

Communication

Gas-phase formation of SiSe in IR laser-co-decomposition of dimethyl selenide and 1,3-disilacyclobutane

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Abstract

A LIF excitation spectrum of SiSe obtained upon IR laser irradiation of gaseous mixture of 1,3-disilacyclobutane and dimethyl selenide reveals that the previously reported infrared multiple photon co-decomposition of both compounds involves formation of SiSe. The SiSe formation is explained in terms of reaction of Se atoms with RHSi: silylenes (R = CH₃, H) and silene, and elimination of RH from silaneselones (RHSiSe, R = CH₃, H).

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1. Introduction

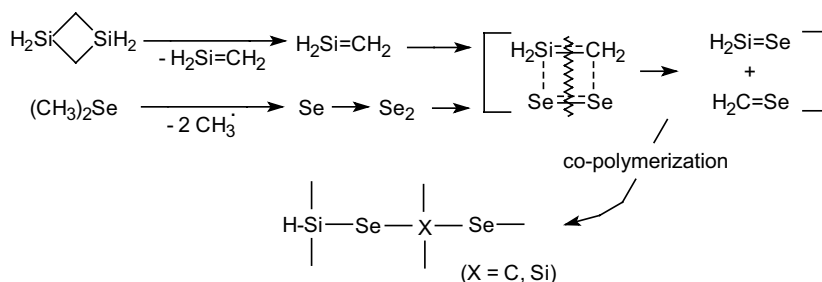
Laser irradiation of 1,3-disilacyclobutane (DSCB) in the mixture with heteroatom (O, S, Se)-containing compounds allows chemical vapour deposition (CVD) of novel polyoxacarbosilanes [1], polythiacarbosilanes [2] and polyselenocarbosilanes [3]. These polymers (ultrafine powders or thin films) can be hardly produced by other techniques, but their gas-phase formation involves a number of reaction steps which are due to the decomposition of the mixture constituents and reactions between products of these decompositions. The proposed steps can be confirmed through detection of transient species, which will help understand the gas-phase chemistry and optimise the process to obtain polymeric materials with required properties.

The IR laser-induced CVD of polyselenocarbosilanes [3] was characterized as the infrared multiple photon-induced, non-interacting homogeneous decompositions of DSCB and dimethyl selenide (DMS), consisting of intermediate formation of silene and elemental selenium as major prod-

ucts, interception of selenium by reactive silene, and formation and polymerization/co-polymerization of transient silaneselone, H₂Si = Se and selenoformaldehyde, H₂C = Se (Scheme 1, [3]).

The interpretation of this process was based on the identification of final products and detection of transient species in the decomposition of DSCB and decomposition of DMS. It is known that the IR laser multiple photon decomposition (IRMPD) of DSCB results in efficient deposition [4] of SiC/H and Si/C materials and is dominated [5–7] by the formation of transient SiCH₄ species (silene (H₂Si=CH₂) and methylsilylene (CH₃)HSi:) that decompose [8,9] into silylene (H₂Si:) and methylene (H₂C:). It is also known that the IR laser-induced decomposition of DMS, affording CVD of elemental selenium and poly(selenoformaldehyde), is dominated by the homolysis of the C–Se bonds [10]. All these steps are feasible in the IR laser-irradiated DSCB–DMS system, despite that the Si–Se–X–Se (X = C, Si) structures of the final solid products can be best reconciled [3] with a sequence of the formation of silene and Se₂, a reaction between these species to silaneselone, and polymerization/copolymerization of silaneselone and selenoformaldehyde (Scheme 1).

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Here we show that the IR laser-irradiated mixture of DSCB and DMS contains SiSe. We report on transient detection of SiSe and explain formation of this molecule in terms of the decomposition of transiently formed silaneselones RHSiSe ($\text{R} = \text{CH}_3, \text{H}$).

2. Experimental

Gaseous mixtures of DSCB and DMS (1:1 ratio, total pressure 0.3 mbar) were irradiated with pulses from a TEA CO_2 laser (Lumonics K-103) laser which operated at the $10\text{P}(26)$ line of the $00^0_1 \rightarrow 10^0_0$ transition at 938.71 cm^{-1} , repetition rate lower than 1 Hz and energies of 0.26 J . The employed wavelength, absorbed by both compounds, was checked with a 16-A spectrum analyzer (Optical Eng. Co.). The laser was equipped with frontal Ge multimode optics (35% reflectivity), a rear diffraction grating with 135 lines/mm and a low jitter trigger device (Lumonics 524) supplying jitters between the IR and UV pulses shorter than 50 ns in the pump and probe experiments. The laser operated with a mixture of CO_2 , N_2 and He in the proportion 8:8:84, the pulse temporal profile being monitored with a photon drag detector (Rofin Sinar 7415). The pulse consisted in a spike (60 ns (FWHM)) and a tail lasting approximately 3 μs .

A Pyrex reactor (605 ml in volume, equipped with a pair of quartz windows orthogonal to the fitting NaCl windows) was placed behind a 24 cm focal lens and used for laser induced fluorescence (LIF) experiments. The output of a N_2 -pumped dye laser (PRA LN107, 0.04 nm bandwidth, 500 ps temporal width), counter-propagating to the infrared laser beam, was focused by a 50 cm quartz lens at the focus of the infrared beam. The LIF experiments were carried out by using coumarin dye 521 (doubled with a KDP crystal) for the 265–272 nm region. The induced fluorescence was collected through a quartz window at the right angle to the laser axis and filtered through a 10 cm-monochromator, 2 mm slit (bandpass of 6.4 nm). The filtered signal was detected by means of a photomultiplier (Hamamatsu R-928) fed with 800 or 1000 V.

The CO_2 laser pulse, picked up with the photon drag detector, triggers a Tektronix TDS 540 digital oscilloscope that is used to collect the LIF signals and send them to a personal computer where they are averaged and analyzed. The delay between the CO_2 and probe laser pulses was con-

trolled by a Berkeley Nucleonics digital delay generator (BNC 7036A) within $\sim 50 \text{ ns}$. Each experimental point in a LIF curve was obtained by averaging over ten measurements. Sample pressures in the cell were measured with (0–1 and 0–10 mbar) MKS Baratron gauges.

The progress of the decomposition of both compounds was monitored with an FTIR spectrophotometer (model Perkin–Elmer 1600) using absorption bands at 650 and at 1432 cm^{-1} for DSCB and DMS, respectively.

3. Results and discussion

The identification of SiSe species in the IR laser irradiated gaseous DMS–DSCB (1:1) mixture is possible by comparing LIF experiments performed on this mixture and LIF experiments performed on (i) pure gaseous DSCB and (ii) gaseous DMS–trisilane mixture in which SiSe species has been previously detected [11].

Our previous study on LIF after IRMPD of DSCB performed by us in the visible spectral region detected the formation of SiH_2 , CH_2 and H_2 [9]. In further experiments in the UV, we have checked that IRMPD of DSCB followed by excitation of the formed species at 265.05 nm give rise to the formation of a LIF signal of long lifetime, in the order of 220 ns (Fig. 1, curve a).

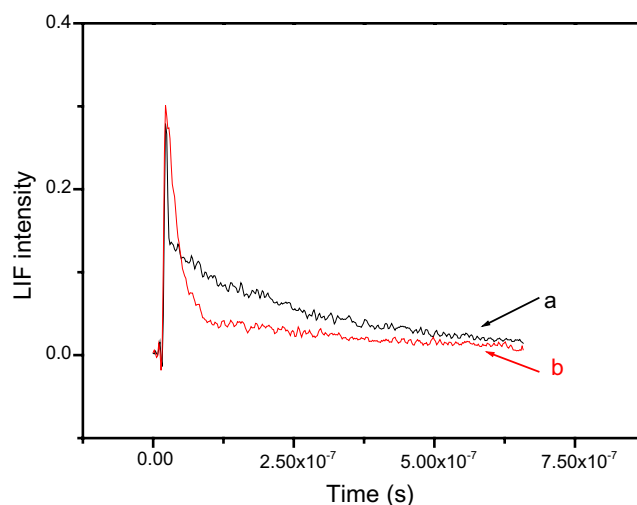


Fig. 1. LIF signals obtained from IRMPD of (a) pure DSCB and (b) DMS–DSCB mixture by exciting at 265.05 nm .

When the LIF experiments are carried out in the DMS–DSCB mixture by exciting at the same wavelength, an intense signal is detected and its temporal profile fitting to a double exponential function with decay constants of around 17 and 300 ns (Fig. 1, curve b) suggests the formation of two different species overlapping in the same spectral region.

We have obtained the excitation spectrum of the LIF signal detected in the decomposition of the DMS–DSCB mixture (1:1) by scanning the probe UV laser beam between 263 and 272 nm. This excitation spectrum is presented in Fig. 2 (curve b) together with the spectrum obtained from the Si₃H₈–DMS mixture (1:1) (curve a, [11]).

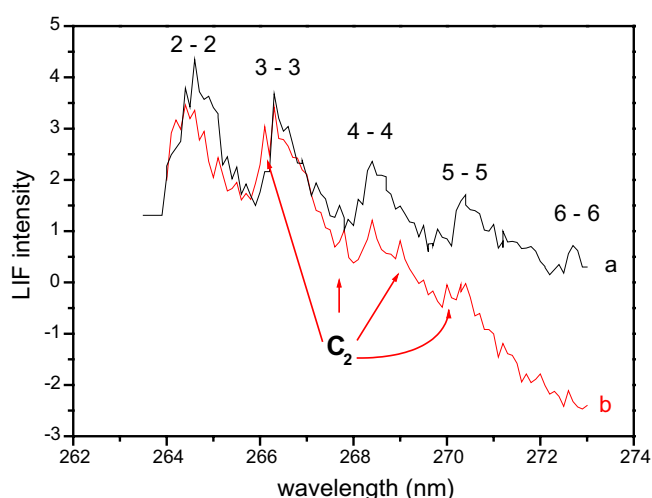
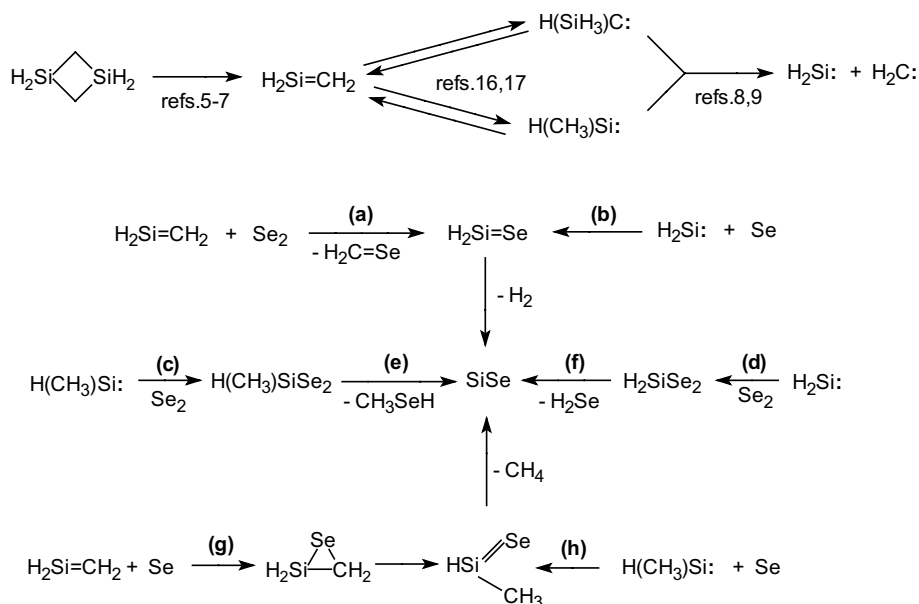


Fig. 2. LIF excitation spectra obtained from IR laser co-decomposition of (a) Si₃H₈–DMS and (b) DMS–DSCB mixtures (both 1:1, total pressure 0.3 mbar).

It is seen that the excitation spectrum obtained from IR laser co-decomposition of DMS–DSCB mixture contains all the bands detected in the Si₃H₈–DMS mixture and assigned to the sequence $\Delta v = 0$ for $v' = 2-6$ of the $E^1\Sigma^+ - X^1\Sigma^+$ system of SiSe [12]. The excitation spectrum also contains small peaks at around 266.0, 267.8, 268.9 and 270.0 nm. All the bands and peaks are overlapped to a continuum background.

The radiative lifetimes of the pure SiSe at the assigned transitions are around 17–20 ns [13], which is coincident with the short lifetime obtained from the DMS–DSCB (1:1) decomposition LIF signal. The long radiative lifetime deduced from the second exponential, as well as the positions of the weak peaks, suggest that these are due to rotational transitions of the $\Delta v = -1$ for $v' = 1-2$ of the $B^3\Pi_g - X^3\Pi_u$ of the Fox-Herzberg system of C₂ [14,15]. From these results we conclude that SiSe and C₂ species are formed in the co-decomposition of DMS–DSCB mixtures.

The formation of SiSe can be best explained (Scheme 2) by reaction of silene and silylenes with selenium (Se and/or Se₂). These silicon-containing transients are well-known products of the homogeneous decomposition of DSCB. Thus, silene [5–7] and silylene [8,9] were detected in the IRMPD of DSCB, and silene and methylsilylene are known [16,17] to exist in thermal equilibrium. Reaction (a) was postulated in our previous work [3] as a step analogous to addition of ³O₂ to silene [1,18], reaction (b and h) was reported [19–22] for kinetically stabilized silylenes, and reaction sequences (c, e and d, f) get support from the previous observation of H₂Se and CH₃SeH products [3] and similarity to reactions of silylene with ³O₂ [23]. However, the dimerization of Se atoms (facilitated by third body stabilization) is in the used low pressure region (0.3 mbar) less



Scheme 2.

probable, which gives more support to reactions initiated by Se atoms (steps b, g and h) than those initiated by Se₂ species.

The reported data on the formation of gaseous SiSe are significant with respect to properties of the solid polymeric films deposited from the IR laser irradiated DMS–DSCB mixture. These films were identified [3] on the basis of X-ray photoelectron and FTIR spectra as composites of elemental selenium and polymer with the Se–X (X = Si, C) and Si–H bonds. It is known that H_n(CH₃)_{3–n}Si–Se– structures possess infrared bands at ca. 390 cm⁻¹ (ν_{Si–Se}, [24,25]) and ~2130–2150 cm⁻¹ (ν_{H–Si(Se)}, [26]), whereas solid SiSe diluted and stabilized in the solid argon matrix has [27] (in agreement with the IR spectra of the gaseous [12] SiSe) a weak absorption band at 572 cm⁻¹. The absence of the SiSe band in the FTIR spectra of the solid polymeric films deposited from the IR laser irradiation of DMS–DSCB mixture indicates that gaseous SiSe is highly reactive and gets lost in sink reactions.

SiSe is isovalent to SiO, the well-known gaseous species [28,29] undergoing fast polymerization to structurally inhomogeneous material (e.g. [30–32]). The absence of infrared absorption at ca. 750 cm⁻¹ (assignable [27] to SiSe₂) rules out the SiSe decomposition (2SiSe → SiSe₂ + Si, [33]). The Si⁺–Se⁻ polarity [13] would favour nucleophilic attack of SiSe to >Si(H)– moieties, leading to the formation of the >Si(H)–Se–Si– structures. Other feasible reactions are insertion into Si–H bonds, addition across silene and combination with silylenes, as deduced from analogous steps of isovalent SiO which behaves [34] as a reactive silylene. All these steps lead to formation of the Si–Se bonds-containing polyselenocarbosilanes [3].

We thus conclude that SiSe is transiently formed in the IR laser-irradiated gaseous DMS–DSCB mixture despite that it is not observed as a component in the solid polymeric product. The gaseous SiSe has yet been observed only when applying discharge to aluminium selenide in quartz tube [35] or silicon tetrachloride with selenium [36]. The formation of SiSe upon IR laser-induced co-decomposition of a pair of Si- and Se-containing volatile compounds ([11] and this work) does not appear promising for deposition of nano-sized SiSe due to high reactivity of this species towards other transients present in the irradiated system, although similar technique has been employed for CVD of other nanosized IV–VI metal chalcogenides [37–40].

4. Conclusions

Further study on the earlier reported [3] IR laser irradiation of gaseous mixture of 1,3-disilacyclobutane and dimethyl selenide allowed identification of a LIF excitation spectrum of SiSe.

The gas-phase formation of this transient species is explained in terms of RH elimination from silaneselones, RHSiSe formed by reaction of Se atoms with silene, H₂Si=CH₂ and silylenes, RHSi: (R = CH₃, H).

The absence of SiSe in the final solid deposited product (Si–Se bonds-containing polyselenocarbosilanes) is ascribed to reactions of SiSe with other components present in the irradiated 1,3-disilacyclobutane–dimethyl selenide mixture.

Acknowledgements

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