the nonspecific methylases of *P. shermanii* to prepare the 12-methyl analogs **2** and **3**, of factors II and III, respectively (Scheme III). Reduction and incubation of these possible intermediates with the corrin-synthesizing cell-free system in the presence of SAM afforded (after esterification) samples of cobester whose specific activities are compared in a control experiment with those of cobester derived from $[^{14}C]$-precorrin **2** and from a mixture of $[^{3}H]$-precorrin **3** and $[^{14}C]$-**2**. As shown in Table I, these ring C-decarboxylated analogues are not substrates for the enzymes of corrin biosynthesis (experiments 2–4), leading to the conclusions that (a) in normal biosynthesis, precorrin **3** is *not* the intermediate which is decarboxylated and (b) decarboxylation occurs at some stage after the fourth methylation (at C_{17}) and by mechanistic analogy, before the fifth methylation at C_{12}. Hence, two isolable *pyrrocorphin* intermediates viz. precorrins **4a**, **4b**[11] should intervene between precorrins **3** and **5**; i.e., precorrin **3** is C-methylated at C_{17} to give precorrin **4a** followed by decarboxylation (→**4b**) and subsequent C-methylations at C_{12a}, C_1, C_5, C_{15}, in that order. Although this sequence differs in the penultimate stages from that reported elsewhere,[4,5] consensus over the timing of decarboxylation in ring C has been reached since identical conclusions have recently been reported by Blanche et al.[15] using *Pseudomonas denitrificans*. The foregoing evidence provides the necessary impetus for the successful isolation of several of the remaining intermediates of the B_{12} pathway proposed in Scheme II.

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Excited-State Proton-Transfer Polymerization of Amorphous Formaldehyde

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Fundamental investigations of photochemical reactions in the solid state are of current interest because they represent a method of inducing localized changes in the chemical composition of solids with use of a high degree of spatial control (e.g., using lasers). A detailed understanding of these processes is important for developing new materials with useful optical and chemical properties (e.g., holographic gratings, photoresists, and high density optical memories).

Crystalline formaldehyde is known to polymerize in the solid state when exposed to ionizing radiation.[1-4] Recently, we reported that polymerization also occurs in amorphous solid films in the presence of a strong acid such as HCl.[5] The films were formed by vapor deposition of chlorine and formaldehyde onto a CsI optical window mounted at the cold tip of a cryogenic refrigerator (10–77 K). Chlorine atoms formed by photodissociation of Cl_2 reacted with CH_2O to form HCl and CHClO. Proton transfer from the HCl to another formaldehyde molecule then initiated oligomerization of nearby formaldehyde molecules to polyoxymethylene (POM). Quantum yield measurements made by infrared absorption spectroscopy showed that the average length of the oligomers was 6.4 ± 1.3 monomer units. This is much lower than the chain lengths of 10^3–10^6 reported for the crystalline solid,[1] and is one consequence of molecular disorder in the amorphous state.

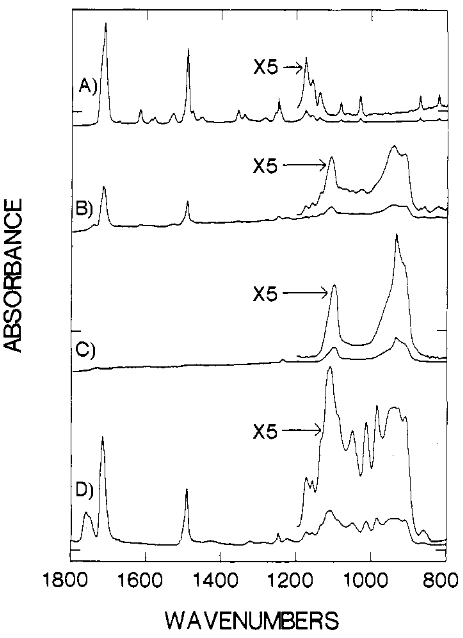

Figure 1. Infrared spectra of solid films of doped formaldehyde deposited on a 77 K CsI window under various conditions. Each tick mark on the vertical axis represents one absorbance unit (base 10): (A) 20:1 mixture of formaldehyde:2-nitrophenol before photolysis, (B) same sample after photolyzing with 4000 pulses at 308 nm (1.06 mJ cm^{-2} $pulse^{-1}$), (C) same sample after warming to room temperature under vacuum, (D) 11:1 mixture of formaldehyde:chlorine after photolyzing with 15 000 pulses at 308 nm (1.0 mJ cm^{-1} $pulse^{-1}$).

In this communication, we report that chain polymerization of formaldehyde can also be initiated by excited-state proton transfer from 2-nitrophenol. This molecule has a pK_a of 9.1 in the ground state, but upon absorption of a photon the molecule is estimated to have a pK_a of about −0.6 in the S_1 state[6] excited at 308 nm. We believe this to be the first example of a solid-state chain reaction which is initiated by proton transfer from an electronically excited dopant molecule. The technique is extremely powerful because it provides a way of temporarily generating a strong acid within a solid for the purpose of inducing transient or irreversible chemical reactions. Photochemical generation of acids has previously been shown by other workers to be useful for photolithography by inducing depolymerization[7] and/or dissolution[8-10] of polymeric photoresists. Photoacids are also known to induce cationic polymerization of several different monomers in liquid solutions.[11] All of the previous work has involved chemical rearrangements which form the acid in its ground state.

Transmission infrared spectra of a 20:1 mixture of CH_2O:2-nitrophenol before and after laser photolysis are shown in Figure 1. Photolysis reduces the intensities of IR bands attributable to formaldehyde[12,13] and 2-nitrophenol.[14] The POM product appears

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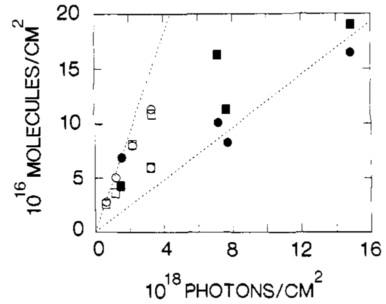

Figure 2. Plot of yields (molecules cm^{-2}) obtained from five separate experiments for reaction of formaldehyde and production of POM (monomer units) versus photons absorbed at 308 nm. In some experiments, data were obtained after two or more successive photolysis periods. The various symbols represent the following measurements: open squares, □, formaldehyde at 1.06 mJ cm^{-2} pulse^{-1}; open circles, O, POM at 1.06 mJ cm^{-2} pulse^{-1}; filled squares, ■, formaldehyde at 4.0 mJ cm^{-1} pulse^{-2}; filled circles, ●, POM at 4.0 mJ cm^{-2} pulse^{-1}. The dotted lines represent quantum yields of 0.012 and 0.045, which encompass most of the experimental data.

as the pair of peaks in the expanded 1200–800-cm^{-1} region of Figure 1b. After warming the sample to room temperature under vacuum, the spectrum in Figure 1c was obtained. The bands due to unreacted monomer and 2-nitrophenol have disappeared as these species are pumped away. The polymer remains on the window, and its spectrum is virtually identical with the literature spectrum of POM.[15]

Figure 2 is a plot of the two-dimensional concentrations of formaldehyde molecules and POM monomer units versus the total absorbed laser fluence. The concentrations are calculated from integrated IR peak intensities by using absorption coefficients which were determined in our previous study.[5] One experiment was performed in which both the 308-nm absorbance due to 2-nitrophenol and its integrated IR band intensity were measured. The UV absorption coefficient was consistent with the literature value.[16] This information allows us to correct for the decreasing concentration of the 2-nitrophenol and determine the actual absorbance at 308 nm throughout each experiment (typically 0.1–0.4). Five experiments run under similar conditions gave quantum yields in the range 0.012–0.045. This range of values is estimated from the data shown in Figure 2. The laser fluence for these experiments was either 1.06 or 4.0 mJ cm^{-2} pulse^{-1}. All of the experiments were conducted at a nominal temperature of 77 K. Transient heating was estimated to be only a few degrees following each laser pulse.

Thus far, we have been unable to directly determine the molecular weight of the POM product. This is partly due to the small size of the sample (approximately 2 × 10^{-6} mol). Also, dissolution of the polymer would probably change its molecular weight, since this would release the reactive ends of the polymer molecules buried in our samples.

Some qualitative information about the size of the polymer can be inferred from its infrared spectrum. The spectrum in Figure 1b bears a close resemblance to the spectrum of mature POM in 1c as well as the literature spectrum of POM.[15] The 1150–850-cm^{-1} region of the C–O–C stretch/bend has two distinct peaks. We note that the IR spectrum of mature POM is reported to be relatively insensitive to molecular weight.[15] On the other hand, the IR spectrum of the oligomer (approximately six monomer units, shown in Figure 1d) has several distinct bands in throughout this region. The oligomer in this case is formed by photolysis of a mixture of CH_2O and Cl_2.[5] On the basis of this indirect evidence, we conclude that each POM molecule formed by excited-state proton transfer is probably composed of 10 or more monomer units.

The results suggest that chain initiation/propagation is an extremely unlikely event. The measured quantum yield is less than 0.05, and the chain length is greater than 10, so the probability of initiation/propagation upon absorption of a photon must be less than 0.005 but quite reasonably may be closer to 0.001 or smaller. The small probability for reaction initiation could be due to rapid quenching of the 2-nitrophenol compared with proton transfer or to depolymerization of short chain-length oligomers. Further studies are underway in our laboratory to more completely characterize reactions which are initiated by excited-state acids in amorphous solids.

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Registry No. CH_2O, 50-00-0; 2-nitrophenol, 88-75-5.

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The Silicon–Carbon Double Bond: Theory Takes a Round

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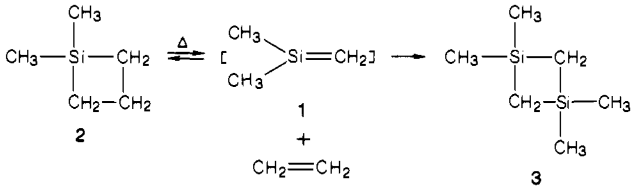
We have observed and assigned several microwave rotational transitions for the transient species 1,1-dimethylsilaethylene (DMSE, **1**). The results agree with the Si–C double bond length of 1.692 Å theoretically predicted for DMSE[1] rather than with the electron diffraction value of 1.815 Å.[2] The experimental methods developed for our study have a wide range of potential applications for observing rotational spectra of other reactive intermediates and determining their properties.

An engaging account of the silaolefins was presented by Schaefer several years ago[1] under the title "The Silicon–Carbon Double Bond: A Healthy Rivalry between Theory and Experiment". The aspect of the rivalry dealt with here is the Si═C bond length in DMSE. This molecule is a short-lived intermediate produced by pyrolysis of 1,1-dimethylsilacyclobutane (DMSCB, **2**).[3] It quickly dimerizes to give the stable product 1,1,3,3-tetramethyl-1,3-disilacyclobutane (TMDSCB, **3**).



The transient nature of DMSE and other silaolefins has made their characterization a continuing challenge. Schaefer described the electron diffraction study of DMSE by Mahaffy et al.[2] as a pioneering, daring experiment. However, its value of 1.83 ± 0.04 Å for r_g(Si═C) is completely outside the range (1.63–1.75 Å) of theoretical predictions. Schaefer reviewed and extended these calculations and suggested that the equilibrium r_e(Si═C) bond distance is 1.705 ± 0.03 Å in both DMSE and the parent silaethylene,[1] 0.12 Å shorter than the electron diffraction result. Our study was undertaken to resolve this discrepancy.[4]

Microwave spectroscopy is used extensively for accurate structural determination of volatile, stable, polar molecules. Also, it has been applied to transient species with lifetimes of a few seconds or longer, generated in heated waveguide cells and in

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