

The Mercury-Sensitized Photolysis of Pentamethyldisilane

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Two primary processes were observed in the Hg-sensitized photolysis of $\text{Me}_5\text{Si}_2\text{H}$: (I) hydrogen abstraction from the Si–H bond with a quantum yield of $\phi(\text{I}) = 0.85$, (V) Si–Si bond breaking with $\phi(\text{V}) = 0.04$. The hydrogen atoms formed in (I) undergo an H atom abstraction reaction ($k(3)$), as well as substitution reactions at the Si centers resulting in the formation of dimethylsilane and trimethylsilyl radical ($k(4)$) or trimethylsilane and dimethylsilyl radical ($k(5)$). The following branching ratios have been determined:

$$\frac{k(3)}{k(3) + k(4) + k(5)} = 0.87, \quad \frac{k(4)}{k(3) + k(4) + k(5)} = 0.096, \quad \frac{k(5)}{k(3) + k(4) + k(5)} = 0.034.$$

The ratio of disproportionation ($k(2)$) to combination ($k(1)$) for the pentamethyldisilyl radical has been determined with MeOH as the scavenger for 1-methyl-1-trimethylsilylsilene, $0.046 \leq k(2)/k(1) \leq 0.071$. A mechanism with pertinent rate constants has been proposed which accounts for the results.

Key words: Hg-sensitized photolysis, pentamethyldisilane, mechanism, substitution reaction, silyl radical disproportionation.

Introduction

The mercury-sensitized photolysis of pentamethyldisilane ($\text{Me}_5\text{Si}_2\text{H}$) was studied for the first time by Jung and Weber about 20 years ago [1]. They observed two main products, decamethyltetrasilane ($\text{Me}_{10}\text{Si}_4$) and octamethyltrisilane (Me_8Si_3), and two minor products 1-hydroheptamethyltrisilane ($\text{Me}_7\text{Si}_3\text{H}$) and 1-hydrononamethyltetrasilane ($\text{Me}_9\text{Si}_4\text{H}$). The formation of $\text{Me}_{10}\text{Si}_4$ was explained by the reaction sequence



All the other products were thought to be of secondary origin, due to direct photolysis of $\text{Me}_{10}\text{Si}_4$ at 254 nm leading to dimethylsilylen (Me_2Si) with concomitant formation of Me_8Si_3 . The insertion of Me_2Si into the Si–H bond of $\text{Me}_5\text{Si}_2\text{H}$ and into the product of this reaction, $\text{Me}_7\text{Si}_3\text{H}$, was thought to be responsible for the formation of the minor products.

Fabry et al. [2] suggested that the H atoms formed in the primary step not only underwent an H atom abstraction reaction from the Si–H bond, but also a substitution reaction yielding either a dimethylsilyl-

or a trimethylsilyl-radical, and the corresponding silane. The silyl radicals combined mainly with Me_5Si_2 radicals yielding $\text{Me}_7\text{Si}_3\text{H}$ and Me_9Si_4 . Therefore in the mechanism of Fabry et al. [2] these two products are of primary origin.

It must be emphasized that in no case of [1, 2] the experimentally observed product yields were in agreement with the suggested mechanism.

Of importance in connection with this work is the publication of Hawari et al. [3], who proposed that dimethylsilylene could be formed by the disproportionation of two pentamethyldisilyl radicals. Me_5Si_2 radicals were generated by the reaction of $\text{t-C}_4\text{H}_9\text{O}$ radicals with $\text{Me}_5\text{Si}_2\text{H}$ in the presence of $\text{t-C}_4\text{H}_9\text{OH}$. There was no evidence for the formation of Me_2Si . The two main products observed, $\text{Me}_{10}\text{Si}_4$ and $\text{Me}_5\text{Si}_2\text{O-t-C}_4\text{H}_9$, were attributed to the combination reaction (1) and the disproportionation reaction



of Me_5Si_2 radicals followed by the scavenging of the silaethylene species by $\text{t-C}_4\text{H}_9\text{OH}$. For the disproportionation to combination ratio an upper limit of $k(2)/k(1) \leq 0.48$ was proposed. We have recently used $\text{Me}_5\text{Si}_2\text{H}$ as a scavenger for Me_2Si [4] and have found it necessary to examine its behaviour with respect to other intermediates as well. This work is also an extension of our previous investigations on the mechanistic pathways of silyl radicals [4–8].

Reprint requests to Prof. P. Potzinger.

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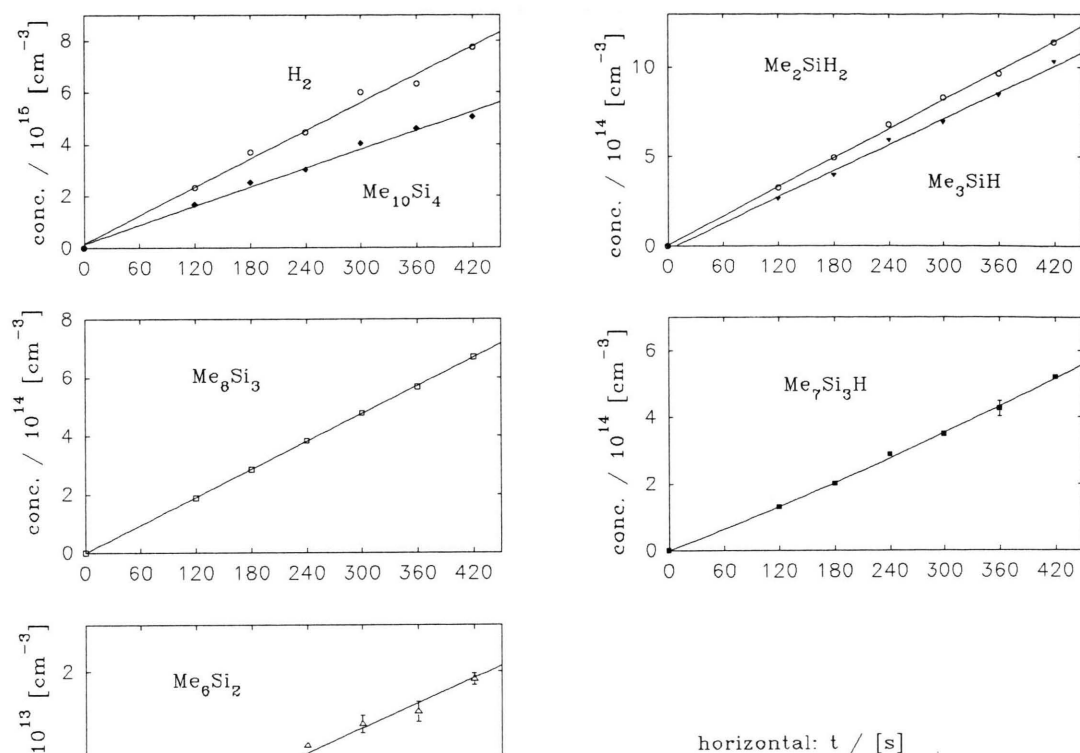


Fig. 1. Dependence of the product concentrations on exposure time in the Hg-sensitized photolysis of $(2.55 \pm 0.07) \cdot 10^{17} \text{ cm}^{-3}$ $\text{Me}_5\text{Si}_2\text{H}$, $I_{\text{abs}} = (2.43 \pm 0.24) \cdot 10^{13} \text{ cm}^{-3} \text{ s}^{-1}$.

Experimental

Static photolyses were carried out as described in [5]. The absorbed light intensity $I_{\text{abs}} [\text{cm}^{-3} \text{ s}^{-1}]$ of the Hg resonance radiation was determined by cis-butene actinometry [9, 10].

All experiments were carried out at room temperature. Endproduct analysis was performed using gas-chromatography (HP 5980, FID, fused silica capillary column OV1, $50 \text{ m} \times 0.32 \text{ mm}$, $1.5 \mu\text{m}$). The inlet system consisted of a multivalve arrangement which could be evacuated, and was heated to 70°C to minimize losses of high boiling products. All samples were analyzed in triplicate, and ethane was used as an internal standard. Response factors were assumed to be proportional to the number of C atoms of the corresponding substance [6]. The photolysis products were identified by a coupled GC-MS (HP 5971 A). Hydro-

gen, which was the only non condensable product, was determined by a simple pressure measurement.

$\text{Me}_5\text{Si}_2\text{H}$ was donated by Prof. Hengge, Graz, and after purification by preparative GC had a purity of 99.6%. The main impurity was hexamethyldisiloxane. The three other substances used, H_2 , NO and MeOH were of commercial origin and of the highest purity grade available.

Results

The Hg-sensitized photolysis of 10 mbar $\text{Me}_5\text{Si}_2\text{H}$ yielded 8 identified products: H_2 , Me_2SiH_2 , Me_3SiH , Me_6Si_2 , $\text{Me}_7\text{Si}_3\text{H}$, Me_8Si_3 , $\text{Me}_{10}\text{Si}_4$ and, in very small yields, $\text{Me}_2\text{HSiSiHMe}_2$. An isomeric unidentified tetrasilane has also been observed. Its retention time was a little shorter than that of $\text{Me}_{10}\text{Si}_4$. The

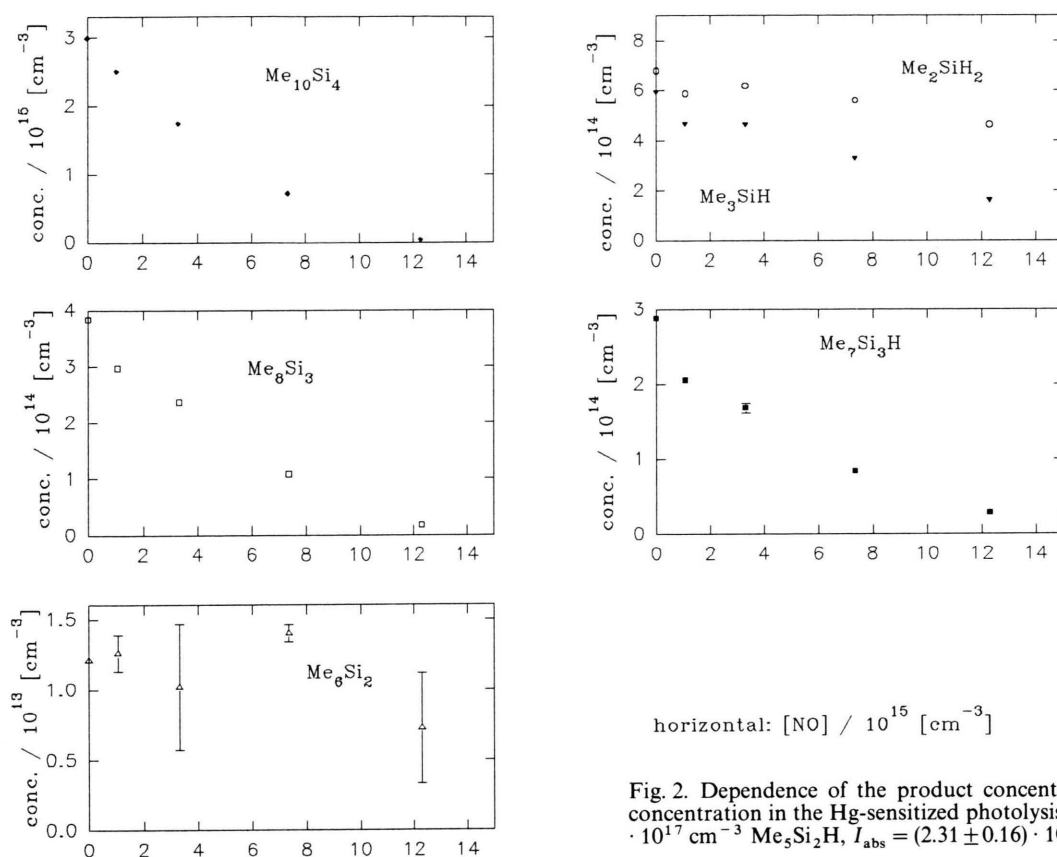


Fig. 2. Dependence of the product concentrations on NO concentration in the Hg-sensitized photolysis of $(2.55 \pm 0.09) \cdot 10^{17} \text{ cm}^{-3} \text{ Me}_5\text{Si}_2\text{H}$, $I_{\text{abs}} = (2.31 \pm 0.16) \cdot 10^{13} \text{ cm}^{-3} \text{ s}^{-1}$.

dependence of the various product yields on irradiation time is shown in Figure 1. With the exception of $\text{Me}_7\text{Si}_3\text{H}$ there is a linear increase of all the product yields with time, indicating that these products are of primary origin. The slope of the straight line divided by I_{abs} gives the quantum yield ϕ which is summarized in Table 1. A second degree polynomial had to be fitted to the experimental points of $\text{Me}_7\text{Si}_3\text{H}$. The coefficient of the linear term was taken equal to ϕI_{abs} . The isomeric tetrasilane shows the typical yield-time behaviour of a substance which reacts further in secondary reactions. Its quantum yield is given in Table 1.

NO is an efficient quencher for silyl-radicals as well as silaethylenes [6]. It is used here to identify products which are formed by a molecular process (with the exception of silaethylenes). Adding high concentration of NO to the reaction mixture leads to the complete disappearance of $\text{Me}_7\text{Si}_3\text{H}$, Me_8Si_3 and $\text{Me}_{10}\text{Si}_4$ (Figure 2). For Me_6Si_2 the picture is unclear. The

Me_2SiH_2 - and Me_3SiH -yields do not drop to zero but seem to reach a plateau value. The quantum yield of product X formation in the presence of NO, denoted by $\phi(\text{X}/\text{NO})$, is also given in Table 1. All the quantum yields of product formation are reported for the highest NO concentration.

The addition of H_2 in excess leads to a new primary process, which has been established as the reaction of excited mercury atoms with hydrogen. This had no influence on the qualitative product spectrum. Only some of the quantum yields changed. As can be seen from Fig. 3, the product yields of Me_2SiH_2 , Me_3SiH , Me_8Si_3 , $\text{Me}_{10}\text{Si}_4$ and $\text{Me}_7\text{Si}_3\text{H}$ as a function of time in the presence of H_2 , are essentially the same as those in the absence of H_2 (Figure 1). The yield of Me_6Si_2 is smaller, and its primary origin unclear. The quantum yields extracted from Fig. 3 are given in Table 1 and are denoted by $\phi(\text{X}/\text{H}_2)$.

The dependence of the product yields on H_2 concentration is shown in Figure 4. In this connection it

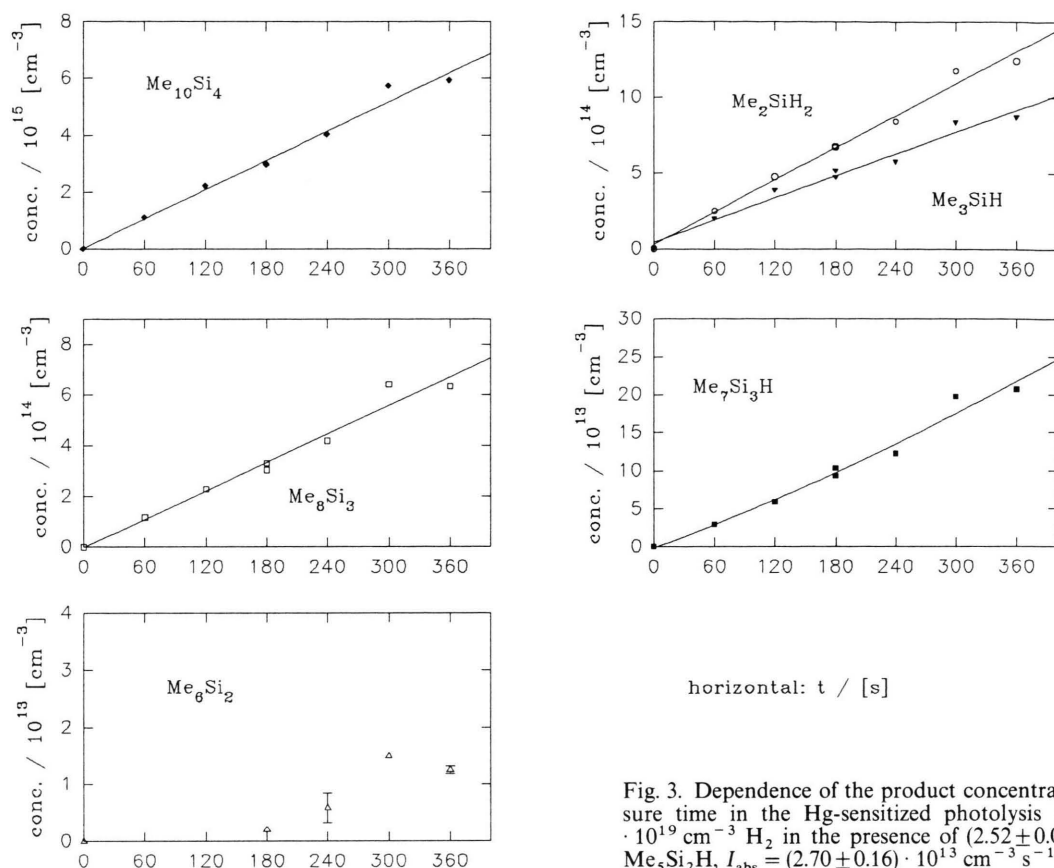


Fig. 3. Dependence of the product concentrations on exposure time in the Hg-sensitized photolysis of $(2.35 \pm 0.03) \cdot 10^{19} \text{ cm}^{-3}$ H_2 in the presence of $(2.52 \pm 0.07) \cdot 10^{17} \text{ cm}^{-3}$ $\text{Me}_5\text{Si}_2\text{H}$, $I_{\text{abs}} = (2.70 \pm 0.16) \cdot 10^{13} \text{ cm}^{-3} \text{ s}^{-1}$.

Table 1. Product quantum yields for various experimental conditions.

Substance X	$\phi(\text{X})$	$\phi(\text{X/NO})$	$\phi(\text{X/H}_2)$	$\phi(\text{X/H}_2, \text{NO})$
H_2	0.75 ± 0.08	—	—	—
Me_2SiH_2	0.11 ± 0.01	$(8.3 \pm 1.0) \cdot 10^{-2}$	0.13 ± 0.01	$(9.8 \pm 1.0) \cdot 10^{-2}$
Me_3SiH	0.10 ± 0.01	$(2.9 \pm 1.0) \cdot 10^{-2}$	$(9.0 \pm 0.8) \cdot 10^{-2}$	$(2.6 \pm 1.0) \cdot 10^{-2}$
$\text{Me}_4\text{Si}_2\text{H}_2$	$\leq 5 \cdot 10^{-4}$	0.00	—	0.00
Me_6Si_2	$(1.8 \pm 0.2) \cdot 10^{-3}$	0.00	—	0.00
$\text{Me}_7\text{Si}_3\text{H}$	$(4.3 \pm 0.5) \cdot 10^{-2}$	0.00	$(1.8 \pm 0.5) \cdot 10^{-2}$	0.00
Me_8Si_3	$(6.6 \pm 0.7) \cdot 10^{-2}$	0.00	$(6.9 \pm 0.6) \cdot 10^{-2}$	0.00
$\text{Me}_{10}\text{Si}_4$	0.50 ± 0.05	0.00	0.64 ± 0.05	0.00
Tetrasilane	$(8 \pm 1) \cdot 10^{-3}$	$(8 \pm 1) \cdot 10^{-3}$	$(2 \pm 0.5) \cdot 10^{-3}$	$(1.5 \pm 0.5) \cdot 10^{-3}$

should be pointed out that for all H_2 concentrations, the H_2 excess is large enough to ensure that the excited mercury atoms react with H_2 only. Changing the primary process has the largest effect on $\text{Me}_7\text{Si}_3\text{H}$; its quantum yield decreases by a factor of 2. A slight increase of Me_2SiH_2 and Me_3SiH is also noted.

Addition of NO had almost the same effect as in the mercury-sensitized photolysis of neat $\text{Me}_5\text{Si}_2\text{H}$

(Figure 5). The quantum yields are denoted by $\phi(\text{X/H}_2, \text{NO})$ and are also given in Table 1.

Addition of MeOH leads to the formation of $\text{Me}_5\text{Si}_2\text{OMe}$. The dependence of this product and of Me_6Si_2 on time is shown in Figure 6. The ratio of the product quantum yields of $\text{Me}_5\text{Si}_2\text{OMe}$ and $\text{Me}_{10}\text{Si}_4$ amounts to 0.071.

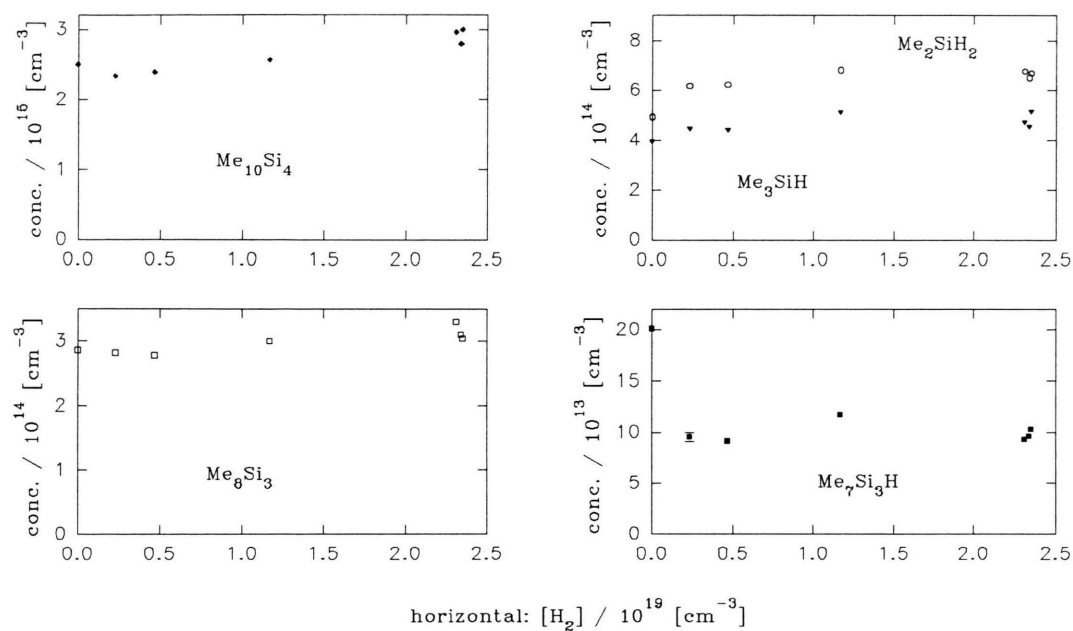


Fig. 4. Dependence of the product concentrations on H_2 concentration in the Hg-sensitized photolysis of H_2 in the presence of $(2.54 \pm 0.08) \cdot 10^{17} \text{ cm}^{-3} \text{ Me}_5\text{Si}_2\text{H}$, $I_{\text{abs}} = (2.58 \pm 0.13) \cdot 10^{13} \text{ cm}^{-3} \text{ s}^{-1}$, $t = 180 \text{ s}$.

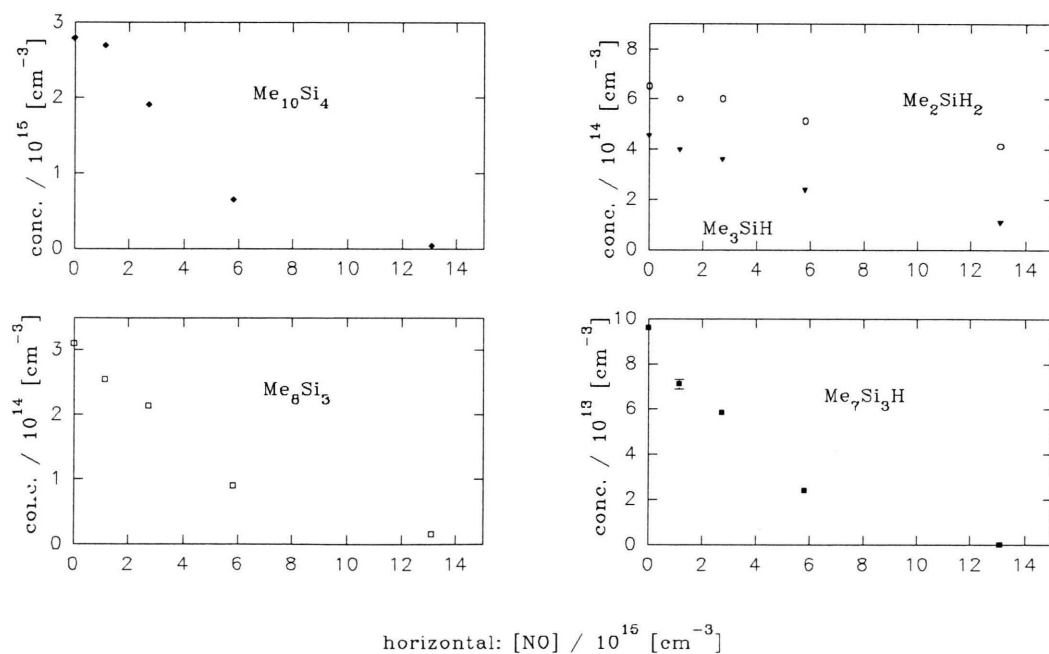


Fig. 5. Dependence of the product concentrations on NO concentration in the Hg-sensitized photolysis of $(2.34 \pm 0.01) \cdot 10^{19} \text{ cm}^{-3} \text{ H}_2$ in the presence of $(2.56 \pm 0.07) \cdot 10^{17} \text{ cm}^{-3} \text{ Me}_5\text{Si}_2\text{H}$, $I_{\text{abs}} = (2.34 \pm 0.18) \cdot 10^{13} \text{ cm}^{-3} \text{ s}^{-1}$, $t = 180 \text{ s}$.

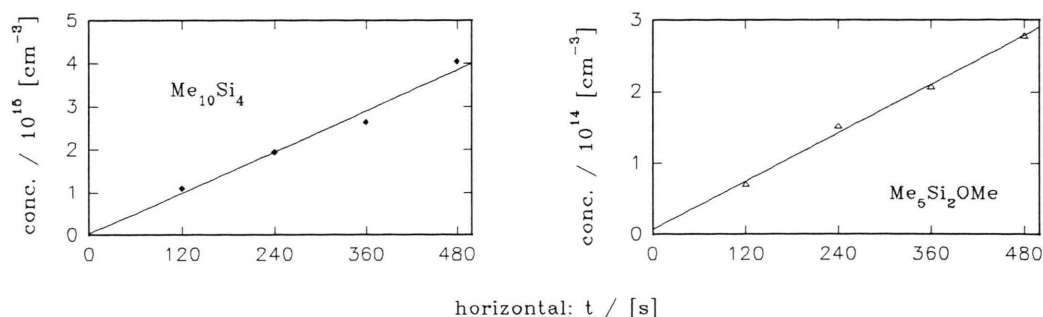


Fig. 6. Dependence of the product concentrations on exposure time in the Hg-sensitized photolysis of $(1.17 \pm 0.01) \cdot 10^{19} \text{ cm}^{-3} \text{ H}_2$ in the presence of $(2.37 \pm 0.08) \cdot 10^{17} \text{ cm}^{-3} \text{ Me}_5\text{Si}_2\text{H}$ and $(1.31 \pm 0.05) \cdot 10^{16} \text{ cm}^{-3} \text{ MeOH}$.

Discussion

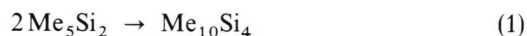
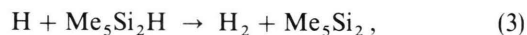
Materialbalance

From the quantum yields $\phi(X)$, given in Table 1, one calculates a quantum yield of 1.31 ± 0.10 for the disappearance of an educt with the formula $\text{Si}_{1.94 \pm 0.15} \text{C}_{4.87 \pm 0.53} \text{H}_{16.00}$. This quantum yield is only a lower limit because besides a loss of Si and C, as discernible from the formula, there will be also a loss of H. The ratio of the stoichiometric numbers of C and Si is $4.87/1.94$, which is very close to $5/2$, suggesting that Si and C are affected in the same way by the various processes leading to an imperfect material balance. We make therefore the assumption that no or very few Si–C bonds and no C–H bonds are broken in the course of reactions, and only Si–H and Si–Si bonds are transformed. We then calculate the loss of a substance with the formula $\text{Me}_{3.37 \pm 0.39} \text{Si}_{1.34 \pm 0.16} \text{H}_{1.00}$ and a quantum yield of 1.89 ± 0.16 . This value is an upper limit because we are assuming that all the H_2 stems from the Si–H bond of $\text{Me}_5\text{Si}_2\text{H}$. It will become evident below, that the true value lies close to this upper limit. This means then that about one third of all Me_5Si_2 entities formed are missing. In the presence of H_2 we are only able to calculate the loss of silicon and the methyl groups. A quantum yield of 1.51 ± 0.10 is observed for the disappearance of Me_5Si_2 . Because the quantum yield of H atoms in the Hg-sensitized photolysis of H_2 lies close to 2 [11], we also expect a quantum yield of approximately 2 for the loss of $\text{Me}_5\text{Si}_2\text{H}$. However, about one third of the observed Me_5Si_2 is unaccounted for. Several reasons for these large losses have been suggested. The first reason could be that the response factors for the higher molecular weight prod-

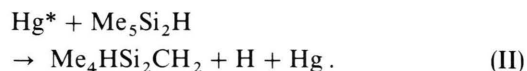
ucts were estimated (see experimental section) incorrectly. However, from our experience with silicon compounds we know that deviations larger than 10% are rare. Therefore it is much more likely that we are not able to transfer the high boiling point products quantitatively to the gaschromatographic column. If we attribute the loss totally to the highest molecular weight product, $\text{Me}_{10}\text{Si}_4$, then a $\phi(\text{Me}_{10}\text{Si}_4)$ of 0.81 instead of 0.5 is expected.

Mechanism

The formation of the two main products H_2 and $\text{Me}_{10}\text{Si}_4$, the similarity of the product spectrum in the presence and absence of H_2 , and our knowledge of the interaction of excited mercury atoms with silanes leave little doubt that the primary process (I), followed by

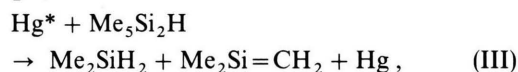


is occurring, as suggested in [1]. There exists also the possibility that the excited Hg atom abstracts a hydrogen atom from a C–H bond. Such a process has been observed to a small extent in the mercury sensitized photolysis of Me_3SiH [5]:



The substituted methyl radical will react predominantly with Me_5Si_2 to yield the isomeric tetrasilane $\text{Me}_4\text{HSi}_2\text{CH}_2\text{Si}_2\text{Me}_5$. One is tempted to assign the unidentified tetrasilane GC peak with this product. Two observations are in favour of this assignment: 1. The quantum yield of this product is smaller in the $\text{Hg}/\text{H}_2/\text{Me}_5\text{Si}_2\text{H}$ system than in the $\text{Hg}/\text{Me}_5\text{Si}_2\text{H}$ sys-

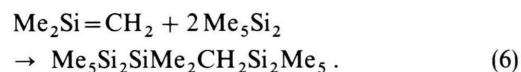
tem [5]. 2. Products with a weak Si–H bond undergo secondary reactions very easily [4]. However there are experimental facts of great weight which argue against such an assignment: 1. The tetrasilane cannot be scavenged by NO and 2. the retention time should be longer and not shorter than for $\text{Me}_{10}\text{Si}_4$. For disilanes it was always observed that isomers with a Si–C–Si frame have a longer retention time than with a Si–Si frame. Even if we are mistaken and the isomeric tetrasilane stands for the primary process (II), its quantum yield (Table 1) would be small in any case. All other products must originate either from other primary processes or from reactions with H and/or Me_5Si_2 which are different from (1) and (2). Me_2SiH_2 and Me_3SiH are produced via a radical reaction, and in a reaction which cannot be scavenged by NO. The nonscavengeable parts of Me_2SiH_2 and Me_3SiH can either be formed by the interaction of excited Hg with $\text{Me}_5\text{Si}_2\text{H}$,



or by a substitution reaction of H atoms with $\text{Me}_5\text{Si}_2\text{H}$,



H atoms can react only termolecularly with NO [12]. Under our experimental conditions $\text{Me}_2\text{Si}=\text{CH}_2$ will react with any radical present [6], and in our system these are mainly Me_5Si_2 radicals:



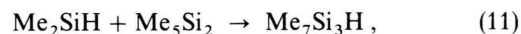
However, the above product has not been detected. The Me_2Si intermediate will insert into the Si–H bond of $\text{Me}_5\text{Si}_2\text{H}$ [13]:



Our experiments with excess H_2 show that an appreciable part of the nonscavengeable fraction of Me_2SiH_2 and Me_3SiH is coming from reactions (4) and (5).

We are not able to exclude the primary processes (II), (III), and (IV) altogether, but their contributions to the overall mechanism will be small and are therefore neglected in our further considerations.

Radical combination reactions explain the remaining products:



The mechanism is still incomplete since the scavengeable part of Me_2SiH_2 and Me_3SiH is not accounted for. One possibility of how Me_2SiH_2 and Me_3SiH could be formed by a radical path are disproportionation reactions accompanying the combination reactions (8)–(12). If we equate $\phi(\text{X}) - \phi(\text{X}/\text{NO})$ with the scavengeable part of $\text{X} = \text{Me}_2\text{SiH}_2$ and Me_3SiH , then the amounts of products formed by disproportionation reactions are of similar magnitude to that formed by combination reactions. This result is very unlikely in view of our previous results [4, 5], which show that disproportionation reactions leading to a Si=C double bonded species make up less than 10% of the pertinent combination reactions. It is in accord, however, with the results given in [3]. We suspected, that the large amounts of $\text{Me}_5\text{Si}_2\text{O}-t\text{-C}_4\text{H}_9$ reported there are due to a dark reaction [14], and our experiments show that disproportionation can be indeed neglected. We find $0.046 \leq k(2)/k(1) \leq 0.071$ depending on the quantum yield of $\text{Me}_{10}\text{Si}_4$ $0.5 \leq \phi \leq 0.81$. We are forced to postulate that silyl-radicals abstract hydrogen from $\text{Me}_5\text{Si}_2\text{H}$. Independent studies [15] have shown that this is indeed the case. We therefore add the reactions



to our mechanism. One can draw up a balance relation for the formation of the Me_2SiH - and Me_3Si -radicals, and from our mechanism

$$\begin{aligned} \phi(\text{Me}_3\text{SiH}/\text{NO}) \\ = 2\phi(\text{Me}_4\text{Si}_2\text{H}_2) + \phi(\text{Me}_5\text{Si}_2\text{H}/(10)) \\ + \phi(\text{Me}_7\text{Si}_3\text{H}) + \phi(\text{Me}_2\text{SiH}_2) \\ - \phi(\text{Me}_2\text{SiH}_2/\text{NO}), \end{aligned} \quad (15)$$

$$\begin{aligned} \phi(\text{l.h.s.}) &= 0.029 \pm 0.010 < \sum \phi(\text{r.h.s.}) \\ &= 0.070 \pm 0.015, \end{aligned}$$

$$\begin{aligned}
&\phi(\text{Me}_2\text{SiH}_2/\text{NO}) \\
&= 2\phi(\text{Me}_6\text{Si}_2) + \phi(\text{Me}_5\text{Si}_2\text{H}/(10)) \\
&\quad + \phi(\text{Me}_8\text{Si}_3) + \phi(\text{Me}_3\text{SiH}) \\
&\quad - \phi(\text{Me}_3\text{SiH}/\text{NO}) \quad (16) \\
&\phi(\text{l.h.s.}) = 0.083 \pm 0.141 < \sum \phi(\text{r.h.s.}) \\
&\quad = 0.141 \pm 0.013,
\end{aligned}$$

one can conclude that reactions (4) and (5) are not able to supply the necessary yields of Me_2SiH and Me_3Si radicals to account for all the products observed. The numbers in relations (15) and (16) have been obtained by neglecting $\phi(\text{Me}_5\text{Si}_2\text{H}/10)$. We assumed that the quantum yield of $\text{Me}_5\text{Si}_2\text{H}$ formed in reaction (10) will be small, in view of the small quantum yields observed for Me_6Si_2 and $\text{Me}_4\text{Si}_2\text{H}_2$.

The difference between the left and right hand side in relations (15) and (16) are approximately the same within the given error limits. For this comparison it should be emphasized that the plateau values of Me_2SiH_2 and Me_3SiH are not very pronounced (Fig. 2) because at higher NO concentration quenching of the H atoms comes into play. To account for the missing Me_2SiH and Me_3Si radicals we postulate a fifth primary process



With the proposed mechanism and the data given in Table 1 we are able to make an assertion about the importance of the primary processes (I) and (V) and the branching ratios for the reactions (3), (4) and (5). The following expressions may be derived:

$$\begin{aligned}
&2\phi(\text{I}) + \phi(\text{V}) \\
&= \phi(-\text{Me}_5\text{Si}_2\text{H}) - \phi(\text{Me}_2\text{SiH}_2) \\
&\quad + \phi(\text{Me}_2\text{SiH}_2/\text{NO}) - \phi(\text{Me}_3\text{SiH}) \\
&\quad + \phi(\text{Me}_3\text{SiH}/\text{NO}) \\
&= 1.73 \pm 0.16 \quad (17)
\end{aligned}$$

$\phi(-\text{Me}_5\text{Si}_2\text{H})$ is taken equal to the upper limit 1.89 ± 0.16 derived in the materialbalance section, because neither C–H nor Si–C bond breaking processes occur within the proposed mechanism.

Further we get

$$\begin{aligned}
\phi(\text{I}) &= \phi(\text{H}_2) + \phi(\text{Me}_2\text{SiH}_2/\text{NO}) \\
&\quad + \phi(\text{Me}_3\text{SiH}/\text{NO}) \\
&= 0.86 \pm 0.08 \quad (18)
\end{aligned}$$

$\phi(\text{V})$ can be calculated in two ways:

$$\begin{aligned}
\phi(\text{V}) &= 2\phi(\text{Me}_6\text{Si}_2) + \phi(\text{Me}_5\text{Si}_2\text{H}/(10)) \\
&\quad + \phi(\text{Me}_8\text{Si}_3) + \phi(\text{Me}_3\text{SiH}) \\
&\quad - \phi(\text{Me}_2\text{SiH}_2/\text{NO}) - \phi(\text{Me}_3\text{SiH}/\text{NO}) \\
&= 0.067 \pm 0.012 \quad (19)
\end{aligned}$$

or

$$\begin{aligned}
\phi(\text{V}) &= 2\phi(\text{Me}_4\text{Si}_2\text{H}_2) + \phi(\text{Me}_5\text{Si}_2\text{H}/(10)) \\
&\quad + \phi(\text{Me}_7\text{Si}_3\text{H}) + \phi(\text{Me}_2\text{SiH}_2) \\
&\quad - \phi(\text{Me}_2\text{SiH}_2/\text{NO}) \\
&\quad - \phi(\text{Me}_3\text{SiH}/\text{NO}) \\
&= 0.041 \pm 0.012 \quad (20)
\end{aligned}$$

For further calculations we take the average value $\phi(\text{V}) = 0.055 \pm 0.015$. With this value we are able to calculate another value for $\phi(\text{I})$ from (17):

$$\phi(\text{I}) = \frac{1.73 - 0.055}{2} = 0.84 \pm 0.08 \quad (21)$$

This value agrees quite well with that obtained in (18), and we use this as a mean value

$$\phi(\text{I}) = 0.85 \pm 0.08 \quad (22)$$

The branching ratios for the reactions of H atoms with $\text{Me}_5\text{Si}_2\text{H}$ are given by

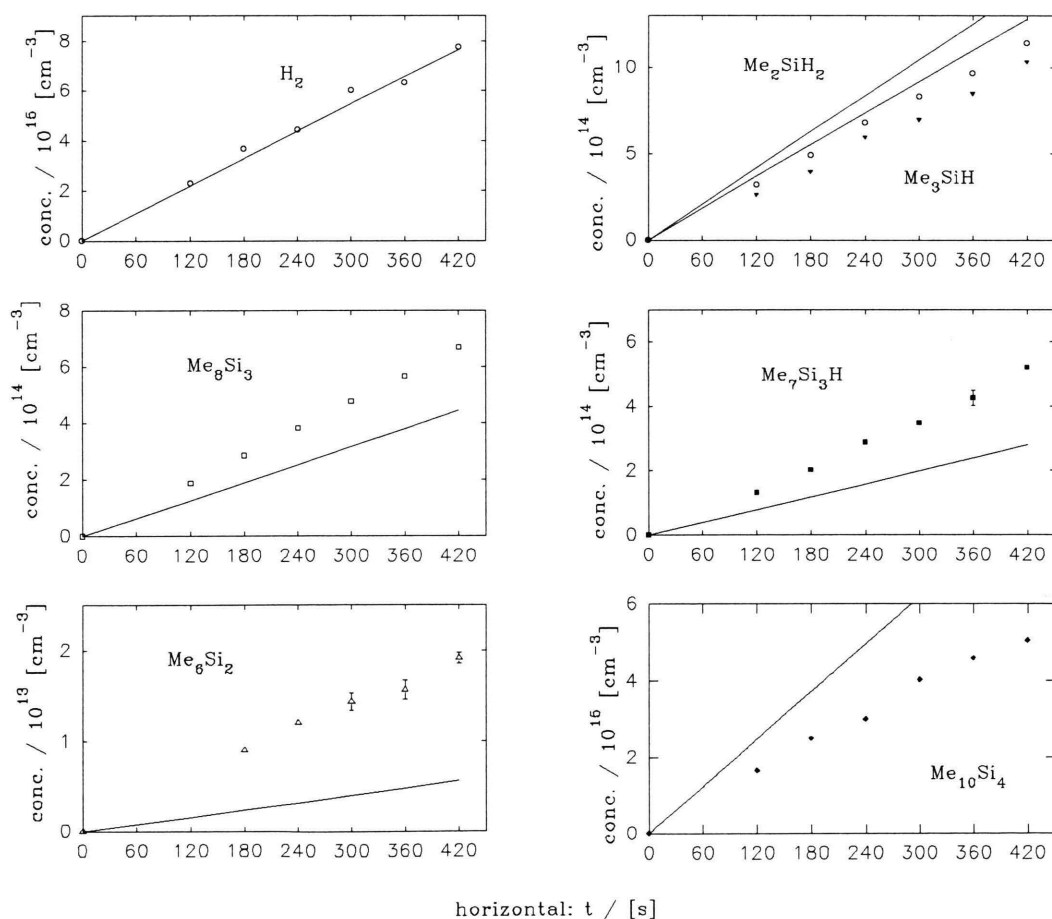
$$\begin{aligned}
&\frac{k(3)}{k(3) + k(4) + k(5)} \\
&= \frac{\phi(\text{H}_2)}{\phi(\text{H}_2) + \phi(\text{Me}_2\text{SiH}_2/\text{NO}) + \phi(\text{Me}_3\text{SiH}/\text{NO})} \\
&= 0.87, \\
&\frac{k(4)}{k(3) + k(4) + k(5)} = 0.096, \quad (23) \\
&\frac{k(5)}{k(3) + k(4) + k(5)} = 0.034.
\end{aligned}$$

Abstraction is the main process. Substitution occurs preferentially at that Si atom which is already bonded to an H atom.

In the presence of excess H_2 , the primary processes (I) and (V) are replaced by the well-known reactions of H_2 with $\text{Hg}(^3\text{P}_1)$ [16–18]. The H atoms generated in these processes enter the proposed mechanism via the reactions (3), (4), and (5). Because of the predominance of reactions (I) and (3) in the Hg-sensitized photolysis of neat $\text{Me}_5\text{Si}_2\text{H}$, no great change in the product spectrum is expected for the addition of excess H_2 . The nonoccurrence of the primary process (V) has the

Table 2. Reactions and rate constants used in computer simulations.

No.		k
	$\text{Hg} \rightarrow \text{Hg}^*$	$I_{\text{abs}} \cdot 10^7 \text{ s}^{-1}$
	$\text{Hg}^* \rightarrow \text{Hg} + h\nu$	$1 \cdot 10^{-10} \text{ cm}^3 \text{ s}^{-1}$
(I)	$\text{Hg}^* + \text{Me}_5\text{Si}_2\text{H} \rightarrow \text{Me}_5\text{Si}_2 + \text{H} + \text{Hg}$	$4.3 \cdot 10^{-10} \text{ cm}^3 \text{ s}^{-1}$
(V)	$\text{Hg}^* + \text{Me}_5\text{Si}_2\text{H} \rightarrow \text{Me}_2\text{SiH} + \text{Me}_3\text{Si} + \text{Hg}$	$3.0 \cdot 10^{-11} \text{ cm}^3 \text{ s}^{-1}$
(3)	$\text{H} + \text{Me}_5\text{Si}_2\text{H} \rightarrow \text{H}_2 + \text{Me}_5\text{Si}_2$	$9.2 \cdot 10^{-13} \text{ cm}^3 \text{ s}^{-1}$
(4)	$\text{H} + \text{Me}_5\text{Si}_2\text{H} \rightarrow \text{Me}_2\text{SiH}_2 + \text{Me}_3\text{Si}$	$1.0 \cdot 10^{-13} \text{ cm}^3 \text{ s}^{-1}$
(5)	$\text{H} + \text{Me}_5\text{Si}_2\text{H} \rightarrow \text{Me}_3\text{SiH} + \text{Me}_2\text{SiH}$	$3.6 \cdot 10^{-14} \text{ cm}^3 \text{ s}^{-1}$
(1)	$2 \text{ Me}_5\text{Si}_2 \rightarrow \text{Me}_{10}\text{Si}_4$	$1.0 \cdot 10^{-11} \text{ cm}^3 \text{ s}^{-1}$
(8)	$2 \text{ Me}_2\text{SiH} \rightarrow \text{Me}_2\text{HSiSiHMe}_2$	$1.0 \cdot 10^{-11} \text{ cm}^3 \text{ s}^{-1}$
(25)	$2 \text{ Me}_2\text{SiH} \rightarrow \text{Me}_2\text{Si} + \text{Me}_2\text{SiH}_2$	$2.0 \cdot 10^{-11} \text{ cm}^3 \text{ s}^{-1}$
(7)	$\text{Me}_2\text{Si} + \text{Me}_5\text{Si}_2\text{H} \rightarrow \text{Me}_7\text{Si}_3\text{H}$	$4.2 \cdot 10^{-11} \text{ cm}^3 \text{ s}^{-1}$
(9)	$2 \text{ Me}_3\text{Si} \rightarrow \text{Me}_6\text{Si}_2$	$3.0 \cdot 10^{-11} \text{ cm}^3 \text{ s}^{-1}$
(10)	$\text{Me}_2\text{SiH} + \text{Me}_3\text{Si} \rightarrow \text{Me}_5\text{Si}_2\text{H}$	$6.0 \cdot 10^{-11} \text{ cm}^3 \text{ s}^{-1}$
(11)	$\text{Me}_2\text{SiH} + \text{Me}_5\text{Si}_2 \rightarrow \text{Me}_7\text{Si}_3\text{H}$	$1.75 \cdot 10^{-11} \text{ cm}^3 \text{ s}^{-1}$
(26)	$\text{Me}_2\text{SiH} + \text{Me}_5\text{Si}_2 \rightarrow \text{Me}_2\text{Si} + \text{Me}_5\text{Si}_2\text{H}$	$1.75 \cdot 10^{-11} \text{ cm}^3 \text{ s}^{-1}$
(12)	$\text{Me}_3\text{Si} + \text{Me}_5\text{Si}_2 \rightarrow \text{Me}_8\text{Si}_3$	$3.5 \cdot 10^{-11} \text{ cm}^3 \text{ s}^{-1}$
(13)	$\text{Me}_2\text{SiH} + \text{Me}_5\text{Si}_2\text{H} \rightarrow \text{Me}_2\text{SiH}_2 + \text{Me}_5\text{Si}_2$	$4.5 \cdot 10^{-16} \text{ cm}^3 \text{ s}^{-1}$
(14)	$\text{Me}_3\text{Si} + \text{Me}_5\text{Si}_2\text{H} \rightarrow \text{Me}_3\text{SiH} + \text{Me}_5\text{Si}_2$	$4.5 \cdot 10^{-16} \text{ cm}^3 \text{ s}^{-1}$

Fig. 7. Dependence of the product concentrations on exposure time in the Hg-sensitized photolysis of $(2.55 \pm 0.07) \cdot 10^{17} \text{ cm}^{-3} \text{ Me}_5\text{Si}_2\text{H}$, $I_{\text{abs}} = (2.43 \pm 0.24) \cdot 10^{13} \text{ cm}^{-3} \text{ s}^{-1}$; curves: simulated concentration vs. time profiles.

greatest influence on the stationary concentration of Me_2SiH ; its decrease is mirrored in the reduction of the $\text{Me}_7\text{Si}_3\text{H}$ quantum yield (Figure 4).

The rate constant ratio $k(4)/k(5)$ can be directly obtained from the quantum yields $\phi(\text{Me}_2\text{SiH}_2/\text{H}_2, \text{NO})$ and $\phi(\text{Me}_3\text{SiH}/\text{H}_2, \text{NO})$:

$$\frac{k(4)}{k(5)} = \frac{\phi(\text{Me}_2\text{SiH}_2/\text{H}_2, \text{NO})}{\phi(\text{Me}_3\text{SiH}/\text{H}_2, \text{NO})} = 3.8. \quad (24)$$

The agreement with (23) is poor and reflects the low precision with which $\phi(\text{Me}_2\text{SiH}_2)$ and $\phi(\text{Me}_3\text{SiH})$ can be obtained in the presence of NO.

Computer Simulations

In Table 2 the reactions which have been considered in the computer calculations (KINAL [19]) are summarized. The quenching cross section for $\text{Hg}^* + \text{Me}_5\text{Si}_2\text{H}$ is not known. To obtain the experimentally observed quantum yield for the disappearance of $\text{Me}_5\text{Si}_2\text{H}$ ($\phi(-\text{Me}_5\text{Si}_2\text{H}) = 1.89$), a very large cross section for the sum of the primary processes (I) and (V) was assumed, being of similar magnitude as for higher alkenes [20]. Radiation imprisonment may have also contributed to this large value. The sum of the rate constants $k(3) + k(4) + k(5)$ for the reactions of H atoms with $\text{Me}_5\text{Si}_2\text{H}$ is known [2]. For the branching ratios of reactions (I) and (V) and for the branching ratios of reactions (3), (4) and (5) the above evaluated figures have been used.

Of the different radical combination reactions only the rate constant for reaction (9) is known [21, 22]. The same value has been assumed for the sum of the rate constants $k(8) + k(25)$. A value for the disproportionation to combination ratio for Me_2SiH has been determined recently [4], and this value has been used in the calculations. For the Me_5Si_2 radical, a smaller value for the combination reaction has been assumed. For cross combination reactions the geometric mean rule has been applied. The disproportionation to com-

bination ratio $k(26)/k(11)$ has been estimated in [15]. The rate constants for the insertion reaction of Me_2Si into $\text{Me}_5\text{Si}_2\text{H}$ [13] and for H atom abstraction from $\text{Me}_5\text{Si}_2\text{H}$ by Me_3Si [15] are known. For Me_2SiH the same value as for the latter reaction has been assumed.

With this set of rate constants we have calculated product yields as functions of time as shown in Figure 7. The agreement is quite satisfactory if one takes into account that no fitting of the rate constants has been undertaken. A substantial improvement in the agreement of calculated and experimental values can be achieved by minor changes in the rate constants, especially for the abstraction reactions (13) and (14).

Conclusion

The mercury-sensitized decomposition of $\text{Me}_5\text{Si}_2\text{H}$ follows in its main channel a reaction type which is known from alkanes and silanes. Process (III), (IV), and (V) are different and quite likely due to the availability of a low lying triplet state. The absorption onset of $\text{Me}_5\text{Si}_2\text{H}$ lies around $\lambda = 230 \text{ nm}$ [23] and is due to a Rydberg transition [24]. The singlet-triplet splitting for this kind of transition is small [25], but may be just large enough to make an energy transfer from $\text{Hg}(^3\text{P}_1)$ to $\text{Me}_5\text{Si}_2\text{H}$ possible. H atoms not only undergo an abstraction reaction, but also a substitution reaction at a Si center, as already discussed in [2]. Preferred attack takes place at the least methylated Si atom. Endproducts can be explained by radical combination reactions and H atom abstraction reactions from $\text{Me}_5\text{Si}_2\text{H}$.

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