higher than would be expected from a homogeneous reaction governed by the presented kinetics or any other investigated homogeneous kinetics system. While the rate constants given here may be somewhat affected by this process, early inflection points should not be altered.

B^{11} Nuclear Magnetic Resonance Spectrum of Benzyldecaborane.—The B^{11} n.m.r. spectrum of benzyldecaborane prepared from $NaB_{10}H_{13}$ and benzyl chloride has been obtained at 12.8 mc. and is comparable to that of the benzyldecaborane prepared from a Grignard synthesis.[4] This spectrum can be interpreted since the B^{11} n.m.r. spectrum of decaborane has been assigned.[12]

Related work reveals that the substitution of an alkyl group for a hydrogen atom upon a boron atom not only collapses that doublet (C^{12} has no nuclear spin) but in all cases thus far observed, the B^{11} chemical shifts are to lower field. The degree of chemical shift appears to be more a function of the specific boron atom substituted than the size or spatial arrangement of the alkyl group. Examples of this shift to lower field have been observed in the alkyldiboranes,[13] 2,4-dimethylenetetraborane, 1- and 2-alkylpentaborane, 2-alkyldecaborane and others. The B^{11} resonances in triethylboron and tripropylboron are also found at the lowest field of some fifty boron containing compounds thus far observed.[14]

(12) Robert E. Williams and I. Shapiro, *J. Chem. Phys.*, **29**, 677 (1958).

(13) R. E. Williams, H. D. Fisher and C. O. Wilson, *J. Phys. Chem.*, **65**, in press (1961).

(14) T. P. Onak, H. Landesman, R. E. Williams and I. Shapiro, *ibid.*, **63**, 1533 (1959).

In consideration of the above information it is apparent that the spectrum recently published for benzyldecaborane prepared *via* the Grignard method is identical to that prepared from decaboranylsodium and decaborane is substituted at either the one or six positions. Such a spectrum would be expected if one quarter of the 1,3 and 6,9 doublet of the decaborane spectrum were collapsed and shifted to lower field by substitution of an alkyl group (Ref. 4, Fig. 2). Conversely, the one quarter collapse of the 5, 7, 8, 10 doublet would have created a different spectrum and the shift to low field would be more than twice as great as any "alkyl shift" to lower field thus far observed.

The 6-position is preferred to the 1-position for several reasons. Attack of an electron donor upon the 6,9-positions most easily explains the deuteration of decaborane in D_2O–dioxane. Substitution at the 6-position could, as mentioned above, deactivate the decaborane molecule at one end allowing three protons (in addition to the bridge protons) to be readily exchanged. In the products of Lewis base attack upon decaborane, *i.e.*, in $B_{10}H_{12}(NCCH_3)_2$ the Lewis base (acetonitrile) is attached to the 6- and 9-positions.[15] It should be noted that small amounts of other space isomers, if they are present, could not be detected by n.m.r. analysis.

Acknowledgments.—We wish to acknowledge the many constructive suggestions received during the course of this work from Dr. George W. Schaeffer and Dr. Manny Hillman.

(15) J. van der Mass Reddy and W. N. Lipscomb, *J. Am. Chem. Soc.*, **81**, 754 (1959).

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA, PENNSYLVANIA]

The Preparation and Properties of Silyl Methyl Ether[1]

BY BURT STERNBACH AND ALAN G. MACDIARMID[2]

RECEIVED JANUARY 9, 1961

Gaseous SiH_4 and gaseous CH_3OH have been found to react at room temperature in the presence of copper metal catalyst to give methoxysilanes. Reaction occurred in the absence of catalyst if liquid CH_3OH was present. The new compound, SiH_3OCH_3, has been prepared from $SiH_3I \cdot N(CH_3)_3$ and CH_3OH, and its physical properties and a number of its chemical properties have been studied. Using B_2H_6 as a reference Lewis acid, SiH_3OCH_3 has been found to be a weaker Lewis base than $(CH_3)_2O$. Diborane was not a sufficiently strong Lewis acid to differentiate between the relative base strengths of SiH_3OCH_3 and $(SiH_3)_2O$.

In a previous paper[3] it was shown that gaseous CH_3OH would combine with gaseous SiH_4 at room temperature in the presence of copper metal catalyst to yield a mixture of methoxysilanes. No methoxysilane (silyl methyl ether), SiH_3OCH_3, was obtained. In one experiment CH_3OH and SiH_4 were found to combine in the absence of catalyst. The present investigation was carried out for the purpose of determining the exact conditions of reaction of CH_3OH with SiH_4 and for the purpose of preparing and studying SiH_3OCH_3—particularly its base strength with respect to the Lewis acid, B_2H_6.

(1) This report is based on portions of a thesis to be submitted by Burt Sternbach to the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Alfred P. Sloan Research Fellow.

(3) B. Sternbach and A. G. MacDiarmid, *J. Am. Chem. Soc.*, **81**, 5109 (1959).

Experimental

Apparatus.—All work was carried out in a Pyrex glass vacuum system. Melting points were determined by a magnetic plunger apparatus.[4] All temperatures below 0° were measured by an iron-constantan thermocouple, standardized by the National Bureau of Standards. Temperatures above 0° were measured by a mercury-in-glass thermometer standardized by the National Bureau of Standards.

Methanol.—Analytical grade methanol was used. Its purity was checked by means of a vapor pressure determination at 0° (found, 30.0 mm., literature value[5] 29.7 mm.).

(4) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933, p. 184.

(5) B. Pesce and V. Evdokimoff, *Gazz. chim. ital.*, **70**, 712 (1940).

Silane.—This was prepared from $SiCl_4$ and $LiAlH_4$. Its purity was checked by measuring its molecular weight (found 32.0, calcd. 32.1) and by comparison of its infrared spectrum with that of a published infrared spectrum.[6]

Silyl Iodide.—This was prepared from SiH_4 and HI.[7] Its purity was checked by means of a vapor pressure determination at 0° (found, 124.2 mm., literature value,[7] 123.9 mm.).

Diborane.—Commercial diborane was purified in the vacuum system and its purity was checked by measuring its vapor pressure at −130.4° (found, 48.0 mm., literature value[8] 48.7 mm.). Its infrared spectrum was identical with a spectrum of pure B_2H_6 furnished by the National Bureau of Standards.

Boron Trifluoride.—Commercial BF_3 was purified in the vacuum system, and its purity was checked by measuring its vapor pressure at −111.8° (found, 306.3 mm., literature value[9] 306.5 mm.). Its infrared spectrum was identical with a spectrum of pure BF_3 furnished by the Harshaw Chemical Company.

Dimethyl Ether.—Commercial $(CH_3)_2O$ was purified in the vacuum system, and its purity was checked by measuring its vapor pressure at −78.6° (found 34.0 mm., literature value[10] 34.4 mm.).

Interaction of Silane with Methanol. A.—SiH_4 (0.0356 g.) and CH_3OH (0.0341 g.) were combined in a 500-ml. vessel. No liquid phase was present and after 5 days at room temperature no H_2 had been produced. After the addition of more CH_3OH (0.5281 g.) to ensure the presence of liquid phase and after an additional 39 hr. at room temperature, 38.3 ml. of H_2 (S.T.P.) had been formed. SiH_4 (0.009 g., identified by infrared spectrum[6]) and a mixture of methoxysilanes and CH_3OH (0.5–0.6 g.) was isolated. Its infrared spectrum indicated the presence of $(CH_3O)_4Si$[3] and $HSi(OCH_3)_3$.[3]

B.—SiH_4 (0.0396 g.), CH_3OH (0.0351 g.) and clean[3] electrolytic dust grade Cu powder (0.4232 g.) were combined in a 500-ml. vessel. After 15 minutes at room temperature, the copper had turned dark brown in color and 39.7 ml. H_2 (S.T.P.) had been produced. After an additional 35 minutes a further 0.39 ml. of H_2 was formed, but during the next 40 minutes no more hydrogen was liberated. No liquid phase was present at any time during the reaction. After removal of unreacted SiH_4 (0.0119 g.) there was isolated $H_2Si(OCH_3)_2$ (0.0054 g., mol. wt. found, 92.3, calcd., 92.2; infrared spectrum identical with that of pure material[3]), $HSi(OCH_3)_3$ (0.0263 g., mol. wt. found, 122, calcd., 122.2; vapor pressure at 0°, found, 18.9 mm., literature value,[3] 18.7 mm.; infrared spectrum identical with that of pure material[3]) and a mixture of $HSi(OCH_3)_3$ and $(CH_3O)_4Si$ (0.0015 g. identified by infrared spectrum[3]). 65% of the starting materials used in the reaction were removed as volatile products. From the darkening in color of the copper catalyst, from experiment C below and from the fact that SiH_3OCH_3 is slowly decomposed by Cu metal, it appears that the remainder of the material underwent complex decomposition.

C.—SiH_4 (0.856 mole) was placed in the reaction vessel used in B, which still contained the Cu catalyst. After 7 days at room temperature, H_2 (6.76 ml., 0.0003 mole) was formed.

Preparation of SiH_3OCH_3. (A).—The reaction of SiH_3I with varying quantities of CH_3OH was investigated in a number of experiments. On all occasions as the reactants warmed from liquid nitrogen temperatures, vigorous reaction accompanied by violent effervescence commenced at approximately −60° and continued up to room temperature. Large quantities of H_2 were evolved and a polymeric film remained in the reaction vessel on removal of volatile materials. Polymeric films also formed in traps in the vacuum system during distillations. Volatile mixtures which could not be identified were obtained in addition to a trace of SiH_3OCH_3 which subsequently was identified by comparison of its infrared spectrum with that of the pure compound prepared in experiment B below.

(B).—Since C_2H_5OH has been reported to react with $SiH_3Cl \cdot N(CH_3)_3$ to give what was presumed to be $SiH_3OC_2H_5$,[11] the analogous reaction involving CH_3OH was investigated.

A slight excess of $(CH_3)_3N$ was mixed with SiH_3I (3.5567 g.) in a 500-ml. bulb at −196° and after warming to room temperature, the excess $(CH_3)_3N$ was distilled from the solid $SiH_3I \cdot N(CH_3)_3$. CH_3OH (0.3694 g.) then was added and the reaction vessel was held at −78° for 9 hr., materials volatile at this temperature being continuously removed by pumping. After an additional 30 minutes at room temperature a further small quantity of volatile material was formed. The volatile material consisted of H_2 (4.7 ml., S.T.P.), SiH_4 (0.027 g., identified by infrared spectrum[6]) in addition to SiH_3OCH_3 which condensed in a −134° trap and distilled slowly from a −112° trap (0.198 g., mol. wt., found 62.3, calcd., 62.15). The SiH_3OCH_3 was analyzed by hydrolyzing a sample (0.0710 g., vapor pressure at −58.9°, found, 91.0 mm., calcd., 91.2 mm.) in 35% aqueous NaOH for two days at room temperature. Silicon was determined as SiO_2,[12] found 45.4%, calcd., 45.21%. Another sample (0.0635 g., mol. wt. found, 62.1, calcd., 62.15; vapor pressure at −60.9°, found 79.6 mm., calcd., 79.8 mm.) yielded upon hydrolysis under similar conditions, 67.83 ml. H_2 (S.T.P.), calcd., 68.64 ml. A portion of the SiH_3OCH_3 used in the vapor pressure study below melted sharply at −98.5 ± 0.1°.

Vapor Pressure of SiH_3OCH_3.—The vapor pressures of SiH_3OCH_3, at a number of temperatures were measured by a mercury manometer. They are recorded in Table I.

TABLE I

VAPOR PRESSURE OF SiH_3OCH_3

T, °C.	P (expt.), mm.	P (calcd.), mm.
−90.2[a]	7.7[a]	8.1[a]
−89.3	8.3	8.7
−87.1	10.3	10.6
−85.5	11.7	12.3
−77.7	23.1	23.3
−72.2	35.7	35.7
−68.2[a]	47.8[a]	47.8[a]
−67.8	50.3	49.3
−65.5	58.0	58.0
−59.1[a]	89.6[a]	90.0[a]
−59.0	90.9	90.5
−57.6	98.9	99.2
−56.9[a]	104.1[a]	104.1[a]

[a] Results of measurements on a different sample.

The data for SiH_3OCH_3 are represented by the equation

$$\log P_{mm.} = (-1320/T) + 8.1196$$

which gives an extrapolated boiling point of −21.1 ± 0.2°, a molar heat of vaporization of 6.04 kcal. and a Trouton's constant of 23.9.

Chemical Properties of SiH_3OCH_3.—All experiments on the chemical properties of SiH_3OCH_3 were performed on material of the following purity: mol. wt. found, 62.3, calcd., 62.15; vapor pressure at −69.2°, found, 44.3 mm., calcd., 44.6 mm.

(A) SiH_3OCH_3 and CH_3OH.—SiH_3OCH_3 (0.0667 g.) and CH_3OH (0.0463 g.) were combined in a 500-ml. vessel and after 15 hr. at room temperature, no hydrogen had been evolved and an infrared spectrum of the mixture showed only the presence of the original reactants. No liquid phase was present. Additional CH_3OH (0.3419 g.) was added to the reaction vessel to ensure the presence of liquid phase and after 23 hr. at room temperature 11.2 ml. H_2 (S.T.P.) had been produced. Fractionation of the materials yielded SiH_3OCH_3 (0.0484 g., identified by infrared spectrum) and a mixture of CH_3OH and methoxysilanes (0.3845 g.) which could not be separated into its constituents. An infrared spectrum indicated the presence of $HSi(OCH_3)_3$ with smaller quantities of $H_2Si(OCH_3)_2$ and $(CH_3O)_4Si$.[3]

(6) J. W. Straley and H. H. Nielsen, *Phys. Rev.*, **62**, 161 (1942).

(7) H. J. Emeléus, A. G. Maddock and C. Reid, *J. Chem. Soc.*, 353 (1941).

(8) H. E. Wirth and E. D. Palmer, *J. Phys. Chem.*, **60**, 911 (1956).

(9) E. Pohland and W. Harlos, *Z. anorg. Chem.*, **207**, 242 (1932).

(10) O. Maass and E. H. Boomer, *J. Am. Chem. Soc.*, **44**, 1712 (1922).

(11) H. J. Emeléus and N. Miller, *J. Chem. Soc.*, 819 (1939).

(12) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1943, p. 406.

(B) SiH_3OCH_3 and H_2O.—SiH_3OCH_3 (0.0674 g.) and distilled H_2O (0.2 g.) were combined in a 500-ml. vessel and after 1 hr. at room temperature there was isolated $(SiH_3)_2O$ (0.0424 g., vapor pressure at −64.9° found, 59.9 mm., literature value[13] 59.0 mm.; mol. wt. found, 78.1, calcd., 78.2; infrared spectrum identical to published spectrum[14]) and CH_3OH (0.193 g.; vapor pressure at 0°, found, 30.5 mm., literature value[6], 29.7 mm.). Yield of $(SiH_3)_2O$ was 100%.

(C) Thermal Stability of SiH_3OCH_3.—SiH_3OCH_3 (0.0579 g.) was allowed to stand for three days at room temperature in a 500-ml. bulb; its infrared spectrum was unchanged. Half the sample was distilled slowly from a trap at −116°. Vapor pressure measurements on the two portions at −64.4° were 62.9 and 63.2 mm. (calcd., 62.8 mm.); 0.0578 g. of the SiH_3OCH_3 was recovered.

(D) SiH_3OCH_3 and HgI_2.—SiH_3OCH_3 (0.0521 g.) and "Analyzed Reagent" grade HgI_2 (0.1782 g.) were allowed to stand in a 500-ml. vessel for 22 hr. at room temperature. No liquid phase was present. There was recovered SiH_3OCH_3 (0.0510 g., mol. wt. found, 62.0, calcd., 62.2) and $SiH_2(OCH_3)_2$ (0.003 g., identified by infrared spectrum[3]).

(E) SiH_3OCH_3 and Cu Metal.—SiH_3OCH_3 (0.930 mmole) and electrolytic dust grade Cu metal[3] (0.7 g.) were allowed to stand in a 500-ml. container for four days at room temperature after which time H_2 (0.208 mmole) had been formed. The Cu metal darkened considerably during this period. An infrared spectrum of the remainder of the material showed it to be pure SiH_3OCH_3.

(F) SiH_3OCH_3 and I_2.—SiH_3OCH_3 (0.0717 g.) and reagent grade I_2 (0.1215 g.) were held in a 250-ml. flask for 10 minutes at room temperature. At the end of this time all the iodine had been consumed and a colorless liquid remained. No hydrogen was evolved. On removing the volatile materials from the reaction vessel a solid glassy material remained. The volatile materials could not be completely separated into pure constituents although one fraction appeared to consist chiefly of SiH_3I (0.1138 g., mol. wt. found 134, calcd., 158; vapor pressure at 0°, found, 123.7 mm., literature value[7] 123.9 mm.). Its infrared spectrum indicated the presence of methoxysilanes.[3] A second, less volatile fraction (0.0203 g., mol. wt. 85 to 90) partly changed to a non-volatile white solid each time it was distilled in the vacuum system.

(G) SiH_3OCH_3 and BF_3. (i).—Equimolar quantities of SiH_3OCH_3 (1.268 mmoles) and BF_3 (1.262 mmoles) were combined at −196° in a 93-ml. glass vessel connected to a mercury manometer. On holding the reaction vessel at −96° for 75 minutes the pressure slowly increased to 22 cm. On cooling to −196° the pressure returned to zero and on raising the temperature to −96° the pressure increased to 22 cm. in 2–3 minutes. After an additional 1 hr. at −96° the pressure had risen to 23 cm. As the temperature was raised slowly to room temperature over a period of 4 hr. the pressure gradually increased and continued to increase at room temperature during an additional ten minutes. No H_2 was formed. Fractionation of the products yielded a mixture of SiH_3F and BF_3 (1.459 mmoles, mol. wt. found, 52.1, calcd. for SiH_3F, 50.08, calcd. for BF_3, 67.82; confirmed by infrared spectrum[15]) containing approximately 1.29 mmoles of SiH_3F and 0.17 mmole of BF_3. In addition there was obtained CH_3OBF_2 (0.765 mmole; mol. wt. found, 75.3, calcd., 79.85; melting point, found 41–42°, literature value[16] 41.5°) and $(CH_3O)_2BF$ (0.260 mmole, mol. wt. found, 91.3, calcd., 91.89).

The above results indicate that at −96° a non-reversible reaction was occurring, and as is shown in experiment (ii) below, SiH_3F was being produced (see equation 8). If it is assumed that CH_3OBF_2 partly disproportionates on formation into $(CH_3O)_2BF$ and BF_3,[17] then, from the quantity of $(CH_3O)_2BF$ isolated, it would appear that 0.520 mmole of CH_3OBF_2 had decomposed in this manner. Thus a total of 1.285 mmoles of CH_3OBF_2 was originally formed in the reaction. Equation 8 therefore represents the chief reaction which occurred.

(ii).—SiH_3OCH_3 (1.103 mmoles) and BF_3 (1.697 mmoles) were combined at −196° in the apparatus used in (i) above. The temperature was raised to −127.8° and held at this value for 45 minutes. The pressure then remained at 23.6 mm. for the next 1 hr. Materials which distilled from the reaction vessel at −127.8° during the next 0.5 hr. (0.699 mmole) were identified by infrared spectrum[15] and mol. wt., (found, 60.4, calcd., for SiH_3F, 50.08, BF_3, 67.82), as an approximately equimolar mixture of SiH_3F and BF_3. During an additional 1 hr. at −127.8° the pressure in the reaction vessel rapidly increased to 21.2 mm. and then remained constant at this value. Material volatile at this temperature (0.203 mmole) then was removed and was found by its infrared spectrum to be a mixture of SiH_3F[15] and BF_3. SiH_3OCH_3 and BF_3 therefore react at −127.8° to produce SiH_3F. It should be noted that if an adduct such as $SiH_3OCH_3 \cdot BF_3$ had been formed at −127.8°, then the excess BF_3 used (0.594 mmole), which is volatile at this temperature, should have been removed readily. However, only approximately 0.35 mmole of BF_3 was recovered during a 0.5 hr. distillation at −127.8°. This strongly suggests that reaction as indicated by equation 8 occurred rapidly at −127.8° and that the SiH_3F liberated immediately combined with the excess BF_3 to give the adduct $SiH_3F \cdot BF_3$. This seems highly likely, since in a previous investigation it was found that $(CH_3)_3SiF$ and BF_3 formed the non-volatile addition compound $(CH_3)_3SiF \cdot BF_3$ at −126°.[18]

(H) SiH_3OCH_3 and B_2H_6.—The apparatus and technique to be employed was first checked by measuring the vapor pressure of the known unstable addition compound $(CH_3)_2O \cdot BH_3$ at −78.2° (found, 16.2 mm., constant for 1.5 hr., literature value[19] 18 mm. at −78.5°). The experiment was carried out using an 80-ml. Pyrex tube attached to a mercury manometer.

(i).—SiH_3OCH_3 (0.417 mmole) and B_2H_6 (0.242 mmole) were combined at −196° and then raised to −78° and recooled to −196° on six occasions to aid mixing. After holding at −78.8° for 2 hr. a constant pressure of 74.4 mm. was observed. The sum of the vapor pressure of SiH_3OCH_3 and gas pressure of B_2H_6 at this temperature is 79.3 mm. The temperature then was reduced to −130.8° and within ten minutes the pressure dropped to a constant value of 35.7 mm. The sum of the vapor pressures of each substance at this temperature is 46.9 mm.[6] Volatile material was then distilled from the reaction vessel at −130.8° during 4–5 minutes. This consisted of B_2H_6 (0.243 mmole, mol. wt. found, 26.5, calcd., 27.69; infrared spectrum identical with that of pure material) and SiH_3OCH_3 (approx. 0.02 mmole, identified by infrared spectrum). This SiH_3OCH_3 was then combined with the material which did not distil from −130.8° and was found to be pure SiH_3OCH_3 (0.414 mmole, mol. wt. found, 62.3, calcd., 62.15; infrared spectrum identical with pure material).

(ii) Experiment (i) was repeated using SiH_3OCH_3 (0.382 mmole) and B_2H_6 (0.210 mmole) but the reaction vessel was alternately held at −78° and −23° every 15 minutes for a total of 90 minutes. After 75 minutes at −130.8°, volatiles were removed at −130.8° during 5–10 minutes as in the previous experiment. There was recovered B_2H_6 (0.207 mmole, mol. wt. found, 29.5, calcd., 27.69; its infrared spectrum showed the presence of small quantities of SiH_3OCH_3) and SiH_3OCH_3 (0.381 mmole, mol. wt. found, 62.3, calcd., 62.15, infrared spectrum identical with that of pure material.)

The low vapor pressures of the SiH_3OCH_3–B_2H_6 mixture at −78.8° and −130.8° in (i) probably are due to solubility effects or some form of extremely weak interaction. Similar observations in the $(SiH_3)_3N$–B_2H_6 system have been attributed to solubility effects.[20]

Infrared Spectrum of SiH_3OCH_3.—Infrared measurements were made with a Perkin-Elmer Model 21 double beam recording spectrophotometer, employing a sodium chloride optical system. Measurements were made on a gaseous sample at 7.5 mm. pressure in a 10 cm. cell having potassium bromide windows cemented with glyptal resin.

(13) R. Wintgen, *Ber.*, **52**, 724 (1919).

(14) R. C. Lord, D. W. Robinson and W. C. Schumb, *J. Am. Chem. Soc.*, **78**, 1327 (1956).

(15) C. Newman, J. K. O'Loane, S. R. Polo and M. K. Wilson, *J. Chem. Phys.*, **25**, 855 (1956).

(16) V. Gasselin, *Ann. chim. phys.*, **3**, 5 (1894).

(17) E. Wiberg and W. Sütterlin, *Z. anorg. Chem.*, **202**, 22 (1931).

(18) E. C. Evers, W. O. Freitag, W. A. Kriner, A. G. MacDiarmid and S. Sujishi, *J. Inorg. Nucl. Chem.*, **13**, 239 (1960).

(19) H. I. Schlesinger and A. B. Burg, *J. Am. Chem. Soc.*, **60**, 290 (1938).

(20) H. M. Manasevit, Doctoral Dissertation, Illinois Institute of Technology, Chicago, Ill., 1959.

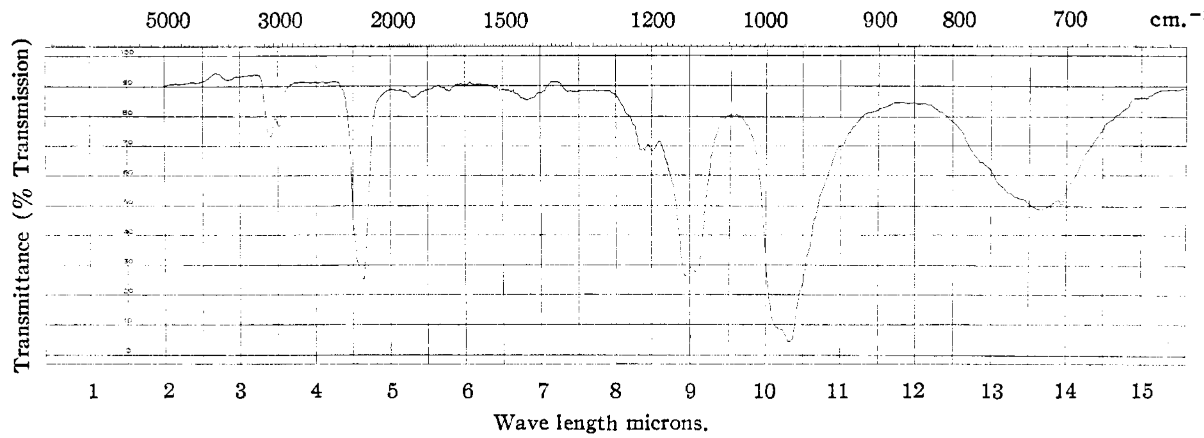

Fig. 1.—Infrared spectrum of silyl methyl ether.

Results and Discussion

Gaseous CH_3OH and gaseous SiH_4 were found to combine at room temperature only in the presence of copper metal catalyst, but if liquid methanol was present reaction occurred in the absence of copper catalyst. The products of the reaction were methoxysilanes and hydrogen.

TABLE II

INFRARED ABSORPTION MAXIMA OF SiH_3OCH_3

Cm.$^{-1}$	Designation
2930 weak, 2830 weak	C–H stretch
2150 medium	Si–H stretch
1890 very weak	Unidentified
1470 very weak	CH_3 deformation
1200 weak, 1178 weak	CH_3 rocking
1117 medium, 1102 medium	Si–O–C stretch
982 strong, 968 strong	SiH_3 deformation
732 medium	SiH_3 rocking

In an attempt to prepare SiH_3OCH_3, the interaction of silyl iodide, SiH_3I, and CH_3OH was investigated. Vigorous reaction commenced at approximately $-60°$ and continued up to and at room temperature. Non-volatile oils, mixtures of liquids which could not be separated, hydrogen and a trace of SiH_3OCH_3 were obtained. It is believed that the SiH_3OCH_3 formed initially in the reaction

$$SiH_3I + CH_3OH \longrightarrow SiH_3OCH_3 + HI \quad (1)$$

was almost entirely consumed in the series of reactions

$$HI + CH_3OH \longrightarrow CH_3I + H_2O \quad (2)$$

$$xHI + SiH_3OCH_3 \longrightarrow I_xSiH_{3-x}OCH_3 + xH_2 \quad (3)$$

$$I_xSiH_{3-x}OCH_3 + xH_2O \longrightarrow (HO)_xSiH_{3-x}OCH_3 + xHI \quad (4)$$

$$y(HO)_xSiH_{3-x}OCH_3 \longrightarrow [O_{x/2}SiH_{3-x}OCH_3]_y + (y/2)H_2O \quad (5)$$

Silanes of the type $(HO)_xSiH_{3-x}OCH_3$ would be expected to be volatile in a vacuum system and to condense spontaneously to polymeric siloxanes. The above reaction sequence is consistant with the fact that, in the methanolysis of $SiCl_4$, some complex polymers are formed[21] and in the ethanolysis of $HSiCl_3$ some $Si(OC_2H_5)_4$ is produced.[22,23] In the former case the formation of CH_3Cl and water is postulated and in the latter case conversion of a Si–H to a Si–Cl linkage by HCl is suggested. If methanolysis of the Si–H bonds in SiH_3OCH_3 also occurred, as is highly likely, the final products would be even more complex.

Attempts to prepare SiH_3OCH_3 by the reduction of Cl_3SiOCH_3 with $LiAlH_4$ or $LiAlH(t\text{-}OC_4H_9)_3$ under a variety of experimental conditions proved unsuccessful, as was also the reaction of SiH_3I with CH_3ONa.

The reaction of the addition compound formed from SiH_3I and $N(CH_3)_3$ with CH_3OH at $-78°$ yielded the new compound SiH_3OCH_3.

$$SiH_3I\ N(CH_3)_3 + CH_3OH \longrightarrow SiH_3OCH_3 + (CH_3)_3N\cdot HI \quad (6)$$

The pure material was thermally stable at room temperature but disproportionated very slowly in the presence of HgI_2. In the presence of copper metal, hydrogen was liberated slowly. It was hydrolyzed quantitatively by pure water. No

$$2SiH_3OCH_3 + H_2O \longrightarrow (SiH_3)_2O + 2CH_3OH \quad (7)$$

reaction occurred with methanol when both components were in the gaseous phase but in the presence of liquid CH_3OH, reaction took place to yield a mixture of methoxysilanes and hydrogen. The Si–O bond in SiH_3OCH_3 was cleaved by iodine at room temperature to yield SiH_3I. This reaction is therefore similar to those occurring between iodine and $(SiH_3)_2O$[24] and $(cyclo\text{-}C_6H_{11}SiH_2)_2O$[25] in which SiH_3I and cyclo-$C_6H_{11}SiH_2I$, respectively, are formed. Silyl methyl ether was not spontaneously inflammable in air, and it underwent no reaction with SiH_3I or with $COCl_2$.

Silyl methyl ether is of particular interest since its preparation completes the series of ethers $(SiH_3)_2O$, SiH_3OCH_3 and $(CH_3)_2O$ which is completely analogous to the corresponding series of amines $(SiH_3)_3N$, $(SiH_3)_2NCH_3$, $SiH_3N(CH_3)_2$ and $N(CH_3)_3$. The smaller electronegativity of silicon (1.8) as compared to carbon (2.5) would suggest that the

(21) W. R. Schwarz and K. G. Knauf, *Z. anorg. allgem. Chem.*, **276**, 176 (1954).

(22) M. E. Havill, I. Joffe and H. W. Post, *J. Org. Chem.*, **13**, 280 (1948).

(23) I. Joffe and H. W. Post, *ibid.*, **14**, 421 (1949).

(24) H. J. Emeléus, A. G. MacDiarmid and A. G. Maddock, *J. Inorg. Nucl. Chem.*, **1**, 194 (1955).

(25) H. H. Anderson, *J. Am. Chem. Soc.*, **81**, 4785 (1959).

silyl ethers and amines should be stronger Lewis bases than their methyl analogs and that the base strength should decrease as silyl groups are replaced by methyl groups. However, in the amine series, the reverse has been found to be the case, $(SiH_3)_3N$ being the weakest base and $(CH_3)_3N$ being the strongest in the series.[20,26] This has been attributed to d_π–p_π bonding involving the lone pair of electrons on the nitrogen and the 3d orbitals of the silicon[20,26–28] It also has been observed by using B_2H_6 as a reference acid that $(SiH_3)_2O$ is a much weaker Lewis base than $(CH_3)_2O$,[29] the latter, but not the former compound forming an adduct with B_2H_6 at $\sim -78°$.[19,29]

The results of the present investigation show that SiH_3OCH_3 is also a much weaker Lewis base than $(CH_3)_2O$ since it forms no addition compound with B_2H_6 at $-78°$. However, diborane is not a sufficiently strong acid to differentiate between the relative base strengths of SiH_3OCH_3 and $(SiH_3)_2O$. Boron trifluoride was of no use in measuring the base strength of SiH_3OCH_3 since SiH_3F was liberated at $-127.8°$ and on warming to room temperature the reaction represented by equation 8 occurred. This reaction is completely analogous

$$SiH_3OCH_3 + BF_3 \longrightarrow SiH_3F + CH_3OBF_2 \quad (8)$$

to that occurring between $(SiH_3)_2O$ and BF_3 under similar experimental conditions.[29,30]

The relative basicities of the ethers given above may be explained in two ways: (1) One SiH_3 group in SiH_3OCH_3 abstracts electrons from the oxygen atom by means of d_π–p_π back-coördination approximately as strongly as do two SiH_3 groups in $(SiH_3)_2O$. Until the Si–O–C bond angle is ascertained, the validity of this somewhat unlikely assumption cannot be determined. (2) The enthalpy for the process

$$B_2H_6 \longrightarrow 2BH_3 \quad (9)$$

is 28.4 kcal./mole.[31] If the interaction energy of a BH_3 group with both SiH_3OCH_3 and $(SiH_3)_2O$ were less than that required to dissociate B_2H_6, then neither ether would form an isolable addition compound with B_2H_6; hence, even if SiH_3OCH_3 were in reality a considerably stronger base than $(SiH_3)_2O$, it would appear to have the same base strength. That this is indeed quite likely is apparent from the fact that $(CH_3)_2O{\cdot}BH_3$ is an unstable compound[19,32] and therefore any slight decrease in electron-donor ability of the oxygen could readily decrease the ether–BH_3 interaction energy to a point where insufficient energy for the B_2H_6 dissociation step would be available.

Acknowledgment.—The authors wish to thank Dr. E. R. Nixon for helpful discussions on the interpretation of infrared spectral data.

(26) A. B. Burg and E. S. Kuljian, *J. Am. Chem. Soc.*, **72**, 3103 (1950).

(27) S. Sujishi and S. Witz, *ibid.*, **76**, 4631 (1954).

(28) A. G. MacDiarmid, *Quart. Rev.*, **10**, 208 (1956).

(29) (a) S. Sujishi, E. L. Gasner and A. D. Payton, Jr., Abstracts of papers presented at 133rd National Meeting of the American Chemical Society, San Francisco, 1958, p. 52-Q. (b) S. Sujishi, Ordnance Research Project No. TB 2-0001-(817), Contract No. DA-11-022 ORD-1264, Final Report, Aug., (1957).

(30) H. J. Emeléus and M. Onyszchuk, private communication, 1954.

(31) R. E. McCoy and S. H. Bauer, *J. Am. Chem. Soc.*, **78**, 206 (1956).

(32) F. G. A. Stone, *Chem. Revs.*, **58**, 101 (1958).

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY, SCHENECTADY, NEW YORK]

The Reaction of Active Nitrogen with Liquid Siloxane Heptamer, D_7

BY JOSEPH L. WEININGER

RECEIVED FEBRUARY 13, 1961

The reaction of active nitrogen with the liquid cyclic siloxane heptamer D_7, $[(CH_3)_2SiO]_7$, was studied quantitatively in a flow system at -24 to 136°. The chemical stability of the siloxane is shown by the fact that atomic nitrogen can be bubbled through the liquid to some extent, giving the characteristic afterglow downstream from the reaction vessel. The nitrogen atoms can, however, attack any bond of the compound D_7 in a reaction which leads mainly to the products HCN and NH_3. The comparable attack of active nitrogen on liquid *n*-hexadecane is more than ten times as vigorous, with 85% of the nitrogen atoms being converted to degradative N-containing gaseous compounds.

In an investigation of the reactions of active nitrogen with compounds in condensed states, the reaction with the cyclic siloxane heptamer D_7[1] was studied. Emphasis was placed on pure starting materials, an extended temperature range over which the reaction was observed, accurate determinations of the concentration of nitrogen atoms as well as reaction products and hence the determination of reaction yields. For comparison of the liquid siloxane with a liquid hydrocarbon the reaction of active nitrogen with *n*-hexadecane also was studied.

Experimental

The condenser-discharge system which was used in the study of the reaction of active nitrogen with polymers[2] was modified for the reaction with liquid siloxane by converting a trap into a reaction vessel. A special glass lock in an inner ground joint surface locked a showerhead in place. This arrangement allowed the exchange of showerheads with orifices of different size as well as their removal to convert the apparatus to solid-state or vapor-phase work. The glass system was not poisoned except insofar as the siloxane vapor may have formed a film on the walls. In the course of an experiment purified dry nitrogen was passed through the discharge tube at the rate of 5 to 8 m./sec. and also flowed through the liquid in the reaction vessel. The liquid level was maintained 5 to 10 mm. above the gas entry ports so that the residence time of the gas in the liquid was at least 0.01 second. In that interval the nitrogen atoms produced in the discharge reacted with the siloxane, others recombined with each other and an appreciable fraction passed through the liquid and gave the yellow afterglow in the system downstream from the reaction vessel. After the reaction the liquid as well as

(1) $[(CH_3)_2SiO]_7$, tetradecyl methyl cycloheptasiloxane, m.p. $-26°$, b.p. 154° (20 mm.).

(2) J. L. Weininger, *J. Phys. Chem.*, **65**, 941 (1961).