considered to be a better value than −31.6° observed as the compound was distilled.

Between 40 and 760 mm., the deviation of the calculated vapor pressures from the experimentally observed pressures is less than 0.5%.

The latent heat of vaporization at the boiling point calculated from the above data using the Clapeyron equation is 5350 cal. per mole. This corresponds to a Trouton constant of 22.15.

Melting Point.—The melting point, −158.5°, was determined from a warming curve using apparatus built by Burger[9] following the design described by Sturtevant.[10] The latent heat of fusion was estimated to be approximately 1900 cal. per mole.

Infrared Spectrum.—The infrared absorption spectra of the substances in the vapor phase were measured over the range 2–15 μ by means of a double-beam Perkin–Elmer spectrometer, Model 21, employing a rocksalt prism and a 10 cm. Pyrex glass cell, with sodium chloride windows sealed to the cell with fluorocarbon wax. To eliminate reaction with the glass walls of the cell, a thin coating of aluminum oxide–phosphoric acid cement was applied to the inside of the cell and caused to set by slow heating with an infrared lamp. For the very reactive fluorine fluorosulfonate, the spectrum was recorded at pressures ranging from 2 to 10 mm.

The region from 15 to 25 μ was studied, using a cell with KBr windows, at a maximum pressure of 10 mm. and a CsBr prism. The pressure limitation was due to reaction of the compound with the windows, resulting in the liberation of free bromine and other reaction products. This interaction was much more pronounced when KI windows were used in an attempt to locate absorption bands in the 25–40 μ region. Brown stains appeared on the windows, presumably due to the formation of triiodide ions. These stains could be removed readily by pumping. After using KBr or KI cell windows for scanning the 15–40 μ regions, the spectrum in the 2–15 μ region was observed on the same sample to ensure that the compound had not completely reacted.

Fluorosulfonic Acid and Methyl Fluorosulfonate.—The acid was prepared by condensing sulfur trioxide and excess hydrogen fluoride in a nickel vessel, allowing it to stand overnight, evaporating off the excess hydrogen fluoride and distilling at atmospheric pressure, while excluding water vapor from the system. Methyl fluorosulfonate was prepared by passing dimethyl ether into fluorosulfonic acid and distilling under reduced pressure.[11]

Acknowledgment.—This work was performed under contract with the Atomic Energy Commission.

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[9] L. L. Burger and G. H. Cady, THIS JOURNAL, **73**, 4243 (1951).

[10] J. M. Sturtevant, Chapter X in A. Weissberger, "Physical Methods of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1945.

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[CONTRIBUTION NO. 691 FROM THE DEPARTMENT OF CHEMISTRY OF INDIANA UNIVERSITY]

The Preparation of Monobromosilane and Organic Silyl Derivatives

BY HERMAN E. OPITZ, JOHN S. PEAKE AND W. H. NEBERGALL

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A method is described for preparing mono- and dibromosilane in quantity. New organic silyl derivatives have been prepared from monobromosilane and their physical constants reported. The infrared spectra of these derivatives are also included and discussed.

Introduction

The chemistry of the methyl radical has received much study, but the analogous silyl radical (SiH$_3$–) has been given little attention. The first silyl compounds were prepared by Stock and Somieski[1] by halogenating silane with hydrogen halide gas in the presence of an aluminum halide catalyst. This type of reaction does not occur with carbon compounds but proceeds stepwise in the case of the silicon hydrides as shown by the equations

$$\mathrm{SiH_4 + HX \xrightarrow{AlX_3} SiH_3X + H_2}$$

$$\mathrm{SiH_3X + HX \xrightarrow{AlX_3} SiH_2X_2 + H_2,\ etc.}$$

Some silyl derivatives have been prepared using vacuum line techniques by treating monohalogenated silanes with amines,[2] zinc alkyls,[10] silver cyanide,[3] phosphorus and sulfur.[4] Using these techniques, Burg and Kuljian[5] synthesized silyl-aminoboron compounds, and Van Artsdalen and Gavis[6] tried unsuccessfully to prepare the silyl Grignard compound by monobromosilane reacting with magnesium. A number of organosilanes also have been made by reduction of the corresponding trihalosilanes with lithium aluminum hydride.[7]

The initial purpose of this work was to prepare a monohalogenated silane in sufficient quantity to make possible further study of the silyl radical. Previously, the extent of such experimentation has been limited by the necessity of using vacuum line techniques or by the availability of the proper trihalosilanes. Monohalogenated silanes can theoretically be prepared by selective reduction of the corresponding tetrahalide, as indicated by Hurd.[8] We have attempted partial reduction of silicon tetrachloride (always present in excess) using lithium aluminum hydride and calcium hydride as reducing agents, with incompatible solvents for the hydride and the silicon tetrachloride, and using low temperatures. All attempts failed to give any monochlorosilane. This is in agreement with the re-

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[1] (a) A. Stock and C. Somieski, *Ber.*, **50**, 1739 (1917); (b) **51**, 989 (1918); (c) **52**, 695 (1919).

[2] (a) A. Stock and C. Somieski, *ibid.*, **54**, 740 (1921); (b) H. J. Emeleus and N. Miller, *J. Chem. Soc.*, 819 (1939).

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[4] B. J. Aylett, H. J. Emeleus and A. G. Maddock, *Research*, **6**, 30s (1953).

[5] A. B. Burg and E. S. Kuljian, THIS JOURNAL, **72**, 3103 (1950).

[6] E. R. Van Artsdalen and J. Gavis, *ibid.*, **74**, 3196 (1952).

[7] (a) A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach and H. I. Schlesinger, *ibid.*, **69**, 2692 (1947); (b) D. G. White and E. G. Rochow, *ibid.*, **76**, 3897 (1954); (c) W. D. English, A. Taurins and R. V. V. Nicholls, *Can. J. Chem.*, **30**, 646 (1952); (d) A. D. Petrov and V. A. Ponomarenko, *Doklady Akad. Nauk. S.S.S.R.*, **90**, 387 (1953); *C. A.*, **48**, 5080h (1954); (e) S. Kaye and S. Tannenbaum, *J. Org. Chem.*, **18**, 1750 (1953).

[8] D. T. Hurd, "An Introduction to the Chemistry of the Hydrides," John Wiley and Sons, Inc., New York, N. Y., 1952, p. 64.

TABLE I

ANALYSES AND PHYSICAL PROPERTIES OF ALKYLSILANES

Silanes	Analyses, % Carbon Calcd.	Analyses, % Carbon Found	Analyses, % Hydrogen Calcd.	Analyses, % Hydrogen Found	B.p. °C.	B.p. Mm.	Yield, %	$n^{25}D$	Density at 25°
Propyl-					21.3	760	62		
Butyl-	54.47	54.38	13.72	14.10	55.5	739.5	53	1.3895	0.6699
t-Butyl-					34.4	760	Low		
Amyl-	58.75	58.59	13.81	13.46	86.8	740.5	58	1.4012	0.7043
Cyclohexyl-	63.08	62.89	12.36	12.09	119.5	739.5	38	1.4464	0.7958
p-Methoxyphenyl-	60.83	61.35	7.29	7.32	180	739.5	Low	1.5251	0.9797
					75–76	21			
1-Naphthyl-	75.90	75.42	6.37	6.86	49.5	0.025	25	1.6030	1.0054
Diamyl-	69.68	69.55	14.03	13.85	204.5	739.5	87	1.4311	0.7610

ported inability to partially reduce organotrichlorosilanes.[9] The partial halogenation of silane, however, can be adapted to give monohalogenated silanes. By use of a catalytic furnace we have been able to produce monobromosilane in a continuous manner and in any desired quantity. Using this monobromosilane as a starting material some organosilanes have been prepared and characterized. Further study of the reactions and derivatives of mono- and dibromosilane is in progress.

Experimental

Part I. Preparation of Monobromosilane.—Silane was prepared by the method of Peake, Nebergall and Chen[10] but with the glass apparatus being replaced by an all-metal system. Pressures of 150 p.s.i. or more were generated to give the unit adequate capacity, and the silane was bled off as needed. Streams of SiH_4 and HBr were caused to react in the gas phase in the presence of an $AlBr_3$ catalyst at 80–100°. The catalyst was supported on asbestos fibers (dried at 600°) within a furnace which allowed reversal of the gas flow at intervals. The resulting SiH_3Br and SiH_2Br_2 were separated with an 11-plate column and collected in brass traps equipped with needle valves. The latter then served as storage cylinders.

Part II. Preparation of Organosilyl Derivatives.—The silyl compounds listed in Table I were prepared by bubbling monobromosilane through a di-*n*-butyl ether solution of the corresponding Grignard reagent. These particular compounds were chosen so that comparisons (especially with regard to infrared spectra) could be made with the disubstituted compounds prepared by West and Rochow.[11] The preparations were carried out under nitrogen in a 500-ml. three-necked flask equipped with a dropping funnel (for organohalide addition in the preliminary Grignard preparation), a flared delivery tube, a magnetic stirrer and a spiral condenser cooled with Dry Ice–methanol mixture. The latter prevented any escape of monobromosilane but allowed nitrogen and non-condensables to pass through to the exhaust. The monobromosilane was introduced through the flared delivery tube from the previously weighed storage cylinder which could be disconnected at intervals and weighed. When the desired amount of monobromosilane had been added, the reaction mixture was stirred for at least another hour, then poured onto a mixture of cracked ice and dilute hydrochloric acid. The ether layer was separated, washed until neutral to litmus and dried over Drierite. The silyl compound was separated from the ether by distillation.

It was found necessary to use di-*n*-butyl ether as the solvent in the preparation of the silyl derivatives, since it proved difficult (if not impossible) to separate some of the lower-boiling silanes from diethyl ether. A coördination effect was postulated between the Si of the silyl group and the O of the ether. This effect was studied with infrared measurements and with the vapor–liquid equilibrium data on the system diethyl ether–butylsilane (Table II). These studies showed no strong coördination effect or azeotrope formation.

TABLE II

VAPOR–LIQUID DATA ON SYSTEM DIETHYL ETHER–BUTYLSILANE

Mole fraction ether in vapor (*y*)	Mole fraction ether in liq. (*x*)	Equilibrium temp. (uncor.), °C.	Mole fraction ether in vapor (*y*)	Mole fraction ether in liq. (*x*)	Equilibrium temp. (uncor.), °C.
0.193	0.062	52.7	0.729	0.585	39.9
.355	.170	49.4	.804	.681	38.5
.460	.270	46.4	.834	.723	37.8
.566	.326	45.1	.878	.802	36.5
.625	.438	42.9	.935	.900	35.0
.656	.476	42.2			

All compounds listed in Table *I* were clear, colorless liquids, stable in air. We were unsuccessful in preparing either mono-2-naphthylsilane or di-2-naphthylsilane starting with mono- or dibromosilane, respectively. While *t*-butylsilane could be prepared in low yields from monobromosilane, it was not possible to synthesize di-*t*-butylsilane from dibromosilane.

Standard carbon and hydrogen analyses were carried out on the *p*-methoxyphenyl-, diamyl-, 1-naphthyl- and cyclohexylsilanes. The butyl- and amyl-silanes exploded when employing the usual combustion furnace techniques, so the analysis procedure had to be modified to obtain the results given in Table I for these compounds. Into a weighed ampule were introduced about 15 mg. of the silane which was frozen in liquid nitrogen and the ampule sealed and weighed. After once more freezing the silane and breaking off the tip of the ampule, the ampule was quickly inserted into the end of the combustion tube. By dropping liquid nitrogen on glass wool surrounding the end of the combustion tube, the sample was allowed to warm up very slowly. Using this technique and air in place of oxygen for the combustion, the sample could be burned without explosion.

Molar refractions were also calculated according to the method of Warrick[12] with an average absolute error of 0.53%. Vapor pressure measurements were made on propyl- and *t*-butylsilanes and the constants calculated for the equation

$$\log P(\text{mm}). = -A/T + B$$

	A	*B*
Propylsilane	−1363	7.510
t-Butylsilane	−1136	6.575

Part III. Infrared Studies.—In addition to the spectra of monobromosilane and dibromosilane reported elsewhere,[13] spectra[14] of *n*-propyl-, *n*-butyl-, *t*-butyl-, cyclohexyl-, 1-

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[9] (a) M. C. Harvey, W. H. Nebergall and J. S. Peake, THIS JOURNAL, **76**, 4555 (1954); (b) P. A. McCusker and E. L. Reilly, *ibid.*, **75**, 1583 (1953).

[10] J. S. Peake, W. H. Nebergall and Yun-Ti Chen, *ibid.*, **74**, 1526 (1952).

[11] R. West and E. G. Rochow, *J. Org. Chem.*, **18**, 303 (1953).

[12] E. L. Warrick, THIS JOURNAL, **68**, 2455 (1946).

[13] D. W. Mayo, H. E. Opitz and J. S. Peake, *J. Chem. Phys.*, **23**, 1344 (1955).

[14] These spectra have been deposited as Document number 4693 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm. microfilm, in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

naphthyl-, and di-*n*-amyl-silane as well as *p*-methoxyphenylsilane were recorded using a Perkin–Elmer Model 21 infrared spectrometer. Where possible, the compounds were examined in the gas phase (using a 10 cm. cell equipped with potassium bromide windows); otherwise the spectra were obtained from a capillary film of the pure liquid.

Discussion of the Spectra

The infrared spectra of the monosubstituted silanes exhibit a band of striking intensity in the 938 to 917 cm.$^{-1}$ region. This exceptional intensity is attributed to the fact that two deformation vibrations of the SiH_3– group occur at very nearly the same frequency.

Absorption in this region also has been reported by West and Rochow[11] for disubstituted silanes; however, no frequency assignments for this region were made in that paper. The spectrum of diamylsilane, a previously unreported compound, is included for comparison.[14] On the basis of our work we can now say that the strong band occurring in the 938 to 917 cm.$^{-1}$ region which is common to disubstituted silanes arises from the deformation mode of the $SiH_2=$ group. The agreement in frequency and intensity of this band with the $SiH_2=$ bending frequency occurring at 953 cm.$^{-1}$ in dichlorosilane[15] and at 940 cm.$^{-1}$ dibromosilane[16] leaves little doubt that the absorption in the 925 cm.$^{-1}$ region for the disubstituted silanes results from the $SiH_2=$ deformation mode. Also it should be noted that absorption in this region remains essentially constant throughout the spectra of 38 compounds[17] containing two or three hydrogen atoms attached to the silicon.

The spectral analogy to halosilanes is further supported by the observation that the SiH_2R_2 compounds exhibit one or two strong bands from 862 to 826 cm.$^{-1}$.[11] This absorption is due in part to silicon–carbon stretching but undoubtedly also arises from a rocking mode of the $SiH_2=$ group. Further, as might be expected from the monohalosilanes, the silyl compounds absorb weakly or not at all in this region.

Regarding other parts of the spectra we also have observed the symmetrical deformation frequency of the methylene groups alpha to a silicon atom as reported by Kaye and Tannenbaum[7e] in the 1200 to 1182 cm.$^{-1}$ region. Also on the basis of our method of preparation we feel that any absorption in the 1130 cm.$^{-1}$ region is not due to ether.

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[15] J. A. Hawkins and M. K. Wilson, *J. Chem. Phys.*, **21**, 360 (1953).

[16] J. A. Hawkins, S. R. Polo and M. K. Wilson, *ibid.*, **21**, 1122 (1953).

[17] Though not reported in this paper, most of these spectra were recorded in connection with this work. Spectra in the literature include references 8e, 10a and 12.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

A Raman Spectroscopic Study of Complexes Involving Dimethyl Ether and HCl, DCl HBr[1,2]

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A detailed investigation of the dimethyl ether–HCl system has been carried out by Raman spectroscopy between −100 and 0° and over the concentration range from 0 to approximately 87 mole per cent. HCl. The results give excellent evidence for the existence of three intermolecular complexes, each having an optimum temperature and concentration range of stability in the liquid. The results of similar investigations of the dimethyl ether–DCl and dimethyl ether–HBr systems are interpreted in support of the designation of the simple 1:1 complex as a hydrogen bonded structure and of the other higher complexes as oxonium compounds. The stoichiometry and possible configuration of the higher complexes are discussed briefly.

Introduction

Considerable interest, theoretical as well as experimental, has been shown recently in the study of complex formation between electron donor molecules and electron acceptors. One such system is that of dimethyl ether and HCl which is often cited as an example of a mixture in which a strong Lewis acid–base interaction occurs between the components. This system is representative of a very large number of quite similar systems involving higher ethers, alcohols and other oxygen containing compounds interacting with strong mineral acids. However, despite the relative simplicity of the molecules involved and the absence of complications introduced by association in the pure components, previous spectroscopic investigations have been limited both in number and in scope and detailed knowledge of the species present in the liquid is quite incomplete. Since information on the nature of complexes present in such mixtures not only is vital to a better understanding of many important organic reaction mechanisms but also is important in the study of complex formation *per se*, suitable experimental methods have been developed and a detailed Raman spectroscopic study has been carried out to supply this information.

No previous infrared examination of the dimethyl ether–HCl system appears to have been made. However, Gordy and Martin[3,4] and Szobel[5] have in-

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[1] Based on a dissertation submitted by Guido L. Vidale in partial fulfillment of the requirements of the Ph.D. degree to the Horace H. Rackham School of Graduate Studies, University of Michigan, September, 1954.

[2] Presented at the Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, June 1954.

[3] W. Gordy and P. C. Martin, *J. Chem. Phys.*, **7**, 99 (1939).

[4] W. Gordy and P. C. Martin, *ibid.*, **9**, 215 (1941).

[5] L. Szobel, *Compt. rend.*, **218**, 347, 834 (1944).