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IR LASER-INDUCED CARBON-ENHANCED THERMOLYSIS OF SILOXANES IN THE LIQUID PHASE

Jaroslav Kupcik[1], Elvira A.Volnina[2],
Ludmila M. Tumanova[3] and Josef Pola[1]*

[1]Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, 165 02 Prague, Czech Republic
[2]Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, V-71 Moscow, Russia
[3] Institute of Spectroscopy, Russian Academy of Sciences, 142092 Troitsk, Russia

Abstract

TEA CO_2 laser induced liquid-phase thermolysis of a series of $[(C_6H_5)_nH_{3-n}Si]_2O$ (n = 1,2), $[(C_6H_5)(CH_3)HSi]_2O$ disiloxanes and $[(CH_3)_2SiO]_3$ in the presence of suspended acidic carbon soot results in the formation of oligomeric siloxanes and is judged to involve assistance of acidic and oxygenated carbon surface sites. The same reaction in the presence of suspended neutral graphite yields volatile hydrocarbons and is similar to homogeneous decomposition of siloxanes in the gas phase.

Introduction

Although extensively studied in the past (e.g. refs.[1-5]), the thermal behaviour of siloxanes is of continuing interest. It has been established that the conventional thermal degradation mechanism operating at hot-surface heterogeneous conditions is the rearrangement of the Si-O bonds. Recent examinations gave attention to specific classes of siloxanes[6] or the use of lasers for inducing siloxanes thermolysis in the gas phase[7-11] to produce hydrido(methyl)silicone powders or polyoxocarbosilane films. It was shown that a homogeneous mechanism occurring in IR laser thermolysis takes place exclusively via cleavage of the Si-C bonds[7,8,10] or by molecular elimination of silane[9,11].

New possibilities for the mechanism and formation of final thermolytic products can be opened through interacting laser radiation with disiloxane aerosol[12] or bulk liquid phase[13].

We have recently reported[13] that IR laser-induced carbon-sensitized decomposition of 1,3-diphenyldisiloxane in the liquid phase proceeds via extrusion/insertion of phenylsilanone and yields a blend of poly(phenylsiloxanes).

In this paper, we examine the interaction of a TEA CO_2 pulsed laser radiation with a series of siloxanes $[(C_6H_5)_nH_{3-n}Si]_2O$ (n = 1,2), $[(C_6H_5)_n(CH)HSi]_2O$ and $[(CH_3)_2SiO]_3$ in the condensed phase and reveal that the feasibility of their thermolysis and products are effected by carbon properties.

Materials and Methods

Experiments were carried with a TEA (transversely excited, atmospheric) CO_2 laser operated at the repetition frequency of 1 Hz on the P(20) line of the $00^01 \rightarrow 10^00$ transition (944.19 cm^{-1}) with a fluence of 0.6 $J.cm^{-2}$. The incident fluence of the focused laser beam was 1 $J.cm^{-2}$. Samples of liquid (0.2 ml) or solid (0.2 g) siloxanes with or without carbon materials (50 mg) were accommodated in a Pyrex vessel furnished with a NaCl window, a sleeve with rubber septum for withdrawing gaseous portions for gas chromatography analysis and by a P.T.F.E. valve (Fig. 1). The vessel was evacuated prior to laser irradiation.

The products obtained by laser irradiation were analysed by FTIR and mass spectroscopy as well as gas chromatography. The analyses of gases were performed on an FTIR Nicolet Impact spectrometer, a Shimadzu QP 1000 quadrupole mass spectrometer (Porapak P), and a GC 14A Shimadzu gas chromatograph (Porapak P and OV 17 column, programmed temperature 30 – 150 ° C). Mass and positive ion MALDI mass spectra of the irradiated liquids were analysed on an MS 80 Kratos GC/MS spectrometer (CBP 10-S50-050 capillary column, or direct inlet sampling, programmed heating of the direct inlet from 50 to 350 ° C) and on a Bruker BIFLEX reflectron time-of-flight mass spectrometer, respectively.

1,3-Diphenyldisiloxane, 1,1,3,3-tetraphenyldisiloxane and 1,3-diphenyl-1,3-dimethyldisiloxane were prepared after reported procedures[14-16] and their purity was checked by gas chromatography and ^{1}H-NMR spectroscopy. Hexamethylcyclotrisiloxane was purchased from Aldrich.

Two carbon powders used were polycrystalline synthetic graphite (SG) (Aldrich) and amorphous carbon soot (CS) (laboratory stock).

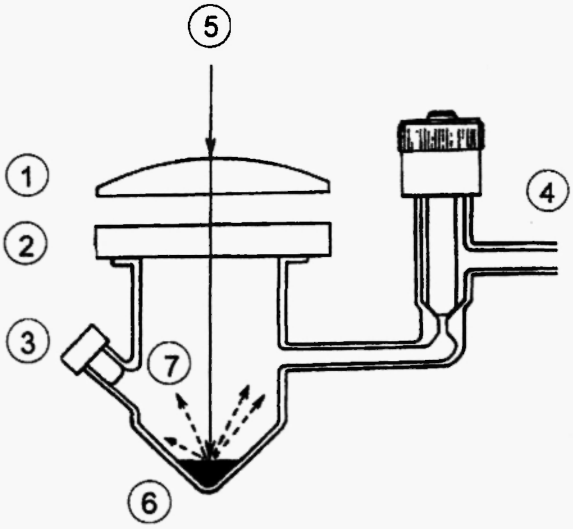

Fig. 1. Reaction vessel
1, KBr lens; 2, NaCl window; 3, sleeve with rubber septum; 4, P.T.F.E. valve; 5, laser beam; 6, irradiated sample; 7, ablation.

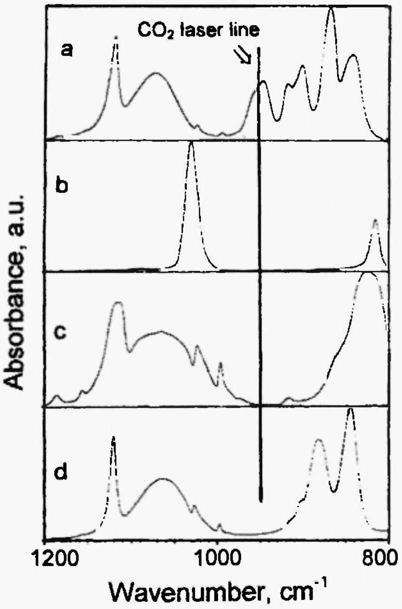

Fig. 2. Segment of FTIR spectrum of $[(C_6H_5)H_2Si]_2O$ (a), and $[(CH_3)_2SiO]_3$ (b), $[(C_6H_5)_2HSi]_2O$ (c) and $[(C_6H_5)(CH_3)HSi]_2O$ (d).

Results and Discussion

The pulsed IR laser irradiation (944.19 cm^{-1}) coincides with a strong $\delta(SiH_2)$ band of $[(C_6H_5)H_2Si]_2O$ (948 cm^{-1}), but absorptivity of the other siloxanes at this wavenumber is rather low, since the strong and broad $\nu(SiO)$ band of the $[(C_6H_5)_nH_{3-n}Si]_2O$ (n = 1,2) and $[(C_6H_5)(CH_3)HSi]_2O$ is located at 1065 cm^{-1} and that of $[(CH_3)_2SiO]_3$ at 1020 cm^{-1} (Fig. 2). We thus assume that the IR laser radiation is directly absorbed only in 1,3-diphenyldisiloxane. Carbon powder suspended in the siloxanes is a very efficient absorber of the CO_2 laser radiation and its particles being heated to high temperatures bring about a temperature jump in nearby layers of siloxanes. The carbon thus acts as a heterogeneous sensitizer[17]. The observation that the laser thermolysis of neat siloxanes does not take place, whereas that of the samples containing suspended carbon particles does (Table 1, Fig. 3) indicates that the role of the sensitization is important. Very fast heating of the irradiated samples of siloxane with carbon was indicated by a violent ablation of the liquid and by visible luminescence on the surface of the sample and on the droplets propelled from the bulk sample after each pulse.

Table 1. Products of laser thermolysis of siloxanes[1]

Initial siloxane (incident fluence)	Products (total yield in wt. %)		
	Neat siloxane	Siloxane with SG	Siloxane with CS
$[(CH_3)_2SiO]_3$ (1.0 J/cm^2)	$[(CH_3)_2SiO]_4$ traces	CH_4, C_2H_4, C_2H_2 C_2H_6, C_3H_6, C_3H_4 C_4H_8, C_4H_6, C_4H_4 (0.14-0.17)	CH_4, C_2H_2, C_2H_6 (0.11) $[(CH_3)_2SiO]_n$, (n=4-7), (20)
$[H_2(C_6H_5)Si]_2O$ (0.6 J/cm^2)	none	C_6H_6, C_4H_4, $C_6H_5SiH_3$ C_2H_6, C_3H_6, C_2H_2 ($3x10^{-3}$)	C_2H_2, CH_4 ($<10^{-3}$) $(C_6H_5)H_2SiO[(C_6H_5)HSiO]_nSiH_2(C_6H_5)$ n=1-3; (29) $[(C_6H_5)HSiO]_n$, n=1-5 (traces)
$[H(C_6H_5)_2Si]_2O$ (0.6 J/cm^2)	none	C_2H_2, C_4H_6, C_6H_6 ($5x10^{-4}$)	None
$[H(CH_3)(C_6H_5)Si]_2O$ (0.6 J/cm^2)	none	C_4H_4, c-C_6H_{12}, C_6H_6 ($6x10^{-4}$)	CH_4, C_2H_2, C_2H_4 ($7x10^{-4}$) $H(C_6H_5)(CH_3)Si[OSi(C_6H_5)(CH_3)]_2H$ (20)

[1] After 10^3 pulses.

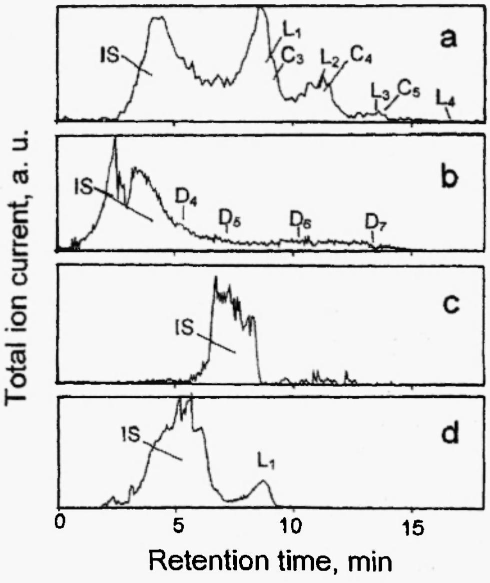

Fig. 3. Total ion current vs. number of scans plot obtained with heated MS direct inlet (50-350 °C). Irradiated $[(C_6H_5)H_2Si]_2O$ (a), and $[(CH_3)_2SiO]_3$ (b), $[(C_6H_5)_2HSi]_2O$ (c) and $[(C_6H_5)(CH_3)HSi]_2O$ (d). Designation: IS = (initial siloxane); a: $C_n = [(C_6H_5)HSiO]_n$, $L_n = (C_6H_5)H_2SiO[(C_6H_5)HSiO]_nSiH_2(C_6H_5)$; b: $D_n = [(CH_3)_2SiO]_n$; d: $L_1 = H(C_6H_5)(CH_3)Si[OSi(C_6H_5)(CH_3)]_2H$.

Products of thermal decomposition of the phenyldisiloxanes and hexamethylcyclotrisiloxane depend on the carbon (SG or CS) used (Table 1) and will be discussed separately for each siloxane.

Irradiation of hexamethylcyclotrisiloxane

The laser irradiation of neat hexamethylcyclotrisiloxane does not lead to any significant products, the only change being formation of traces of octamethylcyclotetrasiloxane.

The irradiation in the presence of SG yields only low amounts of C_1-C_4 hydrocarbons, which confirms the cleavage of the Si-C (and possibly Si-H) bond(s). This indicates that the decomposition mechanism is similar to that observed in the gas phase[18], wherein concomitantly produced $Si{=}CH_2$–containing fragments polymerise to higher polysiloxanes and escape detection.

The irradiation in the presence of CS affords low amounts of C_1 - C_2 hydrocarbons together with important quantities of higher cyclic dimethylsiloxanes $[(CH_3)_2SiO]_n$, (n=4-7). The relative amounts of these products show that the major decomposition route is a rearrangement at the Si-O bond as observed[18-20] in the thermolysis of $[(CH_3)_2SiO]_n$ (n>3) but not in that of $[(CH_3)_2SiO]_3$. Siloxane bond redistribution with $[(CH_3)_2SiO]_3$ can only occur as a catalyzed reaction[21].

Irradiation of 1,3-diphenyldisiloxane

The laser irradiation of neat 1,3-diphenyldisiloxane failed to induce any chemical change.

The irradiation in the presence of SG yields trace amounts of benzene, ethyne and butadiyne as the only observable products and is in line with the Si-C and Si-H bond cleavage. It is plausible[20] to assume that trace amounts of higher polymers not detectable by mass spectroscopy were formed too.

The irradiation in the presence of CS results in the formation of traces of ethane and methane. These gaseous products are accompanied with great amounts of linear $(C_6H_5)H_2SiO[(C_6H_5)HSiO]_nSiH_2(C_6H_5)$ (n=1-5) and small amounts of cyclic $[(C_6H_5)HSiO]_n$, n=1-5 oligomers. MALDI spectra indicate rich mixtures of oligomers with molecular weight 500 -1400 Da. Differences of 78 u or 60u observed between individual components correspond to losses of benzene and silicon dioxide. Two mechanisms are plausible[13], (1) intermolecular exchange of hydride and siloxy groups on silicon, and (2) intramolecular elimination of phenylsilanone which inserts into the Si-O bond of initial disiloxane and of products of this insertion. The latter mechanism gets support from the formation of polycyclosiloxanes that could be only produced by cyclomerization of transient phenylsilanone.

Irradiation of 1,3-diphenyl-1,3-dimethyldisiloxane

The laser irradiation into neat 1,3-diphenyldisiloxane does not lead to any chemical change.

The irradiation in the presence of SG yields traces of butadiyne, cyclohexane and benzene the formation of those can be interpreted as initiated by cleavage of the Si-C and Si-H bonds.

The irradiation in the presence of CS produces methane, ethene and ethyne and trisiloxane in very small amounts as well as trisiloxane $H(C_6H_5)(CH_3)SiOSi(C_6H_5)(CH_3)OSiH(C_6H_5)(CH_3)$ whose formation can be explained by the two mechanisms suggested to operate in the thermolysis of 1,3-diphenyldisiloxane.

Irradiation of 1,1,3,3-tetraphenyldisiloxane

Similarly as in the previous cases, no chemical changes were seen upon irradiation of the neat sample.

The irradiation in the presence of SG yields low quantities of ethyne, butadiene and benzene as the only observable products. These hydrocarbons are in line with a cleavage of the Si-C and Si-H bonds and with ensuing polymerisation of geminal Si-centered radical fragments.

The irradiation in the presence of CS does not lead to any chemical change.

Inferences on reaction mechanism

The different effects of SG and CS on the laser thermolytic products can be explained by a property in which both materials differ. Both carbons exert similar BET surface (SG - 585 m^2/g, CS - 593 m^2/g), the size of particles (SG - 1-2 μm, CS - 0.5-2 μm) and concentration of radical centers (SG - 1.3×10^{17}/g, CS - 3.4×10^{18}/g), but differ in acidity (SG – 1 μmol/g, CS - 400 μmol/g) and in oxygen content. The FTIR spectrum of SG showed only very weak bands of C-H bonds (at 2919 and 2851 cm^{-1}), whereas that of CS possessed bands at 2909 and 2848 cm^{-1} (Csp^3-H bonds), 1699 cm^{-1} (C=O), 1577 cm^{-1} (conjugated C=O in a quinone configuration or aromatic ring bonds) and 1162 cm^{-1} (C-O in $-CO_2H$). This spectral pattern is in keeping[22,23] with the presence of acidic and oxygenated surface functional groups.

Higher acidity of and/or the presence of surface functional groups in CS suggests that the observed oligomerization of polysiloxanes from linear hydridosiloxanes occurs via the intermolecular mechanism involving acid catalysis and/or specific interaction of oxygenated surface sites. Similar intermolecular mechanism was earlier described for acid clay-catalyzed reversible interchange of hydrogen and siloxy substituents on silicon wherein neither Lewis or Brönsted acids nor carbon blacks functioned as catalysts[24]. Considering that catalytic activity of carbon is mostly associated with carbon surface reactions[25], we suggest that the exchange of H and siloxy substituents in the laser-induced reaction takes place at oxygenated surface sites. The presence of cyclooligomers in the decomposition of 1,3-diphenyldisiloxane is, however, consistent with at least partial operation of the intramolecular pathway[13]. The fact that the laser-induced reaction is less efficient with Ph and Me groups, or with two Ph groups on silicon implies that other substituents than H make this oligomerization less feasible.

Laser decomposition of hexamethylcyclotrisiloxane in suspended CS giving cyclooligomers has similar course as acid-catalyzed polymerization of cyclic siloxanes[21] and can be due to acidic sites of SG.

The decomposition of phenylhydridosiloxanes and also of hexamethylcyclotrisiloxane induced in the suspended SG proceeds via cleavage of Si-C bonds. This decomposition step is also observed in the homogeneous decomposition of siloxanes[7,8] where heterogeneous effect of hot surface is avoided, but not in hot glass tubes[1-3]. It thus appears that graphite particles do not affect the decomposition of siloxanes as do polar surfaces.

Conclusion

We thus reveal that acidic carbon soot containing oxygenated surface sites can function as a catalyst of thermolytic oligomerization of hydridosiloxanes induced in a hot microenvironment of carbon particles by laser pulses. We also show that laser-induced neutral graphite-photosenstized decomposition of siloxanes bears resemblance to homogeneous pyrolysis of siloxanes in the gas phase.

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