been present. It is possible that higher molecular weight species might have been present if higher temperatures had been achieved earlier in the vaporizations.

The presence of series 2 species probably arises from the reactivity of B_2Se_3 with $H_2O(g)$ even at low H_2O pressures. This hydrolysis reaction would be expected to introduce an oxygen contaminant also into the sample. The presence of oxygen in some species was deduced for sets of ions at masses 71, 108, and 136 as discussed previously. The presence of series 2 species $H_2BSe_2^+$ and $H_2B_2Se_3^+$ is assumed to be caused by parent species also bearing H atoms, probably $H_2BSe_2(g)$ and $H_2B_2Se_3(g)$.

The data reported in Tables I–III indicate that the gaseous molecules BSe_2 and B_2Se_3 are thermally stable to 700°.

The results of this study of the boron selenides show some similarities to the studies of the vaporization of B_2S_3;[4,5,8] the gaseous species observed were BS_2, B_2S_3, and their polymers. In the earlier studies,[4,5] as the vaporization proceeded by heating to progressively higher temperatures, the higher molecular weight species decreased in importance leaving only $B_2S_3(g)$. In the study by Chen and Gilles,[8] the gas composition was studied as a function of the composition of the condensed B–S phase. Congruent vaporization of B_2S_3 was found to produce only $B_2S_3(g)$ and its polymers. If the sample was S rich in comparison to B_2S_3, $BS_2(g)$ and its polymers were found also. If the sample was S poor, then $B_2S_2(g)$ was detected in addition to BS_2^+ and $B_2S_3^+$. In the study of the thermal decomposition of HBS_2,[6,7] it was concluded that HBS_2 initially lost large amounts of $H_2S(g)$, samples then lost gaseous polymers of HBX_2, and finally the mass spectra of boron sulfides similar to those of the earlier studies were observed.

The appearance in this study of the vaporization of $B_2Se_3(s)$ of series 1 gaseous species may be compared with what occurred with the similar vaporization of $B_2S_3(s)$ by Gilles, *et al.*[4,5,8] The initial appearance of selenium and its polymers suggests that these B_2Se_3 samples were of high selenium activity. In later stages of the vaporization of these samples, the species $BSe_2(g)$ and $B_2Se_3(g)$ were observed. Gilles, *et al.*, in addition to $BS_2(g)$ and $B_2S_3(g)$, found gaseous polymers of BS_2 and B_2S_3. If polymers of BSe_2 or B_2Se_3 were present, their importance was significantly less than in the case of the boron sulfides. The fact that vaporizations terminating at high temperatures led to B_2S_3 and BSe_2 (BSe_2^+ may be a fragmentation product at the end of the vaporization) and B_2Se_3 as the important gaseous molecular species shows the similarities in sulfur and selenium chemistry.

In the case of the boron selenides, the hygroscopic nature of the sample introduced H (and O) into the condensed phase. Initial stages of the vaporization showed large amounts of $H_2Se(g)$. In addition, $H_2BSe_2(g)$ was observed. These results show similarities to the thermal decomposition of $HBS_2(s)$ studied by Gilles, *et al.*,[6,7] in the case of HBS_2, $H_2S(g)$ and $HBS_2(g)$ were observed. Further heating of the HBS_2 sample gave gaseous products as found in the vaporization of $B_2S_3(s)$. In this study of the B–Se system, further heating of samples showing H species, see Table III, gave rise to $B_2Se_3(g)$ just as vaporization of a sample showing only series 1 species.

The Formation of Silene and Germene from the Pyrolyses of Disilane and Digermane and the Relative Insertions of Silene into Silanes

BY PETER ESTACIO, M. D. SEFCIK, E. K. CHAN, AND M. A. RING

The products from the pyrolysis of disilane-d_6 and methylsilane were silane-d_4 and $CH_3SiH_2SiD_2H$. These results demonstrate that the pyrolysis of disilane yields silene (probably singlet) and silane. The rate of insertion of silene into silicon–hydrogen bonds appears to increase greatly with an increase in the hydridic character. The pyrolysis of digermane was found similar to that of disilane.

Introduction

We have proposed that the pyrolysis of disilane occurs *via* the formation of silene and silane.[1] This proposed mechanism (eq 1 and 2) was based on the fact

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$$Si_2H_6 \longrightarrow SiH_2 + SiH_4 \qquad (1)$$
$$SiH_2 + Si_2H_6 \longrightarrow Si_3H_8 \qquad (2)$$
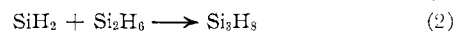
that the pyrolysis of disilane with low-temperature trapping yielded only silane and trisilane (eq 3).

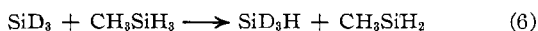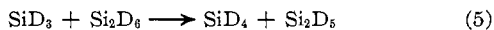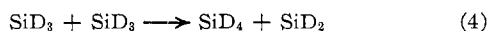$$2Si_2H_6 \longrightarrow SiH_4 + Si_3H_8 \qquad (3)$$
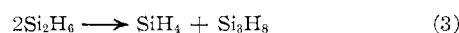
In this paper we report our results on the trapping of silene-d_2 by methylsilane and on relative rates of silene insertion into silanes. We also report our results on the pyrolysis of digermane.

Results

The results listed below were obtained in flow systems which contained a cold trap which set the pressure of the reactants and which condensed the volatile products except silane or germane which are stable at the reaction temperatures.

1. Thermal Reaction of Si_2D_6 with CH_3SiH_3.—The products from the pyrolysis of disilane-d_6 in the presence of excess ($\sim$6.7:1) methylsilane at 375° were silane-d_4 and $CH_3SiH_2SiD_2H$. The very small hydrogen fraction obtained was all D_2. The absence of HD demonstrates that deuterium atoms were not present since they would abstract hydrogen atoms from methylsilane. Thus the initial step in the pyrolysis of disilane must be either the formation of silyl radicals or the formation of silene and silane (eq 1). The formation of CH_3SiH_2-SiD_2H clearly demonstrates that the reactive species from the disilane pyrolysis is the silene radical (methylsilane is stable below 500°).[2]

The silene radical could be formed either from eq 1 or from the initial formation of silyl radicals followed by the conversion of silyl to silene.[3] The conversion of silyl radicals could occur by a decomposition to silene and deuterium which we can eliminate (no HD) or by a deuterium abstraction reaction. In this case, the abstraction reactions would be

$$SiD_3 + SiD_3 \longrightarrow SiD_4 + SiD_2 \qquad (4)$$

$$SiD_3 + Si_2D_6 \longrightarrow SiD_4 + Si_2D_5 \qquad (5)$$

$$SiD_3 + CH_3SiH_3 \longrightarrow SiD_3H + CH_3SiH_2 \qquad (6)$$

From concentration and even activation energy[4] considerations, the relative rates for these three reactions must be eq 6 > eq 5 ≫ eq 4. Since silane-d_3 was not observed, we can eliminate reaction 6 and thus also reaction 4. Therefore, we can conclude that silene-d_2 was produced according to eq 1 which is the initial decomposition step in the pyrolysis of disilane.

2. Thermal Reaction of Si_2H_6 with $(CH_3)_2SiH_2$.—The products from the pyrolysis of disilane in the presence of dimethylsilane $\{[Si_2H_6]/[(CH_3)_2SiH_2] \cong 0.93/1.00\}$ at 412° were 1,1-dimethyldisilane and trisilane in a 1.44:1 ratio. This experiment measured the relative rate of silene insertion into dimethylsilane and disilane. With a correction for steric factors, this result demonstrates that insertion into the silicon–hydrogen bond of dimethylsilane was favored over that of disilane by about 7:1. This result suggests that silene acts as a electrophilic reagent.

3. Thermal Reaction of Si_2H_6 with $ClSiH_3$.—The silene insertion product from the pyrolysis of disilane at 400° in the presence of a small excess of chlorosilane

was trisilane with no evidence for the formation of chlorodisilane. This result confirms the fact that silene acts as an electrophile during insertion reactions into silicon–hydrogen bonds.

4. Pyrolysis of Digermane.—The results from the pyrolysis of digermane are listed in Table I. These
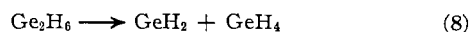
TABLE I
PYROLYSIS OF DIGERMANE

Temp, °C	Ge_2H_6 consumed, mmol	Amt of products, mmol			Time, hr
		GeH_4	Ge_3H_8	H_2	
230	0.01	0.004	0.004	...	3
240	0.08	0.04	0.04	...	3
240	0.05	0.02	0.02	...	3
250	0.06	0.03	0.01	0.005	2.5

results show that the pyrolysis of digermane (eq 7) is

$$2Ge_2H_6 \longrightarrow GeH_4 + Ge_3H_8 \qquad (7)$$
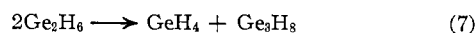
similar to that of disilane. The low quantity of hydrogen produced demonstrates that hydrogen atoms were not formed in the initial decomposition.

5. Thermal Reaction of Ge_2H_6 with $C_2H_5GeD_3$.—The products from the pyrolysis of digermane in the presence of ethylgermane-d_3 at 280° were germane, trigermane, and ethyldigermanes while diethyldigermanes were not observed. These results strongly argue that digermane decomposes into germene and germane (eq 8). If digermane had decomposed into germyl

$$Ge_2H_6 \longrightarrow GeH_2 + GeH_4 \qquad (8)$$

radicals, reaction 8 should have produced germane-d_1 and a diethyldigermane.

Discussion

1. Pyrolysis of Disilane and Digermane.—It is well known that disilane is thermally less stable than ethane or peralkyl- or peraryldisilanes.[5] Ethane and hexamethyldisilane decompose by carbon–carbon[6] or silicon–silicon[7] bond fission with activation energies of 89.5 and 67 kcal/mol, respectively. Though the silicon–silicon bond energy in disilane is open to question, the best value appears to be 81 kcal/mol.[8] Therefore, if disilane were to decompose into silyl radicals, the activation energy would be about 80 kcal/mol and disilane would be essentially as thermally stable as ethane and the organodisilanes. Thus, the different decomposition mode found for disilane explains its lower thermal stability. We have estimated that the activation energy for this process is 57 kcal/mol. This value is based on an A factor of 16 and data from the pyrolysis of disilane reported by Tebben and Ring.[1] It is also of interest that the pyrolysis of digermane appears to proceed through the formation of germene and germane.

The formation of silene and silane from disilane suggests that the activated complex has a bridging hydro-

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gen atom similar to what exists in diborane. Since silicon has low-lying vacant "d" orbitals available for bonding, the apparent formation of the bridged intermediate in place of silicon–silicon bond fission seems reasonable. In ethane, with no low-lying vacant orbitals, the formation of such an intermediate must require a higher energy than simple carbon–carbon bond fission. It is interesting that methyl groups do not form bridged intermediates in hexamethyldisilane. Again, this is reminiscent of diborane where methyl groups do not form stable bridged compounds.

2. Silene Insertion Reactions.—The fact that silene insertion into methylsilane occurred without any scrambling of products strongly argues that the silene was in its singlet state. If it were triplet silene, hydrogen extraction would be expected followed by random radical recombinations. It is not known what the ground state of silene is, but singlet silene[9] has been observed spectroscopically from the flash photolysis of phenylsilane and from the flash discharge of silane.

If silene is in its singlet state in our reactions, then its selectivity toward insertion into silicon–hydrogen bonds greatly exceeds the selectivity observed for singlet carbene insertion into carbon–hydrogen bonds. This high selectivity could be due to the nature of silene compared to carbene or due to a greater polarizability of silicon–hydrogen bonds compared to carbon–hydrogen bonds.

Experimental Section

All pyrolysis experiments were carried out in flow systems previously described[1,2] which contained an automatic Toepler pump and a cold trap.

The silicon hydrides and ethylgermane-d_3 were prepared by the lithium aluminum hydride or deuteride reduction of the corresponding chloro compounds. Digermane was prepared from the electric discharge decomposition of germane. The purity of disilane, disilane-d_6, and digermane was verified by a mass spectrum which consisted only of ions with a heavy-atom skeleton—$E_2H(D)_{6-x}^+$ and $EH(D)_{3-x}^+$ ($E = Si, Ge$), whose infrared spectrum and vapor pressure demonstrated that silane or germane was absent. The purity of the methylsilanes and ethylgermane-d_3 was verified in the same manner. The infrared spectrum of disilane-d_6 and ethylgermane-d_3 demonstrated that only a few per cent of the silicon–hydrogen or germanium–hydrogen bonds were not deuterated.

1. Thermal Reaction of Si$_2$D$_6$ with CH$_3$SiH$_3$.—Disilane-d_6 (0.725 mmol) and methylsilane (1.88 mmol) were pyrolyzed at 375° for 30 hr. The product trap was at $-95°$ (toluene slush) where the vapor pressures were 12 and 83 mm, respectively. The products and reactants were separated by trap to trap distillations. The fraction passing a $-196°$ trap (0.02 mmol) was identified as D$_2$ by a mass spectrum.

The product condensed in the $-196°$ trap was silane-d_4 (0.372 mmol). The infrared spectrum demonstrated that only a trace of silane-d_3[10] was present while strong bands from silane-d_2[10] and -d_1[11] were not observed. The fraction condensed in the $-160°$ trap (1.88 mmol) was identified by an infrared spectrum and a mass spectrum as a mixture of methylsilane and disilane-d_6 in a 4.26:1 ratio. This ratio was determined from the mass spectrum which was compared to the mass spectrum of an analytical mixture. The fraction which condensed in the $-112°$ trap was

CH$_3$SiH$_2$SiD$_2$H (0.278 mmol) while the fraction condensed in the $-95°$ trap (0.005 mmol) was too small to identify completely but appeared to be CH$_3$SiH$_2$SiD$_2$H. The identification of CH$_3$SiH$_2$-SiD$_2$H was based on the following observations.

(1) The proton nmr spectrum (10%) in carbon tetrachloride consisted of three sets of resonances with δ values of 3.50, 3.00, and 0.17 ppm (external standard) with relative intensities 1.96:1.00:3.02. These were assigned to $-SiH_2$, D$_2$SiH$-$, and H$_3$C$-$. For methyldisilane (18% in cyclohexane) these resonances were observed at δ 3.83, 3.33, and 0.40 ppm.[12] The resonance at δ 3.50 ppm was complex as expected while that of the methyl group was a well-resolved triplet with $J_{H-H'} = 4.6$ cps compared to 4.2 cps reported for methyldisilane. The resonance at 3.00 ppm was a broadened triplet with $J_{H-H'} = 2.7$ cps compared to the well-resolved triplet in methyldisilane with $J_{H-H'} = 2.5$ cps. The values of J_{H-D} in SiH$_3$D and SiHD$_3$ are 0.427 and 0.412 cps[13] and it seems reasonable to expect similar values for J_{H-D} in CH$_3$SiH$_2$SiD$_2$H. If J_{H-D} in CH$_3$SiH$_2$SiD$_2$H is about 0.4 cps, the D$_2$SiH$-$ resonance would be a broadened triplet with an expected $J_{H-H'}$ of about 2.5 cps.

(2) The mass spectrum of methyldisilane has a strong parent peak at m/e 76 with much weaker peaks at m/e 77 and 78 due to ^{29}Si and ^{30}Si. As expected, our sample had a strong parent peak at m/e 78 and much weaker peaks at m/e 79 and 80 (see Table II).

				m/e				
	80	79	78	77	76	75	74	73
CH$_3$SiH$_2$SiD$_2$H	4.2	10	64	37	31	27	21	27
CH$_3$Si$_2$H$_6$[12]			2.7	5.6	32.1	22.7	25.7	13.5

(3) The infrared spectrum consisted of the following absorptions in cm^{-1}: 2970 (m), 2150 (vs), 1560 (s), 1270 (m), 940 (s), 885 (vs), 790 (vs), 715 (s), 665 (vs), 630 (m), and 555 (m). The intensity of the silicon–hydrogen stretching frequency was stronger than the silicon–deuterium stretching frequency which would be expected for CH$_3$SiH$_2$SiD$_2$H but not for CH$_3$SiH$_2$SiD$_3$.

2. Thermal Reaction of Si$_2$H$_6$ with (CH$_3$)$_2$SiH$_2$.—Disilane and dimethylsilane (1.23 mmol each) were pyrolyzed in a flow system at 412° for 24 hr. The product trap was at $-78°$ (Dry Ice-2-propanol) where the vapor pressures were 28 and 30 mm, respectively. The products were separated by trap to trap distillations. Hydrogen (0.30 mmol) passed the $-196°$ trap. The fraction condensed in the $-196°$ trap was identified as silane (0.60 mmol) by an infrared spectrum. The fraction condensed in the $-160°$ trap was dimethylsilane (0.84 mmol). The fraction condensed in the $-78°$ trap (0.66 mmol) was a mixture of 1,1-dimethylsilane and trisilane in a ratio of 1.44:1. This mixture was identified by an infrared spectrum which contained only those bands reported for 1,1-dimethyldisilane[14] and trisilane[15] and an nmr spectrum which was a composition of that reported for 1,1-dimethyldisilane[14] and trisilane.[16] The ratio was determined from the relative intensities of the silicon–hydrogen absorptions and the carbon–hydrogen absorptions. The fraction condensed in the $-45°$ trap was a trace of tetrasilane. In similar experiments the ratio of 1,1-dimethyldisilane to trisilane was 2.1 and 2.8 for pyrolysis at 410 and 400°, respectively.

In a separate control experiment, dimethylsilane was pyrolyzed in the same flow system at 420° for 24 hr with the product trap at $-78°$ without any decomposition.

3. Thermal Reaction of Si$_2$H$_6$ with ClSiH$_3$.—The pyrolysis of a disilane–chlorosilane mixture was conducted at 400° for 7 hr with the product trap held at $-95°$. The products were silane,

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trisilane, and some dichlorosilane. Chlorodisilane[17] was not obtained.

4. Pyrolysis of Digermane.—The pyrolysis of digermane was examined in the same flow apparatus as previously described.[1] The product trap was set at $-45°$. Germane was found in the $-196°$ trap, digermane was found in the $-130°$ trap having passed a $-95°$ trap, and trigermane passed a $-36°$ trap and condensed in a $-63°$ trap. The trigermane was identified by a mass spectrum which contained only peaks from the ions of heavy-atom skeletons, Ge_3^+ (25.5%), Ge_2^+ (64.3%), and Ge^+ (10.2%). The infrared spectrum was identical with that reported by MacKay and Robinson[18] while the strong 812-cm^{-1} absorption from germane[19] and the strong 750-cm^{-1} absorption from digermane[20] were absent.

5. Thermal Reaction of Ge_2H_6 with $C_2H_5GeD_3$.—Digermane (0.41 mmol) and ethylgermane-d_3 (1.80 mmol) were pyrolyzed at $280°$ for 24 hr with the product trap set at $-63°$. Under the conditions, very small quantities of products were obtained. The product fraction condensed in the $-196°$ trap was identified by infrared and mass spectra to be germane. The strong 706-cm^{-1} band of germane-d_1[21] was absent from the infrared spectrum. The fraction condensed at $-95°$ was the unreacted ethylgermane-d_3. The fraction which passed the $-45°$ trap and condensed in the $-63°$ was a mixture of ethyldigermanes and trigermane. The mass spectrum of this mixture consisted of ions with the following heavy-atom skeletons: Ge_3^+ (7.2), $C_2Ge_2^+$ (22.2), Ge_2^+ (100), C_2Ge^+ (68.9), and Ge^+ (62.2). No diethyldigermanes were observed.

In a control experiment, no products were observed from the 5-hr pyrolysis of ethylgermane-d_3 at $320°$ with the trap set at $-54°$, which gave a higher reaction pressure than with the bath set at $-63°$.

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The Direct Synthesis of Organic Derivatives of Silicon Using Nonhalogenated Organic Compounds

BY W. E. NEWTON[1] AND E. G. ROCHOW

Some trialkoxysilanes, $(RO)_3SiH$ ($R = CH_3$, C_2H_5, n-C_3H_7, i-C_4H_9), and tetraalkoxysilanes were prepared directly by the reactions of the appropriate primary alcohol with a silicon–copper contact mixture. Similar attempts with secondary and tertiary alcohols, ethers, and secondary amines gave no silicon-containing products.

Introduction

With the discovery in 1940 of the direct synthesis, the problems of large-scale production of organosilicon halides were solved, in large part. The first paper described the high-temperature reaction of chloromethane with elemental silicon, in the presence of a copper catalyst in a flow system, from which mixtures of methylchlorosilanes were obtained.[2] This process was discovered independently and later by two other chemists.[3] Since that time, much effort has been spent on attempts to elucidate the mechanism of this process and also to extend its application. The scope of the direct synthesis has now been successfully widened to include the reactions of: (a) other aliphatic chloro compounds, *e.g.*, *n*-propyl, isopropyl, etc.;[4-8] (b) aromatic halo compounds, *e.g.*, bromobenzene and chlorobenzene;[9-11] (c) olefinic chloro compounds, *e.g.*, allyl chloride;[12-15] (d) polyfunctional compounds, *e.g.*, dichloroalkanes;[16-21] (e) silicon-containing aliphatic chlorides, *e.g.*, γ-chloropropylmethyldichlorosilane;[22-28] (f) other elements, *e.g.*, germanium, tin, thallium,

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