

Laser powered homogeneous decomposition of 2,2-diethenylhexamethyltrisilane: Complex mechanism and gas-phase deposition of polycarbosilane

Radek Fajgar^a, Karl Hassler^b, Josef Pola^{a,*}

^aLaser Chemistry Group, Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, 16502 Prague, Czech Republic

^bInstitut für Anorganische Chemie, Technische Universität, A-8010 Graz, Austria

Received 29 September 2004; accepted 24 February 2005

Available online 24 March 2005

Abstract

IR laser-induced SF₆-photosensitized decomposition of gaseous 2,2-diethenylhexamethyltrisilane yields acetylene, volatile organylsilanes (vinyltrimethylsilane, trimethylsilane) and organyldisilanes (1,1- and 1,2-bis(trimethylsilyl)ethenes and 3,3-dimethyl-3,5-disilacyclopent-4-ene), and affords chemical vapour deposition of solid polycarbosilane film. The mechanism of the decomposition is discussed on the basis of quantification of gaseous products and scavenging experiments with buta-1,3-diene and revealed to involve both molecular and radical steps. The first experimental evidence on direct extrusion of central silylene unit from trisilanes is reported.

© 2005 Elsevier B.V. All rights reserved.

Keywords: 2,2-Diethenylhexamethyltrisilane; Homogeneous decomposition; Mechanism of decomposition; Polycarbosilanes deposition

1. Introduction

Thermolysis studies on low-molecular weight polysilanes in the gas phase (e.g. Refs. [1–6]) have attracted much interest because of the use of polysilanes as photoresists, precursors to new polymers and ceramic materials and also because of mechanistic reasons. Further studies on the mechanism of thermolysis of polysilanes are helpful in explanation of photo-thermal and thermal laser ablation of these compounds, which can be used in lithography and for deposition of novel materials.

The mechanism of the decomposition of hexamethyldisilane is affected by pressure [1] and consists of a number of radical steps (initial Si–Si bond cleavage, [H] abstraction by (CH₃)₃Si radical, (CH₃)₃Si group Si → C rearrangement, radical combinations and dimethylsilene cyclodimerization) that result in the formation of (CH₃)₃SiH, (CH₃)₄Si,

(CH₃)₃SiCH₂Si(CH₃)₂H and [–(CH₃)₂SiCH₂Si(CH₃)₂CH₂–] compounds [1].

The same reactions and addition of trimethylsilyl radical to dimethylsilene, silene → silylene isomerizations, silylene intramolecular cyclizations and elimination of trimethylsilane from tri- and hydrido(polymethyl)tetrasilanes are considered to take place in the thermolysis of octamethyltrisilane and yield monosilanes (CH₃)₃SiH (a major product), (CH₃)₄Si and (CH₃)₂SiH₂ together with cyclic products having two or three –(CH₃)₂Si– (or one CH₃HSi and one(CH₃)₂Si) groups and 2–CH₂– groups in the ring [5].

The mechanism of thermolysis is dramatically changed upon substituting two central methyl groups in octamethyltrisilane by ethyl groups. Thus, the thermolysis of 2,2-diethylhexamethyltrisilane is judged [6] to proceed via a multitude of the above steps and additionally via [H] abstraction from the CH₃ group and from two different sites of the CH₃CH₂ group. It yields only ethylene (a major product), (CH₃)₃SiH and (CH₃)₃SiCH=CH₂ together with minute amounts of products containing three and four Si atoms. Trimethylsilane was considered as originating from

* Corresponding author. Tel.: 420 2 203 90308; fax: 420 2 209 20661
E-mail address: pola@icpf.cas.cz (J. Pola).

hydrido(methyl)ethyltrisilanes as well as from [H] abstraction by $(\text{CH}_3)_3\text{Si}$ radical, whereas ethylene and vinyltrimethylsilane were judged as arising from cleavage of sila- and disilacyclopropanes [6].

Silylenes are considered to play a minor role in these decompositions and cyclic adducts reportedly formed (but not described) upon scavenging by 2,3-dimethylbuta-1,3-diene of $\text{H}_n(\text{CH}_3)_{2-n}\text{Si}$: and $\text{C}_2\text{H}_5(\text{H})\text{Si}$: in thermolysis of $(\text{CH}_3)_3\text{Si}(\text{C}_2\text{H}_5)_2\text{Si}(\text{CH}_3)_3$ [6] and of $(\text{CH}_3)_2\text{Si}$: in thermolysis of $(\text{CH}_3)_3\text{Si}(\text{CH}_3)_2\text{SiSi}(\text{CH}_3)_3$ [5] were supporting transient occurrence of these species. The scavenged products could not, however provide unequivocal evidence on the direct (initial) extrusion of the central silylene units from linear trisilanes, since the silylenes could be rationalized as produced by other steps.

In the context of our interest in the gas-phase laser-powered homogeneous decomposition (LPHD [7,8]) of organic and organosilicon compounds (e.g. [9–12]), we considered interesting to examine thermolysis of 2,2-diethenylhexamethyltrisilane under conditions circumventing heterogeneous contributions to the decomposition progress. We report here on LPHD of 2,2-diethenylhexamethyltrisilane, provide quantitative analysis of volatile products and give the first evidence on direct extrusion of central silylene as one of many paths occurring in the system.

2. Experimental

2.1. Laser-induced decomposition

Laser-induced decomposition of 2,2-diethenylhexamethyltrisilane was conducted by irradiating 2,2-diethenylhexamethyltrisilane (0.2 Torr)– SF_6 (1.3 Torr) without or in the presence of buta-1,3-diene (1.5 Torr) in a stainless-steel cell (inner diameter 32 mm, 140 mm long) equipped with a port with rubber septum and with a pair of NaCl windows (tightened to the cell body by rubber O-rings). A transversally excited atmospheric pressure (TEA) CO_2 laser (Plovdiv university) operating on the P(20) line of the $00^0_1 \rightarrow 10^0_0$ transition (949.19 cm^{-1}) with a repetition frequency of 1 Hz and providing an energy in pulse of 0.8 J on incident area of 1.0 cm^2 was used. The wavelength and fluence were checked by a spectrum analyzer (a model 16-A, Opt. Eng. Co.) and a pyroelectric detector (a ml-1 JU, Charles University). The cell was furnished with a metal needle valve connecting it to a standard vacuum manifold (equipped with Barocell and Pirani manometers) and both 2,2-diethenylhexamethyltrisilane and SF_6 were introduced to the cell as gases.

In some experiments liquid 2,2-diethenylhexamethyltrisilane ($15 \mu\text{l}$) was injected by a syringe through the septum of the cell that was heated to 110°C , which allowed to increase pressure of gaseous 2,2-diethenylhexamethyltrisilane. The irradiation of 2,2-diethenylhexamethyltrisilane (11.3 Torr)– SF_6 (1.3 Torr) by a focused laser beam (incident pulse energy 3.5 J/cm^2) was carried out to achieve chemical

vapour deposition of solid film on substrates (Al or Cu sheets) accommodated in the cell. These substrates covered with the deposited material, were transferred for measurements of physical properties of the deposited material by photoelectron spectroscopy and electron microscopy.

2.2. Analysis of products

Changes in the composition in the irradiated gaseous mixtures were monitored by a Fourier transmission infrared resonance (FT-IR) (Nicolet, model Impact 400) spectrometer by determining integrated absorbances of the diagnostic bands of 2,2-diethenylhexamethyltrisilane at 3004 cm^{-1} .

The identification of the gaseous products after the irradiation was accomplished by GC/MS (gas-chromatography/mass spectrometry) method (a Shimadzu GC/MS QP 1000 mass spectrometer) and by a GC–FT-IR method (a homemade interface) through comparison of the MS spectra with authentic samples or literature data. The quantification of these products was performed by gas chromatography (a Shimadzu GC 14A gas chromatograph with flame ionization detector (FID) detector coupled with a Chromatopac C-R5A computing integrator). All the instruments were equipped with SE-30 (3.3 m long, i.d. 3 mm, support material Chromatron N) column and operated at the programmed temperature ($20\text{--}140^\circ\text{C}$) using He carrier gas.

The films of solid products were deposited during the laser irradiation on KBr lumps that were accommodated in the cell prior to irradiation. The lumps were fixed on a metal frame and positioned into the probing IR beam after evacuation of the cell.

2.3. Model compound and chemicals

2,2-Diethenylhexamethyltrisilane was prepared from 2,2-dichlorohexamethyltrisilane.

2,2-Dichlorohexamethyltrisilane [13]. To a solution of 2,2-diphenylhexamethyltrisilane [14] (29.1 g) in 150 mL of benzene containing catalytical amount of AlCl_3 was introduced anhydrous HCl and then the mixture was heated to reflux. 2,2-Dichlorohexamethyltrisilane was obtained by distillation (bp $93\text{--}97^\circ\text{C}/21 \text{ Torr}$) in 78% yield.

2,2-Diethenylhexamethyltrisilane. 2,2-Dichlorohexamethyltrisilane (17.2 g) was mixed with dry THF (200 mL) and cooled to 0°C . Vinylmagnesium bromide (Aldrich, 0.1 M) in THF was slowly added to the stirred solution of 2,2-dichlorohexamethyltrisilane (17.2 g) at 0°C and then the solution was stirred at room temperature for 1 h. 2,2-Diethenylhexamethyltrisilane was distilled at $103^\circ\text{C}/30 \text{ Torr}$ in 50% yield.

^1H NMR spectrum (CDCl_3): δ 5.6–6.3 (m, 6H), 0.14 (s, 18H); ^{29}Si NMR spectrum (CDCl_3): δ -16.21 (TMS), -50.91 ($\text{Si}^* < \text{Si}_2$); ^{13}C NMR spectrum (CDCl_3): δ 133.8 (CH), 132.6 (CH_2). Mass spectrum [m/z (relative intensity, %)]: 228 ($M^{+\bullet}$, 1), 213 (21), 185 (12), 169 (17), 155 (38), 154 (21), 139 (18), 127 (23), 116 (36), 113 (59), 85 (19), 73

Download English Version:

<https://daneshyari.com/en/article/10547553>

Download Persian Version:

<https://daneshyari.com/article/10547553>

[Daneshyari.com](https://daneshyari.com)