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Laser-induced decomposition of silacyclobutane: extensive H(Si)/H(C) scrambling via 1,2-H shift in silene and radical reactions

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Abstract

The mechanism of the silacyclobutane decomposition has been further refined through a study of the laser induced decomposition of 1,1-dideuterio-1-silacyclobutane. It is concluded that the identified volatile and solid products and the hydrogen and deuterium content in them are in accord with 1,2-H(D)-shift in intermediate silene and with radical reactions. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Silacyclobutane; Laser-induced decomposition; Silene; H(Si)/H(C)scrambling

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1. Introduction

Thermolysis of silacyclobutane ($H_2\overline{SiCH_2CH_2CH_2}$, SCB) has attracted much attention [1–6] and the renewal of interest in this reaction stems from the suitability of SCB to serve as a precursor for chemical vapour deposition of silicon carbide [7–10]. The distribution of products and consequently the mechanism of SCB decomposition is affected by the decomposition conditions.

The major decomposition pathways in the conventional low pressure (hot wall assisted) pyrolysis (at ca. 0.1 Torr) or pyrolysis in stirred flow (N_2 stream) reactor—(i) the cleavage into silene and ethene, and (ii) the cleavage into silylene and propene [5] via transient *n*-propylsilylene and methylsilacyclopropane [6]—were derived from the observation of volatile silicon non-containing products (ethene and propene), scavenging of three silicon-containing, short-lived transients (silene, methylsilylene and silylene) with butadiene and hexamethylcyclotrisiloxane [1,4], and from kinetic studies [5].

The predominant initial products in the hot substrate-assisted decomposition in a cold wall low-pressure reactor (above 1000°C) are [7] dihydrogen and ethene in the ratio H_2:C_2H_4 ca. 2, the latter being in accord with the silene extrusion, while the former remaining unexplained, though its formation together with 1-silacyclobutylidene is in accord with the known ease of 1,1-H_2 elimination from mono- and diorganylsilanes [11–14]. The observation of cyclopropane under the same conditions suggests a direct extrusion of silylene from SCB.

Ethene, poly(silaethene) being the major and ethyne and silane being minor products of UV laser photolysis [9] show that this decomposition is governed by silene polymerization.

The almost twice higher ethene/propene ratio in the IR laser induced decomposition (IR multiphoton decomposition, IRMPD) as compared to the conventional pyrolyses, as well as the stoichiometry (C/Si ca. 1) of and H content in the solid deposit, are in line with a preference of silene formation when surface effects are excluded, and with silene and methylsilylene dehydrogenation followed by polymerization of $SiCH_n$ ($n < 4$) species [10].

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All these findings support the involvement of the initial steps given in Scheme 1 and suggest that the transient silene, methylsilylene and silylene may relax by a multitude of consecutive reactions. The pivotal molecule silene has been unambiguously detected in the gas phase only very recently by monitoring its milimeter wave spectrum [15,16]. Time-resolved UV spectra of the transients in SCB decomposition induced by TEA (transversely excited atmospheric) CO_2, or ArF laser are in accord with complex kinetics involving at least two decay channels for silene and the onset of reactions of other unidentified transients at higher fluences [17].

Although better understanding of the later decomposition stages was attempted through the identification of minor volatile products and the analysis of the deposited solid material [7,10], the present state of knowledge of the SCB decomposition leaves considerable uncertainty.

In our preceding papers we reported on the IR and UV laser induced decomposition of several silacyclobutanes with different substituents at the silicon [18–22] and on the TEA CO_2 or ArF laser induced decomposition of SCB [9,10,16,17]. We have also examined the TEA CO_2 laser-induced decomposition of SCB under various decomposition conditions [10]. Extending these results, we present in this paper GC/MS and GC/FTIR analyses of the final products of the TEA CO_2 laser induced decomposition of $D_2\overline{SiCH_2CH_2C}H_2$ (SCB-d_2) and show that these products can be explained by assuming that the earlier established initial molecular fissions into silene and silylene are accompanied by extensive H/D scrambling which is due to 1,2-H(D) shift occurring in silene and in the course of radical reactions. These views are supported by additional experiments on the TEA CO_2 laser induced decomposition of SCB and $H_2\overline{SiCD_2CHDC}D_2$ (SCB-d_5).

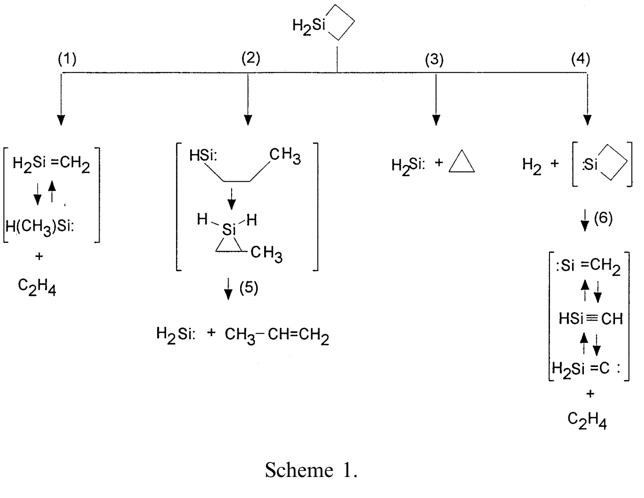
2. Experimental details

Laser-induced homogeneous SF_6-photosensitized decomposition (LPD) of SCB-d_2, and also of SCB and SCD-d_5, was carried out using a grating-tuned TEA CO_2 laser (P. Hilendarski Plovdiv University, 1300 M model) operated on the P(20) line of the $00^01 \rightarrow 10^00$ transition (944.2 cm^{-1}). The wavelength was confirmed by a model 16-A spectrum analyzer (Optical Engineering). The incident laser beam was rectangular (1.8 and 1.0 cm per side), repetition frequency and incident fluence in all experiments was 1 Hz and 0.5–0.8 J cm^{-2}, respectively.

Irradiation of gaseous SCB, SCB-d_5 and SCB-d_2 (each 3–5 Torr), SF_6 (3–6 Torr), N_2 (30–40 Torr) was conducted in a cylindrical (3.6 cm i.d., 10 cm long) Pyrex cell which was furnished with NaCl windows, a PTFE stopcock and a port for rubber septum for withdrawal of samples by a syringe. The irradiation parameters and pressure of the components were selected to match those at which LPD of SCB were previously examined [10].

Changes in the composition of the irradiated cell content were monitored by FTIR (Nicolet, model Impact 400) spectroscopy. The withdrawn gaseous samples were analyzed by gas chromatography (a gas chromatograph Shimadzu 14 A coupled with Chromatopac CR5A data processor), GC-MS (Shimadzu, model QP 1000 quadrupole spectrometer), and GC-FTIR (Nicolet, model Impact 400 coupled to a home-made chromatograph/interface) techniques. For chromatographic separation of the decomposition products, a programmed temperature (20–150°C) and a column packed with Porapak P (1.3 m) were employed. The decomposition progress was monitored by using diagnostic IR bands at 2146 (SCB), 1566 (SCB-d_2), and 2146 cm^{-1} (SCB-d_5). FTIR spectra of the solid products were recorded for materials deposited on the NaCl cell windows and on a NaCl plate accommodated in the cell prior to irradiation.

Samples of SCB-d_2 and also of SCB and SCB-d_5 were prepared according to previously reported procedures (SCB-d_2 and SCB, ref. [23]; SCB-d_5, ref. [16]) and their purity ($>99\%$) was checked by gas chromatography. Isotopic purity of SCB-d_2 and SCB-d_5 ($>95\%$) was confirmed by GC/MS technique and FTIR spectroscopy. The observed mass spectral fragmentations of SCB and SCB-d_2 were identical to those reported earlier [6,18]. Sulfur hexafluoride was purchased from Fluka. Authentic samples of trimethylsilane, trimethylsilane-d_1 $(CH_3)_3SiD)$, ethane-d_1 and methane-d_1 were from laboratory stock.



Scheme 1.

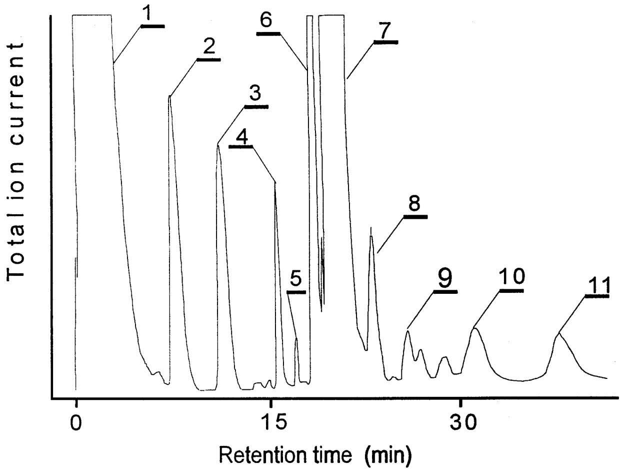


Fig. 1. Typical GC-MS trace of the mixture of products obtained by LPD of SCB-d_2. Column Porapak P. Peak identification: 1, methane, SF_6, N_2 and ethene (C_2H_4); 2, methylsilane (mostly $D_2HC{-}SiD_2H$); 3, propene (C_3H_5D); 4, dimethylsilane ($SiC_2D_5H_3$); 5, butane (C_4H_9D); 6, propylsilane ($SiC_3D_3H_7$ and $SiC_3D_4H_6$); 7, SCB-d_2; 8, trisilane ($Si_3H_5D_3$); 9, disilapentane (mostly $Si_2C_3H_6D_6$); 10, methyldisilacyclopentene (mostly $Si_2C_4H_6D_4$); 11, 1,3,5-trisilacyclohexane ($Si_3C_3D_2H_{10}$) and 1,2,4-trisilacyclopentane ($Si_3C_2H_7D_3$). The formulae in the brackets designates only the isotopomer with highest number of D, though others with less D are also present.

3. Results and discussion

The LPD of SCB-d_2 induced with SCB-d_2 (3–5 Torr), SF_6 (3–6 Torr), N_2 (38–55 Torr) mixtures at incident laser fluence 0.5–0.8 J cm^{-2} and 50–5000 pulses affords a mixture of products of which some are blends of several isotopomers. A typical GC/MS trace and FTIR spectra for each peak of the trace are given in Figs. 1 and 2, respectively. As reported previously by us with the CO_2 laser induced multiphoton decomposition of SCB [10], also the relative amounts of products formed by LPD of SCB-d_2 are, within the range of the irradiating conditions, practically independent of the decomposition progress. This is documented in Fig. 3. Residual pressure in the irradiated cell after freezing the volatile compounds in a trap cooled with liquid nitrogen indicated the presence of some H_2, D_2 or HD. The GC/MS trace reveals ethene as a major product, which indicates that mostly silene gives rise to formation of observed organosilicon products. The volatile organosilicon products were identified by combining the potential of GC/MS and GC/FTIR techniques as singly, and multi (di-, tri- and tetra) deuterium-substituted methylsilane, dimethylsilane, propylsilane, disilapentane, methyldisilacyclopentene, 1,3,5-trisilacyclohexane, 1,2,4-trisilacyclopentane and trisilane (Table 1, Fig. 2). Although we are unable to give quantities of the particular isotopomers, the GC/MS and GC/FTIR analyses (more specifically mass fragmentation and IR absorptivity at ν_{C-H}, ν_{Si-H} and ν_{Si-D}) allow us to determine these species qualitatively. Absorption bands due to ν_{C-D} (their partial overlap with those of ν_{Si-H}) do not hamper our analysis, since (i) the ν_{C-D} band of RD ($R{-}CH_3$, C_2H_5) has its Q branch or maximum at 2200 cm^{-1} which is well separated from the ν_{Si-H} absorption bands of all the volatile products (Fig. 2), and (ii) absorptivity of the ν_{C-D} band of R–D ($R{-}CH_3$, C_2H_5) is by ca. 2 orders of magnitude lower than that of ν_{Si-H} as checked with the RD and $(CH_3)_3Si{-}H$ as model compounds.

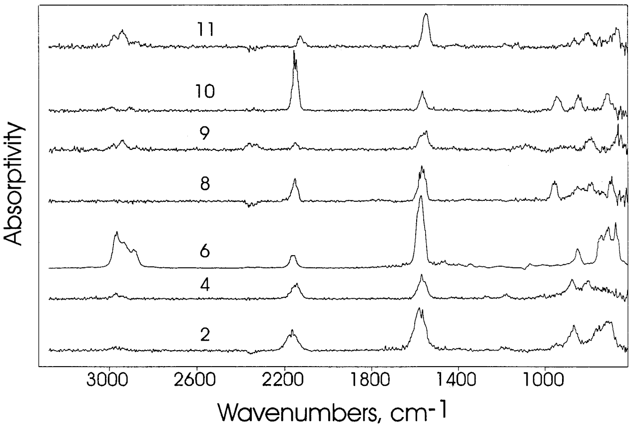


Fig. 2. FTIR spectra of the products of LPD of SCB-d_2 separated by gas chromatography (column Porapak P). The numbering of the products is the same as in Fig. 1.

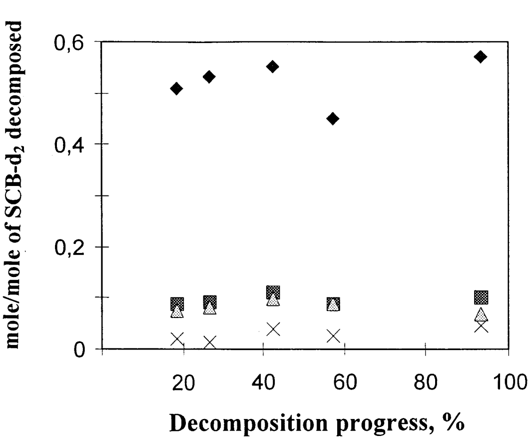


Fig. 3. Product distribution (in mol mol^{-1} of SCB-d_2 decomposed) in LPD of SCB-d_2. Product designation: ◆ ethene, ■ propene, △ methylsilane (mostly $D_2HC{-}SiD_2H$), **X** dimethylsilane ($SiC_2D_5H_3$). 19% decomposition—SCB-d_2 (4.6 Torr), SF_6 (3 Torr), N_2 (55 Torr), 2000 pulses; 27% decomposition—SCB-d_2 (3.3 Torr), SF_6 (3 Torr), N_2 (55 Torr), 5000 pulses; 43% decomposition—SCB-d_2 (4.1 Torr), SF_6 (6.0 Torr), N_2 (38 Torr), 60 pulses; 57% decomposition—SCB-d_2 (4.0 Torr), SF_6 (4.0 Torr), N_2 (38 Torr), 1500 pulses; 94% decomposition—SCB-d_2 (3.0 Torr), SF_6 (3.0 Torr), N_2 (38 Torr), 2000 pulses; all runs with fluence of 0.5 J cm^{-2}.

The relative amounts (in mol mol^{-1} of SCB decomposed) of these products formed from SCB-d_2 within the decomposition progress 10–50%, methane (traces), ethene (only C_2H_4, 0.45–0.55); methylsilanes (mostly $D_2HC{-}SiD_2H$, 0.08–0.1), propene (only C_3H_5D, ca.

Table 1
Mass and IR Spectra of GC-separated Fractions from SCB-d_2 Decomposition[a]

Product	MS spectra m/z (relative intensity, %)	IR spectra[b]	
		$A(\nu_{C-H}):A(\nu_{Si-H})$	$A(\nu_{Si-D}):A(\nu_{Si-H})$
Ethene	14(3), 25(16), 26(93), 27(100), 28(100), 29(7)	—	—
Methylsilane	28(40), 32(40), 44(35), 45(36), 46(100), 47(42), 48(62), 49(14), 50(7)	0.23	2.28
Propene	28(28), 39(51), 40(58), 41(54), 42(100), 43(76), 44(16), 45(4), 46(4)	—	—
Dimethylsilane	28(52), 44(85), 45(94), 60(82), 61(90), 62(100), 63(51), 64(22), 65(4)	0.31	1.44
Butane	28(63), 29(44), 42(53), 43(100), 44(74), 58(11), 59(21)	—	—
Propylsilane	28(30), 43(73), 44(92), 45(64), 61(28), 62(100), 74(27), 75(19), 76(5), 77(7)	5.9	5.9
Trisilane[c]	28(20), 42(5), 43(10), 44(15), 45(8, 46(2), 86(14), 87(40), 88(72), 89(100), 90(57), 91(34), 92(40), 93(13), 94(3), 95(2)	—	1.95
Disilapentane	28(26), 43(31), 44(22), 76(33), 77(55), 78(38), 88(52), 100(9), 101(12), 102(28), 103(51), 104(53), 105(60), 106(100), 107(71), 108(25), 109(15), 110(12)	2.06	2.87
Methyldisilacyclo-pentene	28(31), 44(38), 70(46), 74(39), 86(36), 90(28), 100(59), 101(99), 102(71), 103(20), 114(28), 115(78), 116(98), 117(100), 118(49)	0.21	0.35
1,3,5-Trisilacyclo-hexane +1,2,4-Trisilacyclo-pentene	28(25), 43(57), 44(100), 71(27), 78(22), 89(97), 90(68), 104(18), 117(12), 119(19), 120(30), 121(11), 132(8), 134(8)	2.22	2.47

[a] Obtained on the basis of GC-MS and GC-FTIR spectroscopy.

[b] A (absorptivity) in the region of 2765–3065 cm^{-1} (ν_{C-H}), 1976–2275 cm^{-1} (ν_{Si-H}) and 1492–1656 cm^{-1} (ν_{Si-D}).

[c] Together with traces of a compound tentatively assigned to 1,3-disilacyclobutane-d_n.

0.1); dimethylsilanes (0.03); butanes (C_4H_{10}, C_4H_9D, 0.006), propylsilanes-d_{2-4} (0.05), trisilanes (0.06–0.08); a disilapentane (0.05–0.07); a methyldisilacyclopentene (ca. 0.04); 1,3,5-trisilacyclohexane and 1,2,4-trisilacyclopentane (0.06–0.07) can be reconciled with reactions in Scheme 2. They indicate that the dominating initial routes (1′) and (2′) are accompanied by a number of other steps and the importance of these reactions is independent of the amount of SCB-d_2 decomposed.

Methylsilane-d_4 and propylsilane-d_4 are likely produced via silylene chain processes discovered [11,24] by O’Neal and Ring (Reaction 7).

$$\mathrm{RDSi{:}} + \mathrm{SCB\text{-}d_2} \rightarrow \mathrm{D_2RSi{-}(D)}\overline{\mathrm{SiCH_2CH_2H}}\mathrm{_2}$$

$$\rightarrow \mathrm{RSiD_3} + \mathrm{{:}Si(CH_2)_3} \qquad (7)$$

$(R = DH_2C,\ DH_2CCH_2CH_2)$

Considering, however, that H_2 is produced upon conventional [6,7] thermal decomposition of SCB and that its important source in IRMPD of SCB is [10] dehydrogenation of $SiCH_4$ ($H_2Si{=}CH_2$ and $(CH_3)HSi{:}$) species, we may admit that an alternative (although slower [25]) route for formation of methylsilane-d_4 and propylsilane-d_4 can be the reaction of methylsilylene-d_2 and propylsilylene-d_2 with D_2 (Reactions 8a,b).

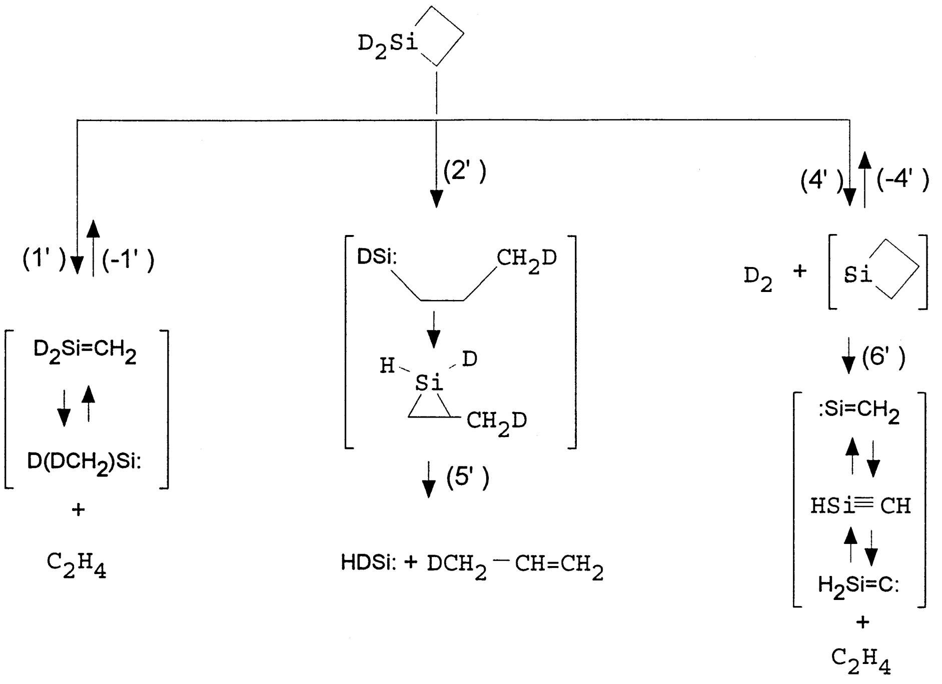
$$[\mathrm{D_2Si{=}CH_2} \rightarrow \mathrm{D(DH_2C)Si{:}}] + \mathrm{D_2} \rightarrow \mathrm{(DCH_2)SiD_3} \qquad (8a)$$

$$\mathrm{DH_2CCH_2CH_2(D)Si{:}} + \mathrm{D_2} \rightarrow \mathrm{DH_2CCH_2CH_2SiD_3} \qquad (8b)$$

The observed methylsilane and propylsilane isotopomers with Si–H bonds (Fig. 2) seem to support this type of reaction with HD or H_2. HD can be provided via short chain radical processes which occur to a small extent as with e.g. the thermolysis of methylsilane [26]. The fact that both HD and H_2 (together with D_2) can be inferred [10] to be produced by dehydrogenation of $SiCH_nD_m$ ($n+m=4$), is supported by the FTIR spectra of the solid deposits (see later).

The other, higher-molecular weight organosilicon products might have been explained as being formed from recombination of silene ($D_2Si{=}CH_2$), methylsilylene ($DH_2C(D)Si{:}$) and silylene ($D_2Si{:}$), or as formed by a sequence of the insertion of silylenes into the Si–D bonds and dehydrogenation steps. However, the D-enrichment (Table 1) and contributions of not only Si–D but also of Si–H vibrations (Fig. 2) observed for the isotopomeric mixtures of these products are not compatible with exclusively these reactions, but they reveal that an important channel in the SCB-d_2 decomposition is H/D scrambling. These H/D exchange reactions are also clearly manifested by the FTIR spectra of the gaseous (Fig. 4) and of solid (Fig. 5) organosilicon products deposited on the inside of the cell.

The FTIR spectrum of all the volatile organosilicon products derived by subtracting the contributions of ethene, propene and SCB-d_2 from the spectrum of the irradiated mixture of SCB-d_2 SF_6-N_2 (Fig. 4a) reveals the ν_{C-H} absorption band at 2948–2985 cm^{-1} and the ν_{Si-H} band at 2145 cm^{-1}, the FTIR spectrum obtained



Scheme 2.

by adding the contributions (Fig. 2) of all the volatile organosilicon products separated by GC/FTIR (Fig. 4b) reveals absorption bands of ν_{C-H} at 2962, ν_{Si-H} at 2159 and ν_{Si-D} at 1567 cm^{-1}, but no ν_{C-D} absorption band at 2200 cm^{-1}. The failure to observe a ν_{C-D} absorption band in the spectrum of the volatile organosilicon products reflects lower oscillator strength of C–D compared to the C–H bond and a higher content of D(Si) than D(C) atoms.

The FTIR spectrum of the solid deposits from SCB-d_2 (Fig. 5b) reveals ν_{C-H} (2861–2919), ν_{Si-H} (2120), ν_{Si-D} (1543), $\nu_{Si-C-Si}$ (1013) and ν_{Si-C} (826 cm^{-1}) absorption bands where $A\nu_{Si-H} > A\nu_{Si-D}$. The spectrum of the solid deposit from SCB-d_5 (Fig. 5), given for the sake of comparison, reveals a similar pattern of absorption bands with an additional broad shoulder at 2238 cm^{-1} which may indicate the occurrence of ν_{C-D} absorption band. It appears that the relative absorptivities of ν_{C-H}, ν_{Si-H}, ν_{Si-D} and $\nu_{Si-C-Si}$ as well as ν_{Si-C} bands in the deposits from SCB-d_2 and SCB-d_5 are very alike,

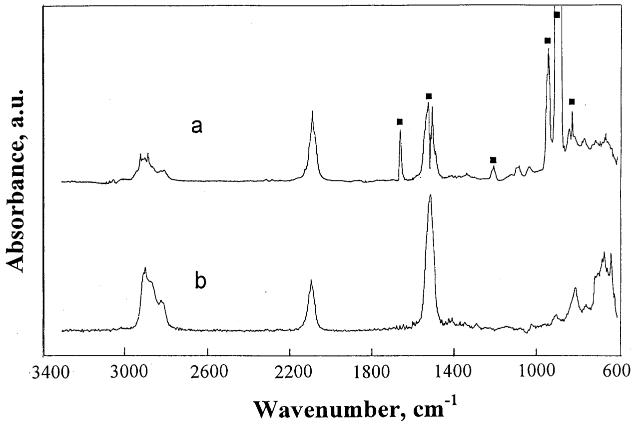


Fig. 4. FTIR spectrum of gaseous silicon-containing products resulting from LPD of SCB-d_2 obtained by (a) subtracting contributions of ethene, propene and SCB-d_2 (peaks designated ■ relate to a fraction of SF_6), and by (b) adding contributions of all the silicon-containing products as separated (Table 1) by the GC-FTIR technique. Irradiation conditions: SCB-d_2 (4 Torr), SF_6 (4 Torr), N_2 (38 Torr), fluence = 0.5 J cm^{-2}, 30% decomposition.

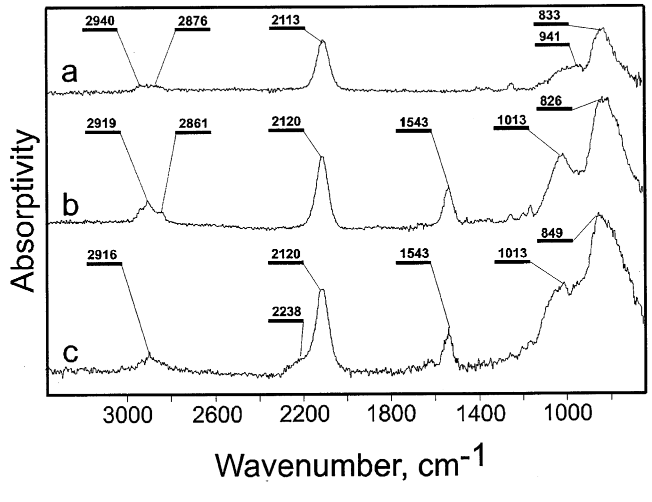


Fig. 5. FTIR spectra of the deposits from SCB (a), SCB-d_2 (b) and SCB-d_5 (c). Irradiation conditions with SCB, SCB-d_2 and SCB-d_5 as in Fig. 4.

Table 2
FTIR spectra of the solid deposits[a]

Solid from	ν_{Si-H}, cm^{-1}	ν_{Si-D}, cm^{-1}	N_{Si-D}/N_{Si-H}	N_{C-H}/N_{Si-H}
LPD of SCB	2115	—	—	1.1
LPD of SCB-d_2	2117	1537	0.60	2.3
LPD of SCB-d_5	2122	1537	0.56	2.2

[a] Obtained upon irradiation of silacycle (3–5 Torr), SF_6 (3–6 torr), N_2 (30–40 Torr) mixtures.

which is consistent with similar distribution of H and D atoms between Si centers in both deposits.

Both spectra, and also that of the deposit from SCB (Fig. 5a) show that all deposits contain less hydrogen than poly(silene), $(H_2Si-CH_2)_n$ (for IR spectrum see ref. [27]) and they are compatible [28–33] with SiC:H(D) and SiC:H films. Provided that (i) the Si–H and Si–D bonds are in the same environment of other (C, Si) atoms and that the integrated absorptivity of ν_{Si-D} and ν_{Si-H} is inversely proportional to the reduced mass [33], and that (ii) the number (N) of the C–H and Si–H bonds can be assessed from the integrated absorptivities of these bonds using an absorption cross section of 0.74×10^{-21} cm^2 for the ν_{C-H} band and 0.71×10^{-20} cm^2 for the ν_{Si-H} band [29–31], we estimate the relative content of the Si–H and Si–D bonds, and that of the C–H and Si–H bonds as shown in Table 2. The N_{Si-D}/N_{Si-H} ratios for LPD of SCB-d_2 (0.6) and SCB-d_5 (0.6) are equal; the same applies to the N_{C-H}/N_{Si-H} ratio which is 2.3 for the LPD of SCB-d_2 and 2.2 for the LPD of SCB-d_5.

We can thus infer that all these films are formed by the sequence of reactions assumed by us in our previous work [10] among those dehydrogenation of $SiCH_nD_m$ $(n+m=4)$ species (Reaction 9), i.e. silene, and methylsilylene (and also silylene) are important steps.

$$HDSi:,\ D_2Si{=}CH_2,\ (DCH_2)DSi{:}{—}[-H_2(-D_2)] \rightarrow H(D)/Si/C_{(solid)} \qquad (9)$$

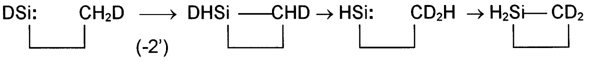
Assuming (i) a major role of Reaction (1′) and a minor role of Reaction (2′) (ethene:propene ratio being ca. 5), and (ii) the polymerization of $D_2Si{=}CH_2$, $D(DH_2C)Si$: and HDSi: as dominant paths forming the solid deposit, the FTIR spectra of the deposits from SCB-d_2 and SCB-d_5 should possess prevailing absorption bands either due to ν_{Si-D} or ν_{Si-H} vibrations, respectively. However, they are (almost equally) constituted by both of Si–H and Si–D bands. The high content of Si–H bonds in the products of LPD of SCB-d_2 (and of Si–D bonds in the products of LPD of SCB-d_5) cannot be explained in terms of Reactions (1′) and (3′), but can be only reconciled in terms of (i) Reaction (6′) producing the $SiCH_2$ species which undergo H migration(s) from carbon to silicon, and/or (ii) 1,2-H(D) shift in the intermediate silene (10),

$$D_2Si{=}CH_2 \leftrightarrow DHSi{=}CHD \leftrightarrow H_2Si{=}CD_2 \qquad (10)$$

the latter possibly taking place [4,34] via intermediary methylsilylenes $DH_2C(D)Si$: and $D_2HC(H)Si$:.

We have observed that (i) SCB-d_2 becomes H(Si) enriched in LPD occurring in the absence of hydrogen, and (ii) it does not become H(Si) enriched when LPD takes place in excess of hydrogen. Thus the irradiation of SCB-d_2 SF_6 (each 4 Torr) in H_2 (63 Torr) driven to 12% conversion leads to ca. 0.5% incorporation of H into SCB-d_2, while that of SCB-d_2 SF_6 (each 4 Torr) in N_2 (30 Torr) driven to 25–35% conversion results in ca. 6% incorporation of hydrogen. We judge that the greater H(Si)-enrichment of SCB-d_2 in the absence of H_2 rather than in its presence is due to the fact that the addition of DHSi=CHD or $H_2Si{=}CD_2$ (rearranged $D_2Si{=}CH_2$) (10, -1′) to ethene is more facile than the reaction of silacyclobutylidene with H_2 (-4′). The excess of the high thermal conductivity hydrogen decreases the temperature in the hot zone of the irradiated system [35,36] and will also decrease the role of (i) elimination [10] of H_2, HD or D_2 from $D_2Si{=}CH_2$, HDSi=CHD and $H_2Si{=}CH_2$ and (ii) polymerization of $D_2Si{=}CH_2$, HDSi=CHD and $H_2Si{=}CH_2$ (which are generated in excess of H_2 in lower concentrations) making these silenes more available for the addition to ethene. Assuming further that (i) both 1,1-D_2 elimination (4′) and 2 + 2 cycloreversion (1′) are reversible (and well documented [37]) processes, and (ii) only silenes ($D_2Si{=}CH_2$, HDSi=CHD and $H_2Si{=}CD_2$) but neither silylenes-d_2 nor 1- or 2-silavinylidenes can add to ethene to yield silacyclobutane, the findings on the H(Si) SCB-d_2 enrichment suggest that the H/D exchange at the silicon occurs via 1,2-H(D) shifts in silene (Reaction 10) and not via 1,2-H shifts in 1-silavinylidene and silyne (Reaction (4′) in Scheme 2). We therefore conclude that of both molecular paths for H/D exchange at the silicon, route (10) is more plausible.

An alternative explanation of the D/H exchange at the silicon via reaction sequence (11) starting from step (-2′) involving silylene γ-insertion into the C–H(D) bond can be ruled out on the following grounds.



(11)

It is known that intermolecular insertions of silylenes into C–H bonds is by at least two and four orders of magnitude slower than reaction of silylene into H_2 or Si–H bonds, respectively [25], and that the former have [38–40], contrarily to the latter [25], sizeable activation energy. Although silacyclic intermediates produced via intramolecular insertions into C–H bonds are accepted intermediates for alkylsilylene decomposition [40–42], the intramolecular insertions into C–H bonds leading to three membered ring formation are favoured over larger ring production [41]. Indeed, only formation of silacyclopropane through β-insertion, but not formation of silacyclobutane via γ-insertion (-2′) has been proved in the examination of the flash vacuum pyrolysis of SCB-d_2 [6]. Apart from that, the reaction sequence (11) should yield D(C) enriched silacyclobutane which should decompose into D-enriched ethene. Our observation of the only ethene isotopomer, C_2H_4 (Table 1) serves as unequivocal proof that path (11) does not take place.

We admit, however, that the H/D scrambling is partly due to radical reactions, since these reactions are proved by the identification of methane, butane, dimethylsilane and perhaps disilapentane and methyldisilacyclopentene among the products. The rate constants at room temperature of the silylene insertion or addition and that of the H-abstraction by silylene from hydrocarbons (methane, ethane) were thought to be ca. 10^{-10}–10^{-11} cm^3 $molecule^{-1}$ s^{-1} [25,43] and ca. $(1 + 0.5)$ 10^{-14} cm^{-3} $molecule^{-1}$ s^{-1} [44], respectively. However, it was admitted that the latter values might correspond to reactions of silylene with impurities, and that the real values of silylene H-abstraction at room temperature must be significantly lower than 10^{-14} cm^{-3} $molecule^{-1}$ s^{-1}. Assuming the typical preexponential factor ca. 10^{-10} cm^3 $molecule^{-1}$ s^{-1} and the activation energy of ca. 8–10 kcal mol^{-1} for bimolecular reactions implies that the reaction constant of the addition of silylene at ca. 1000 K (effective temperature in the laser hot zone) is only several times higher than the reaction constant for the H abstraction by silylene. This estimation is in favour of the occurrence of H-abstraction reactions from the main H(C) containing products (the parent compound or mostly ethene, propene-d_1) which can further initiate short chain radical reactions resulting in the H/D scrambling (Reactions 12 and 13).

$$\mathrm{D(H_2DC)Si{:}} + \mathrm{RH} \rightarrow \mathrm{D(H_2DC)HSi^{\bullet}} + \mathrm{R^{\bullet}} \qquad (12a)$$

$$\mathrm{D(H_2DC)HSi^{\bullet}} \rightarrow \mathrm{D(H)Si{:}} + {}^{\bullet}\mathrm{CH_2D} \qquad (12b)$$

$$\mathrm{DHSi{:}} + \mathrm{RH} \rightarrow \mathrm{DH_2Si^{\bullet}} + \mathrm{R^{\bullet}} \qquad (13a)$$

$$\mathrm{DH_2Si^{\bullet}} \rightarrow \mathrm{H_2Si{:}} + \mathrm{D} \qquad (13b)$$

In conclusion, we show that SCB-d_2 decomposition is not only controlled by initial silylene and silene extrusions but also by extensive H/D scrambling reactions. Apart from the earlier demonstrated 1,2-hydrogen shift from Si to C producing *n*-propylsilylene [6], we reveal that other modes of H/D scrambling occur via the 1,2-H(D) shift in silene and also by radical chain reactions initiated by H-abstraction by silylenes.

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