

## Photolysis of hexamethyldisilane at 206 nm

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### Abstract

The photolysis of  $\text{Me}_6\text{Si}_2$  at 206 nm results in two main decomposition processes: simple Si–Si bond breaking with a quantum yield of  $\Phi = 0.21 \pm 0.03$ , and  $\text{Me}_3\text{SiH}$  elimination with the concomitant formation of  $\text{Me}_2\text{SiCH}_2$  with  $\Phi = 0.18 \pm 0.01$ . There is also a minor decomposition channel with a very small quantum yield,  $\Phi = (5.6 \pm 0.2) \times 10^{-3}$ , which results in the formation of  $\text{Me}_3\text{Si}$  and  $\text{Me}_2\text{Si}$ . The main fate of the excited  $\text{Me}_6\text{Si}_2$  molecule produced during photolysis is stabilization by collisional deactivation. The end products observed indicate that the reaction pathways followed by the main intermediates,  $\text{Me}_3\text{Si}$  and  $\text{Me}_2\text{SiCH}_2$ , are the same as those found in the photolysis of  $\text{Me}_4\text{Si}$  (Ahmed et al., *J. Photochem. Photobiol. A: Chem.* 86 (1995) 33). © 1997 Elsevier Science S.A.

**Keywords:** Hexamethyldisilane; Photolysis

### 1. Introduction

In a previous paper from this laboratory [1], we reported the photolysis of  $\text{Me}_4\text{Si}$  in the long-wavelength absorption region. A detailed account of the mechanism of decomposition was given, and some insight was gained into the photo-physics of the  $\text{Me}_4\text{Si}$  molecule. We concluded that the two decomposition processes of Si–C bond breaking and molecular methane elimination took place from the excited state, and molecules reaching the electronic ground state were mostly deactivated. Our aim in this work is to investigate the effect on the photolytic behaviour of the replacement of a methyl group in  $\text{Me}_4\text{Si}$  by an  $\text{Me}_3\text{Si}$  group.

$\text{Me}_6\text{Si}_2$  has been used as a precursor for the photolytic generation of  $\text{Me}_3\text{Si}$  radicals [2–4]. Brix et al. [3] also investigated the decomposition channels in the stationary photolysis at 206 nm. It was found that two processes accounted for 98% of the  $\text{Me}_6\text{Si}_2$  decomposed: Si–Si bond breaking (71%) and molecular  $\text{Me}_3\text{SiH}$  elimination (27%). No quantum yields were given and the material balance was poor. These deficiencies have been remedied in more recent work [1,5,6]. In this paper, we describe the determination of the quantum yields of the various primary processes occurring during the photolysis of  $\text{Me}_6\text{Si}_2$ , and examine the mechanism leading to the formation of the end products.

### 2. Experimental details

The photolysis system, gas handling and product analysis techniques employed in this work have been described previously [1,5]. The 206 nm radiation was produced by a microwave discharge lamp. The lamp was thermostatically controlled at 18 °C, resulting in a very stable light output. Photon fluxes in the photolysis cell were determined by HBr actinometry ( $\Phi(\text{H}_2) = 1.0$  [7]), and amounted to  $(2-3) \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$ .

All compounds were of commercial origin and of the highest purity available.  $\text{Me}_6\text{Si}_2$  was dried before use by passing the vapour through a  $\text{P}_2\text{O}_5$  column.

End products were separated on an OV1 fused silica capillary column, and identified on a coupled gas chromatography–mass spectrometry (GC–MS) apparatus (HP 5971A). Response factors were taken to be proportional to the number of C atoms in the compound under consideration [1], and  $\text{C}_2\text{H}_6$  was used as an internal standard. All the products, with one exception, could be identified by their retention times and/or mass spectra. The GC retention time classified the unknown product quite clearly as a tetrasilane.

The absorption spectrum of  $\text{Me}_6\text{Si}_2$  was recorded on a single beam apparatus incorporating a stabilized deuterium lamp (Hamamatsu C1518), a vacuum UV monochromator (Minuteman 302VM) and a photomultiplier (EMR 54-IN-06). Measurements were taken at several different pressures of  $\text{Me}_6\text{Si}_2$ , and each measurement was preceded and followed by a blank.

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### 3. Results

The absorption cross-section of  $\text{Me}_6\text{Si}_2$  in the wavelength region 175–240 nm is shown in Fig. 1. Agreement with a previously published spectrum [8] is good, and a value for the cross-section at 206 nm of  $\sigma(\text{base e}) = (9 \pm 1) \times 10^{-18} \text{ cm}^2$  was obtained.

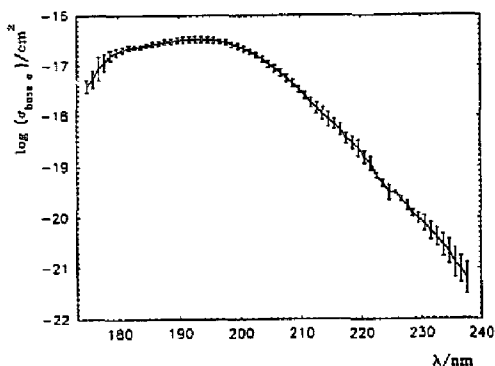


Fig. 1. Absorption cross-section of  $\text{Me}_6\text{Si}_2$  as a function of wavelength near the absorption onset.

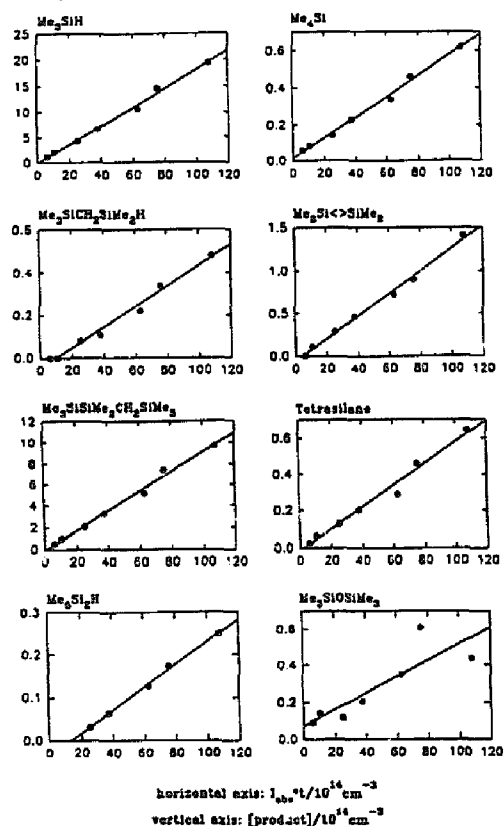


Fig. 2. Dependence of the product yields on the number of absorbed quanta.

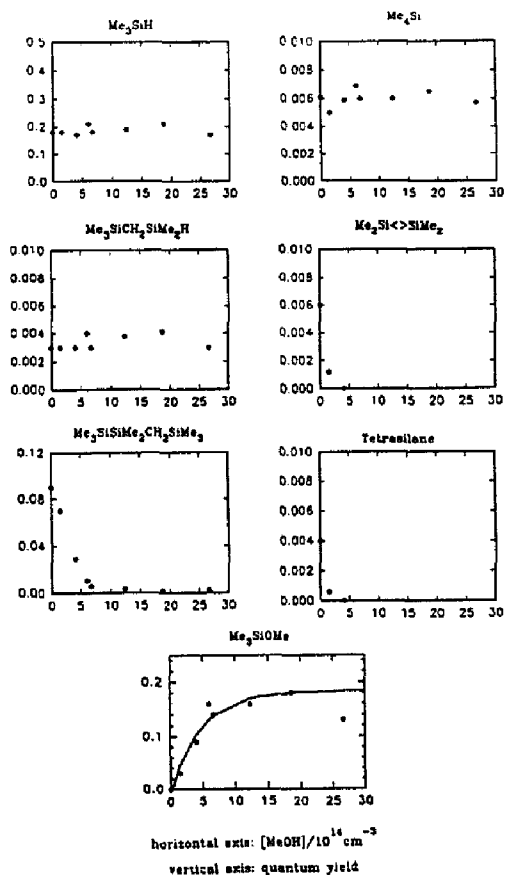


Fig. 3. Dependence of the product quantum yields on the MeOH concentration.

The concentrations of the various products as a function of photolysis time are shown in Fig. 2. In all cases, a linear relationship was obtained, a behaviour which is usually taken as an indication that a primary product is involved. For both  $\text{Me}_3\text{SiCH}_2\text{SiMe}_2\text{H}$  and  $\text{Me}_6\text{Si}_2\text{H}$ , a large negative intercept is observed. The quantum yields of the various products and the relative intercept  $X/\Phi$  (obtained from Fig. 3 by dividing the intercept  $X$  by the corresponding quantum yield) are listed in Table 1.

The effect of the addition of MeOH on the quantum yields of the products is shown in Fig. 3.  $\text{Me}_3\text{SiCH}_2\text{SiMe}_2\text{CH}_2$  (in the figures, the notation  $\text{Me}_2\text{Si} <> \text{SiMe}_2$  was used),  $\text{Me}_3\text{SiSiMe}_2\text{CH}_2\text{SiMe}_3$  and the tetrasilane disappear, whereas  $\text{Me}_3\text{SiH}$ ,  $\text{Me}_4\text{Si}$  and  $\text{Me}_3\text{SiCH}_2\text{SiMe}_2\text{H}$  remain unaffected. The product of the scavenging process,  $\text{Me}_3\text{SiOMe}$ , is also shown in Fig. 3.

When the photolysis is carried out in the presence of NO, all the products, with the exception of  $\text{Me}_3\text{SiH}$  and  $\text{Me}_4\text{Si}$ , disappear (Fig. 4). To determine the overall quantum yield of  $\text{Me}_6\text{Si}_2$  decomposition,  $\text{Me}_6\text{Si}_2$  was photolysed in the pres-

Table 1  
Product quantum yields and relative intercepts from Fig. 2

Product	$\Phi$ ( $10^{-2}$ )	$X/\Phi$ ( $10^{14}$ cm $^{-1}$ )
Me <sub>3</sub> SiH	18.2 ± 0.6	-0.55
Me <sub>3</sub> SiSiMe <sub>2</sub> CH <sub>2</sub> SiMe <sub>3</sub>	9.2 ± 0.4	-1.09
Me <sub>2</sub> SiCH <sub>2</sub> SiMe <sub>2</sub> CH <sub>2</sub>	1.32 ± 0.04	-4.55
Me <sub>3</sub> SiSiMe <sub>2</sub> CH <sub>2</sub> SiMe <sub>2</sub> CH <sub>2</sub> SiMe <sub>3</sub>	0.59 ± 0.04	-3.39
Me <sub>4</sub> Si	0.56 ± 0.02	3.57
Me <sub>3</sub> SiOSiMe <sub>3</sub>	0.50 ± 0.1	14.0
Me <sub>3</sub> SiCH <sub>2</sub> SiMe <sub>2</sub> H	0.48 ± 0.03	-10.4
Me <sub>3</sub> Si <sub>2</sub> H	0.27 ± 0.08	-13.7
Me <sub>3</sub> SiOMe/MeOH	18 ± 2	
-Me <sub>6</sub> Si <sub>2</sub> /NO	40 ± 4	
Me <sub>3</sub> SiH/GeH <sub>4</sub>	60 ± 5	
Me <sub>3</sub> Si <sub>2</sub> H/Me <sub>3</sub> SiH	0.48 ± 0.03	

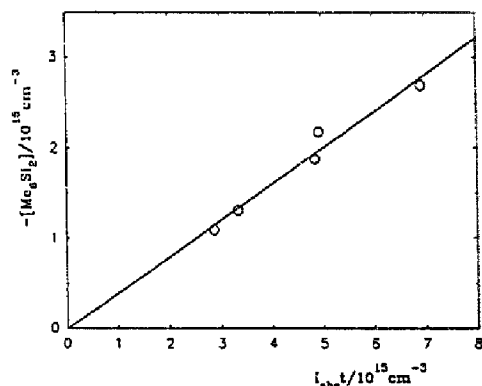


Fig. 5. Dependence of the reactant concentration on the number of absorbed quanta in the presence of NO.

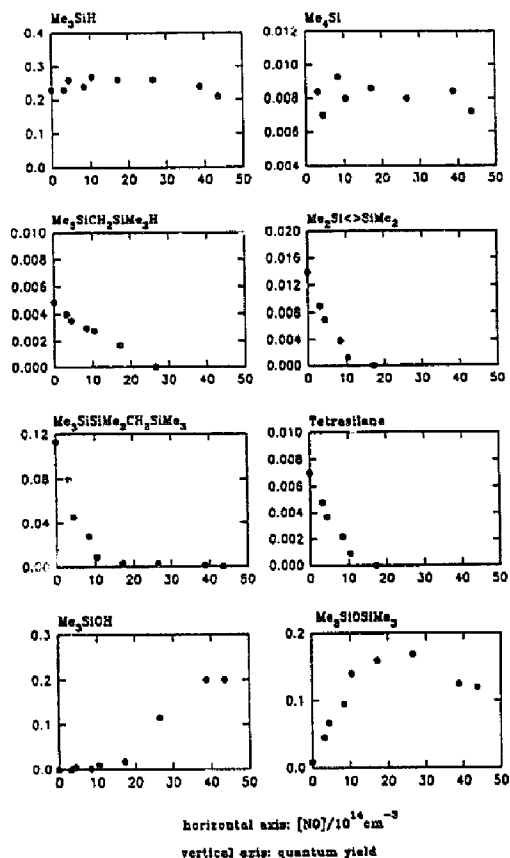


Fig. 4. Dependence of the product quantum yields on the NO concentration.

ence of an excess of NO. A value of  $\Phi(-\text{Me}_6\text{Si}_2) = 0.40 \pm 0.04$  was obtained (Fig. 5).

The result of the addition of GeH<sub>4</sub> on the product concentrations is depicted in Fig. 6. Me<sub>3</sub>SiCH<sub>2</sub>SiMe<sub>2</sub>H, Me<sub>3</sub>SiSiMe<sub>2</sub>CH<sub>2</sub>SiMe<sub>3</sub> and the tetrasilane disappear completely at higher GeH<sub>4</sub> concentrations. The data points for Me<sub>3</sub>Si, Me<sub>3</sub>Si<sub>2</sub>H and Me<sub>2</sub>SiCH<sub>2</sub>SiMe<sub>2</sub>CH<sub>2</sub> are rather scat-

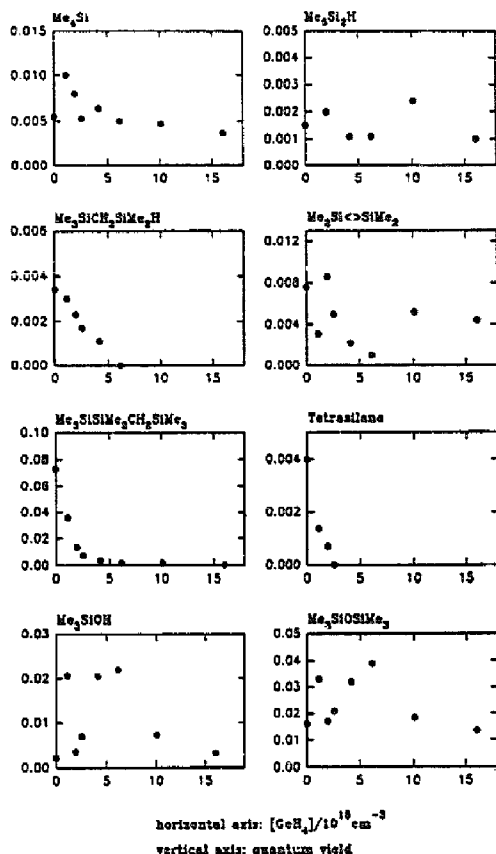


Fig. 6. Dependence of the product quantum yields on the GeH<sub>4</sub> concentration.

tered, but seem to be little influenced by the presence of GeH<sub>4</sub>. Me<sub>3</sub>SiH, on the other hand, increases with increasing GeH<sub>4</sub> concentration and reaches a plateau value (Fig. 7).

Me<sub>3</sub>SiOSiMe<sub>3</sub> and Me<sub>3</sub>SiOH are formed in the presence of NO by an unknown mechanism. Their formation in the presence of GeH<sub>4</sub> is likely due to traces of water.

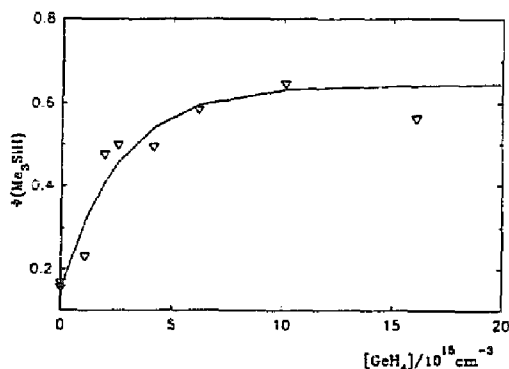


Fig. 7. Dependence of  $\Phi(\text{Me}_3\text{SiH})$  on the  $\text{GeH}_4$  concentration.

To elucidate the origin of  $\text{Me}_3\text{Si}_2\text{H}$ , we added  $\text{Me}_3\text{SiH}$  to the reaction mixture. The quantum yield of  $\text{Me}_3\text{Si}_2\text{H}$  increases in the presence of  $\text{Me}_3\text{SiH}$  and reaches a plateau value of  $4.8 \times 10^{-3}$  (Table 1).

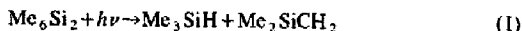
## 4. Discussion

### 4.1. The primary decomposition channels

To infer from the observed end products the nature of the decomposition channels of the excited reactant and the mechanism leading to the formation of stable products, product retrieval must be as complete as possible. A first indication that a good material balance has been achieved is the agreement between the empirical formula calculated from the observed products and the formula of the reactant. From the data in Table 1, we calculate that 0.27 molecule of a substance with the formula  $\text{Si}_{2.03 \pm 0.04}\text{C}_{6.1 \pm 0.2}\text{H}_{18.0}$  is decomposed per absorbed quantum. The decomposition quantum yield of 0.27 is a lower limit to the actual quantum yield because higher weight products may have gone undetected. However, there was no indication of polymer formation on the walls of the cuvette. The small value of the decomposition quantum yield must mean either that an appreciable number of the excited molecules are collisionally deactivated, or that radical recombination reactions regenerate the reactant. The quantum yield of  $\text{Me}_6\text{Si}_2$  decomposition in the presence of an excess of NO,  $\Phi(-\text{Me}_6\text{Si}_2/\text{NO}) = 0.40 \pm 0.04$ , indicates that deactivation is the most important channel open to the excited molecules. The question of whether the difference between the two decomposition quantum yields is due to an incomplete product recovery or to radical recombination processes must wait for an inspection of the individual product quantum yields.

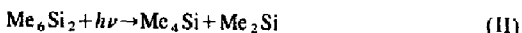
The quantum yields of  $\text{Me}_3\text{SiH}$  and  $\text{Me}_4\text{Si}$  are almost unaffected by the additives used in the photolysis experiments. In particular, the radical scavenger NO does not decrease the quantum yields of either  $\text{Me}_3\text{SiH}$  or  $\text{Me}_4\text{Si}$ .  $\text{GeH}_4$ , which is an efficient H atom donor to silyl radicals [1], increases the yield of  $\text{Me}_3\text{SiH}$  but leaves that of  $\text{Me}_4\text{Si}$  unchanged.

We therefore postulate that  $\text{Me}_3\text{SiH}$  is formed in a primary photochemical decomposition process, accompanied by the formation of  $\text{Me}_2\text{SiCH}_2$



Typical stable products of this intermediate, such as  $\text{Me}_2\text{SiCH}_2\text{SiMe}_2\text{CH}_2$  and  $\text{Me}_3\text{SiSiMe}_2\text{CH}_2\text{SiMe}_3$ , are indeed observed (see below).

A second primary decomposition process takes place with the formation of  $\text{Me}_4\text{Si}$



This is a minor decomposition channel, the quantum yield of  $\text{Me}_4\text{Si}$  being only  $(5.6 \pm 0.2) \times 10^{-3}$ . The correspondingly small amount of  $\text{Me}_2\text{Si}$  formed is accordingly difficult to demonstrate. This problem is taken up in Section 4.2.

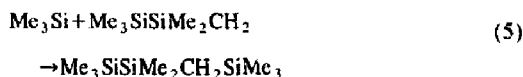
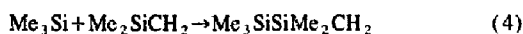
The product  $\text{Me}_3\text{SiSiMe}_2\text{CH}_2\text{SiMe}_3$  is not only characteristic of the formation of  $\text{Me}_2\text{SiCH}_2$ , but also requires the presence of  $\text{Me}_3\text{Si}$  radicals. A further sign that  $\text{Me}_3\text{Si}$  radicals are formed is the increase in the  $\text{Me}_3\text{SiH}$  quantum yield in the presence of  $\text{GeH}_4$ . We attribute the formation of  $\text{Me}_3\text{Si}$  radicals to the primary decomposition channel



Evidence for the occurrence of two other processes, which play an important role in the photochemistry of  $\text{Me}_6\text{Si}_2$ , was pursued. One is Si–C bond splitting, which has been postulated in a previous publication [3], and the other is the molecular elimination of  $\text{CH}_4$ .  $\text{CH}_4$  can be easily detected, but was not observed. A primary process in which Si–C bond breaking takes place will lead to the generation of two new radicals,  $\text{CH}_3$  and  $\text{Me}_3\text{SiSiMe}_2$ . These two radicals will be mostly scavenged by radicals present with the highest stationary concentration. It is shown below that, in our system,  $\text{Me}_3\text{Si}$  and  $\text{Me}_2\text{SiCH}_2$  are the scavengers in question. As in the photolysis of  $\text{Me}_4\text{Si}$ , where the same intermediates are present, we expect  $\text{Me}_3\text{SiSiMe}_2\text{Et}$ ,  $\text{Me}_3\text{Si}$  and  $\text{Me}_3\text{SiSiMe}_2\text{SiMe}_3$  as products. Neither  $\text{Me}_3\text{SiSiMe}_2\text{Et}$  nor a decrease in  $\text{Me}_4\text{Si}$  in the presence of NO or  $\text{GeH}_4$  was observed.  $\text{Me}_3\text{SiSiMe}_2\text{SiMe}_3$  was also absent from our product spectrum. We must therefore conclude that Si–C bond splitting does not occur in a primary decomposition process, or occurs with a quantum yield smaller than  $2 \times 10^{-3}$ , our approximate detection limit.

### 4.2. Mechanism and material balance

The two main primary processes (I) and (III) generate  $\text{Me}_2\text{SiCH}_2$  and  $\text{Me}_3\text{Si}$  radicals, whose pathways to stable products have already been studied. In the direct photolysis of  $\text{Me}_4\text{Si}$ ,  $\text{Me}_3\text{Si}$  radicals and  $\text{Me}_2\text{SiCH}_2$  molecules were formed in similar proportions, in addition to  $\text{CH}_3$  radicals. The mechanism advanced for  $\text{Me}_4\text{Si}$  [1] should also describe our present system if all reactions involving  $\text{CH}_3$  radicals are omitted.



This mechanism is somewhat simplified in that the addition of  $\text{Me}_3\text{Si}$  to the carbon side of the  $\text{SiC}$  double bond has been neglected. This process is of only minor importance, however [1].

To complete the mechanism, we must add the reactions involving dimethylsilylene. It is known that  $\text{SiMe}_2$  inserts very easily into an  $\text{Si-H}$  bond [9], adds to electron-rich double bonds [10] and combines to form  $\text{Si}_2\text{Me}_4$  [11]. At the beginning of the photolysis, only two reaction pathways seem to be open for  $\text{SiMe}_2$ : self-recombination



which proceeds at close to the collision-controlled rate [11], and addition to the  $\text{SiC}$  double bond of silaethene



The reaction (process (6) or (7)) of importance in our system depends on the rate constants of the two reactions and the stationary concentration of the  $\text{Me}_2\text{SiCH}_2$  intermediate. Reaction (7) has not yet been studied, but if we make the assumption that the  $\text{SiC}$  double bond shows a similar reactivity towards  $\text{SiMe}_2$  as the  $\text{CC}$  double bond in propene [10], the ratio of the two rate constants becomes  $k_6/k_7 \approx 3$ . The stationary concentration of  $\text{Me}_2\text{SiCH}_2$ , which is mainly determined by reactions (3) and (4), is given by

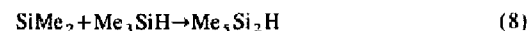
$$k_3[\text{Me}_2\text{SiCH}_2]^2 + k_4[\text{Me}_2\text{SiCH}_2][\text{Me}_3\text{Si}] = \Phi(I)I_{\text{abs}}$$

and the stationary concentration of  $\text{Me}_3\text{Si}$ , which is mainly determined by reactions (1) and (4), is given by

$$k_1[\text{Me}_3\text{Si}]^2 + k_4[\text{Me}_2\text{SiCH}_2][\text{Me}_3\text{Si}] = 2\Phi(\text{III})I_{\text{abs}}$$

From our previous investigations [1,12], we know that  $k_1 \approx k_3 \approx k_4 \approx k = 3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ . Furthermore  $\Phi(\text{I})/\Phi(\text{III})$ , which means that  $[\text{Me}_3\text{Si}] \approx 2^{1/2}[\text{Me}_2\text{SiCH}_2]$ . This leads to  $[\text{Me}_2\text{SiCH}_2]_{\text{ss}} = \Phi(\text{I})I_{\text{abs}} / [(1 + \sqrt{2})k]^{1/2} = 2 \times 10^{11} \text{ cm}^{-3}$ . From this value, it can be calculated that approximately 30% of the  $\text{SiMe}_2$  intermediates disappear by self-recombination, and the rest by addition to the  $\text{SiC}$  double bond.

Both reactions (6) and (7) will lose importance with increasing photolysis time because of the increasing concentration of  $\text{Me}_3\text{SiH}$  and, at the same time, reaction (8) will become increasingly important

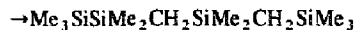
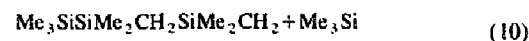


The time  $t$  at which the rate of reaction (8) and the rates of reactions (6) and (7) become equal can be calculated from the relation

$$(2k_6[\text{SiMe}_2] + k_7[\text{Me}_2\text{SiCH}_2])/k_8\Phi(\text{I})I_{\text{abs}}t = 1$$

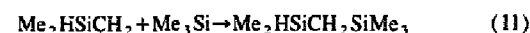
Taking into account that  $2k_6[\text{SiMe}_2] \approx 0.4k_7[\text{Me}_2\text{SiCH}_2]$  and  $k_8 \approx 5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  [9], we obtain  $t = 0.5 \text{ s}$ . Our shortest photolysis time is 30 s, which means that, even if we take into account that our calculations are only order of magnitude estimates, to a very good approximation only reaction (8) needs to be considered as a sink of  $\text{SiMe}_2$ . Although reaction (8) must be rated as a secondary reaction, a plot of  $[\text{Me}_3\text{Si}_2\text{H}]$  vs. time should give a straight line, but with a negative intercept. The intercept observed in Fig. 2 is certainly larger than that expected from our calculations, and this may be an indication that the rate constants, especially for reaction (7), are larger than those assumed.

Our mechanism does not yet explain the formation of the observed tetrasilane. Here we face the additional difficulty that the structure of this compound has not been determined. From our experiments with  $\text{MeOH}$  and  $\text{GeH}_4$  we know, however, that  $\text{Me}_2\text{SiCH}_2$  and  $\text{Me}_3\text{Si}$  radicals are involved in the formation of this compound. From the very fast disappearance of tetrasilane in the presence of  $\text{MeOH}$ , similar to disilacyclobutane (Fig. 3), we conclude that two  $\text{Me}_2\text{SiCH}_2$  units are involved in the formation of tetrasilane. The formation of tetrasilane occurs via reaction (4) followed by processes (9) and (10)



Such an oligomerization of  $\text{Me}_2\text{SiCH}_2$  was proposed in our first investigation of the photolysis of  $\text{Me}_4\text{Si}$  [13], but was not observed there. The reason that such a step can be seen in the present system is due to the smaller steady state concentration of the radicals present.

Finally, we must discuss the formation of the product  $\text{Me}_2\text{HSiCH}_2\text{SiMe}_3$ . This compound has a large negative intercept (Table I) and may therefore be of secondary origin. In the photolysis of  $\text{Me}_4\text{Si}$ , the same product was observed with a similar quantum yield to that found in the present system, and primary as well as secondary processes contributed to its formation [1].  $\text{Me}_2\text{SiCH}_2$  is not a precursor of  $\text{Me}_2\text{HSiCH}_2\text{SiMe}_3$ , as might be suspected from the  $\text{Si-C-Si}$  arrangement in the molecule; the compound is formed by a radical-radical process



However, we are unable to give a satisfactory explanation for the formation of the  $\text{Me}_2\text{HSiCH}_2$  radical. In Ref. [1], the isomerization of a vibrationally excited  $\text{Me}_3\text{Si}$  radical was offered as a possible explanation.

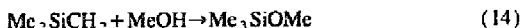
Silaethene reacts very rapidly with water, and traces of the latter contained in our reactants led to the formation of disiloxane



In the presence of  $\text{GeH}_4$ ,  $\text{Me}_3\text{Si}$  radicals abstract hydrogen giving trimethylsilane [1]



$\text{MeOH}$  reacts very rapidly with silaethenes [14]



$\text{NO}$  scavenges  $\text{Me}_3\text{Si}$  as well as  $\text{Me}_2\text{SiCH}_2$ , the mechanism of which is not well known.

With the mechanism given above, we can now derive the quantum yields for the primary processes and set up material balances. The quantum yield of primary process (1) is given by

$$\Phi(\text{I}) = \Phi(\text{Me}_3\text{SiH}) - \Phi(\text{Me}_3\text{SiH}/(2)) + \Phi(\text{Me}_5\text{Si}_2\text{H}) \quad (15)$$

where  $\Phi(\text{Me}_3\text{SiH}/(2))$  represents the quantum yield of  $\text{Me}_3\text{SiH}$  formed in reaction (2).  $\Phi(\text{Me}_3\text{SiH}/(2))$  should, in principle, be measurable from the decrease in  $\Phi(\text{Me}_3\text{SiH})$  in the presence of  $\text{NO}$ . In practice,  $\Phi(\text{Me}_3\text{SiH})$  increases slightly, as does  $\text{Me}_5\text{Si}_2$ , and we attribute this to a systematic error in this series of experiments.  $\Phi(\text{Me}_3\text{SiH}/(2))$  can, however, be calculated from the  $\text{Me}_6\text{Si}_2$  quantum yield formed in reaction (1) [5,6] via the relation

$$\Phi(\text{Me}_3\text{SiH}/(2)) = 0.067\Phi(\text{Me}_6\text{Si}_2/(1)) \quad (16)$$

$\Phi(\text{Me}_6\text{Si}_2/(1))$  is not accessible to direct measurement, but can be calculated from relation (17)

$$\begin{aligned} 1/2[\Phi(\text{Me}_3\text{SiH}/\text{GeH}_4) - \Phi(\text{I})] \\ = \Phi(\text{Me}_6\text{Si}_2/(1)) + \Phi(\text{Me}_3\text{SiH}/(2)) \\ + \Phi(\text{Me}_3\text{SiSiMe}_2\text{CH}_2\text{SiMe}_3) \\ + \Phi(\text{Me}_2\text{HSiCH}_2\text{SiMe}_3) \\ + \Phi(\text{Me}_3\text{SiSiMe}_2\text{CH}_2\text{SiMe}_2\text{CH}_2\text{SiMe}_3) \end{aligned} \quad (17)$$

Insertion of Eq. (15) and Eq. (16) into Eq. (17) yields  $\Phi(\text{Me}_6\text{Si}_2/(1)) = 0.10 \pm 0.03$  and  $\Phi(\text{Me}_3\text{SiH}/(2)) = (6.7 \pm 2.0) \times 10^{-3}$ . Since the quantum yield of  $\text{Me}_3\text{SiH}$  formed in reaction (2) is small, and lies within the error limits of the total  $\text{Me}_3\text{SiH}$  quantum yield, it need not be considered further. We then obtain  $\Phi(\text{I}) = 0.18 \pm 0.01$ .

$\Phi(\text{II})$  simply equals the quantum yield of  $\text{Me}_4\text{Si}$ , and hence  $\Phi(\text{II}) = (5.6 \pm 0.2) \times 10^{-3}$ .

$\Phi(\text{III})$  is given by the relation

$$\Phi(\text{III}) = 1/2[\Phi(\text{Me}_3\text{SiH}/\text{GeH}_4) - \Phi(\text{I})] \quad (18)$$

which yields  $\Phi(\text{III}) = 0.21 \pm 0.03$ .

The sum of the quantum yields of the three processes (I)–(III) should equal the total loss of  $\text{Me}_6\text{Si}_2$  in the presence of a radical scavenger

$$\Phi(-\text{Me}_6\text{Si}_2/\text{NO}) = \Phi(\text{I}) + \Phi(\text{II}) + \Phi(\text{III}) \quad (19)$$

Substitution of the  $\Phi$  values derived above into the right-hand side of this expression gives  $0.40 \pm 0.03$ , in excellent agreement with the experimental value  $\Phi(-\text{Me}_6\text{Si}_2/\text{NO}) = 0.40 \pm 0.04$ . This excludes the participation of any other important primary process. Subtracting the quantum yield of  $\text{Me}_6\text{Si}_2$ , which is re-formed in reaction (1), from the total quantum yield, we calculate that  $0.30 \pm 0.04$   $\text{Si}_2\text{C}_6\text{H}_{18}$  molecules are decomposed per photon absorbed. This may be compared with the value of 0.27 calculated from all the products observed. Our material balance is entirely satisfactory.

From the mechanism, we can derive the relations

$$\Phi(\text{Me}_2\text{SiCH}_2) = \Phi(\text{Me}_3\text{SiH}) + \Phi(\text{Me}_5\text{Si}_2\text{H}) \quad (20)$$

$$\Phi(\text{Me}_2\text{SiCH}_2) = \Phi(\text{Me}_3\text{SiOMe}/\text{MeOH}) \quad (21)$$

$$\begin{aligned} \Phi(\text{Me}_2\text{SiCH}_2) = 2\Phi(\text{Me}_2\text{SiCH}_2\text{SiMe}_2\text{CH}_2) \\ + \Phi(\text{Me}_3\text{SiSiMe}_2\text{CH}_2\text{SiMe}_3) \\ + 2\Phi(\text{Me}_3\text{SiSiMe}_2\text{CH}_2\text{SiMe}_2\text{CH}_2\text{SiMe}_3) \\ + 2\Phi(\text{Me}_3\text{SiOSiMe}_3) \end{aligned} \quad (22)$$

As can be seen from Table 1,  $\Phi(\text{Me}_3\text{SiOMe}/\text{MeOH})$  does in fact equal very closely the sum of  $\Phi(\text{Me}_3\text{SiH})$  and  $\Phi(\text{Me}_5\text{Si}_2\text{H})$ . Summation of the product quantum yields in Eq. (22) gives a value for the right-hand side of  $0.14 \pm 0.01$ , somewhat less than the sum of the quantum yields of  $\text{Me}_3\text{SiH}$  and  $\text{Me}_5\text{Si}_2\text{H}$  ( $0.185 \pm 0.003$ ). Thus not all the  $\text{Me}_2\text{SiCH}_2$  reacted is accounted for in the products found. A similar deficiency was observed in the case of  $\text{Me}_4\text{Si}$  [1]. This could be an indication that  $\text{Me}_2\text{SiCH}_2$  undergoes an as yet unidentified reaction which leads to higher molecular weight products.

For  $\text{Me}_2\text{Si}$ , the following predictions can be derived from our mechanism

$$\Phi(\text{SiMe}_2) = \Phi(\text{Me}_4\text{Si}) \quad (23)$$

$$\Phi(\text{SiMe}_2) > \Phi(\text{Me}_3\text{Si}_2\text{H}) \quad (24)$$

$$\Phi(\text{SiMe}_2) = \Phi(\text{Me}_5\text{Si}_2\text{H}/\text{Me}_3\text{SiH}) \quad (25)$$

As can be seen from Table 1,  $\Phi(\text{Me}_5\text{Si}_2\text{H})$  is smaller than  $\Phi(\text{Me}_4\text{Si})$  by a factor of two, a difference larger than expected. The value of  $\Phi(\text{Me}_5\text{Si}_2\text{H})$ , in the presence of  $\text{Me}_3\text{SiH}$ , although not very precise, is equal to that of  $\Phi(\text{Me}_4\text{Si})$  within their combined error limits.

## 5. Conclusions

The photolytic behaviour of  $\text{Me}_6\text{Si}_2$  has much in common with that of  $\text{Me}_4\text{Si}$ . In both cases, three pathways are open to the excited molecule: deactivation, molecular elimination of  $\text{Me}_2\text{SiCH}_2$  and, to a very minor extent, elimination of  $\text{SiMe}_2$  and breaking of the weakest bond in the molecule. The deactivation of an appreciable fraction of the excited molecules suggests that the relative importance of the different decom-

position channels should be pressure dependent if the reaction occurs from the ground potential energy surface. Since the molecular eliminations observed in this work do not show pressure dependence, it follows that they do not occur from the ground state. The experimental evidence is less compelling with respect to the bond breaking process. In the case of  $\text{Me}_4\text{Si}$ , RRKM calculations show that molecules which reach the ground state live long enough to become deactivated [1]. This behaviour is even more likely for  $\text{Me}_6\text{Si}_2$ , because of its greater number of internal degrees of freedom. The somewhat smaller bond dissociation energy will be almost cancelled out by the smaller excitation energy. The higher number of internal degrees of freedom will increase the chances of the excited molecule leaking to the ground state, where it will be deactivated. Decomposition must therefore occur from the excited state, as in the case of  $\text{Me}_3\text{Si}$ .

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