metal–ammonia solutions, we propose the mechanism[21–23]

$$e^- + GeH_4 \longrightarrow GeH_3^- + H \tag{4}$$

$$H + e^- \longrightarrow H^- \tag{5}$$

$$H^- + NH_3 \longrightarrow NH_2^- + H_2 \tag{6}$$

$$2H \longrightarrow H_2 \tag{7}$$

$$GeH_4 + NH_2^- \longrightarrow GeH_3^- + NH_3 \tag{3}$$

$$GeH_4 + NH_2^- \longrightarrow GeH_3NH_2 + H^- \tag{8}$$

The formation of hydride ion as an intermediate seems plausible because when potassium silyl ($KSiH_3$) is prepared from the reaction of silane with potassium in 1,2-dimethoxyethane, potassium hydride is formed as a by-product.[21,22] We assume that subsequent ammonolysis of GeH_3NH_2 to $Ge(NH_2)_4$ or $Ge(NH)_2$ proceeds rapidly.[24,25] In this mechanism,[5] one would expect the rate of formation of amide ion (which catalyzes the $Ge(NH)_2$-producing reaction), relative to the rate of reaction 4, to increase with increasing metal concentration. The mechanism thus explains the excess hydrogen formed at high metal concentrations. The same mechanism is applicable to the analogous reactions of silane and stannane if we assume that, on going from SiH_4 to GeH_4 to SnH_4, the protonic acidity increases and the susceptibility to displacement of hydride ion by amide ion decreases.

Acknowledgments.—This work was sponsored by the U. S. Atomic Energy Commission and the National Science Foundation.

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[21] The following reaction[22] is another conceivable source of hydride ion: $GeH_4 + 2e^- \rightarrow GeH_3^- + H^-$. However, we omit this reaction because its inclusion would not change the qualitative conclusions and because a dinegative activated complex seems implausible to us. In either case, reaction 5 (or a combination of reactions 5 and 6) should be included because the corresponding aqueous reaction proceeds at a diffusion-controlled rate.[23]

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[24] The rate-determining step in the formation of $Ge(NH_2)_4$ is probably reaction 8, because the germanium would become more positive as the number of amino groups increases (inductive effect) and, consequently, more susceptible to nucleophilic attack by amide.[25] From the data in Table II, we calculate $k_8/k_3 = 0.18$.

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The Preparation and Properties of Germyl Methyl Ether and Germylmethyl Methyl Ether[1]

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Received June 2, 1967

The synthesis, characterization, and some properties of GeH_3OCH_3 and $GeH_3CH_2OCH_3$ are described. The donor properties of the compounds have been investigated by an infrared hydrogen-bonding study. Germyl methyl ether acts as a stronger Lewis base than $(CH_3)_2O$, and $GeH_3CH_2OCH_3$ acts as a weaker Lewis base than $CH_3CH_2OCH_3$, with methanol as reference acid. The results are compared with data for the corresponding silicon compounds and discussed in terms of electronegativity and π-bonding considerations.

Interest in the structure and bonding of hydrogen compounds of the lower group IV elements continues to be strong. Most of the work reported thus far has been concerned with the silicon hydrides and their derivatives.[2–4] Much less work has been reported for the corresponding derivatives of germanium. Synthesis and stability problems have greatly hindered the study of these latter hydride derivatives and only recently have many of these difficulties been overcome.

Central to an evaluation of the factors which influence the physical properties and bonding in the germanium hydride derivatives is the availability of compounds on which specific physical measurements can be performed. In a previous paper,[5] the preparation of GeH_3OCH_3 was reported as part of a study of the mercury-sensitized photolysis of carbon, silicon, and germanium hydride systems. Only a small amount of material was isolated by using this technique, but contrary to the prediction of earlier workers,[6] the compound was found to be reasonably stable in the vacuum line. This has prompted us to investigate a more conventional preparation of GeH_3OCH_3 and to determine some of its physical and chemical properties. In addition, the new compound germylmethyl methyl ether, $GeH_3CH_2OCH_3$, has been synthesized and studied. The Lewis base strengths of these compounds relative to their silicon and carbon counterparts have been measured to study the basicity of the oxygen atom in the Ge–O–C linkage and the inductive effect of the GeH_3

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[1] Presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

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[3] F. G. A. Stone, "Hydrogen Compounds of the Group IV Elements," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962.

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group relative to the CH_3 and SiH_3 groups in simple ether systems.

Experimental Section

A conventional Pyrex-glass high-vacuum system was used to manipulate all volatile substances. Stopcocks and ground-glass joints were lubricated with Apiezon N grease. Standard vacuum-line techniques were employed throughout.[7] Mass spectra were obtained by means of a CEC Model 21-103C or an AEI Model MS-9 mass spectrometer. All fragment patterns were measured by using 70-v electrons. Infrared absorption spectra (excluding spectra for the hydrogen-bonding studies) were recorded with a Perkin-Elmer 137B Infracord spectrophotometer on the gaseous phase at room temperature with the sample confined in a 10-cm cell fitted with KBr windows. Proton nuclear magnetic resonance spectra were recorded on a Varian Associates A-60 spectrometer at room temperature. The spectra were individually calibrated by the standard audiofrequency side-band interpolation technique. A magnetic plunger apparatus was used for the determination of melting points.[8] Gas chromatographic separations were performed on a slightly modified Varian–Aerograph Model A-90-P3 gas chromatograph equipped with a 20 ft × $^3/_8$ in. aluminum column packed with 25% Carbowax 400 on Chromosorb W support (60–80 mesh). A special inlet and collection system was constructed which allowed the samples to be chromatographed without exposure to air. The unit was operated at a flow rate of 100 ml of He min^{-1} and at a column temperature of 30°. Infrared data on the hydrogen-bonding systems were obtained on a Beckman IR 9 spectrophotometer. Techniques employed for these measurements were identical with those previously reported.[9] Although phenol is generally employed as the reference acid in most hydrogen-bonding studies, it was not used in the present study since it appeared to react chemically with certain of the ethers. No problems were encountered when methanol was employed as reference acid. Spectra of the methanol–ether–carbon tetrachloride solutions (in an 0.08-mm cell) were taken after each base strength measurement to confirm the purity of the ether under study.

Materials.—GeH_4 (mol wt: found, 76.6; calcd, 76.6; confirmed by its infrared[10] and mass spectra) was prepared from GeO_2 and $NaBH_4$.[11,12] Commercial $ClCH_2OCH_3$ (Eastman) was purified in the vacuum line (passed through a trap cooled to −46°; stopped in a trap cooled to −64°). The purity was confirmed by infrared spectrum[13] and gas chromatography (retention time 32.5 min). Analytical grade methanol was dried over BaO and distilled in the vacuum line. GeH_3Cl (vapor pressure at 0° 225.7 mm, lit.[14] 234.5 mm, confirmed by infrared spectrum[15]) was synthesized from GeH_4 and HCl.[14] $(GeH_3)_2S$ (purity checked by infrared spectrum[16]) was synthesized from GeH_3I and red HgS.[16,17] $NaGeH_3$ was obtained by the reaction of GeH_4 with sodium in liquid ammonia.[18,19]

Preparation of GeH_3OCH_3.—An attempt was made to prepare GeH_3OCH_3 by the interaction of CH_3OH with $(GeH_3)_2S$. A similar method has been used to prepare SiH_3OCH_3.[20] $(GeH_3)_2S$ (0.15 mmole) and CH_3OH (0.33 mmole) were combined and kept at 0° for 48 hr. An infrared spectrum of the material after this time period was identical with that of a CH_3OH–$(GeH_3)_2S$ mixture.

GeH_3OCH_3 was successfully prepared by the reaction of GeH_3Cl with $NaOCH_3$ in diglyme. Since previous workers failed to isolate GeH_3OCH_3 by a similar method,[21] a typical preparation is described below.

$NaOCH_3$ was prepared by allowing sodium (0.090 g, 3.9 mg-atoms) to react with CH_3OH (approximately 3 ml) in an evacuated 50-ml two-neck flask (Claissen type). One neck of the flask led to the vacuum line, while the other was fitted with a 100-ml pressure-equalizing addition funnel which contained approximately 30 ml of diglyme. When the Na–CH_3OH reaction was complete, both H_2 and the excess CH_3OH were pumped out of the vessel. The diglyme was added through the addition funnel and GeH_3Cl (0.433 g, 3.90 mmoles) was then condensed in. The contents of the flask were held at −78° for 1.5 hr. No noncondensable material (at −196°) was produced in the reaction. The products were allowed to distil out of the reaction flask (kept at −78°) and through successive traps held at −64, −96, and −196°. Small amounts of CH_3OH (identified by infrared spectrum[22]) and diglyme collected in the −64° trap while small amounts of GeH_4 and Ge_2H_6 (identified by infrared spectra[10,23]) collected in the −196° trap. The crude GeH_3OCH_3 (approximately 0.4 g) which collected in the −96° trap was further purified by similar distillations to yield the pure compound (0.236 g, 2.15 mmoles, 55%, mol wt: found, 105.8; calcd, 106.6; confirmed by infrared spectrum[5]). The pure sample had a melting point of −44.5 ± 0.5°.

All attempts to purify GeH_3OCH_3 by gas chromatography met with failure. Only CH_3OH was eluted from the column. Various stationary phases, supports, and column materials were tried without success.

Vapor Pressure of GeH_3OCH_3.—The vapor pressures of a freshly purified sample of GeH_3OCH_3 at a number of temperatures were measured by a mercury manometer. The inner surface of the manometer had been pretreated with a separate sample of GeH_3OCH_3 for several hours. Data are recorded in Table I. Vapor pressures in the range −45.8 to −23.2° are given by the equation

$$\log P_{\mathrm{mm}} = -\frac{1823.0}{t + 273.16} + 9.0090$$

which gives an extrapolated boiling point of 24.3°, a molar heat of vaporization of 8.340 kcal, and a Trouton's constant of 28.0 cal deg^{-1} $mole^{-1}$.

Table I

Vapor Pressures of GeH_3OCH_3[a,d]

Temp, °C	P, mm		Temp, °C	P, mm	
	Obsd	Calcd		Obsd	Calcd
−45.8	9.4	9.8	−31.0	30.4	30.3
−45.8[c]	10.0	9.8	−31.0[b,c]	30.9	30.3
−41.2[b,c]	14.3	14.1	−26.8[b]	39.1	40.7
−40.8	14.3	14.6	−24.4[c]	50.1	47.9
−36.0[c]	22.0	21.0	−23.2	49.6	52.0
−35.8	21.4	21.3	−196[c]	0.0	. . .

[a] Duration of experiment 5.5 hr. [b] Pressure observed on decreasing the temperature. [c] Results of a separate study on a different sample. [d] The infrared spectrum of the sample at the conclusion of each experiment indicated that some decomposition had occurred, since a trace of CH_3OH was present. This was not present at the beginning of the experiment. Also, a trace of yellow deposit was observed in the finger tube.

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Thermal Stability of GeH_3OCH_3.—A sample of pure GeH_3OCH_3 (0.110 g) partly in the liquid phase and partly in the vapor phase was held at 0° for 17.5 hr in a 10-ml all-glass tube. No noncondensable material (at −196°) was observed at the conclusion of the experiment. An infrared spectrum of the volatile material (0.095 g) clearly indicated that the bulk of the material was unchanged GeH_3OCH_3, but that significant amounts of CH_3OH, GeH_4, and possibly $(GeH_3)_2O$ were also present.[10,16,22] The latter material was tentatively identified by the strong doublet absorption centered at 790 cm^{-1}, observed in $(GeH_3)_2O$ but not in GeH_3OCH_3.[5,16] All attempts to separate quantitatively the CH_3OH, GeH_3OCH_3, and $(GeH_3)_2O$ were unsuccessful.

Reaction of GeH_3OCH_3 with H_2O.—GeH_3OCH_3 (0.044 g) and distilled H_2O (0.203 g) were allowed to react in a 500-ml all-glass vessel for 1 hr at room temperature. No noncondensable material (at −196°) was formed. An infrared spectrum of the products (separated from the excess water by distillation through a −64° trap) indicated the presence of CH_3OH, $(GeH_3)_2O$, GeH_3OCH_3, and a trace amount of GeH_4.[5,10,16,22] The bulk of the material appeared to be CH_3OH and $(GeH_3)_2O$. Despite various attempts, the CH_3OH, $(GeH_3)_2O$, and GeH_3OCH_3 could not be quantitatively separated by any type of fractionation. Similar results were obtained when the products were allowed to react with a second sample of H_2O. A mass spectrum of the products confirmed the presence of $(GeH_3)_2O$ and GeH_3OCH_3 in the sample.

Synthesis of $GeH_3CH_2OCH_3$.—$ClCH_2OCH_3$ (0.805 g, 10.0 mmoles) and freshly prepared solid $NaGeH_3$ (approximately 10 mmoles, small amount of NH_3 present) were allowed to react at temperatures between −78 and 0° for 1 hr in a 150-ml vessel. The $GeH_3CH_2OCH_3$ formed in the reaction was partially purified in the vacuum line by distillation through a −64° trap and condensation in a −96° trap. The crude material isolated in the −96° trap (0.258 g) was contaminated with $(CH_3O)_2CH_2$ (identified by mass spectrum; infrared[24] and nmr spectra were identical with spectra obtained for an authentic sample of $(CH_3O)_2CH_2$). These two materials could not be separated in the vacuum line. The $GeH_3CH_2OCH_3$ was purified by gas chromatography (yield 0.134 g, 1.1 mmoles, 11.1%; mol wt: found, 119.5; calcd, 120.6; retention time 25 min). The $(CH_3O)_2CH_2$ had a retention time of 32 min. A sample of purified $GeH_3CH_2OCH_3$ was analyzed.[25] *Anal.* Calcd for C_2H_8GeO: C, 19.90; H, 6.68; Ge, 60.19. Found: C, 20.19; H, 6.70; Ge, 59.98. $GeH_3CH_2OCH_3$ melts sharply at $-121.6 \pm 0.3°$.

Vapor Pressure and Thermal Stability of $GeH_3CH_2OCH_3$.—Vapor pressure–temperature data obtained for $GeH_3CH_2OCH_3$ in a pretreated mercury manometer system are listed in Table II. Vapor pressures in the range −64.0 to 0° are given by the equation

$$\log P_{\mathrm{mm}} = -\frac{1678.6}{t + 273.16} + 8.1674$$

which gives an extrapolated boiling point of 44.4°, a molar heat of vaporization of 7.679 kcal, and a Trouton's constant of 24.2 cal deg^{-1} $mole^{-1}$. The fact that the vapor pressure curve is reversible on decreasing the temperature indicates that little, if any, thermal decomposition of the compound had occurred during the experiment. No apparent decomposition of the $GeH_3CH_2OCH_3$ was ever observed after normal vacuum system manipulations.

Infrared, Nuclear Magnetic Resonance, and Mass Spectra of GeH_3OCH_3 and $GeH_3CH_2OCH_3$.—Infrared, nmr, and mass spectral data for GeH_3OCH_3 have been reported in a previous communication.[5] Weak infrared absorptions attributed to trace amounts of CH_3OH and $(GeH_3)_2O$ in the previous communication have been completely removed in the present work. Assignments for the absorptions and data for $GeH_3CH_2OCH_3$ are listed in Table III. The spectra of GeH_3OCH_3 (at pressures of 14.5 and 7.5 mm) and $GeH_3CH_2OCH_3$ (at pressures of 22 and 6 mm) are shown in Figure 1.

TABLE II

VAPOR PRESSURES OF $GeH_3CH_2OCH_3$[a,c]

Temp, °C	*P*, mm Obsd	*P*, mm Calcd	Temp, °C	*P*, mm Obsd	*P*, mm Calcd
−64.0	1.3	1.4	0.0	103.2	105.3
−49.3	4.7	4.7	−21.6[b]	31.7	31.3
−45.8	6.2	6.1	−31.4[b]	17.4	16.8
−36.0	12.6	12.3	−45.8[b]	6.3	6.1
−31.1	17.2	17.1	−64.0[b]	1.3	1.4
−24.6	26.1	26.0	−196.	0.0	...
−21.8	31.3	30.9			

[a] Duration of experiment, 12.0 hr. [b] Pressure observed on decreasing the temperature. [c] The infrared spectrum of the sample at the conclusion of the experiment was identical with that of the pure material.

TABLE III

INFRARED ABSORPTION MAXIMA OF GeH_3OCH_3 AND $GeH_3CH_2OCH_3$ (CM^{-1})

GeH_3-OCH_3	GeH_3-CH_2OCH_3[a]	Assignment	Ref
$\left.\begin{matrix}2950\\2890\end{matrix}\right\}$ d, w	3030 sh 2915 w 2865 sh	C–H str	*b*, *c*
2109 sh 2096 sh 2084 s	2092 s	Ge–H str	*c*, *d*
1458 vw	1445 vw	CH_3 sym def	*b*, *c*, *e*
$\left.\begin{matrix}1089\\1076\end{matrix}\right\}$ d, s	$\left.\begin{matrix}1119\\1107\end{matrix}\right\}$ d, s	Str vibration associated with the COC or COGe linkage	*b*, *c*, *d*
$\left.\begin{matrix}866\\855\end{matrix}\right\}$ d, vs	824 vs	GeH_3 sym def	*d*

[a] Unassigned absorptions for this compound are at 1269 vw; 1188, 1175 d, w; 932 w; and 707 w. [b] L. J. Bellamy. "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958. [c] R. J. Cross and F. Glockling, *J. Organometal. Chem.* (Amsterdam), **3,** 146 (1965). [d] Ref. 15. [e] M. P. Brown, R. Okawara, and E. G. Rochow, *Spectrochim. Acta,* **16,** 595 (1960).

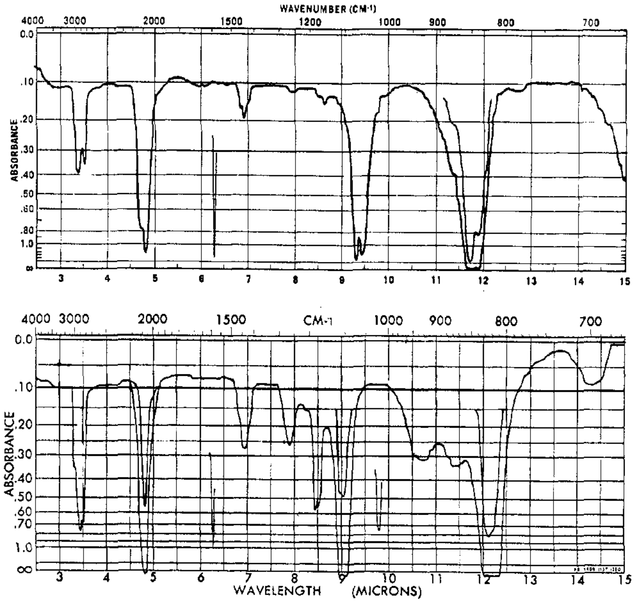

Figure 1.—Infrared absorption spectra of GeH_3OCH_3 (top) and $GeH_3CH_2OCH_3$ (bottom). Peak at 1601 cm^{-1} is a polystyrene calibration.

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The high-resolution proton nuclear magnetic resonance spectrum of $GeH_3CH_2OCH_3$ in cyclohexane or tetramethylsilane (20% solution by volume) consisted of two unresolved peaks at τ 6.42 ($\pm$0.01) and 6.77 ($\pm$0.01) in a ratio of 5:3. Apparently the CH_2 protons and the GeH_3 protons have identical chemical shifts in these solvents. When the spectrum was determined in benzene (20% solution by volume, a drop of TMS added), the GeH_3CH_2 chemical shift coincidence was removed and a complex A_3B_2 spectrum resulted for this part of the molecule. Excluding the absorption due to the CH_3 protons at τ 6.89 ($\pm$0.01), 20 assignable transition frequencies were obtained. The CH_2 and GeH_3 chemical shift values and the H–H′ coupling constant were obtained by fitting the observed spectrum with a calculated spectrum. Computation was performed with the iterative least-squares program LAOCN3[26] on an IBM 7040 computer. The following data were obtained: τ_{GeH_3} 6.39; τ_{CH_2} 6.54; $J_{H-H'} = 3.10$ cps. Line positions were reproducible to 0.10 cps. The observed and calculated spectra (obtained on a Cal-Comp plotter) for the GeH_3CH_2 portion of the molecule are shown in Figure 2.

The mass spectrum of $GeH_3CH_2OCH_3$ is in complete agreement with the proposed structure. All major fragments expected for this compound were observed and the germanium-containing fragments were in general accord with the known isotopic distribution of germanium. No major peaks were observed above mass number 124, the parent ion of $^{76}GeH_3CH_2OCH_3$. The most intense peak of the spectrum was at *m/e* 29 (HCO^+).

Results and Discussion

Synthesis and Properties of GeH_3OCH_3 and $GeH_3CH_2OCH_3$.—The synthesis of simple ether derivatives of the germanium hydrides has been quite a challenge to inorganic chemists.[6,16,27] Although $(GeH_3)_2O$ has now been prepared from HgO and $(GeH_3)_2S$,[16] the only reported synthesis of GeH_3OCH_3 has been by the mercury-sensitized photolysis of a CH_3OH–GeH_4 mixture.[5] This photolysis technique is quite tedious and is not suitable for producing large amounts of material. In the present investigation it has been determined that GeH_3OCH_3 can be conveniently prepared in good yield by the reaction of GeH_3Cl with $NaOCH_3$ in diglyme at −78°

$$GeH_3Cl + NaOCH_3 \xrightarrow[\text{diglyme}]{-78°} GeH_3OCH_3 + NaCl \qquad (1)$$

A solvent must be used in this reaction and the products must be allowed to distil out of the reaction flask at −78°.

Germyl methyl ether can be handled in routine manipulations about the vacuum line with little or no decomposition. However, over a period of several hours it decomposes slowly in the liquid phase, even at temperatures below −23°. Since CH_3OH is the only volatile product produced under these conditions, the decomposition is probably best represented by eq 2,

$$xGeH_3OCH_3 \longrightarrow (GeH_2)_x + xCH_3OH \qquad (2)$$

where $(GeH_2)_x$ represents the orange-yellow deposit observed. At higher temperatures and over a longer time period, the decomposition appears to be much more complex, with GeH_4 and $(GeH_3)_2O$ being produced in addition to CH_3OH and $(GeH_2)_x$. All attempts to purify GeH_3OCH_3 by using gas chromatographic techniques were unsuccessful. Since CH_3OH was the only product eluted from the column, the main decomposition reaction is presumed to be that represented by eq 2.

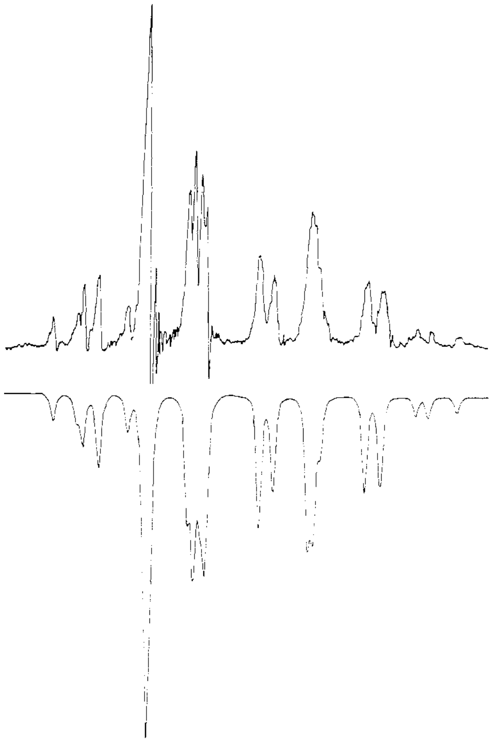

Figure 2.—High-resolution proton nmr spectrum of the GeH_3CH_2 portion of $GeH_3CH_2OCH_3$ at 60 Mc. The upper part is the observed spectrum; the lower part is the calculated spectrum. H_0 increases from left to right; the distance between the first and last absorptions represents approximately 20 cps.

The chief reaction of GeH_3OCH_3 with water is shown in eq 3. It parallels the reaction of SiH_3OCH_3 with

$$2GeH_3OCH_3 + H_2O \rightleftarrows 2CH_3OH + (GeH_3)_2O \qquad (3)$$

water, except that in the present case an equilibrium appears to exist. Silyl methyl ether is quantitatively hydrolyzed to CH_3OH and $(SiH_3)_2O$ under similar conditions.[28]

The new compound germylmethyl methyl ether, $GeH_3CH_2OCH_3$, has been prepared by the reaction of $ClCH_2OCH_3$ with solid $NaGeH_3$ (eq 4). It was identi-

$$ClCH_2OCH_3 + NaGeH_3 \longrightarrow GeH_3CH_2OCH_3 + NaCl \qquad (4)$$

fied by chemical, mass spectral, infrared, and proton nmr analyses. The compound is quite stable thermally and unlike GeH_3OCH_3 can be purified by using gas chromatographic techniques. It represents the first carbon-substituted oxygen derivative of CH_3GeH_3 to be reported in the literature and is the third member of the series of compounds which has the general formula $MH_3CH_2OCH_3$ (M = C, Si, Ge).

The coupling reaction used in the synthesis of $GeH_3CH_2OCH_3$ appears to be quite general, since various alkylgermanes can be prepared in the same manner.[3,19] The present system is somewhat more com-

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[26] This is a revised version of the LAOCOON II computer program: S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964).

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[28] B. Sternbach and A. G. MacDiarmid, *J. Am. Chem. Soc.*, **83**, 3384 (1961).

plex, however, since there is more than one possible cleavage site in $ClCH_2OCH_3$, *viz.*, at the C–Cl and the C–O bonds. Since $(CH_3O)_2CH_2$ was formed in the present reaction in addition to $GeH_3CH_2OCH_3$, it appears that both the C–Cl bond and the $ClCH_2$–O bond are cleaved to some extent. A reaction sequence which would account for $(CH_3O)_2CH_2$ is

$$ClCH_2OCH_3 + NaGeH_3 \longrightarrow ClCH_2GeH_3 + NaOCH_3 \quad (5)$$

$$NaOCH_3 + ClCH_2OCH_3 \longrightarrow NaCl + (CH_3O)_2CH_2 \quad (6)$$

This is only a *postulated* sequence and the fate of the $ClCH_2GeH_3$ has not been determined. It is tempting to postulate reaction 7 for part of its disappearance.

$$NaOCH_3 + ClCH_2GeH_3 \longrightarrow NaCl + GeH_3CH_2OCH_3 \quad (7)$$

It should be noted that this type of reaction has been successfully applied to the synthesis of GeH_3OCH_3. In the over-all reaction, decomposition reactions are most likely occurring to a considerable extent, since the yield of $GeH_3CH_2OCH_3$ was only 11.1%. The nature of these decomposition reactions has not been established.

Base Strength Studies of GeH_3OCH_3, $GeH_3CH_2OCH_3$, and Related Compounds.—Base strength measurements of ether derivatives of silicon have yielded a considerable amount of information about the nature of the silicon–oxygen bond.[29] Very little information is available for the analogous germanium–ether systems.[6] In the present work, the Lewis basicities of GeH_3OCH_3 and $GeH_3CH_2OCH_3$ relative to the basicities of $(CH_3)_2O$, SiH_3OCH_3, $CH_3CH_2OCH_3$, and $SiH_3CH_2OCH_3$ as proton acceptors in hydrogen-bond formation have been determined by means of an infrared hydrogen-bonding study. The extent of interaction between the ethers and the OH proton of methanol was determined by observing the difference ($\Delta\nu$ in cm^{-1}) between the free OH and the hydrogen-bonded OH stretching frequencies in the infrared spectrum of a solution containing both the ether and the methanol. It has been well established that the ether which shows a greater value of $\Delta\nu$ with a given reference alcohol is the stronger base.[9,30] The results obtained for GeH_3OCH_3, $GeH_3CH_2OCH_3$, and other compounds previously studied are listed in Table IV.

The relative electronegativities of carbon, silicon, and germanium would be expected to have a considerable effect on the relative base strengths of CH_3OCH_3, CH_3OSiH_3, and CH_3OGeH_3. The same would be true for the series of compounds $CH_3CH_2OCH_3$, $SiH_3CH_2OCH_3$, and $GeH_3CH_2OCH_3$ except that in these cases the effect might be smaller owing to the intervening methylene group. Although the exact values for the electronegativities of silicon and germanium are in some dispute, both atoms are less electronegative than carbon.[31,32]

TABLE IV

Methanol Frequency Shift Data for MH_3OCH_3 and $MH_3CH_2OCH_3$ Compounds (M = C, Si, and Ge)[a]

Ether	Ether concn, *M*	$\Delta\nu_{OH}$, cm^{-1}, methanol
CH_3OCH_3[b]	0.25	128
CH_3OSiH_3[c]	0.25	92
CH_3OGeH_3	0.14	155
	0.08	153
$CH_3OCH_2CH_3$	0.12	142
$CH_3OCH_2SiH_3$[d]	0.12	...
$CH_3OCH_2GeH_3$	0.19	126

[a] Solvent, CCl_4; methanol concentration, 0.01 *M;* experimental values reproducible to ± 3 cm^{-1}. [b] Reference 9. [c] C. H. Van Dyke and A. G. MacDiarmid, unpublished results. [d] No hydrogen-bonded OH absorption was observed with methanol as reference acid. $\Delta\nu = 246$ cm^{-1} with phenol as reference acid. A discussion of $CH_3OCH_2CH_3$ and the monomethoxy isomers of CH_3SiH_3 will appear in a separate communication.

In the series of MH_3OCH_3 (M = C, Si, and Ge) compounds, simple electronegativity concepts would predict that SiH_3OCH_3 and GeH_3OCH_3 should act as stronger Lewis bases than $(CH_3)_2O$. The fact that SiH_3OCH_3 is a weaker base than $(CH_3)_2O$ is, however, in accord with experimental observations of other workers.[28,33] For example, by using B_2H_6 as a reference acid, SiH_3OCH_3 is a much weaker base than $(CH_3)_2O$, since the latter but not the former forms an adduct at −78°.[28] The lack of appreciable donor activity appears to be a general phenomenon in siloxanes and alkoxysilanes and has been explained on the basis of one or both lone pairs of electrons on oxygen becoming involved in (p → d) π bonding with silicon.[2,3,29] For SiH_3OCH_3, and alkoxysilanes in general, a model has been proposed where only one pair of p-orbital electrons on the oxygen is involved in π bonding with the silicon, the second lone pair being involved in some type of hybrid orbital (approximating an sp^2 hybrid) at the oxygen.[29,33] The lone pair in the hybrid orbital would not have the correct symmetry to form appreciable overlap with the d orbitals of silicon and hence the molecule would have some (but reduced overall) base character.

The near equality of the electronegativities of silicon and germanium and the fact that GeH_3OCH_3 acts as a stronger Lewis base than SiH_3OCH_3 indicate that (p → d) π bonding in the Ge–O linkage is much less important than it is in the Si–O linkage. In other words, although (p → d) π bonding may exist in the Ge–O bond of GeH_3OCH_3, it does not appreciably alter the electron-donor character of the oxygen toward Lewis acids. The relative base strengths of $(CH_3)_2O$ and GeH_3OCH_3 can be explained on the basis of simple electronegativity considerations. There is other evidence in the literature which supports this conclusion about the relative importance of π bonding in the Si–O and Ge–O linkages.[6,16,34,35]

It is of interest to note that simple electronegativity factors cannot be used to explain the relative Lewis basicities of the $MH_3CH_2OCH_3$ (M = C, Si, and Ge)

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series of compounds. It is unlikely that steric factors are responsible for the trend, since alcohols have low steric requirements for interaction.[9,29] The results indicate that to a CH_2 group, the CH_3 group is more electron releasing than the SiH_3 or GeH_3 groups. These results are not in agreement with the order of electron release suggested by Srivastava and Onyszchuk[36] for the GeH_3 and CH_3 groups, from their infrared studies of the acetate derivatives of CH_4 and GeH_4. The results are not strictly comparable, however, since the compounds involved are structurally different. The order is also not consistent with the experimental inductive effects of the related $(CH_3)_3C$, $(CH_3)_3Si$, and $(CH_3)_3Ge$ groups, although again different systems were studied.[37] The possibility of an interaction between the lone pairs of electrons on oxygen and the d orbitals of silicon or germanium through a CH_2 group should be given some further consideration in light of the present results.[38]

Acknowledgments.—The authors wish to thank Drs. S. Castellano and A. A. Bothner-By for making their LAOCN3 computer program available to them and for discussions pertaining to the nmr spectra. Thanks are also extended to Mr. David Welsh, who helped to design and set up the original apparatus for the preparation of $GeH_3CH_2OCH_3$. Computer time was made available through the Computation Center of the Carnegie Institute of Technology. The A-60 spectrometer was purchased with funds from a Department Instruments Grant from the National Science Foundation.

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On the Acidity of Substituted Methylenediphosphonates and Their Interaction with Alkali Metal Ions

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Received May 1, 1967

The acidity of and Li^+, Na^+, K^+, and Cs^+ complexing with a series of substituted methylenediphosphonates have been determined at 25° in 0.5 *M* tetramethylammonium chloride. The acid properties of the alkyl-substituted methylenediphosphonates have been shown to be correlated with the electron-donor ability of the substituents attached to the bridging carbon atom. Also, $\log \beta_{\mathrm{MH}_i\mathrm{L}}$ $(i = 0, 1)$ is predicted by an equation involving the reciprocal of the radius of the bare cation and the sum of the Taft σ^* values. For 1-hydroxyethylidene-1,1-diphosphonic acid evidence is presented for intramolecular binding of the protons and the metal ions by the hydroxyl group.

Introduction

Previous studies[1-3] on methylene- and polymethylenediphosphonic acids, $H_2O_3P(CH_2)_nPO_3H_2$, showed that the p*K* values for the least acidic hydrogen atom and the values of the formation constants of alkaline earth metal ion complexes both decreased with increase in the value of *n*. The largest decrease in the interaction of diphosphonates with cations was noted in going from methylenediphosphonic acid, MDP, to dimethylenediphosphonic acid.

This paper includes a study of the effect on proton dissociation and alkali metal complexing upon substituting alkyl and hydroxy groups for the methylene hydrogens in MDP. In particular, an objective is to determine if the interaction of alkali metal ions with these diphosphonates is primarily ionic and specific site binding in character as opposed to a random nonspecific interaction. In the case of condensed phosphates[4] and isohypophosphate,[5] evidence obtained from ^{31}P nmr studies suggested specific site binding. Unfortunately, the changes in the ^{31}P nmr chemical shifts and spin–spin coupling constants for the phosphonate polyanions upon metal complexing are too small to be used for such a study.

Experimental Section

Chemicals.—Methylenediphosphonic acid (MDP) was prepared as previously described[6] but was further purified by crystallization of a tetrasodium salt. *Anal.* Calcd for $H_2C(PO_3)_2Na_4 \cdot 9H_2O$: C, 2.8; H, 4.7; P, 14.5. Found: C, 2.9; H, 4.6; P, 14.5. Aqueous solutions of the MDP salt were converted to the free acid by cation exchange with the hydrogen form of a Dowex 50 resin.

Ethylidene-1,1-diphosphonic acid, $CH_3CH(PO_3H_2)_2$ (EDP), and isopropylidenediphosphonic acid, $(CH_3)_2C(PO_3H_2)_2$ (PDP), were prepared by hydrolysis of their tetraethyl esters. The esters were prepared by stepwise methylation of the carbanion

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