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Supplementary Material Available: A table of anisotropic temperature factors (Table VII) and a listing of observed and calculated structure factors from the final cycle of least-squares refinement (13 pages). Ordering information is given on any current masthead page.

Infrared Laser Photochemistry of SiH_4–HCl Mixtures[1]

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Abstract: The infrared laser photochemistry of SiH_4–HCl mixtures has been studied in a pressure range of 28–60 torr and in a temperature range of 295–414 K. The gaseous products observed are H_2, Si_2H_6, SiH_3Cl, SiH_2Cl_2, and $SiHCl_3$ with trace amounts of Si_3H_8 and Si_2H_5Cl. As is usual in silane decompositions, a solid product containing silicon, hydrogen, and perhaps very small amounts of chlorine was also formed. The photochemical conversion is best described by initial decomposition of SiH_4 to SiH_2 and H_2 followed by competition of SiH_4 and HCl for SiH_2 molecules. The simultaneous formation of all chlorosilanes suggests that decomposition of the initial product of SiH_2–HCl reaction leads in turn to SiHCl and $SiCl_2$ molecules. Studies of the temperature dependence of the rates of the competing reactions indicate that the activation energy for insertion of SiH_2 into HCl is less than 1.3 kcal/mol.

Recent studies of the infrared laser induced decomposition of pure SiH_4,[2,3] SiH_4–SiF_4[4] mixtures, and SiH_4–PH_3[5] mixtures have shown that the predominant primary photodecomposition is to SiH_2 and H_2, paralleling what is thought to be the mechanism of the purely thermal homogeneous decomposition of SiH_4. It therefore appears that the infrared laser induced decomposition of SiH_4 would be a good source of SiH_2 for study of the interaction of these reactive molecules with other substrates.

It is known that SiH_2 will insert readily into Si–H bonds.[2,4,6–12] Moreover, there is evidence that silylenes insert into the O–H bonds of alcohols[10] and into Si–Cl bonds in halosilanes.[11,12] The insertion of SiH_2 into the strong H–H bond of molecular hydrogen has been reported,[13] and it is of interest to inquire if SiH_2 will insert into an equally strong bond involving hydrogen that resides in an equally simple molecule. Hence, we have conducted a study of the infrared laser photochemistry of SiH_4–HCl mixtures. This paper is a report of 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, led directly into the ionization source of a time-of-flight mass spectrometer. 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. Molecules leaving the cell, along the axis of the flight tube of the mass spectrometer, reach the ionization source after a transit time of, at most, 2–3 ms.

The source of infrared radiation was a CO_2 TEA laser (Lumonics Research Ltd., Model 103-2) pulsed at a frequency of 0.5 Hz. All irradiations were carried out with an unfocussed beam and with the laser turned to the P(20) line of the 10.6 μm 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 5.94 cm^2, and the incident energy, as measured by a GenTec joulemeter and an evacuated photolysis cell, was 4.17 J/pulse, resulting in an incident fluence of 0.70 J/cm^2. The laser beam illuminated approximately 64% of the photolysis cell volume.

During a photolysis the concentrations of SiH_4, HCl, H_2, Si_2H_6, SiH_3Cl, SiH_2Cl_2, and $SiHCl_3$ were determined mass spectrometrically by measurement of the intensities of the ions at m/z 31, 36, 2, 62, 64, 99, and 133, respectively, which are generated in the ion source of the mass spectrometer. Calibrations for quantitative measurements at the above masses, in which ion currents are related to molecular concentrations, were carried out by using pure samples of SiH_4, HCl, H_2, Si_2H_6, SiH_2Cl_2, and $SiHCl_3$. A pure sample of SiH_3Cl was not available, and so the initial rates of formation of this substance were calculated by the material balance in (1). This assumes, of course, that all of the chlorine atoms

$$\left(\frac{d[SiH_3Cl]}{dt}\right)_0 = -\left[\left(\frac{d[HCl]}{dt}\right)_0 + 2\left(\frac{d[SiH_2Cl_2]}{dt}\right)_0 + 3\left(\frac{d[SiHCl_3]}{dt}\right)_0\right] \qquad (1)$$

from the reacted HCl remain in the gas phase as SiH_3Cl, SiH_2Cl_2, and $SiHCl_3$. Using a reported mass spectrum[14] and estimates of the ionization cross section of SiH_3Cl from interpolation of cross sections for SiH_4, SiH_2Cl_2, $SiHCl_3$, and $SiCl_4$, it is clear that the preponderance of the Cl in the reacted HCl appears as SiH_3Cl and that the initial rate of SiH_3Cl formation determined by (1) is not in serious error, certainly not more than 15%.

SiH_4 was obtained from the Matheson Co. and further purified by vacuum distillation. Si_2H_6 was synthesized by using methods described previously[15] and was also purchased from Merck and Co. SiH_2Cl_2 was obtained from Petrarch Systems, and $SiHCl_3$ was purchased from Alfa

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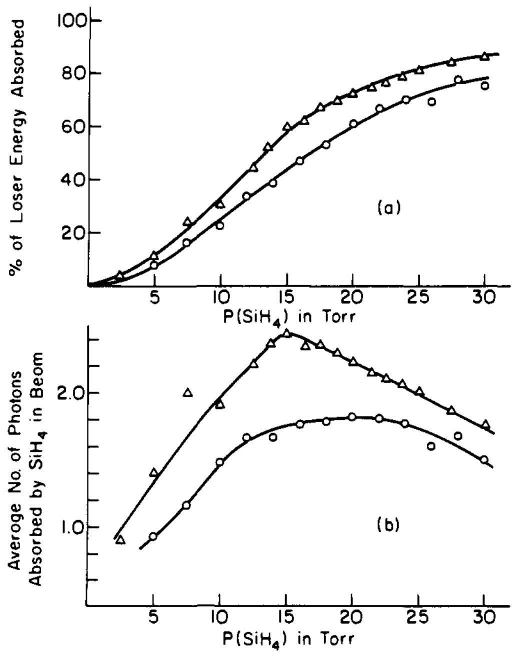

Figure 1. Absorption of Laser energy by silane as a function of pressure: (a) percent of laser energy absorbed; (b) average number of photons per silane molecule in the beam path; ○, pure SiH_4; △, equimolar SiH_4–HCl mixture.

Products. All compounds were subjected to freeze–pump–thaw cycles on the high-vacuum line prior to use. All gas mixtures were prepared by using a Saunders-Taylor apparatus.[16]

Results and Discussion

1. Absorption of Energy. As pointed out by Deutsch,[17] the P(20) line of the 10.6-μm band from the CO_2 laser (944.19 cm^{-1}) closely matches an R-branch transition in the ν_4 mode of SiH_4 at 944.21 cm^{-1}, and is, therefore, an efficient frequency at which to carry out the photodecomposition. As may be seen in Figure 1a, in which the % absorption of the beam is plotted vs. the partial pressure of SiH_4, energy absorption is not described by Beer's law but rather exhibits an increasing slope with increasing pressure up to about 50% absorption. As in previous studies[2,4,5,17] of the infrared photochemistry of SiH_4, this behavior is due principally to the fact that collisions redistributing the absorbed vibrational energy are aiding the absorption process. In such a case the average number of photons absorbed per SiH_4 molecule, $\bar{\upsilon}$, is a more useful parameter by which to describe the absorption coefficient. Plots of $\bar{\upsilon}$ vs. the partial pressure of SiH_4 are shown in Figure 1b. As may be seen in parts a and b of Figure 1, the absorption at a given SiH_4 partial pressure is enhanced by the presence of HCl, although HCl does not absorb at this frequency. This means that HCl–SiH_4 collisions also redistribute vibrational energy efficiently, thereby continuously providing SiH_4 molecules in low ν_4 states. This enhancement effect by foreign gases has been observed before.[2,4,5,18]

2. Products of the Reaction. Mass spectrometric analysis of the contents of the reaction cell as a function of the irradiation time, or, equivalently, of the number of pulses, leads to the conclusion that both SiH_4 and HCl are reacted, with the principal products being H_2, Si_2H_6, Si_3H_8, SiH_3Cl, SiH_2Cl_2, $SiHCl_3$, and a solid containing silicon and hydrogen. The extent of formation of the solid silicon hydride depends sharply on the pressure of SiH_4. At the lowest pressures of SiH_4 employed (13–20 torr) the solid appears as a poorly adherent film on the cell window and walls while, at the higher pressures, the solid appears immediately as suspended particulate matter in the gas phase of the photolysis cell. Minor products probably observed are SiH_3SiH_2Cl and Si_4H_{10}, although the intensities were too low for quantitative measurement.

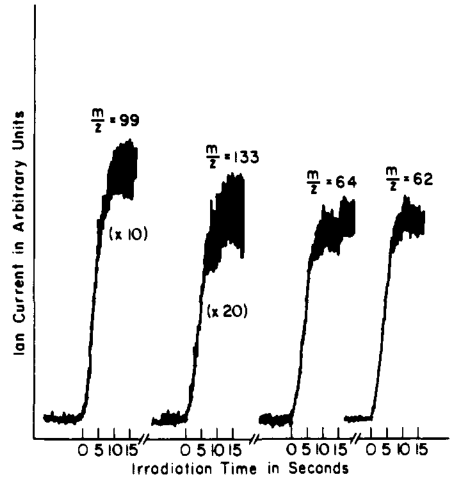

Figure 2. Dependence of ion currents of reaction products on irradiation time.

As is evident from Figure 2, in which the ion currents of $Si_2H_6^+$ (*m/z* 62), $SiHCl^+$ (*m/z* 64), $SiHCl_2^+$ (*m/z* 99), and $SiCl_3^+$ (*m/z* 133) are plotted vs. irradiation time, all products are formed simultaneously and are, therefore, primary products of the infrared photodecomposition of SiH_4 in the presence of HCl.

3. Mechanism of the Photochemical Reaction. (a) Formation of Disilane and Monochlorosilane. On the basis of previous studies[2–5] of the infrared laser induced decomposition of SiH_4, we interpret the simultaneous formation of Si_2H_6, SiH_3Cl, SiH_2Cl_2, and $SiHCl_3$ to be a consequence of the competition of SiH_4 and HCl for SiH_2 molecules formed in the primary photodecomposition. Thus, the mechanism of formation of the principal products Si_2H_6, SiH_3Cl, and H_2 may be described by (2)–(8).

$$SiH_4 + nh\nu \rightarrow SiH_2 + H_2 \tag{2}$$

$$SiH_2 + SiH_4 \underset{-3}{\overset{3}{\rightleftharpoons}} Si_2H_6^* \tag{3}$$

$$SiH_2 + HCl \underset{-4}{\overset{4}{\rightleftharpoons}} SiH_3Cl^* \tag{4}$$

$$Si_2H_6^* \rightarrow SiH_3SiH + H_2 \tag{5}$$

$$Si_2H_6^* + M \rightarrow Si_2H_6 + M \tag{6}$$

$$SiH_3Cl^* \rightarrow SiHCl + H_2 \tag{7}$$

$$SiH_3Cl^* + M \rightarrow SiH_3Cl + M \tag{8}$$

A standard kinetic treatment of this mechanism leads to the following expression for the ratio of the initial rate of SiH_3Cl formation to that of Si_2H_6:

$$\frac{R(SiH_3Cl)}{R(Si_2H_6)} = \left(\frac{k_4}{k_3}\right)\left(\frac{k_8}{k_6}\right)\left(\frac{k_{-3} + k_5 + k_6[M]}{k_{-4} + k_7 + k_8[M]}\right)\frac{[HCl]}{[SiH_4]} \tag{9}$$

The expression in (9) predicts that, if the total pressure (i.e., [M]) is fixed, the ratio of rates should vary linearly with the ratio $[HCl]/[SiH_4]$.

The data in Figure 3 depict the results of such experiments at several temperatures, in the range of 295–357 K, in which the partial pressure of SiH_4 was maintained constant at 30 torr, the partial pressure of HCl was varied from 0 to 20 torr, and He was added at a partial pressure of 30 − P(HCl) to maintain constancy of the total pressure. It is clear from the data in Figure 3 that the initial rate ratio $R(SiH_3Cl)/R(Si_2H_6)$ does vary linearly with $[HCl]/[SiH_4]$ as predicted by (9). Furthermore, it is also clear from Figure 3 and from the Arrhenius plot in Figure 4 (namely, the slopes of the lines in Figure 3, vs. $1/T$) that within experimental error the temperature coefficient of the initial rate ratio is zero. The temperature range covered by the data in Figure 4 is 295–414 K, and the scale of the ordinate covers the range expected for a temperature coefficient of ±5 kcal/mol.

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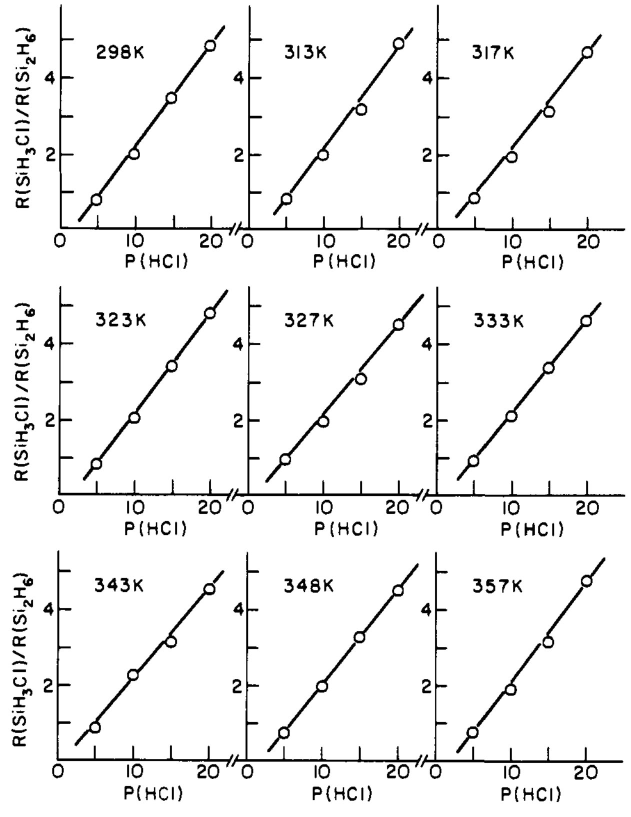

Figure 3. Dependence of the initial rate ratio $R(SiH_3Cl)/R(Si_2H_6)$ on partial pressure of HCl at various temperatures ($P(SiH_4)$ = 30 torr).

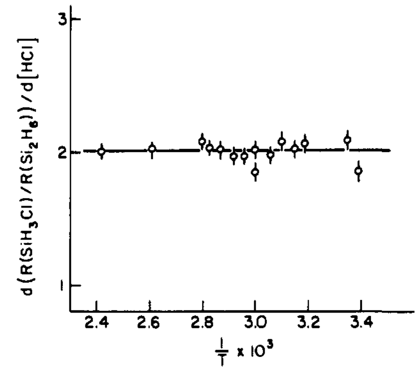

Figure 4. Arrhenius plots of data in Figure 3: i.e., $dR[(SiH_3Cl)/R(Si_2H_6)]/d[HCl]$ vs. $1/T$.

The meaning of the temperature coefficient, or lack of it, in Figures 3 and 4 warrants some discussion, since the energy input to the gas must cause a transient temperature change of several hundred degrees before cooling at the walls restores the original conditions.[19]

One interpretation is that because of the temperature rise caused by the absorption of laser energy, the effect of varying the initial gas temperature from 295 to 414 K is negligible. As a result one would observe a temperature coefficient of zero, as indicated by Figures 3 and 4.

We favor an alternate interpretation as follows: Given the simplicity of the molecule, the unimolecular decomposition of SiH_4^* molecules that contain energy above the lowest dissociation threshold, i.e., (2), will be veryfast; indeed the RRKM minimum rate constant, defined by[20]

$$k_{\min}(E_0^*) = \frac{L^\dagger}{hN(E_0^*)} \tag{10}$$

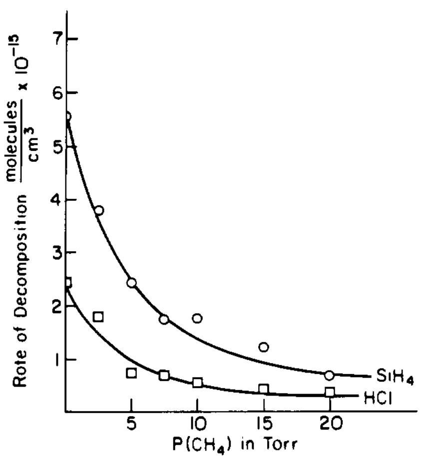

Figure 5. Dependence of the decomposition rates of SiH_4 and HCl on pressure of an inert third body at $[HCl]/[SiH_4]$ = 1.0: ○, SiH_4; □, HCl.

(where $L^\dagger$ is the number of ways the decomposition can occur, h is Planck's constant, and $N(E_0^*)$ is the density of states of SiH_4 at the dissociation threshold), is 5.6×10^8 s^{-1} and so the mean lifetime of SiH_4^* is $\sim 2 \times 10^{-9}$ s. The rate constant for insertion of SiH_2 into SiH_4 is such[13] that at 300 K the half-life of SiH_2 under our conditions is less than 1 μs. Assumption of a typical V–T relaxation time,[21] which under our conditions is 50–100 μs, leads to the conclusion that the dissociation of SiH_4^* and the chemical reactions subsequent to it will be essentially complete before any significant temperature rise of the system occurs. Therefore, the initial temperature will play a significant role in the chemical reaction. Recently, we have carried out similar studies of the infrared photochemistry of SiH_4–GeH_4 mixtures, and the observation of a significant temperature dependence supports this latter, alternative explanation.

Consideration of the nature of the rate constants in (9) suggests that any temperature coefficient of the initial rate ratio should reflect principally the activation energy difference, $E_4 - E_3$. As discussed in more detail below, Figures 3 and 4, therefore, indicate that within experimental error $E_4 = E_3$.

Inspection of (9) reveals that if the total pressure is sufficiently high, such that $k_8[M] >> k_{-4} + k_7$ and $k_6[M] >> k_{-3} + k_5$, the expression reduces to that in (11) and the ratio of rates should be independent of total pressure at a fixed ratio of concentrations. We must consider if (11) applies under our conditions.

$$\frac{R(SiH_3Cl)}{R(Si_2H_6)} \approx \frac{k_4}{k_3}\frac{[HCl]}{[SiH_4]} \tag{11}$$

The effect of an increase in an inert third-body concentration, at fixed concentrations of SiH_4 and HCl, is to decrease the rates of formation of all products and decrease the rates of decomposition of SiH_4 and HCl. This is clearly seen in Figure 5, in which the initial rates of decomposition of SiH_4 (20 torr) and HCl (20 torr) are plotted vs. the partial pressure of added CH_4, this latter gas being inert toward reaction with SiH_2. The decrease in rates of decomposition (and of product formation) are most probably due to vibrational deactivation of SiH_4^* formed initially by absorption of infrared photons. That is, (2) in the mechanism is actually comprised of several steps, namely, (2a), (2b), and (2c). The role of CH_4 in Figure 5 is to deactivate SiH_4^*, as shown in eq 2c.

$$SiH_4 + nh\nu \rightarrow SiH_4^* \tag{2a}$$

$$(SiH_4^*)_{n\geq 21} \rightarrow SiH_2 + H_2 \tag{2b}$$

$$(SiH_4^*)_{n\geq 21} + CH_4 \rightarrow (SiH_4^*)_{n<21} + CH_4^* \tag{2c}$$

Of course, SiH_4 and HCl play the same third-body role as CH_4 but, in the experiments of Figure 5, the concentrations of these

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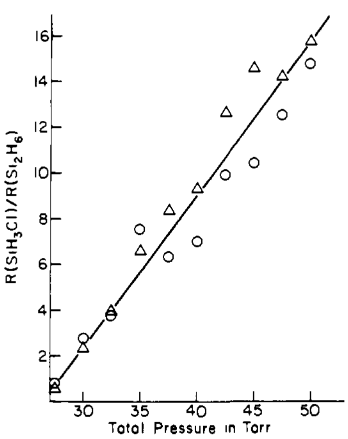
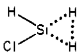
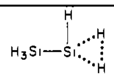


Figure 6. Dependence of the initial rate ratio $R(SiH_3Cl)/R(Si_2H_6)$ on total pressure at $[HCl]/[SiH_4]$ = 1.0.

Table I. Frequencies (ν, cm^{-1}) for Energized Molecules and Transition States in the Unimolecular Decomposition of SiH_3Cl^* and $Si_2H_6^*$

SiH_3Cl^*		$Si_2H_6^*$	
2266 (1)	2266 (1)	2154 (4)	2154 (3)
977 (1)	977 (1)	2179 (2)	2179 (2)
567 (1)	567 (1)	909 (1)	909 (1)
2249 (2)	2249 (1)	844 (1)	844 (1)
978 (2)	978 (2)	940 (2)	940 (2)
680 (2)	680 (2)	929 (2)	929 (2)
		625 (2)	625 (2)
		379 (2)	379 (2)
		434 (1)	434 (1)
		200 (1)	200 (1)

species are fixed. In experiments conducted at a constant total pressure, such as the bulk of them in this work, one may for kinetic simplicity describe the primary process (2) by a single step, since the fraction of SiH_4^* deactivated is, to a first approximation, constant.

In view of the differing molecular complexity of SiH_3Cl and Si_2H_6, it is likely that the lifetime of the excited molecules, with respect to unimolecular decomposition, also differ appreciably. Thus, in the pressure range studied, $Si_2H_6^*$ may be more effectively deactivated than SiH_3Cl^*, a phenomenon that can be examined by studying the effect of total pressure on the ratio of the initial rates of formation of Si_2H_6 and SiH_3Cl at a constant ratio of the concentrations of SiH_4 and HCl. Such a plot is shown in Figure 6, for replicate experiments conducted several months apart, in which the ratio of initial rates, i.e., $R(SiH_3Cl)/R(Si_2H_6)$, in an equimolar mixture of SiH_4 and HCl is plotted vs. the total pressure.

The increase in the rate ratio with increasing pressure seen in Figure 6 is most easily rationalized within the framework of (9) by the assumption that under our conditions: $(k_{-3} + k_5) << k_6[M]$ and $(k_{-4} + k_7) >> k_8[M]$. With these assumptions (9) reduces to (12), rather than to (11). At constant concentrations of HCl

$$\frac{R(SiH_3Cl)}{R(Si_2H_6)} \cong \left(\frac{k_4}{k_3}\right)\left(\frac{k_8}{k_{-4} + k_7}\right)\frac{[HCl]}{[SiH_4]}[M] \qquad (12)$$

and SiH_4, (12) predicts that $R(SiH_3Cl)/R(Si_2H_6)$ should vary linearly with [M]. In support of this rationalization, the linear plot in Figure 6 indicates that this is indeed true.

To examine the validity of this rationalization further we have estimated, using RRKM theory,[20] the unimolecular decomposition rates of SiH_3Cl^* (energized to the extent of 81 kcal/mol by virtue of its formation via addition of SiH_2 to HCl)[22] and $Si_2H_6^*$ (energized analogously by addition of SiH_2 to SiH_4 to the extent of 50 kcal/mol.[13] The frequencies used in the calculation are given in Table I. The calculated average lifetimes of SiH_3Cl^* and $Si_2H_6^*$ are 6×10^{-12} s and 2×10^{-6} s, respectively; however, in view of the great uncertainties in the energetics of SiH_3Cl decomposition the former number should be considered only as semiquantitative. This very large difference is consistent with the observation from Figure 6a and (12) that, at the total pressures obtaining in the experiments (40–60 torr), SiH_3Cl formation is in the third-order region and Si_2H_6 formation is in the second-order region. That Si_2H_6 formation is in the second-order region is also in agreement with the finding of John and Purnell.[13]

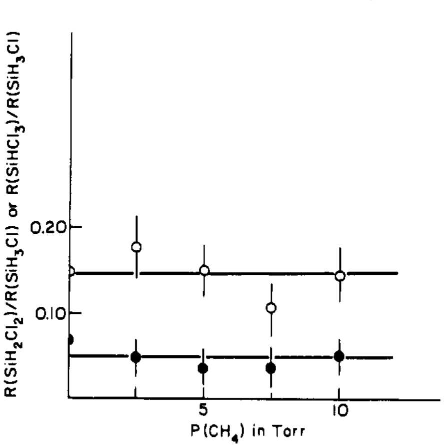


Figure 7. Dependence of the initial rate ratios on pressure of an inert third body at $[HCl]/[SiH_4]$ = 1.0: ⊙, $R(SiH_2Cl_2)/R(SiH_3Cl)$; ●, $R(SiHCl_3)/R(SiH_3Cl)$.

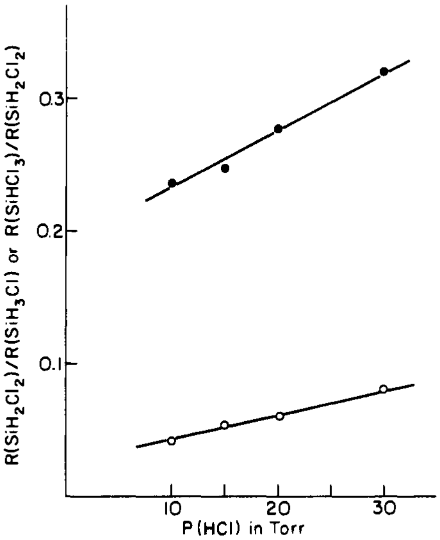


Figure 8. Dependence of the initial rate ratios on $[HCl]/[SiH_4]$ at constant total pressure of 60 torr: ⊙, $R(SiH_2Cl_2)/R(SiH_3Cl)$; ●, $R(SiHCl_3)/R(SiH_2Cl_2)$ ($P(SiH_4)$ = 30 torr; $P(He) = 30 - P(HCl)$ in torr; $[HCl]/[SiH_4] = (1/30)P(HCl)$.

The formation of SiH_3Cl and Si_2H_6 thus appears to be described adequately by the mechanism embodied in (2)–(8), with the realization that (2) really must be described by (2a), (2b), and (2c), with all substrates taking part in the deactivation step (2c). At the pressures studied deactivation of $Si_2H_6^*$to Si_2H_6 is much more efficient than that of SiH_3Cl^* to SiH_3Cl.

According to (12), then, the temperature dependence of the initial rate ratio $R(SiH_3Cl)/R(Si_2H_6)$ reflects the temperature dependence of the quantity:

$$\left(\frac{k_4}{k_3}\right)\left(\frac{k_8}{k_{-4} + k_7}\right)$$

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Since the energization process to form SiH_3Cl^* is chemical activation by insertion of SiH_2 into HCl, it is not likely that there is any significant temperature coefficient of k_{-4} and k_7. The collisional deactivation rate constant k_8 is not likely to be temperature dependent, it generally being taken as being the rate constant for molecular collisions. Therefore, we conclude that the observed temperature dependence, or lack of it, seen in Figures 3 and 4 reflects the fact that under our conditions $E_4 \approx E_3$. E_3 has been reported[13] to be 1.3 kcal/mol.

(b) Formation of Dichlorosilane and Trichlorosilane. In view of the facts that SiH_2 is the predominant reactive species produced in the infrared multiphoton decomposition of SiH_4[2-5] and that SiH_2Cl_2 and $SiHCl_3$ are formed simultaneously with SiH_3Cl and Si_2H_6, the most feasible mechanism for formation of dichlorosilane and trichlorosilane is as shown in (13)–(17). The very small amounts of what we believe to be SiH_3SiH_2Cl most probably result from insertion of SiHCl into SiH_4, as shown by (18) and (19).

$$SiHCl + HCl \rightleftarrows SiH_2Cl_2^* \tag{13}$$

$$SiH_2Cl_2^* \rightarrow SiCl_2 + H_2 \tag{14}$$

$$SiH_2Cl_2^* + M \rightarrow SiH_2Cl_2 + M \tag{15}$$

$$SiCl_2 + HCl \rightleftarrows SiHCl_3^* \tag{16}$$

$$SiHCl_3^* + M \rightarrow SiHCl_3 + M \tag{17}$$

$$SiHCl + SiH_4 \rightleftarrows Si_2H_5Cl^* \tag{18}$$

$$Si_2H_5Cl^* + M \rightarrow Si_2H_5Cl + M \tag{19}$$

$SiCl_2$ will most likely also insert into SiH_4, (20), although we have not detected the ultimate product of this reaction.

$$SiCl_2 + SiH_4 \rightleftarrows Si_2H_4Cl_2^* \tag{20}$$

A standard kinetic treatment of the mechanism leads to the following expressions for the rate ratios $R(SiH_2Cl_2)/R(SiH_3Cl)$ and $R(SiHCl_3)/R(SiH_2Cl_2)$:

$$\frac{R(SiH_2Cl_2)}{R(SiH_3Cl)} = \left(\frac{k_7k_{15}/k_8}{k_{-13} + k_{14} + k_{15}\,[M]}\right) \frac{(k_{13}/k_{18})\ ([HCl]/[SiH_4])}{1 + (k_{13}/k_{18})\ ([HCl][SiH_4])} \tag{21}$$

$$\frac{R(SiHCl_3)}{R(SiH_2Cl_2)} = \left(\frac{k_{14}k_{17}/k_{18}}{k_{-16} + k_{17}[M]}\right) \frac{(k_{16}/k_{20})([HCl]/[SiH_4])}{1 + (k_{16}/'k_{20})([HCl]/[SiH_4])} \tag{22}$$

We have already noted, e.g., (9) and (12), that unimolecular decomposition of the chemically activated monochlorosilane appears to be very rapid relative to collisional deactivation in the pressure regime studied. The same is very likely true for $SiH_2Cl_2^*$ and $SiHCl_3^*$, since the number of internal degrees of freedom is the same. Therefore, we assume $(k_{-13} + k_{14}) >> k_{15}[M]$ and $k_{-16} >> k_{17}[M]$. With these assumptions, we see that for experiments at constant $[HCl]/[SiH_4]$, the rate ratios in (21) and (22) should be independent of third-body concentration or, equivalently, of total pressure. That this is true within experimental error may be seen in Figure 7, in which the ratios $R(SiH_2Cl_2)/R(SiH_3Cl)$ and $R(SiHCl_3)/R(SiH_3Cl)$ are plotted vs. the partial pressure of CH_4.

On the other hand, for experiments at constant total pressure, but increasing $[HCl]/[SiH_4]$, the rate ratios should increase in a linear fashion. As in Figure 8, this prediction is also born out by the experimental facts. It is to be seen from Figure 8 that the plots do not go through the origin as predicted by (21) and (22). We believe this is due to the presence of very small amounts of chlorosilanes as impurities in the silane and the intercepts of Figure 8 simply reflect the ratios of these impurities. The impurities arise, of course, from the synthesis of silane via the reduction of silicon tetrachloride.

Finally, the linearity seen in Figure 8 for $[HCl]/[SiH_4]$ up to a value of 1.0, suggests that

$$k_{13}/k_{18} << 1 \qquad k_{16}/k_{20} << 1$$

This effect of chlorine substitution in reducing silylene reactivity toward insertion into the H–Cl bond is in accord with the reactivity order reported for insertion into Si–H bonds.[23]

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Registry No. SiH_4, 7803-62-5; HCl, 7647-01-0; H_2, 1333-74-0; Si_2H_6, 1590-87-0; SiH_3Cl, 13465-78-6; SiH_2Cl_2, 4109-96-0; $SiHCl_3$, 10025-78-2; Si_3H_8, 7783-26-8; Si_2H_5Cl, 14565-98-1; Si, 7440-21-3.

Metal Cluster Electronic and EPR Properties: SCF–Xα–SW Prediction of the Magnetogyric (g) and Superhyperfine Tensors of Trigonal-Bipyramidal Charged Silver Clusters Ag_5^{q+} (where $q = 2$ or 4)

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Abstract: The effect of gradually depleting valence electronic charge from a model, neutral pentaatomic ligand-free cluster, Ag_5^0, is investigated by using the SCF–Xα–SW method. Specifically, electronic ground- and excited-state wave functions, charge distributions, and eigenvalues are calculated for trigonal-bipyramidal Ag_5^{q+} (q = 0–4) clusters. First ionization potentials for q = 0–4 and excitation energies for q = 0, 2, and 4 are computed and discussed in terms of optical spectroscopic trends as a function of charge on the cluster. Isotropic and anisotropic magnetogyric (g) and hyperfine tensor components are calculated from first principles using the SCF–Xα–SW–MO charge and spin-density distributions for isotopically pure $^{109}Ag_5^{q+}$ for q = 2 and 4. Trends in their EPR parameters and predicted spectra as a function of charge on the cluster are discussed. Calculations of this type are expected to be useful for deciphering optical and EPR spectra of neutral and/or cationic silver clusters entrapped in, for example, rare gas solid, zeolite, or aqueous glassy matrices.

Interest in ligand-free metal clusters has grown steadily over the past decade.[1] A major trend has been an attempt to correlate the structure and bonding of the low nuclearity clusters with their spectroscopic properties, ultimately to gain an understanding of

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