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Hg-sensitized photolysis of Me_3SiH
I. A quantitative approach to the mechanism

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Abstract

The mercury-sensitized photolysis of Me_3SiH was studied as a function of the exposure time, substrate pressure and light intensity, and in the presence of the additives MeOH and H_2. Two primary processes were observed: hydrogen abstraction from the Si–H bond and, to a minor extent, from the C–H bond. The sum of the quantum yields of the two primary processes is only 0.8. The main part of the reaction mechanism, which concerns the reactions of the Me_3Si radical, can be quantitatively explained by a previous investigation of the direct photolysis of Me_4Si (Ahmed et al., *J. Photochem. Photobiol. A: Chem.*, *86* (1995) 33). With the rate constants given by Ahmed et al., the experimental values can be satisfactorily reproduced by computer simulations. In particular, it is confirmed that silaethylene reacts in an almost collision-controlled manner with radicals and the disproportionation reactions of Si-centred radicals leading to an Si=C double bond play only a minor role. The ratio of disproportionation to combination of the Me_3Si radical was determined to be 0.07 ± 0.01.

Keywords: Mercury; Photolysis; Sensitization

1. Introduction

We have recently performed a detailed study of the direct photolysis of Me_4Si [1]. In the primary processes, three intermediates (CH_3, Me_3Si and Me_2SiCH_2) are generated and their mechanistic pathways to different end-products have been determined. We also attempted to simulate the experimental results by proposing a number of hitherto unknown rate constants. It is desirable to test this mechanism and the proposed rate constants in a different but related system (related in the sense that the same set of reactions plays a dominant role in both systems). The mercury-sensitized photolysis of Me_3SiH seemed to be an ideal candidate. It is known from earlier studies that an H atom and an Me_3Si radical are generated in the primary process [2]. Conditions can be chosen such that the H atoms abstract an H atom from the Si–H bond of Me_3SiH generating a second Me_3Si radical. It is also known that Me_3Si radicals undergo both disproportionation and combination reactions [3–10]. Disproportionation leads to Me_2SiCH_2, an intermediate also obtained in the photolysis of Me_4Si [1]. The main mechanistic differences between the Hg-sensitized photolysis of Me_3SiH and the direct photolysis of Me_4Si are the absence of CH_3, a different steady state concentration of Me_3Si and Me_2SiCH_2 and the presence of a molecule with an abstractable H atom.

The Hg-sensitized photolysis of Me_3SiH has been studied by Nay et al. [2] and has been used by different groups to determine the ratio of the disproportionation to recombination of Me_3Si radicals [3–10]. Qualitatively, the reaction mechanism is known. In this work, the quantitative aspects are emphasized. Precise quantum yield determinations were performed and attempts were made to achieve a material balance as complete as possible. The observation that Hg atoms take part in the mechanism was another impetus to the reinvestigation of this system.

2. Experimental details

Static photolyses were carried out in a 180 cm^3 cylindrical quartz cell with an optical path length of 10 cm. The cell was attached to a conventional vacuum line equipped with two capacitance manometers (MKS Baratron 122A 1000 mbar, MKS Baratron 220BA 10 mbar).

The light source, a low-pressure mercury lamp (Gräntzel Type 5), thermostatically controlled and purged by a continuous N_2 flow, was operated in d.c. mode. The lamp current was kept constant by a home-built power supply. Of the impurity lines present, only the 185 nm line was removed by a Vycor filter. The 254 nm light intensity transmitted through the photolysis cell was monitored either by a UV photodiode

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(Gigahertz Optik) or a photomultiplier (9783 R, Thorn Emi). In both cases, a 254 nm bandpass filter (full width at half-maximum (FWHM), 25 nm) was mounted in front of the detector.

The light intensity absorbed by the Hg atoms was determined by three different actinometers: Hg-sensitized *cis*-butene to *trans*-butene conversion (Φ(*trans*-butene) = 0.5 [11,12]); Hg-sensitized N_2O photolysis ($\Phi(N_2) = 1.0$ [13]); Hg-sensitized propane photolysis ($\Phi(H_2) = 0.58$ [11,14–16]). The most precise results were obtained using the butene actinometer (Fig. 1). The N_2O experiments showed a somewhat larger scatter, but the results of the two actinometers agreed within 2%. In the photolysis of 387 mbar propane, the quantum yield of H_2 formation declined continuously as a function of the irradiation time (Fig. 2). The value of the H_2 quantum yield obtained at the longest photolysis time agrees with the literature value [15,16].

The light intensity absorbed I_{abs} (cm^{-3} s^{-1}) depends on the Hg concentration in the photolysis cell. To place reproducible amounts of Hg in the cell, the Hg reservoir was either thermostatically controlled or the Hg concentration was determined by an absorption experiment. All experiments described in this paper were carried out with an Hg concentration of 3.6×10^{13} cm^{-3}. At lower Hg concentrations, a depletion of Hg was observed with a concomitant increase in the transmitted light intensity, making quantum yield determinations more difficult. The highest intensity employed was $I_{abs} = 8 \times 10^{13}$ cm^{-3} s^{-1}. Lower values of I_{abs} could be used by inserting calibrated wire meshes into the light path.

All experiments were carried out at room temperature (296 ± 2 K).

All substances were of commercial origin and degassed before use. The gas chromatographic purity of Me_3SiH was better than 99.5%, the main impurity being Me_3SiOH.

End-product analyses were undertaken by gas chromatography (HP 5980 Series II) and, for H_2, the only non-condensable product at 77 K, by a simple pressure measurement. Chromatographic separations were performed on a 50 m × 0.32 mm (1.5 μm) fused silica capillary column OV1. Further details, especially the determination of response factors, are described in a previous publication [1]. Propane was used as an internal standard and all samples were analysed at least three times. The photolysis products were identified by a coupled gas chromatography-mass spectrometry (GC-MS) apparatus (HP 5971 A).

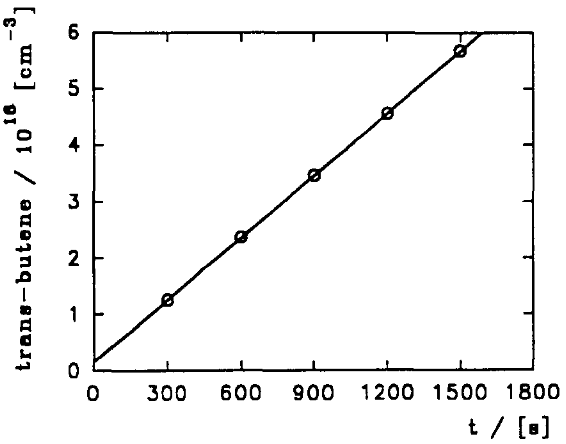

Fig. 1. Dependence of the *trans*-butene concentration on the exposure time during the Hg-sensitized photolysis of 4.15×10^{18} cm^{-3} *cis*-butene.

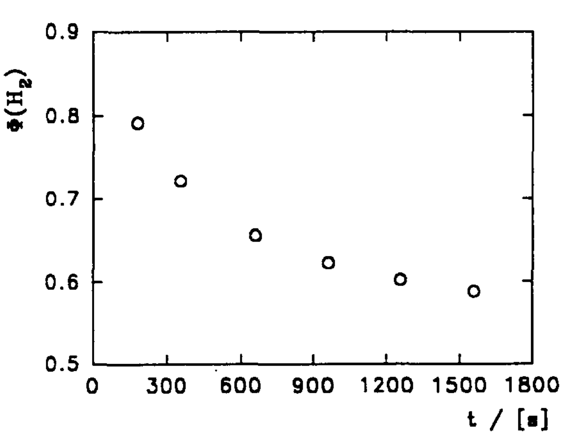

Fig. 2. Dependence of the H_2 quantum yield on the exposure time during the Hg-sensitized photolysis of 9.41×10^{18} cm^{-3} propane.

3. Results

The Me_3SiH/Hg system was studied as a function of the exposure time, substrate pressure and light intensity, and in the presence of the additives MeOH and H_2. The dependences of the photolysis products on these different parameters are shown in Figs. 3–12. In all cases, the experimental values are represented by symbols and the calculated values by lines.

The mercury-sensitized photolysis of Me_3SiH yielded five products: H_2, two disilanes $(CH_3)_3SiSi(CH_3)_3$ and $(CH_3)_3SiCH_2Si(CH_3)_2H$, a trisilane $(CH_3)_3SiSi(CH_3)_2CH_2Si(CH_3)_3$ and in very small amounts $(CH_3)_2SiCH_2Si(CH_3)_2CH_2$. The compounds are abbreviated to Me_6Si_2, SiCSiH, SiSiCSi and DSCB in this publication. In

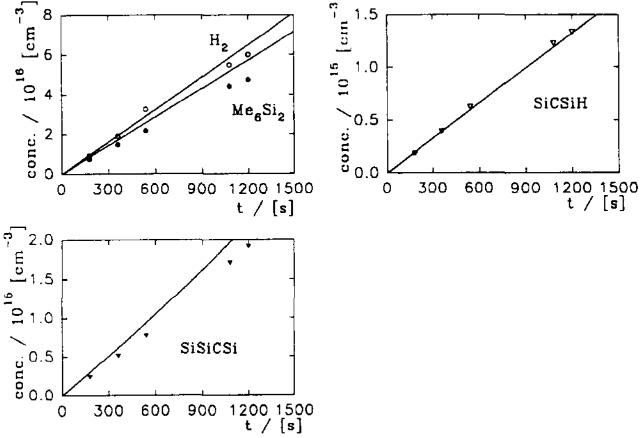

Fig. 3. Dependence of the product concentrations on the exposure time during the Hg-sensitized photolysis of 4.33×10^{18} cm^{-3} Me_3SiH at low conversion. $I_{abs} = 6.8 \times 10^{13}$ cm^{-3} s^{-1}.

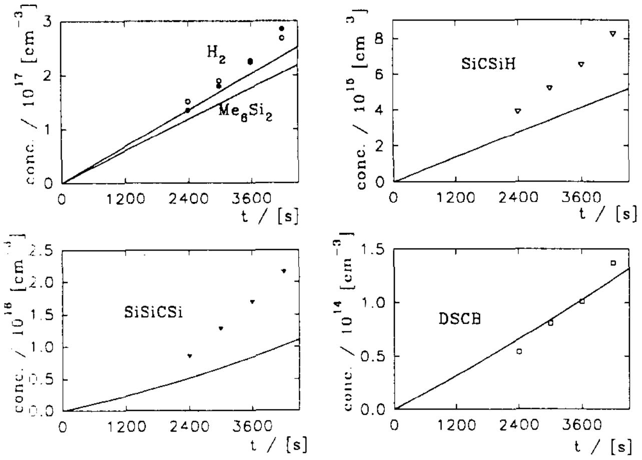

Fig. 4. Dependence of the product concentrations on the exposure time during the Hg-sensitized photolysis of 4.33×10^{18} cm^{-3} Me$_3$SiH at high conversion. $I_{abs}=7.0\times10^{13}$ cm^{-3} s^{-1}.

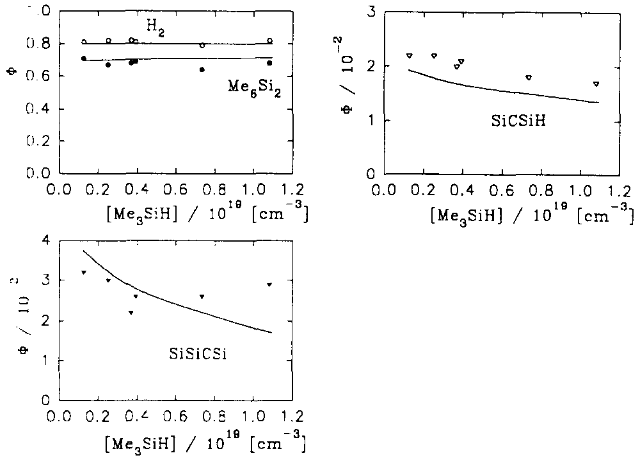

Fig. 5. Dependence of the product quantum yields on the substrate pressure during the Hg-sensitized photolysis of Me$_3$SiH. [Me$_3$SiH]/t = constant.

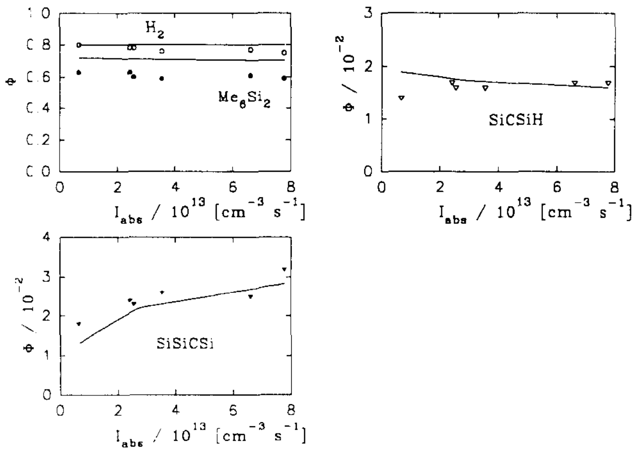

Fig. 6. Dependence of the product quantum yields on the light intensity during the Hg-sensitized photolysis of 4.43×10^{18} cm^{-3} Me$_3$SiH. $I_{abs}\times t$ = constant.

addition to these products, (CH$_3$)$_3$SiOCH$_3$ (Me$_3$SiOMe) was observed when the photolysis was performed in the presence of methanol. Solid films were deposited on the cell

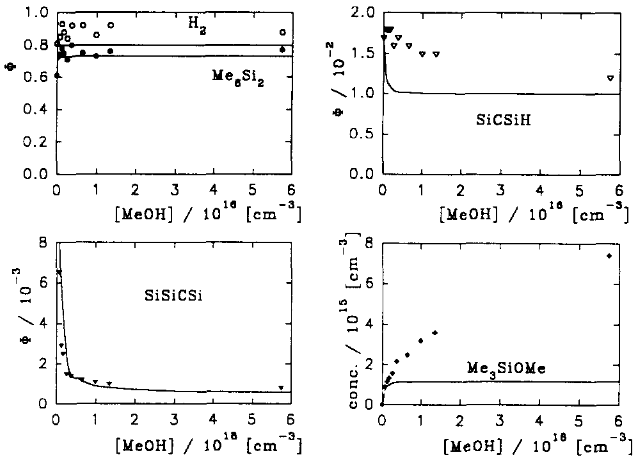

Fig. 7. Dependence of the product quantum yields on the MeOH concentration during the Hg-sensitized Me$_3$SiH photolysis; 4.46×10^{18} cm^{-3} Me$_3$SiH, $I_{abs}=6.9\times10^{13}$ cm^{-3} s^{-1}.

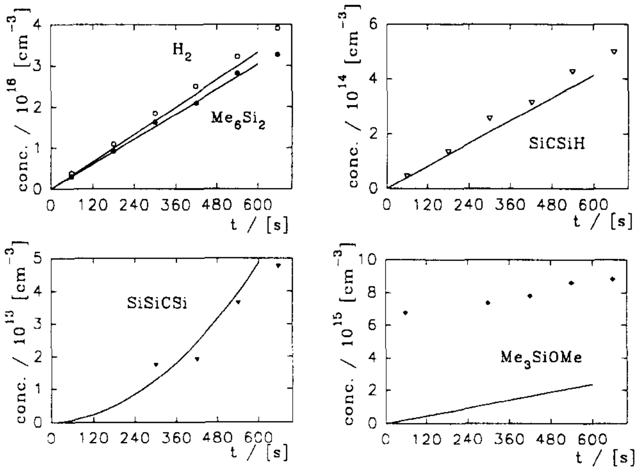

Fig. 8. Dependence of the product concentrations on the exposure time during the Hg-sensitized Me$_3$SiH photolysis in the presence of MeOH; 4.46×10^{18} cm^{-3} Me$_3$SiH, 5.80×10^{16} cm^{-3} MeOH, $I_{abs}=6.9\times10^{13}$ cm^{-3} s^{-1}.

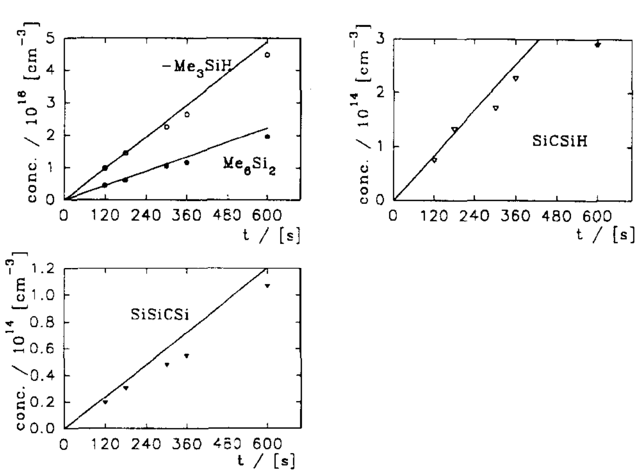

Fig. 9. Dependence of the product concentrations on the exposure time during the Hg-sensitized photolysis of 1.34×10^{19} cm^{-3} H$_2$ and 1.07×10^{17} cm^{-3} Me$_3$SiH. $I_{abs}=5.3\times10^{13}$ cm^{-3} s^{-1}.

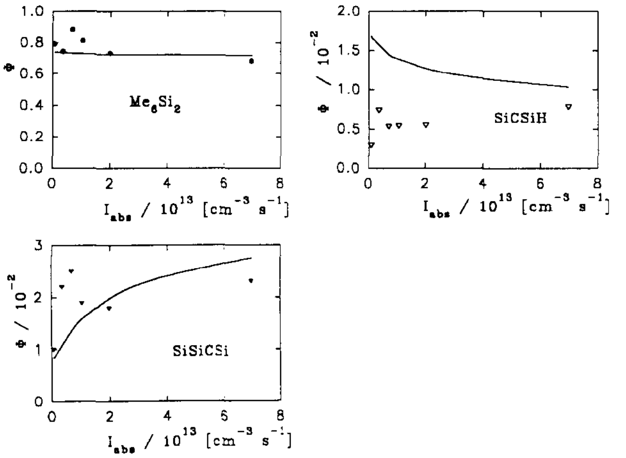

Fig. 10. Dependence of the product quantum yields on the light intensity absorbed during the Hg-sensitized Me_3SiH decomposition. $[Me_3SiH] = 2.97 \times 10^{18}$ cm^{-3}, $[H_2] = 2.00 \times 10^{19}$ cm^{-3}, $I_{abs} \times t$ = constant.

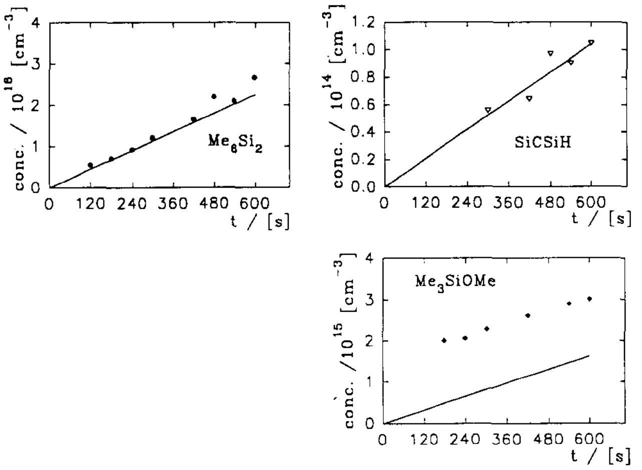

Fig. 11. Dependence of the product concentrations on the exposure time during the Hg-sensitized Me_3SiH decomposition; 1.68×10^{18} cm^{-3} Me_3SiH, 1.55×10^{19} cm^{-3} H_2, 1.70×10^{16} cm^{-3} MeOH, $I_{abs} = 5.1 \times 10^{13}$ cm^{-3} s^{-1}.

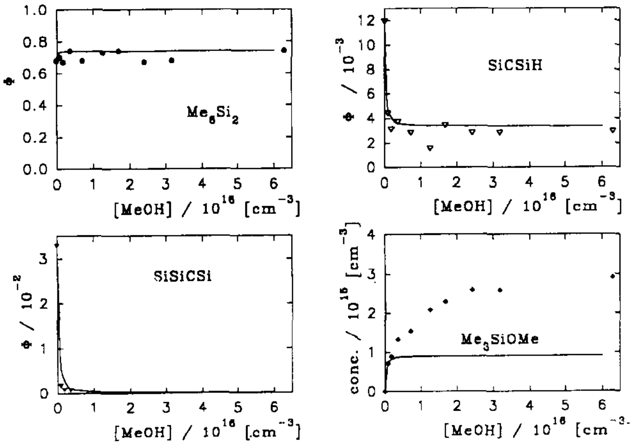

Fig. 12. Dependence of the product quantum yields on the MeOH concentration in the Hg-sensitized Me_3SiH decomposition; 1.70×10^{18} cm^{-3} Me_3SiH, 1.60×10^{19} cm^{-3} H_2, 0 $cm^{-3} \leq [MeOH] \leq 6.30 \times 10^{16}$ cm^{-3}, $t = 300$ s, $I_{abs} = 5.6 \times 10^{13}$ cm^{-3} s^{-1}.

windows during experiments with long exposure times. All of these products, with the exception of DSCB, were observed by Nay et al. [2], but only Me_6Si_2 and H_2 were considered as true primary products. In a later publication, they revised their opinion and also considered SiSiCSi as a primary product [10].

The time dependence of the photolysis products was investigated at low (0.4%–2.7%) and medium (7%–12.4%) conversions. As can be seen from Fig. 3, all four products observed at low conversion are primary photolysis products; their quantum yields are given in Table 1 denoted by $\Phi(\text{product}/t)$. In the experiments at medium conversions, DSCB was also detected (Fig. 4). Again all products show a linear yield–time dependence but, with the exception of H_2, an extrapolation to zero photolysis time results in a strong negative intercept. Therefore only an upper limit for the quantum yield of DSCB can be given (Table 1).

Changing the substrate pressure from 50 to 450 mbar has no effect on the quantum yields of H_2 and Me_6Si_2, in agreement with the results of Nay et al. [2]. The quantum yields of SiCSiH and possibly SiSiCSi undergo a slight decrease with increasing pressure, although in the case of SiSiCSi this trend is somewhat obscured by the experimental scatter (Fig. 5). In Ref. [2], a decrease in SiSiCSi relative to Me_6Si_2 was also observed.

Reducing the light intensity by more than a factor of ten affected only the quantum yield of SiSiCSi, which decreased with decreasing light intensity (Fig. 6).

The product quantum yields obtained under conditions of varying substrate pressure and light intensity can also be found in Table 1 and are denoted by $\Phi(\text{product}/Me_3SiH)$ and $\Phi(\text{product}/I_{abs})$. For computational purposes, we used the following quantum yields: $\Phi(H_2) = 0.80 \pm 0.03$, $\Phi(Me_6Si_2) = 0.64 \pm 0.03$, $\Phi(\text{SiCSiH}) = 0.023 \pm 0.003$ and $\Phi(\text{SiSiCSi}) = 0.031 \pm 0.005$. $\Phi(H_2)$ and $\Phi(Me_6Si_2)$ are averages over all experiments (the errors indicate the 99% confidence limit) and $\Phi(\text{SiCSiH})$ and $\Phi(\text{SiSiCSi})$ are extrapolated from their dependence on I_{abs} and the substrate pressure.

From these quantum yields, we conclude that the products are formed from a compound with the formula $Si_1C_{3.00}H_{10.10}$ and the quantum yield of its disappearance is given by $\Phi(-Si_1C_{3.00}H_{10.10}) = 1.42$. This value is a lower bound to the quantum yield of $\Phi(-Me_3SiH)$. Furthermore, it must hold that

$$\Phi(H_2) = \Phi(Me_6Si_2) + \Phi(\text{SiCSiH}) + 2\Phi(\text{SiSiCSi}) + 2\Phi(\text{DSCB})$$

From the quantum yields given above, we calculate that $90.8\% \pm 5.2\%$ of the silicon-containing products have been detected relative to hydrogen formation. This value can be used to calculate an upper limit to $\Phi(-Me_3SiH) \leq 1.42(1/0.908) = 1.56$.

The addition of MeOH influences the quantum yields of all the products. $\Phi(H_2)$ and $\Phi(Me_6Si_2)$ increase slightly,

Table 1
Quantum yields

	X						
	H_2	Me_6Si_2	SiCSiH	SiSiCSi	DSCB	Me_3SiOMe	$-Me_3SiH$
$\Phi(X/t)$	0.81 ± 0.02	0.61 ± 0.01	0.017 ± 0.001	0.023 ± 0.001	$<7 \times 10^{-4}$		
$\Phi(X/Me_3SiH)$	0.81 ± 0.02	0.68 ± 0.01	0.023 ± 0.002	0.031 ± 0.005			
$\Phi(X/I_{abs})$	0.77 ± 0.02	0.60 ± 0.01	0.016 ± 0.001	$\geqslant 0.030$			
$\Phi(X/MeOH)$	0.88 ± 0.05	0.75 ± 0.02	0.014 ± 0.001	0.0		0.052 ± 0.006	
$\Phi(X/H_2,t)$		0.68 ± 0.01	0.012 ± 0.001	0.033 ± 0.003			1.53 ± 0.02
$\Phi(X/H_2,MeOH)$		0.79 ± 0.02	0.003 ± 0.0005	0.0		0.045 ± 0.001	

while $\Phi(SiCSiH)$ decreases (Fig. 7). SiSiCSi disappears completely at small MeOH concentrations. At higher conversions, SiSiCSi is also formed in secondary reactions, giving the appearance of a non-scavengable portion of SiSiCSi by MeOH (Figs. 7 and 8). Taking an average of all experiments in the presence of MeOH, we obtain $\Phi(H_2/MeOH) = 0.88 \pm 0.03$, $\Phi(Me_6Si_2/MeOH) = 0.75 \pm 0.02$ and $\Phi(SiCSiH/MeOH) = 0.014 \pm 0.002$. Contrary to the results obtained in the photolysis of Me_4Si [1], MeOH does not act exclusively as a selective scavenger for Me_2SiCH_2, but also reacts with Me_3SiH in a dark reaction [10]. The only product of this dark reaction was Me_3SiOMe and no H_2 was found. In agreement with this observation, an intercept was found in the product vs. time plot of Me_3SiOMe but not of H_2 (Fig. 8). A small portion of Me_3SiOMe is also formed by photochemical means. From the slope in Fig. 8, we obtain $\Phi(Me_3SiOMe/MeOH,h\nu) = 0.052 \pm 0.006$. The intercept agrees quite well with the Me_3SiOMe yield obtained from a blind sample treated in the same way except for irradiation.

By adding excess H_2, a new primary process was established: the reaction of excited mercury atoms with hydrogen. This had no influence on the product spectrum. The same products were observed as in the Hg-sensitized photolysis. In this case, $\Phi(H_2)$ is not amenable to measurement, but $\Phi(-Me_3SiH)$ can be measured (Fig. 9). The quantum yields obtained in Fig. 9 are given in Table 1 (Φ(product/H_2,t)). A dependence of the product yields on the H_2/Me_3SiH ratio, which varied from 7 to 125, was not found. Changing the intensity absorbed (Fig. 10) seems to affect SiCSiH and SiSiCSi, but scatter in the experimental results does not allow a definite answer.

The determination of $\Phi(-Me_3SiH/H_2)$ again allows a material balance to be set up independent of the mechanism

$$\Phi(-Me_3SiH/H_2) = 2\Phi(Me_6Si_2/H_2)$$
$$+ 2\Phi(SiCSiH/H_2) + 3\Phi(SiSiCSi/H_2)$$

The product recovery is 97%.

Adding MeOH to the Hg/H_2/Me_3SiH system leads to a slight increase in the quantum yield of Me_6Si_2. Φ(SiCSiH/H_2,MeOH) is clearly reduced by almost a factor of four and SiSiCSi completely disappears (Figs. 11 and 12). The Me_3SiOMe quantum yield $\Phi(Me_3SiOMe/H_2,MeOH,h\nu)$ is 0.045 ± 0.001. The dependence of the different product quantum yields on the MeOH concentration (Fig. 12) shows the expected picture: no influence on $\Phi(Me_6Si_2/H_2,MeOH)$, complete disappearance of SiSiCSi and a large reduction in the SiCSiH quantum yield at very small MeOH concentrations. It also shows a fast increase of Me_3SiOMe (Fig. 12) due to photochemically initiated processes and a much slower increase due to dark reactions.

4. Discussion

4.1. Primary processes

On the basis of previous investigations [2], there is no doubt that excited Hg atoms abstract hydrogen from the Si–H bond in Me_3SiH

$$Me_3SiH + Hg^* \longrightarrow Hg + H + Me_3Si \qquad (1)$$

and Eq. (1) is the main process. The involvement of HgH in reaction (1) is unlikely [17], but has not been rigorously excluded.

Other primary reactions (Eqs. (2)–(5)) are energetically possible and should be investigated as possible candidates for minor processes occurring parallel to Eq. (1)

$$Me_3SiH + Hg^* \longrightarrow Hg + H + Me_2HSiCH_2 \qquad (2)$$

$$Me_3SiH + Hg^* \longrightarrow Hg + CH_3 + Me_2HSi \qquad (3)$$

$$Me_3SiH + Hg^* \longrightarrow Hg + CH_4 + Me_2Si \qquad (4)$$

$$Me_3SiH + Hg^* \longrightarrow Hg + H_2 + Me_2SiCH_2 \qquad (5)$$

Reactions (1)–(5) can be viewed as unimolecular decomposition channels of Me_3SiH excited by triplet–triplet energy transfer. In addition, reactions (1) and (2) can occur by a simple photoreaction.

Primary processes (3) and (4) can be dismissed for the following reasons. CH_3 and Me_2HSi would be scavenged by the predominant radical present in the system, Me_3Si, yielding Me_4Si and Me_5Si_2H. Me_2Si would insert into the Si–H bond of Me_3SiH yielding again Me_5Si_2H. Neither Me_4Si nor CH_4 has been observed. Channel (5) cannot be discarded for such simple reasons: both H_2 and Me_2SiCH_2 are genuine products, although produced by other processes as well (see below). However, arguments exist which show that Eq. (5) is also unimportant. The quantum yield of Me_3SiH disappearance $\Phi(-Me_3SiH)$ is very nearly twice as large as $\Phi(H_2)$ signifying the unimportance of a molecular hydrogen elimination process. The second argument concerns the product SiSiCSi. The quantum yield of this product should be the same in the experiments with and without H_2 as an additive (see mechanism below) under the condition that Eq. (5) does not play any role and $\Phi(-Me_3SiH)$ is the same in both cases. This condition is fulfilled with $\Phi(-Me_3SiH) \leqslant 1.56$ compared with $\Phi(-Me_3SiH/H_2) = 1.53$. Me_2SiCH_2 is observed predominantly as the stable product SiSiCSi. We therefore expect that $\Phi(\text{SiSiCSi}) = \Phi(\text{SiSiCSi}/H_2)$ if reaction (5) is unimportant; this is indeed the case. Finally, there exists a spectroscopic argument against a triplet–triplet energy transfer process between $Hg(^3P_1)$ and Me_3SiH and therefore against the occurrence of reactions (3)–(5). The absorption onset at approximately 170 nm is most probably a Rydberg state. Rydberg states are known for their small singlet–triplet separation of a few thousand wavenumbers [18]. The energy transfer process would therefore be highly endothermic.

What remains to be investigated is the importance of reaction (2). If this process is taking place, we expect the appearance of SiCSiH as a product. The substituted methyl radical generated in reaction (2) should be scavenged predominantly by Me_3Si yielding SiCSiH in a combination reaction (Eq. (6)) or Me_3SiH and Me_2SiCH_2 in a disproportionation reaction (Eq. (7))

$$Me_2HSiCH_2 + Me_3Si \longrightarrow Me_3SiCH_2SiMe_2H \qquad (6)$$

$$Me_2HSiCH_2 + Me_3Si \longrightarrow Me_2SiCH_2 + Me_3SiH \qquad (7)$$

Of the total SiCSiH yield ($\Phi(\text{SiCSiH}) = 0.023$) only $\Phi(\text{SiCSiH/MeOH}) = 0.014 \pm 0.002$ can be attributed to Eq. (6), and the difference between these quantum yields indicates that SiCSiH is not only formed via reaction (6) but also via Me_2SiCH_2. The quantum yield $\Phi(\text{SiCSiH/MeOH})$ is a lower limit for the quantum yield of reactions (2) and (8)

$$Me_3SiH + H \longrightarrow H_2 + Me_2HSiCH_2 \qquad (8)$$

because of the possible occurrence of Eq. (7). Reaction (8) comes into play because H atoms generated in Eq. (2) may create another dimethylsilylmethyl radical.

Reaction (7) could be prominent because of the low Si–H bond dissociation energy in the Me_2HSiCH_2 radical

$$\begin{aligned} &DH^{\ominus}(Me_2CH_2Si\text{–}H) \\ &\quad = DH^{\ominus}(Me_3Si\text{–}H) - B_\pi(Me_2Si{=}CH_2) \\ &\quad = 390\ \text{kJ mol}^{-1}\ [19] - 150\ \text{kJ mol}^{-1}\ [20] \\ &\quad = 240\ \text{kJ mol}^{-1} \end{aligned}$$

We can demonstrate, however, that Eq. (7) is not the main fate of the Me_2HSiCH_2 radical. In the experiments with excess H_2, we also observe SiCSiH, but with a much lower quantum yield, $\Phi(\text{SiCSiH}/H_2,\text{MeOH}) = 0.003 \pm 0.0005$. This is attributed to the processes (8) and (6). Let us compare the two quantum yields $\Phi(\text{SiCSiH/MeOH}) = 0.014 \pm 0.002$ and $\Phi(\text{SiCSiH}/H_2,\text{MeOH}) = 0.003 \pm 0.0005$ with the two Me_2SiCH_2 quantum yields, manifested in the product Me_3SiOMe, in the presence and absence of H_2, $\Phi(Me_3SiOMe/MeOH,h\nu) = 0.052 \pm 0.006$ and $\Phi(Me_3SiOMe/H_2,MeOH,h\nu) = 0.045 \pm 0.001$. If all the Me_2SiCH_2 generated in our system came from reaction (7), then $\Phi(Me_3SiOMe/MeOH,h\nu)$ should also change by a factor of 3/14 on adding excess H_2. This is obviously not the case. If we assume that the quantum yield difference

$$\Phi(Me_3SiOMe/MeOH,h\nu) - \Phi(Me_3SiOMe/H_2,MeOH,h\nu) = 0.007 \pm 0.006$$

is completely due to reaction (7), then k_7/k_6 can be estimated

$$\frac{k_7}{k_6} \approx \frac{\Phi(Me_3SiOMe/MeOH,h\nu) - \Phi(Me_3SiOMe/H_2,MeOH,h\nu)}{\Phi(\text{SiCSiH/MeOH}) - \Phi(\text{SiCSiH}/H_2,\text{MeOH})} = \frac{0.007 \pm 0.006}{0.011 \pm 0.002} = 0.64 \pm 0.57$$

This value is very much larger than any other disproportionation to recombination ratio known leading to an Si=C double bond, but in view of the easy abstraction of the H atom on the Si atom this is not unrealistic. We are now able to calculate $\Phi(2) + \Phi(8)$

$$\Phi(2) + \Phi(8) = \Phi(\text{SiCSiH/MeOH})\,\frac{k_6 + k_7}{k_6} = 0.023 \pm 0.009$$

$\Phi(8)$ can be obtained from our experiments with excess H_2

$$\Phi(8) = \tfrac{1}{2}\Phi(\text{SiCSiH}/H_2,\text{MeOH})\,\frac{k_6 + k_7}{k_6} = \tfrac{1}{2}0.032(1 + 0.64) = 0.003 \pm 0.002$$

The factor 1/2 takes care of the fact that, with H_2 in excess, two H atoms are generated in the primary process.

The quantum yield for process (2) is given by

$$\Phi(2) = 0.020 \pm 0.008$$

It will be shown in the next section that H atoms formed in Eq. (1) react under our conditions exclusively by H atom abstraction from Me_3SiH

$$\Phi(1) = \Phi(H_2) - \Phi(2) = 0.80 - 0.020 = 0.78 \pm 0.03$$

The fact that $\Phi(1) + \Phi(2)$ is smaller than unity will be discussed below.

4.2. The mechanism

Having established the two primary processes (Eqs. (1) and (2))

$$\mathrm{Me_3SiH + Hg^* \longrightarrow Hg + H + Me_3Si} \qquad (1)$$

$$\mathrm{Me_3SiH + Hg^* \longrightarrow Hg + H + Me_2HSiCH_2} \qquad (2)$$

followed by

$$\mathrm{Me_3SiH + H \longrightarrow H_2 + Me_3Si} \qquad (9)$$

$$\mathrm{Me_3SiH + H \longrightarrow H_2 + Me_2HSiCH_2} \qquad (8)$$

we transfer our knowledge of the mechanistic pathways of the $\mathrm{Me_3Si}$ radical in the photolysis of $\mathrm{Me_4Si}$ [1] to this system, and postulate the following reactions

$$\mathrm{2Me_3Si \longrightarrow Me_6Si_2} \qquad (10)$$

$$\mathrm{Me_2HSiCH_2 + Me_3Si \longrightarrow Me_3SiCH_2SiMe_2H} \qquad (6)$$

The combination of two $\mathrm{Me_2HSiCH_2}$ radicals need not be taken into account because $\Phi(1)+\Phi(9) \gg \Phi(2)+\Phi(8)$ and therefore $[\mathrm{Me_3Si}]_{ss} \gg [\mathrm{Me_2HSiCH_2}]_{ss}$. It will be shown below that H atoms are more selective than Hg* in abstracting hydrogen from the Si–H bond. It can be easily demonstrated that the reactions of H atoms with the radicals present in our system, above all $\mathrm{Me_3Si}$, do not play any role under our conditions. The relative rates of reactions (9) and (11)

$$\mathrm{H + Me_3Si \longrightarrow Me_3SiH} \qquad (11)$$

are given by

$$\frac{R_9}{R_{11}} = \frac{k_9[\mathrm{Me_3SiH}]}{k_{11}[\mathrm{Me_3Si}]}$$

The steady state concentration of $\mathrm{Me_3Si}$ is given by

$$[\mathrm{Me_3Si}]_{ss} \leqslant \sqrt{\frac{I_{abs}}{k_{10}+k_{12}}}$$

where reaction (12) is given by

$$\mathrm{2Me_3Si \longrightarrow Me_2SiCH_2 + Me_3SiH} \qquad (12)$$

The rate constants are either known or can be reliably estimated: $k_9 = 2.6\times10^{-13}$ cm^3 s^{-1} [21], $k_{10}+k_{12} = 3\times10^{-11}$ cm^3 s^{-1} [9] and $k_{11} = 2\times10^{-10}$ cm^3 s^{-1} [22]. With $I_{abs} = 5\times10^{13}$ cm^{-3} s^{-1}, we obtain $[\mathrm{Me_3Si}]_{ss} \leqslant 1.3\times10^{12}$ cm^{-3} and, finally, $R_9/R_{11} \geqslant 10^3$.

In agreement with the findings in Ref. [1], combination reactions are sufficient to explain the main products, but disproportionation reactions (Eqs. (12) and (7)) must be introduced to account for all the products observed.

$\mathrm{Me_2SiCH_2}$ is a highly reactive intermediate and either combines to yield DSCB or adds to a radical

$$\mathrm{2Me_2SiCH_2 \longrightarrow DSCB} \qquad (13)$$

$$\mathrm{Me_3Si + Me_2SiCH_2 \longrightarrow Me_3SiSiMe_2CH_2} \qquad (14)$$

$$\mathrm{Me_3Si + Me_2SiCH_2 \longrightarrow Me_3SiCH_2SiMe_2} \qquad (15)$$

The two radicals formed in Eqs. (14) and (15) combine with $\mathrm{Me_3Si}$ to yield the yet unaccounted for product SiSiCSi

$$\mathrm{Me_3Si + Me_3SiSiMe_2CH_2 \longrightarrow Me_3SiSiMe_2CH_2SiMe_3} \qquad (16)$$

$$\mathrm{Me_3Si + Me_3SiCH_2SiMe_2 \longrightarrow Me_3SiSiMe_2CH_2SiMe_3} \qquad (17)$$

Reactions (16) and (17) will be accompanied by disproportionation reactions

$$\mathrm{Me_3Si + Me_3SiSiMe_2CH_2 \longrightarrow Me_6Si_2 + Me_2SiCH_2} \qquad (18)$$

$$\mathrm{Me_3Si + Me_3SiCH_2SiMe_2 \longrightarrow Me_3SiCH_2SiMeCH_2 + Me_3SiH} \qquad (19)$$

$$\mathrm{Me_3Si + Me_3SiCH_2SiMe_2 \longrightarrow SiCSiH + Me_2SiCH_2} \qquad (20)$$

Eq. (20) gives one possible explanation for the dependence of the SiCSiH quantum yield on MeOH. The complete disappearance of SiSiCSi in the presence of MeOH due to reaction (21) is also correctly described by the mechanism

$$\mathrm{Me_2SiCH_2 + MeOH \longrightarrow Me_3SiOMe} \qquad (21)$$

Carbon-centred radicals may also abstract hydrogen from $\mathrm{Me_3SiH}$

$$\mathrm{Me_2HSiCH_2 + Me_3SiH \longrightarrow Me_3SiH + Me_3Si} \qquad (22)$$

and

$$\mathrm{Me_3SiSiMe_2CH_2 + Me_3SiH \longrightarrow Me_6Si_2 + Me_3Si} \qquad (23)$$

These two minor reactions explain the slight decrease in Φ(SiCSiH) and Φ(SiSiCSi) with increasing $\mathrm{Me_3SiH}$ pressure (Fig. 5).

At high conversions, $\mathrm{Me_6Si_2}$ is also attacked by Hg*

$$\mathrm{Me_6Si_2 + Hg^* \longrightarrow Hg + H + Me_3SiSiMe_2CH_2} \qquad (24)$$

The radical formed in Eq. (24) will react with $\mathrm{Me_3Si}$ to yield SiSiCSi, which is observed as a secondary product in the presence of MeOH (Fig. 8).

From the mechanism, we derive the following quantum yields

$$\Phi(\mathrm{H_2}) = 1.0$$

$$\begin{aligned}\Phi(-\mathrm{Me_3SiH}) &\approx 2\Phi(\mathrm{H_2}) - \Phi(\mathrm{Me_2SiCH_2})\\ &= 2\Phi(\mathrm{H_2}) - \Phi(\mathrm{Me_3SiOMe/MeOH}, h\nu)\end{aligned}$$

In the expression for $\Phi(-\mathrm{Me_3SiH})$, we have assumed that, for every $\mathrm{Me_2SiCH_2}$ molecule, an $\mathrm{Me_3SiH}$ molecule is formed. The postulated quantum yields for $\mathrm{H_2}$ and for $\mathrm{Me_3SiH}$ reduction are appreciably larger than the experimentally observed values, $\Phi(\mathrm{H_2}) = 0.80$ and $\Phi(-\mathrm{Me_3SiH}) \leqslant 1.56$. This discrepancy will be examined after a discussion of the photolysis experiments in the presence of $\mathrm{H_2}$.

With excess $\mathrm{H_2}$, reactions (1) and (2) must be replaced by the well-known mechanism for the Hg-sensitized photolysis of $\mathrm{H_2}$ [23–25]

$$\mathrm{Hg^* + H_2 \longrightarrow HgH + H} \tag{25}$$

$$\mathrm{Hg^* + H_2 \longrightarrow 2H + Hg} \tag{26}$$

$$\mathrm{HgH + M \longrightarrow H + Hg + M} \tag{27}$$

$$\mathrm{HgH + R \longrightarrow RH + Hg} \tag{28}$$

where M is a third body and R is a radical or an H atom.

If Eq. (27) is the predominant reaction of HgH, then the two systems Hg/Me_3SiH and Hg/H_2/Me_3SiH differ from each other only by the different importance of reactions (2) and (8). If, however, Eq. (28) plays a role, the quantum yield for the loss of Me_3SiH will be reduced. This quantum yield is given by

$$\Phi(-\mathrm{Me_3SiH/H_2}) \approx 2(\Phi(25) + \Phi(26)) - \Phi(25) \times \left(1 - \frac{k_{27}[\mathrm{M}]}{k_{27}[\mathrm{M}] + k_{28}[\mathrm{R}]}\right) - \Phi(\mathrm{Me_2SiCH_2})$$

Values for $\Phi(25)$, $\Phi(26)$, k_{27} and k_{28} have been reported in the literature [23–25].

Reaction (28) does not play a role for R≡H because of the high Me_3SiH concentration ($[\mathrm{Me_3SiH}] \geqslant 1 \times 10^{17}$ $\mathrm{cm^{-3}}$) implying a small stationary H atom concentration

$$[\mathrm{H}]_{\mathrm{ss}} \leqslant \frac{2I_{\mathrm{abs}}}{(k_8 + k_9)[\mathrm{Me_3SiH}]} = 4 \times 10^9\ \mathrm{cm^{-3}}$$

and because of the small lifetime of HgH due to a high M concentration ($\mathrm{M} \equiv \mathrm{H_2} \geqslant 2.4 \times 10^{19}\ \mathrm{cm^{-3}}$). However, the reaction between Me_3Si and HgH must be considered. For $[\mathrm{Me_3Si}]_{\mathrm{ss}}$, we have already deduced a value of $[\mathrm{Me_3Si}]_{\mathrm{ss}} \leqslant 1.3 \times 10^{12}\ \mathrm{cm^{-3}}$. If we take the smaller of the two published values for $k_{27} = 1.6 \times 10^{-16}\ \mathrm{cm^3\ s^{-1}}$ [24] and use the same value for k_{28} as determined for R≡H [24], $k_{28} = 2.6 \times 10^{-10}\ \mathrm{cm^3\ s^{-1}}$, we obtain a lower limit for the quantum yield of Me_3SiH disappearance, $\Phi(-\mathrm{Me_3SiH/H_2}) \geqslant 1.93 - 0.052 = 1.88$.

A comparison with the experimental value shows quite clearly that we experience the same situation as in the direct mercury- sensitized photolysis of Me_3SiH: the experimental value for $\Phi(-\mathrm{Me_3SiH})$ is much smaller than the value expected from the mechanism. However, in the Hg/Me_3SiH system we can always postulate a reaction

$$\mathrm{Hg(^3P_1) + Me_3SiH \longrightarrow Hg(^1S_0) + Me_3SiH^v} \tag{29}$$

to explain the low quantum yield for $\Phi(-\mathrm{Me_3SiH})$, our knowledge of the Hg/H_2 system prevents such a facile explanation. In the analysis above, the quantum yield for H atom generation in the Hg/H_2 system is close to two and this is corroborated by experiment [26,27]. Obviously there is a reaction (or reactions) missing which regenerates Me_3SiH. We immediately think of reaction (11) as a probable candidate but, as shown above, this reaction is unimportant in our system. At the moment we do not know what this reaction might be. The Hg compound detected in our system is speculated to be a possible candidate. Our present knowledge of this compound will be summarized in Part II of this series.

Two points of our mechanism remain to be addressed: the DSCB quantum yield and the portion of the SiCSiH quantum yield which is scavengable by MeOH.

DSCB is only observed at high conversions. From our mechanism, we expect

$$\frac{\Phi(\mathrm{DSCB})}{\Phi(\mathrm{SiSiCSi})} \approx \frac{k_{12}k_{13}}{(k_{14} + k_{15})^2}$$

if we approximate the stationary concentration of Me_2SiCH_2 by

$$[\mathrm{Me_2SiCH_2}]_{\mathrm{ss}} \approx \frac{k_{12}}{k_{14} + k_{15}}[\mathrm{Me_3Si}]_{\mathrm{ss}}$$

If we take $k_{12} = 0.07k_{10}$ (see below) and use the rate constant values suggested in Ref. [1], we arrive at $\Phi(\mathrm{DSCB})/\Phi(\mathrm{SiSiCSi}) = 0.02$. Fig. 4 shows that, at an irradiation time of 600 s, we expect a DSCB concentration of $2 \times 10^{13}\ \mathrm{cm^{-3}}$. This is about our detection limit. At long irradiation times, we expect a DSCB yield of $2 \times 10^{14}\ \mathrm{cm^{-3}}$ instead of the $0.5 \times 10^{14}\ \mathrm{cm^{-3}}$ observed. This discrepancy may partially be caused by erroneous rate constants, but there is certainly an additional route for the loss of Me_2SiCH_2 (see below).

The second point concerns the formation of that part of SiCSiH which can be scavenged by MeOH. A possible route for its formation is given by Eq. (20). Our results in the case of Me_4Si [1] strongly argue against such an explanation, however. There, it was shown that Me_3Si radicals add preferentially at the Si side of the Si=C double bond giving rise to a carbon radical. Transferring this value to our system, we have

$$\frac{\Phi(\mathrm{Me_3SiSiMe_2CH_2})}{\Phi(\mathrm{Me_3SiCH_2SiMe_2})} = 14$$

$$\begin{aligned}\Phi(\mathrm{Me_3SiSiMe_2CH_2}) + \Phi(\mathrm{Me_3SiCH_2SiMe_2}) &= \Phi(\mathrm{SiSiCSi}) + \Phi(\mathrm{SiCSiH}) - \Phi(\mathrm{SiCSiH/MeOH}) \\ &= 0.031 + 0.009 = 0.040\end{aligned}$$

giving $\Phi(\mathrm{Me_3SiCH_2SiMe_2}) = 0.003$. Even if we make the absolutely unrealistic assumption that the $Me_3SiCH_2SiMe_2$ radical undergoes only the disproportionation reaction (Eq. (20)), we arrive at a value for $\Phi(\mathrm{SiCSiH/MeOH})$ which is too small by a factor of three.

For the same reason, another possibility, hydrogen abstraction from Me_3SiH by the vibrationally excited silyl radical formed in Eq. (15), can be abandoned. The formation of SiCSiH via Me_2SiCH_2 was not observed in the direct photolysis of Me_4Si [1], and we therefore suspect that Me_3SiH with its weaker Si–H bond is somehow responsible for its appearance. We use reaction (30) as a type of place keeper in our mechanism

$$\mathrm{Me_2SiCH_2 + Me_3SiH \longrightarrow Me_3SiCH_2SiMe_2H} \tag{30}$$

Table 2
Reaction mechanism

No.	Reaction	k ($cm^3\ s^{-1}$)
(1)	$Me_3SiH + Hg^* \rightarrow Hg + H + Me_3Si$	1.97×10^{-10}
(2)	$Me_3SiH + Hg^* \rightarrow Hg + H + Me_2HSiCH_2$	3.60×10^{-12}
(3)	$Me_3SiH + Hg^* \rightarrow Hg + CH_3 + Me_2HSi$	
(4)	$Me_3SiH + Hg^* \rightarrow Hg + CH_4 + Me_2Si$	
(5)	$Me_3SiH + Hg^* \rightarrow Hg + H_2 + Me_2SiCH_2$	
(8)	$Me_3SiH + H \rightarrow H_2 + Me_2HSiCH_2$	7.00×10^{-16}
(9)	$Me_3SiH + H \rightarrow H_2 + Me_3Si$	2.60×10^{-13}
(10)	$2Me_3Si \rightarrow Me_6Si_2$	3.00×10^{-11}
(12)	$2Me_3Si \rightarrow Me_2SiCH_2 + Me_3SiH$	2.10×10^{-12}
(6)	$Me_2HSiCH_2 + Me_3Si \rightarrow SiCSiH$	1.88×10^{-11}
(7)	$Me_2HSiCH_2 + Me_3Si \rightarrow Me_2SiCH_2 + Me_3SiH$	1.12×10^{-11}
(13)	$2Me_2SiCH_2 \rightarrow DSCB$	3.00×10^{-11}
(14)	$Me_3Si + Me_2SiCH_2 \rightarrow Me_3SiSiMe_2CH_2$	4.80×10^{-11}
(15)	$Me_3Si + Me_2SiCH_2 \rightarrow Me_3SiCH_2SiMe_2$	3.30×10^{-12}
(16)	$Me_3Si + Me_3SiSiMe_2CH_2 \rightarrow SiSiCSi$	3.00×10^{-11}
(18)	$Me_3Si + Me_3SiSiMe_2CH_2 \rightarrow Me_6Si_2 + Me_2SiCH_2$	2.10×10^{-12}
(17)	$Me_3Si + Me_3SiCH_2SiMe_2 \rightarrow SiSiCSi$	3.00×10^{-11}
(19)	$Me_3Si + Me_3SiCH_2SiMe_2 \rightarrow Me_3SiCH_2SiMeCH_2 + Me_3SiH$	
(20)	$Me_3Si + Me_3SiCH_2SiMe_2 \rightarrow SiCSiH + Me_2SiCH_2$	
(21)	$Me_2SiCH_2 + MeOH \rightarrow Me_3SiOMe$	1.00×10^{-12}
(25)	$Hg^* + H_2 \rightarrow HgH + H$	
(26)	$Hg^* + H_2 \rightarrow 2H + Hg$	2.00×10^{-10}
(27)	$HgH + M \rightarrow H + Hg + M$	
(28)	$HgH + R \rightarrow RH + Hg$	
(11)	$Me_3Si + H \rightarrow Me_3SiH$	
(29)	$Me_3SiH + Hg(^3P_1) \rightarrow Hg(^1S_0) + Me_3SiH^v$	
(31)	$Me_2SiCH_2 + Me_3SiOH \rightarrow Me_3SiOSiMe_3$	2.50×10^{-12}
(30)	$Me_2SiCH_2 + Me_3SiH \rightarrow SiCSiH$	
(30a)	$Me_2SiCH_2 \rightarrow SiCSiH$	$15\ s^{-1}$
(22)	$Me_2HSiCH_2 + Me_3SiH \rightarrow Me_3SiH + Me_3Si$	3.00×10^{-19}
(23)	$Me_3SiSiMe_2CH_2 + Me_3SiH \rightarrow Me_6Si_2 + Me_3Si$	3.00×10^{-19}
(24)	$Me_6Si_2 + Hg^* \rightarrow Hg + H + Me_3SiSiMe_2CH_2$	9.00×10^{-11}

In Table 2, the most important reactions in our mechanism are summarized. We wish to emphasize once again that this mechanism cannot explain the deviation of $\Phi(H_2)$ from unity. The involvement of Hg and an unknown Hg compound has not been included in this mechanism simply because our knowledge of these reactions is too poor. We should be aware of changes and/or additions to this mechanism due to the involvement of these compounds.

4.3. Material balance and relative rate constants

With the mechanism given in Table 2, the following relations can be set up

$$\Phi(Me_2HSiCH_2) = \Phi(SiCSiH/MeOH) + z\Phi(Me_2SiCH_2)$$

$$z = \frac{\Phi(Me_2SiCH_2)_{rxn.(7)}}{\Phi(Me_2SiCH_2)}$$

$$\Phi(Me_2SiCH_2)_{rxn.(7)} = \frac{k_7}{k_6}\Phi(SiCSiH/MeOH)$$

$$\Phi(Me_2HSiCH_2) = \Phi(SiCSiH/MeOH)\left(1 + \frac{k_7}{k_6}\right) \qquad (I)$$

$$\begin{aligned}&\Phi(Me_2SiCH_2)\\ &\quad = \Phi(Me_3SiOMe/MeOH,h\nu)\\ &\quad = (SiSiCSi) + \Phi(SiCSiH) - \Phi(SiCSiH/MeOH) \qquad (II)\end{aligned}$$

$$\begin{aligned}\Phi(Me_3Si) &= 2\Phi(Me_6Si_2) + 2(1-z)\Phi(Me_2SiCH_2)\\ &\quad + 2\Phi(SiSiCSi) + \Phi(SiCSiH/MeOH)\\ &= 2\Phi(Me_6Si_2) + 2\Phi(SiSiCSi)\\ &\quad + 2\Phi(Me_3SiOMe/MeOH,h\nu)\\ &\quad + \left(1 - 2\frac{k_7}{k_6}\right)\Phi(SiCSiH/MeOH) \qquad (III)\end{aligned}$$

$$\begin{aligned}\Phi(H_2) &= \tfrac{1}{2}\Phi(Me_3Si) + \tfrac{1}{2}\Phi(Me_2HSiCH_2)\\ &= \Phi(Me_6Si_2) + \Phi(SiSiCSi)\\ &\quad + \Phi(Me_3SiOMe/MeOH,h\nu)\\ &\quad + \Phi(SiCSiH/MeOH)\\ &= \Phi(Me_6Si_2) + \Phi(SiCSiH) + 2\Phi(SiSiCSi) \qquad (IV)\end{aligned}$$

$$\begin{aligned}\Phi(-\mathrm{Me_3SiH}) &\\ &= 2\Phi(\mathrm{H_2}) - \Phi(\mathrm{SiSiCSi})\\ &= 2\Phi(\mathrm{Me_6Si_2}) + 2\Phi(\mathrm{SiCSiH}) + 3\Phi(\mathrm{SiSiCSi})\end{aligned}$$

Relation (IV) has already been used to show that there is a loss of Si and C of 9.2% in our products and we are now able to trace these losses back to losses of Me_2SiCH_2 and Me_3Si. The loss of Me_2SiCH_2 in the Hg/Me_3SiH system can be calculated by comparing $\Phi(\mathrm{Me_3SiOMe/MeOH}, h\nu)$ with Eq. (II), and it turns out to be a rather large 23.1%. This Me_2SiCH_2 loss makes a contribution of approximately

$$\frac{k_{12}}{k_{10}} 23.1\% = 1.6\%$$

to the total loss of products. The rest (7.6%) must be attributed to Me_3Si. The reasons for these losses are manifold. Two reasons can be clearly identified. Firstly, Me_2SiCH_2 reacts with Me_3SiOH, an impurity which could not be completely removed

$$\mathrm{Me_2SiCH_2} + \mathrm{Me_3SiOH} \longrightarrow \mathrm{Me_3SiOSiMe_3} \qquad (31)$$

Reaction (31) competes with the radical addition reactions (Eqs. (14) and (15)) and leads to the observed dependence of $\Phi(\mathrm{SiSiCSi})$ and $\Phi(\mathrm{SiCSiH/H_2})$ on I_{abs}. Secondly, high boiling products such as SiSiCSi are difficult to detect quantitatively. In some of our experiments, e.g. in the time dependence of the product formation in the presence of H_2, better results were obtained, where the losses of Me_2SiCH_2 and Me_3Si were 6% and 3% respectively. The last result is important in so far as it shows that $\Phi(\mathrm{Me_3SiOMe/MeOH}, h\nu)$ is a measure of $\Phi(\mathrm{Me_2SiCH_2})$ despite its additional formation in a dark reaction.

The following relative rate constants can be calculated from our results: k_1/k_2, k_9/k_8 and k_{12}/k_{10}. k_9/k_8 can be directly obtained from our Hg/Me_3SiH/H_2 system

$$\frac{k_9}{k_8} = \frac{\Phi(\mathrm{Me_3Si/H_2})}{\Phi(\mathrm{Me_2HSiCH_2/H_2})}$$

The two quantum yields can be obtained from relations (I) and (III), and with $k_7/k_6 = 0.64 \pm 0.57$, we obtain

$$\frac{k_9}{k_8} = 308 \pm 107$$

If we compare this value with the ratio of the known rate constants $k(\mathrm{H}+\mathrm{Me_3SiH}) = (2.6 \pm 0.1) \times 10^{-13}$ cm^3 s^{-1} [21] and $k(\mathrm{H}+\mathrm{Me_4Si}) = (1.3 \pm 0.4) \times 10^{-16}$ cm^3 s^{-1} [28], a large discrepancy is noted. The reason could simply be that an additivity relationship does not hold and the comparison is invalid. We consider this to be unlikely, however, because the values of the two rate constants are far from collision controlled. On the other hand, experimental errors of this magnitude cannot be excluded either. The value of k_9/k_8 depends very much on k_7/k_6, which is only poorly known. However, even if we set $k_7/k_6 = 0$ to obtain an upper limit of k_9/k_8

$$\frac{k_9}{k_8} < 506 \pm 79$$

this is still a factor of four too small. The error could also lie in the absolute rate constants, especially the A factor of $k(\mathrm{H}+\mathrm{Me_4Si})$ which could be a factor of 2–3 too small.

For k_1/k_2, we derive the following relation

$$\begin{aligned}\frac{k_1}{k_2} &= \frac{(\Phi(\mathrm{Me_3Si})/\Phi(\mathrm{Me_2HSiCH_2}))[2(k_8/k_9)+1]-1}{2-(k_8/k_9)(\Phi(\mathrm{Me_3Si})/\Phi(\mathrm{Me_2HSiCH_2}))}\\ &\approx \frac{(\Phi(\mathrm{Me_3Si})/\Phi(\mathrm{Me_2HSiCH_2}))-1}{2-(k_8/k_9)(\Phi(\mathrm{Me_3Si})/(\mathrm{Me_2HSiCH_2}))}\end{aligned}$$

In this case, the value of k_8/k_9 does not exert a great influence on k_1/k_2 and, with the value given above, we derive

$$\frac{k_1}{k_2} = 26 \pm 11$$

This time the ratio is larger than expected from the absolute rate constants $k(\mathrm{Hg}^* + \mathrm{Me_3SiH}) = 2.50 \times 10^{-10}$ cm^3 s^{-1} [2,29] and $k(\mathrm{Hg}^* + \mathrm{Me_4Si}) = 4 \times 10^{-11}$ cm^3 s^{-1} [2,29]. The discrepancy cannot be explained by experimental error and it must be concluded that simple additivity rules fail. Our results of the Hg-sensitized decomposition of Me_2SiH_2 [30] agree with this conclusion. An increase in the corresponding k_1/k_2 ratio of about two is expected, but no H abstraction from the C–H bond was observed. Our experiments show quite clearly that an H atom is a much more selective agent than $\mathrm{Hg}(^3P_1)$.

The value of the rate constant ratio k_{12}/k_{10} has been the subject of many studies [3–10]; most of them utilized the Hg-sensitized photolysis of Me_3SiH to generate Me_3Si radicals. In the latter case, it has always been assumed that the mechanism consists solely of steps (1), (9), (10) and (12). In such a case, k_{12}/k_{10} is simply given by

$$\frac{k_{12}}{k_{10}} = \frac{\Phi(\mathrm{Me_2SiCH_2})}{\Phi(\mathrm{Me_6Si_2})}$$

$\Phi(\mathrm{Me_2SiCH_2})$ has been equated to $\Phi(\mathrm{Me_3SiOMe/MeOH}, h\nu)$ in the presence of MeOH. Widely scattered values were obtained by different groups [4–7] mainly because it was not recognized that Me_3SiOMe is also formed in a dark reaction. Only Safarik et al. [10] evaluated $\Phi(\mathrm{Me_3SiOMe/MeOH}, h\nu)$ from the time dependence of the products, and in this respect it is the only trustworthy determination of k_{12}/k_{10}.

On the basis of the mechanism given in Table 2, the value of k_{12}/k_{10} is given by the ratio of the quantum yield of Me_2SiCH_2 formed in reaction (12), $\Phi(\mathrm{Me_2SiCH_2})_{\mathrm{rxn.}(12)}$, and the quantum yield of Me_6Si_2 formed in reaction (10), $\Phi(\mathrm{Me_6Si_2})_{\mathrm{rxn.}(10)}$

$$\frac{k_{12}}{k_{10}} = \frac{\Phi(\mathrm{Me_2SiCH_2})_{\mathrm{rxn.}(12)}}{\Phi(\mathrm{Me_6Si_2})_{\mathrm{rxn.}(10)}}$$

The two quantum yields can be expressed by the following relations

$$\Phi(\mathrm{Me_2SiCH_2})_{\mathrm{rxn.(12)}} = \Phi(\mathrm{Me_3SiOMe/MeOH},h\nu) - \frac{k_7}{k_6}\,\Phi(\mathrm{SiCSiH/MeOH}) \qquad \text{(V)}$$

$$\begin{aligned}\Phi(\mathrm{Me_6Si_2})_{\mathrm{rxn.(10)}} &= \Phi(\mathrm{Me_6Si_2}) - \frac{k_{18}}{k_{16}}\,\Phi(\mathrm{SiSiCSi}) \\ &+ \frac{k_{18}}{k_{16}}\,\frac{k_{15}}{k_{14}+k_{15}}\,(\Phi(\mathrm{Me_3SiOMe/MeOH},h\nu) \\ &- \Phi(\mathrm{SiCSiH}) + \Phi(\mathrm{SiCSiH/MeOH}) \qquad \text{(VI)}\end{aligned}$$

To evaluate k_{12}/k_{10}, a number of relative rate constants are needed. The value for k_7/k_6 has already been discussed above; fortunately, the large uncertainty will be diminished by the small value of Φ(SiCSiH/MeOH) in Eq. (V). In a previous publication, a value for $k_{15}/(k_{14}+k_{15}) = 1/15$ has been derived [1]. For k_{18}/k_{16}, we must rely on an analogous rate constant ratio, the ratio of disproportionation to combination of CH_3 and Me_3Si. A value of less than 0.08 was estimated and we use $0 < k_{18}/k_{16} < 0.1$. With these values, the third term in Eq. (VI) makes a negligible contribution and we obtain finally

$$\frac{k_{12}}{k_{10}} = \frac{\Phi(\mathrm{Me_3SiOMe/MeOH},h\nu) - (k_7/k_6)\,\Phi(\mathrm{SiCSiH/MeOH})}{\Phi(\mathrm{Me_6Si_2}) - (k_{18}/k_{16})\,\Phi(\mathrm{SiSiCSi})} \qquad \text{(VII)}$$

In the case of the time dependence of the $Hg/Me_3SiH/H_2$ experiments, we can also use relation (II) to derive

$$\frac{k_{12}}{k_{10}} = \frac{\Phi(\mathrm{SiSiCSi}) + \Phi(\mathrm{SiCSiH}) - [1 + (k_7/k_6)]\,\Phi(\mathrm{SiCSiH/MeOH})}{\Phi(\mathrm{Me_6Si_2}) - (k_{18}/k_{16})\,\Phi(\mathrm{SiSiCSi})} \qquad \text{(VIII)}$$

Using $0 < k_{18}/k_{16} < 0.1$ and $0 < k_7/k_6 < 1$, we derive an upper and a lower bound to k_{12}/k_{10}. For $Hg/H_2/Me_3SiH$, we obtain from relation (VIII)

$$0.057 < \frac{k_{12}}{k_{10}} < 0.062$$

Using relation (VII)

$$0.057 < \frac{k_{12}}{k_{10}} < 0.061$$

For the Hg/Me_3SiH system, we obtain from relation (VII)

$$0.059 < \frac{k_{12}}{k_{10}} < 0.082$$

A value of $k_{12}/k_{10} = 0.07 \pm 0.01$ covers the range of values obtained in our experiments.

4.4. Computer simulations

Computer simulations with sensitivity analysis (*KINAL* [31–33]) have been undertaken with the set of reactions compiled in Table 2. The mechanism given explains most of our experimental results, with the following exceptions.

It does not address the problem of the low quantum yield for H_2 formation and Me_3SiH disappearance. It has been assumed that all excited mercury atoms are deactivated in a reactive process (Eqs. (1), (2) and (26)). This leads to a quantum yield of unity for H_2 formation instead of the value of 0.8 observed experimentally. To allow a better comparison with the experimental results, all calculated quantum yields have been multiplied by a factor of 0.8. The formation of that part of SiCSiH which is scavengable by MeOH is dealt with in a very crude way by the non-stoichiometric relation (30a). Reaction (30) gives unsatisfactory results, incorrectly postulating a dependence of SiCSiH on the Me_3SiH concentration. Our mechanism does not account for the experimentally observed Me_3Si loss. Secondary photolysis clearly occurs at higher conversions (Fig. 4) and is not reproduced by our mechanism. The secondary formation of SiSiCSi in the presence of MeOH is, however, taken into account by reaction (24). The formation of Me_3SiOMe in a dark reaction is also not described by the mechanism. There is therefore a shift between the experimental points and computed line in Figs. 8 and 11. The convex increase in Me_3SiOMe in Figs. 7 and 12 is interpreted as being due to an increasing dark reaction with increasing MeOH pressure. The jump-like increase in Me_3SiOMe at small MeOH concentrations is thought to be due to photolytic formation. The calculated Me_3SiOMe concentration reaches a plateau value at a small MeOH concentration in agreement with this interpretation. Reaction (31) has been added to the mechanism as an additional route for the removal of Me_2SiCH_2 and acounts for the difference between the amount of Me_2SiCH_2 which is produced and found in the products. It has been assumed that Me_3SiH contains 0.5% Me_3SiOH as an impurity.

The rate constants given in Table 2 can be split into three categories: (A) the absolute rate constants reported in the literature have been used without alteration; (B) known relative rate constants and rate constants obtained in computer simulations have been followed as far as possible; (C) unknown rate constants.

To category A belong the rate constants k_1 [29], k_9 [21], k_{10} [9,34], k_{13} [20], k_{26} [35] and k_{24} [29]. Reaction (24) has been used to simulate the secondary formation of SiSiCSi. In the presence of MeOH (Fig. 8) this was only successful if, for k_{24}, an appreciably smaller value than that in the literature was used. On the other hand, with this smaller value, we were unable to account for the secondary yield of SiSiCSi at long irradiation times (Fig. 4).

To category B belong the rate constants k_{14}–k_{17} and k_{21}. The values of all these rate constants have been reported in Ref. [1]. Of importance is the confirmation of the large rate constants for the addition of the Me_3Si radical and MeOH molecule to the Si=C double bond. The rather slow decrease in Φ(SiCSiH) in Fig. 7 is considered to be an experimental artefact. This view is supported by the results in Fig. 12. The fast addition of radicals to the Si=C bond is the reason why very little DSCB is observed in systems where, in addition to Me_2SiCH_2, radicals are formed.

Sensitivity analysis reveals that only some of the rate constants in category C are sensitively connected to a certain product, e.g. the calculated yield of SiSiCSi in the presence of H_2 depends on the ratio k_8/k_9 and, to a lesser extent, on k_6/k_7. It is not possible to give independent values for these two rate constant ratios. We can only state that k_8/k_9 varies from 1.3×10^{-3} to 3.4×10^{-3} when k_6/k_7 takes values between 1.0 and 0.1. A similar situation holds for k_2/k_1; again only a range of values can be given, $1.4\times10^{-2}<k_2/k_1<2.1\times10^{-2}$, rather than a precise value. For k_{12}/k_{10}, we are in the fortunate situation that Me_6Si_2 as well as SiSiCSi depend predominantly on these two rate constants. We arrive at a similar small value as in Section 4.3. The ratio k_{18}/k_{16} is only weakly coupled to SiSiCSi formation and the same value as for k_{12}/k_{10} has been assumed. To account for the slight decrease in Φ(SiCSiH) and Φ(SiSiCSi) with increasing Me_3SiH pressure, we introduced reactions (22) and (23). The rate constants are a factor of 2–3 smaller than the values for the corresponding CH_3 radicals [36]. The value for k_{31} should be considered with reservation; firstly, reaction (31) represents all losses of Me_2SiCH_2 and, secondly, the concentration of the Me_3SiOH impurity is not well known.

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References

[1] M. Ahmed, P. Potzinger and H.Gg. Wagner, *J. Photochem. Photobiol. A: Chem., 86* (1995) 33.
submitted for publication.

[2] M.A. Nay, N.C. Woodall, O.P. Strausz and H.E. Gunning, *J. Am. Chem. Soc., 87* (1965) 179.

[3] S.K. Tokach and R.D. Koob, *J. Phys. Chem., 83* (1979) 774.

[4] E. Bastian, P. Potzinger, A. Ritter, H.P. Schuchmann, C. von Sonntag and G. Weddle, *Ber. Bunsenges. Phys. Chem., 84* (1980) 56.

[5] L. Gammie, I. Safarik, O.P. Strausz, R. Roberge and C. Sandorfy, *J. Am. Chem. Soc., 102* (1980) 378.

[6] S.K. Tokach and R.D. Koob, *J. Am. Chem. Soc., 102* (1980) 376.

[7] B.J. Conett, K.Y. Choo and P.P. Gaspar, *J. Am. Chem. Soc., 102* (1980) 377.

[8] D.J. Doyle, S.K. Tokach, M.S. Gordon and R.D. Koob, *J. Phys. Chem., 86* (1982) 3626.

[9] T. Brix, E. Bastian and P. Potzinger, *J. Photochem. Photobiol. A: Chem., 49* (1988) 287.

[10] I. Safarik, A. Jodhan and O.P. Strausz, *Chem. Phys. Lett., 142* (1987) 115.

[11] G.R. De Maré, *J. Photochem., 7* (1977) 101.

[12] M. Termonia and G.R. De Maré, *Chem. Phys. Lett., 25* (1974) 402.

[13] R.J. Cvetanovic, W.E. Falconer and K.R. Jennings, *J. Chem. Phys., 35* (1961) 1225.

[14] S. Bywater and E.W.R. Steacie, *J. Chem. Phys., 19* (1951) 319.

[15] Y. Rousseau, *Dissertation*, University of Alberta, 1963.

[16] T.L. Pollock, *Dissertation*, University of Alberta, 1971.

[17] T. Brix, U. Paul, P. Potzinger and B. Reimann, *J. Photochem. Photobiol. A: Chem., 54* (1990) 19.

[18] M.B. Robin, *Higher Excited States of Polyatomic Molecules*, Academic Press, 1985.

[19] R. Walsh, Thermochemistry, in S. Patai and Z. Rappoport (eds.), *The Chemistry of Organic Silicon Compounds*, Wiley, 1989, p. 371.

[20] T. Brix, N.L. Arthur and P. Potzinger, *J. Phys. Chem., 93* (1989) 8193.

[21] N.L. Arthur, P. Potzinger, B. Reimann and H.P. Steenbergen, *J. Chem. Soc., Faraday Trans. II, 84* (1989) 1447.

[22] R. Ellul, P. Potzinger and B. Reimann, *J. Phys. Chem., 88* (1984) 2793.

[23] A.B. Callear and P.M. Wood, *J. Chem. Soc., Faraday Trans. II, 68* (1972) 302.

[24] D. Wyrsch, H.R. Wendt and H.E. Hunziker, *Ber. Bunsenges. Phys. Chem., 78* (1974) 204.

[25] K. Oka and R.J. Cvetanovic, *J. Chem. Phys., 68* (1978) 4391.

[26] T.L. Pollock, E. Jakubowski, H.E. Gunning and O.P. Strausz, *Can. J. Chem., 47* (1969) 3474.

[27] C. Kerst and P. Potzinger, unpublished results, 1990.

[28] N.L. Arthur, P. Potzinger and B. Reimann, *J. Chem. Soc., Faraday Trans. II, 86* (1990) 1407.

[29] A.J. Yarwood, O.P. Strausz and H.E. Gunning, *J. Chem. Phys., 41* (1964) 1705.

[30] C. Kerst, P. Potzinger and H.Gg. Wagner, to be published.

[31] T. Turanyi, T. Berces and S. Vajda, *Int. J. Chem. Kinet., 21* (1989) 83.

[32] T. Turanyi, *Comp. Chem., 14* (1990) 253.

[33] T. Turanyi, *Math. Chem., 5* (1990) 203.

[34] N. Shimo, N. Nakashima and K. Yoshihara, *Chem. Phys. Lett., 125* (1986) 303.

[35] A.B. Callear, *Chem. Rev., 87* (1987) 335.

[36] R.E. Berkley, I. Safarik, H.E. Gunning and O.P. Strausz, *J. Phys. Chem., 77* (1973) 1734.