(SiH_3)_3$ and $N(SiD_3)_3$

| | Relative Intensity | | | Relative Intensity | |
|---|---|---|---|---|---|
| m / e | $(SiH_3)_3N$ | $(SiD_3)_3N$ | m / e | $(SiH_3)_3N$ | $(SiD_3)_3N$ |
| 28 | 10.9 | 13.9 | 71 | 25.6 | 8.40 |
| 29 | 7.84 | 0.99 | 72 | 90.0 | 25.6 |
| 30 | 2.13 | 14.2 | 73 | 14.5 | 5.48 |
| 31 | 7.90 | 0.89 | 74 | 100.0 | 94.2 |
| 32 | 0.58 | 3.41 | 75 | 15.7 | 10.6 |
| 33 | 0.32 | 0.82 | 76 | 27.2 | 12.3 |
| 34 | - | 14.1 | 77 | 3.65 | 9.01 |
| 35 | 0.23 | 1.09 | 78 | 1.96 | 100.0 |
| 35.5 | 0.39 | - | 79 | - | 11.5 |
| 36 | - | 1.16 | 80 | - | 13.3 |
| | | | 81 | - | 5.06 |
| 41 | 0.31 | - | 82 | - | 28.6 |
| 42 | 0.57 | 0.64 | 83 | - | 3.50 |
| 43 | 0.61 | 0.22 | 84 | - | 2.40 |
| 44 | 2.26 | 0.64 | | | |
| 45 | 0.26 | - | 98 | 4.90 | 2.57 |
| 46 | 0.21 | 4.50 | 99 | 1.96 | - |
| | | | 100 | 3.23 | 0.70 |
| 52 | 3.39 | - | 101 | 2.74 | - |
| 52.5 | 2.00 | - | 102 | (shoulder) | 1.83 |
| 53 | 0.56 | - | 103 | 46.9 | - |
| | | | 104 | 32.6 | 1.31 |

TABLE III-1 (continued)

| | | | | | |
|---|---|---|---|---|---|
| 55 | - | 4.27 | 105 | 37.7 | - |
| 56 | 2.00 | 4.36 | 106 | 93.2 | (shoulder) |
| 57 | 1.84 | 0.91 | 107 | 64.4 | - |
| 58 | 0.71 | 2.24 | 108 | - | 49.4 |
| 59 | 0.39 | - | 110 | - | 32.4 |
| 60 | - | 0.72 | 112 | - | 30.8 |
| | | | 114 | - | 94.0 |
| 70 | 84.0 | 76.4 | 116 | - | 54.5 |

TABLE III-2

Mass Spectral Data for $N(SiH_3)_3$ - $N(SiD_3)_3$ Exchange

Below are listed the intensities in scale divisions of the upper mass region of an equimolar mixture of $(SiH_3)_3$ and $(SiD_3)_3N$ (before and after heating to 100° for 14 hours).

| m / e | I before | I after |
|---|---|---|
| 98 | 27 | 22.5 |
| 99 | - | 7.8 |
| 100 | 16 | 9.0 |
| 101 | 12 | 9.6 |
| 102 | - | 11.2 |
| 103 | 169 | 35.7 |
| 104 | 128 | 73.3 |
| 105 | 143 | 118 |
| 106 | 332 | 174 |
| 107 | 272 | 226 |
| 108 | 233 | 261 |
| 109 | - | 261 |
| 110 | 101 | 252 |
| 111 | - | 235 |
| 112 | 93 | 214 |
| 113 | - | 180 |
| 114 | 277 | (shoulder) |
| 115 | - | " |
| 116 | 165 | " |

In an effort to determine whether hydrogen exchange did indeed take place, the above mixture was reacted with DCl liberating silyl chloride. A slight excess of DCl was added to the mixed silylamines and the resulting condensables fractionated. An infrared spectrum was obtained of the silyl chloride fraction and showed the presence of species other than just $SiH_3Cl$ and $SiD_3Cl$. Thus it can be concluded that hydrogen exchange did take place (in light of the results of section 3). Group exchange may also have occurred. It may be that one or the other of the processes (group exchange or hydrogen exchange) is predominant at lower temperatures or in the liquid phase and this will be examined more carefully.

2. Exchange Between Trisilylamine and Silyl Chloride-$d_3$

Although a quaternary type of salt containing four silyl groups is unstable, it might have a transitory existence sufficient to induce exchange. To check this possibility 0.105 mmole of $(SiH_3)_3N$ was mixed with 0.287 mmole of $SiD_3Cl$ in the gas phase. After suitable lengths of time, the mixture was passed into a -112° bath, the more volatile fraction sampled and its infrared spectrum determined. The original Si-D stretching frequency had now decreased and the hitherto absent Si-H stretch became significant in the recovered silyl chloride. No peaks were present that could not be accounted for in terms of a mixture of $SiD_3Cl$ and $SiH_3Cl$. Thus exchange of silyl groups had occurred. It is possible that exchange occurred only in the liquid state present in the fractionation procedure. That such exchange did

actually occur in the liquid state was shown by passing another sample immediately after mixing directly through a -112° trap. The infrared spectrum of the more volatile fraction confirmed that exchange had occurred.

Further studies of this system will be carried out during the coming year.

3. Reaction of Trisilylamine with Deuterium Chloride

To determine whether any exchange occurs in the reaction of trisilylamine with hydrogen chloride, 0.206 mmole $(SiH_3)_3N$ and 0.655 mmole of DCl were allowed to react in a small flask for one hour at room temperature. After fractionation an infrared spectrum of the resulting silyl chloride was taken and showed the absence of any Si-D stretching frequency. Thus, no hydrogen exchange occurred during the reaction; it was observed that the reaction is essentially quantitative (a yield of 99.0% of $SiH_3Cl$ was obtained, based on the amount of DCl used).

With a deficiency of DCl, there was no indication of formation of any intermediate species such as $D_2NSiH_3$ or $DN(SiH_3)_2$.

## PART IV

## INTRODUCTION

In recent years a number of compounds have been obtained by substitution of phosphorous containing ligands for carbon monoxide in nickel carbonyl. Molecules of the general formula $Ni(CO)_{4-x}L_x$ are known and several members of each type from x equaling one to four have been reported[1,2]. The phosphorous-containing ligands generally

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1. J. Chatt and F. Hart, J. Chem. Soc., 1378 (1960).
2. J. Meriwether and M. Fiene, J. Amer. Chem. Soc., 81, 4200 (1959).

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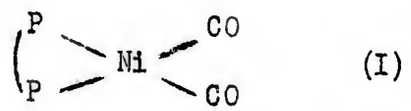
employed are of the type $PX_3$ (X = halogen), $PR_3$ or $P(OR)_3$ (R = alky or aryl). These phosphine substituted nickel complexes evidently owe their stability to the existence of partial multiple bond character in the P-Ni bond.

Difunctional phosphines have also been studied in this type of reaction. Chatt[1] has shown that nickel carbonyl reacts with diphosphines $C_2H_4(PR_2)_2$ (R = Et and Ph) and $O\text{-}C_6H_4(PR_2)_2$ (R = Me, Et and Ph) to yield the chelated product

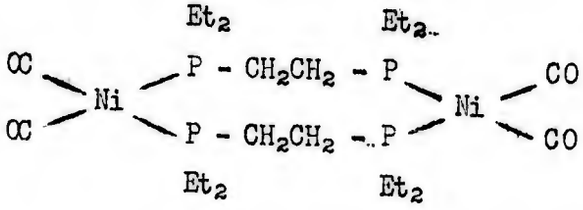


(I)

where $\binom{P}{P}$ signifies $R_2PCH_2CH_2PR_2$ or $O\text{-}C_6H_4(PR_2)_2$. These are solids with fair thermal stability. By reacting some of these compounds of type I with additional diphosphine, several products of type II were obtained.

(II)

These were colored solids with good thermal stability but readily attacked by air. Chatt also reports isolating a small amount of material with the structure



which rearranged to the type I compound in boiling solvent.

Burg[3] reported that $P_2(CF_3)_4$ reacted with $Ni(CO)_4$ to give a red-

3. A. Burg and W. Mahler, J. Amer. Chem. Soc., 80, 2334 (1958).

black solid having the formula $(OC)_3Ni\text{-}P(CF_3)_2P(CF)_2\text{-}Ni(CO)_3$ indicated by the stoichiometry. This observation is in accord with other information that biphosphine derivatives can act as dibases. Thus, $P_2(CH_3)_4 \cdot 2BH_3$ and $P_2[N(CH_3)_2]_4 \cdot 2BH_3$ are both reported[4,5], and $P_2I_4$ forms a diadduct with $BBr_3$[6].

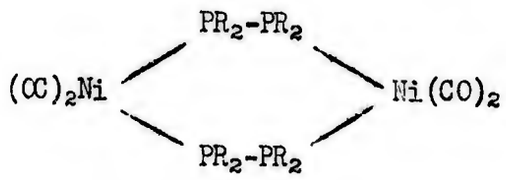
4. A. Burg, J. Amer. Chem. Soc., 83, 2226 (1961).

5. H. Nöth and H. Vetler, Ber., 94, 1505 (1961).

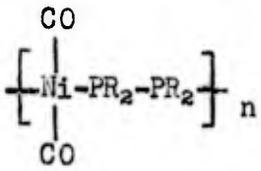
6. J. Tarible, Comp. Rend., 132, 204 (1901); confirmed by recent work in this laboratory.

An extensive study of reactions of biphosphine derivatives with nickel carbonyl appears promising with respect to the synthesis of interesting molecules. Since biphosphine molecules are not large enough to span the distance between adjacent coordination positions in tetrahedral Ni(0) complexes, they can only serve to link nickel atoms

when acting as dibases by replacing two CO molecules from nickel carbonyl. This may lead to interesting molecules of the type



and polymers of the types



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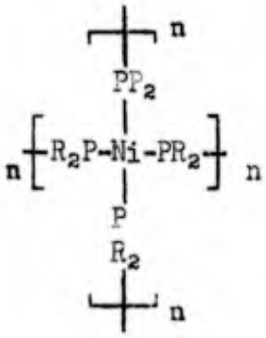


The possibility also exists of reacting biphosphines with phosphine-carbonyl-nickel complexes of the type $Ni(PR_3)_2(CO)_2$ to form similar compounds. The ability of phosphorous to engage in $d_\pi - d_\pi$ bonding with nickel should give considerable stability to such materials and in polymeric forms might lead to extensive electron delocalization.

Preliminary work has been started on these systems to investigate the reactivity of biphosphines with nickel carbonyl and the nature of the reactions. Preparation and characterization of other intermediates has also been initiated.

# DISCUSSION

## 1. Reaction of Nickel Carbonyl with Biphosphines

It has been found that tetramethylbiphosphine, $P_2Me_4$, reacts readily with nickel carbonyl in sealed tubes below room temperature, with displacement of carbon monoxide. Results of experiments conducted are given in Table IV-1.

TABLE IV-1

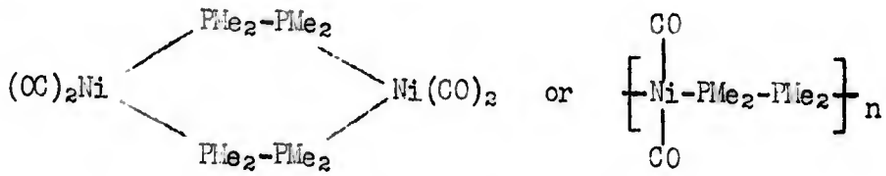
Reactions of Biphosphines with Nickel Carbonyl

| | Reactants | | Products and Recovered Reactants (mmoles) | | | |
|---|---|---|---|---|---|---|
| | $P_2Me_4$ | $Ni(CO)_4$ | CO | $P_2Me_4$ | $Ni(CO)_4$ | Product |
| 1. | 1.38 | 2.8 | 2.74 | - | 0.07 | liquid |
| 2. | 1.01 | 3.81 | 2.16 | - | 1.75 | liquid |
| 3. | 1.10 | 1.11 | 1.98 | - | - | solid |
| 4. | 2.21 | 2.2 | - | - | - | solid |
| 5. | 1.08 | 0.55 | 1.07 | 0.44 | - | solid |
| 6. | 2.84 | 0.60 | 1.14 | 2.24 | - | solid |

Experiments 1 and 2 in which the ratio of $Ni(CO)_4$ to $P_2Me_4$ was greater than two to one produced two moles of CO per mole of $P_2Me_4$ and the recovered $Ni(CO)_4$ corresponded to that in excess of twice the amount of $P_2Me_4$. Thus, the product, a yellow-brown, non-volatile oil, most probably has the composition $(OC)_3Ni\text{-}PMe_2\text{-}PMe_2\text{-}Ni(CO)_3$. The

infrared spectrum of this material has been obtained, but other structural or analytical data have not yet been determined. A sample of the oil gradually heated to 100° did not volatilze, but decomposed to liberate carbon monoxide and nickel carbonyl in the ratio of one to two and leave a deep brown solid residue. The oil was attacked by air on prolonged exposure.

In reaction 3 containing equimolar amounts of $P_2Me_4$ and $Ni(CO)_4$ all reactants were consumed and produced two moles of CO per mole of $P_2Me_4$. This product, as well as that of reaction 4, was a pale yellow solid, stable towards air and water. A sample of the substance heated in a glass capillary began to darken at 125° and decomposed at 235°. No data other than the infrared spectrum has been obtained, although a preliminary X-ray powder pattern indicates crystallinity. From the stoichiometry involved, one of the two following structures seems probable:




It is hoped that continuing work will elucidate the structure of this material.

In reaction 5 and 6, containing $P_2Me_4$ to $Ni(CO)_4$ ratios of two to one and four to one, respectively, the amount of displaced carbon monoxide did not exceed two moles per mole of $Ni(CO)_4$. Since the stoichiometry shows a combining ratio of one $P_2Me_4$ to one $Ni(CO)_4$, it is

tempting to assume that the pale yellow solid products are identical to that obtained from reactions 3 and 4. It has been observed, however, that while the latter material is stable in air, the solid from reaction 5 is slightly darkened and that from reaction 6 is spontaneously flammable. The explanation of these observations should prove interesting and of considerable importance. It is significant that the first two molecules of CO are readily displaced from nickel carbonyl by the biphosphine but further substitution under these conditions does not occur.

The biphosphine $P_2I_4$ has been found to react with $Ni(CO)_4$ in carbon tetrachloride solution at room temperature. Reactions using $P_2I_4$ to $Ni(CO)_4$ ratios of 1 to 2, 1 to 1 and 2 to 1 have all yielded deep purple-black, finely powdered solids which have not undergone further study.

2. Reaction of $PF_3$ with $Ni(CO)_4$

Although the tetrasubstituted $Ni(PF_3)_4$ has been prepared[7], no

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7. G. Wilkinson, J. Amer. Chem. Soc., 73, 5501 (1951).

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isolation of lower substituted $PF_3$-carbonyl-nickel complexes has been reported[8]. The molecule $Ni(PF_3)_2(CO)_2$ would be very desireable

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8. J. Chatt and A. Williams, J. Chem. Soc., 3061 (1951).

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with respect to reaction with a biphosphine, since this may lead to more stable derivatives not containing carbonyl groups.

A vapor phase mixture of $PF_3$ and $Ni(CO)_4$ in a two to one ratio, heated for 90 minutes at 100°, produced a mixture of substitution products. Careful fractional condensation in the vacuum system, working with a total of 2 mmoles of material, produced fractions having average molecular weights of 223 and 271. The calculated molecular weights of $Ni(CO_3)PF_3$ and $Ni(CO)_2(PF_3)_2$ are 230.7 and 290.7, respectively. By using larger quantities of material, the probability of isolating pure samples of the mono- and disubstituted species by repeated fractionation seems high and this will be pursued.

## EXPERIMENTAL

### 1. Reaction of Nickel Carbonyl with Biphosphines

Tetramethylbiphosphine was prepared by the reaction[9]

$$Me_2\underset{\underset{S}{\|}}{P}\text{-}\underset{\underset{S}{\|}}{P}Me_2 + 2Bu_3P \rightarrow Me_2P\text{-}PMe_2 + 2Bu_3PS \quad \text{at } 150°$$

9. G. Parshall, J. Inorg. Nucl. Chem., 14, 291 (1960).

Tributylphosphine was obtained from the reaction of n-butyl magnesium bromide $PCl_3$, and tetramethylbiphosphine disulfide was prepared by the action of methyl magnesium iodide on $PSCl_3$.

Nickel carbonyl was purchased from the Matheson Company and purified by fractional condensation in the vacuum system.

Glass reaction tubes equipped with break-off tips were sealed directly to the vacuum system for introduction and removal of materials. Quantitities of reactants and products are listed in the preceeding

table. Carbon monoxide was collected and measured in a Toepler pump system. Volatile materials removed after reaction were identified by vapor pressures and/or molecular weights determined by vapor density.

In all mixtures of $P_2Me_4$ and $Ni(CO)_4$ observed, reaction started immediately after melting of the reactants and evolution of CO proceeded vigorously for 2 to 3 minutes. This apparent case of CO displacement by the biphosphine is striking, since most of the monophosphine substitutions on nickel carbonyl require heating for substitution to progress. Furthermore, the accumulation of a carbon monoxide pressure in the sealed tube evidently does not inhibit the reaction.

In reactions 5 and 6, containing excess $P_2Me_4$, just two moles of CO per mole of $Ni(CO)_4$ were displaced. After removal of the initially displaced CO from the reaction tube with the other contents held at liquid nitrogen temperature, the tubes were resealed and allowed to again warm to room temperature but no additional CO was liberated under these conditions.

The biphosphine, $P_2I_4$[10], reacted with $Ni(CO)_4$ in carbon

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10. M. Baudler, Z. Naturforsch, 13b, 266 (1958).

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tetrachloride solution under a nitrogen atmosphere at a much slower rate than did $P_2Me_4$. Four to six hours at room temperature were required for the slow CO evolution to cease. Purple-black powdered products were obtained as the reaction progressed and were isolated by pumping

off the solvent and other volatile materials after reaction stopped. The products melted with decomposition at 300° in sealed capillaries.

2. Reaction of $PF_3$ with $Ni(CO)_4$

A gas phase mixture of 4.37 mmoles $PF_3$ (prepared from $ZnF_2$ and $PCl_3$) and 2.2 mmoles $Ni(CO)_4$ in a 125 cc flask was heated for 90 minutes in a steam bath. After removal of carbon monoxide, the mixture was roughly separated by fractional condensation in the vacuum line using a fractionation train of -63.5°, -78.6°, -157° and -196° baths. Recovered $PF_3$ amounting to 0.7 mmole passed through to the -196° bath. A fraction amounting to 0.22 mmole passed readily through the -78.6° bath and had an average molecular weight of 174, indicating that it was essentially unreacted $Ni(CO)_4$. Another fraction slowly passed through the -78.6° bath with continuous pumping, amounted to 0.38 mmole and had an average molecular weight of 189. In a similar way, a first fraction readily passed through the -63.5° bath while a second fraction (the remainder of all products) came through the -63.5° bath slowly with pumping. The first fraction amounted to 0.58 mmole and had an average molecular weight of 223, while the second fraction amounted to 1.09 mmoles and had an average molecular weight of 271. Repeated fractionations of larger quantities of materials should be successful in isolating reasonable amounts of the pure mono- and disubstituted complexes.

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