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The Formation and Cleavage of the Germanium–Germanium Bond in Digermane

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Digermane was prepared from the reaction between potassium germyl and chlorogermane. Catalyzed decompositions of digermane going to germane were examined with lithium chloride, bromide, and hydride. The reaction of either digermane or germane with potassium hydride produced potassium germyl. The results from these reactions and similar reactions with disilanes are discussed.

Introduction

Alkali metal salt catalyzed disproportionation reactions of disilane have recently been described.[1] Since germanium lies directly below silicon in the periodic table, it should be of interest to examine similar reactions for digermane.

At this time, the best synthesis for digermane appears to be the passing of germane through an electric discharge.[2] Since coupling reactions have been successful for the preparation of disilane[3] and germylsilane,[4] we have also examined the coupling reaction between potassium germyl and chlorogermane.

Experimental Section

The cleavage and coupling reactions were carried out in 100-ml round-bottom flasks which were fitted with either Teflon needle valves or stopcocks and ground joints to allow for transfer of volatile compounds between the vacuum line and the reaction vessels. The reaction vessels were also fitted with a side tube through which solids could be added. Infrared spectra were obtained in 5- or 10-cm gas cells, fitted with sodium chloride or potassium bromide windows using a Perkin-Elmer Model 337 spectrophotometer. The proton nmr spectrum was obtained on a Varian Model A-60 spectrometer.

Germane was prepared by the reduction of germanium oxide[2] and purified by passage through a −130° trap. The germane was identified by a vapor pressure of 40 torr at −131°, lit.[5] value 40 torr, and confirmed by an infrared spectrum[6] in which the very strong 755-cm⁻¹ absorption of digermane[7] was absent. Chlorogermane was prepared from the reaction of germane with silver chloride[8] and identified by a high pressure (∼300 torr) infrared spectrum[9] which demonstrated that hydrogen chloride was absent and also from a proton nmr spectrum which had only one absorption at τ 4.86, lit.[10] value τ 4.89.

Potassium hydride (50% slurry in Bayol 85), lithium hydride, lithium deuteride, hydrogen chloride, silver chloride, and germanium dioxide were obtained commercially and were used without purification.

The 1,2-dimethoxyethane (bp 83–85°) was mixed with a large amount of potassium sand in an evacuated flask equipped with a stopcock. The flask was stored in a −78° bath when not in use to maintain the deep blue color.

The lithium halides were stored for approximately 12 hr in a vacuum oven at 125° prior to use. After transfer to the reaction vessel, the lithium halides were heated again for 1 hr under dynamic vacuum.

Potassium germyl was prepared by the method reported by Kennedy, *et al.*, for potassium silyl.[3] Excess potassium sand was treated with germane in 1,2-dimethoxyethane at −78° until the solution turned blue (2–40 hr) at which time the solvent was distilled from the reaction vessel. Treatment of the potassium germyl with hydrogen chloride yielded germane and digermane in 80 and 15% yields, respectively, based on the germane consumed in the preparation of potassium germyl. The excess potassium sand was present during the reaction with hydrogen chloride.

1. **Preparation of Digermane.**—(a) Potassium germyl (∼2.5 mmol) prepared in 1,2-dimethoxyethane as described above was filtered to remove the excess potassium. The solvent was removed by distillation until the salt was just free flowing. Chlorogermane (2.46 mmol) was condensed onto the potassium germyl. After 12 hr at room temperature, the volatile components were distilled into the vacuum system for separation. The condensate in the −196° trap was germane (0.55 mmol) identified as previously described. The condensate in the −130° trap was digermane and chlorogermane, and the condensate in the −95° trap was chlorogermane. The similarity in the vapor pressures of digermane and chlorogermane made it expedient to destroy the chlorogermane by a hydrolysis reaction with water for 2 hr. Digermane is unaffected by contact with water for 24 hr. The digermane isolated (0.45 mmol) after treatment with water and distillation through a trap cooled to −95° was identified by an infrared spectrum[17] in which the strong 431-cm⁻¹ band of chlorogermane and the strong 819-cm⁻¹ band of germane were absent. The vapor pressure of the digermane was 0 at −130° (no germane) and 3 torr at −78°; lit.[5] value 3 torr. The quantity of chlorogermane initially condensed in the −95° trap and retained in the water was 1.5 mmol.

(b) Chlorogermane (2.46 mmol) was condensed onto potassium

(1) J. A. Morrison and M. A. Ring, *Inorg. Chem.*, **6**, 100 (1967).
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(3) R. C. Kennedy, L. P. Freeman, A. P. Fox, and M. A. Ring, *J. Inorg. Nucl. Chem.*, **28**, 1373 (1966).
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(7) D. A. Downs and R. M. Hexter, *J. Chem. Phys.*, **24**, 1029 (1956).
(8) K. M. MacKay, P. Robinson, E. J. Spanier, and A. G. MacDiarmid, *J. Inorg. Nucl. Chem.*, **28**, 1377 (1966).
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(10) E. A. V. Ebsworth, S. G. Frankiss, and A. G. Robiette, *J. Mol. Spectry.*, **32**, 299 (1964).

germyl (~2.5 mmol) which had not been filtered so that the excess potassium sand was still present. The solvent was again removed. After 6 hr at room temperature, the volatile fraction found consisted of germane (0.62 mmol), digermane (0.92 mmol), and chlorogermane (0.72 mmol) all identified as described in section 1a.

The yields of digermane ranged from a few per cent to about 50% based on the chlorogermane consumed. When low yields of digermane were obtained, germane was obtained in large quantities. The factors which appeared to contribute to the best yields were: (1) the use of freshly prepared potassium sand in the preparation of potassium germyl; (2) the use of potassium germyl soon after it was prepared; (3) the almost complete removal of the 1,2-dimethoxyethane from the potassium germyl so that the salt was just free flowing.

2. **Control Reactions.**—(a) Digermane (0.17 mmol) was allowed to react with potassium sand for 48 hr at room temperature with only trace amounts of germane being produced while essentially all of the digermane was recovered.

(b) Chlorogermane (0.82 mmol) was condensed onto excess dry potassium sand. After 30 min at room temperature, the products found were germane (0.16 mmol) and only trace amounts of digermane and chlorogermane. Treatment of the solid product with hydrogen chloride (2 mmol) yielded 0.62 mmol of products consisting of germane, some chlorogermane, and trace quantities of digermane.

3. **Reactions of Digermane. a. LiCl–Ge₂H₆.**—Digermane (0.25 mmol) was allowed to react with excess lithium chloride partially dissolved in 1,2-dimethoxyethane (5 ml) for 90 hr. The volatile fraction was analyzed as previously described and found to consist of digermane (0.16 mmol) and germane (0.08 mmol). The solid product did not react with hydrogen chloride.

b. **LiBr–Ge₂H₆.**—In a similar reaction, digermane (0.14 mmol) was allowed to react with lithium bromide in 1,2-dimethoxyethane (5 ml) for 280 hr after which time the volatile fraction consisted of 0.05 mmol of digermane and 0.10 mmol of germane.

c. **LiH–Ge₂H₆.**—Digermane (0.43 mmol) was treated with lithium hydride in 1,2-dimethoxyethane (10 ml) for 84 hr. No noncondensables were observed. Germane (0.44 mmol) was the only volatile product. Treatment of the solid fraction with hydrogen chloride for 10 hr yielded noncondensables (1 mmol) and trace amounts of germane, chlorogermane, and digermane. In a similar reaction between lithium deuteride and digermane, the germane obtained was pure GeH₄ since the infrared spectrum of the germane did not contain the strong Ge–D stretching band[11] at 1529 cm⁻¹.

d. **KH–Ge₂H₆.**—The reaction between excess potassium hydride and digermane was examined in 1,2-dimethoxyethane (6 ml) for various reaction times. After the volatile fraction (including the solvent) was distilled into the vacuum system for separation, excess hydrogen chloride was condensed onto the solid products. The quantities of germane and digermane formed in these reactions were assumed to represent the quantities of potassium germyl and potassium digermanyl formed in the initial reaction. The results from these reactions are listed in Table I.

4. **Reactions of Germane. a. LiH–GeH₄.**—Germane (0.93 mmol) was allowed to react with excess lithium hydride in 1,2-dimethoxyethane (5 ml) for 67 hr. Germane (0.92 mmol) was recovered unreacted.

b. **KH–GeH₄.**—Germane (0.72 mmol) was treated with excess potassium hydride in 1,2-dimethoxyethane (5 ml) for 65 hr. All of the germane had reacted to form a white solid that produced germane (0.70 mmol) and trace amounts of digermane and chlorogermane when treated with excess hydrogen chloride. In a similar reaction, germane (2.54 mmol) was allowed to react with excess potassium hydride. After 4.5 hr, 1.05 mmol of germane was left unreacted; while after an additional 17 hr, 0.37 mmol of germane was still unreacted.

(11) L. P. Lindeman and M. K. Wilson, *J. Chem. Phys.*, **22**, 1723 (1954).

TABLE I

RESULTS OF THE DIGERMANE–POTASSIUM HYDRIDE REACTIONS

| Ge₂H₆ $\xrightarrow{\text{KH}}$	GeH₄ +	KGeH₃ +	KGe₂H₅	Reaction
		mmol		time, min
0.29	0.27	0.18	0.03	<3
0.27	0.18	0.29	0.02	3
0.37	0.03	0.50	0.07	60
0.57	0.00	0.94	0.08	600

Discussion

1. **Preparation of Digermane.**—The coupling reaction between potassium germyl and chlorogermane does produce digermane. However, as in the analogous preparation of disilane[3] the yields vary depending on the reaction conditions. Since large quantities of germane were obtained when the digermane yield was low, it is possible that some digermane undergoes a salt-catalyzed disproportionation reaction after initial formation or that the germyl ion and chlorogermane react to produce germane directly. When the coupling reaction is carried out in the "near" absence of the solvent, reasonable yields can be obtained; however, it is difficult to determine just when the potassium germyl is desolvated enough to ensure reasonable yields.

2. **Reactions of Germane and Silane.**—We have found that germane reacts with potassium hydride in 1,2-dimethoxyethane

$$GeH_4 + KH \longrightarrow KGeH_3 + H_2 \qquad (1)$$
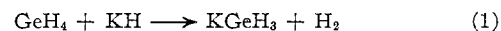
This result is not surprising in view of the fact that germane reacts with potassium hydroxide to yield potassium germyl.[12] It is interesting to note that lithium hydride does not react with germane and that potassium hydride does not react with silane.[13]

3. **Reactions of Digermane.**—The alkali metal salt catalyzed decomposition reactions of disilane,[1] some alkyldisilanes,[14] and now digermane have been investigated. When lithium chloride or hydride is the salt, the reaction can be represented by the equation

$$xGe_2H_6 \xrightarrow{\text{LiX}} xGeH_4 + (1/x)(-GeH_2-)_x \qquad (2)$$
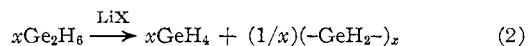
The formula for the solid product is based on a mass balance and therefore represents an average. The polymer obtained did not react with hydrogen chloride.

The relative rates of these reactions (2) are in the order: Si₂H₆ > Ge₂H₆ ≃ CH₃Si₂H₅ > (CH₃)₂Si₂H₄. This order is reasonable if one assumes that the salts are base catalysts which attack the silicon or germanium atoms. Since silicon is more electropositive than germanium, the silicon atoms in disilane should be more positive than the germanium atoms in digermane. Similarly, the methyl groups release electron density to the silicon atoms[15] which decreases the positive charge on the silicon atoms in the methyldisilanes compared to those in disilane.

The potassium hydride catalyzed decompositions of disilane and the methyldisilanes can be represented by
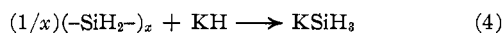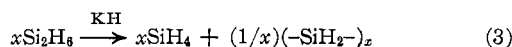
(12) W. L. Jolly, *Inorg. Chem.*, **6**, 1435 (1967).
(13) J. A. Morrison and M. A. Ring, unpublished observation, 1966.
(14) W. M. Ingle, E. A. Groschwitz, and M. A. Ring, *Inorg. Chem.*, **6**, 1429 (1967).
(15) V. N. Krishnamurthy and S. Soundararagan, *J. Inorg. Nucl. Chem.*, **27**, 2341 (1965).

$$x\text{Si}_2\text{H}_6 \xrightarrow{\text{KH}} x\text{SiH}_4 + (1/x)(-\text{SiH}_2-)_x \tag{3}$$

$$(1/x)(-\text{SiH}_2-)_x + \text{KH} \longrightarrow \text{KSiH}_3 \tag{4}$$
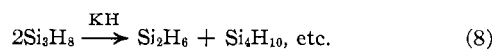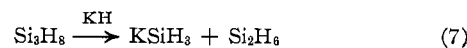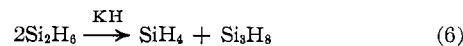
The reaction represented by eq 3 is very fast while the reaction represented by eq 4 is slow. A reaction similar to route 4 was also observed in the disilane–lithium hydride reaction.

The decomposition of digermane by potassium hydride is much faster than any of the disilane decompositions. The change in the order of the relative rates with potassium hydride suggests that a different reaction path is followed. Germane does react with potassium hydride to form potassium germyl but not fast enough to account for the rapid appearance of potassium germyl in the digermane–potassium hydride reaction. These results suggest that digermane and potassium hydride may react primarily without going through a polymer (M_xH_{2x+2}, where $x = 3$ or more, M = Si or Ge) as must be the case for disilane with potassium hydride[1]

$$\text{KH} + \text{Ge}_2\text{H}_6 \longrightarrow \text{KGeH}_3 + \text{GeH}_4 \tag{5}$$
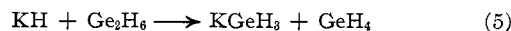
Thus, the potassium hydride–digermane reaction may be a fairly simple cleavage reaction while the potassium hydride–disilane reaction may involve numerous disproportionation and cleavage reactions in which disilane is regenerated

$$2\text{Si}_2\text{H}_6 \xrightarrow{\text{KH}} \text{SiH}_4 + \text{Si}_3\text{H}_8 \tag{6}$$

$$\text{Si}_3\text{H}_8 \xrightarrow{\text{KH}} \text{KSiH}_3 + \text{Si}_2\text{H}_6 \tag{7}$$

$$2\text{Si}_3\text{H}_8 \xrightarrow{\text{KH}} \text{Si}_2\text{H}_6 + \text{Si}_4\text{H}_{10}, \text{ etc.} \tag{8}$$

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Electron Impact Fragmentation of B₁₀H₈(N₂)₂ and Isotopic Composition of Decaborane(14)[1]

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The mass spectrum of $B_{10}H_8(N_2)_2$ which has a closed polyhedral boron skeleton was examined and compared with that of decaborane(14) which has an open-faced icosahedral fragment boron skeleton. There is less boron fragmentation from $B_{10}H_8(N_2)_2$ than from $B_{10}H_{14}$. Prominent ions were $B_{10}H_8N_4{}^+$ and $B_{10}H_8N_2{}^+$, with no evidence of similar ions with fewer than eight hydrogens. The ion current patterns of these ions were used to determine the per cent of boron-10 in the sample. Overlapping $B_{10}H_x{}^+$ ion currents were resolved to show large contributions from species with x even and small or negligible contributions for x odd. Appearance potential differences are 0.60 ± 0.05 V for the loss of one N_2 molecule and 1.80 ± 0.05 V for the loss of two N_2 molecules. Metastable ions indicate the reactions $B_{10}H_8N_4{}^+ \rightarrow B_{10}H_8N_2{}^+ + N_2$ and $B_{10}H_8N_2{}^+ \rightarrow B_{10}H_8{}^+ + N_2$ take place in the spectrometer.

Decaborane, $B_{10}H_{14}$, has an icosahedral fragment skeleton of boron atoms in which the bonding is best described as delocalized or aromatic.[2] Electron impact ionization results in fragmentation favoring loss of H_2 and BH_3 units, to give $B_{10}H_n{}^+$ ions of greater abundance for n even than for n odd and $B_xH_y{}^+$ ions in appreciable abundance.[3] Derivatives of the $B_{10}H_{10}{}^{2-}$ ion have a closed polyhedral boron skeleton in which the bonding is probably completely delocalized ellipsoidally rather than having an open face as in decaborane. Electron impact ionization of 1,10-$B_{10}H_8(N_2)_2$, a relatively volatile derivative of $B_{10}H_{10}{}^{2-}$,[4] was investigated to determine if the fragmen-

tation processes from a closed polyhedral structure are significantly different from those from the open-faced polyhedral fragment structure of decaborane. In addition, relative ion currents were used to determine the boron isotopic composition.

Results

The natural isotopic composition of boron is about 80% ^{11}B and 20% ^{10}B. For a group of ten borons, $^{11}B_8{}^{10}B_2$ is the most probable isotopic composition, but six others have probabilities greater than 1% of the most probable composition. Table I gives the relative abundances of $B_{10}H_8$ and $B_{10}H_8N_4$ species calculated from often quoted natural abundances of B (19.6% ^{10}B), H ($1.5 \times 10^{-2}\%$ ^{2}H), and N (0.36% ^{15}N), and also from 20.20% ^{10}B and natural abundances of H and N isotopes. Values are changed only in the fourth significant figure by neglecting the effect of ^{2}H. Similar calculations were performed at 0.10% intervals for ^{10}B from 19.00 to 21.00%. Masses 175, 147, and 119 arise from species containing ^{2}H or ^{15}N.

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(2) For a discussion of structures and bonding, see W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963.

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