

Cw CO₂-laser-induced reaction between silane and methyl methacrylate

^aJ. POLA, ^bR. ALEXANDRESCU, ^bJ. MORJAN, and ^bD. SORESCU

^a*Institute of Chemical Process Fundamentals, Czechoslovak Academy of Sciences, CS-165 02 Prague*

^b*Laser Department of the Institute of Physics and Technology of Radiation Devices, Central Institute of Physics, Bucharest — Magurele*

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Infrared laser homogeneous heating of monosilane SiH₄—methyl methacrylate (MMA) mixtures results in the formation of gaseous methane, acetylene, butenes, and carbon monoxide along with solid silicone polymer. Mechanism of this reaction is assumed to be initiated by the dissociation of silane into silylene and the addition of the latter to MMA. The results resemble those obtained when the reaction between SiH₄ and MMA is induced *via* multiphoton decomposition of silane.

Инфракрасное лазерное гомогенное нагревание смесей моносилана SiH₄ с метилметакрилатом (ММА) приводит к образованию газообразных метана, ацетилен, бутенов и монооксида углерода наряду с твердым силиконовым полимером. Предполагается, что механизм реакции инициируется диссоциацией силана на силилен и присоединением последнего к ММА. Эти результаты подобны результатам, полученным при изучении реакции между SiH₄ и ММА, индуцируемой посредством мультифотонного разложения силана.

The infrared laser-induced decomposition of monosilane into molecular hydrogen and very reactive silylene has recently been intensively studied [1—5]. The silylene is known [3—26] to react with variety of molecules such as oxygen [6], dimethylacetylene [6], ethylene [6, 8], methane [8], alcohols [14, 15], halosilanes [17, 18], hydrogen [8, 18], deuterium [19], hydrogen chloride [20], germane [10, 11, 21], phosphine [22], acetylene [14, 23], cyclopentadiene [24], and 1,3-butadiene [7, 14, 25—28]. All these reactions afford high yields of volatile and low yields of solid silicon-containing compounds. Conversely, solid silicon-containing films can be obtained as major reaction products by infrared multiphoton decomposition (IRMPD) of silane [29—31] or by the IRMPD of silane in the presence of methyl methacrylate (MMA) [32] which add to the potential of this technique for chemical vapour deposition of electronically significant materials.

Our previous results [32] on the silicone polymer deposition by pulsed CO₂-laser-induced decomposition of silane in the presence of MMA revealed that silylene reaction with MMA is strongly favoured over silylene insertion into the

Si—H bond of silane and thus indicated that the addition of silylene to the double bond of olefins is facilitated by α -carbalkoxy group. This suggestion was based on the assumption that $\text{SiH}_4 \rightarrow \text{SiH}_2 + \text{H}_2$ dissociation occurs prior to possible decomposition of MMA. Here we wish to report on the reaction between SiH_4 and MMA induced by a continuous-wave CO_2 laser. Due to its thermal nature, this reaction can be explained consulting the papers on thermal laser-induced [4, 5] and conventional [33—36] decomposition of silane and reports [37, 38] on thermal decomposition of MMA.

Experimental

Silane (Matheson or Lachema), helium (Messer Griesheim), and methyl methacrylate (Fluka) were commercial samples.

Silane and its mixtures with helium or MMA were irradiated by continuous-wave (cw) CO_2 lasers operating at the P(20) line (944 cm^{-1}) of the $00^{\circ}1 \rightarrow 10^{\circ}0$ transition in a cylindrical (3 or 4 cm inner diameter, 10 cm long) Pyrex cell that was equipped with KCl or NaCl windows and valve. Two lasers were used, namely one with 25 W output in a beam of 2.5 mm diameter (power density around 500 W cm^{-2}) and another [39] the beam (output 15 W) of which was focused by a Ge lens to obtain incident power density 300 W cm^{-2} .

The samples to be irradiated were introduced into the cell by using a standard vacuum-line technique as reported previously [32]. Changes in the composition of the irradiated samples were followed by recording IR spectra on Specord 75 model (Zeiss) and Perkin—Elmer, model 621 spectrometers. Depletion of silane was monitored using absorptivity at $\tilde{\nu} = 920 \text{ cm}^{-1}$ and determined as the ratio $\log T^{-1} : \log T_0^{-1}$ where T and T_0 are the transmissions before and after the irradiation.

Gaseous reaction products, *i.e.* carbon monoxide ($\tilde{\nu} = 2140 \text{ cm}^{-1}$), methane ($\tilde{\nu} = 1300 \text{ cm}^{-1}$), and acetylene ($\tilde{\nu} = 730 \text{ cm}^{-1}$) were identified by their infrared absorption bands (Fig. 1); these compounds along with butenes were identified also *via* their mass fragmentation on a Shimadzu model QP 1000 GC/MS quadrupole spectrometer (column packed with alumina deactivated with silicone oil).

Results and discussion

Interaction of the radiation of both continuous-wave CO_2 lasers (incident power density 300 and 500 W cm^{-2}) with different SiH_4 ($p = 0.6\text{—}2.5 \text{ kPa}$)—MMA ($p = 0.9\text{—}1.5 \text{ kPa}$) mixtures results in the depletion of both compounds and the formation of gaseous methane, carbon monoxide, and butenes together with a solid deposition on both windows and surface of the cell (Fig. 1). Infrared spectra of solid deposited material are consistent with siloxane structure and show very low intensity of the absorption band at $\tilde{\nu} = 2950 \text{ cm}^{-1}$. These results, *i.e.* the infrared spectra of siloxane deposit and the gaseous

products, are the same as those obtained in the study of the TEA CO_2 -laser-induced reaction between SiH_4 and MMA [32] which was assumed to be initiated by the multiphoton absorption in and by the dissociation of silane.

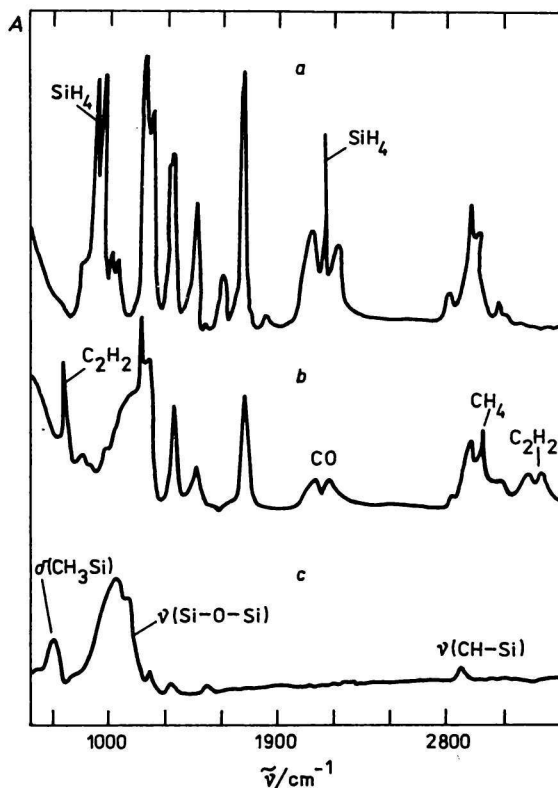


Fig. 1. Infrared spectra before (a) and after (b) the irradiation of SiH_4 —MMA mixtures and that of solid polymer (c) after the evacuation of the cell.

Here reported reaction induced by cw CO_2 laser has obviously thermal nature. The absorption of the laser radiation (the P(20) line from $10.6\ \mu\text{m}$ band) in the ν_4 mode of silane leads to primary vibrational excitation of this compound and further fast V-T energy collisional transfer to MMA molecules, which finally produces an increase in temperature. Under these conditions several reactions can take place, namely the hydrosilylation of MMA [40–42] or of products of thermal MMA decomposition, reaction of MMA with silylene, reaction of MMA fragments with silane [43], and finally reaction between silylene and MMA fragments.

Thermal decomposition of silane attracted lot of attention [33—36], much care being taken to eliminate surface contributions to reaction stages [5, 44], and has been concluded [36] to proceed by a nonchain mechanism, starting from the dissociation of silane



Thermal decomposition of MMA studied under conditions not obviating surface participation favours decarboxylation over decarbonylation [37], but laser-powered homogeneous decomposition of MMA can be described as decarbonylation leading to methacrylaldehyde that further decomposes into formaldehyde and propene, this homogenous reaction having Arrhenius parameters $E_a = 342 \text{ kJ mol}^{-1}$ and $\log A = 18.3 \text{ s}^{-1}$ [38]. Should MMA decompose, the latter process involving decarbonylation is to be expected under our conditions.

The known Arrhenius parameters of both SiH_4 and MMA thermal homogeneous decompositions allow to estimate which of these reactions is easier. Arrhenius plots of kinetic data for MMA and SiH_4 homogeneous decompositions are shown in Fig. 2 and reveal that decomposition of MMA is, within a wide temperature range, appreciably slower than decomposition of silane. The addition of silane to MMA (hydrosilylation) does not seem probable, since no products of such a reaction were detected. The above facts allow to assume that the major reaction pathway occurring in the SiH_4 —MMA mixture upon the

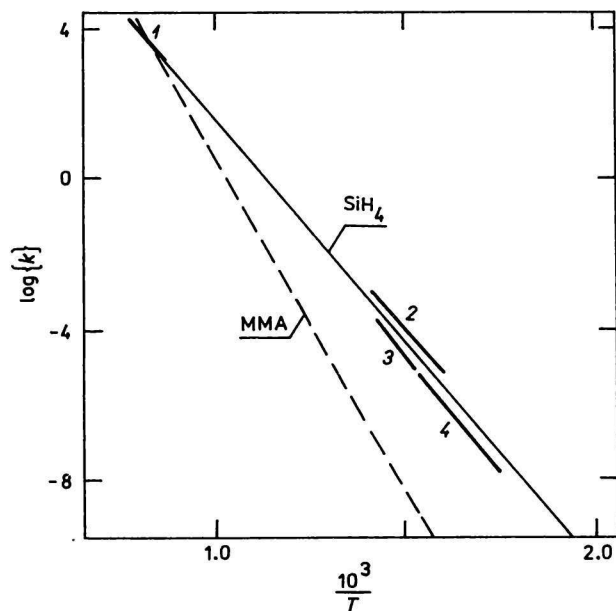
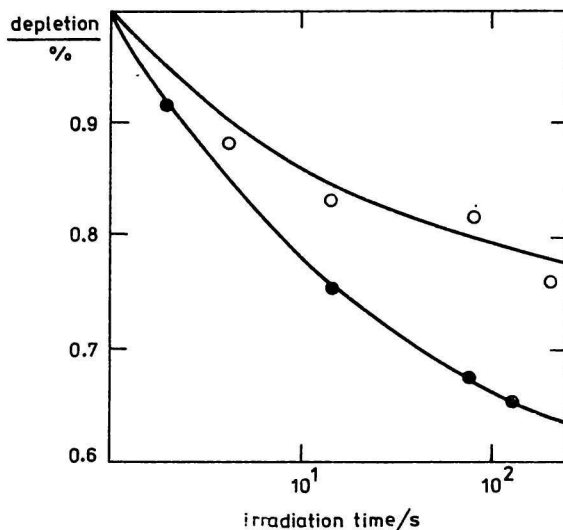


Fig. 2. Arrhenius plots for thermal decomposition of silane (lines 1—4 relate in the given order to Ref. [44, 36, 34, and 35]) and thermal decomposition of methyl methacrylate (Ref. [38]).

Fig. 3. The time variation of the depletion of silane ($p = 2.5$ kPa) (○) and silane ($p = 2.5$ kPa) in mixture with MMA ($p = 1.2$ kPa) (●) using laser power density 500 W cm^{-2} .



irradiation with cw CO_2 laser is the dissociation of silane and reaction of silylene with MMA. We note that the depletion of silane in the mixture with MMA is much faster than that of silane alone (Figs. 3 and 4, Table 1). It was observed earlier [3] that the addition of helium increases energy absorption and the decomposition of silane during the process of IRMPD, and this was explained by collisions between SiH_4 and He leading to pressure broadening of the SiH_4 absorption line. Under our conditions different mechanism has to operate and

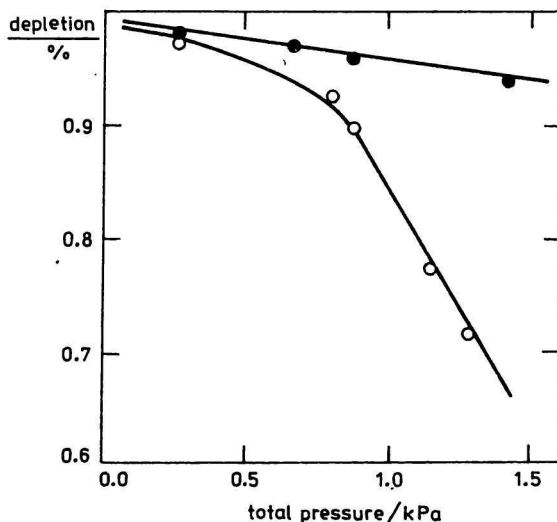


Fig. 4. Dependence of silane depletion on total pressure with mixtures of silane ($p = 0.7$ kPa) with helium (●) or MMA (○). (Laser power density and irradiation time were 500 W cm^{-2} and 90 s).

Table 1

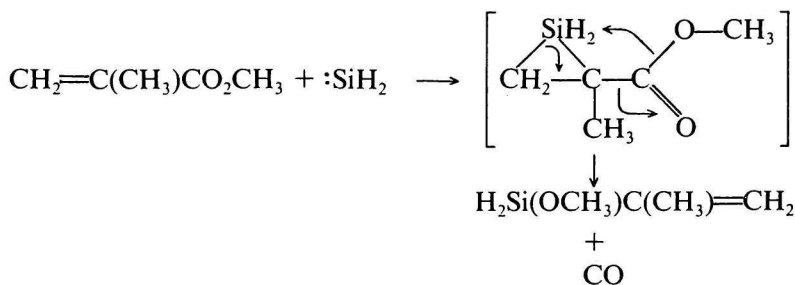
Depletion of SiH₄ at pressure thresholds^a

System	Pressure threshold	Depletion
	kPa	%
SiH ₄	0.9	3
SiH ₄ + He ^b	0.7	5
SiH ₄ + MMA ^b	0.6	22

a) Upon irradiation with power density 500 W cm⁻² for 90 s; b) equimolar mixture.

we believe that the acceleration of the SiH₄ depletion by MMA is brought about by a shift in the equilibrium (eqn (A)) through easy trapping of silylene by MMA. Such a promotion of silane dissociation appears plausible. There are no disilane and trisilane observed to be formed, which was also pointed out during the interaction of TEA CO₂ laser with the SiH₄—MMA mixture [32], and their absence can be explained by faster reaction of silylene with MMA compared to that with silane. The formation of gaseous compounds suggests that thermal reaction between SiH₄ and MMA has a complex nature and that it involves not only an addition of silylene to the double bond of MMA but also a molecular reorganization of the SiH₂—MMA adduct (expulsion of CO). The occurrence of methane, acetylene, and butenes indicates that other, radical processes have to be important as well.

We can speculate that the molecular channel may consist of the following reaction steps



leading to methoxy(propenyl)silane which can undergo the disproportionation (intermolecular exchange of H and OCH₃ groups) and subsequently final condensation to siloxane.

Similarly to the deposit from the SiH₄—MMA reaction induced by TEA CO₂ laser [32], the deposit obtained through the here described cw CO₂-laser-induced

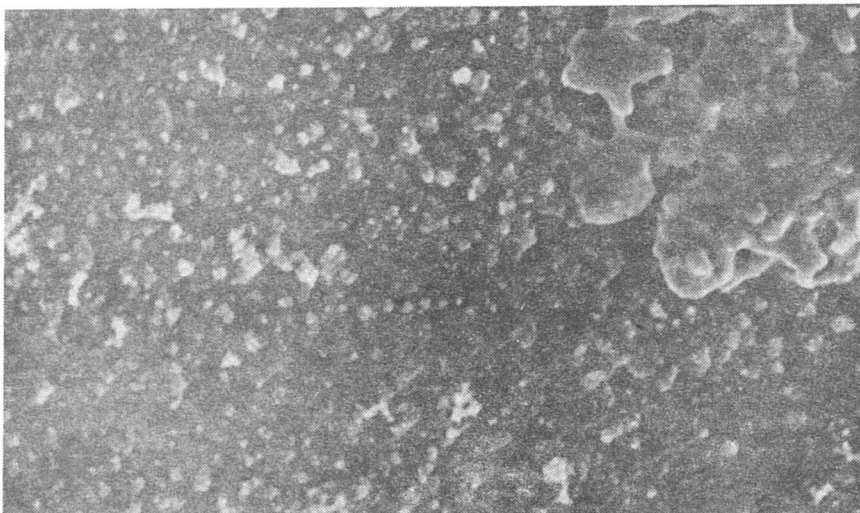
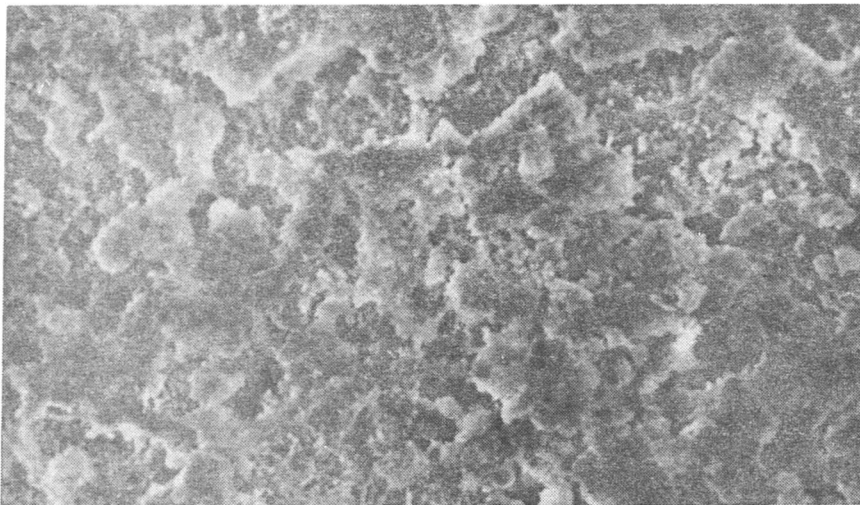


Fig. 5. SEM of the deposit showing structure of agglomerates.
Magnification is 10^3 .

SiH_4 —MMA reaction is not homogeneous and consists of regions of different morphology (Fig. 5).

We continue to study reactions of silylene with structurally different oxygen-containing olefins to attempt to find whether olefin structure is important for silicone formation.

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