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

The Preparation of Methoxysilanes by the Interaction of Monosilane and Methanol[1]

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Monosilane and methanol have been found to react at room temperature to produce di-, tri- and tetramethoxymonosilanes. Infrared spectra and other physical properties of the above substances have been measured.

Introduction

Of the four possible methoxymonosilanes only $Si(OCH_3)_4$ and $HSi(OCH_3)_3$ previously have been reported. $Si(OCH_3)_4$, which has been completely characterized, can be prepared readily from $SiCl_4$ and CH_3OH.[2] Helferich and Hausen[3] reported the formation of $HSi(OCH_3)_3$ (b.p. 104–106°) by the interaction of $HSiCl_3$ and CH_3OH. Reuther[4] also prepared $HSi(OCH_3)_3$ by this reaction, but reported a boiling point of 84° for the material.

It has been stated previously that SiH_4 and CH_3OH do not react even in the presence of $LiOCH_3$.[5] However, since recent work[6] indicates that the reaction of an Si–H bond with an alcohol is catalyzed by copper metal the present investigation was performed in order to study the reaction of SiH_4 with CH_3OH both in the presence and absence of copper metal catalyst in order to attempt to prepare and thoroughly characterize the mono-, di- and trimethoxysilanes.

Experimental

Apparatus.—All work was carried out in a Pyrex glass vacuum system. Melting points were determined by means of a magnetic plunger apparatus.[7] 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 also standardized by the National Bureau of Standards.

Monosilane.—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.[8]

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[9] 29.7 mm.)

Interaction of Monosilane with Methanol.—The experimental results are summarized in Table I.

Experiment 1.—The reactants were combined in a 500-ml. bulb to which had been added 0.1061 g. of electrolytic dust grade Cu powder and a mixture of 0.8 g. of Cu wire and foil which previously had been washed with dilute HNO_3 and water and then dried. Reaction commenced immediately, at, or slightly below room temperature as evidenced by gas evolution from the small amount of liquid phase which was in contact with some of the copper. After removal of hydrogen and unreacted SiH_4, $HSi(OCH_3)_3$ was identified by molecular weight (found, 122.3, calcd., 122.2) and by analysis,[10] (C found, 29.24%, calcd., 29.49%; H found, 8.45%, calcd., 8.25%; Si found, 23.35%, calcd., 22.97%). The infrared spectrum of the $Si(OCH_3)_4$ and its molecular weight (found 134; mol. wt. $Si(OCH_3)_4$, 152; CH_3OH, 32.0) indicated that it was contaminated with a small quantity of unreacted CH_3OH from which it could not be separated.

Experiment 2.—During the course of the experiment the CH_3OH vapor was allowed to pass slowly into a 3-liter reaction vessel containing the SiH_4. The reaction vessel contained Cu similar to that described in experiment 1. At no time during the experiment could a liquid phase be observed in the reaction vessel. The products isolated after removal of hydrogen, unreacted SiH_4 and CH_3OH were identified as reported: $H_2Si(OCH_3)_2$ (mol. wt. found, 91.3, calcd. 92.2; C found, 25.94%, calcd., 26.07%; H found, 8.76%, calcd., 8.85%); $HSi(OCH_3)_3$ (mol. wt. found, 121.2, calcd., 122.2; C found, 29.65%, calcd., 29.49%; H found, 8.35%, calcd., 8.25%); $Si(OCH_3)_4$ (mol. wt. found, 148, calcd., 152; C, found, 31.77%, calcd., 31.56%; H found, 8.10%, calcd., 7.95%; vapor pressure at 0°, 2.5 mm.).

Experiment 3.—The reaction was carried out in a 500-ml. bulb. The products were separated from hydrogen and unreacted SiH_4 and were identified as $Si(OCH_3)_4$ (mol. wt. found, 152, calcd., 152; vapor pressure at 0°, found, 2.4 mm., pure material (expt. 2), 2.5 mm.) and a mixture which could not be separated. Molecular weight (mol. wt. 49.3), vapor pressure and infrared measurements indicated that this was probably a mixture of unreacted CH_3OH and $HSi(OCH_3)_3$.

Infrared Absorption Spectra.—These were made by means of a Perkin–Elmer model 21 double beam recording spectrophotometer with a sodium chloride prism. Spectra were made at approximately 20° in a 10 cm. cell having potassium bromide windows. The absorption maxima are listed in Table II.

Properties of Trimethoxy- and Dimethoxysilane.—Vapor pressure data on trimethoxysilane and dimethoxysilane are given in Table III.

The data for $HSi(OCH_3)_3$ are represented by the equation

$$\log P_{\mathrm{mm}} = \frac{-1919}{T} + 8.297$$

which gives an extrapolated boiling point of 81.1 ± 0.3°, a molar heat of vaporization of 8,782 cal./mole and a Trouton's constant of 24.8. The above boiling point is considered to be more reliable than that of 84° reported by Reuther[4] which was determined on material whose purity had not been confirmed by analysis.

A sample of $HSi(OCH_3)_3$, (vapor pressure at 0°, found 18.4 mm., pure $HSi(OCH_3)_3$, 18.7 mm. (Table III)), melted sharply at −114.8 ± 0.2°.

The data for $H_2Si(OCH_3)_2$ are represented by the equation

$$\log P_{\mathrm{mm}} = \frac{-1645}{T} + 8.243$$

which gives an extrapolated boiling point of 33.5 ± 0.2°, a molar heat of vaporization of 7,528 cal./mole and a Trouton's constant of 24.8. A sample of this material melted sharply at −99.8 ± 0.2°.

Discussion

Contrary to a previous report[5] it has been demonstrated that SiH_4 and CH_3OH react slowly at room temperature to produce methoxymonosilanes and

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[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) D. F. Peppard and W. C. Johnson, THIS JOURNAL, **68**, 70 (1946).

(3) B. Helferich and J. Hausen, *Ber.*, **57**, 795 (1924).

(4) H. Reuther, *Chem. Tech. Berlin*, **2**, 331 (1950).

(5) J. S. Peake and W. H. Nebergall, THIS JOURNAL, **74**, 1526 (1952).

(6) W. H. Nebergall and J. S. Peake, *ibid.*, **79**, 5604 (1957).

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

(8) J. W. Straley and H. H. Nielsen, *Phys. Rev.*, **62**, 151 (1942).

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

(10) All carbon, hydrogen and silicon analysis performed by Galbraith Laboratories, Knoxville, Tenn.

TABLE I

Expt.	Reaction time at room temp. (hr.)	Reactants, g. SiH_4	Reactants, g. CH_3OH	Materials recovered, g. SiH_4	Materials recovered, g. CH_3OH	Materials recovered, g. $Si(OCH_3)_4$	Materials recovered, g. $HSi(OCH_3)_3$	Materials recovered, g. $H_2Si(OCH_3)_2$
1	63	0.4838	0.4834	0.3167	Nil	0.0374	0.5080	Nil
2	90	1.004	.3260	.8559	0.0149	.0429	.2261	0.0397
3	140	0.4[a]	.4[a]	.3260	[b]	.2202	[b]	Nil

[a] Approximate values. [b] Identification not confirmed.

TABLE II

INFRARED ABSORPTION SPECTRA OF $Si(OCH_3)_4$, $HSi(OCH_3)_3$, AND $H_2Si(OCH_3)_2$

$Si(OCH_3)_4$,[a] cm.$^{-1}$	$HSi(OCH_3)_3$,[b] cm.$^{-1}$	$H_2Si(OCH_3)_2$,[c] cm.$^{-1}$	Designation
2980 medium	2955 weak	2890 very weak	C–H stretch
2875 medium	2870 weak	2860 very weak	
....	2210 weak	2180 weak	Si–H stretch
1472 very weak	1470 very weak	....	CH_3 deformation
1195 medium	1195 medium	1190 very weak	CH_3 rocking
1097 strong	1097 strong	1097 medium	Si–O–C stretch
....	....	933 strong	SiH_2 deformation
888 weak	880 strong		
848 strong	785 very weak	792 very weak	Unidentified
	703 very weak	691 weak	

[a] Pure gaseous $Si(OCH_3)_4$ at 5 mm. pressure—sample from experiment 2. [b] Pure gaseous $HSi(OCH_3)_3$ at 5 mm. pressure—sample from experiment 2. The spectrum was identical to that of the $HSi(OCH_3)_3$ prepared in experiment 1. [c] Pure gaseous $H_2Si(OCH_3)_2$ at 4 mm. pressure.

TABLE III

VAPOR PRESSURE OF $HSi(OCH_3)_3$

T, °C.	0.0	0.0	26.5	30.0	31.3	34.6	42.6	43.4
Pmm (expt.)	18.7	19.0[a]	79.3	92.7	100.8	116.6	164.6	173.1
Pmm (calcd.)	18.8	18.8	78.7	92.9	99.1	116	167	173

VAPOR PRESSURE OF $H_2Si(OCH_3)_2$

T, °C.	−54.2	−40.8	−31.8	−24.2	−14.4
Pmm (expt.)	5.4	14.5	27.0	43.4	77.6
Pmm (calcd.)	5.4	14.6	26.9	43.4	77.5

[a] Vapor pressure at end of experiment.

hydrogen. The rate of the reaction is increased considerably by copper metal, in the presence of which monosilane and methanol react in the vapor phase at room temperature to produce di-, tri- and tetramethoxysilanes. A large excess of monosilane and a slow addition of methanol to the reaction system favor the formation of less highly substituted silane derivatives but under the conditions of the experiments performed, no monomethoxysilane is formed.

It may therefore be concluded that the rate of reaction of an Si–H bond with methanol increases when the silicon atom has methoxy groups attached. The inductive effect of the attached methoxy group would tend to make the silicon more positive and hence increase the ease of nucleophilic attack of the silicon by an approaching methanol molecule. This effect apparently more than compensates for any decrease in reaction rate caused by steric effects due to the presence of relatively bulky methoxy groups.

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