Reaction of O(³P) with Hexamethyldisilane[†]

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The title reaction has been investigated at room temperature in a discharge flow system and also by stationary Hg(${}^{3}P_{1}$)-sensitized N₂O photolysis experiments. By far the most important reaction is the insertion of O(${}^{3}P$) atoms into the Si–Si bond yielding a vibrationally excited hexamethyldisiloxane. The rate constant for this reaction has been measured to be $(1.3 \pm 0.3) \times 10^{-13}$ cm³ s⁻¹. The vibrationally excited hexamethyldisiloxane could not be stabilized at pressures up to 1 bar, decomposing mainly by Si–C bond cleavage. A reaction mechanism is proposed to account for the observed products.

Introduction

In a recent publication¹ we reported on the reaction of O atoms with trimethylsilane in which the primary step is hydrogen abstraction from the silicon center. The present work is concerned with the reaction of O atoms with hexamethyldisilane. Three different reaction modes can be envisaged: (i) hydrogen abstraction from the C-H bond, expected by analogy with oxygen atom attack on alkanes to be a rather slow process,² (ii) substitution at a silicon center analogous to the reaction of hydrogen atoms with disilanes,^{3,4} and (iii) insertion into the Si-Si bond forming a vibrationally excited siloxane molecule. In this paper it will be shown that the reaction proceeds predominantly by mechanism (iii). The kinetics and mechanism of the reaction have been investigated by the discharge flow technique, and by a complementary study of the products formed in stationary photolysis experiments.

Experimental Section

The discharge flow apparatus has been described in detail in our previous paper.¹ All flow experiments were carried out either in the quartz reactor with Teflon rings inserted at regular distances (reactor B, see ref 1), or in the Pyrex reactor coated with halocarbon wax (reactor C). Argon or helium was used as the carrier gas, and O atoms were generated by titration of N atoms with NO. Rate constants were determined with O atoms in excess (1.2 $\times 10^{14}$ cm⁻³ \leq [O] $\leq 6.5 \times 10^{14}$ cm⁻³, with [Me₃SiSiMe₃] smaller by a factor of 15-75).

Stationary photolysis experiments were performed in the same manner as described previously.¹ The noncondensable fraction was analyzed by mass spectrometry (MAT 311A) and its pressure measured by a membrane manometer (Datametrics 511-10); all other products were analyzed quantitatively by gas chromatography (Carlo Erba 2000, 50-m glass capillary column OV 1).

Product peaks with a retention time shorter than Me₃SiSiMe₃ were identified by comparison with authentic reference samples. Most of the more abundant higher molecular weight products like Me₃SiOSiMe₂OMe, Me₃SiSiMe₂CH₂Me, Me₃SiOSiMe₂OSiMe₃, and Me₃SiOSiMe₂OSiMe₂OSiMe₃ were associated with the different GC peaks by means of their known mass spectra. One mass spectrum, consisting of the major fragment peaks m/e 149 (100), m/e 133 (60), and m/e 75 (25), was tentatively assigned to the substance Me₃SiOSiMe₂OH for the following reasons: methylated disiloxanes are characterized by a m/e (parent-15) peak and a m/e (parent-31) peak;⁵ m/e 75 is characteristic of a Me₂SiOH group in the molecule. The GC peak exhibits tailing in a similar way to that shown by Me₃SiOH, thus providing further evidence for the presence of the SiOH group.

The purities of gases as stated by the manufacturers were as follows: He 99.996%, Ar 99.997%, $N_2 \ge 99.99\%$, O_2 99.995%, NO > 99.8%, $N_2O \ge 99.0\%$, and $Me_3SiSiMe_3 \ge 99.6\%$. Argon was passed over P_2O_5 to remove traces of moisture. N_2 and O_2

were used as delivered. NO was passed over Ascarite (Fluka) to remove higher oxides. N_2O , whose main impurities were N_2 and O_2 , was degassed before use by several freeze-pump-thaw cycles. $Me_3SiSiMe_3$ contained two impurities, $Me_3SiOSiMe_3$ (0.3%) and $Me_3SiCH_2SiMe_2H$ (0.03%).

Quantum yield determinations were accomplished by using mercury-sensitized N_2O photolysis in the presence of butene-1 as an actinometer. The N_2 quantum yield was assumed to be unity.⁶

Results and Discussion

The rate constant for

$$O(^{3}P) + Me_{3}SiSiMe_{3} \rightarrow products$$
 (1)

has been measured under pseudo-first-order conditions (O(³P) in excess) by following the decay of Me₃SiSiMe₃ at m/e 146 and m/e 131. A typical first-order plot is shown in Figure 1. The dependence of the pseudo-first-order rate constants, $k^1(1)$, on oxygen atom concentration is presented in Figure 2, from which we derive the bimolecular rate constant $k(1) = (1.33 \pm 0.09) \times 10^{-13}$ cm³ s⁻¹ (95% confidence limits, precision only; the corresponding accuracy is estimated to $\approx 23\%$). This rate constant is smaller by an order of magnitude than that for the corresponding reaction with trimethylsilane, which involves hydrogen abstraction from the silicon center,¹ but is still too large for abstraction from a C-H bond:

$$O(^{3}P) + Me_{3}SiSiMe_{3} \rightarrow OH + Me_{3}SiSiMe_{2}CH_{2}$$
(1-1)

The rate constant obtained in the present work can be compared with a rate constant calculated from the relation given by Huie and Herron² for hydrogen abstraction by O atoms from the corresponding alkane, Me₃CCMe₃. Our rate constant is a factor of 20 higher than that for O atom attack on the alkane. Further evidence that abstraction from the C-H bond is not an important process is provided by the absence of H₂O in the products of the flow experiments. If abstraction had occurred, the OH radical produced in (1-1) would have formed H₂O by a further H abstraction reaction.

The behavior of O atoms toward $Me_3SiSiMe_3$ and Me_3SiH is similar to that shown by the reactions of H atoms with these two substances: the rate constant for the reaction H + $Me_3SiSiMe_3$ is a factor of 10 lower⁴ than for H + Me_3SiH .⁷ Since the attack of H atoms on $Me_3SiSiMe_3$ is known to proceed by a substitution reaction, this suggests that the corresponding O atom reaction might also proceed by this mechanism (1-2)

 $O(^{3}P) + Me_{3}SiSiMe_{3} \rightarrow Me_{3}SiO + Me_{3}Si$ (1-2)

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[†]Dedicated to Prof. Dr. D. Schulte-Frohlinde on the occasion of his 60th birthday.

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Figure 1. First-order plot for reaction 1 with O atoms in excess. I and I_0 are the intensities at m/e 146 with discharge on and discharge off, respectively. z is the distance between the tip of the injector and the first skimmer.



Figure 2. Dependence of the pseudo-first-order rate constant $k^{1}(1)$ on O atom concentration. Open circles: reactor B, carrier gas Ar, substrate decay measured at m/e 146. Filled circles: reactor B, carrier gas Ar, substrate decay measured at m/e 131. Squares: reactor C, carrier gas He, substrate decay measured at m/e 146.

The only products observed in the flow experiments were CH_3 , CH_4 , and CH_2O . CH_4 and CH_3 can be explained in terms of the combination of O atoms with the silyl radicals formed in (1-2) to give vibrationally excited siloxy radicals, which under these conditions subsequently decompose. Formaldehyde is formed in the reaction of O atoms with CH_3 . These kinds of reactions were shown to be responsible for the same products observed in the system $O + Me_3SiH$.¹

At this point in our discussion of the likely mechanism for the reaction of O atoms with Me₃SiSiMe₃ we introduce evidence from our experiments involving the Hg sensitized photolysis of N₂O in the presence of Me₃SiSiMe₃. If reaction 1-2 is the major primary process, the products of the reaction should be very similar to those of the corresponding $Hg/N_2O/Me_3SiH$ system.¹ By analogy with this system, the silvl radicals would be expected to either combine with a siloxy radical yielding Me₃SiOSiMe₃, or abstract oxygen from N2O producing a second siloxyl radical. Two siloxy radicals would also form Me₃SiOSiMe₃, but the mechanism involved is not yet characterized. (One possibility, explicitly referred to in ref 1, involves combination of two siloxy radicals, thus yielding bis(trimethylsilyl)peroxide which is subsequently decomposed at the hot GC column.) Thus we expect N_2 and Me₃SiOSiMe₃ to be the two main products. This expectation is not fulfilled by the product spectrum given in Table I. From the table, two things are noteworthy, the presence of large amounts of ethane, and the presence of the SiOSi group in most of the silicon containing compounds.

We also carried out the photolysis over a wider range of N_2O pressures (1.2 × 10⁴-9.7 × 10⁴ Pa). No major changes in the product distribution were observed except that the quantum yield of N_2 increased from 1.4 to 1.8.

The appearance of methyl radicals (which combine to give ethane) as the main product is difficult to explain unless by a

TABLE I: Product Quantum Yields in the Hg-Sensitized Decomposition of N_2O in the Presence of Hexamethyldisilane^a

N ₂	1.5
CH ₄	0.03
C_2H_6	0.25
Me₄Si	0.01
Me ₃ SiOH	0.11
Me ₃ SiOSiMe ₃	0.05
Me ₃ SiOSiMe ₂ OMe	0.10
Me ₃ SiOSiMe ₂ OH	0.23
Me ₃ SiSiMe ₂ CH ₂ Me	0.07
Me ₃ SiOSiMe ₂ OSiMe ₃	0.05
Me ₃ SiOSiMe ₂ OSiMe ₂ OSiMe ₃	0.06

^aExperimental conditions: 0.16 Pa of Hg, 133 Pa of Me₃SiSiMe₃, 2.5 \times 10⁴ Pa of N₂O.

unimolecular decomposition of a chemically activated species. The only process which can supply enough energy to overcome stabilization at pressures up to 10^5 Pa in this system which has a rather large number of internal degrees of freedom is the spin forbidden insertion of O atoms into the SiSi bond:

$$O(^{3}P) + Me_{3}SiSiMe_{3} \rightarrow Me_{3}SiOSiMe_{3}$$
 (1-3)

This reaction undoubtedly involves a number of mechanistic steps. Presumably the O atoms add to the hexamethyldisilane forming a complex in the triplet state. This complex must then undergo interconversion in the singlet state with concomitant formation of two Si–O bonds and the breaking of the Si–Si bond. Reaction 1-3 is exothermic by 670 kJ/mol^{8,9} which means that the Me₃SiOSiMe₃ is highly vibrationally excited. Within the limited pressure range, up to 10^5 Pa, no stabilization was observed.

A plausible reaction mechanism, which explains the products observed is given in Figure 3. The energetically most favorable decomposition pathways are the formation of a silaethylene with concomitant generation of methane (2) ($\Delta H(2) \simeq 190 \text{ kJ/mol}$,¹⁰ $E_a \simeq 300 \text{ kJ/mol}^{11}$), and the formation of a dimethylsilaethylene together with Me₃SiOH (3). The latter process has a larger endothermicity, $\Delta H(3) \simeq 300 \text{ kJ/mol}$,¹⁰ than the methane forming reaction, but it is unlikely that its activation energy will be very much higher.

Simple bond breaking processes must also be considered. These reactions have a high energetic requirement but they also have high A factors and may, in the case of large internal excitation, successfully compete with the two low energy processes. Simple RRK considerations suggest that a likely process of this kind is Si–C bond cleavage ($E_a \simeq 360 \text{ kJ/mol}^{10}$), which in this case leads to CH₃ radical formation, reaction 4. Table I shows that this reaction not only occurs but that it is the major pathway for the decomposition of the excited siloxane species.

A number of products like C_2H_6 , Me₃SiOSiMe₂OSiMe₂OSiMe₃, Me₃SiOSiMe₂OMe, and Me₃SiOSiMe₃ can be explained in a straightforward manner by radical combination if one assumes in addition that Me₃SiOSiMe₂. radicals abstract oxygen from N₂O (5). A similar reaction involving O atom abstraction from N₂O has been shown to occur with trimethylsilyl radicals.¹ Reaction 5 also accounts for our finding that the N₂ quantum yield is in excess of unity.

However, there are products, notably $Me_3SiOSiMe_2OH$, which are not taken account of by these reactions. The most straightforward reaction to explain the formation of $Me_3SiOSiMe_2OH$ would be

$$Me_3SiOSiMe_2O + Me_3SiSiMe_3 \rightarrow$$

 $Me_3SiOSiMe_2OH + Me_3SiSiMe_2CH_2$ (10)

There are, however, some objections against (10). This reaction has been shown not to be an important process in the Me_3SiO + Me_3SiH system.¹ Further, in the present work only 30% of the

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Figure 3. Reaction mechanism. Stable end products, in boxes, have been measured quantitatively; results are shown in Table I.

 $Me_3SiSiMe_2CH_2$ radical was recovered in the products. One would expect that the $Me_3SiSiMe_2CH_2$ radical would combine with one of the three most abundant radicals, CH_3 (16), $Me_3SiOSiMe_2$, and $Me_3SiOSiMe_2O$, yielding $Me_3SiSiMe_2CH_2Me$, $Me_3SiSiMe_2CH_2SiMe_2OSiMe_3$, and $Me_3SiSiMe_2CH_2OSiMe_2OSiMe_3$. Only $Me_3SiSiMe_2CH_2Me$ has been identified.

Disproportionation of a $Me_3SiOSiMe_2$ with a $Me_3SiOSiMe_2O$ -radical, reaction 11, would be another route to the silanol product, $Me_3SiOSiMe_2OH$.

$$Me_{3}SiOSiMe_{2} + Me_{3}SiOSiMe_{2}O \rightarrow Me_{3}SiOSiMe_{2}OH + Me_{3}SiOSiMe_{2}CH_{2} (11)$$

Some could also come from a reaction of $Me_3SiOSiMe=CH_2$ with water (12), whose presence in trace amounts is difficult to avoid.

We are then left to find an explanation for the formation of $Me_3SiOSiMe_2OSiMe_3$ and tetramethylsilane. It is possible to explain these products within the framework of reaction 1-3 if one postulates a substitution reaction

$$\begin{array}{r} Me_{3}SiOSiMe_{2}O \cdot + Me_{3}SiSiMe_{3} \rightarrow \\ Me_{3}SiOSiMe_{2}OSiMe_{3} + SiMe_{3} \cdot (13) \end{array}$$

It seems to us more likely, however, that primary process 1-2 occurs followed by the radical combination reactions 14 and 15.

Reaction 1-1 has also been included in Figure 3 because its complete absence has not been shown. What can be shown, however, is the predominance of reaction 1-3. From the data given in Table I one calculates a quantum yield of 0.9 for reaction 1-3.

Additional support for the proposed mechanism comes from liquid-phase experiments involving the insertion of oxygen atoms into the Si-Si bond of organodisilanes¹² as well as from the fact

that hexamethyldisiloxane undergoes the same decomposition pathways with other modes of excitation.^{5,13-15} A very detailed study of the decomposition of liquid Me₃SiOSiMe₃, excited by 185-nm photons, has been reported by Schuchmann et al.¹⁵ From their product analysis they deduced four decomposition channels: reactions 2, 3, 4, and to a very minor extent C-H bond cleavage. Reactions 2 and 4 make up 94% of the overall decomposition.

The mechanism for the reaction of O atoms with hexamethyldisilane has no counterpart in the alkane series, but shows similarities with the mechanism of O atoms with alkenes.¹⁶

The Si–Si bond also shows similarities with a C==C double bond in other reactions. Di- and polysilanes not only exhibit chargetransfer complexes with strong acceptor molecules^{17,18} but also undergo catalyzed $[\sigma_{2s} + \pi_{2s}]$ cycloaddition reactions.¹⁹

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Registry No. Me₃SiSiMe₃, 1450-14-2; O₂, 7782-44-7.

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