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SELF-REACTION OF PENTAMETHYLDISILYL RADICALS: IS DIMETHYLSILYLENE A PRODUCT? *

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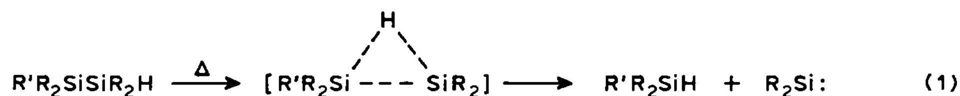
Summary

The self-reaction of the pentamethyldisilyl radical was investigated, in solution, at 298 K. Products due to the disproportionation and combination of these radicals were detected in a ratio $\leqslant 0.48$. However, there was no evidence for silylene formation. These results suggest that silylenes, which are formed during polysilane photolysis, are not produced from the self-reaction of polysilyl radicals but must be photo-extruded from the polysilane itself.

Introduction

Photolysis [1,2] or thermolysis [3–6] of polysilanes are known to give both silyl radicals and silylenes as reaction products. For polysilanes which contain Si–H bonds, the mechanism for silylene formation is thought to involve a 1,2-hydrogen shift (eq. 1) [3–6]. In essence, this is the reverse of the well authenticated insertion of



$$R'R_2SiSiR_2H \xrightarrow{\Delta} [R'R_2Si \overset{H}{---} SiR_2] \longrightarrow R'R_2SiH + R_2Si: \qquad (1)$$

(R = H , Me ; R' = H , Me or polysilyl)

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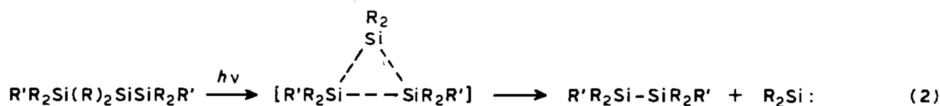
silylenes into the Si–H bonds of silanes [1,3–6]. Activation energies for the latter [6] are much less than the strength of the Si–H bond [7,8] implying that the process is concerted and that it does not involve an abstraction-recombination mechanism.

Hydrogen migration will obviously not occur in organopolysilanes that do not contain Si–H bonds. Nevertheless, these compounds give silylenes and silyl radicals on photolysis. For examples, photolysis of dodecamethylcyclohexasilane gives dimethylsilylene exclusively [1] while linear polysilanes give a mixture of silylenes and silyl radicals [2]. Two straightforward mechanisms can account for the observations. First, silylenes might be formed by a simple extrusion process (eq. 2). Second, Si–Si



bond cleavage to give silyl radicals might be followed by a radical–radical reaction which leads to silylene formation (eq. 3, 4). This reaction would be about as exothermic as the disporportionation reaction between silyl radicals which gives silenes and silanes (eq. 5) [7,8] and which competes with the simple radical combination process (eq. 6) [9–11].

$$R'R_2Si\text{–}SiR_2R' \xrightarrow{h\nu} 2R'R_2Si\cdot \quad (3)$$

$$2R'R_2Si\cdot \rightarrow R'_2SiR_2 + R_2Si: \quad (4)$$

$$2R'R_2Si\cdot \rightarrow R'R_2SiH + R'RSiR(-H) \quad (5)$$

$$2R'R_2Si\cdot \rightarrow R'R_2Si\text{–}SiR_2R' \quad (6)$$

In this work we have studied the chemistry of the pentamethyldisilyl radical in solution, to see whether the self-reaction of a polysilyl radical can indeed give rise to silylene formation.

Experimental

Materials. Di-t-butyl peroxide (K and K) was passed through a column of alumina and was further purified (> 99%) by preparative GC (Varian Aerograph 920, fitted with a 10′, 3/8″ aluminum column containing SE-30 on 60–80 mesh Chromosorb G support). Pentamethyldisilane [12] was a gift from Dr. J. Lusztyk and was also purified (> 97%) by preparative GC. 1,4,5,6-Tetraphenyl-2,3-benzo-7,7-dimethyl-7-silanorbornadiene was prepared by a literature method [13]. All other materials were commercially available and were used without further purification.

Product studies. All samples were deoxygenated by purging with nitrogen before use. In a typical experiment, mixtures containing pentamethyldisilane (0.2–1.0 *M*) and t-butyl alcohol (0.2–0.5 *M*) in di-t-butyl peroxide (2 ml) as solvent, were purged with nitrogen and were photolyzed with 350 nm UV light in a Rayonet reactor. Pyrex sample tubes were always used since these cut off wavelengths below ca. 310 nm. After photolysis, decane (1 μl) was added to serve as a GC standard. The products were identified by GC-mass spectrometry (Hewlett Packard 5995) and were quantified by GC (Hewlett–Packard 5890 A) using 10 m, 0.2 mm diameter cross-linked methyl silicon columns.

Results and discussion

The pentamethyldisilyl radical was generated by hydrogen abstraction from its parent disilane using t-butoxyl radical as the abstracting agent. Di-t-butyl peroxide was used as a photochemical soure of t-butoxyl and as the solvent (eq. 7, 8). In

$$\text{t-BuO–OBu-t} \xrightarrow{h\nu} \text{2t-BuO}\cdot \quad (7)$$

$$\text{t-BuO}\cdot + Me_3Si(Me)_2SiH \rightarrow \text{t-BuOH} + Me_3Si\dot{S}iMe_2 \quad (8)$$

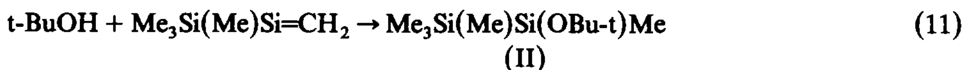
addition, t-butyl alcohol (ca. 0.5 M) was included in the reaction mixture to serve as a silylene trap (eq. 9). The samples were contained in Pyrex tubes and were

$$\text{t-BuOH} + Me_2Si: \rightarrow \underset{\text{(I)}}{\text{t-BuOSi(Me)}_2\text{H}} \quad (9)$$

irradiated with UV light at room temperature. The use of the peroxide as solvent and of Pyrex sample tubes which cut off wavelengths below 310 nm, ensured that cleavage of the peroxide was the dominant photochemical reaction.

Sample analysis by GC/mass spectrometry showed that a large number of products were formed in these reactions. However, the major products were t-butoxypentamethyldisilane (II), and decamethyltetrasilane (III), which were presumably formed in reactions 10–13. For example, at 36% conversion of the starting

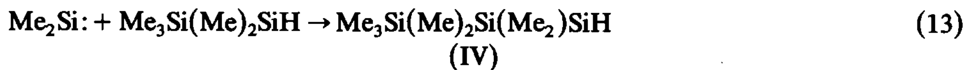
$$2Me_3Si\dot{S}iMe_2 \rightarrow Me_3Si(Me)_2SiH + Me_3Si(Me)Si{=}CH_2 \quad (10)$$



$$\text{t-BuOH} + Me_3Si(Me)Si{=}CH_2 \rightarrow \underset{\text{(II)}}{Me_3Si(Me)Si(\text{OBu-t})Me} \quad (11)$$

$$2Me_3Si\dot{S}iMe_2 \rightarrow \underset{\text{(III)}}{Me_3Si(Me)_2SiSi(Me)_2SiMe_3} \quad (12)$$

pentamethyldisilane in a mixture containing disilane 0.2 M) and t-butyl alcohol (0.5 M) in di-t-butyl peroxide, these products represented 39% of the material consumed. The remaining products were each present in such low concentrations that they could not be properly identified. However, there was no sign of I or IV which would have been formed by the reaction of dimethylsilylene with t-butyl alcohol and pentamethyldisilane, respectively (eq. 9, 13).



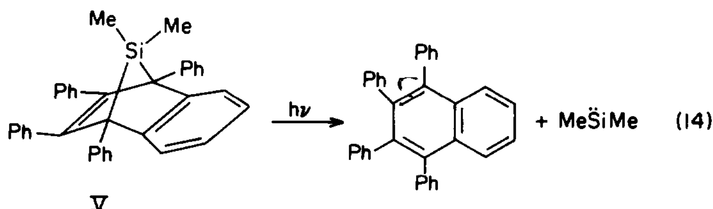
$$Me_2Si: + Me_3Si(Me)_2SiH \rightarrow \underset{\text{(IV)}}{Me_3Si(Me)_2Si(Me_2)SiH} \quad (13)$$

Photolysis of the sample to high conversion of the pentamethyldisilane increased the complexity of the product mixture and there was a concurrent increase in the ratio of II/III which was 0.48 at 36% conversion and 0.55 at 97% conversion. In view of these changes with conversion a value of 0.48 must be regarded as an upper limit for the disproportionation: recombination ratio for the self-reaction of the pentamethyldisilyl radical i.e. k_{10}/k_{12}. In principle, II could have been formed in a diffusion controlled reaction between t-butoxyl and the pentamethyldisilyl radical thus affecting these conclusions. However, for all practical purposes this route was inconsequential. The relatively high concentration of pentamethyldisilane (0.2–1 M) and the low rate of initiation ($< 10^{-4}$ M s^{-1}) used in these experiments, ensured

that t-butoxyl must have been consumed ca. 10^5 times more rapidly in reaction with the disilane [14] (eq. 8) than in any possible radical–radical process.

We were not able to achieve a significant reduction in the number of reaction products by varying the concentrations of starting materials or the conversion. The complexity of the product mixture was presumably caused by a variety of side reactions. Abstraction of the silyl hydrogen in pentamethyldisilane is a rapid process ($k_8 = 1.7 \times 10^7$ M^{-1} s^{-1}) [14]. Nevertheless attack at the methyl hydrogens is likely to occur to some extent, particularly because an anchimeric effect operates in its favour [15]. Equally, attack by t-butoxyl at the parent peroxide and at t-butyl alcohol add further possible complications [16]. Moreover, the variation in the ratio of disproportionation recombination products seem to suggest that III is being steadily destroyed under the reaction conditions. In short, to fully demonstrate that dimethylsilylene was not formed in the self-reaction of pentamethyldisilyl, it was necessary to prove that the products of the silylene reactions would have been detected under the experimental conditions.

Dimethylsilylene was deliberately generated under the reaction conditions by photolyzing a mixture of the 1,4,5,6-tetraphenyl-2,3-benzo-7,7-dimethyl-7-silanorbornadiene (V) (0.13 M), t-butyl alcohol (0.1 M) and pentamethyldisilane (0.06 M) in toluene as solvent. As before, the samples were contained in pyrex tubes but di-t-butyl peroxide was deliberately omitted in case its photolysis became a complicating factor. Products which were due to the insertion of dimethylsilylene into the alcohol and silane respectively were easily detected (eq. 9, 13, 14). The ratio of



these products, when combined with the relative concentrations of the starting materials led to a value of 3.2 for k_9/k_{13}. These products were not detected in the chromatograms for the disilyl radical reactions and allow us to set an upper limit of 2%, based on the sensitivity of the instrument, for the yield of dimethylsilylene in the self-reaction of pentamethyldisilyl radicals.

As final controls, dimethylsilylene was generated, eq. 14, by photolysis of a benzene/cyclohexane solution of V (3×10^{-3} M) at 350 nm containing di-t-butyl peroxide (1 M). While a variety of polysilanes were detected, no products due to the insertion of the silylene into the O–O bond of the peroxide were found. This is presumably due to steric protection of O–O linkage by the bulky t-butyl groups. Unfortunately, it was not possible to use the peroxide as solvent, as has been the case in the first product study, because its high optical density would have interferred with the photolysis of V. As an additional safeguard, we therefore repeated the above experiment in the presence of t-butyl alcohol (0.1 M) to unequivocally establish that dimethylsilylene was indeed being formed in the presence of the peroxide. The O–H insertion product, I, was easily detected (eq. 9), which established that di-t-butyl peroxide did not interfere with silylene generation (eq. 14).

Conclusion

The results described above suggest that silylenes are not formed to a significant extent in the self-reaction of thermally equilibrated polysilyl radicals. Their formation in the photolysis of linear and cyclic polysilanes must therefore be a result of a photochemically induced extrusion and does not result from self-reactions of silyl radicals which are frequently formed under these conditions.

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