The Reaction of Hydrogen Atoms with Silyl Radicals; the Decomposition Pathways of Chemically Activated Silanes

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Dedicated to Prof. G. O. Schenck on the occasion of his 70th birthday

The reactions of hydrogen atoms with silane and the methylated silanes — with the exception of tetramethylsilane — have been investigated in a fast flow reactor. Under our experimental conditions hydrogen abstraction from the Si–H bond is followed by combination of hydrogen atoms with the corresponding silyl radicals. The molecules formed in this way are activated by about 375 kJ/mol of vibrational energy. Two decomposition channels have been unequivocally identified, namely the elimination of molecular hydrogen and of methane, both with concomitant formation of the respective silylenes. In a subsequent step, silylene inserts into the substrate under formation of disilanes. With increasing degree of methylation, stabilization of the activated molecule competes with decomposition and dominates the kinetics in the case of trimethylsilane. With methyl- and dimethyl-silyl, methyl radicals are observed as an additional reaction product. On the basis of RRKM calculations it is unlikely that they originate from a direct decomposition of the activated molecules.

Absolute values for the room temperature rate constants of the abstraction reactions are given; for H + CH₃SiH₄, Arrhenius parameters have been determined.

Introduction

The reactions of hydrogen atoms with silane and the methylsilanes have been the subject of a number of studies [1]. There exists agreement that the primary step comprises a simple abstraction reaction (1)

\[ \text{H} + \text{R}_3\text{SiH} \rightarrow \text{H}_2 + \text{R}_3\text{Si}. \] (1)

Investigating this type of reaction by the flow technique, the primary step is inevitably followed by a very fast reaction (2)

\[ \text{H} + \text{R}_3\text{Si} \rightarrow \text{R}_3\text{SiH}(v) \] (2)

not only under the condition of atoms in excess but also when the substrate is introduced in ten to hundred fold excess, due to the small rate constant for the dimerisation of the silyl radicals compared to (2) [2]. The fate of the silane molecule generated in (2) and possessing approximately 375 kJ/mol excess energy has been investigated by Michael and co-workers [3]. In the case of trimethylsilane complete stabilization of the molecule activated by (2')

\[ \text{D} + \text{R}_3\text{Si} \rightarrow \text{R}_3\text{SiD}(v) \] (2')

was found under flow conditions. This is in agreement with findings in our group [4]. In the case of silane, mono- and dimethyl-silane all the activated molecules were thought to decompose by simple bond breaking processes, a silicon-hydrogen split in the case of SiH₄ and a silicon-carbon split otherwise. Further reactions of the radicals with D atoms lead ultimately to CD₄ and SiD₄.

Based on our knowledge at present it is improbable that silane and the methylsilanes activated by (2) decompose as suggested by [3]. Energetically much lower fragmentation pathways — silylene formation with concomitant loss of H₂ or CH₄ — are available and are not only realized in thermally activated systems [5, 6, 7] but also in chemically activated methylsilanes, produced by ethylene insertion into the Si–H bond [8].

It has been pointed out by us [9, 10] and others [3] that flow experiments involving silanes are severely hampered by wall effects and this also holds true with pyrolysis experiments [5] leading in the latter case at least to a contamination of the reaction mechanism by radical reactions. Accordingly, the scatter of the reported rate constants is large especially for the systems H/SiH₄ and H/CH₃SiH₃ [1].

We have therefore decided to repeat the experiments of Michael et al. [3] taking special care to minimize wall effects. Rate constants as well as de-
composition pathways of vibrationally excited silane, mono-, di- and trimethylsilane as measured in a flow reactor are reported. The experimental results are compared with RRKM calculations. To test the quality of our results obtained in the flow experiment we also measured the Arrhenius parameters for reaction (3)

\[ H + CH_3SiH_3 \rightarrow H_2 + CH_3SiH_2 \]  

in a virtually wall free experiment by time resolved Lyman \( \alpha \) resonance absorption resp. resonance fluorescence.

**Experimental**

\( SiH_4 \) (\( \equiv 99.999\% \)) was purchased from Air Liquid, \( CH_3SiH_3 \), \( (CH_3)_2SiH_2 \) and \( (CH_3)_3SiH \) from PCR. \( He (99.996\%) \), \( H_2 (99.999\%) \), and \( D_2 \) (isotopic purity 99.6\%) were passed through molecular sieve cooled by liquid nitrogen to remove any trace of moisture. \( Ar (99.997\%) \) was dried over \( P_2O_5 \). Propane (Phillips research grade) was used as received.

Methyldisilane was prepared by reaction of disilane with methyllithium [13]. 1,2-Dimethyldisilane was prepared by reduction of 1,2-dimethyltetra-chlorodisilane with LiAlH\(_4\). 1,1,2-Trimethyldisilane and 1,1,2,2-tetramethyldisilane were not available as pure substances for calibration purposes, only their mass spectra are known from earlier work [14]. The intensity of the prominent fragment ions of the four methylated disilanes are given in Table 1. The mass spectra of methyldisilane and 1,2-dimethyldisilane are not in good agreement with published spectra by Longeway and Lampe [15].

Our flow reactor is basically of the same design as that of Wagner and coworkers [11]. Differences occur in a) the mass spectrometer; a quadrupole mass spectrometer has been used, and b) the signal processing; the molecular beam was chopped in the first vacuum chamber allowing phase sensitive detection to be employed. A detailed description of the apparatus is given in [12]. A special problem was posed in the flow experiments by the high wall activity of the atom-silane systems. Measurements of rate constants using a plain quartz reactor were virtually impossible. Poisoning of the surface with diluted HF, halocarbon wax, or methylated chlorosilanes brought only a slight improvement. An appreciable decrease of the influence of the walls has been achieved by inserting teflon rings of 6 mm height with a conical opening (smallest diameter 22.7 mm, largest diameter 25 mm) into the reactor. The teflon rings were inserted with the sharp edge of the smaller opening facing the streaming gas at regular distances of 3.5 cm. The working hypothesis made was that at high flow velocities the rings would lead to a contraction of the flow leading to a "wallless" reactor. The effective cross section of the reactor was reduced in this way by a factor of 1.5. No extensive investigations to substantiate this proposition have been carried out. What has been shown, however, is that in the case of the \( D + (CH_3)_3SiH \) reaction, where wall effects are less severe, consistent results are obtainable both with and without the teflon rings. For the reaction \( D + \text{transbutene} \) the rate constant \( k (D + \text{trans-C}_4\text{H}_8) = (7 \pm 1) \times 10^{-13} \text{cm}^3\text{s}^{-1} \) (experimental details: flow velocity 25.3 m s\(^{-1}\), \( P = 425 \text{ Pa} \), \([D]_o = 4.3 \times 10^{14} \text{cm}^{-3} \), \([\text{trans-C}_4\text{H}_8]_o = 4 \times 10^{13} \text{cm}^{-3} \) was obtained with teflon rings in satisfactory agreement with the literature [16].

The time resolved Lyman \( \alpha \) absorption technique has been described previously [17]. It is very similar to a conventional flash photolysis-resonance absorption system, the main difference being the production of H atoms by means of pulsed mercury radiation. This is achieved by putting a fast mechanical shutter in front of a DC powered low pressure mercury lamp. The gas mixture in the reaction cell

### Table 1. Intensities of the four most prominent fragment ions of four methylated disilanes.

<table>
<thead>
<tr>
<th>Substance</th>
<th>m/e</th>
<th>43</th>
<th>44</th>
<th>45</th>
<th>58</th>
<th>59</th>
<th>73</th>
<th>76</th>
<th>90</th>
<th>104</th>
<th>118</th>
</tr>
</thead>
<tbody>
<tr>
<td>( CH_3SiH_3 )</td>
<td></td>
<td>65</td>
<td>40</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>( 1,2-(CH_3)_2SiH_2 )</td>
<td></td>
<td>53</td>
<td>72</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>69</td>
<td></td>
</tr>
<tr>
<td>( 1,1,1-(CH_3)_3SiH_3 )</td>
<td></td>
<td>46</td>
<td>49</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>( 1,1,2,2-(CH_3)_4Si_2H_2 )</td>
<td></td>
<td>54</td>
<td>86</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>44</td>
<td></td>
</tr>
</tbody>
</table>
consists of ~65 kPa He, ~1 kPa H₂, ~0.1 Pa Hg, and various, but well known amounts of substrate in the order of a few Pa. The mercury light creates thermal H atoms which react with the substrate under pseudo first order conditions. Systematic variation of the substrate partial pressure yields absolute values of the bimolecular rate constant for the reaction of H atoms with the substrate.

The advantage of this experimental setup lies in the way the H atoms are produced. Up to the present time, most investigations employing time resolved resonance techniques for the study of H atom reactions involved H₂O photolysis as an atom source. There the H atoms are generated with a varying amount of undesirable translational energy, depending on the wavelength of the photolysing radiation. In addition, the creation of one OH radical for each H atom invariably complicates the kinetics. Neither of these disadvantages is present with the chemical quenching of Hg(^1P₁) by H₂. The translational excess energy of the H atoms is very low and no radical species are created besides H.

A few other points make this method convenient. Firstly, the light pulses are obtained with high reproducibility (~5% pulse to pulse variation). Secondly, absolute intensity calibrations are easily performed by propane actinometry [18], and finally, systematic variations of the light intensity are simply achieved by either varying an iris or by attenuating the radiation by means of neutral density filters.

A disadvantage is the limited shutter closing time which sets an upper limit of ~250 s⁻¹ to the range of pseudo first order rate constants.

A few improvements have been made over the apparatus of [17]: In order to avoid product build-up in the reaction cell, a slow flow system has been incorporated. The premixed gases are supplied from a 20 l glass vessel and the pressure in the cuvette is kept constant using an automatic pressure controller (MKS 250A). The closure time of the shutter in front of the Hg lamp was reduced to ~1 ms by inserting a circular disc (~1 cm) to cut off the central light rays. In the resonance fluorescence experiments a combination of mechanical shutter and electrical lamp shut off has been used. The light pulses are generated by opening the shutter with a moderately fast rise time of 2-3 ms. After a pre-selected time interval, typically of 10-20 ms duration, the lamp is electrically shut off with a fall time of less than 50 μs. Immediately after the lamp shut down the shutter is closed too and the mercury arc is turned on again. The pulse repetition rate used in these experiments is in the range of 1 to 0.1 s⁻¹.

Photon pulse counting was employed exclusively for signal detection. The data accumulated in the Nicolet signal averager were subsequently transferred to a mainframe computer for further processing.

All errors quoted are single standard deviation and are precision only.

Results

The system H/SiH₄ and D/SiH₄

The rate constants for the abstraction of hydrogen from silane by hydrogen atoms (4)

H + SiH₄ → H₂ + SiH₃

as well as by deuterium atoms (4’) have been determined in a flow experiment. For k (4) a value of (4.4 ± 0.7) · 10⁻¹³ cm³ s⁻¹ at room temperature was obtained under the following experimental conditions: the argon volume flow F varied in 6 experiments from (1.4—1.5) · 10⁴ cm³ s⁻¹, the pressure P from 220—240 Pa, the initial atom concentration |H₀| ranged from (2—3.6) · 10⁻⁷ cm⁻³ and the atom-substrate ratio |H₀|/SiH₄₀ from 160 to 270. k (4’) equals (3.9 ± 0.7) · 10⁻¹³ cm³ s⁻¹ and is an average value of 7 determinations. The following experimental conditions were used: 0.85 · 10⁻⁴ ≤ F ≤ 1.4·10⁻³, 225 ≤ P ≤ 640, 2.6·10⁻¹⁴ ≤ |D₀| ≤ 4.3·10⁻¹⁴, 5 < |D₀|/SiH₄₀ < 230. In all cases the disappearance of SiH₄ was measured at m/e 31. The H and D atom concentrations have been determined mass spectrometrically.

The products observed in the system D/SiH₄ can be inferred from Fig. 1 and Figure 2. At reactant ratios |SiH₄₀|/|D₀| ≈ 2 only Si₂H₆ and Si₂H₃D are observed in the ratio of ~2 and no deuterated silanes are formed. For smaller |SiH₄₀|/|D₀| ratios higher deuterated disilanes are formed and SiD₄ is observed in increasing amounts. Interestingly, a quantitative evaluation of the mass spectra of the silane part (Fig. 2) does not show the appearance of any partially deuterated silanes. Finally, it should be mentioned that m/e 56 at medium reactant ratios cannot be explained solely as a fragment peak of the differently deuterated disilanes.
The system $H/CH_3SiH_3$ and $D/CH_3SiH_3$

For reaction (3)

$$H + CH_3SiH_3 \rightarrow H_2 + CH_3SiH_2 \quad (3)$$

and its isotopic analogue (3'), hydrogen abstraction by D atoms, the rate constants obtained by the flow technique are $k(3) = (3.9 \pm 0.7) \cdot 10^{-13} \text{cm}^3\text{s}^{-1}$ and $k(3') = (3.5 \pm 0.4) \cdot 10^{-14}$. The following experimental conditions prevailed for reaction (3): 8 experiments measured either on $m/e$ 44 or $m/e$ 45, $1.38 \cdot 10^4 \leq F \leq 1.53 \cdot 10^4$, $226 \leq P \leq 246$, $2.4 \cdot 10^{14} \leq H_0 \leq 3.75 \cdot 10^{14}$, $160 \leq H_0/CH_3SiH_3 \leq 250$, room temperature; for reaction (3') 5 experiments measured on $m/e$ 45, $1.35 \cdot 10^4 \leq F \leq 1.38 \cdot 10^4$, $P = 234$, $3.4 \cdot 10^{14} \leq |D_0| \leq 3.8 \cdot 10^{14}$, $160 \leq |D_0|/CH_3SiH_3 \leq 230$, room temperature.

The rate constant for reaction (3) has also been determined in a real time experiment at pressures around 1 bar where wall effects are negligible. Most experiments have been done by a pulsed mercury resonance photolysis – Lyman x resonance absorption technique. For determination of the room temperature rate constant the following experimental conditions applied: $|He| = 1.5 \cdot 10^{19} \text{cm}^{-3}$, $|H_2| = 1.7 \cdot 10^{17} \text{cm}^{-3}$, $|H_0|$ varied from $5 \cdot 10^{10} - 1 \cdot 10^{12} \text{cm}^{-3}$.

Because of the anticipated large difference in the rate constants for (3) and (5)

$$H + CH_3SiH_2 \rightarrow CH_2SiH_3(v) \quad (5)$$

a study of the intensity dependence of the apparent rate constant was regarded advisable. Such a dependence was indeed observed but in the resonance absorption experiments the limiting low intensity rate constant has not been reached. We have therefore extrapolated the pseudo-first-order rate constant by assuming a linear dependence on the square root of the mercury light intensity. This procedure was sug-

Fig. 1. Comparison of the mass spectra of $Si_2H_6$ and $Si_2D_6$ with product spectra of the silane system for different $[SiH_4]/[D]$ ratios.

Fig. 2. Profiles of masses $m/e 28 - m/e 34$ for different $[SiH_4]/[D]$ ratios.
gested by a computer simulation of a reaction system containing the three steps (3), (5) and (6)

\[
2\text{CH}_3\text{SiH}_2 \rightarrow \text{CH}_3\text{H}_2\text{SiSiH}_2\text{CH}_3
\]

(6)
to give a lower bound to the true rate constant. All pseudo first order rate constants graphed in Fig. 3 by open circles were obtained in this way. In the case of the resonance fluorescence experiments, where a better signal to noise ratio has been achieved, we believe that the true rate constant for (3) has been reached (Figure 4). The values obtained by this method are filled in Fig. 3 by black circles. From Fig. 3 one obtains for the bimolecular rate constant for reaction (3)

\[k(3) = (3.8 \pm 0.2) \times 10^{-13} \text{ cm}^3\text{s}^{-1}\]

Exploratory experiments on the temperature dependence of \(k(3)\) have shown that the activation energy obtained was the same within experimental error regardless of whether the rate constants were extrapolated to zero mercury light intensity or the rate constants at a specific mercury light intensity were used. The data shown in Fig. 5 were all obtained with a mercury light intensity of \(3.4 \times 10^{-13}\) cm\(^3\)s\(^{-1}\). The activation energy obtained for reaction (3) was \(E_A(3) = 10.1 \pm 0.8\) kJ mol\(^{-1}\). Using the extrapolated room temperature rate constant an \(A\) factor of \(A(3) = (2.3 \pm 0.9) \times 10^{-11}\) cm\(^3\)s\(^{-1}\) is obtained.

Product analyses for \(\text{H} + \text{CH}_3\text{SiH}_3\) as well as \(\text{D} + \text{CH}_3\text{SiH}_3\) have been carried out with substrate in excess. The results are shown in Figure 6. Peaks with positive intensities are product peaks while the negative intensities give the minimum amounts of the reactant peaks that have disappeared. A closer inspection of the spectra immediately suggests that 1,2-dimethyldisilane, methylsilane and methane are products of reactions initiated by (3). Methylsilane has a parent peak at \(m/e 76\) which is not occupied by a fragment ion of dimethylsilane according to our reference spectrum (Table 1) as well as that of Longeway and Lampe [15]. In the system D/CH\(_3\)SiH\(_3\) the formation of dimethylsilane-d\(_1\) and methylsilane-d\(_1\) is observed as well and also CD\(_4\) besides CH\(_4\). The observation of CD\(_4\) indicates the appearance of methyl radicals which undergo repetitive atom addition followed by unimolecular decomposition of vibrationally excited methane [3]. Subsequently it was indeed possible to show the presence of methyl radicals at high flow velocities by the use of low voltage spectra. The following relative ionization cross sections have been determined \(\sigma(m/e 16 \leftarrow \text{CH}_4)\): \(\sigma(m/e 76 \leftarrow \text{CH}_3\text{Si}_2\text{H}_4)\): \(\sigma(m/e 90 \leftarrow (\text{CH}_3)_2\text{Si}_2\text{H}_4) = 1.0:0.2:0.15\) which allow us to deduce from Fig. 6 the following relative product yields \((\text{CH}_3)_2\text{Si}_2\text{H}_4 : \text{CH}_3\text{Si}_2\text{H}_5 : \text{CH}_4 = 1 : 0.2 : 0.16\). One further result can be extracted from Fig. 6b, the ratios \((\text{CH}_3)_2\text{H}_3\text{DSi}_2\) / \((\text{CH}_3)_2\text{SiH}_4 \approx 0.4\) and \(\text{CH}_3\text{Si}_2\text{H}_3\text{D} / \text{CH}_3\text{Si}_2\text{H}_5 \approx 2\).

The spectrum in Fig. 6b might suggest that methylsilane-d\(_1\) is also a prominent product mani-
fested in the appearance of a peak at m/e 46. But as can be seen from Fig. 6a, the relative “negative” intensity of m/e 45 is much too small as compared to the mass spectrum of pure methylsilane, suggesting that m/e 45 is a prominent product peak. This is supported by the reference spectra of the methylated disilanes (see Table 1). In the D/CH₃SiH₃ system this product peak will partly show up at m/e 46.

The system H/(CH₃)₂SiH₂ and D/(CH₃)₂SiH₂

The evaluation of the data in these two systems is much more difficult due to a number of factors. First of all lack of reference substances allows only a qualitative interpretation of the product spectrum, secondly partially stabilization of the chemically activated dimethylsilane, generated in analogy to reaction (5) and interference by product peaks falsify the rate constant determinations.

In Fig. 7 the product spectrum of the system D/(CH₃)₂SiH₂ is shown. The peak group around m/e 120 is due to tetramethyldisilane, partially isotopically substituted. More specifically we will assume, for reasons given later, that the product is 1,1,2,2-tetramethyldisilane. According to the known reference spectrum of this substance there appear to be no fragment ions at m/e 104 and m/e 105, splitting off a methyl group yields m/e 103 of approximately the same intensity as the parent peak. This means that m/e 104 and m/e 105 in the product spectrum must be predominantly due to trimethyl-dsilane. Here again we find isotopically substituted and unsubstituted products of approximately the same concentration. If the mass spectrometric sensitivity for the parent peaks of tri- and tetramethyldisilane is not too different, then the two substances are formed in approximately equal amounts. As in the case of methylsilane we find CH₄, CH₃D, CD₄ and also methyl radicals.

The loss spectrum of dimethylsilane shows much too small intensities for m/e 58 and m/e 59. This can be qualitatively explained by the very intensive fragment peaks at m/e 58 and m/e 59 of tri- and tetramethyldisilane which will show up partially at m/e 60 in the case of reaction with D atoms. For m/e 46 this explanation is insufficient because tri- as well as tetramethyldisilane show only very small fragment peaks at m/e 45. We therefore have to

Fig. 6a. Mass spectrum of the system H + CH₃SiH₃ obtained in the flow system. Peaks with positive intensities are product peaks while the negative intensities give the minimum amounts of the reactant peaks that have disappeared.
Fig. 6b. Mass spectrum of the system D + CH₃SiH₃.
assume that \( m/e 46 \) originates predominantly from 
\((\text{CH}_3)_2\text{SiH}_2\) formed by reaction (7)

\[
(\text{CH}_3)_2\text{SiH} + \text{D} \rightarrow (\text{CH}_3)_2\text{SiHD}.
\] (7)

If we neglect higher molecular weight product
contributions to \( m/e 46 \) and \( m/e 45 \) altogether then
we arrive at a stabilization fraction of deuterated
dimethylsilane formed via (7) of \(~40\%\).

The rate constants for the abstraction reaction by
H atoms (8)

\[
\text{H} + (\text{CH}_3)_2\text{SiH}_2 \rightarrow \text{H}_2 + (\text{CH}_3)_2\text{SiH}
\] (8)
as well as by D atoms (8') have been determined in
a flow experiment with atoms in excess. The
disappearance of dimethylsilane as a function of reaction
time was monitored at \( m/e 59 \). (Other experimental conditions for a) \( \text{H}/(\text{CH}_3)_2\text{SiH}_2 \): 5
determinations, \( F = 1.4 \cdot 10^4, P = 234, 1.9 \cdot 10^{14} \leq \text{H}_0 \leq 2.6 \cdot 10^{14}, 80 \leq \text{H}_0/(\text{CH}_3)_2\text{SiH}_2 \leq 160, \text{room}
temperature; b) \( \text{D}/(\text{CH}_3)_2\text{SiH}_2 \): 7 determinations,
\( F = 1.35 \cdot 10^4, P = 240, 3.4 \cdot 10^{14} \leq \text{D}_0 \leq 4.1 \cdot 10^{14},
130 \leq \text{D}_0/(\text{CH}_3)_2\text{SiH}_2 \leq 360, \text{room temperature}.\)

The rate constants obtained are
\( k (8) = (2.8 \pm 0.2) \cdot 10^{-13} \text{ cm}^3\text{s}^{-1}, \quad k (8') = (2.2 \pm 0.2) \cdot 10^{-13} \text{ cm}^3\text{s}^{-1}.\)

Two error sources influence these values. Dimethyl-
silane formed by (7) leads to too small a decrease of
\( m/e 59 \) so that the rate constant \( k (8) \) has to be in-
creased by the stabilization fraction while \( k (8') \) has
to be increased by only half of this value (neglecting
isotope effects). The second error source concerns
the heavy contributions of tri- and tetramethyl-
disilane to \( m/e 59 \) but here one has to take into
account that for every disilane molecule formed a
second dimethylsilane molecule is used up (see below)
so that this error will largely cancel itself.

The system \( \text{D}/(\text{CH}_3)_3\text{SiH} \)

The rate constant of the reaction

\[
\text{D} + (\text{CH}_3)_3\text{SiH} \rightarrow \text{HD} + (\text{CH}_3)_3\text{Si}
\] (9')

has been determined in the usual way to \( k (9') =
(1.4 \pm 0.2) \cdot 10^{-13} \text{ cm}^3\text{s}^{-1}. \)

Experimental conditions: 7 determinations, substrate concentration measured at \( m/e 59,
1.07 \cdot 10^4 \leq F \leq 1.5 \cdot 10^2, 192 \leq P \leq 351, 3.7 \cdot 10^{14}
< \text{D}_0 \leq 6.6 \cdot 10^{14}, 15 \leq \text{D}_0/(\text{CH}_3)_3\text{SiH}_0 \leq 180, \text{room}
temperature.

The product spectrum is shown in Figure 8. With
the mass spectrum of trimethylsilane-d in mind [4]
it is immediately clear that \( (\text{CH}_3)_3\text{SiD} \) is the main
product. There are higher deuterated species formed
as well as can be seen from \( m/e 61, m/e 62 \) and
\( m/e 74, m/e 75 \). The appearance of a negative
Fig. 8. Mass spectrum of the system D + (CH$_3$)$_3$SiH.

$m/e$ 73 indicates that other reaction channels than (10)

$$D + (CH_3)_3Si \rightarrow (CH_3)_3SiD$$

contribute to the disappearance of the trimethylsilyl radicals formed in (9'), but no higher molecular weight products have been found. The product loss seems to be dependent on the atom substrate ratio. At large ratios the loss is negligible while at smaller values it increases to almost 50%. Small amounts of CD$_4$ have also been found.

Discussion

It is generally well accepted [19] that the Si–H bond dissociation energy in silane and the methylated silanes is hardly dependent on the degree of methylation. Accordingly one expects no great variation in the rate constants for hydrogen abstraction in going from silane to trimethylsilane. This expectation is borne out by our experimental results. Our rate constant for H/SiH$_4$ and D/SiH$_4$ is in very good agreement with earlier measurements from our laboratory using a flow- [9] as well as a pulse radiolysis- Ly $\alpha$ resonance absorption-experi-

ment [10], and with the recommended value by Arthur and Bell [1] in their critical review on hydrogen abstraction reactions from silanes. This finding is of importance for the main subject of the present work because it shows that wall effects to which flow experiments with silanes are especially prone have been successfully suppressed. Michael and co-workers [3] in their paper on the very same subject obtained a much smaller rate constant with atoms in excess ($k_{app} = 0.5 \cdot 10^{-13} \text{cm}^3 \text{s}^{-1}$) and a much higher rate constant ($k_{app} = 52 \cdot 10^{-13} \text{cm}^3 \text{s}^{-1}$) with substrate in excess.

The reported rate constants for hydrogen abstraction from methylsilane by H atoms cover almost a power of ten ranging from $(1.5 \pm 0.4) \cdot 10^{-13} \text{cm}^3 \text{s}^{-1}$ [20] over $(6.1 \pm 1.0) \cdot 10^{-13} \text{cm}^3 \text{s}^{-1}$ [21] to $(11.5 \pm 2) \cdot 10^{-13} \text{cm}^3 \text{s}^{-1}$ [3]. Here again the value obtained in a flow experiment is the highest one. Our two room temperature values obtained by different techniques are in agreement with each other and also with the value of Lampe et al. [21] within the combined error limits. There exists no other measurement of the Arrhenius parameters to compare our values with. Activation energy as well as A factor are very similar to the values obtained for the systems D/SiH$_4$ [9] and D/(CH$_3$)$_3$SiD [17]. The small differences in the activation energies merely reflect the minor variations in the SiH bond dissociation energies, while the expected increase of A factors with the number of Si–H bonds per molecule seems to be buried in experimental uncertainties.

Our rate constants for the systems H/(CH$_3$)$_2$SiH$_2$ and D/(CH$_3$)$_2$SiH$_2$ are only lower bounds due to difficulties inherent in these systems (see experimental part). Relative rate determinations by Lampe et al. [21] and Strausz et al. [22] yielded considerably larger values.

The reason for reporting another set of rate constants is to show that our efforts to diminish wall effects were successful and that the product measurements are not falsified by heterogeneous processes.

Michael et al. found SiD$_4$ as the only product of the decomposition of chemically activated SiH$_3$D(v) generated by the reaction sequence (4') and (11)

$$D + SiH_3 \rightarrow SiH_3D(v).$$

They explained this by a primary Si–H bond split of SiH$_3$D(v) followed by successive D atom addition and Si–H bond rupture. For the thermal de-
composition of SiH₄. Ring et al. [23] proposed the same primary step while Purnell and his group [24] favoured a silylene mechanism
\[
\text{SiH}_4 \rightarrow \text{SiH}_2 + \text{H}_2 \quad (12)
\]
which has been finally agreed on [25].

Our results at large |SiH₄/D₀| ratios are in qualitative accordance with the latter mechanism:
\[
\begin{align*}
\text{SiH}_3\text{D}(v) & \rightarrow \text{SiH}_2 + \text{HD} \quad (13) \\
& \rightarrow \text{SiHD} + \text{H}_2 \quad (14) \\
\text{SiH}_2 + \text{SiH}_4 & \rightarrow \text{Si}_2\text{H}_6 \quad (15) \\
\text{SiHD} + \text{SiH}_4 & \rightarrow \text{Si}_2\text{H}_5\text{D} \quad (16)
\end{align*}
\]

Neglecting isotope effects, a ratio of one for the two disilane products should be observed, while Si₂H₆ in twofold excess has been found experimentally. An explanation could be reaction (17)
\[
\text{SiH}_3 + \text{D} \rightarrow \text{SiH}_2 + \text{HD} \quad (17)
\]
competing with (11). At smaller |SiH₄/D₀| ratios, SiD₄ as well as higher deuterated disilanes are observed (see Figs. 1 and 2). The reaction sequence leading to these products is possibly initiated by a reaction of the D atoms with SiH₂.

There are additional reaction channels open for methylated silanes excited by about 375 kJ/mol [19]:

1. Deactivation
\[
(\text{CH}_3)_n\text{SiH}_{4-n}(v) + \text{M} \rightarrow (\text{CH}_3)_n\text{SiH}_{4-n} + \text{M} \quad (18)
\]
where in our case M is predominantly argon and (18) is certainly a multistep process.

2. Elimination of molecular hydrogen with concomitant formation of silylene
\[
(\text{CH}_3)_n\text{SiH}_{4-n}(v) \rightarrow \text{H}_2 + (\text{CH}_3)_n\text{SiH}_{2-n} \quad (19)
\]

3. Elimination of methane with concomitant formation of silylene
\[
(\text{CH}_3)_n\text{SiH}_{4-n}(v) \rightarrow \text{CH}_4 + (\text{CH}_3)_{n-1}\text{SiH}_{3-n} \quad (20)
\]

4. Elimination of molecular hydrogen with concomitant formation of silaethylene
\[
(\text{CH}_3)_n\text{SiH}_{4-n}(v) \rightarrow \text{H}_2 + (\text{CH}_3)_{n-1}\text{H}_3-n\text{Si} = \text{CH}_2 \quad (21)
\]

5. Breaking of a silicon-carbon bond
\[
(\text{CH}_3)_n\text{SiH}_{4-n}(v) \rightarrow \text{CH}_3 + (\text{CH}_3)_{n-1}\text{SiH}_{4-n} \quad (22)
\]

Reactions (19) and (20) have been observed in the thermal decomposition of methylsilane [5, 6, 7]. For hydrogen elimination (19) an activation energy of about 270 kJ/mole⁻¹ has been reported, while for reaction (20) a somewhat higher activation energy as well as a lower A factor has been estimated [7]. Both reaction channels are clearly observed in our methylsilane system; the silylenes formed in reactions (19) and (20) will yield the observed products 1,2-dimethyldisilane and methyldisilane via an insertion reaction in methylsilane, e.g.

\[
\text{CH}_3\text{SiH} + \text{CH}_3\text{SiH}_3 \rightarrow \text{CH}_3\text{SiH}_2\text{SiH}_2\text{CH}_3 \quad (23)
\]

The observation of monodeuterated products in the system D/CH₃SiH₃ is in accordance with this explanation. By analogy with the methylsilane system we associate the mass spectrum in Fig. 7 with 1,1,2,2-tetramethyldisilane and 1,1,2-trimethyldisilane. In the case of trimethylsilane these two decomposition pathways are not observable anymore due to reaction (18).

Concerning the other reaction channels our results do not allow similar definitive conclusions as for reactions (19) and (20).

We expect increasing importance of reaction (18) with increasing methylation and indeed there is no SiH₄D observed in the silane system while (CH₃)₄SiD is clearly the main product in the D/(CH₃)₄SiH system. A quantitative assertion to the occurrence of (18) in the dimethylsilane system is difficult to make and in the methylsilane system even a qualitative statement cannot be made.

Reaction (21) has not been discussed in the investigations of the thermal decompositions of methylsilane despite the fact that the exothermicity of reaction (21) is at least as large as those for reactions (19) and (20) [19]. Nothing is known about the activation energy of reaction (21). If it is taking place we would expect very fast addition of deuterium atoms to silaethylene [26] leading to a chemically activated (CH₃)ₙ₋₁H₃₋ₙSiDCH₂D(v) which incorporates two D atoms. These two D atoms should then, at least partially, show up in the reaction products. Our results are ambiguous. In the case of methylsilane we do not observe higher deuterated disilane products while in the dimethylsilane case deuterated tetramethyldisilane shows up. Deuteration at the methyl group is also observed with trimethylsilane. But other reaction paths lead-
ing to these products can be envisaged and the whole problem must be considered unsettled.

Methyl radicals are observed in the methyl- and dimethyl-silane system and one is inclined to attribute this product to reaction (22). But reaction (22) is close to thermoneutral and despite its expected large A factor it is questionable whether it can compete with the other decomposition channels. In order to gain more quantitative insight we carried out RRKM calculations.

The input data are given in Tables 2, 3, and 4. The vibrational frequencies for the molecules have been taken from Ball et al. [27] while the necessary energetic parameters were taken from Walsh [19] with the exception of the activation energies for reactions (19) and (20). In the case of methyl- and dimethylsilane the activation energy for (19) has been measured by Neudorff and Strausz [5] and for (20) a value has been suggested by Davidson and Ring [7] for the methylsilane system, all other values are estimated. The transition state models for the three processes have been chosen to achieve agreement with A factors reported in the literature for the same or similar reactions [5, 7, 28]. For reaction (22) a Gorin type transition state has been used with free tumbling motion of the two fragments. However, in the case of trimethylsilane this leads to too large an A factor and therefore the sum tumbling motion has been restricted [29]. Direct count of states has been employed for the sum of states of the activated complex of reaction (22); in all other cases the Whitten-Rabinovitch approximation has been used.

The results of these calculations (Table 2, 3, and 4) substantiate our surmise made above, that reaction (22) cannot compete with the energetically favoured channels (19) and (20). In the case of methylsilane reaction, (22) amounts to only 0.3% of the total decomposition and this value may be even further lowered by competing deactivating collisions. Taking up a suggestion by Hase et al. [30] to approximate the unknown Lennard-Jones parameters of the methylsilanes we can calculate a collision frequency of the activated molecules with the carrier gas Ar of $\omega = 2 \cdot 10^7$ s$^{-1}$. In the case of dimethylsilane the occurrence of reaction (22) can be excluded with certainty. The calculations further suggest that methylsilane cannot be stabilized under our experimental conditions, that trimethylsilane is completely and dimethylsilane is partially stabilized. In this connection one has to keep in mind that Ar is not a strong collider for the very exothermic

<table>
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<tr>
<th>Model</th>
<th>CH$_3$SiH$_3$</th>
<th>(CH$_3$ ... SiH$_3$)*</th>
<th>(CH$_3$HSi ... H$_2$)*</th>
<th>(H$_2$Si ... CH$_4$)*</th>
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| $E_0^l$ [kJ mol$^{-1}$] | 360 | 260 | 269 |
| $E_0^{2}$ [kJ mol$^{-1}$] | 393 | 376 | 376 |
| $\Delta A$ [s$^{-1}$] | 17.0$^d$ | 15.0$^e$ | 14.6$^f$ |
| $k$ ($E^*$) [s$^{-1}$] | 2.2$\cdot 10^7$ | 6.6$\cdot 10^{9}$ | 1.0$\cdot 10^9$ |

$^a$ tumbling motion; $^b$ $\sigma = \sigma_\text{ext} \cdot \sigma_\text{int}$; $^c$ factor 2 comes from the tumbling motion of planar CH$_3$; $^d$ $T = 950$ K; $^e$ $T = 660$ K; $^f$ $T = 900$ K.
Table 3.

<table>
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<th>(CH$_3$...Si(CH$_3$)$_2$)$^*$</th>
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<th>(CH$_3$)HSi...CH$_4$)$^*$</th>
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</table>

Moments of inertia [10$^{-40}$ g cm$^2$]

| $I_x$          | 169.5               | 754                           |                               |                          |
| $I_y$          | 51.2                | 71                            |                               |                          |
| $I_z$          | 138.7               | 711                           |                               |                          |
| $I_{rot(CH_3)}$| 4.9                 | 4.9                           |                               |                          |
| $I_{(CH_3)}$   | 2.95                |                               |                               |                          |
| $I_{(SiH_2)CH_3}$ | 30$^*$            |                               |                               |                          |

Symmetry number $\sigma$

| 18             | 18                 | 18                            | 3/2 $^b$                      |

$E_0^*$ [kJ mol$^{-1}$]

| 356            | 280                | 395                           | 378                          |

$E_0^*$ [kJ mol$^{-1}$]

| 17.4 $^c$      | 14.6 $^d$          | 14.5 $^e$                     | 1.4 $\cdot 10^6$            |

$\lg A$ [s$^{-1}$] $^a$ mean value; $^b$ factor 1/2 due to optical activity of the activated complex; $^c$ $T = 950$ K; $^d$ $T = 660$ K; $^e$ $T = 900$ K.

Table 4.

<table>
<thead>
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<th>Model</th>
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<th>(CH$_3$...SiH(CH$_3$)$_2$)$^*$</th>
<th>((CH$_3$)$_2$Si...H$_2$)$^*$</th>
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<td>$r$ (Si–C) [Å]</td>
<td>1.87</td>
<td>5.8</td>
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</tr>
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</table>

Moments of inertia [10$^{-40}$ g cm$^2$]

| $I_x$          | 153                | 802                           |                               |                          |
| $I_y$          | 153                | 177                           |                               |                          |
| $I_z$          | 260                | 888                           |                               |                          |
| $I_{rot(CH_3)}$| 5.1                | 5.1                           |                               |                          |
| $I_{(CH_3)}$   | 2.95               |                               |                               |                          |
| $I_{(SiH_2)CH_3}$ | 80 $^a$        |                               |                               |                          |

Symmetry number $\sigma$

| 81             | 54                 | 9                             |                               |

$E_0^*$ [kJ mol$^{-1}$]

| 363            | 293                | 397                           | 387                          |

$E_0^*$ [kJ mol$^{-1}$]

| 17.45 $^b$     | 14.6 $^c$          | 6.6 $\cdot 10^2$              | 1.7 $\cdot 10^4$            |

$\lg A$ [s$^{-1}$] $^a$ mean value; $^b$ $T = 950$ K; $^c$ $T = 900$ K.
reactions (19) and (20) and $\omega$ has to be multiplied by a collisional deactivation efficiency factor.

We are still left with the question: where do the CH$_3$ radicals come from? There is of course the possibility of formation by wall reactions. A second possibility might be a reaction sequence suggested by O’Neal [31] and formulated here for the methyl-silane system:

$$\text{CH}_3\text{SiH} + \text{H} \rightarrow \text{CH}_3\text{SiH}_2(v).$$

$$\text{CH}_3\text{SiH}_2(v) \rightarrow \text{CH}_3 + \text{SiH}_2.$$  (25)

A number of assumptions must be made for this mechanism:

1. Reaction (24) must be fast enough to compete with the rapid silylene insertion reaction; under our condition of high atom concentration this might well hold true.

2. The difference in the activation energies of (24) and the back reaction of (25) must be lower than the exothermicity of (25).

3. The exoergic reactions (26), (27)

$$\text{CH}_3\text{SiH}_2(v) \rightarrow \text{CH}_3\text{Si} + \text{H}_2$$

$$\rightarrow \text{SiH} + \text{CH}_4$$

must not compete with (25). This calls for activation energies for the reversed reactions (−26) and (−27) of about 80 kJ/mole. The activation energies for (−19) and (−20) are about that order of magnitude and higher values are expected for (−26) and (−27), so condition 3 seems to be fullfilled. RRKM calculations given in Table 5 suggest that 4 kJ/mol and 20 kJ/mol of excess energy are necessary for the CH$_3$SiH$_2$ radical and the (CH$_3$)$_2$SiH radical, resp., in order to decompose via (25).

Our experiments do not allow an extraction of rate constants for the different decomposition pathways. Therefore, our RRKM calculations cannot be tested quantitatively. However, the agreement between theory and experiment with respect to the stabilization of the dimethylsilane molecule indicates that our calculations are quantitatively not too far off. Simons and coworkers [30, 8] investigated the decomposition of methylsilanes activated by CH$_2$ insertion into the Si–H bond e.g.

$$\text{CH}_2 + \text{CH}_3\text{SiH}_3 \rightarrow (\text{CH}_3)_2\text{SiH}_2(v)$$  (28)

and gave rate constants for the different product channels. Our calculated rate constants $k(19) = 6.7 \cdot 10^3$ s$^{-1}$, $k(20) = 4.0 \cdot 10^8$ s$^{-1}$ and $k(22) = 6.5 \cdot 10^9$ s$^{-1}$ are in reasonably good agreement with the experimental results if the free available energy of the dimethyl silane molecule is simply computed from the exothermicity of reaction (28). Taking into
account an excess energy of methylene as high as suggested by Simons [32] leads to values too large for the various rate constants.

Conclusions

Silane and the methylated silanes produced by reacting hydrogen atoms with the corresponding silyl radicals decompose mainly by the ejection of hydrogen or methane with the concomitant formation of silylenes. The observed formation of methyl radicals is in all probability not due to a decomposition of the activated molecule, but rather to secondary reactions. RRKM calculations show that the results obtained by thermal and chemical activation are consistent.