namely, 2-phenyl-1-pyrroline, is substituted for 1-phenylcyclobutylamine; (6) if benzylamine is substituted for **1**. The last control confirms the report of Tan et al.[17] who also observed no ESR signal with MAO B and benzylamine in the presence of PBN. It also indicates that the signals are not coming from hydrogen peroxide or any products of normal substrate turnover, although we have not yet identified the structure of the radical product. A typical control ESR spectrum is shown in Figure 1C. The possibility that a trace contaminant of cytochrome P-450, which has been shown to generate radical intermediates,[18] is responsible for the observed signals was negated on the basis of the following experiments: (1) pretreatment of the enzyme with acetylene, a known inactivator of cytochrome P-450,[27] had no effect on the generation of the ESR signal; (2) increasing amounts of PBN did not inhibit the generation of the ESR signal, as would be expected on the basis of the results of Augusto et al.[18] We have yet to be able to prepare the oxidation product of **1**, 2-benzoyl-1-pyrrolidine, presumably because of its instability.

These results provide the first direct evidence for a radical intermediate in the MAO-catalyzed oxidation of a substrate amine. The scope of this observation currently is under investigation.

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Mechanism of the Photochemical Degradation of Poly(di-*n*-alkylsilanes) in Solution

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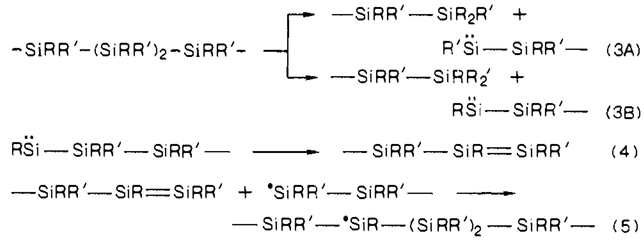
The photodegradation of polysilanes[2] $(RR'Si)_n$ with UV light in the neat solid[3-5] or in solution[6,7] is of considerable current interest. We now communicate the results of a mechanistic study of this process. Primary solution products are believed to be the silylenes RR'Si: identified by trapping with Et_3SiH and polysilyl radicals $-SiRR'-SiRR''^{\bullet}$. The latter are implicated by the isolation of the silanes $H(SiRR')_2H$ and $H(SiRR')_3H$ after exhaustive irradiation at 254 nm. Irradiated solutions of polysilanes induce the polymerization of olefins providing further evidence for the homolytic cleavage route.[8] Since the photon energies are insufficient for simultaneous generation of two silyl radicals and a silylene by the cleavage of two adjacent SiSi bonds, we believe that silylene extrusion (eq 1) and homolytic cleavage (eq 2) are competing processes. Both processes are known in short-chain oligosilanes.[9,10]

$$-SiRR'-(SiRR')_2-SiRR'- \xrightarrow{h\nu} -SiRR'-SiRR'-SiRR'- + RR'Si: \quad (1)$$

$$-SiRR'-(SiRR')_2-SiRR'- \xrightarrow{h\nu} -SiRR'-SiRR''^{\bullet} + {}^{\bullet}SiRR'-SiRR'- \quad (2)$$

Recently, the structures of the persistent radicals present in irradiated solutions have been assigned as $-SiRR'-{}^{\bullet}SiR-SiRR'-$ and $-SiRR'-{}^{\bullet}SiR'-SiRR'-$.[11] To account for their formation a minor third chain cleavage path was proposed starting from either (3A) or (3B); steps 4 and 5 produce the observed radical structures.



Support for this proposal was provided by GC-MS observation of trialkylsilyl-terminated short chains upon exhaustive irradiation at 248 nm. We now report results that support the existence of separate paths (eq 1 and 2) which dovetail nicely with the previously proposed[12] interpretation of the photophysical behavior of alkylated polysilanes.

In cyclohexane-Et_3SiH (1:1), exhaustive irradiation of poly(di-*n*-hexylsilane)[p-(Hx_2Si)] or poly(di-*n*-butylsilane)[p-(Bu_2Si)] at 248 nm (pulsed) or at 254 nm (cw)[6] produces the silylene trapping product Et_3SiSiR_2H and the homolytic cleavage products $H(SiR_2)_nH$ ($n = 2, 3$, R = Hx or Bu), respectively. Use of Et_3SiD yields Et_3SiSiR_2D and $H(SiR_2)_nH$ ($n = 2, 3$, R = Hx or Bu). Previous work did not rule out the possibility that R_2Si: is only produced from very short photodegraded silicon chains and not from the high polymer. However, in the irradiation of p-(Bu_2Si), the $Et_3SiSiBu_2H$ appears with no induction period and we thus conclude (i) that reaction 1 occurs from the high polymer. The quantum yield of $Et_3SiSiBu_2H$ decreases as the irradiation wavelength increases (GC-MS, internal standard) and falls to zero above 300 nm, while the polymer absorption band at 315 nm still disappears rapidly and persistent ESR signals are observed.

We conclude therefore that (ii) silylene production and radical formation indeed occur as two distinct processes, presumably reactions 1 and 2, and that (iii) the proposed[4] thermal fragmentation of polysilyl radicals with a sequential loss of single RR'Si: units (see below) does not occur at room temperature. This

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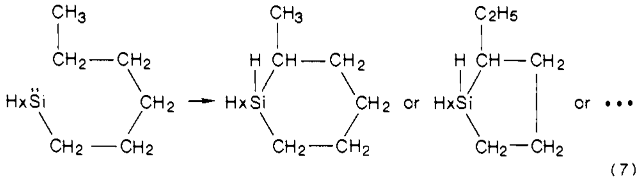
has also recently been shown for $Me_3SiSiMe_2^{\bullet}$.[13] Above 300 nm, products such as $H(SiR_2)_nH$ (n = 2, 3) are not formed either, since Si_nR_{n+2} is transparent for $n < \sim 7$.[14]

$$-SiR_2-SiR_2-SiR_2^{\bullet} \not\rightarrow -SiR_2-SiR_2^{\bullet} + R_2Si:$$

Irradiation (308 nm) of p-(Hx_2Si) or p-(Hx_2Si-β-D), fully β-deuterated on the n-hexyl side chains in pentane, pentane-d_{12}, cyclohexane, cyclohexane-d_{12}, or Et_3SiD, produces only Si–H and no Si–D bonds (IR); p-(Hx_2Si-α-D), fully α-deuterated on the hexyls, forms Si–D and no Si–H bonds. We conclude (iv) that in addition to likely recombination, the primary radicals undergo disproportionation[2,7,9] but not a more or less random hydrogen abstraction from solvent[2] or polymer side-chains to yield carbon radicals.[4] Similarly there is no evidence of intermolecular radical abstraction from Et_3SiD when incorporated in the solvent.

$$2\,-SiHx_2-{}^{\bullet}SiHx(CH_2)_5CH_3 \rightarrow -SiHx_2-SiHHx_2 + -SiHx_2SiHx{=}CH(CH_2)_4CH_3 \quad (6)$$

Repetition of steps 2 and 6 accounts for the observed formation of $H(SiHx_2)_nH$ (n = 2, 3). We have no information on the subsequent fate of the silene formed in (6) such as dimerization or addition of $-SiHx_2-{}^{\bullet}SiHx_2$ followed by further transformations. The formation of Si–H in addition to Si–D bonds upon 248-nm irradiation of p-(Hx_2Si-α-D) is, however, not due to the previously proposed[7] β-hydrogen abstraction from the silene, since it is suppressed in the presence of Et_3SiD. They must originate from Hx_2Si: by intramolecular C–H insertion (see below) either photochemical as in t-Bu_2Si:[15] or more likely thermal.



(7)

Consistently an isomer of Hx_2Si: was detected among the products from exhaustive 248-nm irradiation of p-(Hx_2Si) in cyclohexane (GC-MS). These results support the mechanism proposed to account for 308-nm laser-desorption mass spectra of neat poly(dialkylsilanes) in a predominately thermal process.[5] In room temperature solution, Hx_2Si: does not insert into C–H bonds intermolecularly (no Si–D bonds appear upon 248-nm irradiation of p-(Hx_2Si) in cyclohexane-d_{12}).

The wavelength dependence of the silylene extrusion process is unusual. Although exceptions do exist, in organic photochemistry such dependence is usually limited to bichromophoric substrates.[16] Although other explanations cannot be dismissed at this time, it is probably not a coincidence that our results fit naturally into the picture of polysilane photophysics developed previously[7,12] with the INDO/S model[17] to accommodate polarized fluorescence data.

Briefly described it is believed that in room temperature solution the long silicon chain is separated by short kinks (e.g., gauche) into a statistical collection of nearly independent chromophores with an approximately all-trans geometry which are in dynamic equilibrium. The longer the segment the lower its excitation energy, until a limiting value is reached in chromophores with about 10–20 silicon atoms. Thus the coherence length of the singlet excitation is defined by the spacing between sharp twists. Energy transfer from short to longer segments competes with fluorescence.

We now propose that only excitation of the shorter chromophores in the polymer chain up to perhaps Si_7 or so causes silylene extrusion (reaction 1), while excitation of the longer ones does not. The homolytic cleavage reaction (reaction 2) may either occur in both types of chromophores and therefore at all wavelengths or in only the long chromophores. In the latter case, energy transfer from short to longer chromophores would need to be the first step following short wavelength excitation.

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Species-Dependent Biosynthesis of Hyoscyamine

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In 1954[2] it was established that ornithine is a precursor of the tropane moiety of the alkaloid hyoscyamine (**11**) in the plant *Datura stramonium.* In particular, it was shown that [2-^{14}C]-ornithine labeled hyoscyamine at the bridgehead carbons. At that time, the method of degradation used to determine the location of ^{14}C did not distinguish between C-1 and C-5. Later[3,4] it was shown that [2-^{14}C]ornithine is incorporated unsymmetrically, all the ^{14}C being found at the C-1 position (having the R configuration). Studies with a root culture of *Datura stramonium* were complementary to these results.[5] The unsymmetrical incorporation of [2-^{14}C]ornithine into hyoscyamine in root cultures of *Datura metel*[6] was in agreement with the earlier feeding involving intact plants. In this same root culture [5-^{14}C]proline also labeled hyoscyamine unsymmetrically.[7]

In contrast to all these results, it has now been discovered that the radioactive hyoscyamine produced in a root culture of *Hyoscyamus albus L.* which was fed DL-[5-^{14}C]ornithine[8] was labeled equally at the C-1 and C-5 positions. It is thus clear that the biosynthetic pathway between ornithine and hyoscyamine must be different in *Datura* and *Hyoscyamus albus.* This dichotomy of biosynthetic pathways is rationalized in Scheme I. It is proposed that ornithine (**1**) reacts with pyridoxal phosphate (delivered from the complex of ornithine decarboxylase and pyridoxal phosphate) to afford the Schiff base **2**. This compound then

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(1) Contribution No. 210 from this laboratory. Part 42 in the series: Chemistry of the Tropane Alkaloids and Related Compounds.

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(8) DL-[5-^{14}C]Ornithine·HCl (0.1 mCi, 0.85 mg) was fed to a root culture of *Hyoscyamus albus L.*[9] for 6 days. The harvested roots (fresh wt 67 g) afforded hyoscyamine (25.4 mg) having a specific activity of 2.49 × 10^7 dpm/mM. The degradation to determine the location of radioactivity is detailed in the Supplementary Material. It is essentially the same as that used previously[2,3,5] with some modifications so that activity at both bridgehead carbons (C-1 and C-5) could be obtained unequivocally.