

Mechanistic study of the $\text{Me}_2\text{SiH}-\text{Me}_3\text{Si}$ radical system

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Di- and trimethylsilyl radicals, generated by the reaction of H atoms with di- and trimethylsilane, react to produce three main products: 1,1,2,2-tetramethyldisilane, pentamethyldisilane and hexamethyldisilane. These products are formed by both radical combination and radical disproportionation reactions. The disproportionation reactions form Me_2Si which inserts into the Si—H bonds of the reactants. From a quantitative determination of the disilane products as a function of the reactant ratio, a value for the branching ratio of cross-disproportionation of di- and trimethylsilyl radicals relative to the branching ratio for the disproportionation of dimethylsilyl radicals can be extracted. Our results provide strong evidence that the ratio of the rate constants for hydrogen abstraction from di- and trimethylsilane by H atoms is larger than absolute rate measurements suggest. Analysis also shows that the geometric mean rule for cross-radical reaction is closely obeyed. Disproportionation reactions yielding silaethenes occur to a minor extent and are responsible for the formation of six trisilanes. Secondary reactions, mainly initiated by H-atom abstraction from tetra- and pentamethyldisilane by silyl radicals, also take place. The relative rate constants estimated for these reactions are in agreement with a previous determination.

Introduction

This paper presents another chapter in our continuing investigation of the mechanistic pathways followed by silyl radicals. So far we have studied the self-reaction of SiH_3 ,¹ Me_2SiH ,² Me_3Si ,³ and Me_5Si_2 radicals, and the cross-reactions of Me_3Si and CH_3 radicals.⁵ For the fully methylated silyl radicals the most important step is combination, while disproportionation leading to silaethene plays only an inferior role: for Me_3Si radicals the branching ratio for disproportionation is only 0.063^{2,3} and a similar value was found for Me_5Si_2 radicals. For silyl radicals containing an Si—H bond a further disproportionation pathway is opened: the formation of silylene. Scavenging experiments with MeOH reveal² that, in the self-reaction of Me_2SiH radicals, two thirds of the radicals choose this path, compared with 42% for SiH_3 radicals.¹

Here, we give an account of the cross-reactions of Me_2SiH and Me_3Si radicals. End-product analysis allows us to evaluate the ratio of rate constants for hydrogen abstraction by H atoms from the reactants, Me_2SiH_2 and Me_3SiH . We are also able to comment on the validity of the geometric mean rule as it applies to the cross-reaction of these two radicals, and to give a value for the branching ratio of cross-disproportionation. Disproportionation reactions leading to silaethenes, and rapid secondary reactions occurring even at small conversions, are identified. To conclude, a computer simulation of the experimental results is described.

Experimental

Gas-handling, photolyses, actinometry and end-product analyses were performed as described in the Hg-sensitized photolyses of Me_3SiH^3 and Me_2SiH_2 .²

Static photolyses were carried out in a 180 cm³ cylindrical quartz cell with an optical path length of 10 cm. The cell was attached to a conventional vacuum line and, at the same time, reproducibly positioned in the optical light path. The light source was a low-pressure mercury lamp (Grüntzel Type 5) operating in dc mode, thermostatically controlled and purged

by a continuous flow of nitrogen. The 185 nm line was removed by a Vycor filter, and the intensity of 254 nm light transmitted through the photolysis cell was monitored by a 254 nm interference filter–photomultiplier arrangement.

The absorbed light intensity was determined by Hg-sensitized N_2O photolysis in the presence of butene, $\Phi(\text{N}_2) = 1.0$.⁶ The Hg concentration in the photolysis cell was measured by an absorption experiment and kept constant in all experiments.

Two capacitance manometers (MKS Baratron 122A 1000 mbar, 220BA 10 mbar), together with calibrated volumes attached to the vacuum line, allowed the preparation of precisely known reactant mixtures. All experiments were carried out at room temperature.

Product analyses were carried out on a HP 5890 gas chromatograph equipped with a flame ionization detector and a 50 m \times 0.32 mm \times 1.5 μm fused silica capillary column (OV1), with He as the carrier gas (200 kPa). The split was adjusted to 1 : 23. The following temperature programme was used to obtain a good separation of the product peaks: 50 °C (7 min)–50 °C min⁻¹–105 °C (0 min)–15 °C min⁻¹–220 °C (8 min). Gas chromatograms with the assigned peaks and retention times are shown in Fig. 1.

$\text{H}_2(6.0)$, Me_3SiH and Me_2SiH_2 were of commercial origin. The gas-chromatographic purity of the latter two compounds was better than 99.5%. Authentic samples of $\text{Me}_4\text{Si}_2\text{H}_2$, $\text{Me}_5\text{Si}_2\text{H}$ and Me_6Si_2 were used in the calibration of the gas chromatograph for analysis of the major products. For the minor products, response factors were taken proportional to the number of C atoms in the molecule.⁵

Results

Our main concern was the precise measurement of the disilane products as a function of reactant composition. 1,1,2,2-Tetramethyldisilane ($\text{Me}_4\text{Si}_2\text{H}_2$), pentamethyldisilane ($\text{Me}_5\text{Si}_2\text{H}$) and hexamethyldisilane (Me_6Si_2) were by far the most important products. From previous studies we know that disilanes with an Si—H bond are susceptible to H atom² and silyl radical⁴ attack. To obtain reliable results, unaffected by secondary processes, it was considered necessary to use high $\text{Me}_3\text{SiH}-\text{Me}_2\text{SiH}_2$ concentrations and high light intensities, and to extrapolate the product ratios to zero photolysis time. In Fig. 2(a)–(c) the concentrations of the three disilanes are

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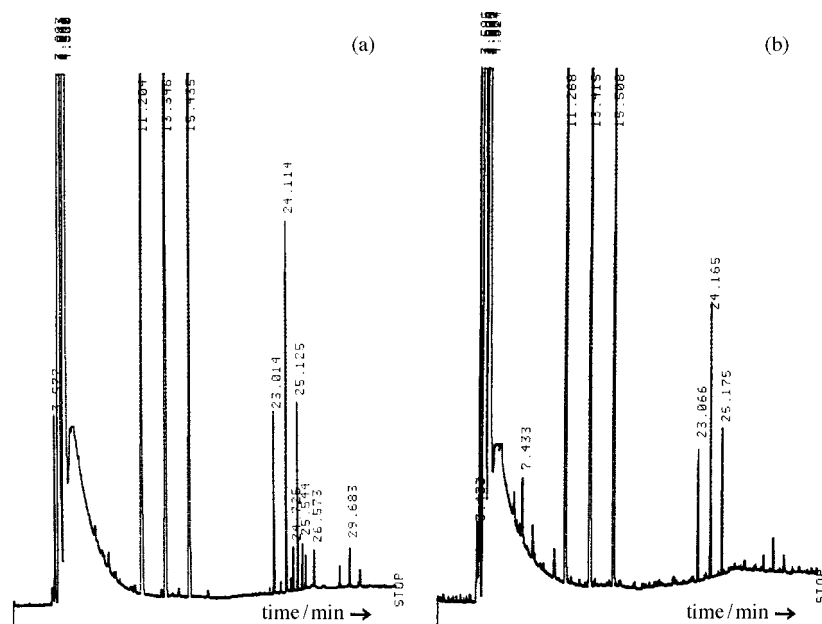


Fig. 1 Typical gas chromatograms after photolysis of a 1 : 1 mixture of Me_2SiH_2 and Me_3SiH : (a) without MeOH , (b) with MeOH . 3.4 min \equiv MeOH , 3.6 min \equiv MeSiH_3 (impurity; $<0.2\%$), 3.9 min \equiv Me_2SiH_2 , 4.4 min \equiv Me_3SiH , 7.4 min \equiv Me_3SiOMe , 11.2 min \equiv $\text{Me}_4\text{Si}_2\text{H}_2$, 13.4 min \equiv $\text{Me}_5\text{Si}_2\text{H}$, 15.5 min \equiv Me_6Si_2 , 17.2 min \equiv $\text{Me}_2\text{HSiCH}_2\text{SiMe}_3$, 23.0 min \equiv $\text{Me}_2\text{HSiSiMe}_2\text{SiMe}_2\text{H}$, 23.5 min \equiv silaethene product, 24.1 min \equiv $\text{Me}_2\text{HSiSiMe}_2\text{SiMe}_3$, 24.5 min \equiv silaethene product, 24.7 min \equiv $\text{Me}_2\text{HSiSiMe}_2\text{CH}_2\text{SiMe}_2\text{H}$, 25.1 min \equiv Me_8Si_3 , 25.5 min \equiv silaethene product, 25.8 min \equiv silaethene product, 26.6 min \equiv $\text{Me}_3\text{SiSiMe}_2\text{CH}_2\text{SiMe}_3$, 28.8 min, 29.7 min, 30.6 min \equiv tertiary products. See Discussion for assignment of silaethene products.

plotted as a function of photolysis time. Deviations from linearity due to secondary reactions are not discernible from such plots but can be seen if the product ratios, $\text{Me}_4\text{Si}_2\text{H}_2/\text{Me}_6\text{Si}_2$ and $\text{Me}_5\text{Si}_2\text{H}/\text{Me}_6\text{Si}_2$, are plotted *vs.* photolysis time [Fig. 2(d)]. Me_6Si_2 does not possess an Si—H bond and is, therefore, not exposed to secondary attack. The

scatter of the experimental points is rather large and the extrapolated intercept is loaded with a correspondingly substantial error. Using smaller Me_3SiH – Me_2SiH_2 concentrations resulted in data of greater accuracy (Fig. 3). The extrapolated intercept values and their errors (2σ) are given in Table 1 for the four reactant ratios studied.

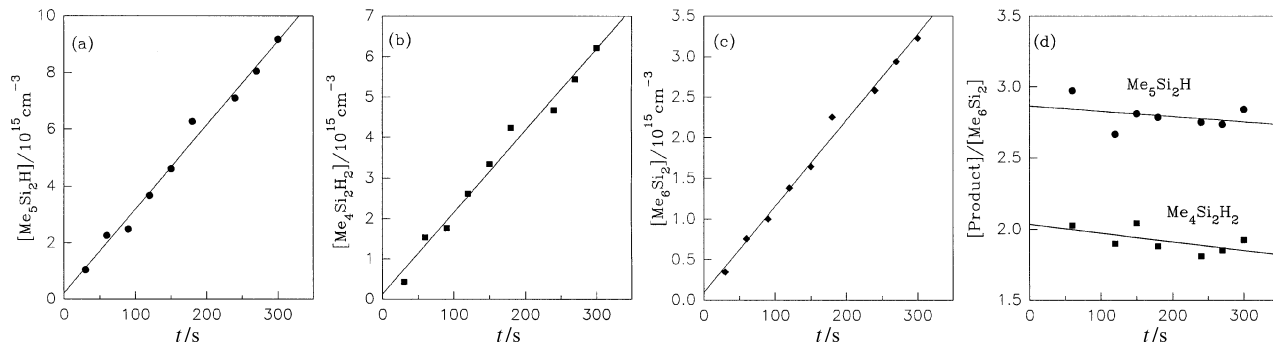


Fig. 2 (a)–(c) Concentration of main products as a function of photolysis time. $[\text{Me}_2\text{SiH}_2] = 7.72 \times 10^{17} \text{ cm}^{-3}$, $[\text{Me}_3\text{SiH}] = 7.76 \times 10^{17} \text{ cm}^{-3}$, $[\text{H}_2] = 2.21 \times 10^{19} \text{ cm}^{-3}$. (d) Relative product concentration as a function of photolysis time.

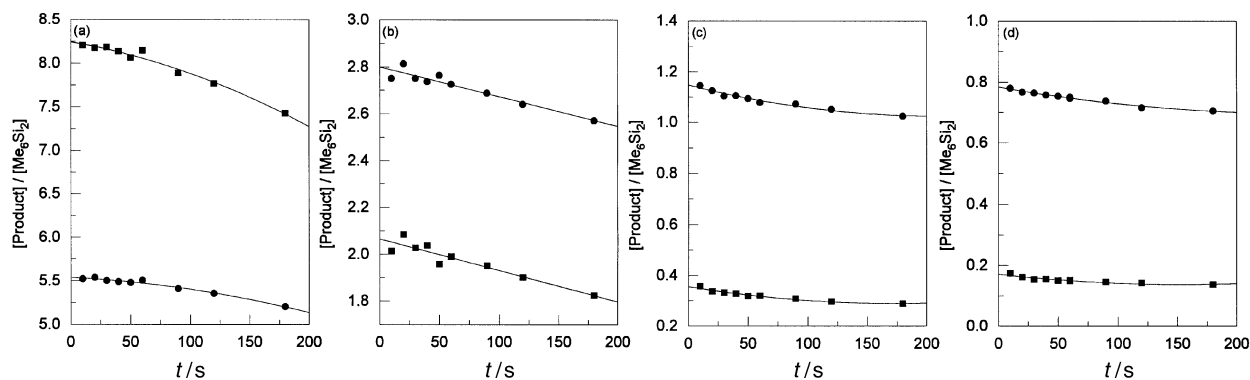


Fig. 3 Relative product concentration as a function of photolysis time for different reactant ratios. (■) $[\text{Me}_4\text{Si}_2\text{H}_2]$, (●) $[\text{Me}_5\text{Si}_2\text{H}]$. (a) $[\text{Me}_2\text{SiH}_2] = 1.63 \times 10^{17} \text{ cm}^{-3}$, $[\text{Me}_3\text{SiH}] = 8.1 \times 10^{16} \text{ cm}^{-3}$, $[\text{H}_2] = 2.2 \times 10^{19} \text{ cm}^{-3}$. (b) $[\text{Me}_2\text{SiH}_2] = 1.21 \times 10^{17} \text{ cm}^{-3}$, $[\text{Me}_3\text{SiH}] = 1.21 \times 10^{17} \text{ cm}^{-3}$, $[\text{H}_2] = 2.2 \times 10^{19} \text{ cm}^{-3}$. (c) $[\text{Me}_2\text{SiH}_2] = 7.0 \times 10^{16} \text{ cm}^{-3}$, $[\text{Me}_3\text{SiH}] = 1.76 \times 10^{17} \text{ cm}^{-3}$, $[\text{H}_2] = 2.2 \times 10^{19} \text{ cm}^{-3}$. (d) $[\text{Me}_2\text{SiH}_2] = 5.3 \times 10^{16} \text{ cm}^{-3}$, $[\text{Me}_3\text{SiH}] = 1.86 \times 10^{17} \text{ cm}^{-3}$, $[\text{H}_2] = 2.2 \times 10^{19} \text{ cm}^{-3}$.

Table 1 Relative product concentration as a function of reactant ratio

	$\text{Me}_2\text{SiH}_2/\text{Me}_3\text{SiH}$			
	2.02 : 1	1 : 1	0.40 : 1	0.29 : 1
$\text{Me}_4\text{H}_2\text{Si}_2/\text{Me}_6\text{Si}_2$		2.04 ± 0.14		
	8.236 ± 0.076	2.064 ± 0.032	0.355 ± 0.008	0.171 ± 0.008
$\text{Me}_3\text{Si}_2\text{H}/\text{Me}_6\text{Si}_2$		2.87 ± 0.18		
	5.537 ± 0.032	2.798 ± 0.026	1.148 ± 0.014	0.784 ± 0.006

Besides these three main products there exists a number of lesser products. Three of these products have already been characterized in previous studies: $\text{Me}_2\text{HSiCH}_2\text{SiMe}_3$, $\text{Me}_2\text{HSiSi}(\text{HMe})\text{CH}_2\text{SiMe}_2\text{H}$ and $\text{Me}_3\text{SiSiMe}_2\text{CH}_2\text{SiMe}_3$. The remaining four primary product peaks in the gas chromatogram form two doublets, with retention times which are typical of trisilanes. These trisilanes are characterized by the ease with which they are scavenged by MeOH [Fig. 1(b)]. It is likely that they all possess the SiCSi structural unit, and are formed by radical addition to a species containing the Si=C bond.

This analysis is supported by the following observations. The retention time difference between $\text{Me}_3\text{SiSiMe}_2\text{CH}_2\text{SiMe}_3$ and Me_8Si_3 is the same as the retention time difference for the first doublet and $\text{Me}_2\text{HSiSiMe}_2\text{SiHMe}_2$, and the same as for the second doublet and $\text{Me}_2\text{HSiSiMe}_2\text{SiMe}_3$. We, therefore, suggest that two out of the three substances $\text{Me}_2\text{HSiSi}(\text{HMe})\text{CH}_2\text{SiMe}_3$, $\text{Me}_3\text{SiSi}(\text{HMe})\text{CH}_2\text{SiHMe}_2$ and $\text{Me}_2\text{HSiSiMe}_2\text{CH}_2\text{SiHMe}_2$ correspond to the first doublet, and two out of the three substances $\text{Me}_2\text{HSiSiMe}_2\text{CH}_2\text{SiMe}_3$, $\text{Me}_3\text{SiSi}(\text{HMe})\text{CH}_2\text{SiMe}_3$ and $\text{Me}_3\text{SiSiMe}_2\text{CH}_2\text{SiHMe}_2$ to the second doublet. The intensity of these peaks was so small, (only a few per cent of the disilane products) that the integrator did not evaluate them most of the time. Quantitative results were therefore difficult to extract but, under favourable experimental conditions, it can be shown that all these products are of primary origin (Fig. 4).

Secondary products are rapidly formed in our system. After a conversion of only 0.3% a triplet of peaks is observed in the gas chromatogram. The size of the peaks grows quadratically with photolysis time (Fig. 5). These three peaks are identified as $\text{Me}_2\text{HSiSiMe}_2\text{SiHMe}_2$, $\text{Me}_2\text{HSiSiMe}_2\text{SiMe}_3$ and Me_8Si_3 . At a conversion of ca. 1.5% the generation of tertiary products is already discernible. Again a triplet of peaks appears, and the retention times are consistent with the products being tetrasilanes.

Discussion

Basic mechanism of the reaction $\text{H} + \text{Me}_2\text{SiH}_2\text{-Me}_3\text{SiH}$

Mercury-sensitized photolysis of H_2 in the presence of a $\text{Me}_2\text{SiH}_2\text{-Me}_3\text{SiH}$ mixture results almost exclusively in the

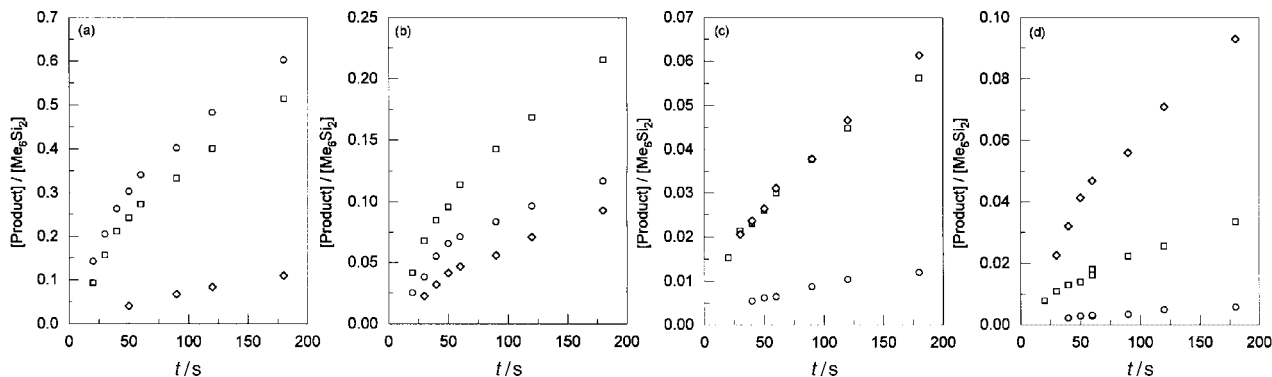


Fig. 5 Relative secondary product concentration as a function of photolysis time for different reactant ratios. (\diamond) $[\text{Me}_3\text{SiSiMe}_2\text{SiMe}_3]$, (\square) $[\text{Me}_2\text{HSiSiMe}_2\text{SiMe}_3]$, (\circ) $[\text{Me}_2\text{HSiSiMe}_2\text{SiHMe}_2]$, reactant concentration as in Fig. 3.

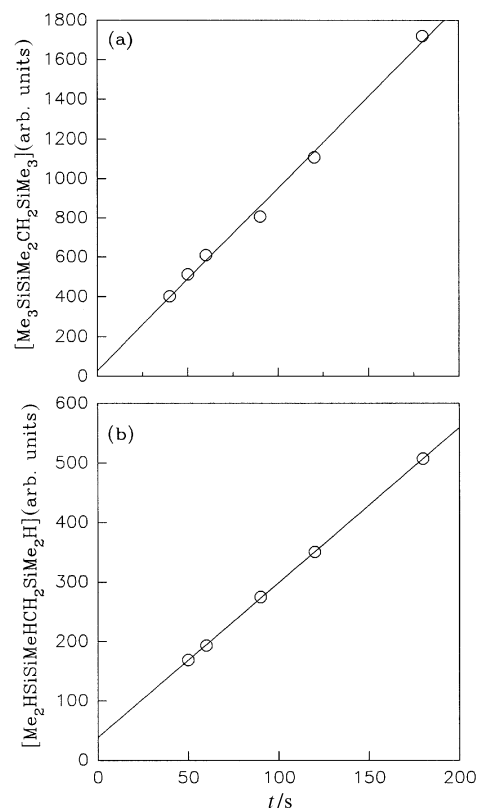
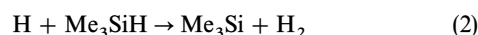
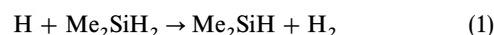


Fig. 4 Concentration of minor products as a function of photolysis time

formation of Me_2SiH and Me_3Si radicals:



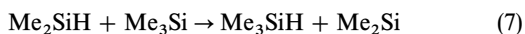
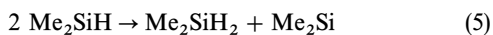
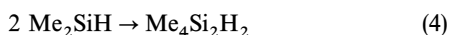
Only for Me_3SiH is it known³ that attack on the methyl group occurs, leading to the formation of $\text{Me}_2\text{HSiCH}_2$:



The branching ratio $k(3)/[k(2) + k(3)]$ is very small, ca. 0.003,³ and reaction (3) will, therefore, be neglected in further discussion. The minor product $\text{Me}_2\text{HSiCH}_2\text{SiMe}_3$ probably results from the occurrence of this reaction. No abstraction

from the C—H bond has been found for the system $\text{H} + \text{Me}_2\text{SiH}_2$.²

The Me_2SiH and Me_3Si radicals produced in our system combine and disproportionate according to the following mechanism:



The dimethylsilylene produced in reactions (5) and (7) inserts into the Si—H bond of Me_3SiH and Me_2SiH_2 .^{7,8}



Analysis of the mechanism

In the mechanism described so far, the disproportionation reactions leading to silaethene formation, and ultimately to minor trisilane products, have been omitted. Neglecting these reactions in the first instance allows us to carry out an analytical treatment of the mechanism within the framework of the familiar steady-state assumption.

To obtain somewhat more manageable expressions, we define the terms: $k(1)[\text{Me}_2\text{SiH}_2]/k(2)[\text{Me}_3\text{SiH}] = n$, $k(4) = (1 - a)k_D$, $k(5) = ak_D$, $k(6) = (1 - b)k_{DT}$, $k(7) = bk_{DT}$, $k(8) = k_T$ and $k(9)[\text{Me}_2\text{SiH}_2]/k(10)[\text{Me}_3\text{SiH}] = q$. k_{DT} is given by the expression $k_{DT} = 2f\sqrt{k_D k_T}$ where f takes into account possible deviation from the geometric-mean rule.

When the steady-state assumption is made for the intermediates Me_2HSi , Me_3Si and SiMe_2 , we arrive at the following expressions:

$$\frac{[\text{Me}_2\text{SiH}]_{ss}}{[\text{Me}_3\text{Si}]_{ss}} = \frac{f}{2} m \sqrt{\frac{k_T}{k_D}} \quad (I)$$

$$[\text{Me}_2\text{Si}]_{ss} = \frac{f\sqrt{k_D k_T} \left\{ \frac{ma}{2} + 2b \right\}}{k_{10}[\text{Me}_3\text{SiH}](q + 1)} [\text{Me}_2\text{SiH}]_{ss} [\text{Me}_3\text{Si}]_{ss} \quad (II)$$

where $m = (n - 1) + \sqrt{(n - 1)^2 + 4n/f^2}$. It is then only a small step to derive expressions for the relative product concentrations:

$$\frac{[\text{Me}_4\text{Si}_2\text{H}_2]}{[\text{Me}_6\text{Si}_2]} = (1 - a)m^2 \frac{f^2}{4} + \frac{q}{q + 1} \left\{ am^2 \frac{f^2}{4} + bm^2 f^2 \right\} \quad (III)$$

$$\frac{[\text{Me}_5\text{Si}_2\text{H}]}{[\text{Me}_6\text{Si}_2]} = (1 - b)mf^2 + \frac{1}{q + 1} \left\{ am^2 \frac{f^2}{4} + bm^2 f^2 \right\} \quad (IV)$$

In the well known case when only combination occurs, $a = 0$, $b = 0$ and $f = 1$, the expressions (III) and (IV) reduce to

$$\frac{[\text{Me}_4\text{Si}_2\text{H}_2]}{[\text{Me}_6\text{Si}_2]} = n^2 \quad (V)$$

$$\frac{[\text{Me}_5\text{Si}_2\text{H}]}{[\text{Me}_6\text{Si}_2]} = 2n \quad (VI)$$

The other extreme case arises when the radicals undergo only disproportionation reactions, corresponding to $a = 1$, $b = 1$, and $f = 1$. This leads to

$$\frac{[\text{Me}_4\text{Si}_2\text{H}_2]}{[\text{Me}_6\text{Si}_2]} = \frac{q}{q + 1} \{n^2 + 2n\} \quad (VII)$$

$$\frac{[\text{Me}_5\text{Si}_2\text{H}]}{[\text{Me}_6\text{Si}_2]} = \frac{1}{q + 1} \{n^2 + 2n\} \quad (VIII)$$

Of the five unknowns n , q , f , a and b , three have been the subject of independent studies. For n to be known, the ratio $k(1)/k(2)$ must be known. Both rate constants have been measured by means of different methods by several groups. The results are summarised in Table 2 as given in ref. 9. The results for $k(1)$ and $k(2)$ show appreciable scatter, but the ratio of the rate constants measured by the same group show much better agreement. For a 99% confidence interval we get $1.01 \leq k(1)/k(2) \leq 1.25$.

The factor q can be evaluated if we know the rate constants $k(9)$ and $k(10)$. Both rate constants have been measured by Walsh and co-workers^{7,8} and, from their values, $k(9)/k(10) = (1.22 \pm 0.18)$.

Simple collision and activated complex theories suggest that the cross-combination rate constant should not be exactly twice the geometric mean of the self-combination rate constants.¹⁴ Furthermore, Arthur and Christie¹⁵ have shown that the factor f introduced in our analysis should always be larger than one. Experimental support is scarce, however, and for radicals with similar masses and similar reaction cross-sections, deviations from $f = 1$ are small and well buried in the uncertainties of the experimental values.

The branching ratio $a = k(5)/[k(4) + k(5)]$ has been determined by a scavenging experiment with MeOH ,² and a value of $a = (0.64 \pm 0.10)$ was found.

If only combination reactions take place, corresponding to $a = 0$, $b = 0$ and $f = 1$, n may be calculated from eqn. (V), (VI) or (IX):

$$\frac{[\text{Me}_4\text{Si}_2\text{H}_2]}{[\text{Me}_6\text{Si}_2]} + \frac{[\text{Me}_5\text{Si}_2\text{H}]}{[\text{Me}_6\text{Si}_2]} = n^2 + 2n \quad (IX)$$

The agreement between experimental and calculated relative product concentrations is astonishingly good. The values of n obtained from the different expressions do not differ very much, and the values for $k(1)/k(2)$ given in Table 3 (entries 1–4) have been calculated from expression (IX) for different values of the reactant ratio, $\text{Me}_2\text{SiH}_2/\text{Me}_3\text{SiH}$. $k(1)/k(2)$ changes very little with the experimental conditions, in any case not in a systematic manner, and the mean value is given by $k(1)/k(2) = (1.41 \pm 0.03)$.

If one also allows f to vary, we have

$$\frac{[\text{Me}_4\text{Si}_2\text{H}_2]}{[\text{Me}_6\text{Si}_2]} + \frac{[\text{Me}_5\text{Si}_2\text{H}]}{[\text{Me}_6\text{Si}_2]} = f^2 m \left(1 + \frac{m}{4} \right) \quad (X)$$

$$\frac{[\text{Me}_4\text{Si}_2\text{H}_2]}{[\text{Me}_5\text{Si}_2\text{H}]} = \frac{m}{4} \quad (XI)$$

for the two unknowns n and f , and the experimental results will be reproduced exactly, independent of the true nature of the mechanism. One expects, however, that a change in the reactant ratio would lead to a change in the calculated $k(1)/k(2)$ and f values if the true and assumed mechanism were not in agreement with each other. Entries 5–8, Table 3, show that only a small increase in the $k(1)/k(2)$ values is observed, 'compensated' for by an f value smaller than one.

Table 2 Literature values of the rate constants for hydrogen abstraction from Me_2SiH_2 and Me_3SiH by H atoms

$k(1)/10^{-13} \text{ cm}^3 \text{ s}^{-1}$	$k(2)/10^{-13} \text{ cm}^3 \text{ s}^{-1}$	$k(1)/k(2)$	ref.
11 ± 3	10 ± 3	1.10 ± 0.45	10
4.1 ± 0.9	3.7 ± 1.0	1.11 ± 0.39	11
3.4 ± 0.4	3.0 ± 0.3	1.13 ± 0.17	12
2.2 ± 0.2^a	1.4 ± 0.2^a	1.57 ± 0.27^a	13
3.1 ± 0.1	2.6 ± 0.1	1.19 ± 0.06	9

^a Rate constants for hydrogen abstraction by D atoms.

Table 3 Relative rate constants for different mechanistic models as a function of reactant ratio

no.	Me ₂ SiH ₂ /Me ₃ SiH	k(1)/k(2)	a	b	f	k(9)/k(10)	Me ₄ Si ₂ H ₂ /Me ₆ Si ₂	Me ₅ Si ₂ H/Me ₆ Si ₂
		>1.01, <1.25 ^a	0.64 ^a			1.22 ± 0.18 ^a		
1	2.02	1.41	0	0	1	—	8.086	5.687
2	1.00	1.42	0	0	1	—	2.020	2.842
3	0.40	1.46	0	0	1	—	0.339	1.164
4	0.29	1.37	0	0	1	—	0.159	0.796
5	2.02	1.45	0	0	0.96	—		
6	1.00	1.42	0	0	1.00	—		
7	0.40	1.48	0	0	0.96	—		
8	0.29	1.39	0	0	0.95	—		
9	2.02	1.41	1	1	1	0.74		
10	1.00	1.42	1	1	1	0.74		
11	0.40	1.46	1	1	1	0.77		
12	0.29	1.37	1	1	1	0.75		
13	2.02	1.41	0.64	0.41	1	1.22		
14	1.00	1.42	0.64	0.40	1	1.22		
15	0.40	1.46	0.64	0.42	1	1.22		
16	0.29	1.37	0.64	0.42	1	1.22		
17	2.02	1.13	0.64	0.55	1.35	1.22		
18	1.00	1.13	0.64	0.57	1.50	1.22		
19	0.40	1.13	0.64	0.68	3.08	1.22		
20	0.29	1.13	0.64	0.67	4.71	1.22		
21	2.02	1.25	0.64	0.49	1.17	1.22		
22	1.00	1.25	0.64	0.50	1.25	1.22		
23	0.40	1.25	0.64	0.59	1.64	1.22		
24	0.29	1.25	0.64	0.55	1.49	1.22		
25	2.02	1.35	0.64	0.44	1.06	1.22		
26	1.00	1.35	0.64	0.44	1.09	1.22		
27	0.40	1.35	0.64	0.51	1.24	1.22		
28	0.29	1.35	0.64	0.45	1.06	1.22		

^a Experimental results.

The results may also be explained by pure disproportionation reactions, for which $a = 1$, $b = 1$ and $f = 1$. The sum of the two relative product concentrations is again given by eqn. (IX), while the product ratio is given by:

$$\frac{[\text{Me}_4\text{Si}_2\text{H}_2]}{[\text{Me}_5\text{Si}_2\text{H}]} = q \quad (\text{XII})$$

The results are documented in Table 3, entries 9–12. $k(9)/k(10)$ is much smaller than the experimental value but changes very little with a change in the reactant ratio.

This analysis shows that, for a mechanism involving only combination ($a = 0$, $b = 0$, $f = 1$), and for one involving only disproportionation ($a = 1$, $b = 1$, $f = 1$), we deduce values for $k(1)/k(2)$, f and $k(9)/k(10)$ which vary very little with a change in the reactant ratio. Both mechanisms cannot be right and, therefore, we have to conclude that the independence of the reactant ratio shown by the evaluated parameters is not a sufficient condition for the correctness of the assumed mechanism. In both cases we derive values for $k(1)/k(2)$ and $k(9)/k(10)$ which deviate greatly from those obtained in more direct experimental determinations, calling both mechanisms into doubt.

Taking disproportionation into account, and assuming the values for $k(1)/k(2)$, $k(9)/k(10)$ and f to be known, one would be tempted to conclude that a and b can be calculated from eqn. (III) and (IV). The two relations can be transformed to

$$qb - \frac{am}{4} = \frac{q+1}{mf^2} \left\{ \frac{[\text{Me}_4\text{Si}_2\text{H}_2]}{[\text{Me}_6\text{Si}_2]} - \frac{m^2f^2}{4} \right\} \quad (\text{IIIa})$$

$$qb - \frac{am}{4} = \frac{q+1}{mf^2} \left\{ mf^2 - \frac{[\text{Me}_5\text{Si}_2\text{H}]}{[\text{Me}_6\text{Si}_2]} \right\} \quad (\text{IVa})$$

It can be clearly seen that only one relation remains for the two unknowns a and b and, taking $f = 1$, there exists an equation for n which we have already met in eqn. (IX). With $a = 0.64$ we calculate the b values given in Table 3, entries 13–16. We expect a b value which is smaller than the a value

and this is indeed observed. The disadvantage of this model is again the large discrepancy between the extracted and the measured $k(1)/k(2)$ value.

This problem can be avoided if we allow f to be varied, assuming n to be known. From the two relations (IIIa) and (IVa) an equation for f can be extracted which is identical to eqn. (X). b can then be determined by either eqn. (III) or (IV). In eqn. (X) and (III) we first introduced the mean value $k(1)/k(2) = 1.13$. As can be seen in Table 3, entries 17–20, the value of f changes systematically with the reactant ratio, not to mention that its absolute value is much too high. A $k(1)/k(2)$ value of 1.13 is, therefore, not able to account for our experimental results. Increasing $k(1)/k(2)$ to the upper confidence limit improves the situation somewhat, but a systematic change in the values of f is still visible, and the b values show large scatter (Table 3, 21–24). Only if $k(1)/k(2)$ is increased to 1.35 is a possible trend in the f values masked by the scatter of the experimental values (Table 3, 25–28).

We must conclude, then, that within the framework of the proposed mechanism we are not able to reproduce the experimental results if we choose a $k(1)/k(2)$ value within the confidence limit, *i.e.* $1.01 \leq k(1)/k(2) \leq 1.25$. Our analysis suggests that $k(1)/k(2) = (1.40 \pm 0.05)$ with an f value very close to one. As the finishing touches were being put to this paper, we learned from Arthur and Miles¹⁶ that they have recently reinvestigated H atom attack on Me₂SiH₂ and Me₃SiH, obtaining $k(1) = (3.95 \pm 0.29) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ and $k(2) = (2.78 \pm 0.19) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$. These give $k(1)/k(2) = (1.42 \pm 0.14)$, thus confirming the value deduced in this work, and reinforcing our analysis of the mechanistic pathway open to Me₂SiH and Me₃Si radicals.

Although a mechanism involving only combination reactions explains our results satisfactorily, we know from a previous study² that the disproportionation reaction (5) does occur, *i.e.* $a \neq 0$. If this is so, our analysis demands that reaction (7) must also occur, and we obtain $b/a = (0.6 \pm 0.1)$, where the standard deviation quoted is a rough estimate, taking into account the errors in n , q , and the product concentrations.

One question remains to be answered: how is it that a model which takes only combination reactions into account, despite the known occurrence of disproportionation reactions, explains the data so well? The answer can be seen in relations (IIIb) and (IVb), which follow straightforwardly from (IIIa) and (IVa). Taking $f = 1$

$$\frac{[\text{Me}_4\text{Si}_2\text{H}_2]}{[\text{Me}_6\text{Si}_2]} = n^2 + \frac{n}{q+1} \{2qb - an\} \quad (\text{IIIb})$$

$$\frac{[\text{Me}_5\text{Si}_2\text{H}]}{[\text{Me}_6\text{Si}_2]} = 2n - \frac{n}{q+1} \{2qb - an\} \quad (\text{IVb})$$

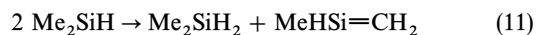
If the value of term $(2qb - an)$ on the right-hand side of eqn. (IIIb) and (IVb) is close to zero, then the same result is obtained as in eqn. (V) and (VI), where only combination reactions are considered. The second term is zero if $b/a = n/2q$ and, from the definitions given at the beginning of this section,

$$\frac{b}{a} = \frac{n}{2q} = \frac{\frac{k(1)}{k(2)}}{2 \frac{k(9)}{k(10)}} = 0.58$$

The value of b/a has to be close to 0.58 so that a mechanism involving only combination accounts for the experimental results.

Computer simulation studies: Expansion of the mechanism

Our analysis so far is incomplete as we have not taken into account the disproportionation reactions of the radicals involved in the formation of the silaethenes. The following reactions have to be considered:



The branching ratio relative to combination for reaction (14) is well known;^{2,3} for reaction (11) we know that it is very small, $k(11)/[k(4) + k(5) + k(11)] \geq 0.007$,² and nothing is known about the branching ratios of reactions (12) and (13). Silaethenes combine and add radicals rapidly, with rate con-

stants similar to those for radical combination reactions.⁵ In our case, the steady-state concentrations of radicals are much higher than those of silaethenes and, therefore, only radical addition will be considered.



The products originating from a silaethene precursor are characterized by an SiSiCSi skeleton. With $\text{R} \equiv \text{Me}_3\text{Si}$, Me_2SiH and $\text{Si}=\text{C} \equiv \text{Me}_2\text{Si}=\text{CH}_2$, $\text{MeHSi}=\text{CH}_2$ we expect eight products: two previously characterized compounds, $\text{Me}_2\text{HSiSi}(\text{MeH})\text{CH}_2\text{SiMe}_2\text{H}$ and $\text{Me}_3\text{SiSiMe}_2\text{CH}_2\text{SiMe}_3$, and two triplets of isomers with, respectively, six and seven methyl groups attached to the SiSiCSi skeleton.

The expected products are listed in Table 4. Experimentally, only two doublets were observed [Fig. 1(a)]. The assignment of these four product peaks was made solely on the basis of computer simulation of the product yields and must, therefore, be regarded with caution. The following rate constant ratios were used as input data: $k(11)/[k(4) + k(5) + k(11)] = 7 \times 10^{-3}$, $k(12)/[k(6) + k(7) + k(12) + k(13)] = 5 \times 10^{-3}$, $k(13)/[k(6) + k(7) + k(12) + k(13)] = 1.6 \times 10^{-3}$, $k(14)/[k(8) + k(14)] = 6 \times 10^{-2}$.^{2,3} The rate constant for reaction (15) was taken as equal to $k(15) = k_D = k_T$, and for reaction (16), $k(16) = k_{DT}$.

The experimental and calculated values (first entry in Table 4) of the two characterized substances, $\text{Me}_2\text{HSiSi}(\text{MeH})\text{CH}_2\text{SiMe}_2\text{H}$ and $\text{Me}_3\text{SiSiMe}_2\text{CH}_2\text{SiMe}_3$, agree well with each other; in particular the different behaviour of the yields of the two substances with respect to the reactant ratio is correctly described.

The two peaks of the first doublet are characterized by an intensity ratio of *ca.* 3 : 1, which is independent of the reactant ratio. The intensity, relative to Me_6Si_2 decreases by more than a factor of 10 as the $\text{Me}_2\text{SiH}_2/\text{Me}_3\text{SiH}$ ratio is varied from 2.02 to 0.29. The computer simulations yield a triplet with two peaks of equal intensity. Our mechanism implies that the yield of R_1SiCR_2 equals that of R_2SiCR_1 . Either $\text{Me}_2\text{HSiSi}(\text{MeH})\text{CH}_2\text{SiMe}_3$ or $\text{Me}_3\text{SiSi}(\text{MeH})\text{CH}_2\text{SiMe}_2\text{H}$ can be correlated with the low-intensity peak, while the calculated intensity of $\text{Me}_2\text{HSiSiMe}_2\text{CH}_2\text{SiMe}_2\text{H}$ agrees with the intensity of the larger peak of the doublet. The dependence on the reactant ratio is again fairly well described by our simulations.

Table 4 Experimental and calculated product concentrations relative to $[\text{Me}_6\text{Si}_2]$ for different reactant ratios

	$\text{Me}_2\text{SiH}_2/\text{Me}_3\text{SiH}$							
	2.02		1.0		0.4		0.29	
	exp	calc ^a	exp	calc ^a	exp	calc ^a	exp	calc ^a
$\text{Me}_2\text{HSiSi}(\text{HMe})\text{CH}_2\text{SiMe}_2\text{H}$	0.039	0.036	0.008	0.006	0.0004	0.0006	—	0.0002
		0.034		0.006		0.0005		0.0002
$\text{Me}_2\text{HSiSi}(\text{HMe})\text{CH}_2\text{SiMe}_3$	0.017	0.017	0.007	0.005	0.0014	0.001	0.001	0.0005
		0.018		0.006		0.0012		0.0007
$\text{Me}_3\text{SiSi}(\text{HMe})\text{CH}_2\text{SiMe}_2\text{H}$		0.017		0.005		0.001		0.0005
		0.004		0.002		0.0004		0.0002
$\text{Me}_2\text{HSiSiMe}_2\text{CH}_2\text{SiMe}_2\text{H}$	0.059	0.051	0.024	0.027	0.007	0.009	0.004	0.006
		0.034		0.018		0.006		0.004
$\text{Me}_2\text{HSiSiMe}_2\text{CH}_2\text{SiSiMe}_3$	0.029	0.018	0.024	0.019	0.017	0.016	0.013	0.014
		0.017		0.019		0.016		0.014
$\text{Me}_3\text{SiSi}(\text{HMe})\text{CH}_2\text{SiMe}_3$		0.004		0.003		0.002		0.001
		0.006		0.004		0.002		0.002
$\text{Me}_3\text{SiSiMe}_2\text{CH}_2\text{SiMe}_2\text{H}$	0.023	0.018	0.018	0.019	0.012	0.016	0.008	0.014
		0.012		0.012		0.011		0.009
$\text{Me}_3\text{SiSiMe}_2\text{CH}_2\text{SiMe}_3$	0.01	0.006	0.016	0.013	0.027	0.028	0.03	0.033
		0.006		0.013		0.028		0.033

^a See text for the method of calculation.

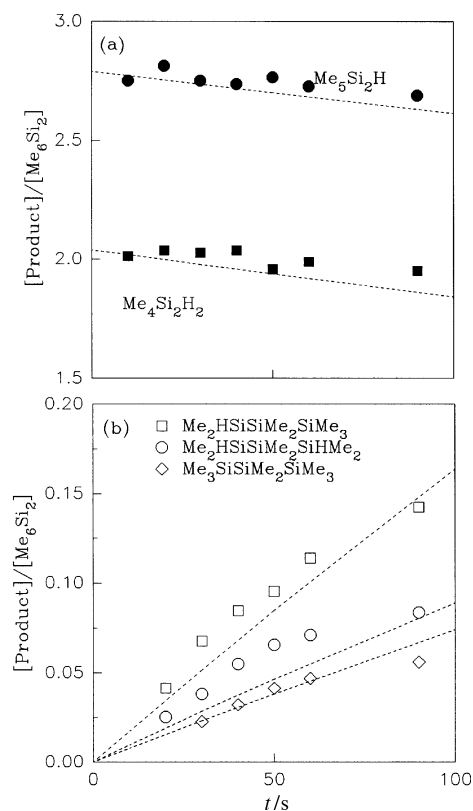


Fig. 6 Calculated relative product concentrations as a function of photolysis time (---). $[\text{Me}_2\text{SiH}_2] = 1.21 \times 10^{17} \text{ cm}^{-3}$, $[\text{Me}_3\text{SiH}] = 1.21 \times 10^{17} \text{ cm}^{-3}$, $[\text{H}_2] = 2.2 \times 10^{19} \text{ cm}^{-3}$. Experimental results are depicted as symbols.

The second doublet consists of two peaks of almost equal intensity which change little with variation in the reactant ratio. Computationally, we obtain the same relative yield for $\text{Me}_2\text{HSiSiMe}_2\text{CH}_2\text{SiMe}_3$ and $\text{Me}_3\text{SiSiCH}_2\text{SiMe}_2\text{H}$ while, for $\text{Me}_3\text{SiSi}(\text{MeH})\text{CH}_2\text{SiMe}_3$, an appreciably smaller yield is calculated. The small change in the product yields with the change of the reactant ratio is also approximately reproduced. In this case one could argue that the small intensity product $\text{Me}_3\text{SiSi}(\text{MeH})\text{CH}_2\text{SiMe}_3$ is hidden under the barely separated two high-intensity peaks and, therefore, only a doublet is observed.

Further simulations of the products associated with the first doublet show that when the mechanism is expanded, and small adjustments are made to the values of the rate constants of the reactions involved, two main products and a minor product are predicted. Just as for the second doublet, we could then argue that the small peak associated with the minor product is hidden by its larger companions.

The mechanism was expanded in the light of our previous result, that radicals add preferentially to the silicon side of the $\text{Si}=\text{C}$ double bond^{5,17} and, also, that the substituted methyl radical may undergo disproportionation as well as combination (16). For the reaction with a trimethylsilylradical we therefore have to include



while, for a dimethylsilylradical, two reactions are possible:

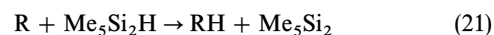
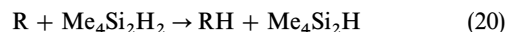


The branching ratio $k(18)/[k(16) + k(18) + k(19)]$ is, presumably, much greater than $k(17)/[k(16) + k(17)]$. In extending the mechanism we took only reaction (18) into account, with $k(18)/[k(16) + k(18)] = 0.3$, and the value for $k(11)/[k(4) + k(5) + k(11)]$ was increased to 1×10^{-2} . The calcu-

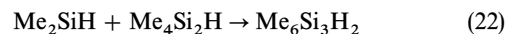
lated values for the relative product yields are given as the second entry in Table 4. No attempt was made to achieve the best possible agreement; the calculations are only intended to show that the mechanism leading to these minor products is by-and-large understood. Beyond that, the calculations confirm that the branching ratio for reaction (11) is much smaller than for reaction (14).

Secondary reactions

The observation of rapid secondary reactions in our system is not unexpected. In the Hg-sensitized photolysis of Me_2SiH_2 similar behaviour was observed. There, the early appearance of secondary products was attributed to the availability of an easily abstractable H atom in the disilane product. H atoms, as well as silyl radicals, are potential reaction partners in this process, forming disilanyl radicals:



where $\text{R} \equiv \text{H}$, Me_2SiH , Me_3Si . The disilanyl radicals will react predominantly with Me_3Si and Me_2SiH , the radicals present in the highest stationary concentration:



The reaction sequence (20)–(25) explains the formation of the secondary trisilane products (Fig. 5). We have also endeavoured to simulate the formation of secondary products by computer calculations. Rate constants for reaction (21) have been reported for $\text{R} \equiv \text{H}$ ¹⁸ as well as for $\text{R} \equiv \text{Me}_2\text{SiH}$, Me_3Si .¹⁹ The rate constants for reaction (20) were taken to be a factor of 1.5 higher. With this set of rate constants, secondary product formation was found to be too large, and the rate constants $k(20)$ and $k(21)$ for $\text{R} \equiv \text{Me}_3\text{Si}$, Me_2SiH had to be reduced by a factor of three to achieve agreement with the experimental results. A similar situation was found when we attempted to simulate the product distribution in our earlier work on the direct photolysis of $\text{Me}_3\text{Si}_2\text{H}$.²⁰ It appears that the relative rate constant $k(21)/[k(8)]^{1/2} = 8 \times 10^{-11} \text{ cm}^{3/2} \text{ s}^{-1/2}$ reported in a previous publication¹⁹ is too large, and a value of $k(21)/[k(8)]^{1/2} = (3 \pm 1) \times 10^{-11} \text{ cm}^{3/2} \text{ s}^{-1/2}$ is more appropriate. The calculated relative di- and trisilane concentrations as a function of photolysis time are plotted in Fig. 6(a) and (b), respectively. Good agreement with the experimental results is obtained, and this is also true for other reactant ratios. Further reactions of the trisilanes have not been taken into account and, therefore, the levelling off of the relative product concentrations is not reproduced.

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