THE 147 nm PHOTODECOMPOSITION OF METHYLSILANE

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Summary

The photodecomposition of methylsilane at 147 nm results in the formation of hydrogen, methane, ethane, dimethylsilane, methyldisilane, dimethyldisilane and a solid deposit on the walls of the vessel. Six primary processes are required to explain the experimental results. These are as follows, with the primary quantum yields given in parentheses:

$$CH_3SiH_3 + h\nu \rightarrow CH_4 + SiH_2 \qquad (0.07) \qquad \text{(a)}$$

$$CH_3SiH_3 + h\nu \rightarrow CH_3 + H + SiH_2 \qquad (0.24) \qquad \text{(b)}$$

$$CH_3SiH_3 + h\nu \rightarrow CH_3SiH + H_2 \qquad (0.24) \qquad \text{(c)}$$

$$CH_3SiH_3 + h\nu \rightarrow CH_3SiH + 2H \qquad (0.07) \qquad \text{(d)}$$

$$CH_3SiH_3 + h\nu \rightarrow CH_2SiH_2 + H_2 \qquad (0.29) \qquad \text{(e)}$$

$$CH_3SiH_3 + h\nu \rightarrow CHSiH_3 + H_2 \qquad (0.09) \qquad \text{(f)}$$

The excess energies of the photodissociations, which must be disposed of by the products of the primary processes, are very large, ranging from 42 to 150 kcal mol^{-1}, so that without doubt the products of the primary processes are internally excited. It is shown specifically that methyl radicals from reaction (b) react some 140 times faster with methylsilane than do methyl radicals without excess internal energy. A mechanism involving further reactions of the products of the primary processes is proposed which is in accord with the experimental facts.

1. Introduction

Although a number of studies of the thermal [1 - 7], mercury-photosensitized [5, 6] and radical-induced [7 - 23] decompositions of methylsilane have been reported, only one investigation of the direct photolysis of

this molecule has appeared in the literature. Over a decade ago, Strausz and coworkers [24, 25] reported a study of the vacuum UV photochemistry of methylsilane based on the irradiation of static systems followed by gas chromatographic measurement of reaction products. We have recently examined the 147 nm photodecomposition of methylsilane by a very different experimental technique, namely irradiation in a flow system in which the photolysis cell is coupled to a mass spectrometer, permitting continuous monitoring of reactant and product concentrations [26 - 28].

2. Experimental

The photolyses were carried out in a cylindrical cell 1.9 cm in diameter and 13.4 cm long which was coupled via a pinhole leak to a time-of-flight mass spectrometer. The apparatus and the xenon resonance lamp used as a source of 147 nm radiation have been described previously [26 - 28]. The partial pressure of methylsilane was 2 Torr and that of the diluent gas, helium, was 38 Torr in all experiments. Under these conditions, absorption [29] of the 147 nm radiation is essentially complete.

The light intensity incident on the reactant mixture was determined by hexafluoroacetone actinometry, *i.e.* $\Phi(C_2F_6) = 1.11$ at 4 Torr [27]. Since the photodecomposition results in the formation of a solid deposit on the window of the photolysis cell that attenuates the light intensity incident on the reactant, it was necessary to make an actinometric measurement prior to each photolysis of methylsilane. The intensity incident on the reactant through a freshly cleaned window (lithium fluoride) was $(2.0 \pm 0.2) \times 10^{15}$ quanta s^{-1}.

Reaction products were identified by comparison of the overall mass spectrum produced by the photolysis with the individual spectra of methane, ethane, dimethylsilane, methyldisilane and dimethyldisilane. Quantitative determinations of the various reaction products were made using the relationship between ion current and pressure, as determined by calibration with pure samples in helium. The ions used for the product determinations were as follows: methane, $m/q = 16$; ethane, $m/q = 26$; dimethylsilane, $m/q = 58$; methyldisilane, $m/q = 76$; dimethyldisilane, $m/q = 90$. Although these masses were chosen so as to minimize interferences from ions due to other products, some corrections were necessary. For dimethylsilane the current at mass 58 had to be corrected for contributions from methyldisilane and dimethyldisilane. Despite the fact that the corrections amounted to nearly 90% of the total ion current at mass 58, a reasonable precision in the determination of dimethylsilane was achieved, as indicated by an average deviation in five replicate experiments of ±13%. The rate of depletion of methylsilane was determined from the decrease in current at mass 41, *i.e.* from the CHSi$^+$ ion, for which interferences from the products were negligible. Since mass spectra for the reaction products methyldisilane and dimethyldisilane have not appeared in the literature, we report such spectra for 50 eV electrons in Fig. 1.

Methylsilane, obtained from PCR Research Chemicals, Inc., was subjected to a freeze–pump–thaw cycle on a high vacuum line prior to use.
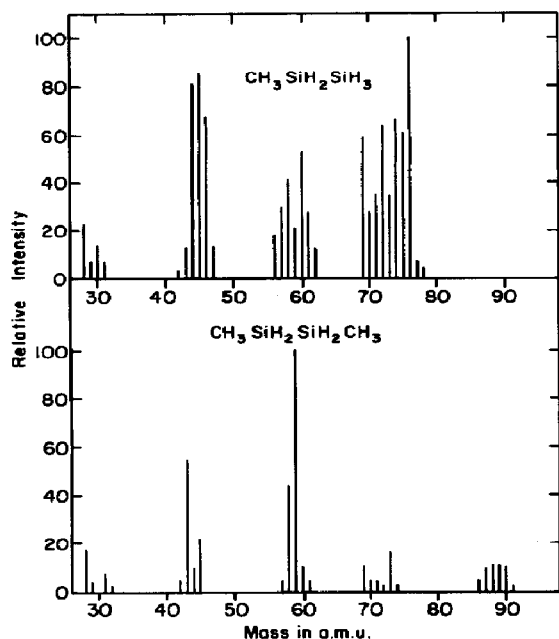
Fig. 1. Mass spectra of methyldisilane and dimethyldisilane at an ionizing energy of 50 eV.

Dimethylsilane was prepared by the lithium aluminum hydride reduction of dichlorodimethylsilane. Methyldisilane was prepared by a batch photolysis of 500 Torr of methylsilane in a 1 l vessel. The methyldisilane was separated from the reactant and other products by vacuum-line distillation and was identified by comparison of the mass spectrum with that [30] of an authentic sample. Dimethyldisilane obtained from Petrarch Systems, Inc., was purified by three freeze–pump–thaw cycles in which warm-up to 59 °C between cycles was permitted. Nitric oxide from Matheson Co. was subjected to a freeze–pump–thaw cycle in which the volatile material first appearing during a slow warm-up period was collected and used. Helium, also from Matheson, was used as received.

3. Results and discussion

The photodecomposition results in the formation of hydrogen, methane, ethane, dimethylsilane, methyldisilane, dimethyldisilane and a solid deposit on the walls and window of the photolysis cell. The form of the dependence of the various ion currents on the photolysis time indicates that all products are primary products of the photodecomposition, an observation in accord with the results of the earlier investigation [25].

3.1. Overall quantum yields

As has been described previously [26 - 28], quantum yields of the photodecomposition were determined from the initial slopes of recorder

tracings of ion currents at the various masses plotted against photolysis time. The yields for the formation of the various products and for the depletion of methylsilane are shown in Table 1. Also shown in Table 1 for comparison are the results of Obi *et al.* [25]. No comparison can be made for the formation of hydrogen and the depletion of methylsilane since we did not measure the former and Obi *et al.* [25] did not measure the latter. The agreement between the results of the two studies is generally very good despite the very different measurement techniques used.

The present values for the quantum yields of methyldisilane and dimethyldisilane are 15 - 20% lower than those of the earlier study [25]. Although in the earlier study uncertainties were not reported, the differences may lie outside experimental error and, if so, may be due to differences in the pressure of methylsilane. Thus Obi *et al.* [25] have shown that an increase in pressure of methylsilane from 3 to 100 Torr resulted in an approximate doubling of the quantum yields for methyldisilane and dimethyldisilane. The pressure effect was attributed to a stabilization of energy-rich disilane products. The fact that our quantum yields for these substances are lower may then be explained by the relatively low partial pressure of 2 Torr of methylsilane that we used. However, the total pressure in our experiments (with helium diluent) was 40 Torr and the fact that our quantum yields for methyldisilane and dimethyldisilane were only 15 - 20% lower suggests that helium serves as a surprisingly effective stabilization gas for internally excited disilanes.

3.2. Effect of light intensity

The reduction in incident light intensity caused by the build-up of solid deposit on the window of the reaction vessel, and the attendant need to evaluate the intensity before each experiment, provides the opportunity to examine the effect of a tenfold variation in light intensity on the quantum yields. With the exception of that for methane formation, which decreased

TABLE 1

Quantum yields in the photodecomposition of methylsilane[a] at 147 nm

Molecule	No. of replicate experiments	Φ(this work)[b]	Φ (ref. 25)
CH_3SiH_3	6	-2.80 ± 0.07	–
H_2	–	–	1.01
CH_4	5	0.138 ± 0.013	0.16
C_2H_6	5	0.062 ± 0.009	0.06
$(CH_3)_2SiH_2$	6	0.063 ± 0.008	0.07
$CH_3SiH_2SiH_3$	6	0.311 ± 0.005	0.36
$CH_3SiH_2SiH_2CH_3$	6	0.360 ± 0.004	0.44

[a]The partial pressure of methylsilane was 2.0 Torr and that of helium was 38.0 Torr.
[b]The uncertainties indicated are average deviations from the average.

with increasing intensity, all quantum yields were independent of light intensity. This may be seen in Fig. 2 in which the quantum yields of several of the products are plotted against the square root of the reciprocal of the light intensity. The reason for plotting in this fashion will be discussed in a later section but it may be said here that the dependence of $\Phi(CH_4)$ on intensity is in accord with the formation of methane being in part via the abstraction of hydrogen from methylsilane by methyl radicals.

3.3. Effect of nitric oxide on quantum yields

Nitric oxide was added to the photolysis system (at partial pressures such that its light absorption was negligible) in order to suppress the reactions of monovalent radicals. It has been shown that divalent silylene radicals are unreactive towards nitric oxide [25]; however, it is well known that monovalent radicals such as methyl and monosilyl are very effectively intercepted by nitric oxide [5, 6].

The effect of nitric oxide on the quantum yields of the various products, which is shown graphically in Fig. 3, is now discussed.

3.3.1. Dimethyldisilane

The quantum yield of this product is clearly suppressed, but only partially, the plateau reached at high nitric oxide concentrations being only 14% below the value of the quantum yield in the absence of nitric oxide. The limited data of Obi et al. [25] relative to this point are ambiguous, although
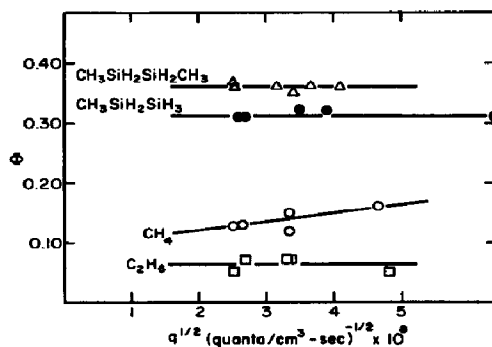

Fig. 2. The dependence of the quantum yields on the light intensity: ○, CH_4; □, C_2H_6; △, $CH_3SiH_2SiH_2CH_3$; ●, $CH_3SiH_2SiH_3$.
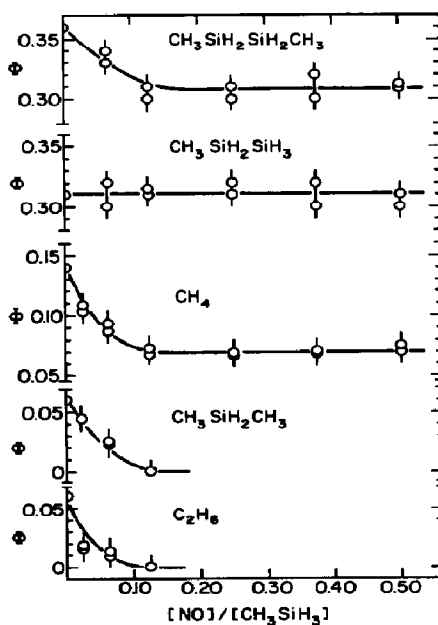
Fig. 3. The effect of nitric oxide on the quantum yields of the reaction products.

they concluded correctly that the major part of dimethyldisilane is formed by a mechanism not involving monoradicals.

3.3.2. Methyldisilane

As may be seen clearly in Fig. 3, the quantum yield is quite unaffected by the presence of nitric oxide and it may be concluded that none of the methyldisilane is produced by reactions of monoradicals. The results of Obi *et al.* [25] are somewhat ambiguous in this matter because they suggest there may be an increase in the yield of methyldisilane as the nitric oxide concentration is increased.

3.3.3. Methane

The quantum yield of this product is partially suppressed by nitric oxide to 51% of the value obtained in the absence of nitric oxide. This indicates that about half of the yield is due to monoradical reactions and that the other half is the result of other processes. Our data on nitric oxide suppression are thus in accord with the mechanistic conclusions of Obi *et al.* [25]. However, although the results in Fig. 3 clearly show the partial suppression by nitric oxide, the limited data of the earlier group [25] suggest an increase in yield with increasing concentration of nitric oxide.

3.3.4. Dimethylsilane and ethane

The addition of nitric oxide completely suppresses the quantum yields of these two products, indicating that both arise solely from reactions of monoradicals. The data and conclusions are in complete accord with the results of Obi *et al.* [25].

3.4. Primary processes

It is known [9, 11, 18] that singlet methylene will insert into Si—H bonds and the fact that dimethylsilane is not a product in the presence of nitric oxide demonstrates that there is no primary process occurring in which methylene is formed. However, silylene must be formed in primary processes in order that methyldisilane be formed in processes not affected by nitric oxide. The yield of methane that is not suppressible by nitric oxide is 0.07 and this must be the quantum yield of the primary process (a), *i.e.*

$$CH_3SiH_3 + h\nu \rightarrow CH_4 + SiH_2 \qquad \Phi_{(a)} = 0.07 \qquad \text{(a)}$$

The fact that the yields of ethane and dimethylsilane are completely suppressed by nitric oxide indicates that these products are formed solely by combination reactions of methyl and methylsilyl radicals. It is not likely that methyl radicals can be formed in this system except in a primary process and the absence of disilane as a product points to the absence of silyl radicals [26]. The only reasonable primary process to account for these observations is (b), *i.e.*

$$CH_3SiH_3 + h\nu \rightarrow CH_3 + H + SiH_2 \qquad \Phi_{(b)} = 0.24 \qquad \text{(b)}$$

with the primary quantum yield being determined by the fact that the total yield of silylene in the primary processes (a) and (b) must equal the overall quantum yield of methyldisilane. A check on the derived value of $\Phi_{(b)}$ may be made by noting that a methyl radical produced in reaction (b) will ultimately form methane (by abstraction of hydrogen from methylsilane) and ethane or dimethylsilane (by radical combination reactions). Appropriate combination of these overall yields gives $\Phi_{(b)} = 0.25$ which is in excellent agreement with the value derived from the yield of methyldisilane.

The non-suppressible part of the quantum yield of dimethyldisilane is undoubtedly due to the insertion of methylsilylene into an Si—H bond of methylsilane. There are two possible primary processes in which methylsilylene may be formed, namely (c) and (d):

$$CH_3SiH_3 + h\nu \rightarrow CH_3SiH + H_2 \tag{c}$$

$$CH_3SiH_3 + h\nu \rightarrow CH_3SiH + 2H \tag{d}$$

The sum of the quantum yields of these two processes must be equal to the non-suppressible yield of dimethyldisilane, i.e. $\Phi_{(c)} + \Phi_{(d)} = 0.31$.

It was not possible to demonstrate the existence of any other primary processes from our data. However, Obi et al. [25] have shown from studies of the photolysis of CH_3SiH_3–CH_3SiD_3 mixtures that (e) and (f) must be occurring as primary processes:

$$CH_3SiH_3 + h\nu \rightarrow CH_2SiH_2 + H_2 \tag{e}$$

$$CH_3SiH_3 + h\nu \rightarrow CHSiH_3 + H_2 \tag{f}$$

Assuming $\Sigma_{(c)\equiv(a)}^{(f)}\Phi_i = 1$, we find that the sum of the quantum yields of the two primary processes (e) and (f) is $\Phi_{(e)} + \Phi_{(f)} = 0.38$.

The abstraction of hydrogen from the Si—H bonds in methylsilane by atomic hydrogen is known to be very fast [21, 23] compared with other possible reactions of atomic hydrogen. We may therefore conclude that all the hydrogen atoms formed in primary processes (b) and (d) will react with methylsilane to form molecular hydrogen and methylsilyl radicals. It was not practical to measure hydrogen quantitatively in our system, but Obi et al. [25] have reported a value for the quantum yield $\Phi(H_2)$ of 1.01. We may utilize this overall quantum yield of hydrogen to obtain values for $\Phi_{(c)}$ and $\Phi_{(d)}$. Thus, since all hydrogen atoms result in hydrogen formation, we may write

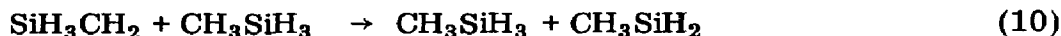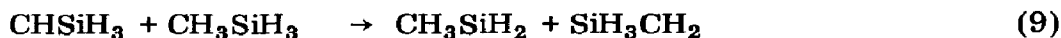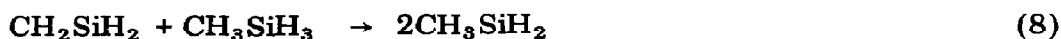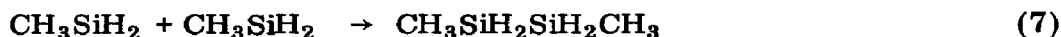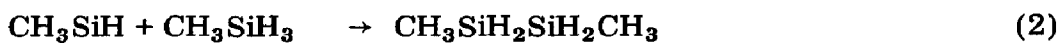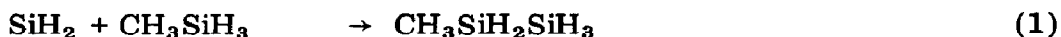$$\Phi_{(b)} + \Phi_{(c)} + 2\Phi_{(d)} + \Phi_{(e)} + \Phi_{(f)} = 1.01$$

and, since $\Phi_{(b)}$, $\Phi_{(c)} + \Phi_{(d)}$ and $\Phi_{(e)} + \Phi_{(f)}$ have already been determined, we obtain $\Phi_{(c)} = 0.23$ and $\Phi_{(d)} = 0.08$.

The depletion of methylsilane occurs with a quantum yield (cf. Table 1) of $\Phi(-CH_3SiH_3) = 2.80$. The primary processes account for the disappearance of one molecule per quantum. Considerations of the secondary reactions show, if it is assumed that the products of processes (e) and (f) other than molecular hydrogen react with methylsilane, a theoretical

yield of $\Phi(-CH_3SiH_3) = 2.5$. If, however, it is assumed that the reactive products of reactions (e) and (f) do not react with methylsilane, then a theoretical yield of $\Phi(-CH_3SiH_3) = 2.1$ is obtained. Although the evidence admittedly is not strong, we suggest that both species silaethylene and silylcarbene react quantitatively with methylsilane. It is not likely that silaethylene will undergo insertion reactions and there is no evidence of formation of the expected insertion products of silylcarbene. Hence we propose that these species react by hydrogen atom abstraction from the Si—H bonds of methylsilane. We are unable to separate the individual yields of $\Phi_{(e)}$ and $\Phi_{(f)}$.

The primary processes and primary quantum yields are summarized in Table 2. Also shown in Table 2 are the corresponding values reported by Obi *et al.* [25] for the 147 nm photolysis of methylsilane-d_3. Considering the very different experimental techniques used and the fact that some differences are expected in a comparison of methylsilane and methylsilane-d_3, even when the photonic energy is very high as is the case here, the agreement is very good.

The secondary reactions, which together with the primary processes complete the mechanistic scheme, are according to the preceding discussion as shown in reactions (1) - (10).

$$SiH_2 + CH_3SiH_3 \rightarrow CH_3SiH_2SiH_3 \tag{1}$$

$$CH_3SiH + CH_3SiH_3 \rightarrow CH_3SiH_2SiH_2CH_3 \tag{2}$$

$$H + CH_3SiH_3 \rightarrow H_2 + CH_3SiH_2 \tag{3}$$

$$CH_3 + CH_3SiH_3 \rightarrow CH_4 + CH_3SiH_2 \tag{4}$$

$$CH_3 + CH_3 \rightarrow C_2H_6 \tag{5}$$

$$CH_3 + CH_3SiH_2 \rightarrow CH_3SiH_2CH_3 \tag{6}$$

$$CH_3SiH_2 + CH_3SiH_2 \rightarrow CH_3SiH_2SiH_2CH_3 \tag{7}$$

$$CH_2SiH_2 + CH_3SiH_3 \rightarrow 2CH_3SiH_2 \tag{8}$$

$$CHSiH_3 + CH_3SiH_3 \rightarrow CH_3SiH_2 + SiH_3CH_2 \tag{9}$$

$$SiH_3CH_2 + CH_3SiH_3 \rightarrow CH_3SiH_3 + CH_3SiH_2 \tag{10}$$

3.5. Kinetic treatment of the mechanism

The fact that all three combination reactions of methyl and methylsilyl radicals, namely (5) - (7), are significant precludes a tractable solution of the steady state rate equations. However, ethane and dimethylsilane are formed solely by reactions (5) and (6) respectively and it is convenient to define the steady state concentrations of methyl and methylsilyl radicals in terms of

TABLE 2

Primary processes and quantum yields in the 147 nm photodecomposition of methylsilane

Process	Products	Excess energy (kcal mol^{-1})	Quantum yield	Quantum yield (ref. 25)
(a)	$CH_4 + SiH_2$	150	0.07	0.09
(b)	$CH_3 + H + SiH_2$	48	0.24	0.26
(c)	$CH_3SiH + H_2$	146	0.23	0.32
(d)	$CH_3SiH + 2H$	42	0.08	0.05
(e)	$CH_2SiH_2 + H_2$	–	0.29[a]	0.23
(f)	$CHSiH_3 + H_2$	–	0.09[a]	0.07

[a]Our data yield only a total of $\Phi_{(e)} + \Phi_{(f)} = 0.38$. These values are obtained using the same ratio of $\Phi_{(f)}$ to $\Phi_{(e)}$ as obtained by Obi et al. [25].

the observed quantum yields and the absorbed light intensity. Thus we obtain from the rates of reactions (5) and (7) and the relationship that the rate equals Φq the expressions (11) and (12):

$$[CH_3] = \left(\frac{q\Phi_E}{k_5}\right)^{1/2} \tag{11}$$

$$[CH_3SiH_2] = \left(\frac{qk_5\Phi_{DMS}^2}{k_6^2\Phi_E}\right)^{1/2} \tag{12}$$

where Φ_E and Φ_{DMS} are the quantum yields of ethane and dimethylsilane respectively, and q is the rate of absorption of quanta. Using these expressions and the standard steady state approximations for the concentrations of all other reactive intermediates, we may then derive in a straightforward way the predicted quantum yields for the products other than ethane and dimethylsilane and for the depletion of methylsilane. The results obtained thus which are in accord with the experimental facts are as follows:

$$\Phi(CH_3SiH_2SiH_3) = \Phi_{(a)} + \Phi_{(b)} \tag{13}$$

$$\Phi(CH_3SiH_2SiH_2CH_3) = \Phi_{(c)} + \Phi_{(d)} + \frac{k_5k_7}{k_6^2}\frac{\Phi_{DMS}^2}{\Phi_E} \tag{14}$$

$$\Phi(CH_4) = \Phi_{(a)} + \left(\frac{k_4}{k_5^{1/2}}\right)[CH_3SiH_3]\left(\frac{\Phi_E}{q}\right)^{1/2} \tag{15}$$

$$\Phi(-CH_3SiH_3) = 1 + \Phi_{(a)} + 2\Phi_{(b)} + \Phi_{(c)} + 3\Phi_{(d)} + \Phi_{(e)} + \Phi_{(f)} +$$
$$+ \left(\frac{k_4}{k_5^{1/2}}\right)[CH_3SiH_3]\left(\frac{\Phi_E}{q}\right)^{1/2} \tag{16}$$

As shown by eqn. (15) the mechanism predicts that $\Phi(CH_4)$ should be dependent on the absorbed light intensity and specifically that it should vary with the inverse square root of q. It is for this reason that the data in Fig. 2 were plotted against $q^{-1/2}$. When the slope of the best straight line through the points for methane in Fig. 2 is combined with the known values of Φ_E and $[CH_3SiH_3]$, using expression (15) we obtain

$$\frac{k_4}{k_5^{1/2}} = (9 \pm 5) \times 10^{-11} \text{ cm}^{3/2} \text{ molecules}^{-1/2} \text{ s}^{-1/2}$$

The value of this ratio for methyl radicals produced by the near UV photolysis of azomethane [17] is 6.3×10^{-13} cm$^{3/2}$ molecules$^{-1/2}$ s$^{-1/2}$, a value some 140 times lower than that obtained in the present system. This implies that the methyl radicals in the present system undergo reaction (4) much more rapidly and/or reaction (5) less rapidly than do methyl radicals that do not contain significant amounts of internal energy, such as are produced in the azomethane photolysis. It is thus indicated that the methyl radicals formed in primary process (b) are vibrationally excited to a very significant extent. This is of course not surprising because, when the photodissociation (b) occurs with 147 nm photons, 48 kcal mol^{-1} must be disposed of by the products of the reaction [31, 32]. If this energy is shared equally by all the vibrational modes of the products of process (b), the methyl radical will contain an excess vibrational energy of 28 kcal mol^{-1}. Since the activation energy of reaction (4) is 8.1 kcal mol^{-1} [17], the presence of this amount of internal energy in the methyl radical would be expected to result in a significant increase in the speed of reaction (4). The excess energies to be disposed of in all the photodissociations are very large (*cf.* Table 2) and the polyatomic products of all the primary processes must contain excess vibrational energy. This is undoubtedly the cause of the pressure effects noted by Obi *et al.* [25]. We can do no more at present than report the total excess energies that must be disposed of in each primary process, as given in Table 2.

Equation (16) predicts that the quantum yield for depletion of methylsilane should decrease with the inverse square root of the light intensity. However, the term containing the intensity in eqn. (16) is so small in comparison with the sum of the intensity-independent terms, *i.e.* a maximum of 0.07 compared with 2.4, that it is not surprising that we were unable to detect experimentally the predicted intensity dependence of $\Phi(-CH_3SiH_2)$.

3.6. Formation of solid deposit

Although the mechanism proposed accounts satisfactorily for the experimental facts concerning the formation of volatile products, it is not a complete mechanism because it does not explain the formation of the solid deposit. The formation of such a deposit is characteristic of the decomposition of all silanes. The solid must be formed by the reaction of silicon-containing intermediates at the walls and window of the photolysis cell. The rate constant of reaction (1) is so large (*i.e.* 1.06×10^{-11} cm^3 molecules^{-1} s^{-1}) [20, 33] that under our conditions the number of silylene radicals

reaching the wall will be insignificant. The same is probably true for the other silylene-type radicals present, namely methylsilylene. This leaves the monoradical methylsilyl and the diradicals silaethylene and silylcarbene as the only silicon-containing reaction intermediates that can reach the wall and can therefore be responsible for the build-up of solid. This conclusion regarding the solid deposition is analogous to those reached previously in the hydrogen-atom-induced decomposition of monosilane [34] and in the 147 nm photodecomposition of monosilane [26] and disilane [30].

Acknowledgment

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