Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Organometallic Chemistry 689 (2004) 2697–2701

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

IR laser decomposition of 1,3-disilacyclobutane in presence of carbon disulfide: chemical vapour deposition of polythiacarbosilane

Marketa Urbanová, Josef Pola *

Laser Chemistry Group, Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, Rozvojova Street 135, 16502 Prague, Czech Republic

Received 8 January 2004; accepted 30 April 2004
Available online 7 July 2004

Abstract

TEA CO_2 laser irradiation of gaseous mixtures of 1,3-disilacyclobutane – carbon disulfide affords chemical vapour deposition of solid polythiacarbosilane films that possess Si–S–X (X = Si, C), S–H and Si–H bonds and undergo slow hydrolysis in air to polyoxothiacarbosilanes containing Si–H, Si–O–Si and (C)S–H bonds. The formation of the polythiacarbosilane is proposed to take place via polymerization of transient silene and incorporation of CS_2 into growing polysilene network.

Keywords: Laser-induced decomposition; 1,3-disilacyclobutane; Carbon disulfide; Chemical vapour deposition; Polythiacarbosilane

1. Introduction

Laser-induced thermal decomposition of gaseous silacyclobutanes and disilacyclobutanes yields transient silenes (and silylenes) that efficiently undergo dehydrogenative polymerization in the gas-phase and allow chemical vapour deposition of solid polycarbosilane films (e.g., [1–6]).

The laser-induced decomposition of silacyclobutanes and 1,3-disilacyclobutane (DSCB) in the presence of molecular oxygen allows interception of generated silenes with $^3O_2$ and leads to transient siladioxetane [7] whose further reactions result in chemical vapour deposition of polyoxocarbosilane films [8].

Similar sulfur-containing polycarbosilanes – (polythiacarbosilanes) – have not been yet purposefully studied, although they are admitted to be initially produced and later decomposed during conventional hot-wall pyrolysis of S-containing organosilicon compounds [9,10].

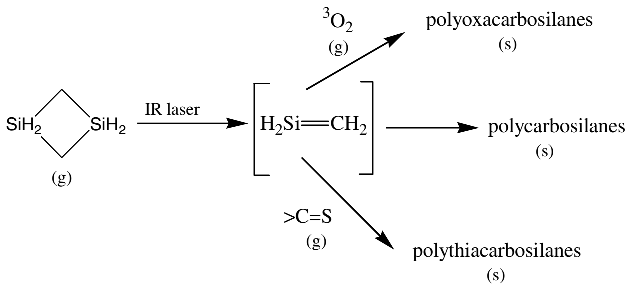
Suitable approach to these polymers can be IR laser generation of silenes in the presence of organic compounds with the C═S bond. The reaction between silenes and thioketones takes place in the course of conventional thermolysis of benzene solution of 1,1-dimethyl- (or 1,1-diphenylsilacyclobutanes) and thiobenzophenone, proceeds via reactive silanethione and yields cyclic dimer of dimethylsilanethione (tetramethylcyclodisilthiane) [11]. The IR laser irradiation of DSCB yielding transient silene in the presence of a C═S group-containing compound in the gas-phase would benefit from the absence of unwanted hot-wall reactions and will circumvent thermal degradation of the once deposited materials. It can extend the potential of the IR laser decomposition of the silacycles for chemical vapour deposition of heteroatom-containing organosilicon polymers (Scheme 1).

It was therefore, of our interest to study the gas-phase reaction between IR laser-generated silene and carbon disulfide, the compound more available than thioketones, and to examine the deposited materials. We report on IR laser decomposition of DSCB in the

---

* Corresponding author. Fax: +42-0220-390308.
E-mail address: pola@icpf.cas.cz (J. Pola).

0022-328X/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2004.04.051



Scheme 1.

presence of CS_2, compare this reaction with IR laser decomposition of DSCB [6] and show it to afford chemical vapour deposition of solid polythiacarbosilane films.

2. Experimental

Laser irradiation experiments were conducted using a grating-tuned transversely excited atmospheric (TEA) CO_2 laser (Plovdiv university, 1300 M model) operated on the R(20) line of the $00^01 \rightarrow 10^00$ transition (975.93 cm^{-1}) as confirmed by a model 16-A spectrum analyzer (Optical Engineering Co.). The incident laser beam was rectangular (1.8 and 1.0 cm per side, or ca. 0.6 and 0.3 cm per side when focused). Focusing of the laser beam was achieved with a Ge lens (focal lens 15 cm). The laser energy (0.75 J) was measured with a laser energy pyroceramic sensor (Charles University ml-1U model).

Gaseous samples of DSCB–CS_2 (molar ratio 1:5 and 5:1; total pressure 60 Torr) and of DSCB (25 Torr) were irradiated in a Pyrex reactor that had two side arms (one fitted with septum and the other connecting to vacuum-line) and was consisting of two orthogonally positioned tubes (both 3 cm in diameter), one 13 cm and the other 9 cm in length, both furnished with pairs of KBr windows. The irradiation was achieved through the shorter tube, while the second tube was used for monitoring IR spectra of the gaseous mixtures after irradiation. The reactor accommodated KBr substrates which, covered with deposited film, were transferred for measuring FTIR spectra.

The chemical changes after the irradiation were monitored directly in the reactor by FTIR spectroscopy (an FTIR spectrometer Nicolet Impact 400) and also, after admitting helium into the reactor to atmospheric pressure, by gas chromatography (a Shimadzu 14 A chromatograph with Porapak P or SE-30 columns, programmed (20–150 °C) temperature, He carrier gas). The gaseous products were identified by FTIR and GC–MS spectrometry (a QP 1000 Shimadzu spectrometer) at the conditions identical to those of gas-chromatography analysis.

The depletion of DSCB was followed using diagnostic bands at 786 and 955 cm^{-1} and that of CS_2 using bands at 1537 and 2331 cm^{-1}. Formation of methane (at 1305 and 3006 cm^{-1}) and ethyne (at 730 cm^{-1}) was also followed by FTIR spectroscopy. Quantitative GC analyses were performed using the FID response factors from the laboratory data base.

DSCB (from the laboratory stock) and carbon disulfide (Aldrich) were distilled prior to use.

3. Results and discussion

The TEA CO_2 laser irradiation of gaseous DSCB–CS_2 mixtures results in infrared multiphoton decomposition (IRMPD, e.g., [12]) of DSCB as the radiation at 975.93 cm^{-1} is efficiently absorbed in its $\delta(SiH_2)$ vibrational mode [6]. Carbon disulfide does not absorb the laser radiation and can, in principle, react only with the major transient product of the decomposition of DSCB, which is mostly silene [6]. Independent TEA CO_2 laser irradiation of gaseous CS_2 alone confirmed high thermal stability [13,14] and no decomposition of CS_2 under the used irradiation conditions.

The final products of the laser irradiation of the DSCB–CS_2 mixtures differ depending on the incident laser energy density and on the composition of the gaseous mixtures (Table 1). In excess of DSCB chemical changes could be accomplished by using unfocused radiation, whereas in excess of CS_2 they can be only achieved by using the focused radiation.

3.1. Unfocused irradiation of DSCB–CS_2

The unfocused irradiation of the mixtures rich in DSCB (Table 1, Run 1) yields minute quantities of gaseous products and results in chemical vapour deposition of whitish films. The gaseous products are methane, ethene, ethyne, C_3-hydrocarbons, methylsilane, dimethylsilane and trimethylsilane. Quantities of these products resemble those observed in the IRMPD of DSCB (Table 1, Run 2), which implies that the major portion of the decomposed DSCB (more than 90%) is used for the formation of the solid films. The depletion of CS_2 is only 8% of that of DSCB, which indicates that most of generated silene underwent polymerization and dehydrogenation as observed in the IRMPD of DSCB [6]. The small depletion of CS_2 and no formation of volatile S-containing products reveals that CS_2 is incorporated into polymerizing silene. Such incorporation is proved by the IR spectrum of the deposit through absorption band of a ν(Si–S) bond (see later).

3.2. Focused irradiation of DSCB–CS_2

The focused irradiation of the mixtures rich in carbon disulfide (Table 1, Run 3) yields small quantities of the same gaseous products together with traces of hydrogen

Table 1
IR laser decomposition of DSCB in presence of CS_2

Run	Irradiated mixture (kPa)	Pulse energy (J)	Focused	No. of pulses	Depletion in (kPa)		Gaseous products[a] (mol/mol of DSCB decomposed × 100)					
					DSCB	CS_2	CH_4	C_2H_4	C_2H_2	C_3H_4	CH_3SiH_3	$(CH_3)_2SiH_2$
1	DSCB (6.7) CS_2 (1.3)	0.75	No	400	0.95	0.075	1.1	0.6	0.6	0.1	0.22	2.4
2[b]	DSCB (3.3)	0.90	No	2000	2.4	–	1.5	0.7	0.2	0.1	4.7	7.0
3	DSCB (1.3) CS_2 (6.7)	0.75	Yes	200	0.63	0.25	15	1.0	28	4.0	4.0	1.0
4[b]	DSCB (3.3)	0.75	Yes	30	1.8	–	3.0	1.0	1.7	0.1	1.0	1.1

[a] Gas-chromatography analysis.
[b] IRMPD of DSCB [6].

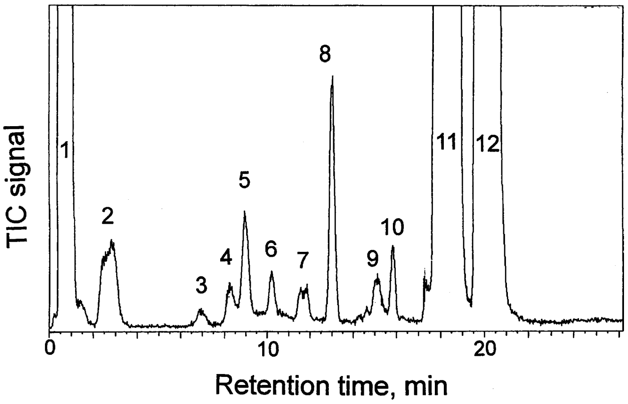


Fig. 1. Typical GC-MS trace of irradiated DSCB (10 Torr)–CS_2 (50 Torr) mixture. Peak designation: (1) CH_4 and air, shoulder C_2H_4, (2) C_2H_2, (3) H_2S, (4) H_2O, (5) CH_3SiH_3, (6) C_3H_6, (7) C_3H_4, (8) $(CH_3)_2SiH_2$, (9) $(CH_3)_3SiH$, (10) unidentified product, (11) CS_2, (12) DSCB.

sulfide (Fig. 1) and results in chemical vapour deposition of greyish films. Methane and ethyne (a high temperature product) are produced in ~10 times higher yields than with the unfocused radiation. The low yields of gaseous products indicate that the major process in the irradiated system is the formation of the solid films. Depletion of CS_2 being ~40% of that of DSCB) is in line with significant incorporation of CS_2 into the solid material. This is confirmed by the FTIR spectrum of the deposit that shows a very intense ν(Si–S) absorption band (see later). The formation of traces of H_2S can be accounted for by reaction of S atoms with H_2 (available in the system [5,6]) or by cleavage of Si–S bonds of the produced solid with traces of H_2O inadvertently present in the system.

3.3. Structure of the deposits assessed from FTIR spectra

The FTIR spectra of the deposits (assigned [15] in Table 2) show pattern (Fig. 2) similar to that of the solid obtained upon similar irradiation conditions from the IRMPD of DSCB, which corresponds [6] to a cross-linked polycarbosilane possessing much less hydrogen than polysilene [16].

The deposit obtained from Run 1 differs slightly and that from Run 3 noticeably from polycarbosilanes by showing a ν(Si–S) absorption band at 490 cm^{-1} and a ν(S–H) absorption band at 2538 cm^{-1} and by having the ν(Si–H) band shifted to higher wavenumbers. This shift confirms that the Si–H bonds experience different local environment due to both inductive effect of S and S back-bonding to Si [17].

Some absorption between 600–800 cm^{-1} (specifically for the deposit from Run 3) is compatible [15] with the presence of ν(C–S–(Si)) (~640 cm^{-1}) and/or of ν(C–S–C) modes.

The absence of bands of sulfur allotropes (S_7 [18] and S_8[19]) and of $—CS_2C—$ bridges [20] at 470 cm^{-1} rules out the presence of elemental sulfur and of disulfide arrangements that might have been produced from decomposition of CS_2.

The deposited films change when exposed to air. This is illustrated by the FTIR spectra (Fig. 2c and d) that show depletion of the ν(Si–S) absorption band at 490 cm^{-1} and a built-up of bands at 2538 cm^{-1} (the ν(S–H) band) and 1040 cm^{-1}. The latter overlaps with the ν($SiCH_2Si$) band and assigns to ν(SiOSi) mode of siloxanes.

These structural changes can be interpreted by hydrolysis of the Si–S bonds. All silicon–sulfur compounds are readily hydrolysed [21] and the observed spectral changes support the assumed presence of the Si–S bonds in the deposit and rule out the less probable and hydrolytically stable disulfidic bridges. The formation of the S–H and Si–O–Si bonds is in line with hydrolysis of Si–S–Si and/or Si–S–C bonds (Scheme 2). The ν(S–H) absorption band at 2538 cm^{-1} in the hydrolyzed films does not get lost after several days, which shows that the HS groups are incorporated in non-volatile polymeric structures.

Table 2
FTIR spectra of deposits

Vibrational mode	Wavenumber (cm^{-1})/absorptivity[a]		
	IRMPD of DSCB in CS_2		IRMPD of DSCB
	Run1	Run 3	Run 2
ν(Si–S)	490/1.2	490/5.0	–
ν(Si–C) and $\rho(CH_3)$	837/9.0	837/2.8	837/9.8
$\delta(H_xC)$ and $\delta(H_xSi)$	956/5.5	956/0.9	956/5.1
$\nu(SiCH_2Si)$	1043/2.7	1043/1.4	1043/4.4
$\delta_s(CH_3Si)$	1253/1.0	1253/1.0	1253/1.0
ν(Si–H)	2135/6.7	2146/1.4	211 0/8.8
ν(S–H)	2538/0.5	–	–
ν(C–H)	2898/0.5	2898/ 0.2	2898/0.4
ν(C–H)	2960/0.5	2960/0.3	2960/0.4

[a] Normalized to absorptivity of $\delta(CH_3Si)$ band.

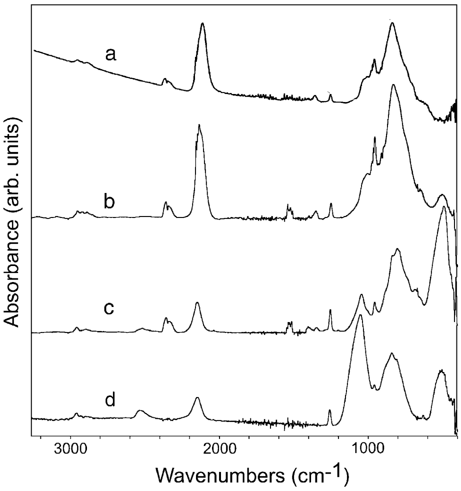
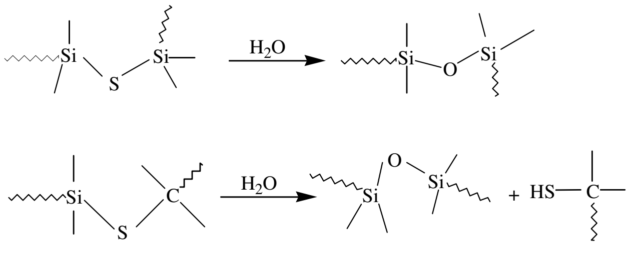


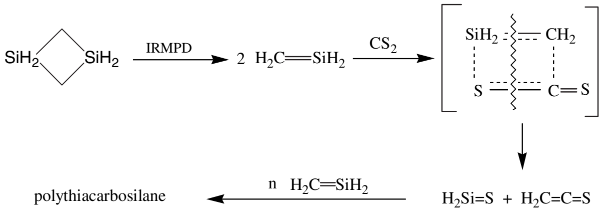
Fig. 2. FTIR spectra of the deposited film from IR laser irradiation of DSCB (a), DSCB (50 Torr)–CS_2 (10 Torr) (b) and DSCB (10 Torr)–CS_2 (50 Torr) (c). The spectrum (d) corresponds to the deposit obtained from DSCB (10 Torr)–CS_2 (50 Torr), which was exposed to air for 24 h.



Scheme 2.

3.4. Gas-phase chemistry

The assessed structure of the solid deposits is apparently the result of an incorporation of CS_2 into polymerizing silene [6].



Scheme 3.

Thermal decomposition of CS_2 is unlikely; this reaction starts only at 1400 K [14] and yields [13,14] CS radical and S atoms dimerizing on walls to S_2 [13]. The formation of the CS in the gas-phase would have lead to its gas-phase polymerization [22] yielding polythiene films with characteristic absorptions of C=S, >C=C<, $S_2C{=}CS_2$, —C–(C=S)–S— and —S–(C=S)–S— configurations. No evidence on elemental sulfur and the absence of the characteristic polythiene absorptions between 1300–1700 cm^{-1} are therefore, compatible with CS_2 reacting mostly with silene and/or silene oligomers.

The more pronounced depletion of DSCB than CS_2 (Table 1) is in accordance with the major channel being polymerization of transient silene together with dehydrogenation of transient silene and its oligomer; CS_2 can be incorporated into polymerizing silene via S-nucleophilic attack initiated 2+2 cycloaddition and cleavage of the adduct into transient silanethione [10] and thioketene [23] (Scheme 3).

Thioketene has not been detected by IR spectroscopy. We assume that both highly reactive silanethione and thioketene undergo much less self-polymerization than reactions with silene and/or silene oligomers. The lower content of the Si–H bonds and the higher content of the CH_3(Si) groups in the films obtained at the focused radiation (Table 2) is associated with higher temperatures and formation of more methylsilylene (through $CH_3(H)Si{:}\leftrightarrow H_2Si{=}CH_2$ equilibrium [24,25]), as well as with more pronounced dehydrogenative steps [6]. We can then speculate that the whole co-polymerization scheme is also contributed by a (yet unknown) methylsilyne reaction with CS_2.

The co-polymerization of silene (and methylsilylene) and of their partially dehydrogenated oligomers with CS_2, silanethione and thioketene can take place via a number of molecular and radical steps to finally yield macromolecules having their skeleton composed of C, Si and S atoms and possessing S–H and Si–H bonds.

4. Conclusion

The TEA CO_2 laser irradiation of gaseous DSCB – CS_2 mixtures affords chemical vapour deposition of a solid polythiacarbosilane films containing Si–S–Si, C–S–Si-, Si–H and S–H bonds.

The formation of polythiacarbosilane is assumed to occur mostly via incorporation of CS_2 molecule into polymerizing silene. More incorporation of CS_2 is achieved with focused laser radiation and higher CS_2/DSCB ratio.

The films are modified in air due to hydrolysis of the Si–S bonds into polyoxothiacarbosilanes containing Si–O–Si, Si–H and (C)S–H bonds.

The IR laser-induced decomposition of DSCB in CS_2 extends the potential of the IR laser decomposition of silacycles for chemical vapour deposition of heteroatom-containing organosilicon polymers.

Acknowledgement

The research was supported by the Ministry of Education, Youth and Sports of the Czech Republic (Grant ME 612).

References

[1] J. Pola, V. Chvalovský, E.A. Volnina, L.E. Gusel'nikov, J. Organometal. Chem. 341 (1988) C13.
[2] J. Pola, E.A. Volnina, L.E. Gusel'nikov, J. Organometal. Chem. 391 (1990) 275.
[3] D. Čukanová, J. Pola, J. Organometal. Chem. 453 (1993) 17.
[4] J. Pola, Rad. Phys. Chem. 49 (1997) 151 and references therein.
[5] L. Khachatryan, E.A. Volnina, R. Fajgar, J. Pola, J. Organometal. Chem. 566 (1998) 263.
[6] Z. Bastl, H. Bürger, R. Fajgar, D. Pokorná, J. Pola, M. Senzlober, J. Šubrt, M. Urbanová, Appl. Organometal. Chem. 10 (1996) 83.
[7] I.M.T. Davidson, C.E. Dean, F.T. Lawrence, J. Chem. Soc., Chem. Commun. (1981) 52.
[8] J. Pola, J. Vitek, Z. Bastl, J. Šubrt, J. Organometal. Chem. 640 (2001) 170.
[9] L.E. Gusel'nikov, N.S. Nametkin, Chem. Rev. 79 (1979) 529.
[10] G. Raabe, J. Michl, Chem. Rev. 85 (1985) 419.
[11] L.H. Sommer, J. McLick, J. Organometal. Chem. 101 (1975) 171.
[12] C.D. Cantrell (Ed.), Multiple-Photon Excitation and Dissociation of Polyatomic Molecules, Springer, Berlin, 1986.
[13] G. Gaydon, G.H. Kimbell, H.B. Palmer, Proc. Roy. Soc. 279 A (1964) 313.
[14] P. Blanchard, P. Le Goff, Can. J. Chem. 35 (1957) 89.
[15] R.G.J. Miller, H.A. Willis (Eds.), Infrared Structural Correlation Tables and Data Cards, Spectrum House, Heyden, London, 1969.
[16] H.-J. Wu, L.V. Interrante, Polym Prepr. (Am. Chem. Soc., Div. Polym. Chem.) (1991) 32.
[17] A.N. Egorochkin, N.S. Vyazankin, S.Ya. Khorshev, Rus. Chem. Rev. 41 (1972) 425.
[18] M. Gardner, A. Rostad, J. Chem. Soc., Dalton (1973) 599.
[19] L.A. Nimon, V.D. Neff, R.E. Cantley, R.O. Buttlar, J. Mol. Spectrosc. 22 (1967) 105.
[20] P.B. Zmolek, H. Sohn, P.K. Gantzel, W.C. Trogler, J. Am. Chem. Soc. 123 (2001) 1199.
[21] D.A. Armitage, in: G. Wilkinson, F. Gordon, A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 2, Pergamon, New York, 1982, p. 168.
[22] R. Tomovska, Z. Bastl, V. Vorlíček, K. Vacek, J. Šubrt, Z. Plzák, J. Pola, J. Phys. Chem. B 107 (2003) 9793.
[23] E. Schaumann, Tetrahedron 44 (1988) 1827.
[24] B.A. Sawrey, H.E. O'Neal, M.A. Ring, D. Coffey, Int. J. Chem. Kinet. 16 (1984) 23;
Int. J. Chem. Kinet. 16 (1984) 31.
[25] A.D. Johnson, J. Perrin, J.A. Mucha, D.E. Ibbotson, J. Phys. Chem. 97 (1993) 12937.