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Oxidation of Trimethylsilyl Radicals by N_2O: A Mechanistic Study

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The reaction of Me_3Si ($Me{\equiv}CH_3$) radicals with N_2O has been studied by analysis of the end products of the mercury-sensitized photolysis of N_2O with Me_3SiH. The main products found were N_2, $Me_3SiSiMe_3$, $Me_3SiOSiMe_3$, and Me_3SiOH. The influence on both major and minor products of reactant pressure, different scavenger and quencher molecules, temperature, and the reactor surface permits the derivation of a reaction mechanism and identification of the intermediates involved. The most important steps comprising the mechanism are oxygen abstraction from N_2O by Me_3Si with formation of Me_3SiO and a chain propagation step, the reaction of Me_3SiO and Me_3SiH with formation of Me_3SiOH and Me_3Si. Although the precise nature of the last step is unknown, it is a multistep reaction. Me_3SiO radicals also undergo combination with Me_3Si radicals. Self-combination under formation of a peroxide does not occur. Vibrationally excited species emerge in Si−O bond-forming processes, and a number of minor products stem from unimolecular decomposition of these excited species. The rate constant of O atom abstraction from N_2O (reaction 5) relative to Me_3Si radical combination (reaction 4) is given by $k_5/k_4^{1/2} = (6.5 \pm 1.3) \times 10^{-12}$ $cm^{3/2}$ $s^{-1/2}$ at room temperature. An activation energy of $E_A(5) = 23 \pm 1$ kJ mol^{-1} is obtained from experiments in the temperature range 295−520 K.

Introduction

Previous investigations of the oxidation of silyl radicals have concentrated so far on the system SiH_3/O_2.[1−4] This can be attributed to the important role the reaction of SiH_3 with O_2 plays in the explosive combustion of SiH_4 and in certain CVD processes in the microelectronics industry. Also, the size of the system is small enough to be successfully treated by ab initio molecular orbital theory.[5−7]

We are interested in the mechanistic pathways open to the siloxy radical, which does not play any role in the SiH_3/O_2 system, and have therefore chosen to examine the reaction of Me_3Si radicals with N_2O. This system offers the advantage over SiH_3/N_2O that the products are more sensitively detected by GC and that it possesses more degrees of freedom, thus inhibiting multistep decomposition.

The reaction between Me_3Si radicals and N_2O has been previously investigated by Hoffmeyer et al.[8] They studied the Hg-sensitized photolysis of N_2O in the presence of Me_3SiH and identified the products N_2, $Me_3SiSiMe_3$, $Me_3SiOSiMe_3$, and Me_3SiOH. The quantum yield of Me_3SiOH was found to be independent of Me_3SiH concentration, and in addition its formation was suppressed in a 4 L spherical photolysis cell of which only 20% was illuminated. It was therefore assumed that the silanol was formed heterogeneously. The quantum yield of N_2 rose from a value of 1 at low N_2O concentration to a plateau value of about 3 at high concentrations. The $Me_3SiOSiMe_3$ quantum yield also grew with increasing N_2O concentration, reaching a value of about 1. The experimental results were explained by the following mechanism. The first step is the well-known Hg-sensitized decomposition of N_2O,[9]

$$Hg(^3P_1) + N_2O \rightarrow O(^3P_1) + N_2 + Hg(^1S_0) \qquad (1)$$

followed by H atom abstraction from the Si−H bond by O and OH:

$$O + Me_3SiH \rightarrow OH + Me_3Si \qquad (2)$$

$$OH + Me_3SiH \rightarrow H_2O + Me_3Si \qquad (3)$$

The combination of the silyl radicals generated in reactions 2 and 3 gives hexamethyldisilane:

$$2\ Me_3Si \rightarrow Me_3SiSiMe_3 \qquad (4)$$

It was postulated that silyl radicals also abstract O atoms from N_2O:

$$Me_3Si + N_2O \rightarrow Me_3SiO + N_2 \qquad (5)$$

The corresponding reaction of SiH_3 radicals has not been

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Table 1. Product Quantum Yields for Three Experiments, A, B and C (see Figure 1)

substance	A (●)	B (▲)	C (○)
N_2	1.56 ± 0.03	2.36 ± 0.07	4.8 ± 0.4
$Me_3SiSiMe_3$	0.18 ± 0.01	$(1.1 \pm 0.1) \times 10^{-2}$	$(3.4 \pm 0.5) \times 10^{-2}$
$Me_3SiOSiMe_3$	0.32 ± 0.02	0.35 ± 0.01	0.43 ± 0.02
Me_3SiOH	0.40 ± 0.01	1.19 ± 0.03	2.9 ± 0.2
CH_4	$(3.5 \pm 0.2) \times 10^{-2}$		
Me_4Si	$(2.9 \pm 0.1) \times 10^{-2}$	$(2.6 \pm 0.1) \times 10^{-2}$	
$Me_3SiOSiMe_2OH$	$(2.8 \pm 0.2) \times 10^{-2}$	$(2.4 \pm 0.1) \times 10^{-2}$	
$Me_3SiOSiMe_2OSiMe_3$	$(1.4 \pm 0.1) \times 10^{-2}$	$(1.5 \pm 0.2) \times 10^{-2}$	
$Me_3SiOSiMe_2SiMe_3$	$(6.5 \pm 0.3) \times 10^{-3}$	$(3.5 \pm 0.2) \times 10^{-3}$	
$Me_3SiSiMe_2CH_2SiMe_3$	$(5.9 \pm 0.3) \times 10^{-3}$	$(3.5 \pm 0.2) \times 10^{-3}$	
$-Me_3SiH$		2.08 ± 0.03	4.0 ± 0.2

observed.[10] Finally, cross combination of silyl and siloxy radicals yields hexamethyldisiloxane:

$$Me_3Si + Me_3SiO \rightarrow Me_3SiOSiMe_3 \qquad (6)$$

Analysis of this mechanism suggests that the N_2 quantum yield should be 2, whereas the observed yield is 3. Introduction of the self-reaction of siloxy radicals

$$2\ Me_3SiO \rightarrow \text{Products} \qquad (7)$$

leads to the predicted N_2 quantum yield of 3, but the quantum yield of $Me_3SiOSiMe_3$ then becomes inconsistent with the observed value of 1.

From this discussion it is evident that the pathways of the siloxy radical to stable products remain largely unexplored. In this paper we present the quantum yields of the main products, and also a number of minor products, as a function of various parameters, including reactant pressure, different scavenger and quencher molecules, temperature, and the influence of the reactor surface.

Experimental Section

All substances were of commercial origin. Me_3SiH contained small Me_3SiCl and $Me_3SiOSiMe_3$ impurities, which were removed by distillation. Me_3SiH, N_2O, and SF_6 were dried before use by repeated distillation through a P_2O_5 column.

Gas handling was performed on a conventional vacuum line. Reactant and product pressures were measured by three capacitance manometers, MKS Baratron-122A (1000 mbar), -220BA (10 mbar), and -622A (1 mbar).

Most of the static photolyses were carried out in a 180 cm^3 cylindrical quartz cell with an optical path length of 10 cm. The photolysis cell was reproducibly positioned in the optical light path and at the same time attached to the vacuum line. It could be removed for analysis of its contents. To investigate the surface dependence of the product yields, cells with different surface-to-volume ratios, as well as cells with chemically modified surfaces, were utilized. The surface-to-volume ratio varied from about 3 cm^{-1} for a cylindrical quartz cell with an optical path length of 1 cm to 0.5 cm^{-1} for a spherical cell with a volume of 1×10^3 cm^3. Chemical modification of the surface involved coating with Teflon and washing with HF and subsequent drying at elevated temperature under vacuum.

The light source was a low-pressure mercury lamp (Gräntzl Typ 5) operating in dc mode, thermostatically controlled, and purged by a continuous flow of nitrogen. The lamp current was kept constant by a FuG MCN 140-65 power supply. A Vycor filter removed the 185 nm line. The intensity of the 254 nm light transmitted through the photolysis cell was measured by a 254 nm interference filter–photomultiplier arrangement. After the lamp had stabilized, the light intensity passing through the empty cell was set to a standard value by adjusting the lamp current. The intensity of the photolysis light could be attenuated by wire meshes of known transmission. Two different Hg concentrations were used: a low concentration with an absorption of approximately 50% (denoted by open symbols in Figures 1–19), resulting in a low but relatively uniform absorbed light intensity, and a high concentration (denoted by solid symbols in Figures 1–19) resulting in the total absorption of the 254 nm radiation and referred to as high-intensity photolysis experiments. At high concentration, Hg was deposited reproducibly in the cell by controlling the temperature of the Hg reservoir.

The photolysis cell could be heated by an oven consisting of two copper blocks tightly enclosing the cell. The blocks could be moved to or from the cell on tracks mounted at right angles to the axis of the cell without interfering with the aligned optical system. The temperature stability was about 1 K.

The absorbed light intensity for different Hg concentrations was determined by N_2O actinometry ($\Phi(N_2) = 1.0$).[9,11,12] A linear dependence was found to exist between the absorbed light intensity and the measured absorption in the range 0–80%.

End product analyses were carried out on a HP 5890II gas chromatograph equipped with either a flame ionization detector or a mass selective detector (HP 5971A). The inlet system consisted of a pneumatically actuated multivalve arrangement which could be evacuated. Gas samples were expanded from the thermostatically controlled photolysis cell into a thermostated sample loop. The pressure in the sample loop was measured by a capacitance manometer. Product separation was performed on a 50 m × 0.32 mm fused silica capillary column coated with dimethylpolysiloxane (1.5 μm, OV1, Weeke). The following temperature program was used to obtain a good separation of the product peaks: 0 °C (10 min)–10 °C/min–220 °C (2 min). All samples were analyzed at least twice. Most of the products have been encountered in previous investigations and were identified by their retention times. In addition mass spectra were taken from all the products evaluated.[13] For quantitative evaluation of the chromatograms by FID an internal standard (*n*-pentane) was used, and response factors were taken to be proportional to the number of C atoms in the molecule. In ref 14 it was shown that this is a good approximation for silicon-containing molecules. The overall amount of noncondensable products was determined by pressure measurement. In the presence of hydrogen the noncondensable product N_2 was determined by mass spectrometry (Varian MAT 331A) with neon as an internal standard.

Results

The Hg-sensitized photolysis of N_2O in the presence of Me_3SiH resulted in the formation of the major

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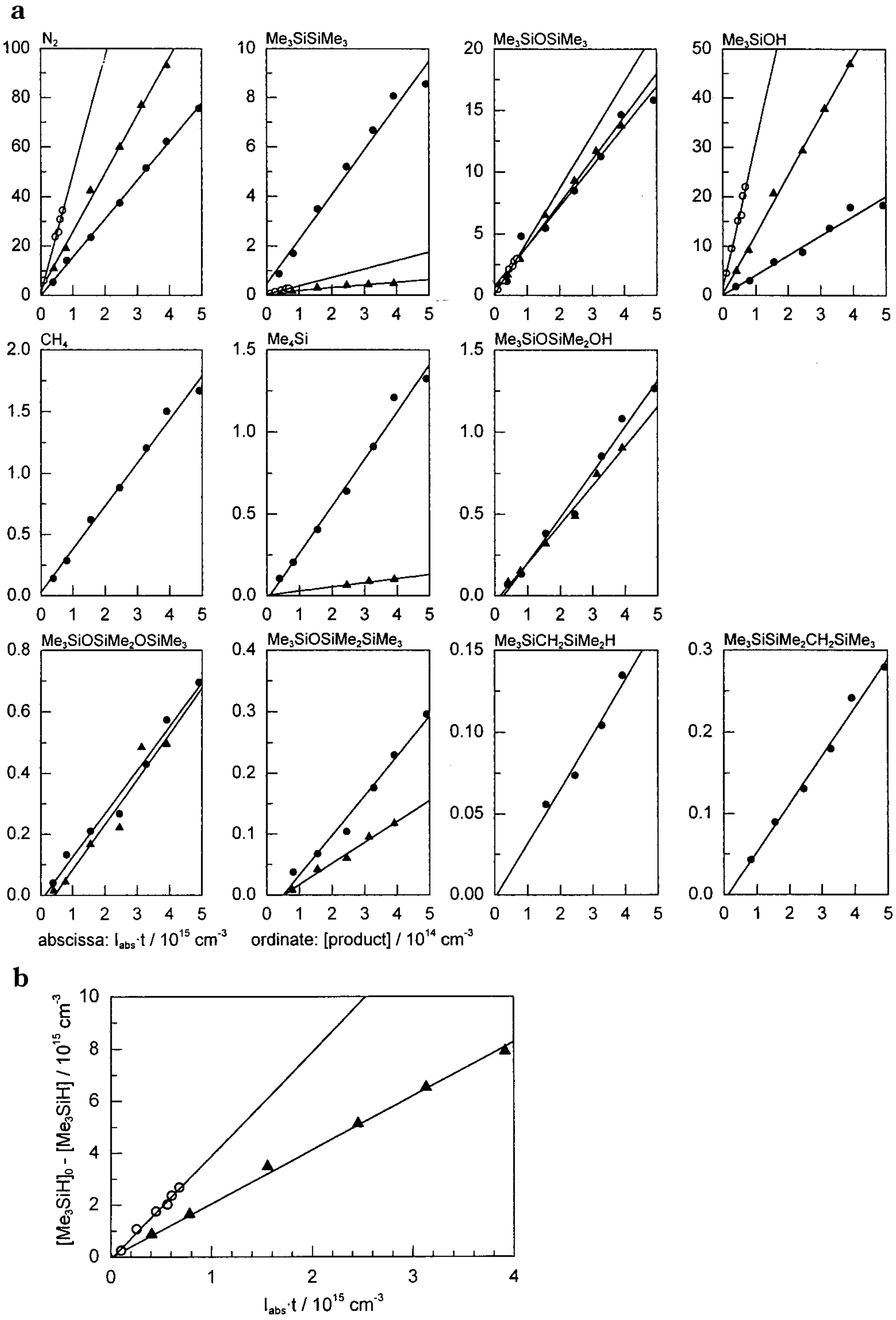

Figure 1. (a) Dependence of the product concentrations on photolysis time in the Hg-sensitized photolysis of N$_2$O/Me$_3$SiH mixtures: (A) [Me$_3$SiH] = (1.13 ± 0.01) × 10^{16} cm^{-3}, [N$_2$O] = (1.21 ± 0.01) × 10^{18} cm^{-3}, I_{abs} = (2.66 ± 0.06) × 10^{13} cm^{-3} s^{-1}, 15 s < t < 180 s (●); (B) [Me$_3$SiH] = (1.20 ± 0.01) × 10^{16} cm^{-3}, [N$_2$O] = (1.22 ± 0.01) × 10^{19} cm^{-3}, I_{abs} = (2.66 ± 0.06) × 10^{13} cm^{-3} s^{-1}, 15 s < t < 150 s (▲); (C) [Me$_3$SiH] = (1.3 ± 0.1) × 10^{16} cm^{-3}, [N$_2$O] = (1.3 ± 0.1) × 10^{19} cm^{-3}, I_{abs} = (2.5 ± 0.6) × 10^{12} cm^{-3} s^{-1}, 60 s < t < 240 s (○). (b) Dependence of the decrease in Me$_3$SiH concentration on photolysis time: (B) [Me$_3$SiH] = (1.20 ± 0.01) × 10^{16} cm^{-3}, [N$_2$O] = (1.22 ± 0.01) × 10^{19} cm^{-3}, I_{abs} = (2.66 ± 0.06) × 10^{13} cm^{-3} s^{-1}, 15 s < t < 150 s (▲); (C) [Me$_3$SiH] = (1.3 ± 0.1) × 10^{16} cm^{-3}, [N$_2$O] = (1.3 ± 0.1) × 10^{19} cm^{-3}, I_{abs} = (2.5 ± 0.6) × 10^{12} cm^{-3} s^{-1}, 60 s < t < 240 s (○).

products N$_2$, Me$_3$SiSiMe$_3$, Me$_3$SiOSiMe$_3$, and Me$_3$SiOH, and in a number of lesser products with quantum yields in the 10^{-2} range, namely, CH$_4$, Me$_4$Si, Me$_3$SiOSiMe$_2$OH, Me$_3$SiOMe, and Me$_3$SiOSiMe$_2$OSiMe$_3$. A few additional products with quantum yields in the 10^{-3} range were also identified, but the quantities formed were determined only in some experiments.

The variation of the concentrations of the products, and of the reactant Me$_3$SiH, on photolysis time under various conditions is shown in Figures 1a and 1b. In

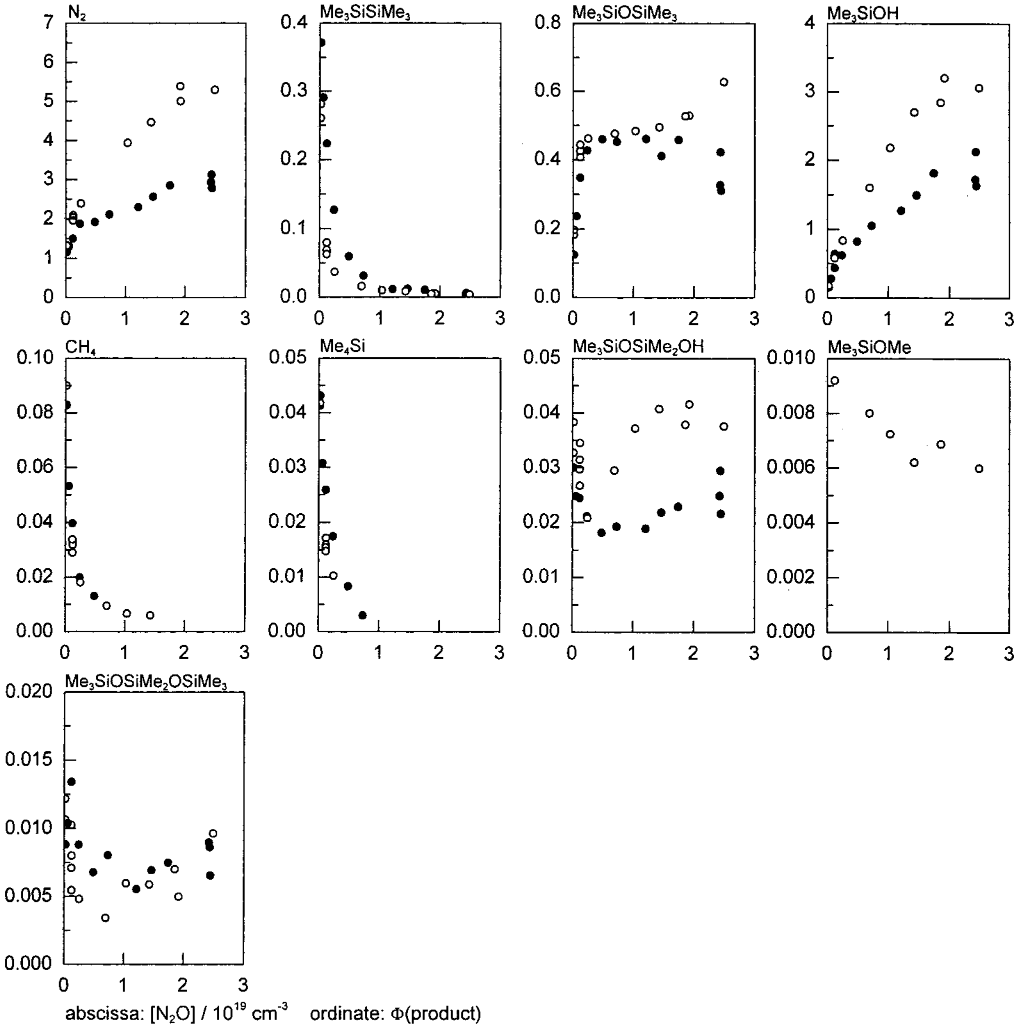

Figure 2. Dependence of the product quantum yields on N_2O concentration. $[Me_3SiH] = (1.22 \pm 0.01) \times 10^{16}$ cm^{-3}, $I_{abs} = (2.66 \pm 0.06) \times 10^{13}$ cm^{-3} s^{-1}, $t = 60$ s, 2.42×10^{17} cm^{-3} < $[N_2O]$ < 2.45×10^{19} cm^{-3} (●); $[Me_3SiH] = (1.25 \pm 0.01) \times 10^{16}$ cm^{-3}, $I_{abs} = (6.3 \pm 0.9) \times 10^{12}$ cm^{-3} s^{-1}, $t = 120$ s, 2.22×10^{17} cm^{-3} < $[N_2O]$ < 2.50×10^{19} cm^{-3} (○).

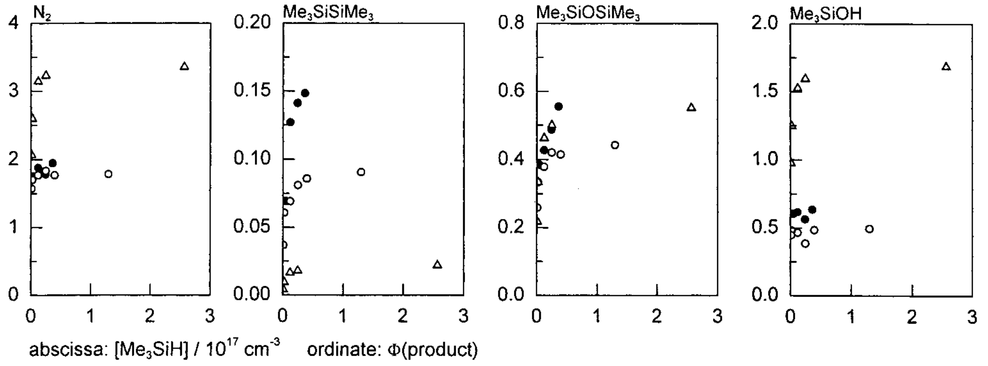

Figure 3. Dependence of the product quantum yields on Me_3SiH concentration in the presence of different N_2O concentrations. $[N_2O] = (2.44 \pm 0.01) \times 10^{18}$ cm^{-3}, $I_{abs} = (2.66 \pm 0.06) \times 10^{13}$ cm^{-3} s^{-1}, $t = 60$ s, 4.81×10^{15} cm^{-3} < $[Me_3SiH]$ < 3.65×10^{16} cm^{-3} (●); $[N_2O] = (1.23 \pm 0.01) \times 10^{18}$ cm^{-3}, $I_{abs} = (7.6 \pm 0.1) \times 10^{12}$ cm^{-3} s^{-1}, $t = 120$ s, 1.27×10^{15} cm^{-3} < $[Me_3SiH]$ < 1.30×10^{17} cm^{-3} (○); $[N_2O] = (6.13 \pm 0.02) \times 10^{18}$ cm^{-3}, $I_{abs} = (7.0 \pm 0.2) \times 10^{12}$ cm^{-3} s^{-1}, $t = 120$ s, 1.24×10^{15} cm^{-3} < $[Me_3SiH]$ < 2.57×10^{17} cm^{-3} (△).

each case the dependence is linear and the intercept is negligible, indicating that all the products qualify as primary. The quantum yields extracted from these plots are summarized in Table 1. The dependence of the product quantum yields on N_2O pressure for two different light intensities is shown in Figure 2. The influence of the Me_3SiH concentration on the main product quantum yields can be seen in Figure 3. This experiment was considered important enough to be repeated under different experimental conditions. To test whether molecules with a Si=C double bond participate in the reaction mechanism, photolyses in the presence of MeOH were undertaken (Figure 4). SF_6 was added as a moderator of vibrationally hot molecules, and its influence on the quantum yields of the products is shown in Figure 5.

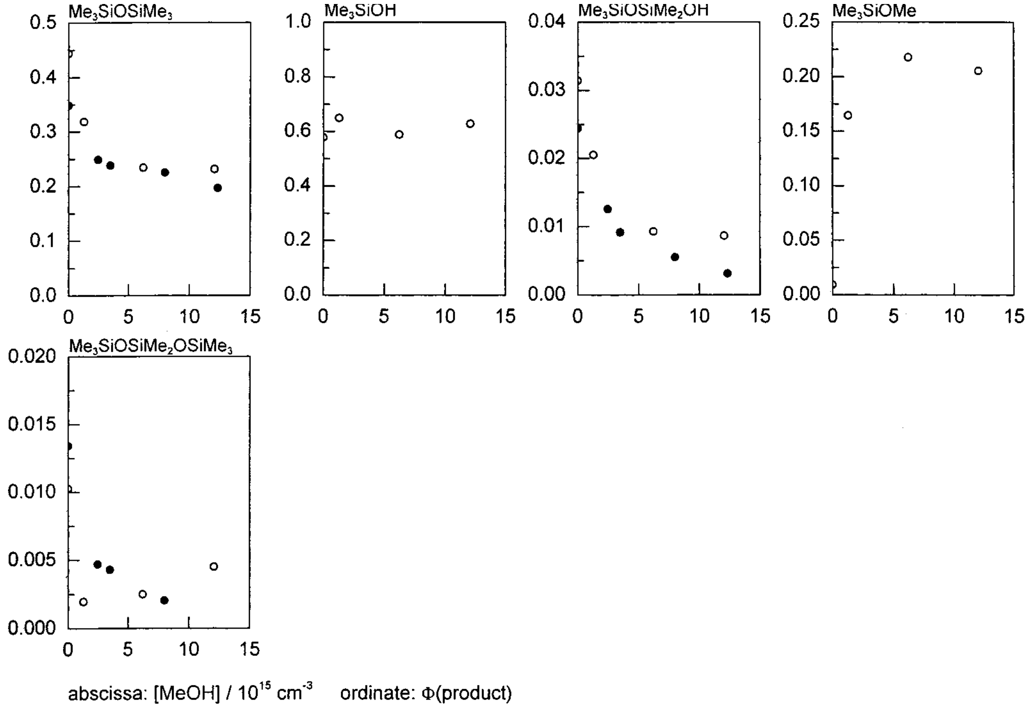

Figure 4. Dependence of the product quantum yields on MeOH concentration. $[Me_3SiH] = (1.24 \pm 0.01) \times 10^{16}$ cm^{-3}, $[N_2O] = (1.23 \pm 0.01) \times 10^{18}$ cm^{-3}, $t = 60$ s, $I_{abs} = (2.66 \pm 0.06) \times 10^{13}$ cm^{-3} s^{-1}, $0 < [MeOH] < 1.24 \times 10^{16}$ cm^{-3} (●); $[Me_3SiH] = (1.24 \pm 0.01) \times 10^{16}$ cm^{-3}, $[N_2O] = (1.23 \pm 0.02) \times 10^{18}$ cm^{-3}, $t = 120$ s, $I_{abs} = (7.4 \pm 0.2) \times 10^{12}$ cm^{-3} s^{-1}, $0 < [MeOH] < 1.21 \times 10^{16}$ cm^{-3} (○).

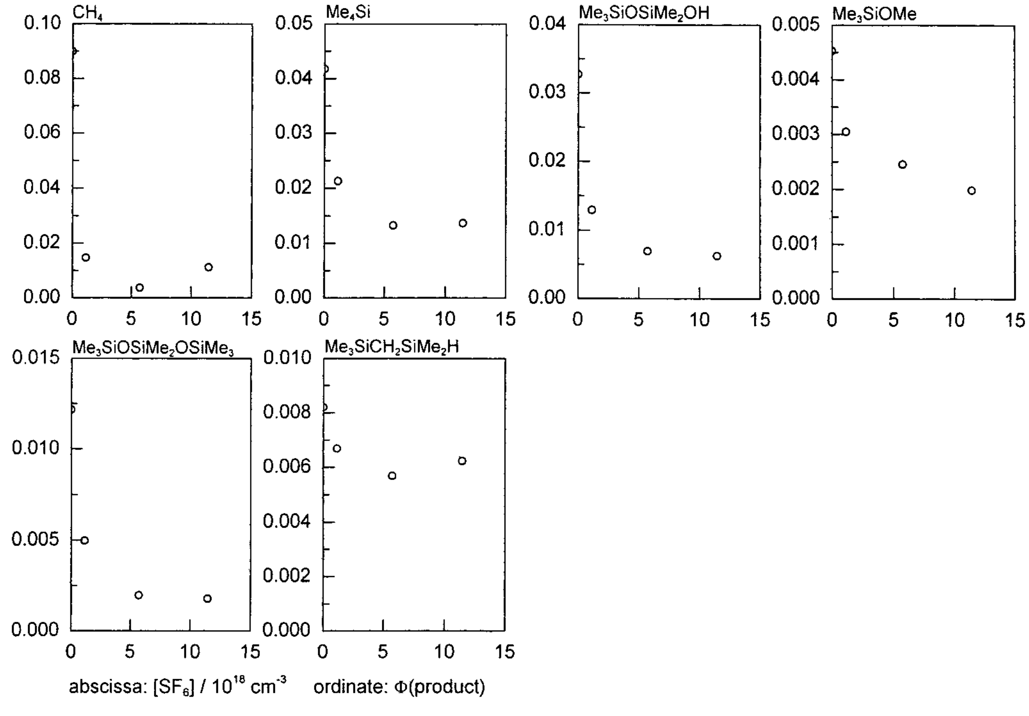

Figure 5. Dependence of the product quantum yields on SF_6 concentration. $[Me_3SiH] = (1.26 \pm 0.00) \times 10^{16}$ cm^{-3}, $[N_2O] = (2.22 \pm 0.01) \times 10^{17}$ cm^{-3}, $I_{abs} = (6.7 \pm 0.6) \times 10^{12}$ cm^{-3} s^{-1}, $t = 120$ s, $0 < [SF_6] < 1.15 \times 10^{19}$ cm^{-3}.

The effect of temperature on all products is pronounced and has been studied in the range from 295 to 520 K (Figure 6). In the high light intensity experiments the reaction mixture was transferred to a bulb and then subjected to GC analysis. This procedure resulted in almost all of Me_3SiOH and $Me_3SiOSiMe_2OH$ being lost. In the low light intensity experiments the reaction mixture was directly transferred from the cuvette to the GC. The reason for the almost complete loss of the silanols in the high-intensity experiments was not elucidated.

The claim in a previous publication of our group[8] that Me_3SiOH is a product of a surface reaction prompted us to investigate this point carefully. First, equivalent experiments to those whose results are shown in Figure 2 were carried out in a photolysis cell with a low surface-to-volume (S/V) ratio. Only 350 cm^3 of the spherical 1 L cuvette was illuminated. Qualitatively the same results

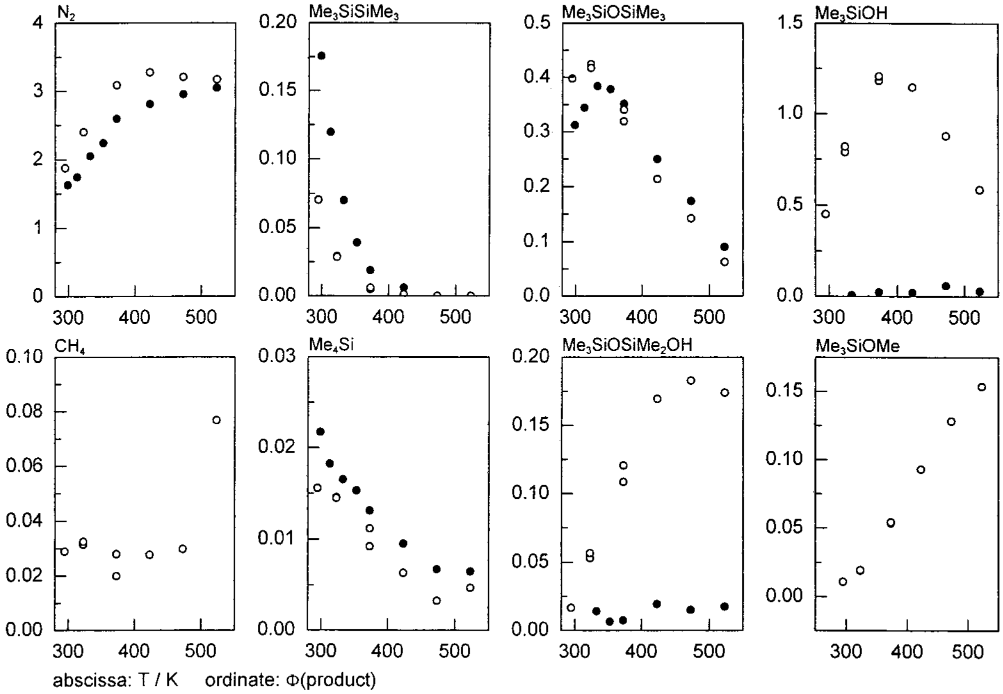

Figure 6. Dependence of the product quantum yields on temperature. [Me_3SiH] = (1.19 ± 0.02) × 10^{16} cm^{-3}, [N_2O] = (1.18 ± 0.04) × 10^{18} cm^{-3}, I_{abs} = (1.75 ± 0.01) × 10^{13} cm^{-3} s^{-1}, t = 90 s, 295 K < T < 520 K (●); [Me_3SiH] = (1.22 ± 0.06) × 10^{16} cm^{-3}, [N_2O] = (1.23 ± 0.06) × 10^{18} cm^{-3}, I_{abs} = (7.6 ± 0.2) × 10^{12} cm^{-3} s^{-1}, t = 120 s, 295 K < T < 520 K (○).

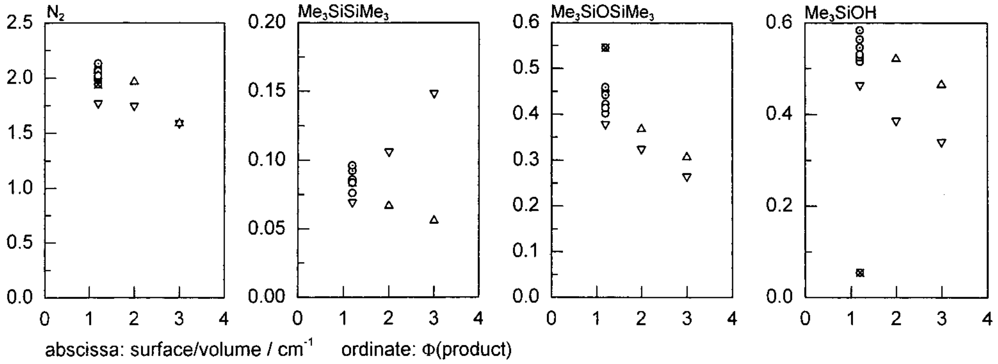

Figure 7. Dependence of the product quantum yields on surface-to-volume ratio. [Me_3SiH] = (1.24 ± 0.01) × 10^{16} cm^{-3}, [N_2O] = (1.23 ± 0.01) × 10^{18} cm^{-3}, $I_{abs}t$ = (9.5 ± 0.6) × 10^{14} cm^{-3}, t = const. ≈ 120 s (△), I_{abs} = const. ≈ 7.9 × 10^{12} cm^{-3} s^{-1} (▽). Dependence of the product quantum yields on the surface character. [Me_3SiH] = (1.22 ± 0.02) × 10^{16} cm^{-3}, [N_2O] = (1.22 ± 0.02) × 10^{18} cm^{-3}, I_{abs} = (7.0 ± 0.5) × 10^{12} cm^{-3} s^{-1}, t = 120 s, Pyrex surface (○), Teflon surface (⊙), acid surface (HF) (⊗).

were obtained as in the cylindrical cells with higher S/V ratios. A slight decrease in the yields of all products with increasing S/V ratio was observed, but no exceptional behavior of Me_3SiOH could be discerned (Figure 7). In another experiment the surface of the cell was coated with Teflon, but again there was no apparent influence on the product quantum yields. Only when the surface was modified to give it an acid character was a change in behavior observed: a decrease in Me_3SiOH together with the formation of $Me_3SiOSiMe_3$ (Figure 7).

In Figure 8 results are presented for a different set of experiments, involving the Hg-sensitized photolysis of H_2 in the presence of Me_3SiH and varying amounts of N_2O. The same products as in the Hg/N_2O/Me_3SiH system were observed. N_2 was identified, but the quantum yield values obtained were loaded with large errors due to the high dilution by H_2. $Me_3SiOSiMe_2OH$ was the minor product most affected by the change of experimental system: its quantum yield decreases below the detection limit for most of the N_2O concentrations. At a N_2O concentration of 1 × 10^{18} cm^{-3} and a total pressure of 320 mbar the quantum yields of CH_4, Me_4Si, and $Me_3SiOSiMe_2OSiMe_3$ are about the same as in the Hg/N_2O/Me_3SiH system at the same total pressure. $Me_3SiSiMe_2CH_2SiMe_3$ is the only product whose concentration increases.

Addition of H_2O to the reaction mixture causes the quantum yield of Me_3SiOH to increase markedly. Φ($Me_3SiOSiMe_2OH$) increases somewhat, while at the same time the yield of $Me_3SiOSiMe_2OSiMe_3$ decreases to a value under the detection limit (Figure 9).

The dependence of the product yields on light intensity in the presence and absence of an excess of H_2 is shown in Figure 10.

Discussion

Material Balance. To draw conclusions about a reaction mechanism from an end product study, product

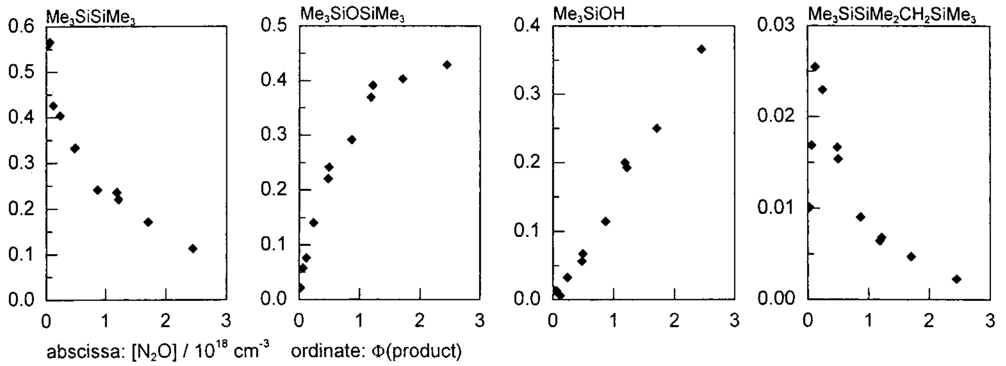

Figure 8. Dependence of the product quantum yields on N_2O concentration in the photolysis of a H_2/Me_3SiH mixture. $[Me_3SiH] = (1.22 \pm 0.01) \times 10^{16}$ cm^{-3}, $P(H_2) = (285 \pm 15)$ mbar, $I_{abs} = (2.66 \pm 0.06) \times 10^{13}$ cm^{-3} s^{-1}, $t = 60$ s, 2.43×10^{17} cm^{-3} < $[N_2O]$ < 2.45×10^{18} cm^{-3}.

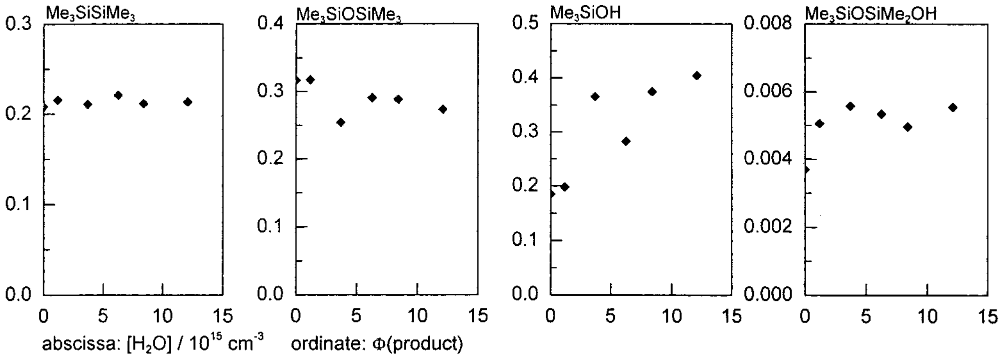

Figure 9. Dependence of the product quantum yields on H_2O concentration in the photolysis of a $H_2/N_2O/Me_3SiH$ mixture. $[Me_3SiH] = (1.22 \pm 0.01) \times 10^{16}$ cm^{-3}, $[N_2O] = (1.21 \pm 0.01) \times 10^{18}$ cm^{-3}, $P(H_2) = 280 \pm 28$ mbar, $I_{abs} = (2.66 \pm 0.06) \times 10^{13}$ cm^{-3} s^{-1}, $t = 60$ s, $0 < [H_2O] < 1.21 \times 10^{16}$ cm^{-3}.

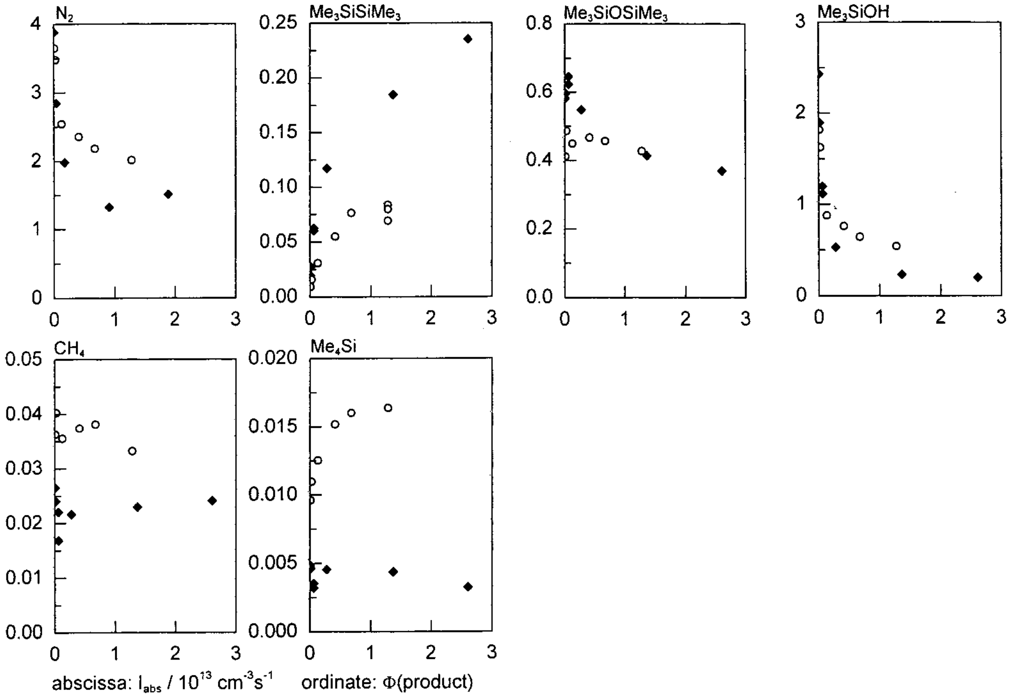

Figure 10. Dependence of the product quantum yields on the light intensity. $[Me_3SiH] = (1.22 \pm 0.01) \times 10^{16}$ cm^{-3}, $[N_2O] = (1.22 \pm 0.0) \times 10^{18}$ cm^{-3}, $P(H_2) = 280 \pm 21$ mbar, $I_{abs}t = (1.58 \pm 0.02) \times 10^{15}$ cm^{-3}, 60 s < t < 24044 s, 6.51×10^{10} cm^{-3} s^{-1} < I_{abs} < 2.61×10^{13} cm^{-3} s^{-1} (◆); $[Me_3SiH] = (1.24 \pm 0.01) \times 10^{16}$ cm^{-3}, $[N_2O] = (1.23 \pm 0.01) \times 10^{18}$ cm^{-3}, $I_{abs}t = (9.1 \pm 0.2) \times 10^{14}$ cm^{-3} 120 s < t < 11204 s, 1.38×10^{11} cm^{-3} s^{-1} < I_{abs} < 1.29×10^{13} cm^{-3} s^{-1} (○).

retrieval should be as complete as possible. The material balance indicates the extent to which this requirement is fulfilled. The product quantum yields of three series of experiments, A, B, and C, and the quantum yield for the Me_3SiH disappearance given in Table 1 show that our product recovery for Si and C is complete, but selective losses for H and O atoms have to be admitted. This is more clearly seen by normalizing Φ(C) to 3 and Φ(N) to 2:

$$\text{A:}\ Si_{1.00\pm0.07}C_3H_{9.30\pm0.61}\quad N_2O_{0.52\pm0.02}$$
$$\text{B:}\ Si_{1.01\pm0.07}C_3H_{9.60\pm0.42}\quad N_2O_{0.69\pm0.03}$$
$$\text{C:}\ Si_{1.00\pm0.04}C_3H_{9.76\pm0.90}\quad N_2O_{0.69\pm0.07}$$

It can be further seen that carbon shows up in the products exclusively in the form of a methyl group. From the reactant Me_3SiH we therefore recover the Me_3Si group almost completely, while the loss of H atoms diminishes with increasing N_2O concentration:

$$\text{A:}\ Me_3Si_{1.00\pm0.07}H_{0.30\pm0.02}$$
$$\text{B:}\ Me_3Si_{1.01\pm0.04}H_{0.60\pm0.02}$$
$$\text{C:}\ Me_3Si_{1.00\pm0.09}H_{0.76\pm0.07}$$

Me_3Si radicals were generated in two ways: (a) Hg-sensitized photolysis of N_2O (reaction 1) followed by the processes 2 and 3 and (b) Hg-sensitized photolysis of H_2 followed by H atom abstraction from the Si−H bond.[11] In case (a) processes 2 and 3 are well established. Park and Wiesenfeld[15] have shown that $O(^3P)$ abstracts hydrogen in a direct process with the formation of OH, and Hoffmeyer et al.[8] detected only D_2O in the system $O(^3P)/Me_3SiD$, supporting the occurrence of reaction 3. H_2O is not part of our product list. If H_2O does not react further, we can explain the loss of the elements H and O. However, from Table 1 we calculate the following stoichiometry from the H and O loss for the three sets of experiments: (A) $H_{1.46}O$, (B) $H_{1.13}O$, and (C) $H_{0.62}O$, showing that the loss of O atoms cannot be explained by the formation of H_2O alone.

The Mechanism. In the absence of N_2O, Me_3Si radicals combine to form $Me_3SiSiMe_3$,[11] as shown in reaction 4. In the presence of increasing amounts of N_2O the $Me_3SiSiMe_3$ quantum yield converges to zero, while the disiloxane quantum yield converges toward an upper limit (Figure 2). From the intensity dependence of $\Phi(Me_3SiSiMe_3)$ (Figure 10) we conclude that the second-order self-combination reaction 4 competes with a pseudo-first-order reaction. Furthermore, in Figure 2 the quantum yield of N_2 is increasing with increasing N_2O concentration and decreasing with increasing light intensity (Figure 10). These results strongly suggest that the abstraction reaction 5 takes place followed by combination (reaction 6). This is not necessarily in contradiction with a previous observation that SiH_3 does not react with N_2O,[10] as the conditions obtained in those experiments allowed observation only of a reaction with $k > 5 \times 10^{-15}\ cm^3\ s^{-1}$.[10] The conclusions drawn up to this point are the same as in our previous publication,[8] but our present investigation adds two important new results: Me_3SiOH is a genuine product, and it is formed in a chain reaction, as can be seen from the values of $\Phi(N_2)$ and $\Phi(Me_3SiOH)$ at high N_2O concentration (Figure 2). As can be seen in Figure 10, $\Phi(Me_3SiOH)$ shows a strong intensity dependence similar to that of $\Phi(Me_3SiSiMe_3)$, but in opposite direction. The quantum yield is decreasing with increasing intensity. From this we deduce that Me_3SiOH is formed in a pseudo-first-order reaction and the participating radical also undergoes a competing radical−radical reaction. The simplest sequence that explains this behavior is reaction 6 and 8:

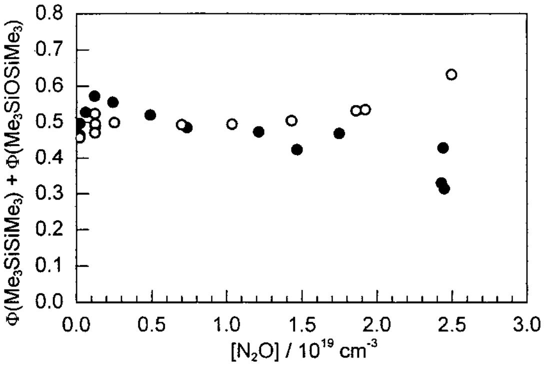

Figure 11. Dependence of $\Phi(Me_3SiSiMe_3) + \Phi(Me_3SiOSiMe_3)$ on N_2O concentration. See Figure 2 for the experimental conditions of (●) and (○).

$$Me_3SiO + Me_3SiH \rightarrow Me_3SiOH + Me_3Si \qquad (8)$$

A similar mechanism has been proposed in the case of Et_3SiH oxidation ($Et \equiv C_2H_5$) by N_2O in the liquid phase.[16] A special feature of our mechanism is the assumption that the Me_3SiO radicals can only abstract hydrogen from Me_3SiH or combine with Me_3Si radicals. Self-combination is not taking place: neither the combination product $Me_3SiOOSiMe_3$ nor $Me_3SiOSiMe_2OMe$, which emerges quantitatively by thermal rearrangement of the peroxide,[17,18] was found.

Reactions 1−6 and 8 comprise the minimum set of chemical steps that explain, at least qualitatively, our experimental results. In the next paragraph we investigate the consequences of the proposed mechanism.

Consequences of the Mechanism. According to the mechanism, the sum of the quantum yields of $Me_3SiSiMe_3$ and $Me_3SiOSiMe_3$ should be constant and independent of the N_2O concentration and the applied light intensity.

$$\begin{gathered}\Phi(Me_3SiSiMe_3) + \Phi(Me_3SiOSiMe_3) = \text{const.} = 1\\ \lim_{N_2O\to0}\Phi(Me_3SiSiMe_3) = 1 \qquad \text{(I)}\\ \lim_{N_2O\to\infty}\Phi(Me_3SiOSiMe_3) = 1\end{gathered}$$

The experiments shown in Figure 2 affirm this prediction of the mechanism at least qualitatively. However, instead of a value of 1 for the sum of the quantum yields of $Me_3SiSiMe_3$ and $Me_3SiOSiMe_3$, a value of only about 0.5 is observed (Figure 11). This value is independent of the light intensity but shows a small dependence on the N_2O concentration. The dependence on N_2O is opposite for the two series of experiments, which suggests that the deviation from the value of about 0.5 is an experimental artifact.

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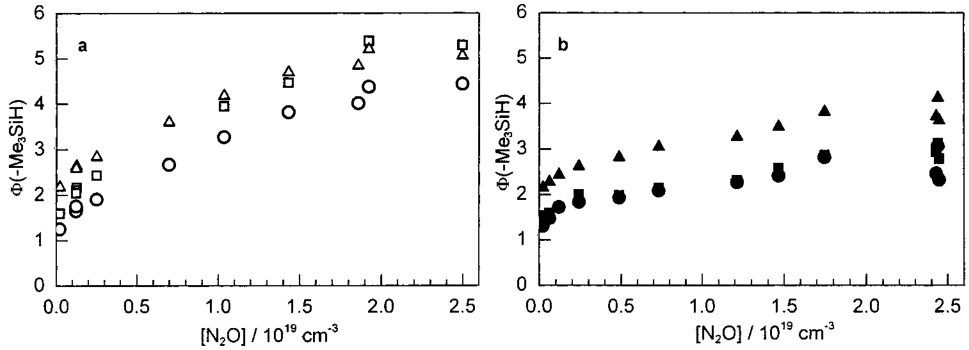

Figure 12. (a and b) Dependence of the Me_3SiH loss during the photolysis on N_2O concentration. Calculated by addition of quantum yields of Si-containing products (○ and ●), by eq III (□ and ■), and by eq IV (△ and ▼). See Figure 3 for experimental conditions, (a) $I_{abs} = (6.3 \pm 0.9) \times 10^{12}$ cm^{-3} s^{-1}, (b) $I_{abs} = (2.66 \pm 0.06) \times 10^{13}$ cm^{-3} s^{-1}.

Further consequences of the mechanism are that the minimum quantum yield for the consumption of Me_3SiH is 2,

$$\Phi(-Me_3SiH) \geq 2 \qquad \text{(II)}$$

and that this value depends on the N_2O concentration and the light intensity. $\Phi(-Me_3SiH)$ has not been measured directly in this series of experiments but can be calculated from the Si-containing products without reference to the mechanism. These results are shown in Figure 12a,b (circles). The N_2O dependence and the much higher consumption at low light intensity are clearly borne out by the experiment, but in both cases the limiting value is not 2 but a value close to 1. The calculated value is a lower limit, as some products may have not been detected. From our material balance we know, however, that the difference between true and calculated values should be small.

Consideration of the mechanism reveals that there exist two other relations by which $\Phi(-Me_3SiH)$ can be calculated:

$$\begin{aligned}\Phi(-Me_3SiH) &= \Phi(N_2) + \Phi(Me_3SiSiMe_3) \qquad \text{(III)}\\ &= 2 + \Phi(Me_3SiOH) \qquad \text{(IV)}\end{aligned}$$

As can be seen from Figure 12, there is good agreement between values calculated from the Si-containing products (circles) and those calculated from eq III for the high-intensity experiments (solid squares) over the whole N_2O concentration range. For the low-intensity experiments (open squares) the agreement is less satisfactory. In both cases the limiting value is much smaller than 2. There exists a large difference between the measured quantum yield for Me_3SiH consumption and the value calculated from eq IV for both low- (open triangles) and high-intensity (solid triangles) experiments.

According to the mechanism, the quantum yield of the product H_2O, which could not be measured, should be 1, equal to the sum of the $Me_3SiSiMe_3$ and $Me_3SiOSiMe_3$ quantum yields, and independent of both N_2O concentration and light intensity:

$$\begin{aligned}\Phi(H_2O) &= 1\\ &= \Phi(Me_3SiSiMe_3) + \Phi(Me_3SiOSiMe_3)\end{aligned} \qquad \text{(V)}$$

It can also be calculated by relation VI:

$$\Phi(H_2O) = {}^1/_2\{\Phi(-Me_3SiH) - \Phi(Me_3SiOH)\} \qquad \text{(VI)}$$

A plot of $\Phi(H_2O)$, calculated according to eq VI, versus N_2O is virtually identical with Figure 11. $\Phi(H_2O)$ is less than 1 and in accord with the second part of relation V.

From a steady-state analysis of the mechanism, for small N_2O concentrations we obtain the following relations:

$$\begin{aligned}\Phi(N_2) &= 1 + \frac{k_5}{(k_4 I_{abs})^{1/2}}[N_2O]\\ \Phi(Me_3SiSiMe_3) &= 1 - \frac{k_5}{(k_4 I_{abs})^{1/2}}[N_2O]\\ \Phi(Me_3SiOSiMe_3) &= \frac{k_5}{(k_4 I_{abs})^{1/2}}[N_2O]\\ \Phi(Me_3SiOH) &= \frac{k_5 k_8}{k_6 I_{abs}}[N_2O][Me_3SiH]\end{aligned} \qquad \text{(VII)}$$

For high N_2O concentrations we obtain

$$\begin{aligned}\Phi(N_2) &= 1 + \left(\frac{k_5 k_8}{k_6 I_{abs}}\right)^{1/2}[N_2O]^{1/2}[Me_3SiH]^{1/2}\\ \Phi(Me_3SiSiMe_3) &= 0\\ \Phi(Me_3SiOSiMe_3) &= 1\\ \Phi(Me_3SiOH) &= \left(\frac{k_5 k_8}{k_6 I_{abs}}\right)^{1/2}[N_2O]^{1/2}[Me_3SiH]^{1/2}\end{aligned} \qquad \text{(VIII)}$$

The expected linear increase of $\Phi(Me_3SiOH)$ with N_2O is best seen in the experiments with excess H_2, where small N_2O concentrations have been utilized (Figure 8). The dependence of $\Phi(N_2) - 1$ and $\Phi(Me_3SiOH)$ versus $[N_2O]$ at high N_2O concentrations is very similar, although not completely following a square root dependence (Figure 2).

We conclude that qualitative agreement exists between experimental results and the prediction of the mechanism, but there are serious quantitative discrepancies.

Enlargement of the Mechanism. The mechanism presented so far is unable to explain the results in the presence of the scavenger molecules MeOH (Figure 4) and H_2O (Figure 9). In the system $Hg/N_2O/Me_3SiH$ the addition of MeOH leads to a substantial decrease of $Me_3SiOSiMe_3$ without affecting Me_3SiOH. Methanol is known to be an effective scavenger for molecules with a Si═C double bond.[19,20] The appearance of the product Me_3SiOMe in the presence of MeOH shows unequivocally that $Me_2Si{=}CH_2$ is formed in our system. These two observations are proof that $Me_2Si{=}CH_2$ is a precursor of $Me_3SiOSiMe_3$. $Me_2Si{=}CH_2$ can be formed by a disproportionation reaction between a Me_3Si radical and the atoms and radicals present in our system. There are four potential reaction partners: O, OH, Me_3Si, and Me_3SiO. O and OH undergo competing reactions with Me_3SiH, which is present in a concentration approximately 5 orders of magnitude larger than Me_3Si. Therefore they are excluded. Disproportionation between Me_3Si radicals is taking place,[21−23] but the branching ratio is small.[11] The most probable reaction leading to the formation of $Me_2Si{=}CH_2$ is

$$\mathrm{Me_3Si + Me_3SiO \rightarrow Me_2Si{=}CH_2 + Me_3SiOH} \quad (9)$$

It is followed by

$$\mathrm{Me_2Si{=}CH_2 + Me_3SiOH \rightarrow Me_3SiOSiMe_3} \quad (10)$$

As water is also present, the following reaction must be considered:

$$\mathrm{Me_2Si{=}CH_2 + H_2O \rightarrow Me_3SiOH} \quad (11)$$

The occurrence of reactions 10 and 11 was shown by photolyzing $Me_3SiSiMe_3$ at 206 nm in the presence of H_2O. $Me_2Si{=}CH_2$ is formed with a quantum yield of 0.18.[24] In the presence of water $Me_3SiOSiMe_3$ and Me_3SiOH were formed with a product ratio dependent on the amount of H_2O added.

In the system $Hg/H_2/N_2O/Me_3SiH$ no water is formed. Only reaction 10 remains as a sink for $Me_2Si{=}CH_2$ besides dimerization and radical addition reactions.[14]

Quantitative Analysis. By carrying out an analysis of various aspects of the extended mechanism (reactions 1−6, 8−11), we can shed further light on some of the reactions involved. We begin by replacing the stoichiometric coefficient of 1 for $O(^3P)$ in reaction 1 by the quantity $a < 1$. We assume that a part of the O atoms generated by reaction 1 is lost. No explanation can be offered for this assumption. It should be remembered that the same situation was encountered in the Hg-sensitized photolysis of H_2/Me_3SiH mixtures.[11] Besides a, we introduce the following quantities:

$$b = k_6/(k_6 + k_9)$$

$$c = \frac{k_{10}[\mathrm{Me_3SiOH}]}{k_{10}[\mathrm{Me_3SiOH}] + k_{11}[\mathrm{H_2O}]}$$

Relations I−V are then transformed to the following:

$$\Phi(\mathrm{Me_3SiSiMe_3}) + \frac{\Phi(\mathrm{Me_3SiOSiMe_3})}{b + c(1-b)} = \text{const.} = a$$

$$\lim_{\mathrm{N_2O}\to 0}\Phi(\mathrm{Me_3SiSiMe_3}) = a \quad \text{(Ia)}$$

$$\lim_{\mathrm{N_2O}\to \infty}\Phi(\mathrm{Me_3SiOSiMe_3}) = a(b + c\,(1-b))$$

$$\Phi(-\mathrm{Me_3SiH}) \geq 2a \quad \text{(IIa)}$$

$$= \Phi(\mathrm{N_2}) + \Phi(\mathrm{Me_3SiSiMe_3}) + a - 1 \quad \text{(IIIa)}$$

$$\Phi(-\mathrm{Me_3SiH}) = 2a + \Phi(\mathrm{Me_3SiOH}) - \frac{2(1-c)(1-b)}{b + c(1-b)}\Phi(\mathrm{Me_3SiOSiMe_3}) \quad \text{(IVa)}$$

$$\Phi(\mathrm{H_2O}) = a - \frac{(1-b)(1-c)}{b + c(1-b)} \quad \text{(Va)}$$

To determine the quantities a, b, and c, we first examine the MeOH scavenging experiments (Figure 4). According to the extended mechanism, the difference between the quantum yields of Me_3SiOH in the absence and presence of an excess of MeOH, denoted by Φ_a and Φ_p, respectively, is given by

$$\Phi_a(\mathrm{Me_3SiOH}) - \Phi_p(\mathrm{Me_3SiOH}) = \frac{(1-b)(1-2c)}{b + c(1-b)}\Phi_a(\mathrm{Me_3SiOSiMe_3}) \quad \text{(IX)}$$

Since the left-hand side is close to 0 and $\Phi_a(Me_3SiOSiMe_3) \neq 0$, either $b = 1$ or $c = 0.5$. From our previous discussion of the mechanism and the definition of b, $b = 1$ can be discarded, and thus $c = 0.5$ remains. It should be emphasized that this value has no universal validity and that it is dependent on the reaction conditions. In a similar way, the difference between the quantum yields of $Me_3SiOSiMe_3$ in the absence and presence of an excess of MeOH is given by

$$\frac{\Phi_a(\mathrm{Me_3SiOSiMe_3}) - \Phi_p(\mathrm{Me_3SiOSiMe_3})}{\Phi_a(\mathrm{Me_3SiOSiMe_3})} = \frac{c(1-b)}{b + c(1-b)} \approx 0.5 \quad \text{(X)}$$

From the experimental results, the value of the left-hand side of eq X is about 0.5. Combining this with $c = 0.5$, we obtain $b \approx 0.3$. This means that the reaction between Me_3Si and Me_3SiO is dominated by disproportionation.

In the series of experiments documented in Figure 2 the quantum yield of $Me_3SiSiMe_3$ extrapolates to 0.55 ± 0.05 at zero N_2O concentration:

$$\lim_{\mathrm{N_2O}\to 0}\Phi(\mathrm{Me_3SiSiMe_3}) = a \approx 0.55 \pm 0.05 \quad \text{(XI)}$$

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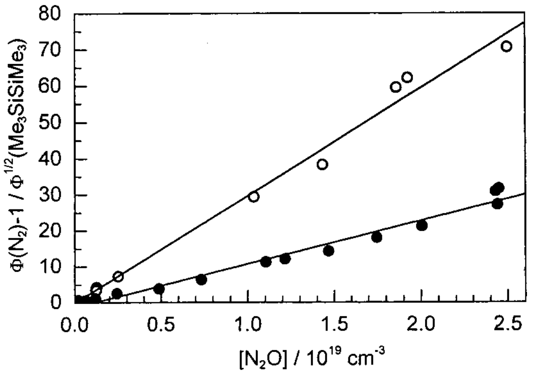

Figure 13. Determination of the relative rate constant $k_5/k_4^{1/2}$ from the experimental results of the N_2O dependence study, employing eq XIIa. $I_{abs} = 6.3 \times 10^{12}$ cm^{-3} s^{-1} (○); $I_{abs} = 2.66 \times 10^{13}$ cm^{-3} s^{-1} (●).

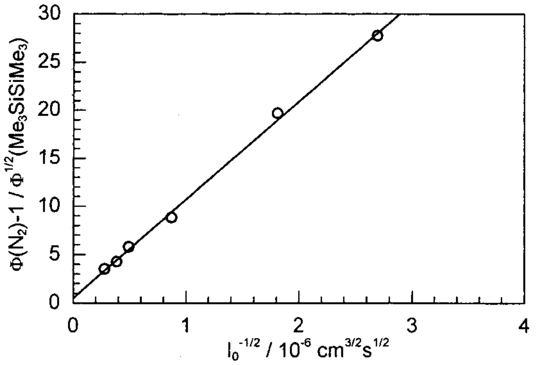

Figure 14. Determination of the relative rate constant $k_5/k_4^{1/2}$ from the experimental results of the dependence on light intensity study, employing eq XIIa. $[N_2O] = 1.24 \times 10^{18}$ cm^{-3}.

The limiting quantum yield of $Me_3SiOSiMe_3$ is very similar to this value, which means that *c* is close to 1 (eq Ia). Under the prevailing conditions $Me_2Si{=}CH_2$ is almost quantitatively converted to $Me_3SiOSiMe_3$ via reaction 10. If this is also true in the system $Hg/H_2/N_2O/Me_3SiH$, then, when H_2O is added in excess (Figure 9), the following relation should apply:

$$\Phi_a(Me_3SiOSiMe_3) - \Phi_p(Me_3SiOSiMe_3) = 0.5(\Phi_p(Me_3SiOH) - \Phi_a(Me_3SiOH))$$

This is approximately observed.

Kinetic Analysis. We are now able to test the mechanism in a more quantitative way and determine the rate constant for reaction 5 relative to the self-combination of Me_3Si radicals, reaction 4.

$$\frac{\Phi(N_2) - 1}{\Phi^{1/2}(Me_3SiSiMe_3)} = \frac{k_5}{k_4^{\ 1/2}}[N_2O]\frac{1}{I_{abs}^{\ \ 1/2}} \quad (XIIa)$$

In eq XIIa we used the fact that the quantum yield of N_2 formed in reaction 5 is given by $\Phi(N_2) - 1$. As can be seen from the results presented in Figures 13 and 14, the dependence of the left-hand side of relation XIIa on both N_2O concentration and $I_{abs}^{-1/2}$ is linear, as predicted by the mechanism.

Combination of the relations Ia, IIa, and IIIa allows $\Phi(N_2) - 1$ to be replaced by $(1 - 2(1 - c)(1 - b))/(1 - (1 - c)(1 - b))\Phi(Me_3SiOSiMe_3) + \Phi(Me_3SiOH)$. In the limit of $c = 1$ we obtain

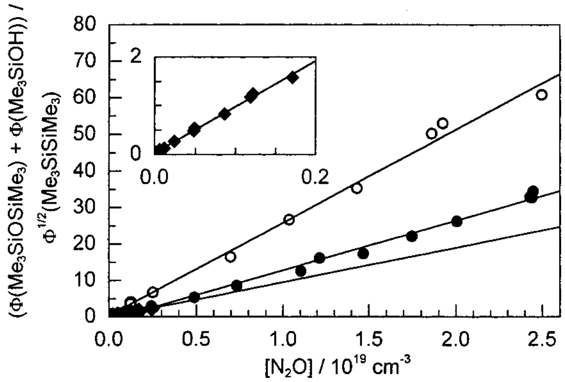

Figure 15. Determination of the relative rate constant $k_5/k_4^{1/2}$ from the experimental results of the N_2O dependence study, employing eq XIIb. $I_{abs} = 6.3 \times 10^{12}$ cm^{-3} s^{-1} (○); $I_{abs} = 2.66 \times 10^{13}$ cm^{-3} s^{-1} (●); $I_{abs} = 2.66 \times 10^{13}$ cm^{-3} s^{-1}, $[H_2] = 1.7 \times 10^{19}$ cm^{-3} (enlarged in the inset) (◆).

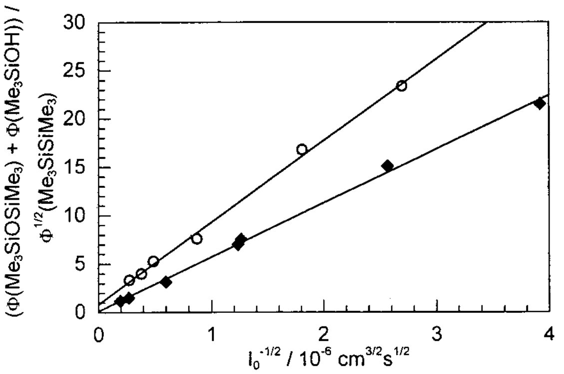

Figure 16. Determination of the relative rate constant $k_5/k_4^{1/2}$ from the experimental results of the dependence on light intensity study, employing eq XIIb. $[N_2O] = 1.24 \times 10^{18}$ cm^{-3} for both experiments, without H_2 (○), $[H_2] = 1.2 \times 10^{19}$ cm^{-3} (◆).

$$\frac{\Phi(Me_3SiOSiMe_3) + \Phi(Me_3SiOH)}{\Phi^{1/2}(Me_3SiSiMe_3)} = \frac{k_5}{k_4^{\ 1/2}}[N_2O]\frac{1}{I_{abs}^{\ \ 1/2}} \quad (XIIb)$$

In the experiments with excess H_2 (Figure 8), the Me_3Si radicals are generated by reaction of H atoms with the Si−H bond. N_2 was not determined or could only be determined with low accuracy. Therefore in this case only relation XIIb can be used to test the mechanism. No H_2O is formed, and therefore the value of *c* should be 1. The required linear dependence of the left-hand side of eq XIIb on N_2O concentration and absorbed intensity is indeed obeyed (Figures 15 and 16). The values of the relative rate constants obtained at room temperature are compiled in Table 2. The mean of these values is given by $k_5/k_4^{1/2} = (6.5 \pm 1.3) \times 10^{-12}$ cm$^{3/2}$ s$^{-1/2}$.

The Formation of Me_3SiOH. The formation of Me_3SiO seems to be correctly described by our mechanism. The next important step, the formation of Me_3SiOH in

Table 2. Values of the Relative Rate Constant $k_5/k_4^{1/2}$

equation	Figure	$k_5/k_4^{1/2}/10^{-12}$ cm$^{3/2}$ s$^{-1/2}$
XIIa	15 (○)	7.5
XIIa	15 (●)	6.2
XIIa	16 (○)	8.3
XIIb	17 (○)	6.4
XIIb	17 (●)	7.0
XIIb	17 (◆)	4.9
XIIb	18 (○)	6.8
XIIb	18 (◆)	4.5

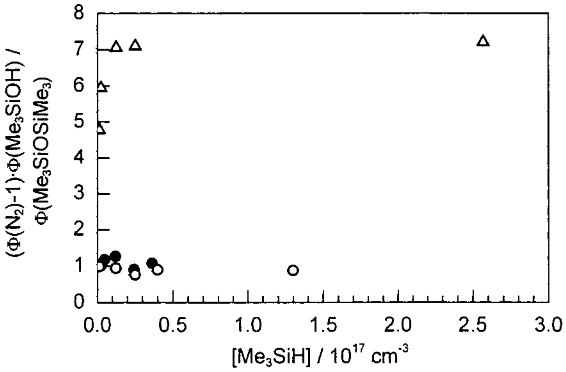

Figure 17. Dependence on Me_3SiH concentration under different experimental conditions, employing eq XIV. $I_{abs} = 7.6 \times 10^{12}$ cm^{-3} s^{-1}, $[N_2O] = 1.24 \times 10^{18}$ cm^{-3} (○); $I_{abs} = 2.66 \times 10^{13}$ cm^{-3} s^{-1}, $[N_2O] = 2.44 \times 10^{18}$ cm^{-3} (●); $I_{abs} = 7.0 \times 10^{12}$ cm^{-3} s^{-1}, $[N_2O] = 6.15 \times 10^{18}$ cm^{-3} (△).

the chain propagating reaction 8, can be tested by the following expression:

$$\frac{(\Phi(N_2) - 1)\Phi(Me_3SiOH(8))}{\Phi(Me_3SiOSiMe_3(6))} = \frac{k_5k_8}{k_6}[N_2O][Me_3SiH]\frac{1}{I_{abs}} \quad (XIII)$$

The quantum yields of Me_3SiOH formed in reaction 8 and of $Me_3SiOSiMe_3$ formed in reaction 6 can be expressed by the total quantum yields of these products. Assuming $c = 1$ we obtain

$$\frac{(\Phi(N_2) - 1)\Phi(Me_3SiOH)}{\Phi(Me_3SiOSiMe_3)} = \frac{k_5k_8}{k_6 + k_9}[N_2O][Me_3SiH]\frac{1}{I_{abs}} \quad (XIV)$$

When the left-hand side is plotted versus $[Me_3SiH]$, a straight line through the origin would be expected. As can be seen from Figure 17, no such dependence is observed, and this leads to the conclusion that the formation of Me_3SiOH is not fully described by our mechanism.

To achieve the observed lack of dependence of the formation of Me_3SiOH on Me_3SiH concentration, at least one additional intermediate has to be introduced into the mechanism. The range of products identified in the present work gives no indication as to the nature of such an intermediate. We therefore restrict ourselves to the discussions of mechanisms closely related to the one given above and for which certain relevant experimental observations exist.

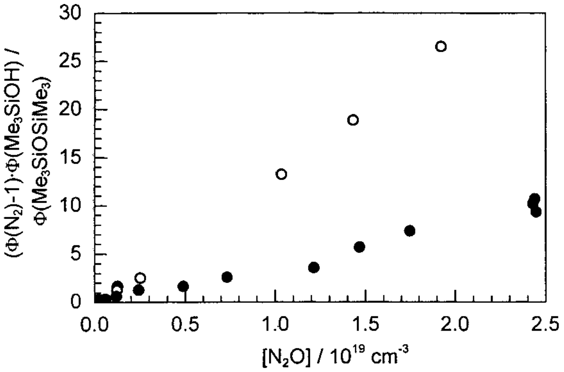

Figure 18. Dependence on N_2O concentration under different experimental conditions, employing eq XV. $[Me_3SiH] = (1.22 \pm 0.01) \times 10^{16}$ cm^{-3}, $I_{abs} = (2.66 \pm 0.06) \times 10^{13}$ cm^{-3} s^{-1}, $t = 60$ s (●); $[Me_3SiH] = (1.25 \pm 0.01) \times 10^{16}$ cm^{-3}, $I_{abs} = (6.3 \pm 0.9) \times 10^{12}$ cm^{-3} s^{-1}, $t = 120$ s (○).

Heterogeneous formation of Me_3SiOH on the reaction vessel wall has been postulated in a previous investigation.[8] The simplest way to make the formation of Me_3SiOH independent of Me_3SiH concentration is to postulate that the diffusion of the Me_3SiO radical to the wall

$$Me_3SiO \rightarrow Me_3SiO_w \quad (12)$$

is the rate-controlling step. In this case the following expression is obtained:

$$\frac{(\Phi(N_2) - 1)\Phi(Me_3SiOH)}{\Phi(Me_3SiOSiMe_3)} = \frac{k_5k_{12}}{k_6 + k_9}[N_2O]\frac{1}{I_{abs}} \quad (XV)$$

As k_{12} is inversely proportional to the pressure, the expression on the left-hand side of eq XV is not only independent of $[Me_3SiH]$ but also independent of the concentration of N_2O, the main component of the reaction mixture. This predicted lack of dependence of relation XV on N_2O concentration is in contradiction with the experimental results (Figure 18).

A more likely alternative to reaction 12 as the rate-determing step is the heterogeneous formation of Me_3SiOH. The lack of dependence of relation XV on the Me_3SiH concentration is only ensured if the abstraction process follows a Langmuir–Rideal type reaction and if the surface is saturated with Me_3SiH over the whole range of Me_3SiH partial pressures.[25] Experimentally there are no indications that the silanol formation is taking place heterogeneously. Increasing the surface-to-volume ratio only decreases the silanol quantum yield (Figure 7). Changing the nature of the surface by Teflon coating has no effect (Figure 7). Only an acid surface causes a drastic decrease of Me_3SiOH accompanied by an increase of $Me_3SiOSiMe_3$. This can be explained by the acid-catalyzed condensation reaction:

$$2\ Me_3SiOH \rightarrow Me_3SiOSiMe_3 + H_2O \quad (13)$$

Another possibility that could explain the lack of dependence of Me_3SiOH formation on Me_3SiH concentration is the involvement of vibrationally excited species in our mechanism. The formation of a Si–O bond

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(25) Laidler, K. J. *Chemical Kinetics*, 3rd ed.; Harper & Row: New York, 1987.

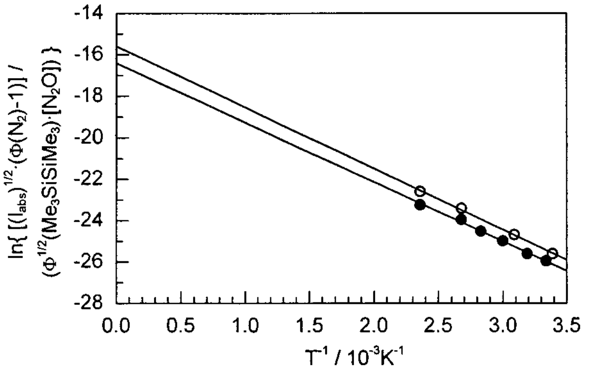

Figure 19. Arrhenius plot for $k_5/k_4^{1/2}$. $I_{abs} = 7.6 \times 10^{12}$ $cm^{-3}\ s^{-1}$, $[N_2O] = (1.23 \pm 0.06) \times 10^{18}\ cm^{-3}$ (○); $I_{abs} = 1.75 \times 10^{13}\ cm^{-3}\ s^{-1}$, $[N_2O] = (1.18 \pm 0.04) \times 10^{18}\ cm^{-3}$ (●).

is a very exothermic process. The heat of reaction for reaction 5 amounts to $\Delta_r H°(5) = -302$ kJ/mol.[13,26,27] It is conceivable that a fraction of the excited Me_3SiO radicals are trapped in a state that undergoes a very fast abstraction reaction independent of the actual Me_3SiH concentration. We were not able to suggest a mechanism along these lines that is also in accord with all other experimental results. In this connection the work of Getoff et al.,[16] who studied the radiolysis of Et_3SiH in the presence of N_2O in the liquid phase, is relevant. Et_3SiOH was also a major product in their experiments, and an identical mechanism, including the analogue of reaction 8, for its formation was suggested. It is unlikely that heterogeneous processes or vibrationally excited species played a role under their experimental conditions. No obvious intermediate presents itself, and we are therefore not able to make any further suggestions regarding the mechanism of formation of Me_3SiOH beyond

$$Me_3SiO + Me_3SiH \rightarrow\rightarrow Me_3SiOH + Me_3Si \quad (8a)$$

Temperature Dependence. The temperature dependence of the system has been studied at a N_2O pressure where $Me_3SiSiMe_3$ is still a major product at low temperature (Figure 6). If reactions 5 and 8a have to overcome an activation barrier, we expect the quantum yields of N_2 and Me_3SiOH to grow and that of $Me_3SiSiMe_3$ to decrease with increasing temperature. As can be seen in Figure 6, this is the case up to 350 K, and we assume that up to this temperature our mechanism is still valid. As a consequence, a plot of the logarithm of the left-hand side of relation XIIa versus $1/T$ should give us $E_A(5) - 1/2E_A(4)$. From the Arrhenius plot shown in Figure 19 and assuming a negligible activation energy for the combination of Me_3Si radicals, the activation energy obtained is $E_A(5) = 23 \pm 1$ kJ/mol. Choosing the literature value[28,29] for $A(4) = k_4 = 3 \times 10^{-11}\ cm^3\ s^{-1}$, we obtain for the A-factor, $A(5) = (6 \pm 3) \times 10^{-13}\ cm^3\ s^{-1}$.

At a temperature of about 400 K a change in the mechanism is discernible. The decrease of $Me_3SiOSiMe_3$ and Me_3SiOH signals a new reaction path either for Me_3Si or for Me_3SiO radicals. The limiting quantum yield of 3 for N_2 proves that Me_3Si radicals still undergo reaction 5 at temperatures higher than 350 K. It must therefore be the Me_3SiO radical for which a new channel is opened. Hints as to the nature of the new channel can be gained from the reaction products Me_3SiOMe and $Me_3SiOSiMe_2OH$, which can be formed in the following reactions:

$$Me_3SiO \rightarrow Me + Me_2Si{=}O \quad (14)$$

$$Me + Me_3SiO \rightarrow Me_3SiOMe \quad (15)$$

$$Me_2Si{=}O + Me_3SiOH \rightarrow Me_3SiOSiMe_2OH \quad (16)$$

Reaction 14 is driven by the large Si−O π-bond energy[26] and is analogous to the splitting off of a methyl group in the Me_3SiCH_2 radical.[30] The methyl radical reacts with the radical present in the largest concentration, Me_3SiO (reaction 15), and silanones are known to react with alcohols[31] as in reaction 16.

Minor Products. The mechanism proposed does not yet take into account the formation of the minor products. All these products, with the exception of $Me_3SiCH_2SiMe_2H$, have in common that their quantum yields decrease with the addition of SF_6 (Figure 5). This indicates the participation of vibrationally excited species in our system, as SF_6 is known to be an efficient moderator of vibrational excitation. The formation of the very strong Si−O bond is a likely cause for the appearance of these minor products. In the mechanism developed so far two such steps occur (reactions 5 and 6). Reaction 6, especially, is very exothermic ($\Delta_r H°(6) = -584\ kJ\ mol^{-1}$),[26] while the heat of reaction 5 is only half as large ($\Delta_r H°(5) = -302\ kJ\ mol^{-1}$).[13,26,27] It is even possible that the exothermicity of reaction 5 is not completely deposited in Me_3SiO.

There are a number of decomposition channels open for vibrationally excited $Me_3SiOSiMe_3$ molecules:

$$Me_3SiOSiMe_3 \rightarrow CH_4 + Me_3SiOSiMe{=}CH_2 \qquad \Delta_r H°(17) \approx 210\ kJ\ mol^{-1} \quad (17)$$

$$\rightarrow Me_3SiOH + Me_2Si{=}CH_2 \qquad \Delta_r H°(18) = 338\ kJ\ mol^{-1} \quad (18)$$

$$\rightarrow CH_3 + Me_3SiOSiMe_2 \qquad \Delta_r H°(19) \approx 370\ kJ\ mol^{-1} \quad (19)$$

From the heats of reaction values we see that splitting off a methane molecule is energetically the least expensive process by far (estimated from the analogous Me_4Si decomposition),[27] but the system has to overcome an additional barrier of unknown height. Processes 18 and 19 are energetically much more demanding[26,27] but are characterized by small and negligible additional activation barriers, respectively. A coarse estimate within RRK theory taking $s_{eff} = 21$ (obtained by neglecting the H atoms in the molecule) and A-factors in the range 10^{14}−$10^{16}\ s^{-1}$ suggests, however, that a unimolecular decomposition according to reactions 18 and 19 would be too slow to compete with collisional deactivation.

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[30] Potzinger, P.; Reimann, B.; Roy, R. S. *Ber. Bunsen-Ges. Phys. Chem* **1981**, *85*, 1119.
[31] Davidson, I. M. T.; Fenton, A. *Organometallics* **1985**, *4*, 2060.

The enthalpy of reaction 14 can be estimated from the analogous unmethylated system[7] to be $\Delta_rH°(14) \approx 100$ kJ mol^{-1}. The activation barrier for the back-reaction is unknown. It may be as small as for the radical addition to the Si═C double bond.[14] The energetically low lying decomposition channel and the small number of internal degrees of freedom compensate for the smaller degree of vibrational excitation and make Me_3SiO a likely candidate for a chemically activated decomposition.

The product CH_4 can be explained most simply by the molecular process 17. This process seems to have just the right activation energy to allow it to be observed at low pressure. As can be seen in Figure 5, the yield of CH_4 drops very fast with increasing vibrational deexcitation via an increase in SF_6 concentration. The molecular formation is also supported by the temperature and intensity experiments (Figures 6 and 10). The concurrent appearance of $Me_3SiOSiMe{=}CH_2$ is also in agreement with the observed products. The formation of the two products $Me_3SiOSiMe_2OH$ and $Me_3SiOSiMe_2OSiMe_3$ can be explained by reactions 20 and 21:

$$Me_3SiOSiMe{=}CH_2 + H_2O \rightarrow Me_3SiOSiMe_2OH \quad (20)$$

$$Me_3SiOSiMe{=}CH_2 + Me_3SiOH \rightarrow Me_3SiOSiMe_2OSiMe_3 \quad (21)$$

At the outset both products decrease with increasing N_2O pressure (Figure 2) but then pass through a minimum, indicating a second path of formation. Addition of MeOH would be expected to cause these two products to diminish, in agreement with the experimental results (Figure 4). $Me_3SiOSiMe_2OH$ drops below the detection limit in the experiments involving the Hg-sensitized photolysis of hydrogen, as there is no H_2O generated during this reaction.

The decomposition of Me_3SiO (reaction 14) supplies two new intermediates, Me and $Me_2Si{=}O$. Methyl radicals undergo radical−radical reactions with those radicals present in the highest stationary concentration:

$$Me + Me_3Si \rightarrow Me_4Si \quad (22)$$

$$Me + Me_3SiO \rightarrow Me_3SiOMe \quad (15)$$

Me_4Si disappears rapidly with increasing N_2O concentration (Figure 2) because the stationary concentration of Me_3Si radicals, as well as the supply of Me, decreases with increasing N_2O pressure. Reaction 14 seems to be much less affected than reaction 17 by an increase in pressure, as can be inferred from the dependence of $\Phi(Me_3SiOMe)$ on N_2O concentration (Figure 2).

Dimethylsilanone reacts with Me_3SiOH in reaction 16, representing another source of $Me_3SiOSiMe_2OH$ which predominates at high N_2O concentration. Addition of Me_3Si or Me_3Si and Me_3SiO radicals to the Si═O double bond explains the formation of the products $Me_3SiOSiMe_2OSiMe_3$ and $Me_3SiSiMe_2OSiMe_3$:

$$Me_2Si{=}O + Me_3Si + Me_3SiO \rightarrow Me_3SiOSiMe_2OSiMe_3 \quad (23)$$

$$Me_2Si{=}O + 2\ Me_3Si \rightarrow Me_3SiSiMe_2OSiMe_3 \quad (24)$$

The product $Me_3SiSiMe_2CH_2SiMe_3$ is always present when $Me_2Si{=}CH_2$ and Me_3Si radicals are generated together in a system and is formed by an analogous reaction to reaction 24.[14] $Me_3SiCH_2SiMe_2H$ has been observed in the Hg-sensitized photolysis of Me_3SiH and was attributed to H abstraction from the CH bond followed by combination with a Me_3Si radical.[11]

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