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A mechanistic investigation of (Me₃Si)₃SiH oxidation

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Abstract

The interaction of (Me₃Si)₃SiH with O_2 is known to afford (Me₃SiO)₂Si(H)SiMe₃ in which the two oxygen atoms arise from the same oxygen molecule. In order to investigate the mechanism of this unusual reaction, the oxidation rates were measured in the temperature range 30–70 °C by following oxygen uptake in the presence and absence of hydroquinone as inhibitor. The rate constant for the spontaneous reaction of (Me₃Si)₃SiH with O_2 was determined at 70 °C to be $\sim 3.5 \times 10^{-5}$ M^{-1} s^{-1}. A sequence of the propagation steps is proposed by combining the previous and present experimental findings with some theoretical results obtained at the semiempirical level. These calculations showed that the silylperoxyl radical (Me₃Si)₃SiOO· undergoes three consecutive unimolecular steps to give (Me₃SiO)₂Si(·)SiMe₃. Evidence has been obtained that the rate determining step is the rearrangement of silylperoxyl radical to a dioxirane-like pentacoordinated silyl radical. Our findings are of considerable importance for the understanding of the oxidation of hydrogen-terminated silicon surfaces.
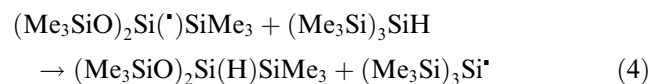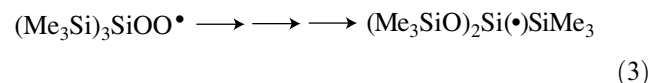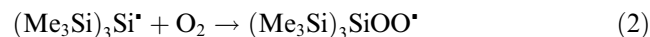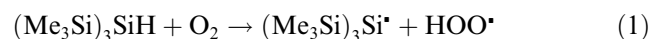© 2004 Elsevier B.V. All rights reserved.

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1. Introduction

(Me₃Si)₃SiH as pure material or in solution reacts spontaneously and slowly at room temperature with air or molecular oxygen, to form the siloxane derivative (Me₃SiO)₂Si(H)SiMe₃ in high yield [1]. The reaction is a radical chain process and it was demonstrated by means of oxygen-labeling experiments that the two oxygen atoms in the final product arise from the same oxygen molecule. However, the reaction sequence is not well understood. It is suggested that the spontaneously formed silyl radical (Eq. (1)) reacts with oxygen to form the silylperoxyl radical (Eq. (2)), which undergoes an unusual structural rearrangement affording another type of silyl radical with a siloxane backbone (Eq. (3)). Hydrogen abstraction from the starting silane by this radical gives the final product (Eq. (4)), thus completing the cycle of this chain reaction.

$$(Me_3Si)_3SiH + O_2 \rightarrow (Me_3Si)_3Si^\bullet + HOO^\bullet \quad (1)$$

$$(Me_3Si)_3Si^\bullet + O_2 \rightarrow (Me_3Si)_3SiOO^\bullet \quad (2)$$

$$(Me_3Si)_3SiOO^\bullet \longrightarrow \longrightarrow \longrightarrow (Me_3SiO)_2Si(\bullet)SiMe_3 \quad (3)$$

$$(Me_3SiO)_2Si(^\bullet)SiMe_3 + (Me_3Si)_3SiH$$
$$\rightarrow (Me_3SiO)_2Si(H)SiMe_3 + (Me_3Si)_3Si^\bullet \quad (4)$$

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Similar conclusions have been reached for the reaction of molecular oxygen with the homologous $(Me_3Si)_2$-Si(H)Me and for poly(hydrosilane)s of type $H(RSiH)_nH$ [2,3]. Kinetic studies carried out by two independent methods allowed the oxidizability of these silicon hydrides to be obtained [2,3]. Reaction (4) is thought to be the slow step of the cycle without concrete evidence and the oxidizability was accordingly assigned.

The rearrangement in Eq. (3) is not straightforward and a few consecutive unimolecular steps should be involved, the driving force being the strength of the silicon–oxygen bond. A possible route has been suggested but it lacks of any support [1]. Based on the above reaction sequence, an analogous mechanistic scheme has been recently proposed for the oxidation of hydrogen-terminated silicon surfaces by molecular oxygen [4]. Moreover, the ability of poly(hydrosilane)s to stabilize polypropylene during multiple extrusion has been assigned in part to their capabilities to scavenge the traces of oxygen present during the extrusion process [5]. In view of the potential application of this reaction in different areas of science [4,6], more information of the reaction mechanism is needed. Herein we report a kinetic investigation of the thermal-induced oxidation of $(Me_3Si)_3$-SiH as well as a theoretical study addressing the mechanism of the unusual rearrangement of Eq. (3).

2. Results and discussion

2.1. Semiempirical calculations

Preliminary investigations indicated that the PM3 method [7] is the most suitable approach to study the reactions of interest. Indeed, the PM3 method gives the best coincidence with experimental geometry and energy values for silicon-containing molecules and their corresponding species as compared with MINDO/3, MNDO and AM1 methods. All calculations were carried out by the unrestricted Hartree–Fock method with PM3 Hamiltonian and with full optimization of all geometrical parameters by the Davidon–Fletcher–Powell procedure [8].

We focused on the unimolecular transformation of silylperoxyl radical (Eq. (3)). The results are summarized in Scheme 1 and are referred as dependence of heats of formation of intramolecular complexes versus a single reaction coordinate.

It was previously suggested that a trimethylsilyl group might undergo an unusual 1,3-shift from the central silicon to the terminal oxygen in the silylperoxyl radical 1 [1,2]. However, this path was not found using the PM3 method in a natural intrinsic coordinate (angle) formed by O–Si–Si. We observed exclusively a 1,2-shift of $SiMe_3$ group to the neighboring oxygen while the terminal oxygen joined the central silicon so that the
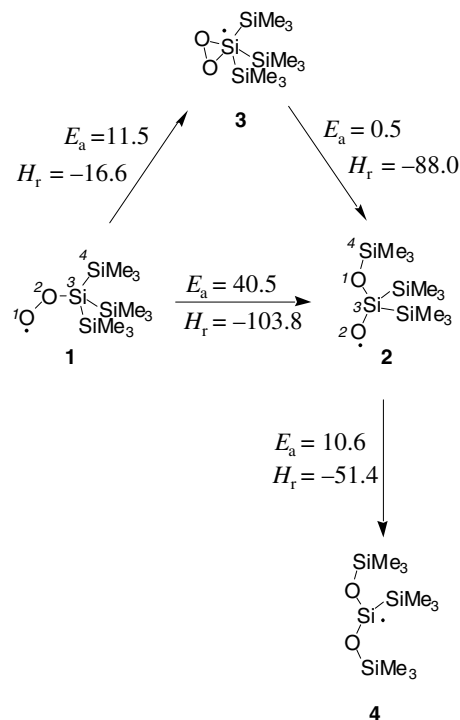
Scheme 1. Reaction barriers (E_a) and reaction enthalpies (H_r) in kcal/mol.

product radical 2 was formed in one step. We have considered two possible conformers of radical 1 for this "concerted" rearrangement. The reaction of the anti conformer (^1O–^2O–^3Si–^4Si) is shown in Scheme 1 (1→2) with a reaction barrier of 40.5 kcal/mol, whereas the reaction of the syn conformer (not shown) was associated with $E_a = 35.5$ kcal/mol. Both reactions lead to the same product and, therefore, they are energetically very similar. It should be noted that the size of 35–40 kcal/mol as reaction barrier is too high to coincide with the group rearrangement conditions observed experimentally. Indeed, the intermediacy of dioxirane-like penta-coordinate silyl radical 3 was found to play an important role in the reaction coordinates. It can be formed with a relatively low reaction barrier ($E_a = 11.5$ kcal/mol) followed by the 1,2-migration of a trimethylsilyl group with a negligible barrier ($E_a = 0.5$ kcal/mol) to give radical 2.
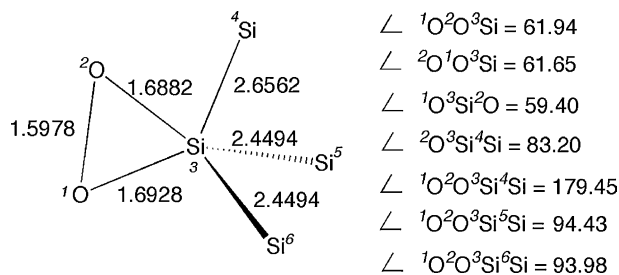
Scheme 2. PM3 optimized structure of radical 3 (methyl groups are omitted for clarity). Bonds in Å and angles in degrees.

The optimized structure of the pentacoordinated silyl radical **3** is shown in Scheme 2 [9]. It is worth mentioning that the two oxygens are nearly equivalent and the Si–Si bond lying on the plane of the three-membered ring is the one that participates in the migration. The schematic energy profile of this stepwise reaction (**1→3→2**) is depicted in Fig. 1 together with the concerted path (dashed line) for comparison. The resulting silyl-oxyl radical **2** is ready for a 1,2-shift of a SiMe$_3$ group to the nearest oxygen with an unpaired electron. Well-described and experimentally supported evidence for similar reactions have been reported [10]. Furthermore, calculations showed that a transition state barrier of 10.6 kcal/mol is needed for this rearrangement (**2→4**). Fig. 1 summarizes the progress of reaction from radical **1** to radical **4** via the intermediacy of radicals **3** and **2**. Barriers of 11.5, 0.5 and 10.6 kcal/mol exist for the three consecutive unimolecular paths with an overall exothermicity of 156 kcal/mol.

2.2. Kinetic studies

The radical chain mechanism reported in Eqs. (1)–(4) is based on oxygen- and deuterium-labeling product studies [1,2]. Furthermore, the oxidation of (Me$_3$Si)$_3$SiH is accelerated by radical initiation and retarded by common radical inhibitors (i.e., substituted phenols). In order to obtain kinetic support for this reaction sequence, the rates of (Me$_3$Si)$_3$SiH oxidation under a variety of conditions were measured by following oxygen uptake.

The oxidation rates (in $M\,s^{-1}$) were calculated by Eq. (5), where 6.82×10^{-4} was the coefficient constant of the manometric apparatus, $V(O_2)$ the volume in ml of oxygen uptake, t the time of oxygen uptake in min and V the sample volume in ml.

$$-\frac{d[O_2]}{dt} = 6.82 \times 10^{-4} \frac{V(O_2)}{Vt} \tag{5}$$

First, an experiment was planned in order to confirm the initiation step (Eq. (1)) and obtain kinetic data related to it. The rate of radical generation in thermal-induced oxidation of (Me$_3$Si)$_3$SiH was determined by the inhibitor method [11]. The hydroquinone (QH$_2$) was chosen as typical trap for peroxyl radicals (Eqs. (6) and (7)) [12].

$$ROO\cdot + HO{-}\langle\bigcirc\rangle{-}OH \longrightarrow ROOH + \cdot O{-}\langle\bigcirc\rangle{-}OH \tag{6}$$

$$ROO\cdot + \cdot O{-}\langle\bigcirc\rangle{-}OH \longrightarrow ROOH + O{=}\langle\bigcirc\rangle{=}O \tag{7}$$

The oxidation of (Me$_3$Si)$_3$SiH in benzene as the solvent was thermally initiated at 70 °C and the volume of oxygen uptake, $V(O_2)$, was measured over time in the absence or presence of QH$_2$. Fig. 2 shows the dependence of $V(O_2)$ vs. time in the absence (solid circles) and presence of 1.02×10^{-4} (open circles) and 1.14×10^{-4} M (solid squares) of QH$_2$. When QH$_2$ was present at concentration higher
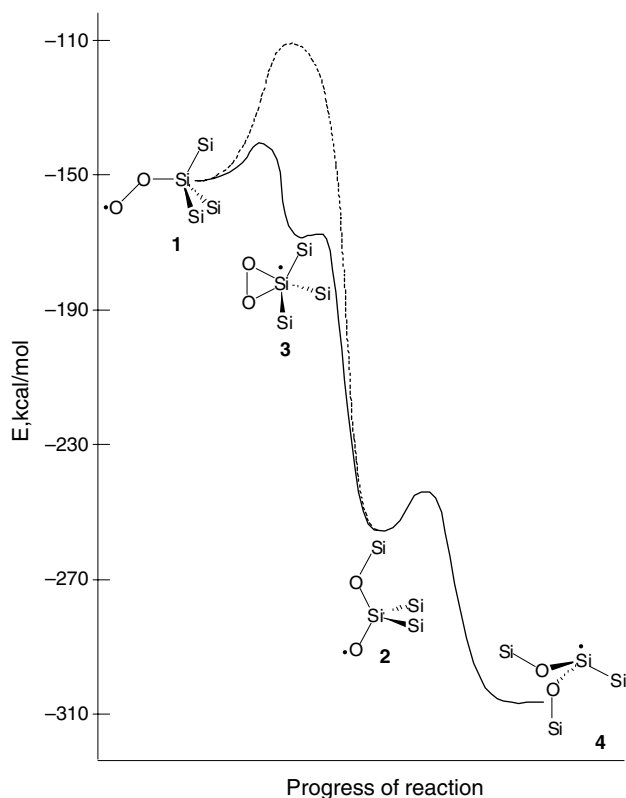

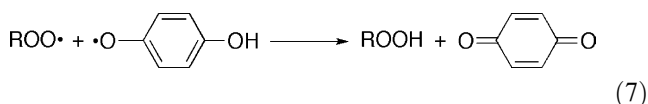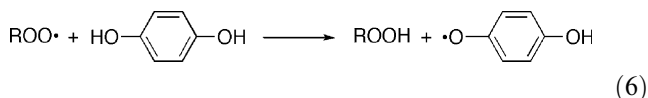Fig. 1. Schematic energy profile of all consecutive unimolecular reactions calculated at PM3 level (see Scheme 1). Methyl groups are omitted for clarity.
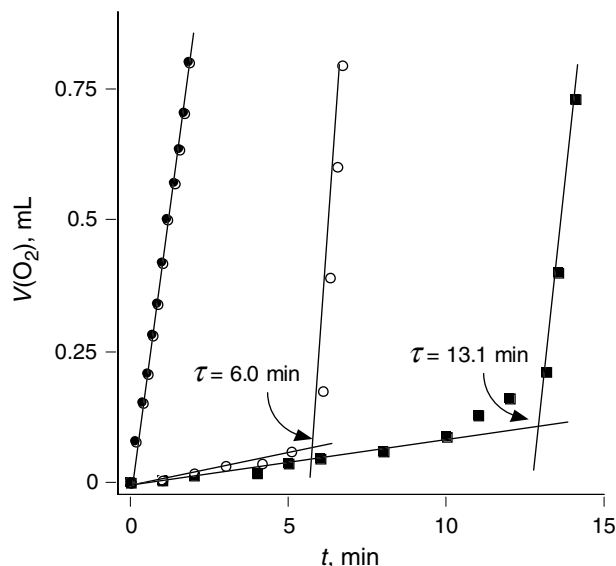
Fig. 2. Oxygen consumption during (Me$_3$Si)$_3$SiH oxidation in benzene at 70 °C: (●) [(Me$_3$Si)$_3$SiH] = 1.62 M; (○) [(Me$_3$Si)$_3$SiH] = 2.98 M, [QH$_2$] = 1.02×10^{-4} M; (■) [(Me$_3$Si)$_3$SiH] = 2.95 M, [QH$_2$] = 1.14×10^{-4} M.

Table 1
Autoxidation of $(Me_3Si)_3SiH$ in benzene and in the presence of hydroquinone (QH_2) at 70 °C

| $[(Me_3Si)_3SiH]$ (M)	$[QH_2]$ (10^{-4} M)	τ (min)	$-d[O_2]/dt$ (10^{-4} M s^{-1})
2.98	1.02	6.0	>3.5
2.95	1.14	13.1	>4.2
2.93	1.27	25.3	>4.8
2.88	1.36	27.5	>4.2
2.85	1.52	33.3	>2.7
2.82	1.65	44.0	>6.4
2.79	1.78	54.5	>3.6
2.76	1.91	64.0	>7.6

than 0.1 mM, the time profile always exhibited an induction period (τ), which can be determined quite accurately as illustrated in Fig. 2 [13]. Table 1 shows that the τ values increase with increasing the concentration of QH_2. The two quantities are related by the equation: $[QH_2] = (R_i/f)\tau$, where R_i is the initiation rate and f is the number of peroxyl radicals trapped by each molecule of QH_2 [14]. From the slope of the plot $[QH_2]$ vs. τ, $R_i/f = (0.26 \pm 0.01) \times 10^{-7}$ M s^{-1} is obtained at 70 °C. If the chain termination (Eqs. (6) and (7)) dominates in the system and the product (quinone) is not active towards chain termination, f is expected to be close to 2 [14]. However this is not the case since quinone reacts very fast with $(Me_3Si)_3Si^\bullet$ radical to give an aryloxyl radical that is able to trap another radical in the system [15]. Therefore, it is reasonable to assume $f \approx 4$ and calculate a $R_i \approx 1.0 \times 10^{-7}$ M s^{-1} at 70 °C. The rate constants for the initiation reaction (Eq. (1)) can be calculated using the equation: $R_i = k_i[(Me_3Si)_3SiH][O_2]$, where the concentration of oxygen is 10^{-3} M [16]. A value of $k_i \approx 3.5 \times 10^{-5}$ M^{-1} s^{-1} at 70 °C is obtained. The reaction enthalpy for this step is calculated to be endothermic of 31.2 kcal/mol based on $DH[(Me_3Si)_3Si–H] = 84.0$ and $DH(H–OO^\bullet) = 52.8$ kcal/mol [17,18].

In Table 1 are also collected the oxidation rates ($-d[O_2]/dt$) after the exit from the induction period. Since the chain length (v) of oxidation is given by the formula: $v = (-d[O_2]/dt)/R_i$, the low limit of v can also be calculated. These low limit values indicate a very long chain length of $(Me_3Si)_3SiH$ oxidation. In the propagation steps, the reaction of silyl radical with oxygen (Eq. (2)) should be fast. Rate constants for the reaction of $R_3Si^\bullet$ radicals with O_2 in solution are missing, although values of ca. 1×10^{10} M^{-1} s^{-1} at room temperature are reported in the gas phase [17]. The resulting silylperoxyl radical is expected to rearrange to the disilyloxysilyl radical (Eq. (3)). How fast? The rate constant for the reaction of cumylperoxyl radical with $(Me_3Si)_3SiH$ is 66.3 M^{-1} s^{-1} at 72.5 °C [19]. Assuming that reaction (8) has a similar rate constant, in neat silane the pseudo-first order rate constant will be $\sim 2.5 \times 10^2$ s^{-1}. Since no species corresponding to hydroperoxide, peroxide, or their

decomposition products were observed in the oxidized samples, the rearrangement should occur with a rate constant $\geqslant 5 \times 10^2$ s^{-1} at $\sim$70 °C. Furthermore, the following observations: (i) 0.1 mM of hydroquinone is found to inhibit the $(Me_3Si)_3SiH$ oxidation at 70 °C, and (ii) alkylperoxyl radical reacts with hydroquinone with a rate constant 5.5×10^5 M^{-1} s^{-1} at 37 °C [12], suggest that the rearrangement (Eq. (3)) should occur with a rate constant close to 10^3 s^{-1}.

$$(Me_3Si)_3SiOO^\bullet + (Me_3Si)_3SiH$$
$$\rightarrow (Me_3Si)_3SiOOH + (Me_3Si)_3Si^\bullet \qquad (8)$$
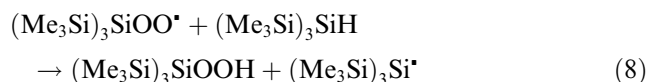
It is worth mentioning that kinetic studies carried out by EPR spectroscopy on the oxidation of $(Me_3Si)_2SiHMe$ initiated by photogenerated t-BuO$^\bullet$ radicals in the presence of 14 mM of α-tocopherol at 50 °C, indicated that not all the silylperoxyl radicals 5 are trapped [2]. Since the rate constant for the reaction of alkylperoxyl radicals with α-tocopherol (under similar experimental conditions) is 4.1×10^6 M^{-1} s^{-1} [20], we calculated a rate constant of ca. $\sim 10^3$ s^{-1} for the unimolecular reaction of silylperoxyl radical 5 (Eq. (9)). It is gratifying to see such an agreement between the estimated rate constants of reactions (3) and (9).

$$(Me_3Si)_2Si(OO\bullet)Me \longrightarrow \longrightarrow \longrightarrow (Me_3SiO)_2Si(\bullet)Me$$
$$\mathbf{5}$$
$$(9)$$
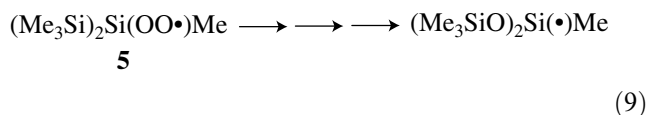
The autoxidation of $(Me_3Si)_3SiH$ was thermally initiated and the volume of oxygen uptake, $V(O_2)$, was measured vs. time at different concentrations of silane in the presence of pure oxygen or air. For example, Fig. 2 shows the linear dependence of $V(O_2)$ vs. time in the presence of 1.62 M of $(Me_3Si)_3SiH$ without an induction period (solid circles). From the slopes of the linear plots the oxidation rates were calculated by using Eq. (5). Table 2 shows that the oxidation rate increases by increasing the concentration of $(Me_3Si)_3SiH$. At 70 °C, the calculated chain lengths are 2450, 4000 and >4900 for silane concentrations of 0.97, 1.30 and 1.62 M, respectively. We could not measure ($-d[O_2]/dt$) values larger than 30×10^{-5} M s^{-1} on our manometric device and, therefore, for the oxidation rate of neat silane (3.24 M) this is the lowest limit value.

The rate of oxidation for pure $(Me_3Si)_3SiH$ at 30 °C was estimated from the following product studies. After 1 h of air bubbling into 1 ml of pure $(Me_3Si)_3SiH$, GC analysis showed that the consumption of the starting silane reached $\sim$50%, whereas the yield of $(Me_3SiO)_2$-$Si(H)SiMe_3$ was nearly with quantitative [1]. We calculated: $-d[O_2]/dt = (d[(Me_3SiO)_2Si(H)SiMe_3]/dt) = [(3.24 \times 0.5)/3600]$ M s$^{-1} = 45 \times 10^{-5}$ M s^{-1}. This value is close to the oxidation rates obtained for higher silane concentrations at 30 °C with the manometric device (cf. Table 2).

Table 2
Autoxidation of $(Me_3Si)_3SiH$ in benzene under oxygen or air pressure of 1×10^5 Pa

T (°C)	$[(Me_3Si)_3SiH]$ (M)	$-d[O_2]/dt$ (10^{-5} M s^{-1})	$-d[O_2]^{air}/dt$ (10^{-5} M s^{-1})	$(-d[O_2]/dt)/(-d[O_2]^{air}/dt)$[a]
30	0.97	0.21		
	1.30	1.5		
	1.62	3.8	1.0	3.8
	1.94	12.2	3.8	3.3
	2.27	28.3	10.2	2.8
	2.59	>41.0		
40	0.97	0.88		
	1.30	3.1		
	1.62	7.8	4.6	1.7[b]
	1.94	18.5	6.8	2.7[b]
	2.27	>30.0		
50	0.97	1.5	0.76	1.9
	1.30	4.8	2.8	1.7
	1.62	13.0	6.7	2.0
	1.94	22.7	11.4	2.0
	2.27	>37.5		
60	0.97	3.2	1.9	1.7
	1.30	9.4	7.6	1.3
	1.62	20.2	11.1	1.8
	1.94	>38.6		
70	0.97	8.3	5.3	1.6
	1.30	18.1	4.7	3.9
	1.62	>27.8		

[a] The experiments with oxygen and air were carried out on the same run unless otherwise mentioned (first with oxygen and after with air).
[b] The experiments with oxygen and air were carried out on different runs.

On the basis of the above findings, the detailed radical chain reaction can be described by the reaction sequence shown in Scheme 3, where $k_{1,3}$, $k_{3,2}$ and $k_{2,4}$ are the rate constants of the three consecutive unimolecular transformations reported in Scheme 1. Furthermore, two possibilities can be drawn for the termination step, depending on which is the rate determining step in the chain sequence. If the unimolecular rearrangement ($1\rightarrow3$) is the slow reaction, then the self-reaction of peroxyl radical **1** will be the main termination step. Alternatively, if the hydrogen abstraction from the starting silane by radical **4** is the slow reaction, then the self-termination of silyl radical **4** will predominate. In the previous kinetic studies of oxidation of $(Me_3Si)_2Si(H)Me$ [2], $H(C_6H_{13}SiH)_nH$ [2] and $H(PhSiH)_nH$ [2,3], the hydrogen abstraction step was assumed to be the slow step of the cycle without evidence. Under these circumstances, the oxidizability is given by $k_H/(2k_t')^{1/2}$ because the overall rate of oxidation is given by Eq. (10).

$$-\frac{d[O_2]}{dt} = \frac{k_H}{(2k_t')^{1/2}}[(Me_3Si)_3SiH](R_i)^{1/2} \qquad (10)$$

The hydrogen abstraction from $(Me_3Si)_3SiH$ by the radical **4** cannot be very slow. Product studies of $(Me_3Si)_3$-SiH oxidation under high dilution showed the formation of siloxane $(Me_3SiO)_3SiOH$. In fact, under high concentrations of silane like in the present study, silyl radical **4** prefers to abstract a hydrogen atom from $(Me_3Si)_3SiH$ rather than to add to another oxygen molecule. Since the oxygen concentration is ~1 mM and the rate of addition to the oxygen should be relative fast, the absence of other oxidation products suggested that the slowest step in the propagation sequence could be the formation of three-membered pentacoordinated silyl radical.

Using the usual steady-state approximation for the mechanism for which the reaction $1\rightarrow3$ is the slow step (Scheme 3), the overall rate of oxidation is given by Eq. (11).

$$-\frac{d[O_2]}{dt} = k_{1,3}\left(\frac{k_i[(Me_3Si)_3SiH][O_2]}{2k_t}\right)^{1/2}$$
$$= \frac{k_{1,3}}{(2k_t)^{1/2}}(R_i)^{1/2} \qquad (11)$$

According to Eq. (11), the oxidation is of half-order in silane and oxygen. The half-order in oxygen is experimentally verified based on the data in Table 2. Indeed, the ratio of oxidation rates in oxygen and air (last column in Table 2) gives an average value of 2.30 which is in excellent agreement with the expectation, which
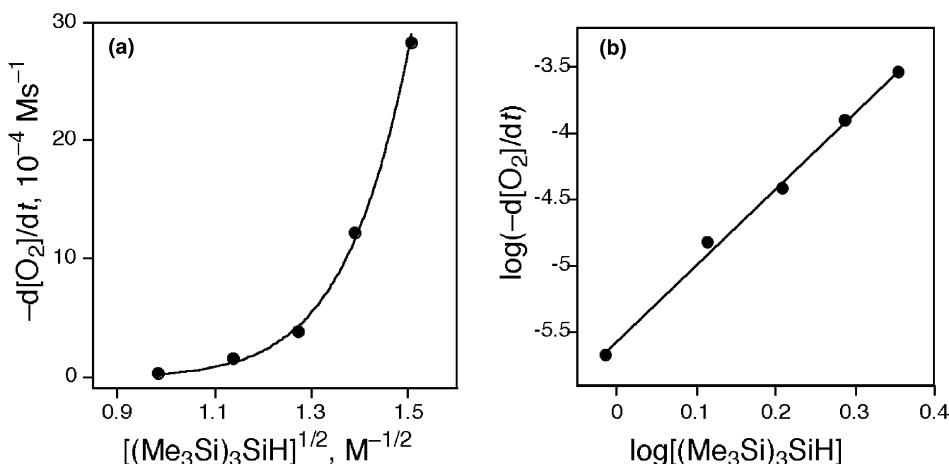
Initiation $(Me_3Si)_3SiH + O_2 \xrightarrow{k_i} (Me_3Si)_3Si\bullet + HOO\bullet$

Propagation $(Me_3Si)_3Si\bullet + O_2 \longrightarrow (Me_3Si)_3SiOO\bullet$
                                                                    1

1 $\xrightarrow{k_{1,3}}$ **3** $\xrightarrow{k_{3,2}}$ **2** $\xrightarrow{k_{2,4}}$ **4**

4 $+ (Me_3Si)_3SiH \xrightarrow{k_H} (Me_3SiO)_2Si(H)SiMe_3 + (Me_3Si)_3Si\bullet$

Termination   **21** $\xrightarrow{2k_t}$ non-radical products

or   **24** $\xrightarrow{2k_t'}$ non-radical products

Scheme 3. The reaction mechanism for the autoxidation of $(Me_3Si)_3SiH$.

yields $(-d[O_2]/dt)/(-d[O_2]^{air}/dt) = ([O_2]/[O_2]^{air})^{1/2} = (1$ atm/0.2 atm$)^{1/2} = 2.24$. It is worth underlining that these findings are in agreement with the mechanism for which the two oxygen atoms arise from the same oxygen molecule.

In benzene, on the other hand, the oxidation rates of $(Me_3Si)_3SiH$ are not directly proportional to the silane concentration or its square root. Fig. 3(a) shows that the oxidation rate decreases sharply upon increasing the square root of $(Me_3Si)_3SiH$ concentration at 30 °C. Fig. 3(b) shows the linear dependence of $\log(-d[O_2]/dt)$ vs. $\log[(Me_3Si)_3SiH]$, where the slope of 5.7 ± 0.2 is the order in silane at 30 °C. This order decreased by increasing the temperature as follows: 5.7 (30 °C), 4.4 (40 °C), 4.0 (50 °C), 3.6 (60 °C) and 2.7 (70 °C). It is evident that benzene behaves as a weak inhibitor for the oxidation of this silane. Indeed, no induction periods are observed.

It is well known that silyl radicals add reversibly to benzene and other aromatic compounds to give cyclohexadienyl radicals (Eq. (12)) [4,17]. For example, the rate constant for the addition of $Et_3Si\bullet$ radicals to benzene is $4.6 \times 10^5 \ M^{-1}s^{-1}$ at 25 °C. Furthermore, it is well known that $(Me_3Si)_3Si\bullet$ radicals add reversibly to olefins the addition rate being similar to other silyl radicals. A reversible addition of $(Me_3Si)_3Si\bullet$ radicals to benzene will afford the cyclohexadienyl radical and perhaps the corresponding cyclohexadiene by hydrogen abstraction from $(Me_3Si)_3SiH$. These cyclohexadienyl derivatives can act as weak inhibitors and therefore, explain the deviation from half-order kinetics as well as the decrease of order in the silane by increasing the temperature, since the reverse reaction (Eq. (12)) will be favored.

$$R_3Si\bullet + \langle\bigcirc\rangle \rightleftharpoons R_3Si\langle\bigcirc\rangle H \quad (12)$$

The rate constant ($k_{1,3}$) for the unimolecular step $1 \rightarrow 3$ can be estimated at 70 °C using Eq. (11) and appropriate values as follows. The rate constant of the termination

step ($2k_t$) in Scheme 3 is unknown. To our knowledge, the only $2k_t$ value for silylperoxyl radicals known is for $Ph_3SiOO\bullet$ at −90 and −40 °C, which allows to calculate a $2k_t = 2.4 \times 10^8 \ M^{-1}s^{-1}$ at 70 °C [21]. Assuming this value for the self-termination of radical **4** together with the initiation rate (R_i) measured above and the oxidation rate for 1.3 M of silane from Table 2 and applying Eq. (11), we obtained $k_{1,3} \approx 4 \times 10^3 \ s^{-1}$ at 70 °C. This value is in good agreement with the ones estimated above and further supports the above mechanistic considerations.

In order to find an inert solvent for the autoxidation of $(Me_3Si)_3SiH$, we tried cyclohexane. The following set of data were obtained at 40 °C and 1×10^5 Pa oxygen pressure: for 0.65, 0.97, 1.30, 1.62, and 1.94 M of $(Me_3Si)_3SiH$ the corresponding oxidation rates are 1.3, 2.4, 9.1, 15.0, and $40.2 \times 10^{-5} \ M \ s^{-1}$. To our surprise the order in silane is 3.1 ± 0.4. Again, no induction periods were observed, indicating C_6H_{12} is a weak inhibitor for the oxidation of $(Me_3Si)_3SiH$. We tentatively suggest that the silyloxyl radical **2** is able to abstract hydrogen from C_6H_{12} and this can explain the deviation from half-order kinetics in the silane. The rate constant for the hydrogen abstraction from cyclohexane by $Me_3CO\bullet$ radicals is reported to be $1.2 \times 10^6 \ M^{-1}s^{-1}$ at 40 °C [22].

All the data available support the reaction mechanism of Scheme 3. Although the order in silane is still an open matter, there are strong evidences that the rate determining step is the unimolecular transformation of peroxyl radical **1**. On the other hand, the hydrogen abstraction from $(Me_3Si)_3SiH$ by silyl radical **4** should be an efficient process. Indeed, theoretical data on bond dissociation enthalpies of $DH(XSiH_2-H)$ show that the replacement of X=H by SiH_3 decreases the bond strength by ca. 2.9 kcal/mol whereas the replacement of H by OH increases the bond strength by ca. 1.2 kcal/mol [4]. In light of these results, the previous mechanistic considerations on poly(hydrosilane)s need some revision.

Fig. 3. (a) Plot of oxidation rate vs. square root of silane concentration: at 30 °C in benzene with oxygen pressure 1×10^5 Pa. (b) Dependence of $\log(-d[O_2]/dt)$ vs. $\log[(Me_3Si)_3SiH]$; the slope = 5.7 ± 0.2 corresponds to the order in silane.

3. Experimental

3.1. Materials

$(Me_3Si)_3SiH$ was commercially available from Fluka and used as received. Benzene and cyclohexane were purified before use by standard methods. Hydroquinone was used as inhibitor and purified by sublimation.

3.2. Kinetic method

The rate of $(Me_3Si)_3SiH$ oxidation was determined from the oxygen consumption as described in the literature [23]. Reactions were carried out in a thermostated glass reactor equipped with a stirrer and attached to a manometric device. All reactions were carried out under pressure of 1.0×10^5 Pa of oxygen or air or oxygen/argon mixtures. The temperature was kept constant (±0.1 °C) during the reaction course. After the addition of a known volume of the solution, the reactor was evacuated and flushed with the appropriate oxygen mixture several times to ensure that the required atmosphere was completely attained in the reaction cell. Sufficient time was given for the solution to attain equilibrium. The stirrer operated at the gas-liquid interface. The experimental error of the rate of oxygen absorption at the manometric apparatus with automatic pressure control was ±1.0%, and the error in the reproducibility of the experiments was 3%.

3.3. Product studies

The mixtures of $(Me_3Si)_3SiH$ and solvent were oxidized in a closed glass vessel (10 ml) and thermostatically controlled within ±1 °C. Molecular oxygen was pumped under a pressure of 1 atm through a needle connected to an oxygen source. After the reaction was complete, the products were analyzed by GC/MS using an HP-5890 Series II chromatograph (HP-5 column, 30 m×0.25 mm; HP-5972 as a mass detector) and identified by comparing their retention times and mass spectra with those of the authentic samples [1,24]. A thin layer chromatography (TLC) analysis of the oxidized $(Me_3Si)_3SiH$ was performed on Silica gel 60 F_{254} (Merck) and Silufol UV_{254} plates (Kavalier Co.).

4. Summary

Our results show that molecular oxygen abstracts hydrogen from $(Me_3Si)_3SiH$ spontaneously but slowly ($k_i \approx 3.5 \times 10^{-5}$ M^{-1} s^{-1} at 70 °C), initiating a free-radical chain oxidation of this silane. The resulting silyl radical adds to oxygen to form a silylperoxyl radical 1 that undergoes three consecutive unimolecular steps and allow the two oxygen atoms in the final product to arise from the same oxygen molecule (Fig. 1). Strong evidence that the rate determining step (~10^3 s^{-1} at 70 °C) is the formation of a dioxirane-like pentacoordinated silyl radical 3 is provided. Up to now similar pentacoordinated silicon centers were only suggested as transition states of homolytic organosilicon group transfer [4]. Obviously the covalent contribution of the Si–O bond in the pentacoordinated center is a matter of further research [25]. We envisage that the reported mechanism of autoxidation of $(Me_3Si)_3SiH$ could serve as a model for the oxidation of poly(hydrosilane)s and of hydrogen-terminated silicon surfaces.

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