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IR laser-induced decomposition of 1,3–dimethyldisiloxane for chemical vapour deposition of nano-structured methyl(hydrido)silicone phases

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The infrared multiphoton decomposition of 1,3-dimethyldisiloxane induced by a TEA CO_2 laser yields gaseous C_1–C_2 hydrocarbons, methylsilane, dimethylsilane, methyldisiloxane and trimethyldisiloxane. These products provide evidence for a range of decomposition steps; amongst these, cleavage of the Si–O bond is important. The process affords chemical vapour deposition of a white solid nano-structured methyl(hydrido)silicone phase that has been characterized by infrared and photoelectron spectroscopy and electron microscopy.

Introduction

There is much continuing interest in silicon oxycarbides due to their importance in various fields of applied materials research (*e.g.* refs. 1–4). Various Si/C/O and Si/C/H/O materials have been produced by pyrolysis of polysiloxane gels (*e.g.* refs. 5–7), pyrolytic laser-aerosol interaction[8] and plasma[9–11] or laser[12–19] interaction with gaseous silicon-containing molecules.

The chemical vapour deposition of solid hydrogenated Si/C/O phases from single organosilicon compounds decomposed by IR laser radiation in the gas phase has been studied with hexamethyldisiloxane,[12,15] methoxytrimethylsilane,[15] tetramethoxysilane,[15] 1,1,3,3-tetramethyldisiloxane[16] and trimethyl(vinyloxy)silane.[19]

The examination of the effect of the structure of the precursors as well as that of the reactions governing the precursor decomposition are important, as it is desired to produce materials with the precise contents of the elements. It has been established that the IR laser-induced thermolysis of hexamethyldisiloxane proceeds exclusively by the cleavage of the weaker Si–C bond,[12,15] which results in the formation of C_1–C_2 hydrocarbons as the only gaseous products and in incorporation of all the Si–O moieties of the precursor into the solid deposited material. We have recently shown[16] that the gaseous products of the infrared multiphoton decomposition (IRMPD) of 1,1,3,3-tetramethyldisiloxane were C_1–C_2 hydrocarbons together with methylsilanes $(CH_3)_nSiH_{4-n}$ ($n=2$, 3). The latter products indicated that, besides cleavage of the Si–C bonds (and perhaps Si–H bonds), cleavage of the strong Si–O bonds also occurs. This process yielded H/Si/C/O films with almost equal numbers of Si, C and O atoms.

Now we report on the IRMPD of a still more hydrogenated disiloxane, 1,3-dimethyldisiloxane, and discuss the reaction steps occurring in the gas phase as they are deduced from the final products. We also show that this decomposition is controlled by cleavage of both Si–C and Si–O bonds and that it results in chemical vapour deposition of a solid nano-structured methylsilicone material with high content of Si–H bonds.

Experimental

1,3-Dimethyldisiloxane (0.7 kPa) was irradiated in a cylindrical Pyrex reactor equipped with NaCl windows, a valve for the connection to a standard vacuum manifold and a sleeve with a rubber septum for the withdrawal by syringe of gaseous samples for analysis. A TEA CO_2 laser (Plovdiv University) operated with a frequency of 1 Hz on the P(42) line of the $00^01 \rightarrow 10^00$ transition ($922.92\ cm^{-1}$) with a fluence of $0.52\ J\ cm^{-2}$ incident upon an area of $0.25\ cm^2$. Deposits were produced on copper and NaCl substrates housed in the reactor before irradiation. Chemical changes in the gas phase during irradiation were monitored by an FTIR Nicolet Impact 400 spectrometer; the depletion of 1,3-dimethyldisiloxane and the build-up of methane and ethyne was followed using diagnostic absorption bands at $1088\ cm^{-1}$, $1305\ cm^{-1}$ and $720\ cm^{-1}$, respectively. After subsequent expansion of helium into the reactor, gaseous samples were analyzed by gas chromatography (a Shimadzu GC 14 A gas chromatograph equipped with FID and coupled with a C-R5A Chromatopac data processor) and by GC/MS technique (a Shimadzu QP 1000 quadrupole spectrometer) using programmed temperature and columns packed with Porapak P and silicone elastomer SE-30. Gaseous products were identified by comparison of their mass spectra and retention times with those of authentic samples. The quantitative analysis of the volatile products relied on the knowledge of the FID response factors of the authentic samples; these factors for methyldisiloxane, 1,3-dimethyldisiloxane and trimethyldisiloxane were taken as 0.16, 0.27 and 0.36, respectively.

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The IR spectra of the deposits on NaCl windows and the NaCl substrate were recorded after evacuation of the reactor.

The photoelectron spectra were acquired using an ESCA 310 (Gammadata Scienta) photoelectron spectrometer equipped with rotating Al anode, monochromator and electron flood gun. The background pressure during spectra acquisition was typically of the order of 10^{-7} Pa. The spectrometer was operated in the fixed analyser transmission mode. The detail spectral scans were taken over Si 2p, O 1s and C 1s regions. In addition, the Si KLL Auger spectrum excited by bremsstrahlung was measured. The latter measurement was carried out in ESCA 3 Mk II (VG Scientific) electron spectrometer with Al K_α unmonochromatized source. The peak positions and areas were determined by fitting the unsmoothed experimental spectra after subtraction of Shirley background.[20] The surface concentrations of elements were calculated using theoretical photoionization cross-sections.[21] The sample surface composition was also determined after mild ion etching (Ar ions, $E = 5$ keV, current 20 µA, time 4 min).

Scanning electron microscopy of the deposits was carried out with a Tesla BS 350 microscope and transmission electron microscopy measurements were performed on a Philips 201 microscope.

1,3-Dimethyldisiloxane was prepared by cleavage of methyl(phenyl)silane with HBr and subsequent hydrolysis of the produced bromo(methyl)silane.[22] Its purity was better than 97% as checked by gas chromatography.

Results and discussion

The IRMPD of 1,3-dimethyldisiloxane by the TEA CO_2 laser irradiation into the strong δ(Si–H) absorption band centered at 922 cm^{-1} affords chemical vapour deposition of a white solid material together with gaseous methane, ethene, ethane, ethyne, methylsilane, dimethylsilane, methyldisiloxane and trimethyldisiloxane. The dependence of the IRMPD progress on the number of pulses has a typical profile as shown in Fig. 1. The yields of these products (in mole/mole of 1,3-dimethyldisiloxane decomposed): methane (0.29–0.34), ethene (0.03–0.05), ethane (<0.1), ethyne (0.01–0.04), methylsilane (0.19–0.27), dimethylsilane (0.08–0.11), methyldisiloxane and trimethyldisiloxane (both 0.02–0.03), do not considerably change within decomposition progress 15–53%. Only minor trends are observed with methane and $(CH_3)_nSiH_{4-n}$ compounds ($n = 1,2$) (Fig. 2): the former shows a slight but steady increase, while the latter reach their insignificant maxima at early decomposition stages (*ca.* 30%) and then they slowly diminish.

Decomposition mechanism

Several plausible decomposition steps for 1,3-dimethyldisiloxane can be anticipated on the basis of the reported data on thermal decomposition of similar molecules. These are 1,1-[H_2] and 1,1-CH_4 extrusions occurring with monoorganylsilanes (*e.g.* refs. 23,24) and molecular cleavage into methylsilane and methylsilanone, this reaction having its prototype in IR laser-induced decomposition of disiloxane $H_3SiOSiH_3$ (ref. 25). Regarding the radical processes, the homolysis of the Si–H and Si–C bonds is more likely than that of the strong Si–O bond. These pathways are as shown in eqns. (1)–(6).

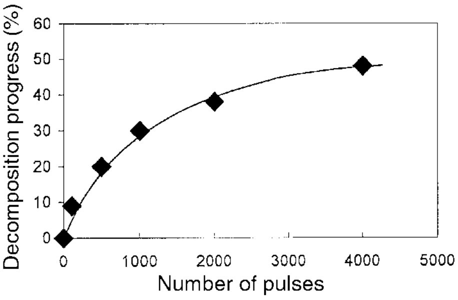

Fig. 1 Progress of IRMPD of 1,3-dimethyldisiloxane as dependent on number of pulses (irradiating conditions as given in Experimental).

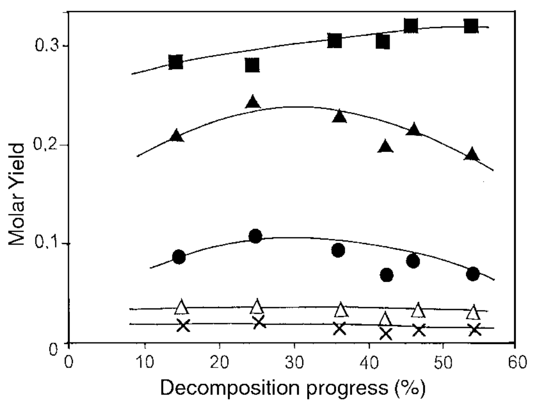

Fig. 2 Distribution of gaseous products in IRMPD of 1,3-dimethyldisiloxane (■ CH_4, ▲ CH_3SiH_3, ● $(CH_3)_2SiH_2$, △ C_2H_4, × C_2H_2; yield given in mole/mole of 1,3-dimethyldisiloxane decomposed).

$$H_2(CH_3)Si{-}O{-}Si(CH_3)H_2 \rightarrow H_2(CH_3)Si{-}O{-}Si(CH_3){:} + H_2 \quad (1)$$

$$H_2(CH_3)Si{-}O{-}Si(CH_3)H_2 \rightarrow H_2(CH_3)Si{-}O{-}SiH{:} + CH_4 \quad (2)$$

$$H_2(CH_3)Si{-}O{-}Si(CH_3)H_2 \rightarrow CH_3SiH_3 + H(CH_3)Si{=}O \quad (3)$$

$$H_2(CH_3)Si{-}O{-}Si(CH_3)H_2 \rightarrow CH_3^{\bullet} + {}^{\bullet}SiH_2{-}O{-}SiH_2(CH_3) \quad (4)$$

$$H_2(CH_3)Si{-}O{-}Si(CH_3)H_2 \rightarrow H^{\bullet} + {}^{\bullet}Si(CH_3)H{-}O{-}SiH_2(CH_3) \quad (5)$$

$$H_2(CH_3)Si{-}O{-}Si(CH_3)H_2 \rightarrow (CH_3)H_2SiO^{\bullet} + {}^{\bullet}SiH_2CH_3 \quad (6)$$

The observed products are in line with the formation of the CH_3 radical being important. Thus, the large yield of methane, even though probably contributed by route (2), can be explained by the abstraction of hydrogen by CH_3 from 1,3-dimethyldisiloxane (eqn. (7)).

$$CH_3^{\bullet} + (CH_3)SiH_2{-}O{-}SiH_2(CH_3) \rightarrow {}^{\bullet}Si(CH_3)H{-}O{-}SiH_2(CH_3) + CH_4 \quad (7)$$

Ethane, ethene and ethyne must also originate from this radical and be produced by the known reactions $2CH_3 \rightarrow C_2H_6$, $CH_3 \rightarrow [{:}CH_2 + H] \rightarrow C_2H_4 + H_2$, *etc.* The presence of the unsaturated C_2 hydrocarbons makes us believe that the irradiated system contains molecular hydrogen and that the formation of methane is partly due to reaction of CH_3 with H and/or H_2.

Significant amounts of methylsilane and dimethylsilane show that the cleavage of the strong Si–O bond is a feasible process. Bellama and Manders (ref. 12) and we (ref. 15) have shown that no Si–O bond cleavage takes place during the IR laser-induced thermolysis of hexamethyldisiloxane, but our recent findings of the high yields of dimethylsilane and trimethylsilane in the IRMPD of 1,1,3,3-tetramethyldisiloxane $[H(CH_3)_2Si]_2O$ (ref. 16) and that of silane in the IRMPD of disiloxane $[H_3Si]_2O$ (ref. 25) revealed that the cleavage of the Si–O bond in hydrogenated disiloxanes is a feasible route. While the mechanism of the cleavage of the Si–O bond in $[H_3Si]_2O$ was interpreted[25] as molecular extrusion of $H_2Si{=}O$ occurring *via* a four-centre transition state, partly hydrogenated disiloxanes can undergo the Si–O cleavage *via* several modes.

We presume that the silicon-centered radicals, which are produced by the Si–C and Si–H homolysis of 1,3-dimethyldisiloxane (eqns. (4), (5)) and by the reaction of CH_3 with 1,3-dimethyldisiloxane (eqn. (7)), undergo cleavage into silanones and the $(CH_3)H_2Si$ radical (eqns. (8), (9)), and that the $(CH_3)H_2Si$ radical forms dimethylsilane and methylsilane by reacting with methyl radical and hydrogen (H or H_2), respectively (eqns. (10), (11)). The occurrence of the Si(R)H–O–$SiH_2(CH_3)$ radicals with R = CH_3 and H is strongly supported by the observation of methyldisiloxane and trimethyldisiloxane among the final products.

$$^{\cdot}SiH_2\text{–}O\text{–}SiH_2(CH_3) \rightarrow H_2Si{=}O + {}^{\cdot}SiH_2(CH_3) \quad (8)$$

$$^{\cdot}Si(CH_3)H\text{–}O\text{–}SiH_2(CH_3) \rightarrow H(CH_3)Si{=}O + {}^{\cdot}SiH_2(CH_3) \quad (9)$$

$$^{\cdot}SiH_2(CH_3) + CH_3^{\cdot} \rightarrow (CH_3)_2SiH_2 \quad (10)$$

$$^{\cdot}SiH_2(CH_3) + H^{\cdot}\ (\text{or } H_2) \rightarrow (CH_3)SiH_3 \quad (11)$$

It is known[26] that Si=O bond-containing molecules are not stable and polymerize easily. The intermediate silanones must therefore give rise to the observed white deposited material. This polymerization is undoubtedly contributed to by other kinds of association reactions of the above open-shell intermediates. The quantification of the observed gaseous products allowed us to determine the exact mass balance and the stoichiometry of the solid deposited material as SiC_xO_y ($x = 0.56$–0.73, $y = 0.59$–0.65). Similarly to the distribution of the gaseous products, this stoichiometry alters with the decomposition progress only insignificantly.

Properties of the solid deposit

FTIR spectra of the deposit taken for different decomposition progress show the same pattern consisting of bands at 767, 867, 1037, 1257, 2150, 2850, 2920 and 2960 cm^{-1} (Fig. 3) which are assignable, in the given order, to ν(Si–C) + ρ(CH_3–Si), δ(SiH_3), ν(Si–O), δ(CH_3Si), ν(Si–H) and ν(C–H) vibrations. The ratio of absorptivities A[ν(C–H)] : A[ν(Si–H)] for the deposit from 1,3-dimethyldisiloxane (0.24) is much higher than the same ratio for gaseous 1,3-dimethyldisiloxane (0.085). This implies that the deposit contains much fewer H(Si) centers relative to H(C) centers than does the precursor. The comparison of the FTIR spectra of the deposits obtained from the IRMPD of 1,3-dimethyldisiloxane and 1,1,3,3-tetramethyldisiloxane reveals (Table 1) that the former are noticeably richer in H(Si) centers and that both possess similar amounts of H(C) centers. The A[ν(C–H)] : A[ν(Si–H)] ratio for the deposit from 1,3-dimethyldisiloxane (0.24) and that for the deposit from 1,1,3,3-tetramethyldisiloxanes (1.1) allow us to estimate[27] the relative concentrations of H(Si) and H(C) centers; the ratios indicate that both types of centers are almost equally present in the former deposit and that H(C) centers are about 4 times as abundant as H(Si) centers in the latter deposit.

The surface stoichiometry calculated from intensities of photoemission lines of the films before ion sputtering, $Si_{1.0}O_{1.0}C_{1.0}$, and the calculated value of the modified Auger parameter, 1711.7 eV, are consistent with data reported in the literature[28] for methylsilicone. Only one chemical state of Si is observed in the Si 2p and Si KLL spectra (Figs. 4, 5). Broadening of the spectra and decrease of the carbon surface concentration ($Si_{1.0}O_{1.1}C_{0.6}$) is observed after ion sputtering. This behaviour is analogous to that which we found experimentally for methylsilicone polymer.

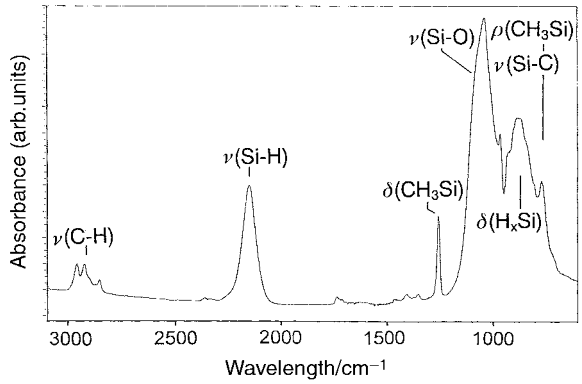

Fig. 3 Typical FTIR spectrum of the deposit from IRMPD of 1,3-dimethyldisiloxane.

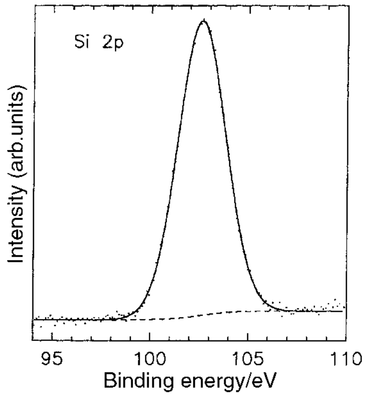

Fig. 4 The Si 2p core level spectrum of the deposit.

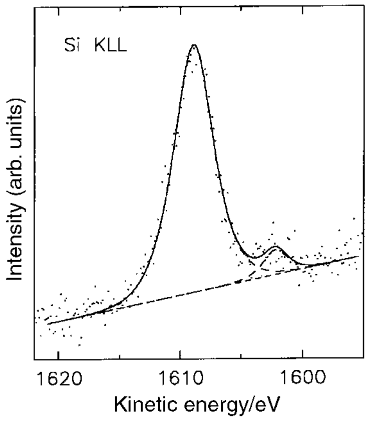

Fig. 5 The Si KLL Auger spectrum of the deposit.

Table 1 FTIR spectra of the solid deposits from IRMPD of $[H_2(CH_3)Si]_2O$ and $[H(CH_3)_2Si]_2O$

	Absorptivity[a]/wavelength in cm^{-1}	
Vibration	Deposit from $[H_2(CH_3)Si]_2O$	Deposit[b] from $[H(CH_3)_2Si]_2O$
ν(Si–C) + ρ(CH_3Si)	0.39/767	0.08/802
ρ(CH_3Si) + δ(SiH)	0.63/867	0.21/902
ν(Si–O)	1.00/1037	1.00/1051
δ(CH_3Si)	0.27/1257	0.25/1263
ν(SiH)	0.42/2150	0.08/2139
ν(CH)	0.1/2960	0.09/2964

[a] Normalized to that of the ν(Si–O) band. [b] Ref. 16.

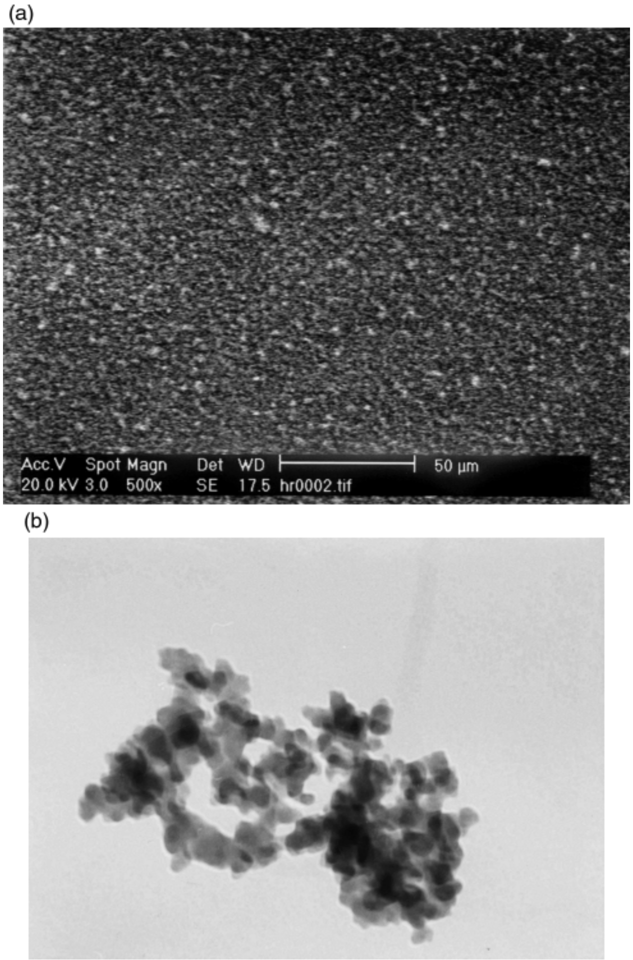

Fig. 6 SEM (a) and TEM (b, magnification 100 000 ×) images of the deposit.

The morphology of the deposited material is represented by agglomerates (Fig. 6a) which are composed of several tens of nm sized chains connected together (Fig. 6b).

The films are insoluble in diethyl ether, ethanol, n-hexane, chloroform and toluene, which shows that they possess a cross-linked structure.

In conclusion, we stress that the reported method of production of the solid methyl(hydrido)silicone material represents an alternative approach to the rather rare silicones having Si–H bonds in the backbone; to our knowledge the only other process leading to similar polymers involves catalysed equilibration of cyclic methylhydridosiloxanes, which affords soluble linear-chain polyhydridomethylsilicones.[29] We also point out that the deposited nano-structured methylsilicone material with the high content of latent Si–H bonds can be easily chemically modified to macromolecules with *e.g.* hydroxy or alkoxy groups and that it may also be a suitable precursor to thin films of Si/C/O glasses.

Acknowledgements

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