Laser powered homogeneous decomposition of tetramethylcyclotetrasiloxane. A source for hydroxy(methyl)silylene

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Abstract

Laser powered homogeneous co-pyrolysis of tetramethylcyclotetrasiloxane and 1,1-dimethyl-1-silacyclobutane affords products in a ratio consistent with the transient existence of hydroxy(methyl)silylene and its addition to transient dimethylsilene. The suggestion that hydroxy(methyl)silylene is very reactive towards dimethylsilene but not towards butadiene is supported by a semiempirical AM1 calculation.

Key words: Methyl; Silylene; Siloxane; Homogeneous co-pyrolysis; Laser

1. Introduction

Hydroxysilylenes HO(R)Si: with (R = H, alkyl) are elusive species which have been treated theoretically [1–4], but identified only for R = H in low temperature matrices after reaction of silicon atoms with water [5], or generated from tetramethoxysilane and detected in the gas phase by collisional-activation and neutralization-reionization mass spectrometry [6]. Indirect evidence for the transient existence of similar, oxygenated $(CH_3)_3Si-O(alkyl)Si:$ silylenes in the gas phase comes from studies of conventional thermolysis of 1,1-bis(allyloxy)tetramethyldisilane [7] and 1,3,5,7-tetramethyl-1,3,5,7-tetrakis(trimethylsilyl)cyclotetrasiloxane [8]. More experimental work is therefore needed to reveal possible approaches to these species and to gain more knowledge of their chemistry.

In this paper, we report the CO_2-laser-photosensitized (SF_6) decomposition of tetramethylcyclotetrasiloxane (($(CH_3(H)SiO)_4$, D_4H) in either the absence or presence of 1,1-dimethyl-1-silacyclobutane (DMSCB), and show that the products observed can be accounted

for in terms of the formation of the previously undetected transient species hydroxy(methyl)silylene, and its reaction with dimethylsilene.

2. Experimental details

Mixtures of D_4H–SF_6(sensitizer) (both 1–1.6 kPa) or D_4H(0.7 kPa)–SF_6(2.6 kPa)–scavenger(buta-1,3-diene, methyl(trimethoxy)silane, trimethylsilane or DMSCB, all 4 kPa) were irradiated in a cylindrical glass reactor equipped with NaCl windows, a valve and a sleeve with rubber septum for the withdrawal by syringe of gaseous samples for analysis. The beam of a CO_2 laser was focused to provide an incident energy power of *ca.* 1 kW cm^{-2} and the laser was operated at 944.2 cm^{-1}. Changes in the composition of the irradiated mixtures were monitored by gas–liquid chromatography/mass spectrometry (GLC/MS) (Shimadzu QP 1000 quadrupole mass spectrometer, columns packed with Porapak P or SE-30, programmed temperature 20–160°C).

The progress of the laser-induced D_4H decomposition in the presence of DMSCB, and the distribution of products in this co-pyrolysis, were also monitored at

appropriate intervals using an apparatus [9] that incorporated a standard vacuum line, a 12-channel sampling valve and a GC 14A Shimadzu gas chromatograph (Porapak P, programmed temperature).

The siloxane D_4H was prepared by the previously described procedure [10] and sulphur hexafluoride (Fluka) was a commercial sample. DMSCB was obtained by the method previously described [11]. Both DMSCB and D_4H were thoroughly dried with calcium hydride and degassed prior to use by several freeze–thaw cycles.

The IR spectra of the material deposited on the NaCl windows of the reactor were recorded on a Specord, model 75, Zeiss IR spectrometer.

Calculations were performed by a standard semiempirical AM1 method included in the program package HYPERCHEM [12].

3. Results and discussion

Laser powered homogeneous decomposition (LPD) of D_4H in the gas phase results in the formation of two volatile compounds, trimethylcyclotrisiloxane $((CH_3(H)SiO)_3, D_3H)$ and pentamethylcyclopentasiloxane $((CH_3(H)SiO)_5, D_5H)$ (Fig. 1(a)) which were identified from their mass fragmentation patterns [13]. After a thorough evacuation of the reactor, a deposit of a non-volatile material on the inside of the reactor was observed, and its IR spectrum (absorption at 760, 900, 1000–1120, 1260, 2170 and 2980 cm⁻¹), which is very similar to that of D_4H (780, 890, 1100, 1260, 2170 and 2970 cm⁻¹), is consistent with a polymethylsiloxane structure. These products can be regarded as being formed by the sequence involving cycloelimination of silanone $CH_3(H)Si=O$, followed by insertion of the latter into D_4H or polymerization (Scheme 1). These reactions have been suggested to occur during conventional thermal decomposition of octamethylcyclotetrasiloxane [14–16]. The absence of products resulting from fission of the Si–C bond (CH_4 and C_2H_6) reveals that, under truly homogeneous conditions [17,18], cycloelimination of $CH_3(H)Si=O$ from D_4H is favoured over the CH_3–Si cleavage, and that cleavage of the CH_3 group from the silicon of D_3H does not take place, although it has been observed in conventional thermolysis of $[(CH_3)_2SiO]_3$ [15].
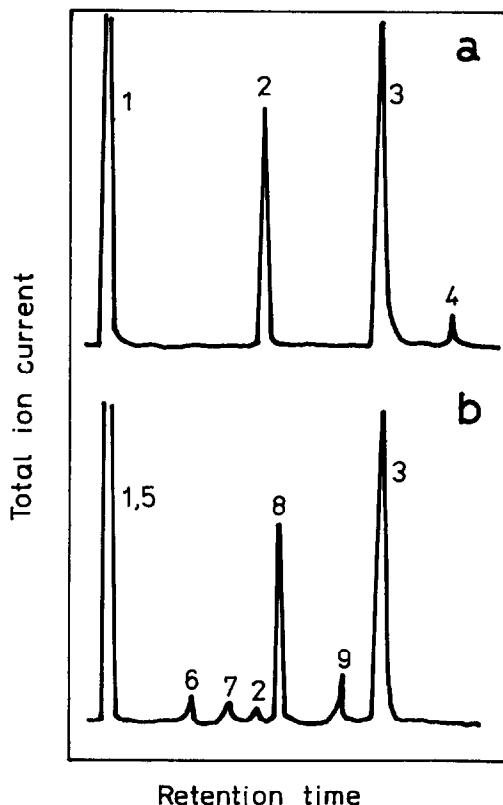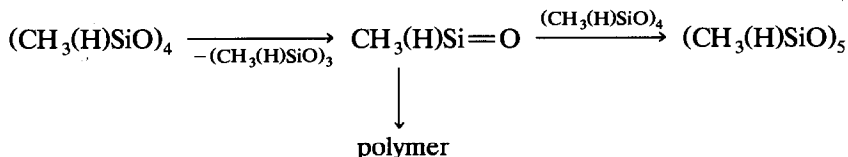

Retention time

Fig. 1. Typical GLC/MS trace of the mixture obtained on laser irradiation of D_4H–SF_6 (a) and D_4H–SF_6–DMSCB (b). Column, SE-30. Peak identification: 1, SF_6; 2, D_3H; 3, D_4H; 4, D_5H; 5, C_2H_4; 6, $(CH_3)_3SiOC_2H_5$; 7, DMSCB; 8, $[(CH_3)_3Si]_2O$; 9, $(CH_3)_2\overline{SiCH_2\text{-}Si(CH_3)_2CH_2}$.
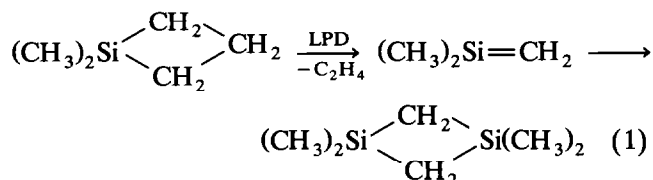
The intermediate methylsilanone $CH_3(H)Si=O$ is known to be of approximately the same energy as hydroxy(methyl)silylene $HO(CH_3)Si$: [3]. In an effort to capture these transients we carried out LPD of D_4H in an excess of trimethylsilane and methyltrimethoxysilane (the scavengers for silanones [19,20]) and butadiene (the scavenger for silylenes [19]), but we failed to observe any product from the scavenging reactions.

Another trapping reagent used was dimethylsilylene $(CH_3)_2Si=CH_2$ which was produced by LPD of 1,1-dimethyl-1-silacyclobutane. The laser irradiation of D_4H–DMSCB–SF_6 mixtures should create conditions in which $CH_3(H)Si=O$ and/or the rearranged $HO(CH_3)Si$: are generated in an excess of the scavenger

$$(CH_3(H)SiO)_4 \xrightarrow[-(CH_3(H)SiO)_3]{} CH_3(H)Si=O \xrightarrow{(CH_3(H)SiO)_4} (CH_3(H)SiO)_5$$

$$\downarrow$$

polymer

Scheme 1.

$(CH_3)_2Si\!=\!CH_2$, since, as observed independently, LPD of DMSCB [21] is much faster than that of D_4H, in accord with the known Arrhenius parameters [15,22] for conventional thermolyses of both compounds. The typical GLC/MS trace, shown in Fig. 1(b), of the mixture of compounds produced on irradiation of D_4H–DMSCB–SF_6–Ar, and also the dependence of the distribution of products on the irradiation time (Fig. 2), strongly suggest the transient existence of hydroxy(methyl)silylene. It is seen that DMSCB does not give the cyclodimer, which is otherwise, together with ethene, the only product from the LPD of DM-SCB (eqn. (1) [21]). The molar cyclodimer to C_2H_4 ratio is, in fact, *ca.* 0.05 (rather than unity), indicating that dimethylsilene is involved in other reactions.

$$(CH_3)_2Si\!\!\begin{array}{c}CH_2\\ \diagup\ \diagdown\\ \diagdown\ \diagup\\ CH_2\end{array}\!\!CH_2 \xrightarrow[-C_2H_4]{LPD} (CH_3)_2Si\!=\!CH_2 \longrightarrow$$

$$(CH_3)_2Si\!\!\begin{array}{c}CH_2\\ \diagup\ \diagdown\\ \diagdown\ \diagup\\ CH_2\end{array}\!\!Si(CH_3)_2 \quad (1)$$

The laser co-pyrolysis of D_4H and DMSCB produces trimethyl(ethoxy)silane and hexamethyldisilox-
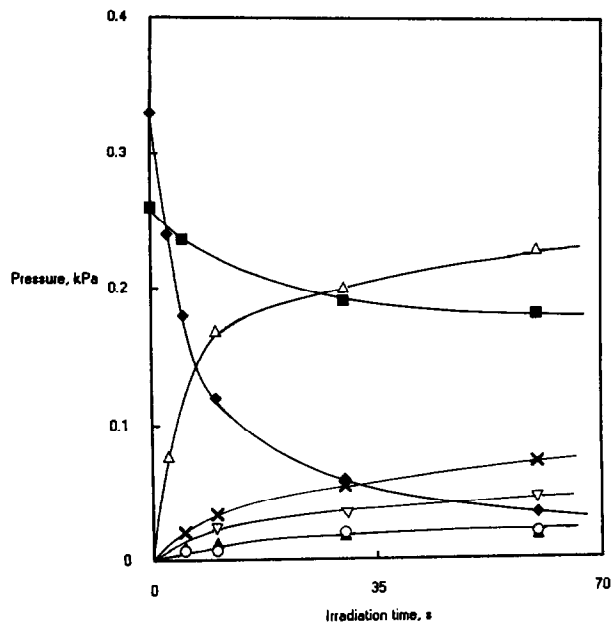
Fig. 2. Compound distribution in irradiated $D_4H(0.27$ kPa)–DMSCB(0.33 kPa)–$SF_6(1.1$ kPa)–Ar(25 kPa): ■; D_4H; ♦, DMSCB; △, C_2H_4; ×, $[(CH_3)_3Si]_2O$; ▲, $(CH_3)_3SiOC_2H_5$; ▽, D_3H; ○, $(CH_3)_2SiCH_2Si(CH_3)_2CH_2$.

$$(CH_3(H)SiO)_4 \xrightarrow[-(CH_3(H)SiO)_3]{} CH_3(H)Si\!=\!O \longrightarrow HO(CH_3)Si\!:$$

$$\Big\downarrow \scriptstyle(CH_3)_2Si\!=\!CH_2$$

$$[(CH_3)_2Si\!\!\begin{array}{c}CH_2\\ \diagup\ \diagdown\\ \diagdown\ \diagup\end{array}\!\!Si]_2O + H_2O \xleftarrow{\quad I \quad} \begin{array}{c}(CH_3)_2Si\!-\!CH_2\\ \diagdown\quad\diagup\\ Si\\ \diagup\quad\diagdown\\ HO\quad CH_3\end{array}$$

II	$\scriptstyle(CH_3)_2Si\!=\!CH_2\Big\downarrow$ **I**

$$\begin{array}{c}(CH_3)_2Si\!-\!CH_2\\ \diagdown\quad\diagup\\ Si\\ \diagup\quad\diagdown\\ (CH_3)_3SiO\quad CH_3\end{array}$$

III

Scheme 2.

$$(CH_3)_2Si\!=\!CH_2 + H_2O \xrightarrow{(2)} (CH_3)_3SiOH \xrightarrow[CH_2\!=\!CH_2]{(3)} (CH_3)_3SiOC_2H_5$$

$$(4)\Big\vert \scriptstyle(CH_3)_2Si\!=\!CH_2$$
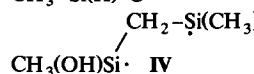
$$\Big\downarrow$$
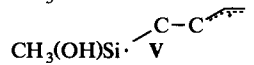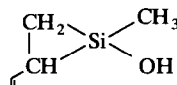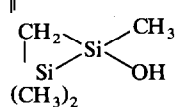
$$[(CH_3)_3Si]_2O$$
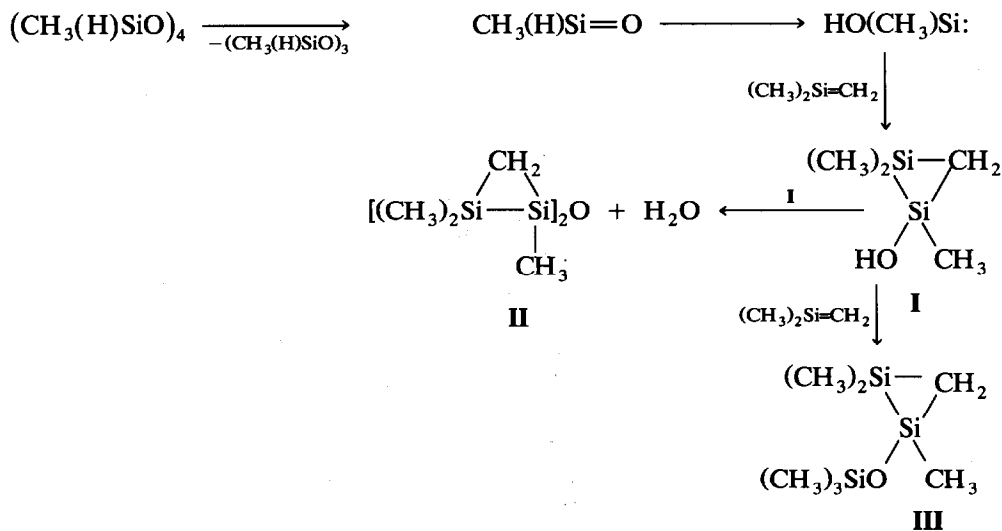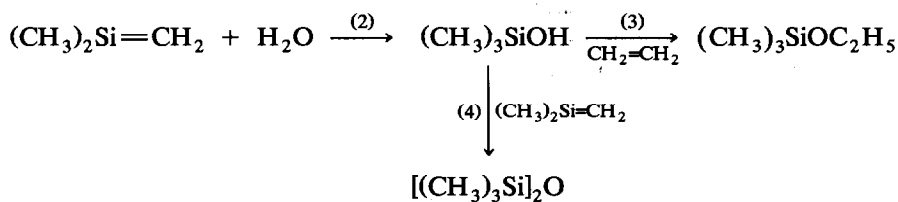
Scheme 3.

ane (Figs. 1 and 2). These unexpected products can be accounted for only in terms of the reactions postulated in Scheme 2. In this scheme transient hydroxy(methyl)-silylene adds across the double bond of transient dimethylsilene to form silanol I, which undergoes dehydration to yield siloxane II and/or reacts with dimethylsilene to afford siloxane III. Neither of these products was detected, perhaps owing to their reactivity (III) or low volatility (II, III). Disilacyclopropanes have, to our knowledge, been assumed as intermediates only in intramolecular rearrangements of silylenes [23–25], and we can infer that their low thermal stability can facilitate the Si–Si cleavage of the three-membered ring in our conditions and participation of the fragments formed (or rearranged species from them) in polymerization reactions. Water produced by the dehydration of I accounts for the formation of the observed trimethyl(ethoxy)silane and hexamethyldisiloxane, since the reactions of H_2O with dimethylsilene (2 [8,26]) and the subsequent reactions of trimethylsilanol with ethene (3 [21]) and dimethylsilene (4 [19,26]) are well documented (Scheme 3).

We stress that the reactions shown in Schemes 2 and 3 are in accord with the observed consumption of D_4H and DMSCB and also with the amounts of $\underline{(CH_3)_3SiOC_2H_5}$, $[(CH_3)_3Si]_2O$, C_2H_4 and $(CH_3)_2\overline{Si}$-$\overline{CH_2Si(CH_3)_2CH_2}$ formed (Fig. 2).

Another possible reaction occurring in the irradiated system is that of dimethylsilene with D_3H, since silenes are known [27,28] to insert into hexamethylcyclotrisiloxane. Since we did not observe the product from such a reaction, we suggest that the reactivity of dimethylsilene towards ROH (R = H, $(CH_3)_3Si$) molecules is much higher than that towards D_3H. It thus appears that the laser powered co-pyrolysis of D_4H and DMSCB is controlled by the initial reaction between the two transients and by the sequence of reactions made possible by the relatively high concentration of dimethylsilene.

We note that silanone-to-silylene rearrangements were, on the basis of similarly indirect evidence, tentatively proposed for $(CH_3)_3Si(R)Si=O$ (R = CH_3, CH_2=CHCH$_2$) [7,8]. In the relevant studies, flash vacuum pyrolysis of 2,2-bis(allyloxy)hexamethyltrisilane or 1,3,5,7-tetramethyl-1,3,5,7-tetrakis(trimethylsilyl)cyclotetrasiloxane was carried out under conditions favouring interaction between the reactant and the hot reactor surface, and so heterogeneous (surface-assisted) steps could not be excluded. Thus in these studies [7,8] the low yields of the products, indicating the intermediacy of the silanone-to-silylene rearrangements, would be consistent with the homogeneous nature of these rearrangements.

TABLE 1. Enthalpy of formation of species assumed to participate in Scheme 2

Species	ΔH$_f$ (kJ mol^{-1})	Method
CH_2=Si(CH$_3$)$_2$	−38.5	AM1/RHF
	−73.6	RHF+CI
(disilacyclopropane)	124.6	AM1/RHF
	55.6	RHF+CI
$^1CH_3$–Si–OH	−191.4	AM1/UHF
$^3CH_3$–Si–OH	−209.4	AM1/UHF
CH_3–Si(H)=O	−161.8	AM1/RHF
CH_3(OH)Si· IV (with CH$_2$–Si(CH$_3$)$_2$ ring)	−400.4	AM1/UHF
CH_3(OH)Si· V (with C–C group)	−212.8	AM1/UHF
(ring: CH$_2$–CH–Si(CH$_3$)(OH))	−214.0	AM1/UHF
(ring: CH$_2$–Si–Si(CH$_3$)(OH), Si(CH$_3$)$_2$)	−411.3	AM1/UHF

In our study, the homogeneous nature of all the involved steps is certain, since the copyrolysis of D_4H–DMSCB at high temperatures (T_{eff} [29] can be estimated as around 750 K) takes place far from the reactor walls [17,18,30,31]. High yields of $[(CH_3)_3Si]_2O$ and $(CH_3)_3SiOC_2H_5$ (Fig. 2) thus reveal the high efficiency of trapping of (HO)CH$_3$Si: with $(CH_3)_2Si$=CH$_2$, and reflect the fact that hydroxy(methyl)silylene is not scavenged on the reactor surface and removed by surface reactions to yield a non-volatile material. These results confirm that D_4H can act as a precursor for the previously unobserved hydroxy(methyl)silylene, and suggest that this transient species, while reacting with the very reactive dimethylsilene, does not react with butadiene. (The failure to trap CH_3(H)Si=O may even indicate the predominance of HO(CH$_3$)Si; and the existence of an active role of this species in producing D_5H in the LPD of D_4H.)

In order to obtain a rationale for the proposed Scheme 2, as well as for the observed lack of scavenging reactivity of butadiene, we performed semiempirical AM1 calculations [12] for all the species that might potentially participate in the reaction with hydroxy(methyl)silylene. The results, summarized in Table 1, show that the triplet hydroxy(methyl)silylene is more stable by 18 kJ mol^{-1} than the singlet form, which is in turn 30 kJ mol^{-1} more stable than methylsilanone. We note that an analogous study of the relative stability of methylsilanone and hydroxy(methyl)silylene, involving ab initio calculations, revealed an extreme sensitivity of
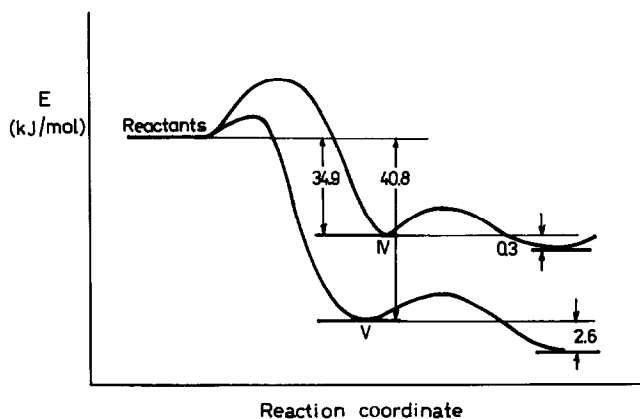
Fig. 3. Schematic reaction profile for reactions of singlet hydroxy-(methyl)silylene with dimethylsilene and buta-1,3-diene.

these structures to the quality of the computational program, and that the reported results suggest a considerable variation in the relative stability of both species [3]. We can assume, however, that the singlet (HO)MeSi: is a primary species generated during our laser decomposition experiments, and that it undergoes addition to scavengers (butadiene, dimethylsilene) to give three-membered ring species (Fig. 3). These additions are very exothermic and apparently occur as stepwise processes. We also obtained data for the biradical intermediates **IV** and **V** formed through the attack of hydroxy(methyl)silylene on buta-1,3-diene and dimethylsilene respectively. It will be seen that the stability of these intermediates is only slightly lower than that of the corresponding products containing a three-membered ring, and so it is apparent that the formation of these biradicals is a very exothermic process. In terms of the Hammond postulate, this implies that the additions involve very early transition states, and this fact accounts for the failure of our computational procedure to locate the transition states. We are thus unable to compare the activation energies for the formation of the two biradicals, but note that the greater exothermicity of the addition of HO(Me)Si: to dimethylsilene (compared to butadiene) is consistent with a higher energy barrier for the addition to butadiene. This inference is in accord with the observed scavenging reactivity of dimethylsilene and the unreactivity of butadiene.

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