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Infrared Multiphoton Decomposition of Monosilane

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Abstract: The decomposition of SiH_4 by infrared radiation from a pulsed CO_2 TEA laser at 944.19 cm^{-1} has been studied in the pressure range of 10–22 torr and at a fluence of 1.0 J/cm^2. The products observed are H_2, Si_2H_6, Si_3H_8, Si_4H_{10}, Si_5H_{12}, and a solid $(SiH_x)_n$. The energy absorption from the laser beam increases with increasing pressure of SiH_4 and/or of He, showing that collisions are necessary to pump molecules into the quasicontinuum from which resonant absorption of the laser photon occurs readily. The addition of He also increases the decomposition rate showing that the decomposition is a multiphoton decomposition and not a purely thermal reaction. The primary dissociation of SiH_4 is to H_2 and SiH_2 and it is the further reactions initiated by attack of SiH_2 on SiH_4 that cause the observed decomposition. It is shown that the results are accounted for by a Boltzmann distribution of infrared photons in SiH_4 and a reaction mechanism identical with that shown to obtain in the pyrolysis of SiH_4.

Among the numerous recent reports in the literature[2-10] on infrared multiphoton chemistry, there have been several papers describing the infrared-laser-induced decomposition of monosilane.[11-15] All of the reports relative to the monosilane decomposition[11-15] agree that collisions are necessary for the initiation of reaction; in the most detailed of these studies,[15] Deutsch has shown that at a fluence of 140 J/cm^2 decomposition cannot be initiated below a pressure of 2 torr. The earlier papers[11-14] describing the monosilane decomposition report the products to be solely Si and H_2 whereas the more detailed study of Deutsch[15] concludes that the reaction products consist of H_2 and the solid polymer $(SiH_x)_n$.

In view of the fact that initiation of the decomposition appears to require collisional pumping of SiH_4 molecules into the quasicontinuum, from which multiple photon absorption can occur readily to the dissociation limit,[2-10] one might expect the infrared-laser-induced decomposition to be similar to the purely thermal decomposition.[16-18] However, in the purely thermal decomposition of SiH_4 both Si_2H_6 and Si_3H_8, as well as H_2, are observed as volatile products, while in the infrared-laser-induced decomposition Deutsch[15] was unable to detect the presence of any Si_2H_6 as a reaction product. Probably the very high conversions of SiH_4 employed (80%) in the experiments[15] precluded the observation of the more reactive Si_2H_6 product.

To examine this question regarding the expected similarity of the infrared-laser-induced decomposition with that of the purely thermal reaction, we have carried out studies of the laser-induced reaction at low conversions (<1.5% per pulse) and with continuous mass-spectrometric monitoring of the volatile reaction products. This paper is a report of our results.

Experimental Section

The source of infrared radiation was a pulsed CO_2 TEA laser (Lumonics Research Ltd., Model 103) operating at 0.5 Hz with the beam stopped down to a diameter of 1.9 cm. All irradiations were carried out with an unfocussed beam and with the laser tuned to the P(20) line of the 10.6 μm band at 944.19 cm^{-1}, corresponding to a photon energy of 0.11706 eV. The incident pulse energy as measured with a GenTec joulemeter and an empty photolysis cell was found to be 2.85 J which corresponds to an incident fluence of 1.0 J/cm^2.

The photodecompositions were carried out in a cylindrical stainless steel cell having a diameter of 1.9 cm and a length of 12.9 cm. One end of the cell consisted of a KCl window, for entrance of the laser beam, while the opposite end was coupled via a pinhole leak to a time-of-flight mass spectrometer. The diameter of the pinhole (35 μm) was such that the average time of a molecule in the photolysis cell was 88 s. The cell was completely illuminated by the unfocussed laser beam.

The energy absorbed by SiH_4 was determined by joulemeter measurement of the difference in energy transmitted by the cell when filled with SiH_4 at a known pressure and when empty. At least 25 replicate measurements were made at each pressure between 10 and 20 torr, with the extent of energy absorption ranging from 16–55%.

During a photolysis the concentrations of SiH_4, H_2, Si_2H_6, and Si_3H_8 were follwed by measurement of the intensities of the ions at m/q 31, 2, 62, and 92 amu, respectively, which are generated in the ion source of the mass spectrometer. By using predetermined mass spectra of the products, the intensities at m/q 31 were corrected for contributions from Si_2H_6 and Si_3H_8 and the intensities at m/q 2 were corrected for the contribution from SiH_4. All currents were measured with use of an ionizing energy of 50 eV.

Reaction rates, in terms of molecules/pulse, were determined from the initial slopes of recorder tracings of ion currents vs. time for decompositions corresponding to 25 pulses (50 s at 0.5 Hz). The mean time between pulses, namely 2 s, is small compared with the mean residence time of molecules in the cell, namely 88 s, so that meaningful initial slopes, and hence initial rates, could be obtained.

SiH_4 was obtained from the Matheson Co., purified by vacuum distillation, and stored in a reservoir on the vacuum line. Si_2H_6 and Si_3H_8 were synthesized for calibration of the mass spectrometer, using methods described previously.[19] Helium, also obtained from Matheson, was used as received. All gas mixtures were prepared with use of a Saunders-Taylor apparatus.[20]

Results

1. Energy Absorption. As pointed out by Deutsch,[15] the P(20) line of the 10.6 μm band from the CO_2 laser is closely matched with an R branch transition in the v_4 mode of SiH_4 at 944.21 cm^{-1}. Energy absorption at this frequency does not adhere to Beer's law behavior in that plots of log (incident fluence/transmitted fluence)

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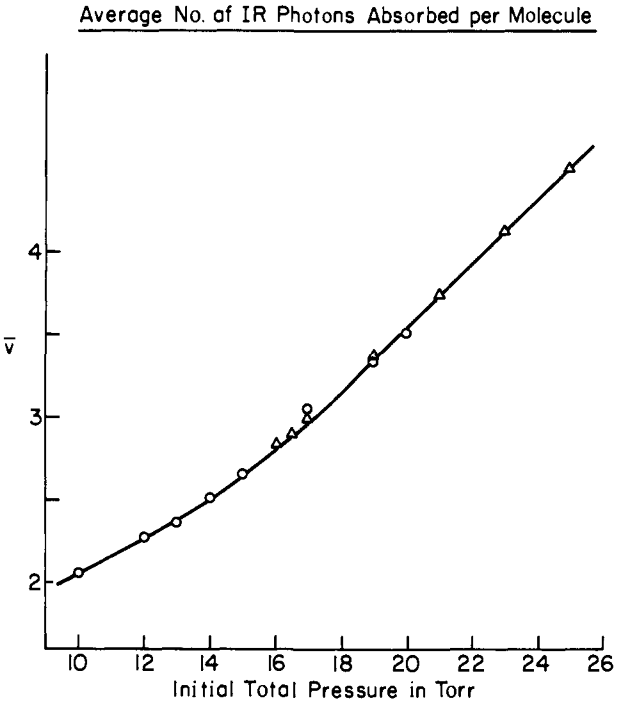

Figure 1. Average number of photons absorbed per molecule per pulse. Fluence = 1.0 J/cm^2. ○, pure SiH_4; △, SiH_4 (15 torr) + He.

vs. density were not linear, but rather showed an increasing slope with increasing pressure. The traditional photochemical concept of absorption coefficient is, therefore, not a useful one in this case. Of much more utility in the kinetic treatment to follow is the average number of photons absorbed per molecule, $\bar{v}$, and this quantity, determined from the energy absorption data, is shown as a function of SiH_4 pressure in Figure 1.

When He is added to 15 torr of SiH_4 the amount of laser energy absorbed per pulse increases with increasing partial pressure of He. Moreover, as shown in Figure 1, the effectiveness of He in increasing the energy absorption is, within experimental error, the same as that of SiH_4. As will be shown later, the amount of decomposition per pulse also increases with increasing partial pressure of He. The reaction is therefore not a thermal reaction, so that it is not V–T relaxation that is responsible for the enhanced absorption due to SiH_4–He collision; rather it is pressure broadening of the rotational fine structure that is responsible for the increase in the average number of photons absorbed per molecule.[21]

2. Nature of the Decomposition. Examination of the mass spectra of the contents of the reaction cell as a function of irradiation time indicates that the products of the reaction are H_2, Si_2H_6, Si_3H_8 traces of Si_4H_{10} and Si_5H_{12}, and, at pressures above 15 torr, a solid containing silicon and hydrogen. As may be seen from Figure 2, in which the ion currents of SiH_3^+ (m/q 31), $Si_2H_6^+$ (m/q 62), and $Si_3H_8^+$ (m/q 92) are plotted vs. irradiation time (or equivalently, the number of pulses), Si_2H_6 and Si_3H_8 are formed simultaneously, i.e., both products, and presumably Si_4H_{10} and Si_5H_{12} also, are primary products of the infrared-induced decomposition of SiH_4.

3. Fractional Yields per Pulse. From the initial slopes of plots of ion currents vs. time, such as shown in Figure 2, it is easy to derive values for the fractional yields per pulse, Y(i), defined as

$$Y(\mathrm{i}) = \frac{1}{N_{SiH_4}{}^\circ}\frac{dN_\mathrm{i}}{dP} = \frac{1}{N_{SiH_4}{}^\circ}\frac{1}{\nu}\lim_{\Delta t\to 0}\frac{\Delta N_\mathrm{i}}{\Delta t} \qquad (I)$$

where $N_{SiH_4}{}^\circ$ is the initial number of molecules of SiH_4 in the photolysis cell, N_i is the number of molecules of substance i at time t, P is the number of pulses, ν is the frequency of the pulsing, and t is the total observation time. Conversion of ion-currents to numbers of molecules in the cell was based on mass spectrometric calibration using the pure gases.

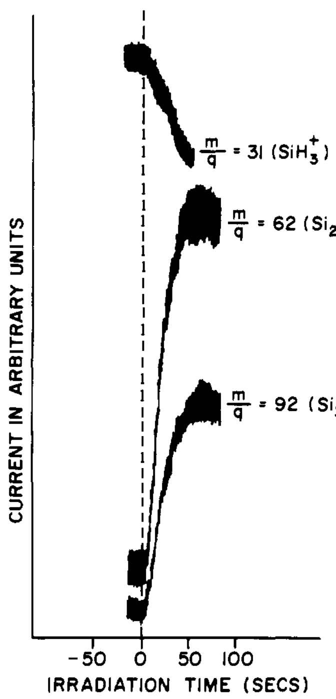

Figure 2. Ion currents due to SiH_4, Si_2H_6, and Si_3H_8 as a function of irradiation time. Fluence = 1.0 J/cm^2.

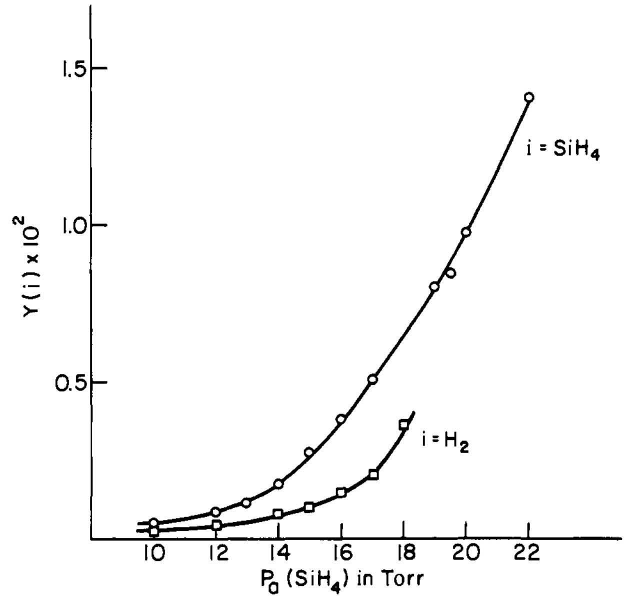

Figure 3. Dependence of the rates of decomposition of SiH_4 and formation of H_2 on SiH_4 pressure. ○, SiH_4 decomposition; □, H_2 formation. Fluence = 1.0 J/cm^2.

The fractional yields per pulse are very strong functions of the pressure of SiH_4, as may be seen in Figures 3 and 4; e.g., log–log plots of the pressure dependence of the SiH_4 depletion indicate that Y increases as $P_{SiH_4}{}^{5.6}$.

4. Effect of Inert Gas on Fractional Yields. The effect of He on the fractional yield of Si_2H_6 at a constant partial pressure of SiH_4 is shown by the dotted line in Figure 4. The addition of He clearly increases the fractional yield although He is not quite as efficient as SiH_4 in promoting this enhancement.

Discussion

1. The Energy-Absorption Process. The data in Figure 1 show that an increase in the pressure of pure SiH_4 or in the partial pressure of He in He–SiH_4 mixtures causes an increase in the average number of photons absorbed per molecule of SiH_4. One

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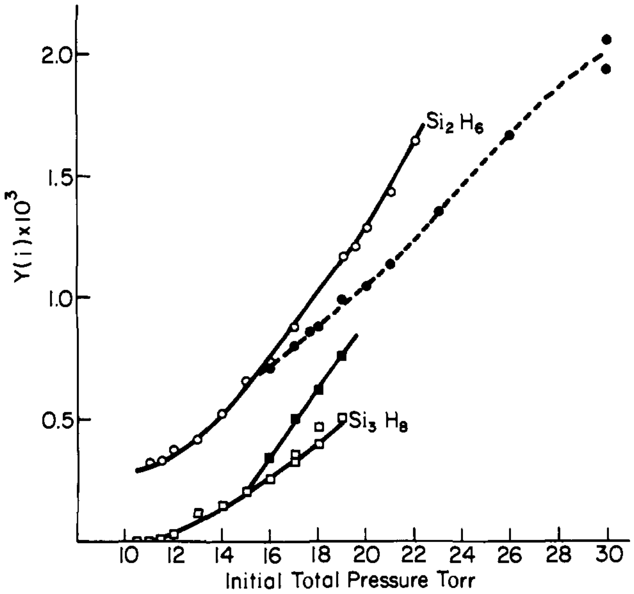

Figure 4. Dependence of the rates of formation of Si_2H_6 and Si_3H_8 on total pressure. ○, Si_2H_6 formation from pure SiH_4; □, Si_3H_8 formation from pure SiH_4; ●, Si_2H_6 formation from SiH_4 (15 torr) + He mixtures; ■, Si_3H_8 formation from SiH_4 (15 torr) + He mixtures. Fluence = 1.0 J/cm^2.

possible explanation for this general phenomenon is that V–T relaxation, with an accompanying temperature rise, provides a steady cycling of SiH_4 between the ground and first excited vibrational states, thus overcoming the vibrational anharmonicity.[21] This may be ruled out, however, because He and SiH_4 are equally efficient in enhancing the average number of photons absorbed per molecule and it is highly improbable that He and SiH_4 would be equally effective in the V–T relaxation of vibrationally excited SiH_4. Secondly, if this explanation were correct, the reaction would have to be classified as a thermal reaction, with the result that an increase in He partial pressure would reduce the fractional yield of reaction because of increased heat capacity and, hence, lower initial temperature rise. As seen in Figure 4, an increase in He partial pressure causes an enhancement of the fractional yield of Si_2H_6, indicating that the reaction is not a thermal one and that, therefore, a different mechanism is responsible for the increase in the energy absorption with increasing pressure.

While an increase in SiH_4 pressure can cause an increase in the energy absorption by both V–V transfer (to keep a steady supply of molecules in the vibrational ground state) and pressure broadening of the rotational fine structure, an increase in He partial pressure can enhance the energy absorption only by the latter mechanism. The equal effectiveness of He and SiH_4 in increasing the energy absorption, as seen in Figure 1, indicates that the pressure broadening of the absorption line through SiH_4–SiH_4 and SiH_4–He collisions must be the dominant mechanism that operates to overcome the vibrational anharmonicity.

2. Mechanism of the Photodecomposition. The infrared photodecomposition of SiH_4 is to be understood in terms of a primary dissociation of highly vibrationally excited SiH_4 molecules followed by secondary reactions of the products of the primary decomposition.

The two primary processes to be considered are shown in (1) and (2). According to available thermochemical and kinetic

$$SiH_4 + nh\nu \rightarrow SiH_2 + H_2 \tag{1}$$

$$SiH_4 + nh\nu \rightarrow SiH_3 + H \tag{2}$$

data,[22-26] the energy barriers of these two reactions are 2.43 and 3.86 eV, respectively. This means that at least 21 photons at 944.19 cm^{-1} must be acquired by SiH_4 to undergo (1), while a minimum of 33 photons is needed for (2) to take place. The difference in energy requirements of the two primary reactions, namely 1.43 eV, is so large that the probability of occurrence of (2) is expected to be negligible in comparison to that of (1). In the pulsed infrared laser induced decomposition of cyclobutanone at pressures in the range of 3–10 torr (collisional region) the lower energy dissociation is 30–60 times more probable than the higher energy one[27,28] while the energy barriers of the two competing primary dissociations differ by only 0.26 eV. Moreover, RRKM calculations[29] of the relative probabilities of (1) and (2), assuming a Boltzmann distribution of vibrational energy, indicate that (2) can be at most 0.8% of (1). Therefore, in our further discussions and kinetic treatment of the mechanism we shall assume that the only significant primary process is (1).

The remainder of the mechanism consists of the reaction of SiH_2, produced in (1), with SiH_4. These reactions, as deduced from studies of the pyrolysis[16-18] and vacuum-ultraviolet photodecomposition[30,31] of SiH_4, are as follows:

$$SiH_2 + SiH_4 \rightarrow Si_2H_6^* \tag{3}$$

$$Si_2H_6^* \rightarrow SiH_4 + SiH_2 \tag{4}$$

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

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

$$SiH_3SiH + SiH_4 \rightarrow Si_3H_8^* \tag{7}$$

$$Si_3H_8^* \rightarrow SiH_3SiH + SiH_4 \tag{8}$$

$$Si_3H_8^* \rightarrow SiH_2 + Si_2H_6 \tag{9}$$

$$Si_3H_8^* \rightarrow SiH_3SiH_2SiH + H_2 \tag{10}$$

$$Si_3H_8^* + M \rightarrow Si_3H_8 + M \tag{11}$$

$$SiH_3SiH_2SiH + SiH_4 \rightarrow Si_4H_{10}^* \tag{12}$$

On the rare occasions that primary process 2 does occur the H-atoms produced will react exclusively by (13) under our con-

$$H + SiH_4 \rightarrow SiH_3 + H_2 \tag{13}$$

ditions;[32-35] further, the only significant gas-phase reaction of SiH_3 will be (14), which forms SiH_2, a species whose only reaction in the system is (3).[36,37] Hence, the inclusion of (2) will have only negligible effects on the observed depletion of SiH_4 and on the formation of the products H_2, Si_2H_6, and Si_3H_8.

$$SiH_3 + SiH_3 \rightarrow SiH_2 + SiH_4 \tag{14}$$

Within experimental error, the mechanism above accounts completely for the observations in the range of 10–14 torr. Above

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14 torr, material balances based on the volatile products fall below 80% and solid products becomes visible in the reaction cell. At these higher pressures, ions containing four and five Si atoms are clearly observed. The solid formation, which is probably due to a gas-phase nucleation of such higher silanes, is not accounted for by the mechanism, so at these higher pressures it is clearly incomplete.

3. Kinetic Treatment of the Mechanism. Since the energy absorption process and the decomposition are strongly dependent on collisions (Figures 1 and 3), we assume that the pulse of infrared radiation creates a Boltzmann distribution of vibrational excitation in the SiH_4 molecules in which the average number of vibrational quanta of 944.19 cm^{-1} (0.1171 eV) in a molecule is determined experimentally, the values being shown in Figure 1. We assume further that all chemical reaction initiated by the occurrence of (1) will be complete before any V–T relaxation takes place. This is a very reasonable assumption because the half-life of the insertion reaction of SiH_2 in the ground vibrational state (and presumably also of SiH_3SiH) at 10 torr is about 3 μs[23] as compared with typical V–T relaxation times of 100 μs.[38]

It is convenient to describe the excitation energy of an energized molecule in terms of the number of quanta, v, of laser frequency, ν, i.e., $\epsilon = vh\nu$. The Boltzmann distribution function for vibrational energy levels of the molecule is

$$F(v) = g(v)e^{-\beta(v/\bar{v})} \tag{II}$$

where β is a numerical constant, $\bar{v}$ is the average number of quanta per molecule, and $g(v)$ is the multiplicity of levels of energy v. Following the usual development in unimolecular rate theory[29] we may approximate the multiplicity by

$$g(v) = N(v)\Delta v \tag{III}$$

where $N(v)$ is the density of states at energy v and Δv is the "width" of the energy level.

The mean lifetime of a state under our conditions is determined by the rate of collisional V–V transfer, and for the mean SiH_4 pressure employed, we estimate[38] it to be ~0.5 μs. Combination of this lifetime with the Heisenberg Uncertainty Principle leads to an estimate of the level "width" of ~10^{-5} cm^{-1} or $\Delta v \simeq 1 \times 10^{-9}$ eV. Comparison of this Δv with the vibrational state density of SiH_4, calculated as a function of v by the Whitten–Rabinovitch approximation,[29] shows that the multiplicity $g(v)$ exceeds unity only for very large values of v, e.g., $v > 37$ for $\bar{v} = 3$. This means that degeneracy of vibrational energy levels of the SiH_4 molecule is not significant in our reaction system, a major reason being that reaction is occurring for relatively low values of $\bar{v}$ (cf. Figure 1).

The normalized, nondegenerate, Boltzmann distribution may then be written[39] as

$$f(v) = \left(\frac{1}{\bar{v}+1}\right)\left(\frac{\bar{v}}{v+1}\right)^{v} \tag{IV}$$

when $f(v)$ is the fraction of molecules that contain v quanta and $\bar{v}$ is the average number of quanta per molecule (cf. Figure 1). The fraction, Ω, of SiH_4 molecules decomposed by the pulse is the fraction that contains at least 21 quanta, i.e.,

$$\Omega = \sum_{v=21}^{\infty} f(v) = 1 - \left(\frac{1}{\bar{v}+1}\right)\sum_{v=0}^{20}\left(\frac{\bar{v}}{\bar{v}+1}\right)^{v} \tag{V}$$

and the concentration of SiH_2 molecules produced by the primary dissociation of SiH_4 is then given by

$$[SiH_2]_0 = [SiH_4]_0\Omega \tag{VI}$$

The dependence of Ω on $\bar{v}$ is shown in Figure 5 for several values of the lower limit to the summation in (V), this lower limit being the minimum number of quanta required for (1) to occur.

Since RRKM calculations for all values of $\bar{v}$ in our experiments (cf. Figure 1) indicate the half-life of (1) to be less than 10^{-10} seconds, we may assume that $[SiH_2]_0$ in (IV) represents an initial concentration produced instantaneously by the pulse. The remainder of the decomposition reaction caused by the pulse is due to the decay of SiH_2 by (3) and the subsequent secondary reactions 4–12.

The rate equation for the decay of SiH_2, according to the mechanism, is

$$-\frac{d[SiH_2]}{dt} = k_3[SiH_4][SiH_2] - k_4[Si_2H_6^*] - k_9[Si_3H_8^*] \tag{VII}$$

Since the fraction of SiH_4 decomposed per pulse is at most 1.4%, we may assume $[SiH_4]$ to be a constant. Then, if we assume that $Si_2H_6^*$, $Si_3H_8^*$ and SiH_3SiH are at steady-state concentrations, we may integrate (VII) to obtain expressions for all reaction transients as functions of time after formation of SiH_2 by the pulse. The result is

$$[SiH_2] = \Omega[SiH_4]_0 \exp\left\{-\frac{(k_5k_{10} + (k_5k_{11} + k_6k_9 + k_6k_{10})[M] + k_6k_{11}[M]^2}{(k_4 + k_5 + k_6[M])(k_9 + k_{10} + k_{11}[M])} \times k_3[SiH_4]_0 t\right\} \tag{VIII}$$

$$[Si_2H_6^*] = \left(\frac{k_3[SiH_4]_0}{k_4 + k_5 + k_6[M]}\right)[SiH_2] \tag{IX}$$

$$[Si_3H_8^*] = \frac{k_3k_5[SiH_4]_0}{(k_4 + k_5 + k_6[M])(k_9 + k_{10} + k_{11}[M])}[SiH_2] \tag{X}$$

$$[SiH_3SiH) = \frac{k_3k_5(k_8 + k_9 + k_{10} + k_{11}[M])}{k_7(k_4 + k_5 + k_6[M])(k_9 + k_{10} + k_{11}[M])}[SiH_2] \tag{XI}$$

If we now write the rate equations for the depletion of SiH_4 and formation of H_2, Si_2H_6, and Si_3H_8, substitute (VIII)–(XI) into the rate equations, and integrate, we may obtain the yields per pulse, Y(i), by evaluation of the resulting expressions as $t \rightarrow \infty$. This process gives the results shown in eq XII–XV.

$$\Omega^{-1}Y(SiH_4) = 2 + \frac{2k_9 + k_{10} + k_{11}[M]}{k_{10} + \frac{k_6}{k_5}\left(k_9 + k_{10} + \frac{k_5k_{11}}{k_6}\right)[M] + \frac{k_6k_{11}}{k_5}[M]^2} \tag{XII}$$

$$\Omega^{-1}Y(Si_2H_6) = \frac{k_9 + \frac{k_6}{k_5}(k_9 + k_{10})[M] + \frac{k_6k_{11}}{k_5}[M]^2}{k_{10} + \frac{k_6}{k_5}\left(k_9 + k_{10} + \frac{k_5k_{11}}{k_6}\right)[M] + \frac{k_6k_{11}}{k_5}[M]^2} \tag{XIII}$$

$$\Omega^{-1}Y(Si_3H_8) = \frac{k_{11}[M]}{k_{10} + \frac{k_6}{k_5}\left(k_9 + k_{10} + \frac{k_5k_{11}}{k_6}\right)[M] + \frac{k_6k_{11}}{k_5}[M]^2} \tag{XIV}$$

$$\Omega^{-1}Y(H_2) = 1 + \frac{k_9 + 2k_{10} + k_{11}[M]}{k_{10} + \frac{k_6}{k_5}\left(k_9 + k_{10} + \frac{k_5k_{11}}{k_6}\right)[M] + \frac{k_6k_{11}}{k_5}[M]^2} \tag{XV}$$

The expressions derived from the mechanism for the observed yields, i.e., eq XII–XV, suggest that we should normalize the observed yields to Ω, namely to the fraction of molecules in the Boltzmann distribution that have acquired enough photons to undergo (1) (cf. eq V). The results of this normalization are shown in Table I, taking 21 photons as the minimum number required

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[38] R. D. Levine and R. B. Bernstein, "Molecular Reaction Dynamics", Oxford University Press, New York, 1974, p 128.

[39] Reference 8, p 36.

Table I. Fractional Reaction Yields per Primary Dissociation of SiH_4

$P(SiH_4)$, torr	$\bar{\nu}$ (Figure 1)	$\Omega \times 10^3$ (eq III)	$\Omega^{-1}Y$ (SiH_4)	$\Omega^{-1}Y$ (Si_2H_6)	$\Omega^{-1}Y$ (Si_3H_8)	$\Omega^{-1}Y(H_2)$
10	2.06	0.24	2.1			1.0
11	2.16	0.34		0.95		
11.5	2.21	0.40		0.83	0.04	
12	2.26	0.46	1.8	0.81	0.13	0.89
13	2.36	0.60	2.0	0.69	0.18	
14	2.51	0.87	2.0	0.60	0.17	0.89
15	2.61	1.19	2.3	0.55	0.17	0.83
16	2.79	1.58	2.4	0.47	0.16	0.95
17	2.96	2.19	2.3	0.40	0.15	0.94
18	3.15	3.02			0.13	1.2
19	3.33	3.98	2.0	0.29		
19.5	3.45	4.74	1.8	0.26		
20	3.52	5.21	1.9	0.25		
22	3.93	7.52	1.9	0.22		

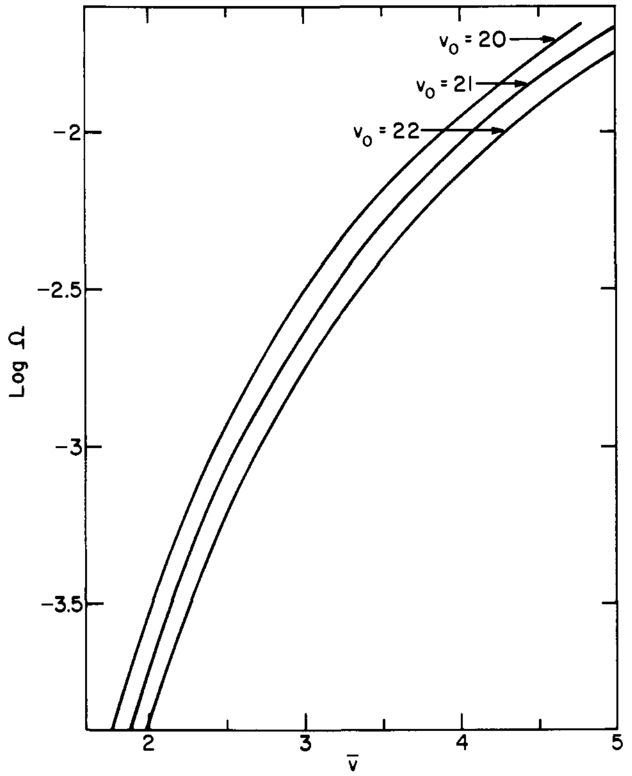

Figure 5. Fraction of SiH_4 in a Boltzmann distribution of vibrational quanta with sufficient energy to decompose for three decomposition thresholds.

in accord with the known thermochemistry.[22-26]

Examination of the normalized yields for SiH_4 depletion (column 4 of Table I) indicates that the very sharp pressure dependence in Figure 3 is accounted for by the Boltzmann factor of eq V. Moreover, comparison with eq XII shows that, within the precision of the data, the mechanism and kinetic treatment account extremely well for the observations. As may be seen in Figure 5, Ω is a very sensitive function of $\bar{v}$ with the result that the experimental uncertainty in $\bar{v}$ (Figure 1) leads to the uncertainty of ~±20% in Ω. There does not appear to be a trend within the precision of the normalized yields for SiH_4 depeletion and the mean value obtained is 2.05 ±0.20. This is consistent with (XII), although our data are not precise enough to detect any influence of the pressure-dependent term in this equation. Consideration of the material balance between SiH_4 consumed and Si_2H_6 and Si_3H_8 produced, in the range of 12–17 torr, indicates that the pressure-dependent term in (XII) should take on values between 0.13 and 0.27 over this range, values which are consistent with the range of the normalized yields in column 4 of Table I.

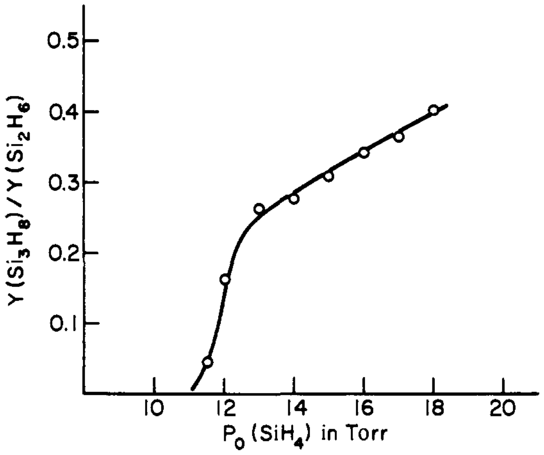

Figure 6. Dependence of Si_3H_8/Si_2H_6 yield ratio on pressure. Fluence = 1.0 J/cm^2.

The pressure dependencies predicted by eq XII–XV are more complicated than may first appear; this is because the rate constants of the unimolecular reactions, i.e., k_5, k_9, and k_{10}, are strongly dependent on pressure as a result of $\bar{v}$ (and, therefore, the average internal energy) being dependent on pressure (cf. Figure 1). For example, the energy barrier of (5) is larger than that of (4) and at some low pressure $\bar{v}$ must be such that k_5 effectively approaches zero. If (5) cannot occur, then a threshold for Si_3H_8 formation will exist and below this threshold only Si_2H_6 and H_2 are formed. Relative to the above discussion, we note the limiting values of eq XII–XV are

$$\lim_{k_5 \to 0} \Omega^{-1}Y(SiH_4) = 2$$

$$\lim_{k_5 \to 0} \Omega^{-1}Y(Si_2H_6) = \lim \Omega^{-1}Y(H_2) = 1$$

$$\lim_{k_5 \to 0} \Omega^{-1}Y(Si_3H_8) = 0$$

which are in accord with the data of Table I at low pressure; moreover, the existence of an effective threshold for Si_3H_8 formation may be seen in Figure 6, in which the ratio of the Si_3H_8 yield to that of Si_2H_6 is plotted vs. the pressure.

The absolute pressure dependencies of the yields of SiH_4 depletion and H_2, Si_2H_6, and Si_3H_8 formation are difficult to calculate with any precision because RRKM calculations of each unimolecular rate constant are necessary at each pressure and, in addition, knowledge of the collisional stabilization rate constants is required. A further complication is the distribution of vibrational energy in the SiH_4 reactant, as well as in the SiH_2 and SiH_3SiH reactants, of (3) and (7), which must be takn into account in determining the internal energies of the Si_2H_6* and Si_3H_8* produced.

We have carried out very crude such calculations with the following assumptions:

(1) A Boltzmann distribution of vibrational quanta in SiH_4 exists with $\bar{v}$ given by Figure 1.

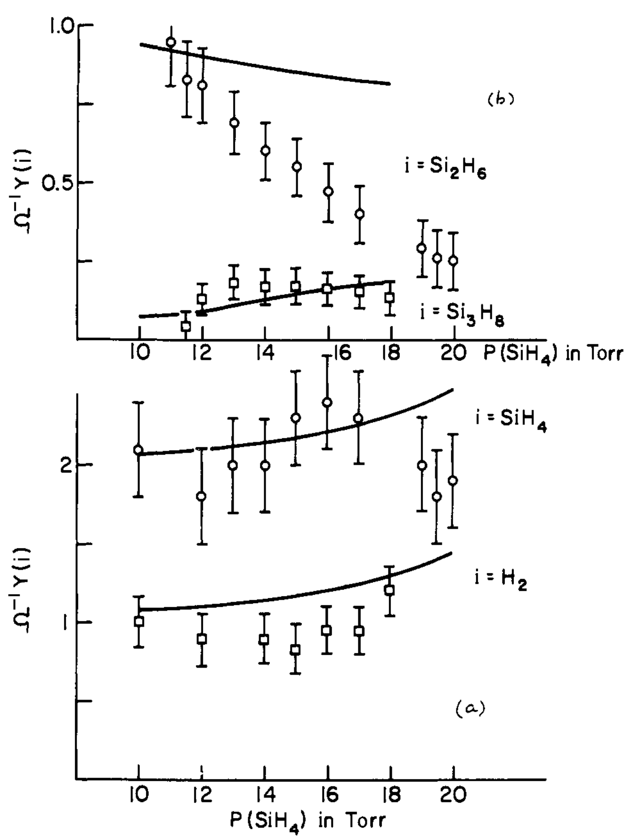

Figure 7. Comparison of calculated normalized yields with experimental values. (a) ○, SiH_4 decomposition; □, H_2 formation. (b) ○, Si_2H_6 formation; □, Si_3H_8 formation. Fluence = 1.0 J/cm^2.

(2) SiH_2 and SiH_3SiH are taken to be at the same *vibrational* temperature as SiH_4 and classical vibrational heat capacities are assumed.

(3) Vibrational frequencies for the Si_2H_6 and Si_3H_8 molecules were taken from the literature.[24,40] The reaction coordinates for (5) and (10) were taken to be Si–H stretching modes while that for (9) was assumed to be a Si–Si stretching mode; the corresponding frequencies were simply removed for the respective transition states of the unimolecular decompositions, (5), (9) and (10).

(4) The collisional stabilization rate constants, k_6 and k_{11}, were taken to be 1.7×10^{-11} cm^3/s as reported from experimental studies of the collisional stabilization of UF_6.[41]

The results of the calculations are shown by the solid lines in Figure 7, while the points shown are the experimental values. Considering the crudeness of the calculations, the agreement with experiment must be considered as satisfactory.

The much more rapid decrease in the observed normalized yield of Si_2H_6, as compared with the calculated yield, is probably due to the occurrence of secondary reactions that destroy the very reactive Si_2H_6.[23] A corresponding destruction of Si_3H_8 would also be expected and while the data seem in accord, it is not as evident as in Si_2H_6 due to the much lower concentration.

4. Effect of He on the Formation of Si_2H_6 and Si_3H_8. The data in Figure 1 show that within experimental error, He is just as effective in promoting absorption of laser energy as is SiH_4. However, the results in Figure 4 show that He is not as effective as SiH_4 in increasing the formation of Si_3H_6 but is more effective than SiH_4 in increasing the formation of Si_3H_8. This is probably to be understood on the basis that He is a less effective third body for the stabilization of Si_2H_6* in reaction 6 than is SiH_4. The data in Figure 4 suggest, and it is born out by experiment, that the rate of reaction of SiH_4 depends only on total pressure for P(SiH_4) $\geq$ 15 torr and, therefore, in view of Figure 1, only on the average number of quanta per molecule.

The addition of He clearly increases the rate of reaction, as shown in Figure 4, and therefore the infrared laser induced decomposition of SiH_4 is a pressure-dependent multiphoton photodecomposition and not a thermal reaction. The success of the treatment employed here indicates that for multiphoton processes in which collisions are necessary to reach the quasicontinuum and in which reaction occurs with $\bar{v}$ in the range of 2–4, one may assume that the vibrational energy from the laser radiation may be taken to be in a nondegenerate Boltzmann distribution characterized by the average number of quanta absorbed per molecule.

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Induced Optical Activity and Liquid Crystal Linear Dichroism of 9,9′-Spirobi[9*H*-fluorene]

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Abstract: A direct confirmation of the mechanism of induction of optical activity proposed by Craig and Stiles for molecules of D_{2d} or S_4 symmetry, on the basis of Jahn–Teller distortion of degenerate excited states producing excited enantiomeric species discriminated in energy in a chiral environment, has been sought by direct measurement of the induced circular dichroism of the spirobifluorene molecule. The shape of the measured induced circular dichroism for the lowest transition in *d*- and *l*-diethyl tartrate is consistent with the Craig–Stiles model, even though other mechanisms of induction of optical activity appear to be active and contribute to the CD signal of this molecule in chiral solvents.

An achiral molecule, dissolved in a chiral solvent, becomes chiral and displays induced circular dichroism (ICD). ICD has been recorded for several molecules in different environments,[2] and theoretical models have been proposed[3-5] to show that ICD may

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