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Excimer laser photolysis of hexamethyldisilazane *

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Abstract

ArF laser-induced photolysis of hexamethyldisilazane $(Me_3Si)_2NH$ in the gas phase yields methane, trimethylsilane, and deposited layers of hydrolysable organosilicon oligomers. Experiments with $(Me_3Si)_2ND$ reveal that early stages of the photolysis are controlled by abstraction of H or N atoms by $(CH_3)_3Si\cdot$ and $CH_3\cdot$ radicals from H(C) and D(N) bonds and by 1,1-elimination of Me_3SiD.

1. Introduction

Hexamethyldisilazane (HMDSZ) has been used as a precursor for chemical vapour deposition (CVD) of various Si/C/N/H materials. These have been produced by decomposition of HMDSZ by use of plasmas [1–4], high temperatures [5–8], and infrared laser radiation [9–12]. In these various processes dissimilar modes of the decomposition are favoured, and can lead to products ranging from refractory powders to dielectric layers.

Excimer laser photolysis of HMDSZ may offer a specific decomposition route as well as giving novel deposited materials. This process has not been studied previously, the only report relating to this topic being a brief examination of CVD in which HMDSZ was photolysed in the presence of air to produce silicon oxide patterns throughout a photomask in contact with the substrate [13].

In this paper, we report on ArF laser-induced photolysis of HMDSZ, identify the early stages of its mechanism, and describe the properties of the deposited organosilicon layers.

2. Experimental details

Gaseous samples of HMDSZ or HMDSZ-d_1 were photolysed by use of a Questek series 2000 excimer laser operating at 193.3 nm with repetition frequency 20 Hz. Experiments were performed in a glass reactor consisting of two orthogonally positioned tubes (2 cm in diameter). Fused quartz plates were mounted at the ends of the shorter (6 cm) tube and NaCl windows were affixed to the ends of the longer (15 cm) one. The reactor had a valve for connection to a standard vacuum-line and a side-arm with a rubber septum. The unfocused beam (energy fluence 140 mJ, FWHM ~ 15 ns) was spatially filtered by a slit (1 cm diameter) and entered the reactor through the quartz plate.

The progress of the photolysis was monitored directly in the reactor with an FTIR (Perkin Elmer, model 1710) spectrometer. The pressure of HMDSZ and HMDSZ-d_1 was determined using the absorption bands at 3392 and 2510 cm^{-1} (absorption coefficient 0.0023 and 0.0046 kPa^{-1} cm^{-1}, respectively), which do not interfere with those of photolysis products.

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Methane, methane-d_1, trimethylsilane, trimethylsilane-d_1 [$(CH_3)_3SiD$] and hexamethyldisilane, respectively, were monitored at 3016 cm^{-1} (0.0062 kPa^{-1} cm^{-1}), 2199 cm^{-1} (0.0020 kPa^{-1} cm^{-1}), 3016 cm^{-1} (0.0045 kPa^{-1} cm^{-1}), 2127 cm^{-1} (0.051 kPa^{-1} cm^{-1}), 1546 cm^{-1} (0.038 kPa^{-1} cm^{-1}), and 723 cm^{-1} (0.034 kPa^{-1} cm^{-1}). The final amounts of methane and ethane were determined by GLC (Packard model 427 chromatograph with FID and alumina column).

HMDSZ, hexamethyldisilane, and methane were commercial samples (Aldrich). HMDSZ-d_1 was prepared by a treatment of HMDSZ with sodium amide and deuterium oxide [14,15]. Trimethylsilanes $(CH_3)_3SiH$ and $(CH_3)_3SiD$ were obtained by reaction of trimethylchlorosilane with lithium aluminium hydride and lithium aluminium deuteride, respectively, whilst methane-d_1 was prepared by deuterolysis of methylmagnesium iodide. All the compounds were checked for purity by GC and IR spectroscopy. The UV spectrum of HMDSZ in hexanes was recorded with a Philips PU 8720 UV/VIS scanning spectrophotometer.

Deposited products were dissolved in hexanes and the solutions evaporated on KBr plates heated at 150°C in an oven and then in a continuously evacuated Büchi GKR-50 furnace heated at the same temperature. A sample of the deposit was analysed on a Perkin Elmer model 10 liquid chromatograph and its molecular weight distribution was determined by use of polystyrene standards in tetrahydrofuran.

3. Results and discussion

HMDSZ can be photolysed with an ArF laser since its absorptivity at the irradiating wavelength (193 nm) is 220 mol^{-1} cm^{-1}. The energy delivered by the photons corresponds to *ca.* 620 kJ mol^{-1}, which is much in excess of the energy needed for the cleavage of the weakest Si–C (~ 370 kJ mol^{-1}) and even the strongest Si–N (420 kJ mol^{-1}) bond. The irradiation of HMDSZ (1.6 kPa) results in the formation of methane, ethane, and trimethylsilane, along with a transparent deposit. Methane dominates over trimethylsilane over the whole decomposition range studied (Table 1) and the ratio $C_2H_6:CH_4$ at large conversions (60–70%) varies between 0.12–0.14. The observed hydrocarbon products suggest the operation of a free radical mechanism involving homolysis of the Si–C bond and radical-molecule reactions ($CH_3\cdot$ radical recombination and abstraction of H) leading to reactive unsaturated organosilicon species. The formation of Me_3SiH indicates a previously unobserved photolytic cleavage of the Si–N bond. Two types of hydrogen [(N)H and (C)H] are available for both suggested routes and it was thus necessary to examine photolysis of $(Me_3Si)_2ND$.

TABLE 1. Product yields [a] in HMDSZ photolysis

Conversion, %	18	32	40	52	70
CH_4	54	59	58	65	72
Me_3SiH	14	18	15	10	7

[a] In mole/mole of HMDSZ decomposed.

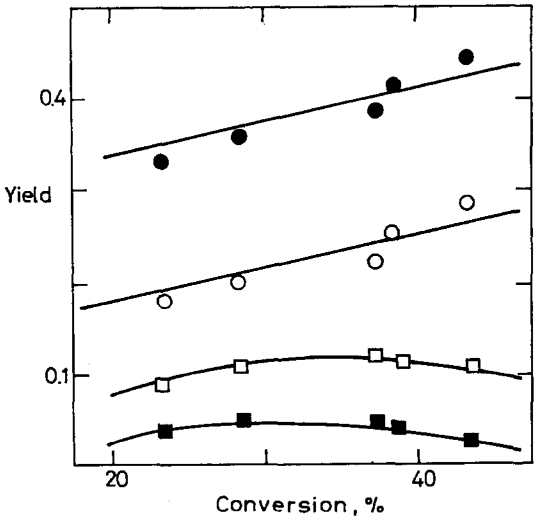
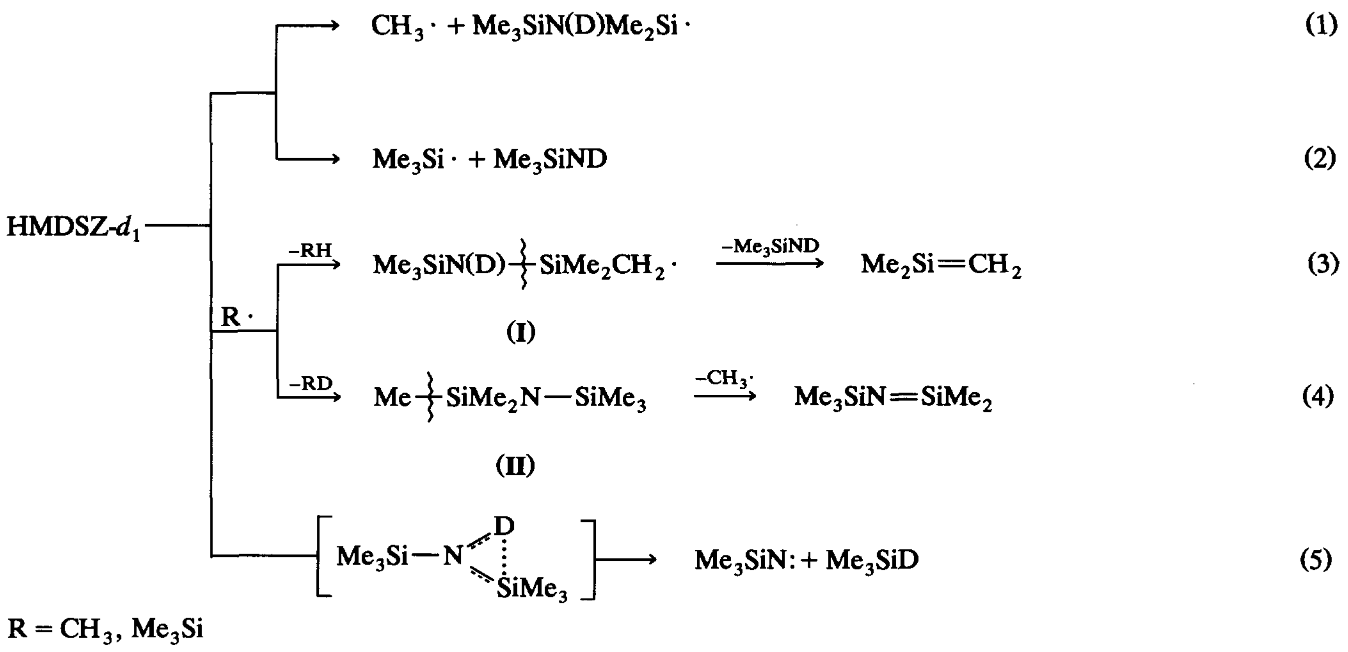


Fig. 1. Product yield as a function of % decomposition of HMDSZ-d_1 (● CH_4, ■ Me_3SiH, ○ CH_3D, □ Me_3SiD).

The laser irradiation of HMDSZ-d_1 (1.6 kPa) yields ethane, CH_4, CH_3D, Me_3SiH, and Me_3SiD. The very small depletion of both methylsilanes observable at later stages of the photolysis can be related to the abstraction of their H (and D) atom by a $CH_3\cdot$ radical, since direct photolysis of either of the two trimethylsilanes occurs to only an insignificant extent. The absence of hexamethyldisilane and the presence of trimethylsilanes indicates that the recombination of $Me_3Si\cdot$ radical is negligible, and that the H and D abstraction route is favoured. This high preference for such abstraction by the $Me_3Si\cdot$ radical from the C–H and N–D bonds may be related to a high energy of the absorbed photons. It is known that the $Me_3Si\cdot$ radical, though quite unreactive in H-abstraction reactions under conditions of Hg-sensitized photolysis [17] and more apt to recombine rather than to disproportionate [18,19], does abstract hydrogen during the photolysis with energy-rich photons at 147 nm [20].

Of the two isotopomers of each product, CH_4 and Me_3SiD are favoured over the photolysis range 20–50% (Fig. 1). The preference for formation of CH_4 over that of CH_3D and of Me_3SiD over that of Me_3SiH indicates that the abstraction by $CH_3\cdot$ radicals of H



Scheme 1.

from HC is faster than that of D from DN, whereas the opposite is the case for abstraction by the $Me_3Si\cdot$ radical from the two centres. The initial (extrapolated) CH_4/CH_3D ratio of 2.6 in our experiments is close to the ratio of rate coefficients $k_{C-H}/k_{N-D} = 1.4$ observed for the abstraction by the methyl radical at 300 K from the similar compound $(CH_3)_2ND$ [16]. The *ca.* 2.5-fold preference for Me_3SiD over Me_3SiH is, however, surprising. The different rate coefficients for H- and D-abstractions from N have been shown [21] to reflect the difference in zero-point energies calculated from vibrational frequencies ν(N(H)) and ν(N(D)) bonds. The very similar (ν(NH)–ν(ND)) value for amines and HMDSZ lends support to the view that the observed Me_3SiD/Me_3SiH ratio is the result (at least in part) of the occurrence of α-elimination from Me_3SiD. We note that similar molecular extrusions have been observed under laser photolysis of some other organometallic compounds [22–25].

Subsequent decays (β-scission) of the radicals produced *via* H and D abstractions by both $CH_3\cdot$ and $Me_3Si\cdot$ radicals can be assumed to be very fast. The most important steps that occur during the photolysis must, therefore, be those in Scheme 1.

The majority of depleting HMDSZ molecules do not photolyse unimolecularly (eqns. (1) and (2) in Scheme 1), but undergo radical attack. The preferential abstraction of the H(C) by $CH_3\cdot$ radical affords intermediate I and a silane (eqn. (3) in Scheme 1), the D(N) abstraction by $Me_3Si\cdot$ radical results in the formation of a silanimine *via* intermediate **II** (eqn. (4) in Scheme 1), and the α-elimination affords trimethylsilylnitrene. All these steps produce very reactive products, which can undergo a myriad of reactions such as silene and silanimine dimerization and the participation in nucleophilic additions [26,27], silylnitrene and radical additions [28], and others.

Yields of trimethylsilanes indicate that most of the silicon of HMDSZ is incorporated in the nonvolatile deposit. The molecular weight distribution of the de-

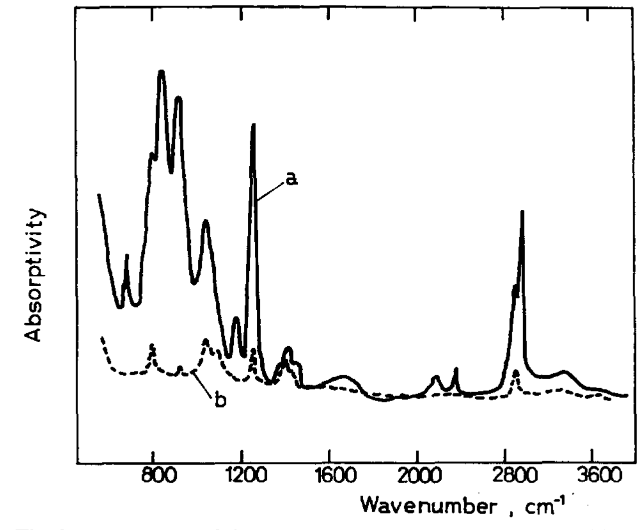


Fig. 2. IR spectrum of the deposit after evacuation of the cell (a) and after exposing it to air (b).

posit was assessed to range between 600–1600 mu, and its IR spectrum (Fig. 2) shows absorptions at 682 (m), 800 (s), 839 (vs), 913 (vs), 1038 (m), 1180 (m), 1253 (vs), 1410 (w), 2901 (m), and 2954 (s) cm^{-1} and reveals [15,29] vibrations of Si–C, CH_3–Si, and Si–N bonds. Upon exposure of the deposit to air (or water) and subsequent heating up to 150°C *in vacuo*, volatile compounds are evolved. This ease of degradation of the oligomer may give rise to interesting applications.

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