Infrared Laser Photochemistry of SiH₄–CH₃Cl Mixtures

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By use of a pulsed CO₂ TEA laser at 944.19 cm⁻¹ and fluences in the range of 0.49–0.71 J/cm², the infrared photochemistry of SiH₄-CH₃Cl mixtures has been studied in a pressure range of 50-100 Torr and over a temperature range of 295-428 K. The gaseous products observed are H_2 , CH_4 , Si_2H_6 , and SiH_3Cl , with trace amounts of Si_3H_8 and perhaps CH_3SiH_2Cl . As is usual in silane decomposition, a brown solid product containing silicon, hydrogen, and, under some conditions, chlorine was also produced. The photochemical conversion is best described by initial decomposition of SiH₄ to SiH₂ and H₂ followed by competition of SiH_4 and CH_3Cl for SiH_2 molecules. The production of CH_4 is believed to occur via the decomposition of highly energized CH₃SiH₂Cl* (formed by SiH₂ insertion into the C-Cl bond of CH₃Cl), yielding CH₄ and SiHCl as products. SiH₃Cl is then formed by the secondary reaction of SiHCl with SiH₄. Studies of the temperature dependence of the rates of competing reactions suggest that the activation energy for insertion of SiH2 into the C-Cl bond of CH3Cl is, within experimental error, equal to that for SiH₂ insertion into the Si-H bond of SiH₄.

Introduction

Studies of the infrared laser induced decomposition of pure SiH_4 - SiF_4^3 mixtures and SiH_4 - PH_3^4 mixtures have shown that the predominant primary photodecomposition is to SiH₂ and H₂. Similarly, the homogeneous thermal decomposition of silane⁵ also produces SiH_2 and H_2 . It therefore appears that the infrared laser induced decomposition of SiH₄ is a good source of SiH₂ for study of the reactions of these labile molecules with other substances.

Silvlenes are known to insert into Si-H bonds.^{1,3,5-19} There is evidence that silylenes will insert into Si–OR bonds, 19,20 Si–Cl bonds of halosilanes,^{10,11} O-H bonds of alcohols^{9,19} and water,¹⁹ and N-H bonds of primary and secondary amines.¹⁹ Insertion into the strong H-H bond of hydrogen has also been reported, and kinetic studies have been carried out.¹⁵⁻¹⁸ Kinetic studies of the insertion reactions of SiH₂ into the P-H bond⁴ of PH₃, the Ge-H bond²¹ of GeH₄, and the H-Cl bond²² of HCl have been

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carried out previously in our laboratory.

It is of interest to determine whether SiH₂ will insert into the C-Cl bond of chloromethane and, if so, to learn what the characteristics of this reaction are. Therefore, we have undertaken a study of the infrared laser photochemistry of SiH₄-CH₃Cl mixtures, and in this paper report our results.

Experimental Section

The infrared laser photodecompositions were carried out in a cylindrical stainless steel cell having a diameter of 3.45 cm and a length of 15.5 cm. A pinhole leak, located in the wall of the photolysis cell, lead directly into the ionization source of a time-of-flight mass spectrometer. The pinhole was covered with a tube packed with glass wool to prevent the plugging of the pinhole by the fine powder particles usually associated with decomposition of silane. The ends of the photolysis cell were fitted with NaCl windows sealed in place by O-ring supports. The cell was mounted so that the laser beam was perpendicular to the axis of the time-of-flight mass spectrometer.

The source of infrared radiation was a CO2 TEA laser (Lumonics Research Ltd. Model 103-2) pulsed at a frequency of 0.5 Hz. All irradiations were carried out with an unfocused beam and with the laser tuned to the P(20) line of the 10.6- μ m band, i.e., at 944.19 cm⁻¹; this corresponds to a photon energy of 0.11706 eV. The average cross section of the beam was 5.66 cm^2 , and the incident energy, as measured by a Gen Tec joulemeter and an evacuated photolysis cell, ranged from 2.79 ± 0.10 to 4.03 ± 0.24 J/pulse, resulting in an incident fluence range of 0.493-0.712 J/cm². The laser beam illuminated approximately 64% of the photolysis cell volume.

During photolyses the concentrations of SiH₄, CH₃Cl, H₂, CH₄, Si₂H₆, and SiH₃Cl were determined mass spectrometrically by measurement of the intensities of the ions at m/z 31, 50, 2, 16, 62, and 64, respectively. Calibrations for quantitative measurements at the aforementioned masses, in which ion currents of reaction products are related to molecular concentrations, were carried out by using respective authentic samples. A pure sample of SiH₃Cl was not available, and so initial rates of formation of this substance were calibrated by several methods²² described previously

SiH₄, CH₃Cl, H₂, Ar, CH₄, C(CH₃)₄, and NO were all purchased from Matheson, while Si₂H₆ was supplied by Merck. SiF₄ was obtained from the Linde Division, Union Carbide Corp. All compounds were subjected to freeze-pump-thaw cycles on a high-vacuum line prior to use. All gas mixtures were prepared by using a Saunders-Taylor apparatus.²³

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Figure 1. Absorption of energy by SiH₄ at a fluence of 0.493 J/cm² as a function of pressure: (a) percent of laser energy absorbed; (b) average number of photons per silane molecule in the beam path; \Box , pure SiH₄; ■, equimolar SiH₄-CH₃Cl mixture.

Results and Discussion

Absorption of Energy. The P(20) line of the 10.6- μ m band from the CO₂ laser (944.19 cm⁻¹), as shown by Deutsch,²⁴ closely matches an R-branch transition in the v_4 mode of SiH₄ (944.21 cm⁻¹) and thus is an efficient frequency at which to carry out the photodecomposition.

In Figure 1a, the percent absorption of the laser beam at a fluence of 0.493 J/cm² is plotted vs the partial pressure of silane, while Figure 1b shows the pressure dependence of \bar{v} , the average number of photons absorbed per molecule. As seen in Figure 1a, the percent energy absorption is enhanced by the presence of an equal amount of chloromethane. In Figure 1b, for pure SiH₄, \bar{v} increases to a maximum at a pressure of 20 Torr and then decreases. At low partial pressures of SiH_4 , for a 1:1 mixture of SiH₄ with CH₃Cl, \bar{v} is much higher compared to that of pure silane and increases with an increase in pressure to a maximum at about 10 Torr (SiH_4) and then decreases. Although energy absorption is enhanced by the presence of CH₃Cl, chloromethane does not absorb radiation at this frequency. This indicates that CH₃Cl-SiH₄ collisions redistribute vibrational energy efficiently, thereby continuously providing SiH₄ molecules in low v_4 states. This enhancement in energy absorption in the presence of foreign gases has been previously observed.^{1,3,4,25,26}

Photolysis at a fluence of 0.712 J/cm² were carried out on gas mixtures in which the pressure of SiH₄ was maintained at 45 Torr and the partial pressure of CH₃Cl was varied from 0 to 45 Torr. Over this range of CH₃Cl partial pressure \bar{v} increased monotonically from 1.44 to 1.66.

Products of the Reaction. Continuous mass spectrometric monitoring of the reaction mixture as a function of time, or number of laser pulses, leads us to conclude that both SiH₄ and CH₃Cl are reacted, although quantitative measurements of the chloromethane depletion were not possible due to the low conversion. The gaseous products observed are H₂, CH₄, Si₂H₆, and SiH₃Cl, with trace amounts of Si₃H₈ and perhaps CH₃SiH₂Cl, although ion intensities for the latter were too low for quantitative measurement. The very low amounts of this latter product were unexpected because, based upon the strong evidence for SiH₂



Figure 2. Dependence of ion currents for SiH₄, CH₄, SiH₃Cl, and Si₂H₆ on irradiation time. Fluence = 0.712 J/cm^2 .

insertion into the H-Cl bond in the IR photochemistry of Si-H₄-HCl mixtures,²² we anticipated that CH₃SiH₂Cl would be the major reaction product rather than CH₄ and SiH₃Cl. Experiments carried out using small amounts of NO, as a monoradical scavenger, added to a 1:1 mixture of SiH₄ and CH₃Cl were negative in the detection of methyl radicals. If methyl radicals were produced in the photolysis, they would have been scavenged by the nitric oxide, the production of methane would be inhibited, and CH₃NO would have been observed.²⁷

As is usual in silane decomposition, a brown solid product containing silicon, hydrogen, and, under some conditions, chlorine was also produced. The extent of formation of the solid silicon hydride depends sharply on the pressure of SiH_4 . At the lowest pressures of SiH₄ employed (25-30 Torr) the solid appears as a poorly adherent film on the cell windows and walls, while at the higher pressures the solid appears immediately as suspended particulate matter in the gas phase of the photolysis cell.

As may be seen in Figure 2, the identical shapes of the recorder tracings of the ion currents for CH_4^+ (m/z = 16), $Si_2H_6^+$ (m/z= 62), and SiHCl⁺ (m/z = 64) indicate that all these reaction products are formed simultaneously and concurrently with the depletion of the reactant SiH₄ (SiH₃⁺, m/z = 31). This means that CH_4 , Si_2H_6 , and SiH_3Cl are all primary products of the infrared photodecomposition of SiH₄ in the presence of CH₃Cl and are not formed by way of further reaction of some product. In our definition here of primary product, we mean stable product since our time resolution does not permit us to see the attainment of steady-state concentration of reactant transients such as SiH₂.

Mechanism of the Photochemical Reaction. We consider the simultaneous formation of products, i.e., Si₂H₆, CH₄, and SiH₃Cl, from the infrared laser photolysis of SiH₄ to be a direct result of the competition of SiH₄ and CH₃Cl for SiH₂ molecules formed in the primary photodecomposition. Therefore, we represent the mechanism for formation of the primary products H₂, CH₄, Si₂H₆, and SiH₃Cl by the reactions shown in (1)-(7).

$$\mathrm{SiH}_4 + nh\nu \to \mathrm{SiH}_2 + \mathrm{H}_2 \tag{1}$$

$$SiH_2 + SiH_4 \rightarrow Si_2H_6$$
 (2)

$$SiH_2 + CH_3Cl \rightarrow CH_3SiH_2Cl^*$$
 (3)

$$CH_3SiH_2Cl^* \rightarrow SiHCl + CH_4$$
 (4)

$$SiHCl + SiH_4 = Si_2H_5Cl^*$$
(5)

$$Si_2H_5Cl^* \rightarrow SiH_2 + SiH_3Cl$$
 (6)

$$Si_2H_5Cl^* \rightarrow H_2 + Si_2H_3Cl \rightarrow solid$$
 (7)

 $Si_2H_5Cl^* + M \rightarrow Si_2H_5Cl + M$ (8)

The formation of Si_2H_6 is more accurately described by eqs 2a-2c; however, results from the study of SiH_4 -HCl mixtures²² in the same pressure range show Si₂H₆ formation to be in the

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Figure 3. Dependence of the initial rate ratio $R(CH_4)/R(Si_2H_6)$ on partial pressure of CH_3Cl at various temperatures ($P(SiH_4) = 45$ Torr). Fluence = 0.712 J/cm².



Figure 4. Arrhenius plots of data in Figure 3: i.e., $\log \{d[R(CH_4)/R(Si_2H_6)]/d[CH_3Cl]\}$ vs 1/T.

second-order region, and therefore, (2) is sufficiently accurate under our conditions.

$$\mathrm{SiH}_2 + \mathrm{SiH}_4 \to \mathrm{Si}_2 \mathrm{H}_6^* \tag{2a}$$

$$Si_2H_6^* \rightarrow SiH_3SiH + H_2$$
 (2b)

$$\mathrm{Si}_{2}\mathrm{H}_{6}^{*} + \mathrm{M} \rightarrow \mathrm{Si}_{2}\mathrm{H}_{6} + \mathrm{M}^{*}$$
(2c)

Comparison of the reaction rates of (2) and (3) was accomplished by monitoring the rates of production of methane and disilane. Although chlorosilane is a major product, we believe it is formed by the reaction of a secondary silylene product, SiHCl, with silane. There are further complicating reactions of SiHCl, discussed later on, which make chlorosilane a poor choice for the monitoring of the rate of reaction 3.

A standard kinetic treatment of this mechanism leads to the following expression for the ratio of the initial rate of CH_4 formation to that of Si_2H_6 :

$$\frac{R(CH_4)}{R(Si_2H_6)} = \frac{k_3[CH_3Cl]}{k_2[SiH_4]}$$
(9)

This expression predicts, of course, that the ratio of rates should vary linearly with the concentration ratio $[CH_3Cl]/[SiH_4]$.

In agreement with (9), the data in Figure 3 show a linear dependence of the ratio of initial rates, $R(CH_4)/R(Si_2H_6)$, on the concentration ratio $[CH_3Cl]/[SiH_4]$ over the temperature range 295-428 K. The slopes of the lines in Figure 3 are the rate constant ratios, k_3/k_2 , and the insensitivity of this ratio to temperature is demonstrated by the Arrhenius plot in Figure 4. Thus,



Figure 5. Dependence of the initial rate of decomposition of SiH₄ on the partial pressure of CH₃Cl added: \blacksquare , 30 Torr of SiH₄; \square , 45 Torr of SiH₄. Fluence = 0.712 J/cm².



Figure 6. Dependence of the initial rate of decomposition of SiH₄ on the partial pressure of SiH₄, for a 1:1 mixture of SiH₄ and CH₃Cl. Fluence = 0.712 J/cm^2 .

provided the ambient temperature in such experiments involving infrared multiple-photon decomposition and the attendant transient heating has any significance, we conclude that the temperature coefficient of the ratio k_3/k_2 is zero.

As we have discussed in a previous paper,²² we believe the ambient temperature does play a significant role because the unimolecular decomposition of SiH₄ and the subsequent reactions of SiH₂ will occur on a time scale that is very short compared with $V \rightarrow T$, R relaxation times and with cooling at the walls.²⁸ Hence, we conclude from our data that $E_3 = E_2$. Moreover, recent measurements have demonstrated that k_2 is so close to the collision rate coefficient that E_2 (and hence E_3) must be very close to zero.

In Figure 5 the initial rates of decomposition of both 30 and 45 Torr of silane are plotted vs the partial pressure of CH₃Cl added. It is evident that an increase in the partial pressure of CH₃Cl has the effect of decreasing the initial decomposition rate for silane. This decrease in the rate of silane decomposition is most likely due to vibrational deactivation of SiH₄* formed initially by absorption of infrared photons. Thus, reaction 1 in the mechanism is actually comprised of several steps, namely, (1a), (1b), and (1c). The role of CH₃Cl in Figure 5 is to deactivate SiH₄*, as in eq 1c.

$$\mathrm{SiH}_4 + nh\nu \rightarrow \mathrm{SiH}_4^*$$
 (1a)

$$\operatorname{SiH}_4^*(n \ge 23) \to \operatorname{SiH}_2 + \operatorname{H}_2$$
 (1b)

 $SiH_4^*(n \ge 23) + CH_3Cl \rightarrow SiH_4^*(n < 23) + CH_3Cl^*$ (1c)

Figure 6 is a plot of the initial rate of decomposition of SiH_4 in a 1:1 mixture of SiH_4 and CH_3Cl vs SiH_4 pressure. It is seen in Figure 6 that, with an increase in silane pressure, there is a sharp increase in the initial rate of silane decomposition. This

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TABLE I: Frequencies $(\nu, \text{ cm}^{-1})$ for Energized Molecules and Transition States in the Unimolecular Decomposition of CH₃SiH₂Cl* and Si₂H₄*

 CH ₃ SiH ₂ Cl*	CH ₃ SiH ₂ Cl ^{‡a}	Si ₂ H ₆ *	Si ₂ H ^{‡a}	
 2973 (2)	2973 (1)	2179 (2)	2179 (2)	
2909 (1)	2909	2155 (2)	2155 (1)	
2184 (2)	2184 (2)	2154 (2)	2154 (1)	
1444 (1)	1444 (1)	2152 (1)	2152 (1)	
1413 (1)	1413 (1)	940 (2)	940 (2)	
1259 (1)	1259 (1)	929 (2)	929 (2)	
956 (1)	956 (1)	909 (1)	909 (1)	
900 (1)	900 (1)	844 (1)	844 (1)	
870 (1)	870 (1)	625 (2)	625 (2)	
748 (1)	748 (1)	424 (1)	424 (1)	
700 (1)	700 (1)	379 (2)	379 (2)	
685 (1)	685(1)	200 (1)	200 (1)	
527 (1)	527 (1)			
508 (1)	508 (1)			
212 (1)	212 (1)			
165 (1)	165 (1)			

^aActivated complex.

effect has been shown¹ to be due to a collisionally induced increase in the average energy content of SiH₄ molecules. The pressure threshold for decomposition of 1:1 mixture of SiH₄ and CH₃Cl is around 44 Torr (22 Torr of SiH_4). It may be noted that in the case of SiH₄-HCl mixtures²² the threshold was approximately 30 Torr (15 Torr of SiH₄), indicating that, as expected, CH_3Cl is a more efficient collisional deactivator of silane than HCl.

Although CH₃SiH₂Cl is expected to be a major photolysis product formed in reaction 3, it is not observed in significant amounts. In order to understand why virtually no CH₃SiH₂Cl is observed, we have estimated, using RRKM theory,²⁹ the unimolecular decomposition rates of CH₃SiH₂Cl* (energized to the extent of 104 kcal/mol by virtue of its formation via addition of SiH_2 to CH_3Cl) and $Si_2H_6^*$ (energized analogously by the addition of silvlene to silane to the extent of 57 kcal/mol).³⁴⁻³⁶ In these and other estimates by RRKM theory (Tables I and II), we have taken the transition-state frequencies to be the same as those of the energized molecules, with the exception of removal of the reaction coordinate. While this may be an oversimplification, we seek only rough comparisons and we feel the uncertainties in the thermochemistry and vibrational frequencies do not justify a more detailed treatment. The chosen decomposition pathways are as follows:

$$Si_2H_6^* \rightarrow SiH_3SiH + H_2$$
 (2b)

$$CH_3SiH_2Cl^* \rightarrow SiHCl + CH_4$$
 (4)

If one uses ΔH° for reaction (calculated from ΔH_{f}° 's)³⁴⁻³⁹ as the activation barrier, E_{2b} and E_4 are 46 and 54 kcal/mol, respectively. The RRKM rate constant for the formation of an activated complex from molecules with excess energy E^* , where $E^* = E_0$ + E^+ (E_0 is the activation energy for the decomposition pathway), is defined²⁹ by eq 10, viz.

$$k_{\rm a}(E^*) = \frac{L^{\dagger} \sum P(E_{\rm vr}^{+})}{h N^*(E^*)} \tag{10}$$

 L^{\ddagger} is a statistical factor representing the number of ways the

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Figure 7. Dependence of the initial rate ratio $R(CH_4)/R(SiH_3Cl)$ on the partial pressure of CH₃Cl ($P(SiH_4) = 45$ Torr). Fluence = 0.712 J/cm².

decomposition can occur (L^{\ddagger} is 6 for Si₂H₆ and has a value of 2 for CH₃SiH₂Cl, $\sum P(E_{vr}^{+})$ is the sum of the number of vibrational-rotational quantum states of all the quantized energy levels of energy less than or equal to E^+ , i.e., the total number of vibrational-rotational quantum states of the activated complex with energies $\leq E^+$, h is Planck's constant, and $N^*(E^*)$ is the density of quantum states for a molecule with energy E^* . The vibrational frequencies for $\text{Si}_2\text{H}_6^{40}$ and $\text{CH}_3\text{SiH}_2\text{Cl}^{41}$ used in the calculation are given in Table I. The calculated rate constants ($k_a(E^*)$'s) are $9.7 \times 10^9 \text{ s}^{-1}$ for k_4 and $4.3 \times 10^7 \text{ s}^{-1}$ for k_{2b} . Therefore, the average lifetimes of CH₃SiH₂Cl^{*} and Si₂H₆^{*} are 1.0×10^{-10} and 2.3×10^{-8} s, respectively. At the highest pressure studied (100) Torr of a 1:1 mixture of SiH_4 and CH_3Cl), the time between collisions is approximately 5×10^{-9} s. Thus, it is clear that Si₂H₆* is very likely to be collisionally stabilized, while this is not the case for CH₃SiH₂Cl*, and CH₃SiH₂Cl would, therefore, not be observed as a product in this system under our conditions.

In our laboratory the IR photochemistry of CH₃SiH₃-HCl mixtures is presently under investigation, and it is observed that in this system CH₃SiH₂Cl is one of the major products of the photolysis. It is suggested that methylchlorosilane in this latter system is formed by the insertion of CH₃SiH into HCl, i.e.

$$CH_3SiH + HCl \rightarrow CH_3SiH_2Cl^*$$
 (11)

 ΔH° calculated for this reaction is -69 kcal/mol. Taking this as the extent of energization of CH₃SiH₂Cl*, and again using (4) as the unimolecular decomposition pathway, the calculated value of $k_{a}(E^{*})$ is 1.7×10^{7} s⁻¹. The lifetime of CH₃SiH₂Cl^{*} in the CH₃SiH₂Cl-HCl system is then 5.9×10^{-8} s, and thus it is much more likely that, in the CH₃SiH₃-HCl system, CH₃SiH₂Cl* will be collisionally stabilized and, therefore, will be observed as a major product.

Treating the mechanism (1)-(8) by standard steady-state kinetics and assuming that $k_7 \gg k_8[M]$ leads to the following relationship:

$$\frac{R(CH_4)}{R(SiH_3Cl)} = 1 + \frac{k_7 + k_8[M]}{k_6} \simeq 1 + \frac{k_7}{k_6}$$
(12)

Equation 12 predicts that the ratio of CH_4 formation rate to that of SiH₃Cl should be independent of the concentration of CH₃Cl and equal to or greater than one.

Figure 7 shows the rate ratio $R(CH_4)/R(SiH_3Cl)$ for a wide range of pressures of CH₃Cl, the pressure of SiH₄ being fixed at 45 Torr. The ratio is roughly equal to 1.85 and is essentially independent of $[CH_3Cl]$ over a 9-fold increase in the concentration as predicted by (12). The fact that only about half as much chlorosilane is formed as methane indicates that some of the chlorosilylene produced in reaction 4 undergoes an alternative reaction (7) to form a nonvolatile product. From (12), $k_7/k_6 \approx$ 0.85.

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Figure 8. Dependence of the initial rate ratio $R(CH_4)/R(SiH_3Cl)$ on total pressure, for a 1:1 mixture of SiH₄ and CH₃Cl. Fluence = 0.712 J/cm².



Figure 9. Dependence of the initial rate ratio $R(\text{SiH}_3\text{Cl})/R(\text{Si}_2\text{H}_6)$ on the partial pressure of CH₃Cl ($P(\text{SiH}_4) = 45$ Torr). Fluence = 0.712 J/cm².

Figure 8 shows the initial rate ratio $R(CH_4)/R(SiH_3Cl)$ for experiments in which the total pressure of a 1:1 mixture of SiH₄ and CH₃Cl was varied. Contrary to (12), which predicts that an increase in total pressure should have no effect, as seen in Figure 8, there is a noticeable increase in the initial rate ratio R- $(CH_4)/R(SiH_3Cl)$. This increase can be rationalized by assuming that at higher pressures the Si₂H₅Cl* formed in (5) is more likely to be collisionally stabilized, and hence the rate of formation of SiH₃Cl by reaction 6 is reduced.

A standard kinetic treatment of the reaction mechanism, with the assumption that $k_7 \gg k_8[M]$ leads to the following expression for the initial rate ratio $R(\text{SiH}_3\text{Cl})/R(\text{Si}_2\text{H}_6)$.

$$\frac{R(\mathrm{SiH}_{3}\mathrm{Cl})}{R(\mathrm{Si}_{2}\mathrm{H}_{6})} = \left(\frac{k_{3}}{k_{7}}\right) \left(\frac{k_{6}}{k_{6}+k_{7}}\right) \frac{[\mathrm{CH}_{3}\mathrm{Cl}]}{[\mathrm{SiH}_{4}]}$$
(13)

Figure 9 shows the rate ratio $R(SiH_3Cl)/R(Si_2H_6)$ as a function of the ratio $[CH_3Cl]/[SiH_4]$, the pressure of SiH_4 in these experiments being fixed at 45 Torr. As predicted by (13), and hence consistent with the proposed mechanism, the ratio of R- $(SiH_3Cl)/R(Si_2H_6)$ shows a linear increase with respect to an increase in the partial pressure of CH_3Cl .

It is possible to again estimate k_7/k_6 , the ratio of rate constants for the decomposition of Si₂H₅Cl^{*}, from the data in Figures 3 and 9. Dividing the slope from Figure 9 by the slope from Figure 3, one obtains a value of 0.25 for $k_6/(k_6 + k_7)$, which leads to an estimate of $k_7/k_6 \approx 3.0$. Although this is not in particularly good agreement with the earlier estimate, combining this value with that obtained earlier from Figure 7 gives the value of $k_7/k_6 \approx 2 \pm 1$.

We have also estimated k_7/k_6 by RRRM theory,²⁹ but given the uncertainties in the energetics and vibrational frequencies of Si₂H₅Cl, such a calculation must be regarded as only a very approximate estimate.

TABLE II: Estimated Fundamental Frequencies (ν , cm⁻¹) for Energized Molecules and Transition States in the Unimolecular Decomposition of Si₂H₅Cl*

	assignment	Si ₂ H ₅ Cl*	Si ₂ H ₅ Cl ^{‡a,b}	Si ₂ H ₅ Cl ^{‡a,c}	Si ₂ H ₅ Cl ^{*a,d}
V1	SiH ₂ str, sym	2170		2170	2170
v2	SiH ₃ str, orig	2200	2200	2200	2200
	degen				
V3	SiH3 str, sym	2180	2180		2180
V4	SiH ₃ def	930	930	930	930
ν_5	SiH ₂ scissors	950	950	950	950
	(def)				
ν_6	SiH ₃ def, sym	900	900	900	900
ν_7	SiH ₂ wag	700	700	700	700
Vs	SiH ₃ rock, sym	560	560	560	560
Vg	Si-Si str	430	430	430	
V10	Si-Cl str	510	510	510	510
ν_{11}	Si-Si-Cl bend	190	190	190	190
V12	SiH ₂ str, antisym	2200	2200	2200	2200
ν_{13}	SiH ₃ str, orig	2200	2200	2200	2200
	degen				
ν_{14}	SiH, def, orig	920	920	920	920
	degen				
V15	SiH ₂ twist	680	680	680	680
V16	SiH ₂ rock	530	530	530	530
V17	SiH ₃ rock,	510	510	510	510
	antisym				
v_{18}	SiH ₃ torsion	160	160	160	160
••	-				

^a Activated complex. ^b Reference 7b. ^c Reference 7a. ^d Reference 6.

Excluding decomposition of Si_2H_5Cl to SiH_2 —SiHCl, on the basis of the high activation barrier reported by Ho et al.⁴² for the analogous decomposition of Si_2H_6 to SiH_2 —SiH₂, there are three energetically feasible paths for the decomposition of $Si_2H_5Cl^*$, namely, (6), (7a), and (7b), viz.

$$Si_2H_5Cl^* \rightarrow SiH_3Cl + SiH_2; \quad \Delta H^\circ = 58 \text{ kcal/mol} \quad (6)$$

 $Si_2H_5Cl^* \rightarrow ClSiH_2SiH + H_2; \quad \Delta H^\circ = 49 \text{ kcal/mol}$ (7a)

$$Si_2H_5Cl^* \rightarrow SiH_3SiCl + H_2; \quad \Delta H^\circ = 52 \text{ kcal/mol}$$
 (7b)

The enthalpy changes for these reactions refer to the ground state of Si_2H_5Cl and are estimated from standard enthalpies of formation in the literature.^{34,36,39,42-44} We assume here that the energy barriers to the unimolecular decompositions in (6), (7a), and (7b) are equal to the enthalpy changes given; i.e., the reverse reactions have negligible activation energies.

Some comment on ΔH° for (6) is warranted. The overall enthalpy change for (5) + (6) as calculated from reported enthalpies of formation ranges from 5 to 12 kcal/mol. We believe, however, that this overall process should be about thermoneutral, since the net effect is to break two Si-H bonds and form two Si-H bonds. Therefore, we chose the lower value for the overall process (5) + (6). This choice leads to an energization²⁹ of the Si₂H₅Cl^{*} molecule of 53 kcal/mol when it is formed from the ground states of the reactants SiHCl and SiH₄, and this energy is below the threshold of (6).

On the other hand, $Si_2H_3Cl^*$ is not usually formed in our system from ground-state reactants. The overall process forming SiHCl, namely, (3) followed by (4), is exothermic by about 50 kcal/mol; if this energy is equipartitioned among the internal degrees of freedom of the products, the SiHCl molecule will be excited to the extent of about 17 kcal/mol. Similarly, each SiH₄, on the average, will contain about 1.5 infrared photons from the laser, which amounts to about 4 kcal/mol. Hence, the energization of Si₂H₅Cl* in our system will, on the average, be about 74 kcal/mol, which is sufficient for (6) to occur and compete with (7).

It has been shown¹ that, under our conditions, the energy distribution in laser-irradiated SiH_4 is adequately represented as a Boltzmann distribution, and we assume the same applies to

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Experiments to examine the effect of an inert third body on

the rate ratio $R(SiH_3Cl)/R(CH_4)$ were carried out with the partial

pressures of SiH₄ and CH₃Cl kept constant at 40 and 30 Torr,

respectively. In these experiments both 20 Torr of SiF₄ and 10

almost to zero; that is, almost no SiH₃Cl was produced. It appears

that if sufficient amounts of inert third body are present, the

reaction of SiHCl going to the solid phase (nucleation) is enhanced. This enhancement is explained by our mechanism as follows.

The SiHCl which is formed in reaction 4 inserts into the Si-H

bond of silane, forming an energized Si₂H₅Cl* which can either decompose by (6) to form SiH₃Cl and regenerate SiH₂ or de-

compose by (7) to form an Si_2H_3Cl diradical species. The barrier

for reaction 6 is higher than that for either reaction 7a or 7b, and

only a certain fraction of the Si₂H₅Cl* formed in (5) may contain enough energy to undergo reaction 6. If an adequate amount of

third body (either SiF₄ or (Me)₄C) is added, the Si₂H₅Cl* (as

well as the SiHCl formed in (4)) is sufficiently collisionally sta-

bilized that there is not enough energy to overcome the activation

barrier for reaction 6 and only reactions 7a and 7b can take place.

DE-ASO2-76ER03416 with the U.S. Department of Energy.

Acknowledgment. This work was supported by Contract No.

Registry No. SiH₄, 7803-62-5; CH₃Cl, 74-87-3; H₂, 1333-74-0; CH₄, 74-82-8; Si₂H₆, 1590-87-0; SiH₃Cl, 13465-78-6; Si₃H₈, 7783-26-8;

Rather surprisingly, the ratio $R(SiH_3Cl)/R(CH_4)$ decreased

Torr of $C(CH_3)_4$ were used as third bodies.

SiHCl. The values of k_6 , k_{7a} , and k_{7b} were therefore averaged over the two Boltzmann distributions, with SiHCl and SiH4 having average energies of 17 and 4 kcal/mol, respectively.

Fundamental frequencies for Si₂H₅Cl were not available from the literature; therefore, we estimated these frequencies based upon analogous assignments and symmetry constraints for chloroethane45 and by combination of various fundamental modes of Si₂H₆,⁴⁰ CH₃SiH₂Cl, CH₃SiHCl₂, CH₂ClSiH₃ and CHCl₂SiH₃.⁴⁰ Table II contains these estimated frequencies for Si₂H₅Cl as well as for the three activated complexes used in calculating k_6 , k_{7a} , and k_{7b} .

Using the energetic values and estmated frequencies just described for the three modes of decomposition of Si₂H₅Cl*, we calculate from RRKM theory that $(k_{7a} + k_{7b})/k_6$ is 17.5, which is to be compared with the value of about 2 that we find experimentally. While the agreement is not particularly good, which is not surprising considering the uncertainties in the frequencies and thermochemistry, it at least tends to confirm the experimental finding that $(k_{7a} + k_{7b}) > k_6$. Moreover, these considerations serve to rationalize the observed increase in $R(CH_4)/R(SiH_3Cl)$ with increasing pressure that is seen in Figure 8. At higher total pressures, the $Si_2H_5Cl^*$ formed in (5) is more likely to be collisionally deactivated, thus making (6) much less favorable and causing the ratio $R(CH_4)/R(SiH_3Cl)$ to increase.

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Shock Tube Pyrolysis of Pyridine[†]

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The kinetics of pyrolysis of pyridine dilute in argon have been studied in a single-pulse shock tube, using capillary column GC together with GC/MS and FTIR spectroscopy for product determination, over the temperature range of 1300-1800 K and total pressures of 7-11 atm. At the lower end of the studied temperatures, cyanoacetylene was found to be the principal nitrogen-containing product. At elevated temperature hydrogen cyanide predominated. Other major products were acetylene and hydrogen. Thermochemical estimates of the isomeric cyclic pyridyls produced in the pyrolysis indicate that the ortho isomer is unique in being able to undergo facile cleavage to an open-chain cyano radical from which cyanoacetylene is produced. Several sources of HCN were identified in the system. The *m*- and *p*-pyridyls may eliminate HCN in a molecular process. An important source of HCN at high temperatures is the addition of H atoms to cyano compounds, especially cyanoacetylene, but also acetonitrile and acrylonitrile which are produced in the pyrolysis. The pyrolysis is a chain process initiated principally by C-H bond fission to form o-pyridyl. A 58-step reaction model is presented and shown to substantially fit the observed profiles of the major product species. From this model we derive a value for the rate constant of the principal initiation reaction, $C_5H_5N \rightarrow o - C_5H_4N + H(1)$, of $k_1 = 10^{15.9\pm0.4} \exp(-98 \pm 3 \text{ kcal mol}^{-1}/RT) \text{ s}^{-1}$ between 1300 and 1800 K and at a total pressure of about 10 atm.

CH₃SiH₂Cl, 993-00-0.

Introduction

on Combustion, Seattle, August 1988.

Heavy fuels such as coal and coal-derived liquids contain considerable amounts of chemically bound nitrogen and the combustion of these fuels can lead to significant amounts of fuel-derived NO_x .¹⁻³ Much of the nitrogen originally bound in the fuel is in the form of aromatic heterocyclic structures containing pyridine and pyrrole ring systems.^{4,5} Under pyrolytic

[†] Presented in part as a Poster Paper at 21st Symposium (International)

conditions these heterocycles may form nitrogen precursors of NO_x so that the rates of pyrolysis and product formation from representative nitrogen heterocycles will determine NO_x formation in the combustion of heavy fuels.

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