TlCl, and TlI. If one also assumes that the electronic and nuclear rotational motions couple according to Hund's case c[2] (and so the molecule is effectively in a singlet state), the entropy calculated is 75 eu at 913°K. This value is just outside the uncertainty range of the experimental value.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AND THE
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Potassium Germyltrihydroborate

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Potassium germyltrihydroborate, KH_3GeBH_3, is formed by the reaction of diborane with potassium germyl. The salt melts with little decomposition at 98–99° and decomposes at 200° to germanium, germanium hydrides, hydrogen, and potassium hydroborate. Alkaline aqueous solutions are fairly stable, but addition of acid causes complete hydrolysis to germane, hydrogen, and boric acid. The infrared and nmr spectra are given.

Although many compounds containing carbon–boron bonds are known, only two compounds containing germanium–boron bonds have been characterized: $[(CH_3)_4N][(C_6H_5)_3GeB(C_6H_5)_3]$ and $[CH_3(C_6H_5)_3P][(C_6H_5)_3GeB(C_6H_5)_3]$.[1] The purpose of this study was to prepare and characterize an unsubstituted hydrogen analog of these compounds: potassium germyltrihydroborate, KH_3GeBH_3. A previous attempt to prepare the corresponding silicon compound, KH_3SiBH_3, had been unsuccessful.[2] Nevertheless, we had two reasons to be optimistic about the synthesis of the germanium compound. First, the carbon compounds LiH_3CBH_3,[3] $LiB(CH_3)_4$,[4] and $NaB(C_2H_5)_3H$[5] have been prepared and are apparently reasonably stable compounds, and many germanium compounds behave more like the analogous carbon compounds than the analogous silicon compounds.[6] Second, data from a study of the reaction of Ge_2Cl_6 with sodium hydroborate suggested that NaH_3GeBH_3 was formed as a stable intermediate.[7] In this study, the synthesis was accomplished by the direct reaction of potassium germyl ($KGeH_3$) with diborane.

Experimental Section

General Material.—Volatile materials were manipulated by standard vacuum-line techniques. Noncondensable gases were collected and measured using a Toepler pump and gas buret, respectively. Moisture- and air-sensitive solids were handled in a polyethylene glove bag flushed with dry argon or nitrogen.

Reagents.—The 1,2-dimethoxyethane was dried with a sodium–potassium alloy and degassed by distilling it into a −78° trap while pumping. Diethyl ether was dried with sodium diphenylketyl[8] and degassed by distilling it into a −196° trap while pumping. Potassium was distilled directly into the reactor *in vacuo*. Germane[9] and diborane[10] were prepared and purified by standard methods.

The identity and purity of volatile materials were determined by infrared spectrometry[11–15] with Perkin-Elmer Infracord spectrophotometers (Models 137B and 137), by mass spectrometry with a Consolidated Engineering Corp. mass spectrometer, Model 21-620, by molecular weight determinations, and by vapor pressure measurements.[16,17] Volatile mixtures were separated, when possible, by fractional condensation in appropriate cold traps. Mixtures of germane, digermane, trigermane, diborane, and 1,2-dimethoxyethane were analyzed for the first four constituents by the following procedure. The mixture was treated with excess 1 *M* aqueous HCl at room temperature for several minutes; the evolved hydrogen was separated and measured, and the equivalent amount of diborane was calculated. The remaining mixture was then separated by fractional condensation in traps cooled to −78° (solvent), −95° (trigermane), −160° (digermane), and −196° (germane).

Reaction Apparatus.—A typical reaction apparatus is illustrated in Figure 1. The apparatus was designed to permit the distillation of potassium from A into B, followed by the sealing off of tube A. Solvent and volatile reactants were distilled into vessel B, and, after reaction, the mixture was inverted and filtered through the fritted disk into C. In one experiment, a similar apparatus with a series of three fritted disks and receiving vessels was used, so that a sequence of reactions and filtrations could be carried out.

Potassium Germyl.—Potassium germyl was prepared[18] by the reaction (during about 36 hr) of excess germane with potassium in 1,2-dimethoxyethane at −63.5°

$$K + GeH_4 \longrightarrow KGeH_3 + {}^1/_2H_2 \qquad (1)$$

In a typical synthesis, 0.435 mmol of germane was consumed, with the evolution of 0.226 mmol of hydrogen (theoretical, 0.218).

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[1] D. Seyferth, G. Raab, and S. O. Grim, *J. Org. Chem.*, **26**, 3034 (1961).

[2] M. A. Ring and D. M. Ritter, *J. Am. Chem. Soc.*, **83**, 802 (1961).

[3] W. C. Price, *J. Chem. Phys.*, **17**, 1044 (1949).

[4] D. T. Hurd, *J. Org. Chem.*, **13**, 711 (1948).

[5] J. B. Honeycutt, Jr., and J. M. Riddle, *J. Am. Chem. Soc.*, **83**, 369 (1961).

[6] F. G. A. Stone, "Hydrogen Compounds of the Group IV Elements," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962, p 73.

[7] R. W. Kopp, Master's Thesis, University of California, Berkeley, Calif., 1962.

[8] G. E. Coates, "Organo-Metallic Compounds," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1960, pp 32, 33.

[9] W. L. Jolly and J. E. Drake, *Inorg. Syn.*, **7**, 34 (1963).

[10] H. G. Weiss and I. Shapiro, *J. Am. Chem. Soc.*, **81**, 6167 (1959).

[11] Good agreement was obtained with the infrared spectra reported in the literature for germane,[12] digermane,[13] trigermane,[14] and diborane.[15]

[12] J. W. Straley, C. H. Tindal, and H. H. Nielsen, *Phys. Rev.*, **62**, 161 (1942).

[13] D. A. Dows and R. M. Hexter, *J. Chem. Phys.*, **24**, 1029 (1956).

[14] J. E. Drake and W. L. Jolly, *J. Chem. Soc.*, 2807 (1962).

[15] American Petroleum Institute Research Project 44, Serial No. 742.

[16] Vapor pressures were observed to be within ±2% of the literature values for germane[9] and diborane.[17]

[17] A. B. Burg, *J. Am. Chem. Soc.*, **74**, 1340 (1952).

[18] We wish to thank Professor D. M. Ritter for his helpful suggestions.

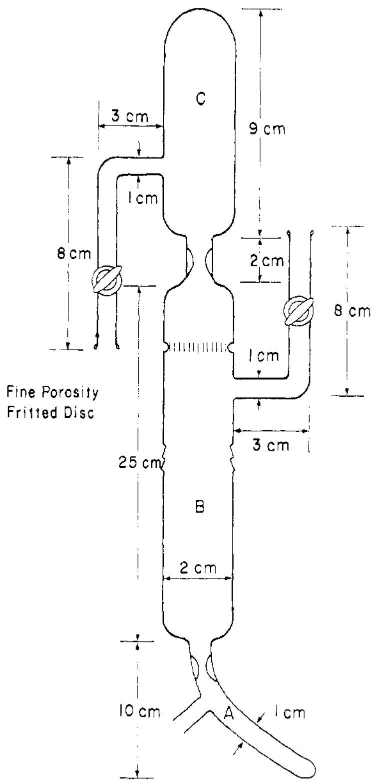

Figure 1.—Typical reaction apparatus.

When the resulting solution of $KGeH_3$ was treated with excess water, 0.444 mmol of germane (102% of theoretical) was evolved.

Reaction of B_2H_6 with $KGeH_3$.—A filtered solution of 1.14 mmol of potassium germyl in 1,2-dimethoxyethane was frozen at −196°; 0.55 mmol of diborane was condensed onto the frozen mass, and the mixture was allowed to warm until all of the 1,2-dimethoxyethane had melted. The mixture was held at −78° for about 15 min with occasional shaking and then warmed to about 25°. A precipitate of potassium hydroborate (identified as such in a separate experiment by X-ray diffraction[19]) was separated by filtration and treated with excess 1 M HCl. Hydrogen (0.535 mmol), corresponding to 0.134 mmol of KBH_4, was evolved. The filtrate remained clear upon standing at room temperature for 2 hr, although traces of germane and hydrogen were evolved. The 1,2-dimethoxyethane solvent was removed at room temperature, and the residue was pumped on for 30 min. During this time, the initially white residue turned partly yellow, and 0.103 mmol of germane and a trace of hydrogen were evolved. The residue was then extracted for 30 min with 2.1 ml of diethyl ether at room temperature, and the solution was filtered. Evaporation of the filtrate yielded 0.813 mmol of potassium germyltrihydroborate. (See below for identification and characterization data.) When the residue, now found to be insoluble in 1,2-dimethoxyethane, was heated to about 200°, hydrogen and traces of condensable gases (presumably germanium hydrides) were evolved;[20,21] the final residue was black and evolved further hydrogen (0.525 mmol) upon treatment with acid.

Characterization of KH_3GeBH_3.—When the potassium germyltrihydroborate isolated above was treated with excess 1 M aqueous hydrochloric acid, 0.813 mmol of germane and 2.44 mmol of hydrogen were evolved. These data correspond to H_2/GeH_4 = 3.00, in exact agreement with the theoretical ratio. Other properties of KH_3GeBH_3 were determined with other samples prepared as described above, except that sometimes the initial removal of KBH_4 by filtration was omitted.

Potassium germyltrihydroborate rapidly deliquesces in moist air. A solution of 0.750 mmol of KH_3GeBH_3 in 2 ml of water evolved 0.015 mmol of germane and 0.025 mmol of hydrogen upon standing for 30 min at about 25°. During a further 2 hr, 0.041 mmol of germane and 0.069 mmol of hydrogen were evolved. A solution of 0.690 mmol of KH_3GeBH_3 in 3 ml of 0.2 M aqueous sodium hydroxide evolved only traces of hydrogen and germane during 10 min at room temperature; no quantitative hydrolysis rate data were obtained.

Several samples of KH_3GeBH_3 were observed to melt (under argon) at 98.0–99.0° (uncorrected). When the molten salt was slowly heated *in vacuo*, it turned light yellow and began to effervesce at about 135°; it turned orange at about 142°, a red solid formed at about 149°, and the material turned black at about 160°. After holding the sample at 200° for 5 min, gas evolution ceased.[20] A 0.0880-mmol sample of KH_3GeBH_3 subjected to this treatment evolved 0.0242 mmol of germane, 0.0061 mmol of digermane, a trace of trigermane, and 0.0310 mmol of hydrogen. An X-ray powder pattern[19] of the black residue corresponded to potassium hydroborate. A 0.220-mmol sample of KH_3GeBH_3, similarly treated, evolved 0.0581 mmol of germane, 0.0102 mmol of digermane, 0.0036 mmol of trigermane, and 0.0832 mmol of hydrogen. The black residue yielded 0.849 mmol of hydrogen upon treatment with excess 1 M HCl. These data may be compared with those expected for the reaction

$$\begin{aligned} KH_3GeBH_3 \xrightarrow{\Delta} {} & [GeH_2] + KBH_4 \\ & \llcorner\!\xrightarrow{\Delta} H_2 + GeH_4 + Ge_2H_6 + Ge_3H_8 + Ge \end{aligned} \qquad (2)$$

For the first sample, the total hydrogen evolved pyrolytically, calculated as H_2, was 0.0977 mmol, as compared with the theoretical 0.0880 mmol. For the second sample, these quantities were, respectively, 0.244 and 0.220 mmol. The 0.849 mmol of hydrogen evolved by hydrolysis compares with the theoretical 0.880 mmol.

A sample of KH_3GeBH_3 was exposed to an atmosphere of dry oxygen for 15 min at room temperature. There was no visible change in the sample, and all of the oxygen was recovered.

Nujol mull infrared spectra of KH_3GeBH_3 are presented in Figures 2 and 3. The Nujol peaks at 3000, 1470, and 1380 cm^{-1} have been deleted. Absorption bands appear at the following frequencies (in cm^{-1}): 2475, 2340, 2290, 1930, 1230, 1120, 1055, 1034, 1007, 920, 830, 735, 526, 509, and *ca.* 400.

The proton magnetic resonance spectrum of the $H_3GeBH_3^-$ ion in the NaOH solution mentioned above was obtained[22] using a Varian Model HA-100 nmr spectrometer and is displayed in Figure 4.

By-Products of the $KGeH_3$–B_2H_6 Reaction.—The mixture formed by the reaction of 0.667 mmol of diborane with 1.348 mmol of potassium germyl in 1,2-dimethoxyethane was held at room temperature for 5 min and then treated with excess 1 M HCl, yielding 4.17 mmol of hydrogen, 0.991 mmol of germane, 0.164 mmol of digermane, and a trace of trigermane. The data may be compared with those expected assuming that the only by-products of the reaction were equimolar amounts of $KGe_2H_5BH_3$ and KBH_4. In accord with this assumption, we note that the original amount of potassium germyl was essentially equal to the total amount of germanium evolved as germane and digermane (0.991 + (2 × 0.164) = 1.319 mmol). We also note that the amount of evolved hydrogen was very close to that calculated from the amounts of germane and digermane [(3 × 0.991) + (7 × 0.164) = 4.121 mmol]. (The hydrolysis of KH_3GeBH_3 yields 3 mol of hydrogen/mol of germane, and the hydrolysis of an equimolar mixture of $KGe_2H_5BH_3$ and KBH_4 yields 7 mol of hydrogen/mol of digermane.) In a similar experiment with 0.621 mmol of diborane and 0.621 mmol of potassium

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[19] We wish to thank Mrs. Helena Ruben for obtaining the X-ray diffraction pattern.

[20] When solid polymeric germanium hydrides (GeH_x) are heated to 200°, they decompose completely to hydrogen, volatile germanium hydrides, and metallic germanium.[21]

[21] P. Royen and R. Schwarz, *Z. Anorg. Allgem. Chem.*, **215**, 295 (1933); P. Royen and C. Rocktaschel, *ibid.*, **346**, 279 (1966).

[22] We wish to thank Mr. Frank Papen for obtaining the spectrum.

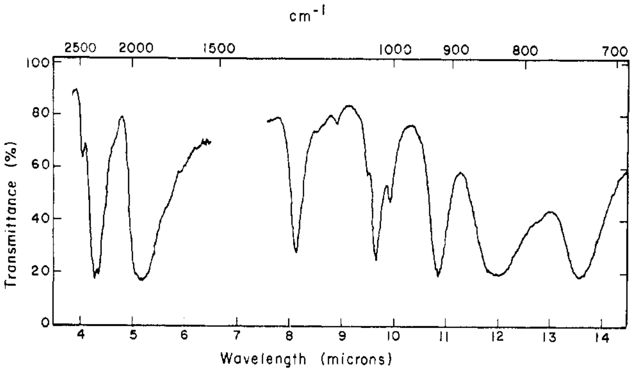

Figure 2.—Infrared spectrum of Nujol mull of potassium germyltrihydroborate, 4–14.5 μ.

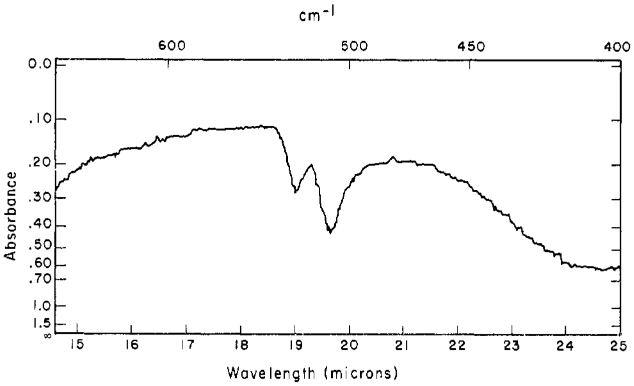

Figure 3.—Infrared spectrum of Nujol mull of potassium germyltrihydroborate, 14.5–25 μ.

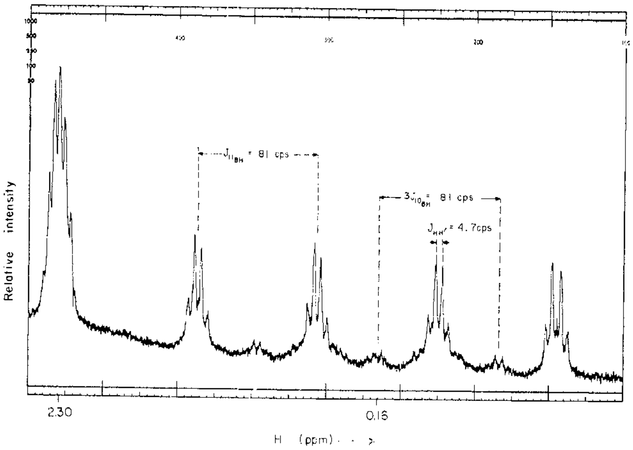

Figure 4.—Proton magnetic resonance spectrum of aqueous KH_3GeBH_3 at 100 Mc/sec.

germyl, equally good germanium and hydrogen checks were obtained.

After allowing 0.904 mmol of diborane and 1.498 mmol of potassium germyl to react in 1,2-dimethoxyethane, the solvent was removed, accompanied by 0.068 mmol of hydrogen, 0.109 mmol of diborane, 0.206 mmol of germane, 0.0605 mmol of digermane, and 0.0048 mmol of trigermane. Extraction of the remaining yellow solid with diethyl ether yielded only 0.015 mmol of KH_3GeBH_3. The insoluble residue was heated to about 200°, yielding 0.907 mmol of hydrogen, 0.0194 mmol of germane, and 0.0157 mmol of digermane.[20] The resulting black solid gave 5.74 mmol of hydrogen upon treatment with excess 1 M HCl. The data may be compared with those expected assuming that the $KGe_2H_5BH_3$ decomposed upon removal of the solvent, yielding a polymeric germanium hydride GeH_x

$$\begin{array}{l} KGe_2H_5BH_3 \longrightarrow 2[GeH_2] + KBH_4 \\ \quad \xrightarrow{ca.\ 25^\circ} GeH_x + GeH_4 + Ge_2H_6 + Ge_3H_8 + H_2 \\ \qquad \xrightarrow{200^\circ} Ge + GeH_4 + Ge_2H_6 + H_2 \end{array} \qquad (3)$$

It may be noted that, in accordance with this assumption, the amount of hydrogen from the last hydrolysis (of hydroborate) was very close to that calculated from the amount of potassium germyl *not* converted to KH_3GeBH_3 [4(1.498 − 0.015) = 5.932 mmol].

A solution of 0.137 mmol of KH_3GeBH_3 in 1.3 ml of 1,2-dimethoxyethane was treated with 0.128 mmol of diborane at room temperature for 10 min. Upon removal of the diborane (0.123 mmol recovered) and solvent, 0.0036 mmol of hydrogen, 0.0335 mmole of germane, 0.0048 mmol of digermane, and a trace of trigermane were evolved. By extraction of the solid with diethyl ether, only 0.007 mol of KH_3GeBH_3 was recovered. Pyrolysis of the residue caused evolution of hydrogen and germane and formation of a black product which evolved hydrogen upon treatment with acid. This experiment and that of the preceding paragraph indicate that diborane promotes the decomposition of KH_3GeBH_3 to KBH_4, H_2, and a mixture of germanium hydrides.

Results and Discussion

The principal reaction between diborane and potassium germyl, when the reagents are in the stoichiometric ratio or when potassium germyl is in slight excess, is

$$KGeH_3 + {}^1/_2B_2H_6 \longrightarrow KH_3GeBH_3 \qquad (4)$$

The physical and chemical properties of the product are consistent with the formulation potassium germyltrihydroborate, the anion consisting of a hydroborate ion in which one of the hydrogen atoms has been replaced by a germyl group (or the equivalent: a germyl anion coordinated to a borane group). Hydrolysis of aqueous solutions proceeds slowly in the presence of base (either added or formed by the self-hydrolysis reaction) but proceeds rapidly upon the addition of acid.

$$H^+ + 3H_2O + H_3GeBH_3^- \longrightarrow 3H_2 + GeH_4 + B(OH)_3 \qquad (5)$$

The salt melts at 98–99° with little apparent decomposition. The decomposition of the salt which occurs at 200° (eq 2) corresponds to a hydride shift from germanium to boron, with subsequent decomposition of the GeH_2 moiety.[20]

Infrared Spectrum of KH_3GeBH_3.—The infrared spectrum of potassium germyltrihydroborate is consistent with the simultaneous presence of the BH_3 and GeH_3 groups, but without a detailed spectral study there is ambiguity in the assignment of many of the absorption bands. The bands at 2340 and 2290 cm^{-1} are probably due to B–H stretching. These frequencies are comparable to those observed in amine boranes[23] and BH_3X^- (X = SCN, F, and CN),[24] but they are 100–200 cm^{-1} higher than those reported for lithium methyltrihydroborate.[3] The broad 1930-cm^{-1} absorption is probably due to Ge–H stretching. This frequency is considerably lower than that usually observed (*ca.*

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[23] R. C. Taylor, "Vibrational Frequencies, Assignments, and Force Constants for Some Compounds Containing Boron-Nitrogen Dative Bonds," in Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964, pp 59–70.

[24] V. D. Aftandilian, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **83**, 2471 (1961).

2100 cm^{-1}) for germyl compounds,[12-14,25] but the lowering is perhaps to be expected.[26,27]

Nmr Spectrum of $H_3GeBH_3^-$.—The nmr spectrum provides confirmation of the $H_3GeBH_3^-$ structure. The signal of the three equivalent BH_3 protons is centered at 0.16 ppm to low field of tetramethylsilane. The signal is split into a 1:1:1:1 quartet by the ^{11}B nucleus (spin $^3/_2$, 81.2% abundance) and a weak 1:1:1:1:1:1:1 septet by the ^{10}B nucleus (spin 3, 18.8% abundance). Each member of the quartet and the septet is further split into a 1:3:3:1 quartet by the three equivalent GeH_3 protons. The coupling constants, $J_{^{11}BH} = 81$ cps and $J_{^{10}BH} = 27$ cps, are essentially the same as those found for the hydroborate ion.[28,29] The observed ratio $J_{^{11}BH}/J_{^{10}BH} = 3.00$ agrees very well with the value 2.99 predicted from the magnetogyric ratios of ^{10}B and ^{11}B. Thus we can rule out the possibility that each member of the quartet hides a member of the septet, corresponding to $J_{^{10}BH} = 40.5$ cps. The coupling constant $J_{HH'} = 4.7$ cps is very plausible for protons separated by two intervening atoms.[30-32] The signal of the three equivalent GeH_3 protons is centered at 2.30 ppm to low field of tetramethylsilane. The signal may be approximately accounted for by considering only the coupling with the BH_3 protons ($J_{HH'} = 4.7$ cps) and the coupling with the ^{11}B nucleus ($J_{^{11}BH'}$). If we assume the latter coupling constant to be of approximately the same magnitude as $J_{HH'}$, we predict an overlapping of the 16 peaks so as to form a septet, as observed.[33] However, because of the serious overlapping of the peaks and the neglect of $J_{^{10}BH'}$, it is not possible to calculate the exact value of $J_{^{11}BH'}$ from the spectrum.

Reaction of Excess B_2H_6 with $KGeH_3$.—The principal by-products in the B_2H_6–$KGeH_3$ reaction are potassium hydroborate and a species, soluble in 1,2-dimethoxyethane, which yields digermane upon acid hydrolysis. We tentatively suggest that the latter species is potassium digermanyltrihydroborate, formed in the reaction

$$2KH_3GeBH_3 \longrightarrow KBH_4 + KGe_2H_5BH_3 \qquad (6)$$

When the solvent is removed from the $KGe_2H_5BH_3$, hydrogen and germanium hydrides are evolved, and a yellow residue, having the characteristics of a mixture of polymeric germanium hydride and potassium hydroborate, is formed. This latter process may be expressed by eq 3. Both of these side reactions are promoted by the presence of excess diborane, particularly during removal of the 1,2-dimethoxyethane solvent. Possibly diborane aids in the formation of germanium dihydride, which then acts as an intermediate in the polymerization reactions

$$H_3GeBH_3^- + {}^1/_2B_2H_6 \longrightarrow GeH_2 + B_2H_7^-$$

$$GeH_2 + H_3GeBH_3^- \longrightarrow Ge_2H_5BH_3^-$$

$$GeH_2 + Ge_2H_5BH_3^- \longrightarrow Ge_3H_7BH_3^-, \text{ etc.}$$

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

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[25] R. C. Lord and C. M. Steese, *J. Chem. Phys.*, **22**, 542 (1954).

[26] The α-C–H stretch frequency is lowered by 76–310 cm^{-1} on going from alcohols to the corresponding alkoxide ions.[27] The CH_3O^- ion may be looked upon as an analog of the $GeH_3BH_3^-$ ion.

[27] F. H. Seubold, Jr., *J. Org. Chem.*, **21**, 156 (1956).

[28] Ogg[29] reported $J_{^{11}BH} = 82$ cps and $J_{^{10}BH} = 27$ for BH_4^-.

[29] R. A. Ogg, *J. Chem. Phys.*, **22**, 1933 (1954).

[30] $J_{HH'} = 8$ cps has been observed for H_3PBH_3;[31] $J_{HH'} = 4.8$ cps for both GeH_3PH_2 and GeH_3AsH_2.[32]

[31] R. W. Rudolph, R. W. Parry, and C. F. Farran, *Inorg. Chem.*, **5**, 723 (1966).

[32] J. E. Drake and W. L. Jolly, *J. Chem. Phys.*, **38**, 1033 (1963).

[33] The observed intensities for the GeH_3 septet are in fair agreement with those expected for the overlap of the 16 peaks.

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Deuterium Isotope Studies on 2,3-Dicarbahexaborane(8)

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Deuterium exchange at various positions on the $C_2B_4H_8$ molecule has been studied. D_2 exchanges with all boron-bonded hydrogen atoms, and B_2D_6 in the presence of diglyme exchanges only at the 4 and 6 terminal positions. The $(CH_3)_2C_2B_4H_6$ and DCl exchange, catalyzed by aluminum chloride, occurs at both apex and base terminal positions. 2,3-Dicarbahexaborane(8)-2,3-d_2, $D_2C_2B_4H_6$, has been prepared by heating B_5H_9 with C_2D_2. The infrared spectrum is given and it is shown that there is no migration of deuterium from carbon to boron during the synthesis.

Introduction

In the course of considering mechanism studies on reactions of 2,3-dicarbahexaborane, it became advantageous to prepare a number of derivatives with deuterium labeling in a variety of specific positions. Described in this report are the results of studies using variously D_2, DCl, and a diglyme solution of B_2D_6 showing the specific positions on the $C_2B_4H_8$ molecule where exchange occurs.

Experimental Section

Materials.—**Deuterium**, D_2, was Matheson CP Grade, 99.5%. A sample of Harshaw chrome catalyst CR-0102T, $^1/_8$ in., was generously donated by the Harshaw Chemical Co. **Deuterium chloride** was prepared by treating Al_2Cl_6 or PCl_3 with D_2O and