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Laser-powered homogeneous pyrolysis of 4-silaspiro[3,3]heptane. A source for 2-silaallene and its polymer

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Abstract

Continuous-wave CO_2 laser-photosensitized (SF_6) decomposition of 4-silaspiro[3,3]heptane is dominated by the transient formation and polymerization of 2-silaallene. The first experimental evidence for 2-silaallene has been achieved via scavenging with alcohols ROH (R = CH_3, CF_3CH_2) to afford dialkoxy(dimethyl)silanes, $(RO)_2Si(CH_3)_2$. ESCA analysis of the polymer demonstrates SiC_2 stoichiometry and indicates the incorporation of oxygen, which may be explained by reaction of the residual Si=C bonds with air.

Keywords: 4-Silaspiro[3,3]heptane; 2-Silaallene; Homogeneous decomposition; Laser; Poly(2-silaallene)

1. Introduction

Conventional thermolysis (CP) of silacyclobutanes is a well-established (2 + 2) cycloreversion affording transient silenes which undergo cyclodimerization (major pathway), rearrangement and/or insertion into Si–H bonds [1–3]. The laser-powered homogeneous decomposition (LPD) and CP of silacyclobutanes $R_2\overline{SiCH_2CH_2CH_2}$ [R = H, CH_3, H_2C=CH, HC≡C and $(CH_2)_4$] are remarkably different in that the transient silenes generated during LPD favour polymerization; thus, LPD is a unique route for the chemical phase deposition (CVD) of polycarbosilanes consisting mainly of silene units [4–9]. The elimination of surface assistance in LPD [10] changes the decomposition mode or the product distribution in many reactions [11–13]. The LPD technique has also proved useful for the initial gas-phase trapping of elusive ClSi≡CH [9] and $(HO)CH_3Si$: [14] species.

Other unsaturated silicon intermediates which continuously attract attention are the silallenes, but only the existence of 1-silaallenes as transients has been known for more than 10 years (see, for example, Refs. [15,16]) and they have recently been synthesized as air-stable compounds [17]. Although discussed theoretically [18–20], 2-silaallene has not been detected experimentally to date and was only suggested as a possible intermediate in the co-pyrolysis of the adduct (2,8-dimethyl-3,9-dichloro-6-silaspiro[5,5]undecatetra-2,4,8,10-ene + methyl acetylenedicarboxylate) and benzaldehyde [21].

In this paper, we report an extension of our LPD studies to 4-silaspiro[3,3]heptane (SSH) and show that the homogeneous decomposition of this silabicycle provides a source of 2-silaallene, and that this process results in a high-yield CVD of a crosslinked poly(2-silaallene).

2. Experimental details

Experiments were carried out using a CW CO_2 laser operating at the P(20) line of the $00^01 \rightarrow 10^00$ transition (944.19 cm^{-1}) with a 10 W output. Mixtures of SSH/SF_6 sensitizer/CH_4 (internal standard) (all at 1.3 kPa)/Ar (at 24 kPa) were irradiated with a focused beam (incident energy, 40 W cm^{-2}) in a vertically positioned glass tube (furnished with NaCl windows) which formed part of a set-up allowing GLC (Shimadzu 14A gas chromatograph coupled with a Chromatopac C-R5A computing integrator, programmed temperature, column packed with Porapak P) monitoring of the disappearance of SSH and the appearance of the gaseous products. Alternatively, the LPD of SSH was monitored

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by FT-IR spectrometry (Nicolet, Impact 400 spectrometer) and GC–MS spectrometry (Shimadzu QP 1000 quadrupole GC–MS spectrometer, programmed temperature, column packed with Porapak P); in this case SSH/SF_6 mixtures (each component at 1.3 kPa) with or without scavenger (methanol or 2,2,2-trifluoroethanol, each at 1.3 kPa) were irradiated in a similar reactor fitted with two NaCl windows and a sleeve with a rubber septum. Depletion of SSH and formation of ethene were determined at 530 and 1126 cm^{-1}, and at 1888 and 1911 cm^{-1}, respectively.

To evaluate the properties of the deposit by FT-IR spectroscopy, SEM and XPS techniques, deposits were produced on different substrates (NaCl, KBr, Al) placed in the reactor before the irradiation. XPS measurements were performed using a VG ESCA 3 Mk II electron spectrometer equipped with an Al Kα X-ray ($h\nu$ = 1486.6 eV) source operated at 220 W. The surface of the deposit was sputtered by Ar ions (energy 4 keV, ion current 20 μA, 5 min). SEM studies of the deposit were conducted on an ultra high vacuum Tesla BS 350 instrument.

Sulphur hexafluoride (Fluka), methanol (Lachema), 2,2,2-trifluoroethanol (Aldrich) and argon (Technoplyn) were commercial samples and SSH was prepared as reported previously [22]. Authentic samples of bis(2,2,2-trifluoroethoxy)dimethylsilane and (dimethoxy)dimethylsilane were prepared by reactions of the appropriate alcohols with dimethyldichlorosilane in ether in the presence of pyridine.

3. Results and discussion

Laser irradiation of $SSH/SF_6/Ar$ mixtures results in the formation of volatile ethene (a major product), together with minor amounts of buta-1,3-diene and silacyclopentene [Figs. 1 and 2(a)] and traces of propene, benzene and toluene. The same simple course for the LPD of SSH is also observed in the absence of Ar. Under both conditions, a transparent material is simultaneously deposited on the cold reactor surface. The mean effective temperature [10] under both types of condition was estimated as being 800°C. The decomposition is driven to completion readily within less than 200 s and the amounts of products (in mol/mol of SSH decomposed) are independent of the decomposition progress: ethene (1.7–1.8), butadiene and silacyclopentene (both below 0.1), and propene (~ 0.03). The very small quantities of silacyclopentene formed indicate that virtually all the silicon of SSH is efficiently utilized in the formation of the deposit.

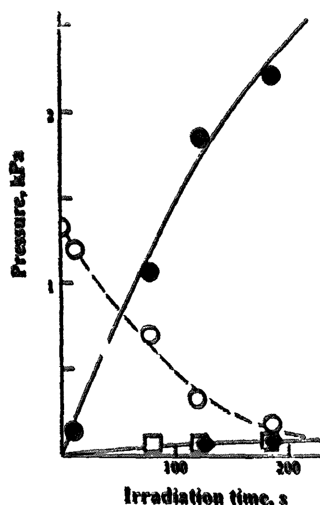


Fig. 1. Compound distribution in irradiated SSH/SF_6 (both at 1.3 kPa)/Ar (at 24 kPa) mixtures. ○, SSH; ●, C_2H_4; □, $CH_2{=}CH{-}CH{=}CH_2$; and ◆, $H_2\overline{SiCH_2CH{=}CHCH_2}$.

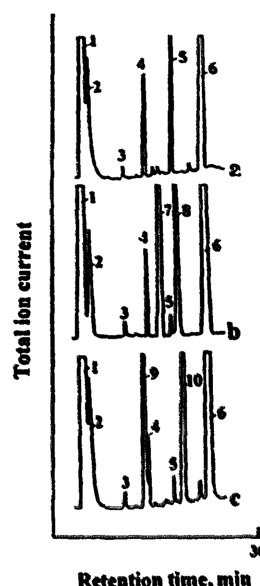
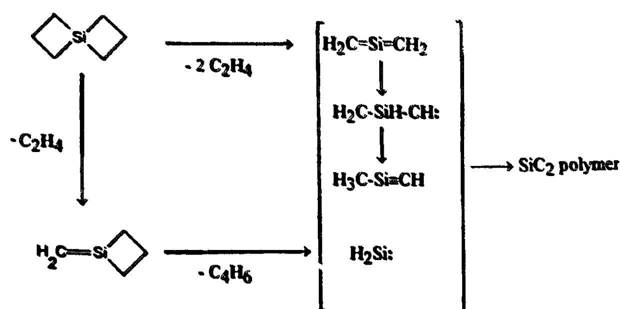


Fig. 2. Typical GLC–MS trace of the mixture obtained on laser irradiation of (a) SSH/SF_6 (both at 1.3 kPa), (b) $SSH/SF_6/CF_3CH_2OH$ (all at 1.3 kPa) and (c) $SSH/SF_6/CH_3OH$ (all at 1.3 kPa). Column: Porapak P. Peak identification: 1, SF_6; 2, C_2H_4; 3, $CH_3CH{=}CH_2$; 4, $CH_2CH{=}CHCH_2$; 5, $H_2\overline{SiCH_2CH{=}CHCH_2}$; 6, SSH; 7, CF_3CH_2OH; 8, $(CF_3CH_2O)_2Si(CH_3)_2$; 9, CH_3OH; and 10, $(CH_3O)_2Si(CH_3)_2$.

This material balance is in keeping with the assumption that the predominant route in the LPD of SSH is a two-fold elimination of ethene yielding 2-silaallene, while minor routes involve the formation of silacyclopentene and its decomposition into butadiene and silylene (Scheme 1). The transient occurrence of 2-silaallene was demonstrated by scavenging experiments with alcohols ROH (R = CH_3 and CF_3CH_2); irradiation of $SSH/SF_6/ROH$ mixtures did not afford a transparent deposit, with volatile dimethyl(dialkoxy)silanes being the dominant products [Fig. 2(b) and (c)]. The formation of $(CH_3)_2Si(OR)_2$ {MS (70 eV, m/z, relative intensity): R = CH_3: 105 (M – CH_3, 49); 75 (50); 59 (13); R = CF_3CH_2: 187 (M – CF_3, 0.3); 173 (0.8); 161 (2); 157 (2); 123 (1); 113 (43)}, ensuing from the two-fold addition of ROH to $H_2C{=}Si{=}CH_2$ and/or



Scheme 1.

$CH_3Si{\equiv}CH$ [Eq. (1)], confirms that $H_2C{=}Si{=}CH_2$ and/or $CH_3Si{\equiv}CH$ species are involved in the process.

$$H_2C{=}Si{=}CH_2 \text{ and/or } CH_3Si{\equiv}CH + 2ROH$$

$$\rightarrow (CH_3)_2Si(OR)_2 \qquad (1)$$

ESCA analysis of the deposit reveals that the stoichiometry of the superficial (5 nm) layers is $Si_{1.0}C_{2.1}O_{0.8}$ (before and after treatment with Ar ions), which is compatible with the major route of the LPD of SSH being the polymerization of SiC_2 transients (Scheme 1). Such analysis also indicates that the deposit is sensitive to air once withdrawn from the reactor. The measured value of the Si 2p core-level binding energy of 102.1 eV as well as that of the modified Auger parameter (1710.8 eV) are in accord [23–25] with an organosilicon polymer containing Si–C units. The FT-IR spectrum (cm^{-1}) of the in situ deposit (Fig. 3) exhibits typical absorptions at 835 ν(Si–C); 1026 $\nu(SiCH_nSi)$; 1250 $\delta(CH_3Si)$; 2117 ν(Si–H); 2924 ν(C–H), and lacks absorption bands typical for the silacyclobutane ring vibrations (956 and 1120 cm^{-1}). The increase in the absorptivity at 1026 cm^{-1} after exposure of the deposit to the atmosphere (Fig. 3) is assignable to ν(Si–O) and ν(C–O) vibrations and consistent with the uptake of oxygen by residual unsaturated bonds between silicon and carbon [26]; a similar residual reactivity of laser chemical vapour-deposited polycarbosilanes from silacyclobutanes has been observed previously [7]. The

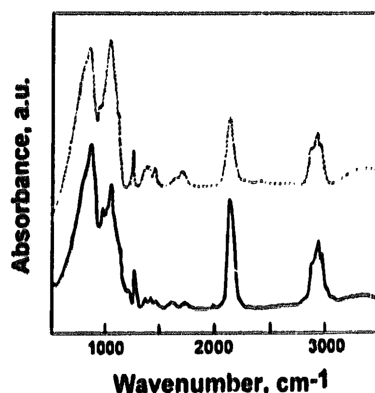


Fig. 3. Infrared spectrum of the deposit before (solid curve) and after (dashed curve) exposure to air.

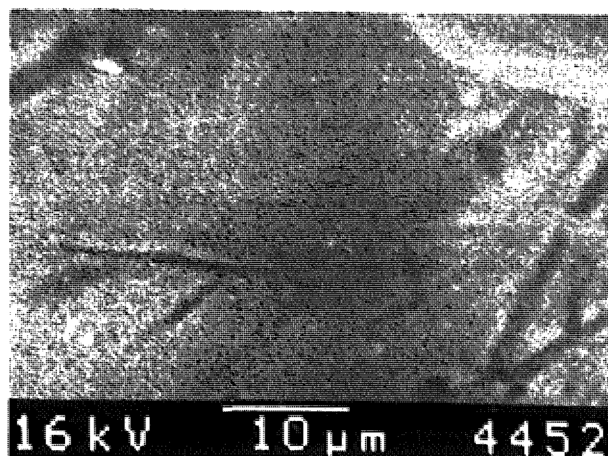


Fig. 4. Scanning electron micrograph of the deposit formed during the reaction.

ν(Si–H) band is obviously related to participation of silylene in polymerization (Scheme 1), the $\delta(CH_3Si)$ band being supportive of the assumed rearrangement of 2-silaallene into the energetically less stable [18] silylethyne. The possible involvement of the methenesilylcarbene intermediate in the polymerization reactions should increase the content of Si–H bonds in the deposit.

Scanning electron microscopy of the deposit (Fig. 4) shows its compact structure with no agglomerates normally produced by LPD of silacyclobutanes [5,7,8]. The deposit is insoluble in tetrahydrofuran and toluene, which suggests that it has a cross-linked structure.

It should be pointed out that the LPD and CP of SSH are competely different, the latter having been reported [27,28] to yield silacyclopentene and elemental silicon as the only silicon-containing products. It should be emphasized that the LPD of SSH leading to the polymerization of 2-silaallene provides a new example of the very efficient polymerization of Si=C bond-containing transients [29] in the gas phase, this polymerization occurring much more readily than that of allene [30,31].

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