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Reaction of Silyl Radical and Silylene with Acetylene and Application of Orbital Symmetry to the Pyrolysis of Silane and Disilane

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The thermal decomposition of SiH_4 and Si_2H_6 was examined in the presence of C_2H_2. The product from reaction of SiH_2 (generated from Si_2H_6) with C_2H_2 was found to be $H_3SiC{\equiv}CH$. The absence of this product, near zero reaction time, in the SiH_4–C_2H_2 pyrolysis system suggests that SiH_2 is not the dominant radical species in the SiH_4 pyrolysis. The products in the SiH_4–C_2H_2 pyrolysis system were consistent with silyl radicals as the dominant silicon radical species. The thermal decomposition of SiH_4 to SiH_2 and H_2 was examined by orbital symmetry considerations. The least motion path must generate a high-energy $^1SiH_2$ to be allowed, while another path yielding ground state $^1SiH_2$ adds a strain energy to the activation energy. These results are consistent with the apparent absence of SiH_2 from the thermolysis of SiH_4.

Introduction

Examinations of the pyrolysis of SiH_4 and related studies have recently been carried out by various groups.[1-3] At this time, no concensus exists concerning the mechanism of the pyrolysis of SiH_4. A detailed kinetic study of the thermal decomposition of SiH_4 was carried out by Purnell and Walsh.[1] The decomposition rate was found to be independent of the surface to volume ratio over a silicon mirror (result confirmed in our laboratory). Purnell and Walsh determined that the initial silane decomposition could be represented by

$$\text{rate} = 10^{(15.2-(55.9/2.3RT))}(\text{SiH}_4)^{3/2}\ \text{mol/(l. sec)} \qquad (1)$$

Purnell and Walsh[1] proposed the following two mechanisms which would be consistent with their results: mechanism A, molecular hydrogen elimination

$$SiH_4 \rightarrow SiH_2 + H_2 \qquad (2)$$

$$SiH_2 + SiH_4 \rightarrow Si_2H_6 \qquad (3)$$

mechanism B, homolytic Si–H bond rupture

$$SiH_4 \rightarrow SiH_3 + H \qquad (4)$$

$$H + SiH_4 \rightarrow SiH_3 + H_2 \qquad (5)$$

$$SiH_3 + SiH_4 \rightarrow Si_2H_6 + H \qquad (6)$$

$$2SiH_3 \rightarrow Si_2H_6 \qquad (7)$$

Purnell and Walsh favored mechanism A but could not rule out mechanism B. In an attempt to demonstrate that only mechanism A was operative, the pyrolyses of equimolar SiH_4–SiD_4 mixtures were examined in a recirculating flow system with a cold trap which removed the product disilanes from the stream.[2] If SiH_4 decomposed solely by mechanism A, the hydrogen fraction produced from such an experiment should have consisted of only H_2 and D_2. The hydrogen fraction contained 31% HD which suggested that mechanism B was also important.

Assuming mechanism B to be predominant, one calculates that the *A* factor for the SiH_4 pyrolysis should be between 10^{12} and 10^{13} which does not agree with the $10^{15.2}$ experimental value.

Recently, John and Purnell have obtained equilibrium constants for reactions of SiH_3 radicals[3] (eq 8, 9). These authors have suggested that the equilibrium data argue in favor of reaction 2 as the primary decomposition mode of SiH_4 and in favor of the SiH_2 diradical as the dominant radical species in SiH_4 decompositions.

$$SiH_3 + H \rightleftarrows SiH_2 + H_2 \quad K_8 = 10^{15.9} \qquad (8)$$

$$2SiH_3 \rightleftarrows SiH_2 + SiH_4 \quad K_9 = 10^{11.3} \qquad (9)$$

The thermal reaction of SiH_4 and acetylene has been examined by White and Rochow.[4] This pyrolysis was carried out in a flow system at 450–510° with a −78° cold trap. The major product was ethynyldivinylsilane with lighter unidentified products containing ethynyl and vinyl groups. These authors were unable to account for the presence of ethynyl groups bonded to silicon.

At this time, two important questions concerning the monosilane pyrolysis remain unanswered. First, what is the dominant reactive intermediate (SiH_3 radical, SiH_2, or both), and second, what is the overall homogeneous mechanism?

In this paper we report our results on the decompositions of SiH_4 and of Si_2H_6 in the presence of C_2H_2. These investigations should allow us to determine the product from reaction of SiH_2 (generated from Si_2H_6) with C_2H_2 and, if this product is absent in the SiH_4–C_2H_2 thermolysis, to eliminate SiH_2 as the dominant radical species in the SiH_4 decomposition.

The reaction of silylenes with acetylenes has been examined in some detail but continues to be of interest in organosilicon chemistry.[5]

Results

I. Application of Orbital Symmetry to the Pyrolysis of Silane and Disilane. Recently, Pearson has discussed the application of orbital symmetry rules to unimolecular reactions.[6] It was concluded that there are no orbital symmetry barriers to reactions of molecules decomposing into a radical and an atom such as the decomposition of SiH_4 into SiH_3 radicals and H atoms (eq 4). However, reactions in which bonds are broken and made in a concerted process (eq 2) can be restricted by orbital symmetry. In the concerted decomposition of SiH_4 into SiH_2 and H_2 (eq 2), the bonds broken and formed must have the same symmetry.[6] The symmetry of the bonds to be broken is C_{2v}. For SiH_4, the silicon–hydrogen bonds (C_{2v} symmetry) have the symmetries $2a_1$, b_1, and b_2 while the hydrogen product has a_1 symmetry. For reaction 2 to be symmetry allowed and follow the least motion path (retain C_{2v} symmetry), the product $^1SiH_2$ must be $a_1^2b_2^2a_1^0b_1^2$ ($^1A_1^*$) while the lowest SiH_2 singlet is $a_1^2b_2^2a_1^2b_1^0$ ($^1A_1$).[7]

The transition of $^1A_1$ to $^1B_1$ ($a_1^2b_2^2a_1^1b_1^1$) has been observed by Dubois[8] in the region 6500–4800 Å. The difference in energy between the a_1 and b_1 levels is at least $43 + s_a$ kcal/mol where s_a is the electron repulsion energy between electrons in the nonbonding a_1 orbital.

The minimum value for the activation energy of reaction 2 (with the back-activation energy zero) forming the lowest energy singlet silylene ($^1A_1$) would be the heat of reaction (~53 kcal/mol),[9] while the minimum activation energy forming the allowed $^1A_1^*$ state would be $139 + s_a + s_b$ kcal/mol where s_b is the electron repulsion energy between electrons in the b_1 orbital. Since the experimental value is 55.9 kcal/mol,[1] it would appear that reaction 2 cannot be an important process in the pyrolysis of monosilane if reaction 2 follows the least motion path.

For reaction 2, the C_s reaction path forming the lowest energy $^1SiH_2$ ($^1A_1$) is allowed but involves considerable strain energy. This path (described as the back-reaction of SiH_2 with H_2) consists of H_2 attack (HOMO)[10] upon the vacant b_1 orbital (LUMO)[10] of the $^1A_1$ SiH_2 state where this orbital is perpendicular to the plane of the silicon–hydrogen bonds and the filled nonbonding a_1 orbital. The strain energy is that required to convert this configuration into SiH_4 (T_d). It is difficult to estimate this energy, but it should be significant. Since the experimental activation energy and the minimum value for the activation energy (from ground-state thermochemistry) differ by only 3 kcal/mol, the incorporation of the strain energy would imply that this path to SiH_2 and H_2 is probably not operative.

It has been established that over a silicon mirror, Si_2H_6 decomposes thermally as described by reaction 10.[11,12]

$$Si_2H_6 \rightarrow SiH_2 + SiH_4 \qquad (10)$$

$$SiH_2 + Si_2H_6 \rightarrow Si_3H_8 \qquad (11)$$

The multiplicity of the SiH_2 generated in the Si_2H_6 pyrolysis has not been established. However, the absence of H–D scrambling in the Si_2D_6–CH_3SiH_3 reaction[11,12] strongly suggests that singlet SiH_2 was the reactive intermediate. It has now been established that SiH_2 has a singlet ground state.[13]

It can be demonstrated that the concerted decomposition of Si_2H_6 into SiH_4 and the lowest energy $^1SiH_2$ ($^1A_1$) is symmetry allowed. The point group of the bonds being broken is C_s or C_1 and their symmetry is a_1. Thus the bonds formed must be a_1. In SiH_4, there are silicon–hydrogen bonds of a_1 symmetry, and the nonbonding electron pair in $^1SiH_2$ which generates the $^1A_1$ state is of symmetry a_1.

II. Thermal Reaction of Disilane with Acetylene. The pyrolysis of Si_2H_6 in the presence of C_2H_2 was carried out at 370° for 4 hr in a recirculating flow system with a –95° cold trap present. Every 15 min, the SiH_4 produced was removed to eliminate the secondary decomposition of SiH_4. Under these conditions, the volatile products were SiH_4, $HC{\equiv}CSiH_3$, Si_3H_8, ethynylvinylsilane, and ethynyldivinylsilane. Vinyl- and divinylsilane were not observed. When this reaction was carried out without the removal of SiH_4 every 15 min, both vinyl- and divinylsilane were observed as products. The above results demonstrate that SiH_2 reacts with C_2H_2 to form ethynylsilane (eq 12) and suggest that the vinylsilane and divinylsilane are produced from species generated from the SiH_4 decomposition. The total reaction will be discussed later.

$$SiH_2 + C_2H_2 \rightarrow HC{\equiv}CSiH_3 \qquad (12)$$

III. Thermal Reaction of Silane with Acetylene. The pyrolyses of SiH_4 in the presence of C_2H_2 were carried out between 420 and 440° in a recirculating flow system with a –119° cold trap present. The volatile products were Si_2H_6, vinylsilane, divinylsilane, ethynylsilane, ethynylvinylsilane, and ethynyldivinylsilane. However, the product ratios were very dependent on the configuration of the thermal zone. The diameter of the entry to the thermal zone was 10 mm. In thermal zone A (diameter 24 mm, with the longest retention time in the thermal zone) the ratio of vinylsilane to ethynylsilane was about 1/1. This ratio increased to 3/1 when the diameter was decreased to 10 mm. The vinylsilane to ethynylsilane ratio increased to 20/1 or more when the reaction zone was shortened from 29 to 10 cm retaining the 10-mm diameter. These results imply that at near zero reaction time, no ethynylsilane would be produced. We conclude that ethynylsilane is a secondary product in the SiH_4–C_2H_2 thermal reaction and thus $^1SiH_2$ is not present in the pyrolysis of SiH_4 except as a secondary product from the decomposition of Si_2H_6 which is generated in the SiH_4 pyrolysis.

Discussion

The use of orbital symmetry applied to reaction 2 ($SiH_4 \rightarrow SiH_2 + H_2$) leads to the conclusion that this reaction is probably not significant in the monosilane pyrolysis. It had been suggested by John and Purnell[3] that even if $^1SiH_2$ were not produced in the initial step in the SiH_4 pyrolysis, it would be generated by the disproportionation reaction

$$2SiH_3 \rightarrow SiH_2 + SiH_4 \qquad (13)$$

It should be pointed out that reaction 13 is a bimolecular reaction involving two radicals. Even if this reaction is very favored, the low concentrations of the radical could render this reaction unimportant.

Our results from the pyrolysis of both SiH_4 and Si_2H_6 in the presence of C_2H_2 have led to the conclusion that $^1SiH_2$ is not present from the SiH_4 pyrolysis except as a product from the decomposition of Si_2H_6, which was generated as a product in the SiH_4 pyrolysis.

The products from the pyrolysis of SiH_4 in the presence of C_2H_2, other than silicon hydrides from the neat pyrolysis and secondary ethynylsilanes due to Si_2H_6 decomposition, were vinyl- and divinylsilane. These vinylsilanes can be accounted for by reaction of silyl radicals with C_2H_2 as in eq 14–18.

$$\cdot SiH_3 + C_2H_2 \rightarrow H_3SiCH{=}\dot{C}H \qquad (14)$$

$$H_3SiCH{=}\dot{C}H \xrightarrow{\text{H abstraction}} H_3SiC_2H_3 \qquad (15)$$

$$H_3SiC_2H_3 \rightarrow H_2\dot{S}iC_2H_3 + H\cdot \qquad (16)$$

$$H_2\dot{S}iC_2H_3 + C_2H_2 \rightarrow C_2H_3SiH_2CH{=}\dot{C}H \qquad (17)$$

$$C_2H_3SiH_2CH{=}\dot{C}H \xrightarrow{\text{H abstraction}} (C_2H_3)_2SiH_2 \qquad (18)$$

We have demonstrated that ethynylsilane was the product of the reaction of SiH_2 (generated from Si_2H_6) with C_2H_2 (eq 12). The formation of the ethynylsilanes can be accounted for by reactions 19–26. These sequences explain our results from the separate pyrolyses of SiH_4 and Si_2H_6 with C_2H_2 and

$$Si_2H_6 \rightarrow SiH_2 + SiH_4 \qquad (19)$$

$$SiH_2 + C_2H_2 \rightarrow H_3SiC_2H \qquad (20)$$

$$H_3SiC_2H \rightarrow H_2\dot{S}iC_2H + H \qquad (21)$$

$$H_2\dot{S}iC_2H + C_2H_2 \rightarrow HC_2SiH_2CH{=}\dot{C}H \qquad (22)$$

$$HC_2SiH_2CH{=}\dot{C}H \xrightarrow{\text{H abstraction}} HC_2SiH_2C_2H_3 \qquad (23)$$

$$HC_2SiH_2C_2H_3 \rightarrow HC_2\dot{S}iHC_2H_3 + H \qquad (24)$$

$$HC_2\dot{S}iHC_2H_3 + C_2H_2 \rightarrow (HC_2)(C_2H_3)SiHCH{=}\dot{C}H \qquad (25)$$

$$(HC_2)(C_2H_3)SiHCH{=}\dot{C}H \xrightarrow{\text{H abstraction}} (HC_2)(C_2H_3)_2SiH \qquad (26)$$

those of White and Rochow[4] which were in fact the joint pyrolysis of SiH_4 and Si_2H_6 in the presence of C_2H_2.

In summary, we conclude that the dominant reactive intermediate in the monosilane pyrolysis is the silyl radical. We cannot resolve the mechanism but conclude the following points about the silane pyrolysis: (i) the reactive species is the SiH_3 radical; (ii) a chain mechanism is probably operative; (iii) the pyrolysis is apparently homogeneous over a silicon mirror; (iiii) the most likely initial step is homolytic silicon–hydrogen rupture yielding SiH_3 radicals and H atoms followed by H atom reaction with SiH_4 forming H_2 and SiH_3 radicals (eq 4 and 5).

The formation of $H_3SiC{\equiv}CH$ from reaction of SiH_2 and $HC{\equiv}CH$ could be accounted for either by direct insertion of SiH_2 into a carbon–hydrogen bond or by addition to C_2H_2 to form silacyclopropene. The insertion of SiH_2 into the carbon–hydrogen bond in CH_3SiH_3 cannot compete with insertion into silicon–hydrogen bonds in CH_3SiH_3 or Si_2H_6[11,12] while SiH_2 addition to butadiene (presumed to be via addition to a double bond) can compete with insertion into silicon–hydrogen bonds in Si_2H_6.[14] Therefore, we suggest that SiH_2 reacts with C_2H_2 to form silacyclopropene. The rupture of a silicon–carbon bond would form $H_2\dot{Si}CH{=}\dot{C}H$ and H atom migration would produce the observed product, $H_3SiC{\equiv}CH$.

Experimental Section

All experiments were performed in a standard vacuum system. Separations were carried out by trap to trap distillation through low-temperature slush baths monitored with a low-temperature thermometer. Infrared spectra were obtained in a 10-cm gas cell, fitted with KBr windows, on a Perkin-Elmer Model 337 spectrophotometer. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6E spectrometer. Small quantities of the products were analyzed and/or separated by glpc. Separations were made on a 5 m × 6 mm column containing 20% squalene on 60–80 mesh aeropac.

Pyrolyses of silane and disilane were carried out in one of three thermal zones. The inner diameters and lengths of the thermal zones were as follows: A, 24 mm × 26 cm; B, 10 mm × 29 cm; C, 10 mm × 10 cm. Each of the thermal zones was wrapped with a heating tape and insulated with asbestos tape. A well was provided for a thermometer. An automatic Toepler pump for cycling reactants was attached following the thermal zone section. A "U" trap was used to trap out heavy products and to set the vapor pressure of the reactants.

Silane and disilane were prepared by the reduction of $SiCl_4$ and Si_2Cl_6 with $LiAlH_4$. Acetylene was prepared by the hydrolysis of Ca_2C. The purity of these reagents was checked by infrared and mass spectroscopies.

Identification of Products. The volatile products (in addition to SiH_4) from the pyrolysis of Si_2H_6 in the presence of C_2H_2 were separated into the following fractions by trap to trap distillations: (a) disilane and ethynylsilane (pass −95°, stop −130°); (b) trisilane and ethynylvinylsilane (pass −78°, stop −95°); (c) ethynyldivinylsilane (pass −23°, stop −36°).

The mass spectrum of fraction a had peaks ranging from *m/e* 64 to *m/e* 54, with major peaks at *m/e* 60 and 56. There were no peaks above *m/e* 64 nor were there any below *m/e* 54 (at 15 V). The parent peak for ethynylsilane is at *m/e* 56 with p − 1 and p − 2 peaks at *m/e* 55 and 54. Disilane has mass spectral peaks from *m/e* 64 to *m/e* 56 with the major peak at *m/e* 60. The infrared spectrum of fraction a showed only the following absorptions: acetylenic C—H (stretching) at 3320 cm^{-1}, Si—H (stretching) at 2150 cm^{-1}, C≡C (stretching) at 2050 cm^{-1}, Si—H (bending) between 950 and 840 cm^{-1}, and acetylenic C—H (bending) at 685 cm^{-1}. Since disilane and ethynylsilane could not be separated on the gas chromatograph, the above spectra were used to identify these compounds. The mass spectrum was consistent only with compounds containing two silicon atoms, one silicon atom and two carbon atoms, or four carbon atoms. The only compounds of the above type that were consistent with the observed infrared spectrum were ethynylsilane, disilane, and butadiyne. Butadiyne, of mol wt 50, was eliminated by the mass spectrum and also by its low volatility. In addition, the infrared spectrum of the mixture was a composite of those for disilane and ethynylsilane.[15]

Fraction b, containing ethynylvinylsilane and trisilane, was separated by glpc. The mass spectrum of ethynylvinylsilane at 15 V showed the expected parent peak at *m/e* 82, as well as p − 1 and p − 2 peaks at *m/e* 81 and 80, respectively. There were no peaks above *m/e* 82 nor were there any below *m/e* 80. At 70 V, the mass spectrum showed fragment peaks at *m/e* 56, due to the loss of an ethynyl group from the p − 1 ion, and *m/e* 54, due to the loss of a vinyl group from the same ion. The infrared spectrum of ethynylvinylsilane contains absorptions assignable to both ethynyl and vinyl groups (cm^{-1}): 3310 (s), 3060 (m), 2960 (m), 2160 (vs), 1980 (s), 1550 (m), 1400 (m), 1340 (m), 1012 (m), 950 (s), 860 (vs), 790 (s), 680 (vs), 630 (s).

The mass spectrum of trisilane at 15 V contained only peaks ranging from *m/e* 94 to *m/e* 84. At 70 V, the spectrum showed a fragment peak at *m/e* 60, which was due to the loss of a silyl group from the p − 2 ion. The infrared spectrum was that of trisilane.[16]

Identification of ethynyldivinylsilane, fraction c, was made by its mass spectrum, infrared spectrum, and NMR spectrum. The mass spectrum at 15 V showed a parent peak at *m/e* 108 and a p − 1 peak at *m/e* 107. There were fragment peaks at *m/e* 82 (loss of ethynyl group from the p − 1 ion) and *m/e* 80 (loss of a vinyl group from the same ion) at 70 V. The infrared spectrum contained absorptions due to vinyl and ethynyl groups (cm^{-1}): 3320 (s), 3060 (s), 2960 (s), 2150 (vs), 2050 (s), 1600 (m), 1410 (s), 1350 (m), 1010 (s), 960 (s), 860 (vs), 810 (vs), 710 (m), 680 (vs), 630 (m). The NMR spectrum was obtained in acetone-d_6 with TMS as the external standard. The NMR spectrum showed a sharp peak at δ 5.48 ($HC{=}CH_2$) and broad peaks at δ 3.82 (Si—H) and δ 2.33 (≡C—H). The relative intensities of these peaks were 5.6:1.0:1.05 (calculated 6:1:1).

The pyrolysis of SiH_4 in the presence of C_2H_2 produced the following fractions which were separated by trap to trap distillations: (a) disilane, ethynylsilane, and vinylsilane (pass −95°, stop −130°); (b) ethynylvinylsilane and divinylsilane (pass −78°, stop −95°); (c) ethynyldivinylsilane (pass −23°, stop −36°).

Fraction a could not be separated by glpc. The mass spectrum at 15 V showed peaks ranging from *m/e* 64 to *m/e* 54 with major peaks at *m/e* 60 (disilane), *m/e* 58 (vinylsilane), and *m/e* 56 (ethynylsilane). There were no peaks above *m/e* 64 nor were there any below *m/e* 54. The infrared spectrum of fraction a was a composite of those for disilane, vinylsilane,[17] and ethynylsilane.[15] Vinylsilane has infrared absorptions at 3050–2950 and at 1600 cm^{-1} which are not present in Si_2H_6 or $HC{\equiv}CSiH_3$. The absence of $C_2H_5SiH_3$ and CH_3SiH_3 cannot be clearly demonstrated by the mass spectrum of this mixture. Methylsilane would have been observed in the glpc spectrum if it were present. Ethylsilane would have been detected in the infrared spectrum at 2950 cm^{-1} (very strong) if it had been present.

Fraction b was separated on the gas chromatograph. This separation gave ethynylvinylsilane (identified above) and divinylsilane which has a mass spectrum at 15 V with the expected parent peak at *m/e* 84, as well as a p − 1 peak at *m/e* 83 and a p − 2 peak at *m/e* 82. There were no absorption peaks below *m/e* 82. The infrared absorptions for divinylsilane were due to vinyl groups but were not due to the ethynyl groups (cm^{-1}): 3120 (m), 3030 (m), 2140 (vs), 1560 (w), 1380 (m), 1140 (m), 1010 (m), 940 (s), 860 (vs), 730 (m), 620 (m). The identification of ethynyldivinylsilane is described above (fraction c).

Analysis of Products. The analysis of mixtures of Si_2H_6, C_2HSiH_3, and $C_2H_3SiH_3$ was obtained from infrared spectra of these mixtures. From neat samples the extinction coefficients for Si_2H_6 and $C_2H_3SiH_3$ were found to be 0.016 and 0.0051 $mmHg^{-1}$ cm^{-1} at 2150 and 710 cm^{-1}, respectively. The extinction coefficient for ethynylsilane at 685 cm^{-1} was determined to be 0.0069 $mmHg^{-1}$ cm^{-1} from a mixture of Si_2H_6 and C_2HSiH_3 where the total pressure was measured and the partial pressure of Si_2H_6 was obtained from its infrared absorbance.

Pyrolysis of Si_2H_6 in the Presence of C_2H_2. The pyrolysis of Si_2H_6 in the presence of C_2H_2 was carried out in thermal zone A. In a typical experiment, Si_2H_6 (7.3 mmol) and C_2H_2 (10.9 mmol) were pyrolyzed at 370° for 4 hr with the "U" trap cooled to −95°. Every 15 min, the pyrolysis was stopped by cooling the cold trap to −196°. The products were distilled through a −160° trap to remove any SiH_4 which was formed. The reactants and other products were recondensed into the cold trap and the pyrolysis was continued. After 4 hr of reaction, the products were separated by trap to trap distillation. The total amount of SiH_4 produced was 2.45 mmol. The fraction condensed at −160° was C_2H_2 (6.8 mmol) while the fraction condensed at −130° contained only Si_2H_6 and ethynylsilane. Infrared spectral analysis of this mixture demonstrated that it consisted of 0.87 mmol of C_2HSiH_3 and 2.17 mmol of Si_2H_6. The fraction condensed at −95° (1.1 mmol) was a mixture of Si_3H_8 and ethynylvinylsilane while the fraction condensed at −78° was ethynyldivinylsilane (0.36 mmol). No vinylsilanes were detected.

In a similar experiment Si_2H_6 (3.36 mmol) and C_2H_3 (9.2 mmol) were pyrolyzed under the same conditions *without* SiH_4 removal. A small amount of H_2 was produced. The other products were separated by trap to trap distillation. The fraction condensed at −196° was SiH_4 (2.1 mmol) while that condensed at −160° was C_2H_2 (1.9 mmol). The fraction condensed at −130° (0.15 mmol) was a mixture of Si_2H_6, ethynylsilane, and vinylsilane. Condensed at −95° was a 1.62-mmol mixture of Si_3H_8, divinylsilane, and ethynylvinylsilane. Ethynyldivinylsilane (0.18 mmol) was condensed at −36°.

Pyrolysis of SiH_4 in the Presence of C_2H_2. 1. Reaction in Thermal Zone A (24 mm × 26 cm). Silane (4.43 mmol) and C_2H_2 (8.55 mmol) were pyrolyzed at 420° for 2 hr with a −119° bath on the "U" trap. After the reaction, 3.06 mmol of SiH_4 remained (condensed at −196°). The fraction condensed at −160° was C_2H_2 (7.7 mmol). The fraction condensed at −130° having passed a −95° trap (1.0 mmol) was analyzed by infrared spectroscopy to contain Si_2H_6, vinylsilane, and ethynylsilane in an approximate ratio of 1:1:1.

2. Reaction in Thermal Zone B (10 mm × 29 cm). Silane (5.75 mmol) and C_2H_2 (5.8 mmol) were pyrolyzed at 420° for 2 hr with the −119° cold trap. With similar separations, SiH_4 (5.3 mmol) and C_2H_2 (5.2 mmol) were found unreacted. The fraction (0.42 mmol) condensed at −130° (pass −95°) was analyzed by an infrared spectrum to contain Si_2H_6, vinylsilane, and ethynylsilane in an approximate ratio of 3:3:1.

3. Reaction in Thermal Zone C (10 mm × 10 cm). Silane (5.25 mmol) and C_2H_2 (5.73 mmol) were pyrolyzed at 440° for 2 hr. The reactants found after the pyrolysis were SiH_4 (5.16 mmol) and C_2H_2 (5.66 mmol). The product fraction (0.2 mmol) condensed at −130° (pass −95°) contained Si_2H_6, vinylsilane, and ethynylsilane in an approximate ratio of 15:50:1 as analyzed by infrared spectroscopy. In a similar experiment this last ratio was found to be approximately 12:20:1.

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Registry No. SiH_4, 7803-62-5; Si_2H_6, 1590-87-0; SiH_2, 13825-90-6; SiH_3, 13765-44-1; $HC{\equiv}CSiH_3$, 1066-27-9; C_2H_2, 74-86-2.

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Microwave Spectrum and Dipole Moment of Methyldifluorophosphine–Borane[1,2]

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The microwave spectra of $CH_3PF_2{\cdot}^{11}BH_3$, $CH_3PF_2{\cdot}^{10}BH_3$, $CH_3PF_2{\cdot}^{11}BD_3$, and $CH_3PF_2{\cdot}^{10}BD_3$ have been assigned. Stark effect measurements gave the following values for the dipole moment and its components: $\mu_a = 3.52$ (5) D, $\mu_b = 1.76$ (5) D, $\mu_c = 0.0$ D, and $\mu = 3.94$ (5) D. The absence of resolvable internal rotation splittings in the ground state yields lower limits of about 2000 cal/mol for the barriers to both CH_3 and BH_3 group internal rotation. By judicious transfer of structural parameters from related molecules r(P–B) was estimated to be 1.84 ± 0.02 Å.

Introduction

Compounds containing P–B dative bonds have recently received considerable attention.[3-9] One particularly interesting facet of their properties is the large variation in their stabilities with respect to dissociation: $H_3P{\cdot}BH_3$[6] is completely dissociated at 273 K, and $F_3P{\cdot}BH_3$[3] is extensively dissociated at the same temperature, whereas $(CH_3)_3P{\cdot}BH_3$[5] may be heated to about 473 K without appreciable dissociation. Attempts to correlate stability with the length of the P–B bond have met with little success; the values for this parameter in the above compounds are 1.937 (5), 1.836 (12), and 1.901 (7) Å, respectively.

The preparation of methyldifluorophosphine–borane, $CH_3PF_2{\cdot}BH_3$, has been recently reported by Foester and Cohn.[10] They studied a series of base displacement reactions and found that CH_3PF_2 was surprisingly basic toward BH_3, and they suggested that an unexpected structural deformation upon adduct formation might be the explanation of this observation. We have recently reported a study of the microwave spectrum of CH_3PF_2[11] as a part of our interest in difluorophosphine derivatives.[12-15] As a continuation of this work, and in an attempt to investigate the speculation of Foester and Cohn about the structure of the complex, we have obtained the microwave spectrum of $CH_3PF_2{\cdot}BH_3$.

Experimental Section

The samples of $CH_3PF_2{\cdot}BH_3$ and $CH_3PF_2{\cdot}BD_3$ were obtained from Dr. K. Cohn. The spectra were recorded at about 220 K and at room temperature with an Hewlett-Packard 8460A microwave spectrometer in the 18–40-GHz frequency region. The spectra of the ^{11}B and ^{10}B isotopic species were assigned in their natural isotopic abundance. The estimated errors in the frequency measurements are ±0.1 MHz.

Spectrum

A projection of the molecule in the *ab* plane is shown in Figure 1. A trial set of rotational constants was calculated from a structure obtained by selection of structural parameters