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Gas-phase photolysis of pentamethyldisilane at 206 nm

C. Kerst, I. Lein, P. Potzinger *

Max-Planck-Institut für Strömungsforschung, Bunsenstraße 10, 37073 Göttingen, Germany

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Abstract

The photolysis of pentamethyldisilane, Me_5Si_2H, is characterized by a large number of decomposition processes of the excited molecule. Quantum yield determinations in the presence and absence of various scavengers support the occurrence of Me_2Si elimination ($\Phi = 0.2$) and Si–Si bond breaking ($\Phi = 0.14$) as the two major decomposition processes. Other processes include the elimination of various silaethylenes and MeHSi. The quantum yield of these processes sum up to $\Phi = 0.16$. However, the most important pathway of the excited molecule is collisional deactivation ($\Phi = 0.5$). The material balance for the various silaethylenes is poor in the absence of traps but can be improved greatly in the presence of MeOH and is in agreement with computer simulations. Experiments with SF_6 suggest that decomposition occurs mainly from the excited states. © 1998 Elsevier Science S.A.

Keywords: Collisional deactivation; Decomposition; Pentamethyldisilane; Photolysis

1. Introduction

This paper is a continuation of our investigation of the photolytic behaviour of simple silicon compounds excited near their absorption limit. Up to now we have studied the two fully methylated mono- and disilanes, Me_4Si and Me_6Si_2 [1,2]. In both cases three pathways are open to the excited molecule: (i) breaking of the weakest bond in the molecule, (ii) molecular elimination of $Me_2Si=CH_2$, and (iii) deactivation. In both cases it was postulated that decomposition of the excited molecule takes place directly from the excited states.

For pentamethyldisilane a new energetically favourable decomposition channel is opened: elimination of Me_2Si with concomitant formation of Me_3SiH. Extrusion of Me_2Si is already observed to a minor extent in the photolysis of Me_6Si_2 but in the case of Me_5Si_2H this process is the energetically lowest decomposition channel of the molecule in its electronic ground state and it proceeds without activation energy [3]. This process has been studied by different authors in the thermally activated system [4–6]. The molecule has also been tested as a photolytic source of Me_2Si and the desired intermediate has indeed been observed [7]. A more detailed picture of the photolytic behavior of the Me_5Si_2H molecule is not known and will be given in this report.

2. Experimental details

The experiments were performed the same way as described in previous publications [1,2]. Gas handling was done on a conventional vacuum line equipped with two membrane manometers (MKS 1000 mbar and 10 mbar). Photolyses were carried out in a 180 cm^3 cylindrical quartz cell with an optical path length of 10 cm which was directly attached to the vacuum line. Radiation at 206 nm was supplied by a homemade microwave driven thermostatted iodine lamp. The stable lamp output was monitored by a monochromator–photomultiplier arrangement. The impurity lines around 175 nm could be completely suppressed by an air gap in which a shutter was placed. The number of photons entering the photolysis cell per unit time were determined by HBr actinometry ($\Phi(H_2) = 1.0$ [8]). All experiments were carried out at room temperature.

Me_5Si_2H was donated by Prof. E. Hengge, Graz, and had a purity of 99.6% after purification by preparative GC. All other substances used, H_2, NO, MeOH, SF_6, and pentane, were of commercial origin. SF_6 was dried before use by repeated distillation through a P_2O_5 column.

Endproduct analyses were performed by gas chromatography using a 50 m × 0.32 mm × 1.5 μm fused silica capillary column OV1 with either a flame ionization or a mass selective detector (HP 5980 and 5971A). Pentane was used as an internal standard. Response factors were taken proportional

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* Corresponding author.

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to the number of C atoms in the molecule [11]. Analyses of permanent gases (H_2, CH_4) were done by MS (MAT 311A).

3. Results

The long wavelength absorption spectrum and the extinction coefficient of Me_5Si_2H at 206 nm are very similar to Me_6Si_2 [2], σ(base e, 206 nm) = $(1.0 \pm 0.1) \times 10^{-17}$ cm^2 (Fig. 1).

In this system the number of recorded photolysis products is much larger than in the case of Me_4Si and Me_6Si_2. A large number of these products occur with low yields and were not identified. The concentration of the major peaks as a function of photolysis time is shown in Fig. 2. Two of these products, $Me_3SiOSiHMe_2$ and $Me_5Si_2SiMeHSiMe_3$ were only tentatively assigned on the basis of GC/MS. The product which we assign to $Me_3SiOSiHMe_2$ shows a base peak at *m/e* 133 in the mass spectrum followed by peaks at *m/e* 44 and 73. It is unclear if this spectrum refers to a penta- or a tetra-methyldisiloxane. The retention time of the second product 2-hydrononamethyltetrasilane, has already been assigned to another product: 1-hydrononamethyltetrasilane (Lein, unpublished results). Formation of the latter product cannot be explained by the mechanism given below even though it is consistent with the mass. It is possible that the retention times of these two products are identical within the error limits of our retention time measurements.

All the products shown in Fig. 2 are rated as primary products and the quantum yields deduced from these plots denoted by $\Phi(X,t)$ are given in Table 1. Also shown in Table 1 is the quantum yield of H_2 formation for this experiment.

A number of added traps were used to indirectly identify the intermediates which are the precursors to the different observed products. MeOH is known to be an effective scavenger of molecules containing a Si=C double bond. Two types of experiments were performed to study the influence of MeOH concentration on product formation: a time dependence with a fixed MeOH concentration and a dependence on the MeOH concentration at a fixed photolysis time. Only the latter is shown in Fig. 3. The quantum yields deduced from both experiments are given in Table 1, denoted by $\Phi(X,\mathrm{MeOH},t)$ and $\Phi(X,\mathrm{MeOH},c)$, respectively. The addition of MeOH leads to a substantial reduction in the number of products as is evident from the much cleaner gas chromatogram. The 1,3-disilacyclobutanes, $Me_5Si_2CH_2SiMe_3$, $Me_2HSiOSiMe_3$ and a number of small intensity products disappear completely, while a number of products show a small but significant increase of their quantum yields. Also recorded was the formation of Me_3SiOMe and $Me_2HSiOMe$.

The addition of NO affects the formation of almost all products (Fig. 4). NO reacts very fast with silaethylenes and with all kinds of radicals. Accordingly, the 1,3-disilacyclobutanes and $Me_5Si_2CH_2SiMe_3$ disappear at small NO concentration. $Me_2HSiSiHMe_2$, Me_6Si_2, Me_8Si_3, and $Me_{10}Si_4$ are also completely scavenged. Other products like Me_3SiH, Me_2SiH_2, and Me_4Si are only partially affected by the presence of NO and their concentrations reach plateau values.

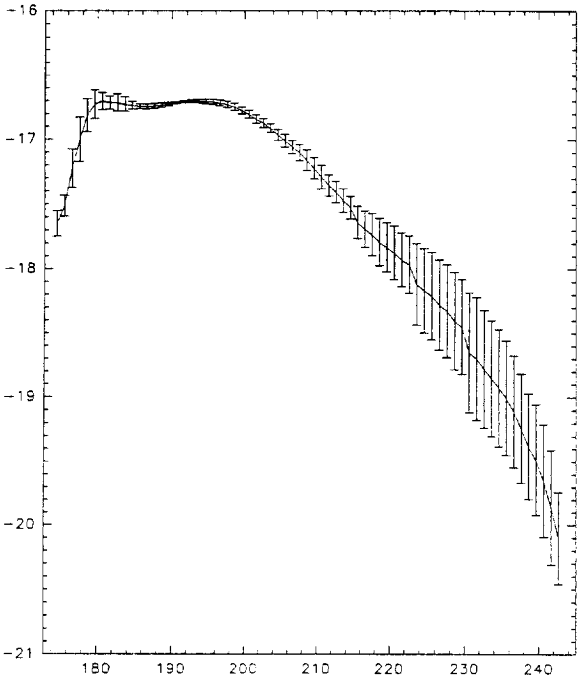

Fig. 1. Absorption cross section of Me_5Si_2H as a function of wavelength near the absorption onset.

SF_6 was introduced as a moderator for vibrationally excited molecules. Contrary to our previous experience [11], all of the recorded products are more or less affected by the addition of SF_6 (Fig. 5). Me_3SiH decreases with increasing SF_6 concentration and reaches a plateau value. A very similar behaviour is shown by $Me_5Si_2SiMe_2H$. The quantum yield change of the two substances is also quite similar. The quantum yield for Me_4Si formation increases with increasing SF_6 concentration, while disilane Me_6Si_2 and $Me_2HSiSiHMe_2$ formation decreases. Me_8Si_3 and $Me_{10}Si_4$ suffer a similar fate. Silaethylene derived products are also quenched by SF_6. In the experiments with SF_6 we also observed an increase in the formation of $Me_2HSiOSiHMe_2$ which suggests trace amounts of water in the SF_6 even though it was dried with P_2O_5. We checked this prediction by performing a Hg-sensitized photolysis of Me_3SiH in the presence of about 700 mbar SF_6. $Me_2Si=CH_2$ is the only intermediate in this system which reacts with H_2O and is formed by disproportionation of two silylradicals. In the absence of a quencher it shows up in the endproduct $Me_5Si_2CH_2SiMe_3$ and to a very minor extent in $Me_2\overline{SiCH_2SiMe_2CH_2}$ [12]. In experiments performed in the presence of SF_6 a small amount of $Me_3SiOSiMe_3$ is observed while $Me_2\overline{SiCH_2SiMe_2CH_2}$ has completely disappeared and $Me_5Si_2CH_2SiMe_3$ is only marginally affected. This suggests that the water impurity in SF_6 must be small.

In another experiment we added different amounts of a mixture of ≈0.1 mole% of H_2O in H_2 to the Me_5Si_2H photolysis system (Fig. 6). Some of the products behave as in

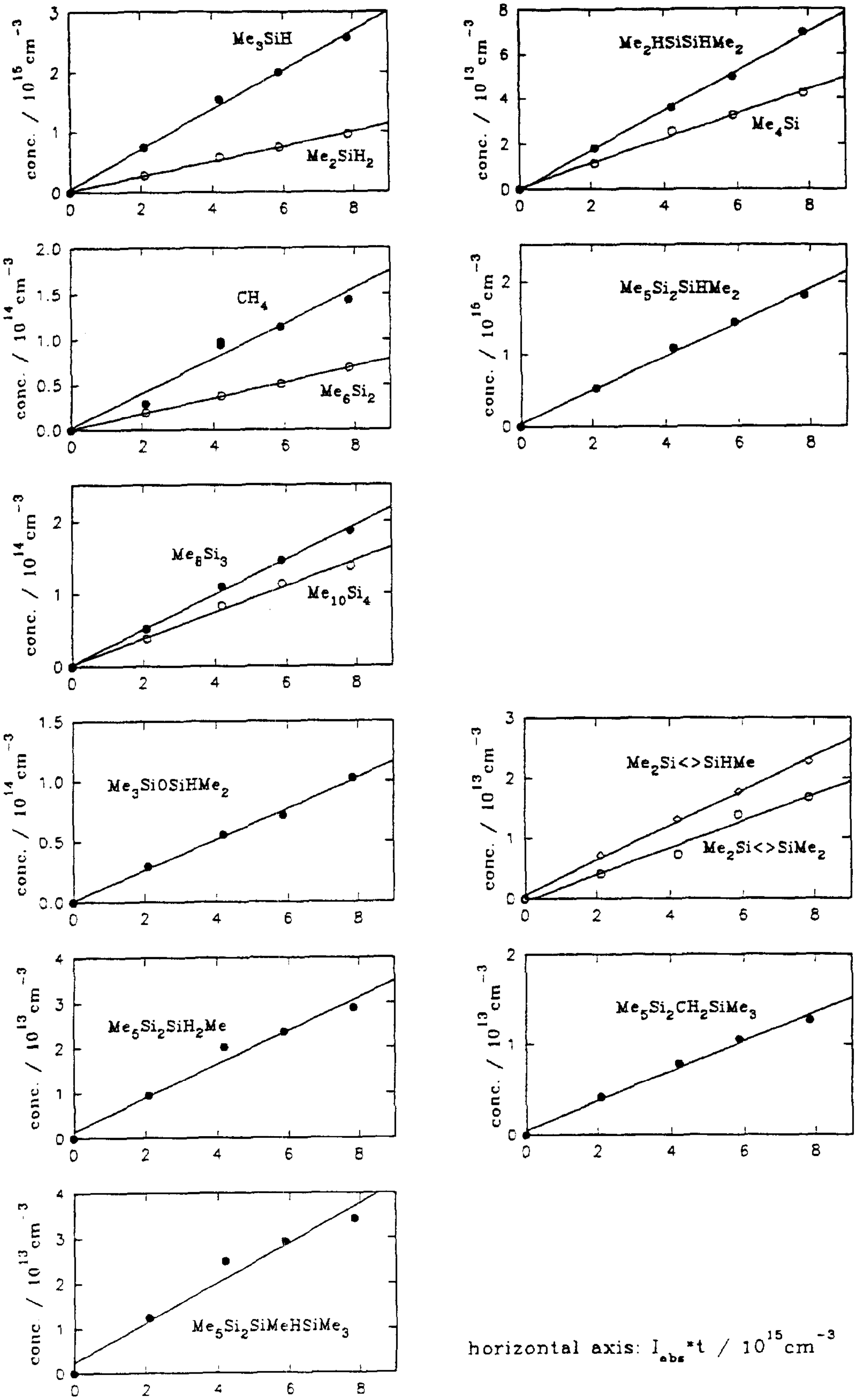

Fig. 2. Dependence of product concentrations on photolysis time; $[Me_5Si_2H] = (1.24 \pm 0.04) \times 10^{17}$ cm^{-3}; $I_{abs} = (3.41 \pm 0.13) \times 10^{13}$ cm^{-3} s^{-1}.

the presence of SF_6. The decrease of Me_3SiH and $Me_5Si_2SiMe_2H$ formation is practically identical with that shown in Fig. 5, and the plateau value is much more clearly identified. The silaethylene products show the expected

Table 1
Photolysis products and their quantum yields under the different experimental conditions

X	$\Phi(X,t)$	$\Phi(X,\mathrm{MeOH},t)$	$\Phi(X,\mathrm{MeOH},c)$	$\Phi(X,\mathrm{NO})$	$\Phi(X,\mathrm{SF_6})$	$\Phi(X,\mathrm{H_2/H_2O})$
$-Me_5Si_2H$		0.78		0.49		
H_2	$(1.2\pm0.4)\times10^{-2}$	n.d.	n.d.	n.d.	n.d.	n.d.
CH_4	$(1.9\pm0.2)\times10^{-2}$	$(1.9\pm0.1)\times10^{-2}$	$(1.8\pm0.1)\times10^{-2}$	$(2.0\pm0.2)\times10^{-2}$	s. Fig. 5	$(1.9\pm0.1)\times10^{-2}$
Me_2SiH_2	0.12 ± 0.01	0.13 ± 0.00	0.12 ± 0.01	$(8.1\pm0.2)\times10^{-2}$	0.11 ± 0.01	0.12 ± 0.00
Me_3SiH	0.33 ± 0.01	0.34 ± 0.01	0.31 ± 0.02	0.26 ± 0.00	0.21 ± 0.02	0.23 ± 0.01
Me_4Si	$(5.4\pm0.3)\times10^{-3}$	$(5.4\pm0.3)\times10^{-3}$	$(5.2\pm0.5)\times10^{-3}$	$(4.3\pm0.0)\times10^{-3}$	increasing	$(5.0\pm0.5)\times10^{-3}$
$Me_2HSiSiHMe_2$	$(8.8\pm0.2)\times10^{-3}$	$(1.1\pm0.0)\times10^{-2}$	$(9.1\pm0.6)\times10^{-3}$	0	→0	decreasing
Me_6Si_2	$(8.7\pm0.1)\times10^{-3}$	$(9.7\pm0.5)\times10^{-3}$	$(9.0\pm0.4)\times10^{-3}$	0	→0	$(7.8\pm0.3)\times10^{-3}$
MeHSi◇SiMe$_2$	$(2.9\pm0.1)\times10^{-3}$	0	0	0	0	0
Me$_2$Si◇SiMe$_2$	$(2.2\pm0.2)\times10^{-3}$	0	0	0	0	0
$Me_5Si_2SiMeH_2$	$(3.7\pm0.3)\times10^{-3}$	$(3.7\pm0.3)\times10^{-3}$	$(3.6\pm0.2)\times10^{-3}$	$(3.9\pm0.1)\times10^{-3}$	$(3.9\pm0.6)\times10^{-3}$	$(3.6\pm0.2)\times10^{-3}$
$Me_5Si_2SiMe_2H$	0.23 ± 0.01	0.23 ± 0.01	0.23 ± 0.01	0.19 ± 0.01	0.12 ± 0.01	0.15 ± 0.01
Me_8Si_3	$(2.4\pm0.1)\times10^{-2}$	$(3.1\pm0.1)\times10^{-2}$	$(2.8\pm0.2)\times10^{-2}$	$(7.5\pm7.1)\times10^{-4}$	decreasing	$(2.3\pm0.1)\times10^{-2}$
$Me_5Si_2CH_2SiMe_3$	$(1.6\pm0.1)\times10^{-3}$	0	0	0	0	decreasing
$Me_5Si_2SiMeHSiMe_3$	$(4.4\pm0.5)\times10^{-3}$	$(1.4\pm0.3)\times10^{-3}$	$(2.1\pm0.3)\times10^{-3}$	$(6.2\pm0.1)\times10^{-3}$	$(4.7\pm0.7)\times10^{-3}$	decreasing
$Me_{10}Si_4$	$(1.8\pm0.1)\times10^{-2}$	$(2.1\pm0.1)\times10^{-2}$	$(2.0\pm0.1)\times10^{-2}$	0	decreasing	$(1.7\pm0.1)\times10^{-2}$
$-MeOH$		0.14 ± 0.02				
Me_3SiOMe		$(7.3\pm0.6)\times10^{-2}$	$(7.3\pm0.4)\times10^{-2}$			
$Me_2HSiOMe$		$(4.2\pm0.2)\times10^{-2}$	$(4.4\pm0.3)\times10^{-2}$			

n.d.: not determined.

reduction in formation, while all other products remain unaffected.

4. Discussion

4.1. Material balance

Since our product recovery is incomplete, a perfect material balance is not expected. From the product quantum yields obtained in the series of experiments shown in Fig. 2, we calculate $\Phi(\mathrm{Si})=1.40$, $\Phi(\mathrm{C})=3.52$, and $\Phi(\mathrm{H})=11.51$. In other words, the recovered products suggest that a substance with a formula $Si_{1.95}C_{4.89}H_{16}$ disappeared with a quantum yield of 0.72. The calculated formula agrees fairly well with that of the reactant, however, the quantum yield represents only a lower limit. In the presence of MeOH a large number of unidentified low intensity products disappear and a better material balance is therefore expected. From the time dependence of the products in the presence of MeOH we calculate that a molecule $Si_{1.96}C_{4.93}H_{16}$ has disappeared with a quantum yield of 0.78.

4.2. Primary processes and mechanism

A number of products are only partially or not at all affected by the various scavenger molecules. The non scavengeable part is therefore assigned to stable products formed in the primary photochemical decomposition processes. The quantum yield of the main photolysis product Me_3SiH decreases to 0.26 in the presence of NO and we therefore postulate that this part is formed in a molecular primary photochemical process. This can be accomplished in two ways:

$$Me_5Si_2H+h\nu \rightarrow Me_3SiH+Me_2Si \qquad (I)$$

$$Me_5Si_2H+h\upsilon \rightarrow Me_3SiH+MeHSi{=}CH_2 \qquad (II)$$

The relative importance of these two processes can be inferred by scavenging processes of Me_2Si and $MeHSi=CH_2$. For example, pentamethyldisilane itself is an excellent scavenger of Me_2Si [9]:

$$Me_2Si+Me_5Si_2H \rightarrow Me_5Si_2SiMe_2H \qquad (1)$$

From Table 1 it can be seen that the quantum yield of $Me_5Si_2SiMe_2H$ decreases in the presence of NO. Under our experimental conditions ($[Me_5Si_2H] \gg [NO]$) NO will not interfere with Eq. (1) [10]. Therefore the decrease is attributed to a radical component in the formation processes of $Me_5Si_2SiMe_2H$. We equate $\Phi(Me_5Si_2SiMe_2H/NO)=0.19$ with the quantum yield of formation of Me_2Si in the primary process (I). The difference between $\Phi(Me_3SiH/NO)=0.26$ and $\Phi(Me_5Si_2SiMe_2H/NO)$ is taken equal to $\Phi(\mathrm{II})=0.07$. The experiments performed in the presence of MeOH can be used as an alternative route to determine $\Phi(\mathrm{II})$. In the presence of MeOH quantitative scavenging of $MeHSi=CH_2$ is expected

$$MeHSi{=}CH_2+MeOH \rightarrow Me_2HSiOMe \qquad (2)$$

and under these circumstances $\Phi(Me_2HSiOMe/MeOH)=0.04$ is equal to $\Phi(\mathrm{Eq.\ (II)})$. The agreement with the value derived above is not very good and we are inclined to give a stronger weight to the directly determined value. We propose the following values for the quantum yields of the primary processes (I) and (II):

$$\Phi(\mathrm{I})=0.20\pm0.01$$

$$\Phi(\mathrm{II})=0.05\pm0.01$$

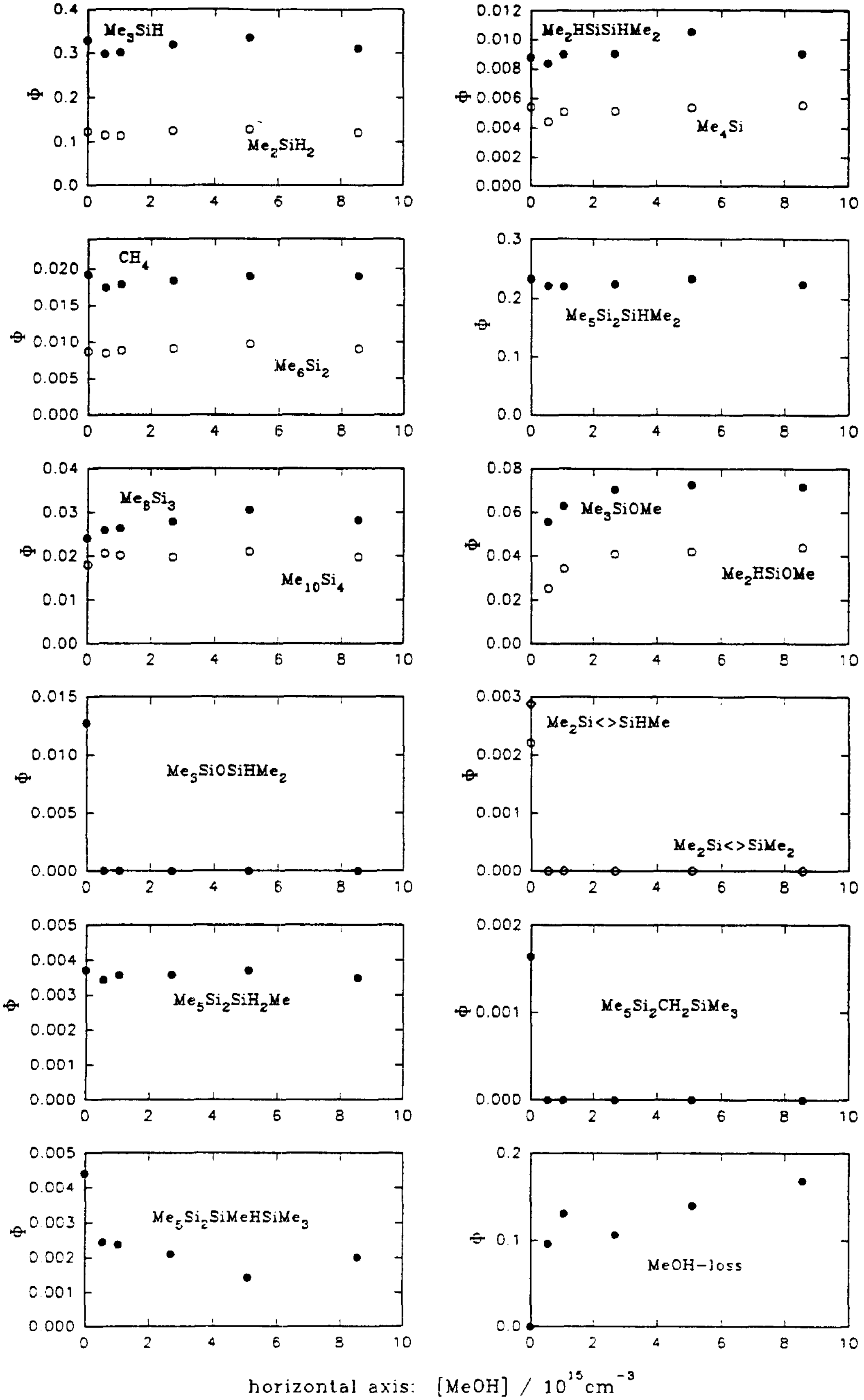

Fig. 3. Dependence of the product quantum yields Φ on MeOH concentration; 0.0 cm^{-3} ≤ [MeOH] ≤ 2.41×10^{16} cm^{-3}; [Me_5Si_2H] = $(1.23 \pm 0.04) \times 10^{17}$ cm^{-3}; I_{abs} = $(3.39 \pm 0.11) \times 10^{13}$ cm^{-3} s^{-1}.

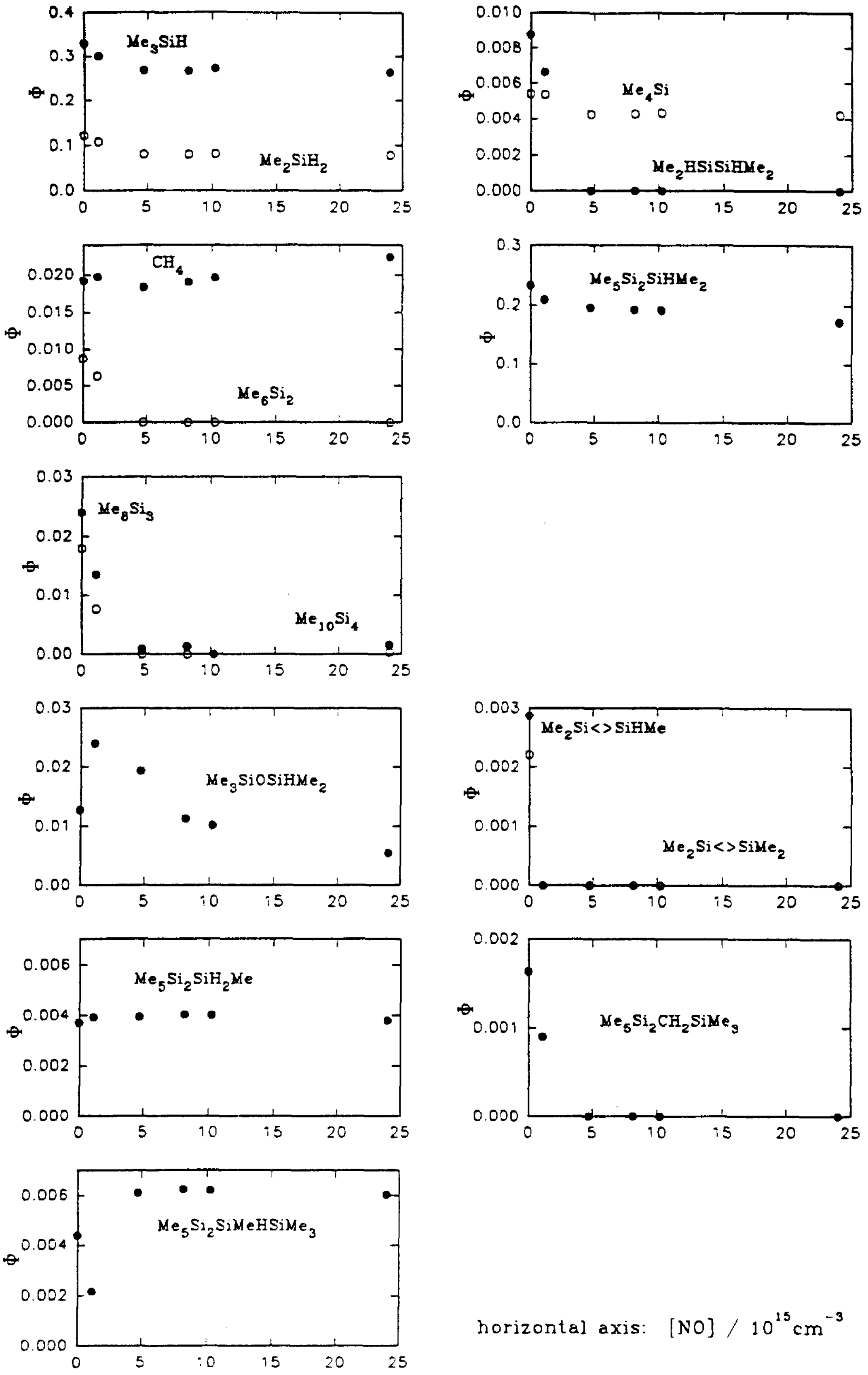

Fig. 4. Dependence of the product quantum yields Φ on NO concentration; 0.0 $cm^{-3} \leq [NO] \leq 8.56 \times 10^{15}$ cm^{-3}; $[Me_5Si_2H] = (1.25 \pm 0.06) \times 10^{17}$ cm^{-3}; $I_{abs} = (3.39 \pm 0.13) \times 10^{13}$ cm^{-3} s^{-1}; $t = 180$ s.

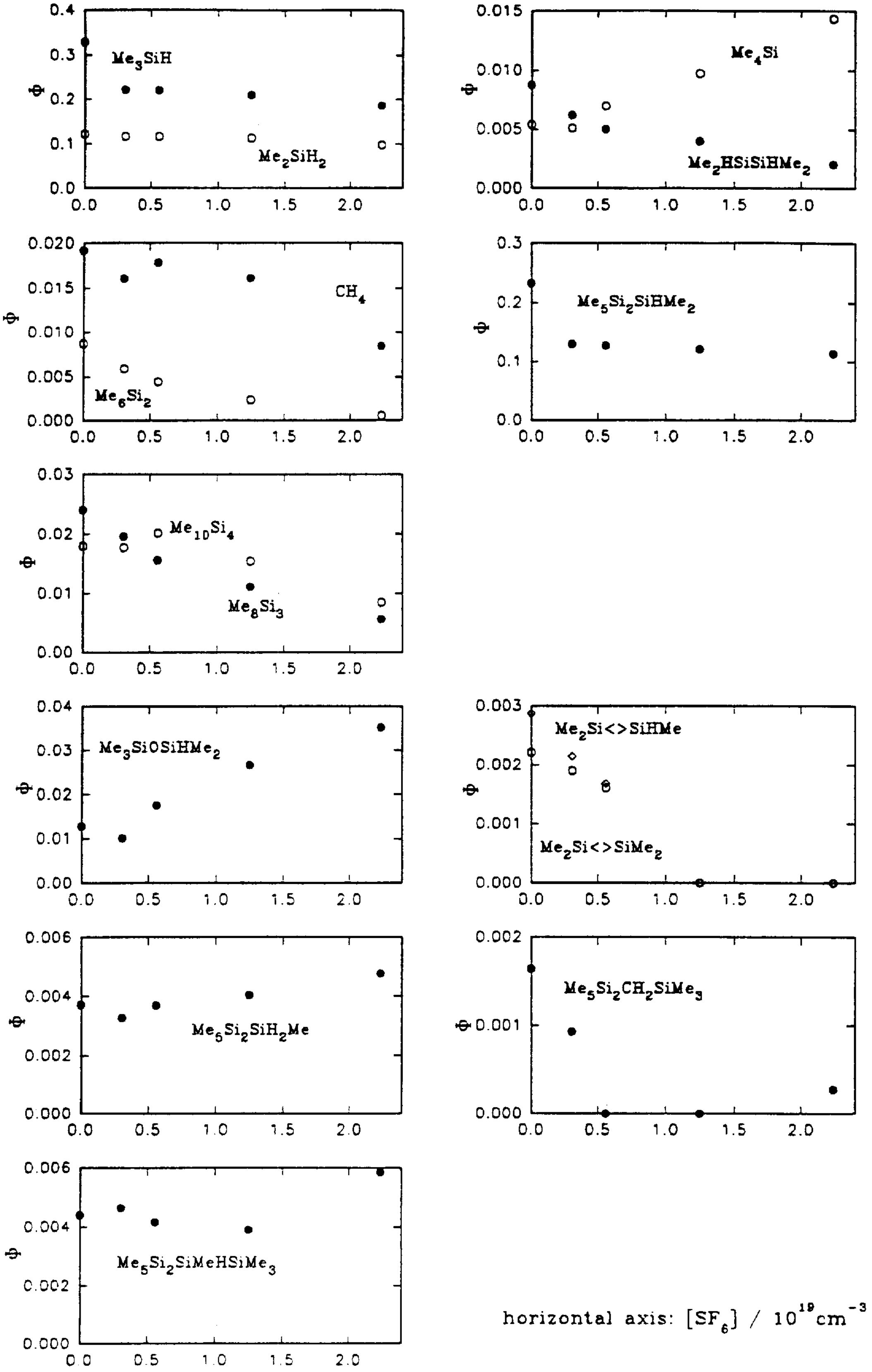

Fig. 5. Dependence of the product quantum yields Φ on SF$_6$ concentration; $0.0\ \mathrm{cm}^{-3} \leq [\mathrm{SF}_6] \leq 2.24 \times 10^{19}\ \mathrm{cm}^{-3}$; $[\mathrm{Me}_5\mathrm{Si}_2\mathrm{H}] = (1.24 \pm 0.04) \times 10^{17}\ \mathrm{cm}^{-3}$; $I_{\mathrm{abs}} = (3.37 \pm 0.13) \times 10^{13}\ \mathrm{cm}^{-3}\ \mathrm{s}^{-1}$; $t = 180$ s.

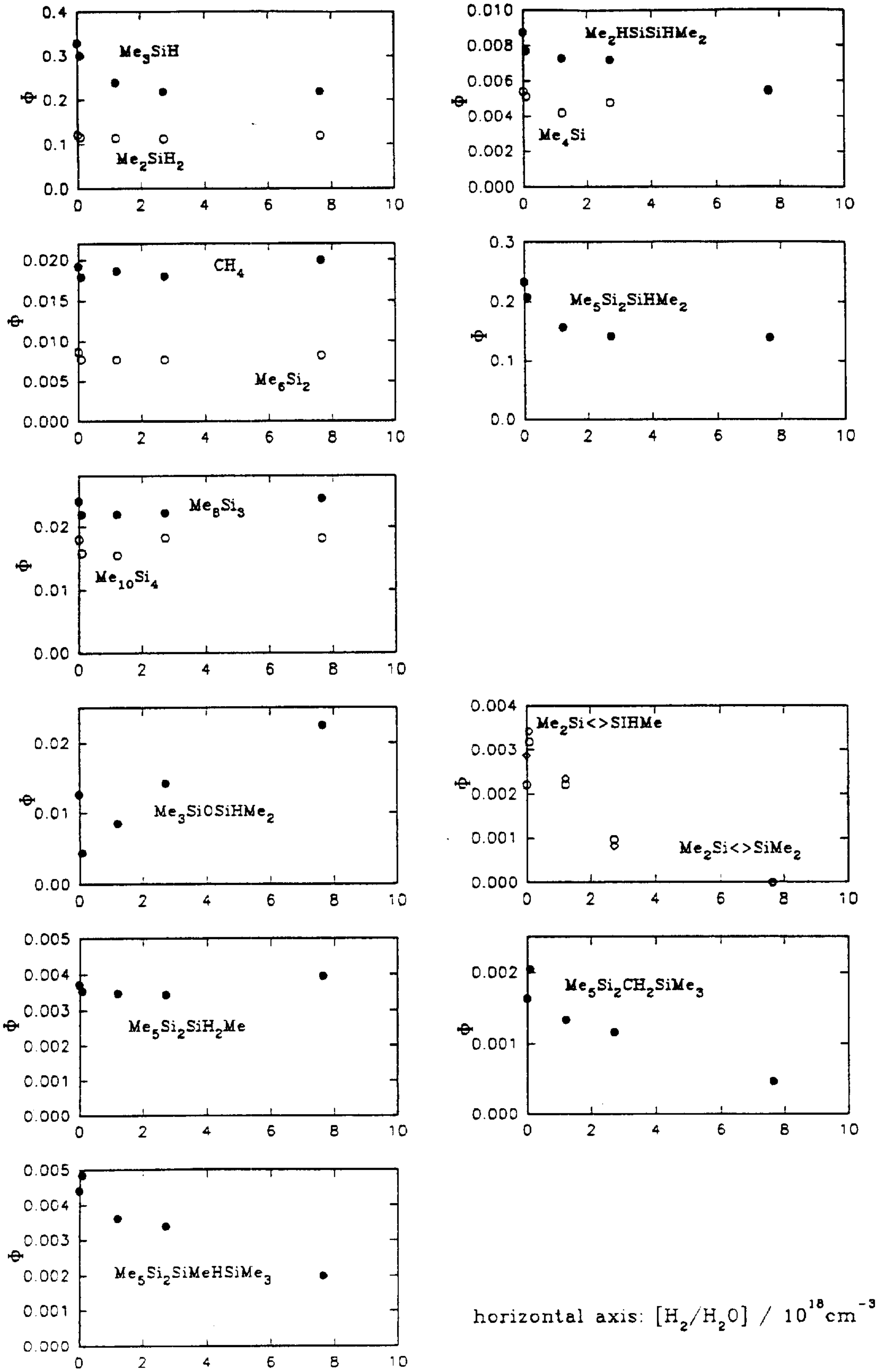

Fig. 6. Dependence of the product quantum yields Φ on the concentration of a H_2/H_2O mixture; 0.0 $cm^{-3} \leq [H_2/H_2O] \leq 7.6 \times 10^{18}$ cm^{-3}; $[Me_5Si_2H] = (1.22 \pm 0.04) \times 10^{17}$ cm^{-3}; $I_{abs} = (3.37 \pm 0.13) \times 10^{13}$ cm^{-3} s^{-1}; $t = 180$ s.

Process (I) can proceed in two mechanistically different ways, either by a transfer of the H atom bonded to silicon to the trimethylsilyl group or by a transfer of a methyl group from the trimethylsilyl to the dimethylsilyl group. Which of the two pathways is more important can only be determined with an isotopically labeled reactant. A clue to the relative importance of the methyl group transfer comes from examining the migration of a methyl group from the dimethylsilyl to the trimethylsilyl group yielding Me_4Si. This process takes place with a very small quantum yield, and indicates that the methyl transfer is unimportant.

$$Me_5Si_2H + h\nu \rightarrow Me_4Si + MeHSi \tag{III}$$

$$\Phi(III) = \Phi(Me_4Si/NO) = 4.3 \times 10^{-3}.$$

In process (II) an H atom is transferred from a methyl group attached to the dimethylsilyl group to the trimethylsilyl group via a four-membered transition state resulting in the formation of $MeHSi=CH_2$. Examining the opposite process, transfer of an H atom to the dimethylsilyl group yields dimethylsilane:

$$Me_5Si_2H + h\nu \rightarrow Me_2SiH_2 + Me_2Si=CH_2 \tag{IV}$$

In fact dimethylsilane is a major photolysis product and partially formed in a molecular manner. We associate $\Phi(Me_2SiH_2/NO) = 8.0 \times 10^{-2}$ with $\Phi(IV)$. This value agrees quite well with $\Phi(Me_3SiOMe/MeOH) = (7.3 \pm 0.6) \times 10^{-2}$. The value for $\Phi(IV)$ is somewhat higher than the value for $\Phi(II)$ which is statistically expected.

$\Phi(CH_4)$ is not influenced by any of the additives and methane must therefore be formed in a primary decomposition process. The following four routes to CH_4 formation from Me_5Si_2H are possible:

$$Me_5Si_2H + h\nu \rightarrow CH_4 + Me_3SiSiMe \tag{Va}$$

$$Me_5Si_2H + h\nu \rightarrow CH_4 + Me_2SiSiMe_2 \tag{Vb}$$

$$Me_5Si_2H + h\nu \rightarrow CH_4 + Me_3SiSi(H)CH_2 \tag{Vc}$$

$$Me_5Si_2H + hv \rightarrow CH_4 + Me_2HSiSi(Me)CH_2 \tag{Vd}$$

The trimethylsilylmethylsilylene is expected to insert into the Si–H bond of Me_5Si_2H:

$$Me_3SiSiMe + Me_5Si_2H \rightarrow Me_5Si_2SiHMeSiMe_3 \tag{3}$$

We attribute the formation of the observed nonamethyltetrasilane to Eq. (3). The latter two products (Vc) and (Vd) should be scavengeable by MeOH, but we were not able to assign any of the GC peaks with the existence of these intermediates. Thus, the sum of the quantum yields of primary processes (Va)–(Vd) equals $(1.9 \pm 0.1) \times 10^{-2}$ and (Va) contributes about 25%

Presumably H_2 is also formed in a primary process as well, as there is no potential reaction following the primary processes which produces H atoms or H_2. Whether H_2 is formed in a molecular or atomic manner is difficult to ascertain, mainly because Me_5Si_2H is a very good H atom scavenger, to compete with the cleavage of the Si–Si and Si–C bonds in the ground and triplet states. The Si–Si as well as the Si–C dissociation channels are energetically, as well as entropically favoured over a Si–H bond breaking process. If splitting off of a methyl radical is taking place at all, it will occur with a very small quantum yield. We therefore assume that the following process is taking place with a quantum yield of $(1.2 \pm 0.4) \times 10^{-2}$:

$$Me_5Si_2H + h\nu \rightarrow H_2 + Me_3SiSi(Me)=CH_2 \tag{VI}$$

We also observe a number of products which are totally or partially scavengeable by NO, e.g., Me_6Si_2, $Me_2HSiSiHMe_2$, $Me_{10}Si_4$, and $Me_5Si_2SiMe_2H$. These products require the presence of Me_3Si, Me_2SiH, and Me_5Si_2 radicals in our reaction system. The generation of the first two radicals is attributed to a further primary process:

$$Me_5Si_2H + h\nu \rightarrow Me_3Si + Me_2SiH \tag{VII}$$

The radical–radical reactions which these two radicals undergo are well known [12–14]; disproportionation reactions leading to silaethylenes are unimportant and were omitted:

$$2\,Me_3Si \rightarrow Me_6Si_2 \tag{4}$$

$$Me_3Si + Me_2SiH \rightarrow Me_5Si_2H \tag{5}$$

$$Me_3Si + Me_2SiH \rightarrow Me_2Si + Me_3SiH \tag{6}$$

$$2\,Me_2SiH \rightarrow Me_2HSiSiHMe_2 \tag{7}$$

$$2\,Me_2SiH \rightarrow Me_2SiH_2 + Me_2Si \tag{8}$$

In the presence of Me_5Si_2H abstraction reactions are taking place [15]:

$$Me_3Si + Me_5Si_2H \rightarrow Me_3SiH + Me_5Si_2 \tag{9}$$

$$Me_2SiH + Me_5Si_2H \rightarrow Me_2SiH_2 + Me_5Si_2 \tag{10}$$

The Me_5Si_2 radicals undergo the following reactions:

$$2\,Me_5Si_2 \rightarrow Me_{10}Si_4 \tag{11}$$

$$Me_5Si_2 + Me_3Si \rightarrow Me_8Si_3 \tag{12}$$

$$Me_5Si_2 + Me_2SiH \rightarrow Me_5Si_2SiMe_2H \tag{13}$$

$$Me_5Si_2 + Me_2SiH \rightarrow Me_2Si + Me_5Si_2H \tag{14}$$

The silaethylenes, which are formed in the various primary processes, undergo addition reactions with silyl radicals. We take this into account in a very coarse way by the following equation:

$$Si=C + 2\,R. \rightarrow products \tag{15}$$

Most of the products formed in reaction (15) have not been identified, since they form low intensity background peaks in the gas chromatograms. Silaethylenes are also scavenged by traces of water impurities. These reactions lead finally to the observed product $Me_3SiOSiHMe_2$.

The mechanism given so far explains qualitatively all our products and their behaviour with respect to the different additives with one exception: The decrease of Me_4Si in the presence of NO. This decrease is small and consequently associated with a large uncertainty. If it does indeed occur we have to postulate another primary process:

$$Me_5Si_2H + h\nu \rightarrow CH_3 + Me_3SiSiHMe \qquad (VIII)$$

The methyl radical will combine with the other three silyl radicals present (Me_3Si, Me_2SiH, Me_5Si_2). In the case of reactions with the latter two the expected products Me_3SiH and Me_6Si_2 are formed by other processes as well, and we are not able to draw any conclusions from them concerning the extent of reaction (VIII). However, we are able to estimate the quantum yield of (VIII) by noting that the Me_5Si_2 radical has approximately a 1.4 times higher stationary concentration as the other two radicals, as can be deduced from stationary state assumptions and computer calculations. Therefore we conclude:

$$\Phi(\mathrm{VIII}) \approx 2.4\ \{\Phi(Me_4Si) - \Phi(Me_4Si/NO)\} = 2.4 \times 10^{-3}$$

The calculation of the quantum yield of primary process (VII) is hindered by an incomplete material balance with respect to the silaethylenes. The products of the radical addition to silaethylenes and their concentrations have to be known in order to calculate $\Phi(\mathrm{VII})$. Because only a small fraction of the silaethylenes formed in (II), (IV), (VI) and possibly also in (Va)–(Vd) appear in the characterized products, one has to suspect that radical addition products were also not identified. In the presence of an excess of MeOH all the silaethylenes are scavenged and the radicals which added to the Si=C double bond should show up as radical combination products. A small increase in radical derived products is indeed observed (Table 1). Within the framework of our mechanism $\Phi(\mathrm{VII}) = 1/2\ \Phi(R)$, where $\Phi(R)$ is the quantum yield of all products formed by radicals:

$$\Phi(R) = \Sigma(\Phi(X_i/\mathrm{MeOH}) - \Phi(X_i/\mathrm{NO})) = 0.224$$

This value is only a lower limit because Eq. (5) has not been taken into account. Assuming the validity of the geometric mean rule, we calculate Φ (Me_5Si_2H/(5)) $= 2.13 \times 10^{-2}$ which must be added to the above figure. Finally we get

$$\Phi(\mathrm{VII}) = 0.14$$

The quantum yield of all the primary processes add up to 0.49, which means that deactivation is the most prominent step of the excited molecule.

In the mechanism given so far the reaction pathways of the various silaethylenes must also be included. From our previous studies [1,16] we know that $Me_2Si{=}CH_2$ reacts by head to tail dimerization or by radical addition. If the other silaethylenes behave similarly we expect in the presence of m silaethylenes and n different radicals $m(m+1)/2$ different 1,3-disilacyclobutanes and $m \times n^2$ different addition products. In our case, $m = 3$ and $n = 3$. The experimental observation that the silaethylenes are distributed as a large number of small intensity products is therefore understandable. We identified only the two 1,3-disilacyclobutanes $Me_2\overline{SiCH_2SiMe_2CH_2}$ and $Me_2\overline{SiCH_2SiHMeCH_2}$ and one addition product $Me_5Si_2CH_2SiMe_3$, which make up only about 10% of all silaethylenes formed. This unsatisfactory material balance does not allow us to discuss the silaethylene reactions in more detail, and we therefore limit the discussion to the mechanism taking place in the presence of an excess of MeOH and NO.

Such a mechanism includes the various radical combination and disproportionation reactions, the silylene insertion reactions and the metathetical reactions (Table 2). Most of the reactions listed in Table 2 have appeared in previous studies, as well as their relative rate constants [1,12,13]. These relative rate constants were deduced from complex reaction systems and it is important to check if they apply to related systems. Therefore computer simulations were performed [17]. For the different silylenes we have assumed that only insertion into the Si–H bond of Me_5Si_2H is taking place. Similarly, silaethylenes are scavenged by MeOH exclusively. Therefore the rate constants for these reactions (Eqs. (1)–(3), 16–18) are not required to be known. The rate constant for Eq. (4) is known [18,19]. The rate constants for the self reaction of the various silyl radicals relative to each other are not known. We have assumed a value of 3×10^{-11} $cm^3\ s^{-1}$ for the sum of rate constants of self-combination and self-disproportionation for each silyl radical. The geometric mean rule is applied for the sum of cross-combination and cross-disproportionation. The rate constants for the hydrogen abstraction reactions (Eqs. (9) and (10)) relative to the radical combination reactions (Eq. (4)Eqs. (7) and (8)) are known [15] as well as the branching ratio of Eqs. (7) and (8) [14]. A value for $k_{14}/(k_{13}+k_{14})$ has also been reported [14] but it is not needed in the present simulation because both reactions Eqs. (13) and (14) followed by Eq. (1) lead to the same endproduct. The branching ratio $k_6/(k_5+k_6)$ is unknown and we assumed a value half as large as for $k_8/(k_7+k_8)$.

A comparison of experimental and calculated quantum yields in the presence of MeOH (Table 3, columns 2,3) show quite clearly that the metathesis Eqs. (9) and (10) are overemphasized. The quantum yield of Me_5Si_2H loss and the quantum yields of Me_2SiH_2 and $Me_{10}Si_4$ formation are calculated to be too large while products formed by Me_3Si and Me_2SiH radicals like Me_6Si_2 and $Me_2HSiSiHMe_2$ are calculated to be too small. A decrease in the rate constants for Eqs. (9) and (10) to 1×10^{-16} $cm^3\ s^{-1}$ agrees quite well with the experimental results (Table 3, column 4). This agreement can be further improved by enlarging k_9 in comparison to k_{10} (Table 3, column 5). The calculated total loss of Me_5Si_2H is also in good agreement with the experimental value.

For the computer calculations in the presence of NO it was assumed that all radicals and all silaethylenes are scavenged by NO and again the agreement with the experimental values is satisfactory (Table 3, columns 6,7).

Table 2
Reaction mechanism and pertinent rate constants

No.	Reaction	Φ
I	$Me_5Si_2H \rightarrow Me_3SiH + Me_2Si$	0.20
II	$Me_5Si_2H \rightarrow Me_3SiH + MeHSi{=}CH_2$	5.0×10^{-2}
III	$Me_5Si_2H \rightarrow Me_4Si + MeHSi$	4.3×10^{-3}
IV	$Me_5Si_2H \rightarrow Me_2SiH_2 + Me_2Si{=}CH_2$	8.0×10^{-2}
Va–Vd	$Me_5Si_2H \rightarrow CH_4 + Me_3SiSiMe$, $Me_2SiSiMe_2$, $Me_3SiSi(H){=}CH_2$, $Me_2HSiSi(Me){=}CH_2$	1.9×10^{-2}
VI	$Me_5Si_2H \rightarrow H_2 + Me_3SiSi(Me){=}CH_2$	1.2×10^{-2}
VII	$Me_5Si_2H \rightarrow Me_3Si + Me_2SiH$	0.14
VIII	$Me_5Si_2H \rightarrow CH_3 + Me_3SiSiHMe$	2.0×10^{-3}
		$k/10^{-11}cm^3 s^{-1}$
1	$Me_2Si + Me_5Si_2H \rightarrow Me_5Si_2SiMe_2H$	
3	$Me_3SiSiMe + Me_5Si_2H \rightarrow Me_5Si_2SiHMeSiMe_3$	
4	$2\ Me_3Si \rightarrow Me_6Si_2$	3.0
5	$Me_3Si + Me_2SiH \rightarrow Me_5Si_2H$	4.3
6	$Me_3Si + Me_2SiH \rightarrow Me_3SiH + Me_2Si$	1.7
7	$2\ Me_2SiH \rightarrow Me_2HSiSiHMe_2$	1.23
8	$2\ Me_2SiH \rightarrow Me_2SiH_2 + Me_2Si$	1.77
9	$Me_3Si + Me_5Si_2H \rightarrow Me_3SiH + Me_5Si_2$	4.7×10^{-5}
10	$Me_2SiH + Me_5Si_2H \rightarrow Me_2SiH_2 + Me_5Si_2$	4.7×10^{-5}
11	$2\ Me_5Si_2 \rightarrow Me_{10}Si_4$	3.0
12	$Me_3Si + Me_5Si_2 \rightarrow Me_8Si_3$	6.0
13	$Me_2SiH + Me_5Si_2 \rightarrow Me_5Si_2SiMe_2H$	} 6.0
14	$Me_2SiH + Me_5Si_2 \rightarrow Me_2Si + Me_5Si_2H$	
16	$MeHSi + Me_5Si_2H \rightarrow Me_5Si_2SiMeH_2$	
2	$MeHSi{=}CH_2 + MeOH \rightarrow Me_2HSiOMe$	
17	$Me_2Si{=}CH_2 + MeOH \rightarrow Me_3SiOMe$	
18	$R_2Si{=}CH_2 + MeOH \rightarrow$ products	

5. Photophysical considerations

The behaviour of the excited Me_5Si_2H molecule follows qualitatively the routes already observed in the photochemistry of Me_4Si and Me_6Si_2 [1,2]. However, quantitatively significant differences are noted. Collisional deactivation is the most important process of the excited molecule. The quantum yield of collisional deactivation ($\Phi = 0.50$) lies between the values observed in Me_4Si ($\Phi = 0.37$) and Me_6Si_2 ($\Phi = 0.60$). Taking the internal degrees of freedom into consideration this trend is expected. The quantum yield for the molecular elimination processes (I)–(VI) ($\Phi = 0.36$) is much higher than for the respective processes in Me_4Si ($\Phi = 0.17$) and Me_6Si_2 ($\Phi = 0.18$). In the case of Me_5Si_2H one has to distinguish between two kinds of elimination processes: those with a high energy barrier for the back reaction (II)–(VI) and those which do not show such a barrier, i.e., primary process (I). In the case of primary process (I), there is no barrier at the ground state potential energy surface, and it seems quite likely that this will be true for the excited singlet states as well. The sum of the quantum yields for the first group amounts to $\Phi = 0.16$. This is, within our error limits, identical with the values observed in the Me_4Si and Me_6Si_2 photolyses. Primary process (I) occurs at least partially at the expense of the Si–Si bond breaking process. The quantum yield of process (VII) ($\Phi = 0.14$) is appreciably smaller than the corresponding process in Me_6Si_2 ($\Phi = 0.21$) The molecular elimination in the Me_4Si and Me_6Si_2 systems was characterized by a complete independence of the quantum yield values on external parameters. It was argued with the help of an energy correlation diagram that these processes occurred from a strongly predissociating state, which is the first excited singlet state and interacts with the ground state. For Me_5Si_2H a very similar energy correlation diagram of the lowest electronic states with the activated molecular decomposition channels (II)–(VI) and the bond breaking channel (VII) applies. In Fig. 7 the energy correlation between the three electronic states and process (IV) as a representative of the activated molecular elimination processes and the two main decomposition modes (I) and (VII) is shown. The necessary thermochemical data were already discussed to a large extent in Ref. [11], the heat of formation of Me_5Si_2H, $\Delta_fH^0(Me_5Si_2H) = -252 \pm 10$ kJ mol^{-1} has been calculated from literature data using an additivity scheme (Potzinger, unpublished results) [20]. For processes (II)–(VI) no pressure dependence was found and we therefore offer the same explanation as in the case of Me_4Si and Me_6Si_2: predissociation from the excited singlet state.

According to Fig. 7, Si–Si bond cleavage can only occur from the triplet or ground state of the Me_5Si_2H molecule. From thermal decomposition studies we know that only process (I) is taking place in the ground state [4–6]. RRKM calculations show that under our experimental conditions even (I) can hardly compete with collisional deactivation of

Table 3
Comparison of experimental and calculated quantum yields in the presence of MeOH and NO

X	$\Phi_{exp}(X, MeOH)$	$\Phi_{calc}(X, MeOH)$	$\Phi_{calc}(X, MeOH)^a$	$\Phi_{calc}(X, MeOH)^b$	$\Phi_{exp}(X, NO)$	$\Phi_{calc}(X, NO)$
$-Me_5Si_2H$	0.78	0.88	0.78	0.79		
CH_4	1.9×10^{-2}	1.9×10^{-2}	1.9×10^{-2}	1.9×10^{-2}	2.0×10^{-2}	1.9×10^{-2}
Me_2SiH_2	0.13	0.175	0.13	0.13	8.1×10^{-2}	7.8×10^{-2}
Me_3SiH	0.33	0.34	0.30	0.31	0.26	0.24
Me_4Si	5.4×10^{-3}	5.4×10^{-3}	5.4×10^{-3}	5.4×10^{-3}	4.3×10^{-3}	5.4×10^{-3}
$Me_2HSiSiHMe_2$	1.1×10^{-2}	1.1×10^{-3}	6.0×10^{-3}	6.0×10^{-3}	0	0
Me_6Si_2	9.7×10^{-3}	2.8×10^{-3}	1.46×10^{-2}	1.0×10^{-2}	0	0
$Me_5Si_2SiMeH_2$	3.7×10^{-3}	5.4×10^{-3}	5.4×10^{-3}	5.4×10^{-3}	3.9×10^{-3}	5.4×10^{-3}
$Me_5Si_2SiMe_2H$	0.23	0.22	0.24	0.24	0.19	0.20
Me_8Si_3	3.1×10^{-2}	2.8×10^{-2}	3.1×10^{-2}	3.0×10^{-2}	7.5×10^{-4}	0
$Me_5Si_2SiMeHSiMe_3$	1.4×10^{-3}	5.0×10^{-3}	5.0×10^{-3}	5.0×10^{-3}	6.2×10^{-3}	5.0×10^{-3}
$Me_{10}Si_4$	2.1×10^{-2}	6.9×10^{-2}	1.6×10^{-2}	2.1×0^{-2}	0	0
$-MeOH$	0.14	0.14	0.14	0.14	–	–
Me_3SiOMe	7.3×10^{-2}	8.0×10^{-2}	8.0×10^{-2}	8.0×10^{-2}	–	–
$Me_2HSiOMe$	4.0×10^{-2}	5.0×10^{-2}	5.0×10^{-2}	5.0×10^{-2}	–	–

[a] k_9 and k_{10} changed to 1.0×10^{-16} cm^{3}s^{-1}.
[b] k_9 changed to 1.5×10^{-16} cm^{3}s^{-1}.

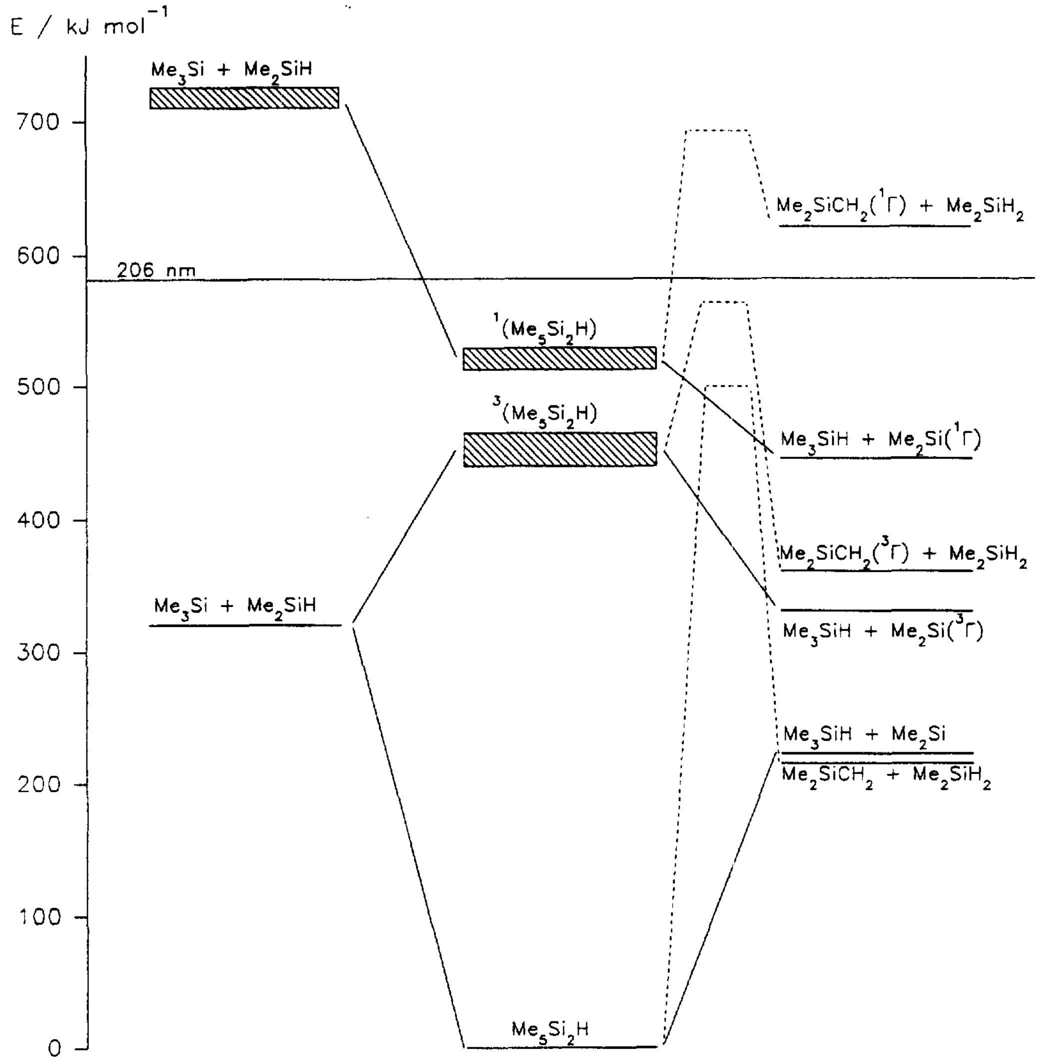

Fig. 7. Energy correlation diagram of the three lowest electronic states of Me_5Si_2H and of the dissociation channels (I), (IV) and (VII).

the excited state. We calculated a microcanonical rate constant of $k(E) = 1.0 \times 10^7 \text{ s}^{-1}$ for decomposition of the excited molecule into Me_2Si and Me_3SiH. We therefore conclude that primary process (VII) is occurring from the triplet state. We arrived at the same result in the case of Me_4Si and Me_6Si_2. In the case of Me_4Si a slight decrease of the bond breaking process in the presence of 1 bar of SF_6 was noted. In the liquid phase radical combination products like C_2H_6 or Me_6Si_2 disappeared almost completely [16]. It was not clear if this was the result of collisional deactivation or cage recombination. SF_6 also reduces the radical combination products in the present case. At first we suspected that this decrease is caused by a water impurity in SF_6. Additional experiments disclosed however that H_2O does not scavenge silyl radicals under our experimental conditions. In agreement with this finding no change in the respective products in the presence of a H_2O/H_2 mixture was found. The experiment also reveals that 1 bar of H_2 is not sufficient to interfere with the Si–Si bond breaking process, and is in agreement with the fact that H_2 is a weaker collider than SF_6. We are now quite convinced that bond breaking processes in photochemically activated methylated silanes can be suppressed and that the almost complete disappearance of products resulting from such processes in the liquid phase is not due to cage recombination of the radicals but due to deactivation of the excited molecule.

Primary process (I) may happen from all three states if no energy barriers exist in the exit channels, as assumed in Fig. 7. To decide from which state the decomposition is actually taking place only few experimental indications are available. The $Me_5Si_2SiMe_2H$ quantum yield can be decreased by SF_6 to a value lower than in the presence of NO. This means that besides process (VII) which leads partially to $Me_5Si_2SiMe_2H$, also molecular elimination process (I) is susceptible to collisional suppression. As can be seen from Figs. 5 and 6, a relatively small pressure of SF_6 or H_2 is enough to decrease the $Me_5Si_2SiMe_2H$ quantum yield to 0.12 and 0.15, respectively. The rest is not influenced by the presence of colliders. We conclude that at least two states are involved in the formation of Me_2Si. The smaller part which can be suppressed probably stems from molecules which made their way to the electronic ground state. The decomposition rate constant $k(E)$ is of such a magnitude that a relatively small pressure suffices to bring this part of process (I) to a standstill. The main part of the Me_2Si molecules must therefore be formed in an excited electronic state.

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