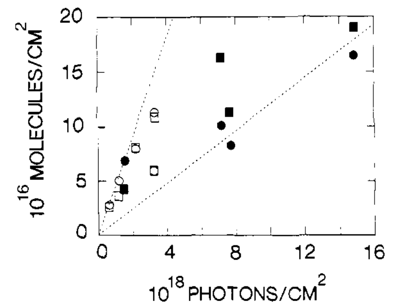

Figure 2. Plot of yields (molecules cm^{-2}) obtained from five separate experiments for reaction of formaldehyde and production of POM (monomer units) versus photons absorbed at 308 nm. In some experiments, data were obtained after two or more successive photolysis periods. The various symbols represent the following measurements: open squares, □, formaldehyde at 1.06 mJ cm^{-2} pulse^{-1}; open circles, ○, 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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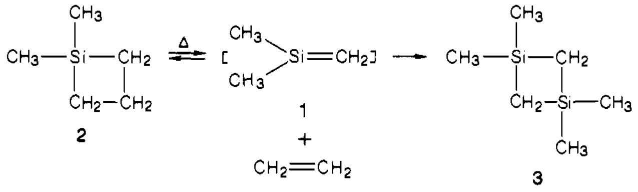
We have observed and assigned several microwave rotational transitions for the transient species 1,1-dimethylsilaethylene (DMSE, **1**). The results agree with the Si–C double bond length of 1.692 Å theoretically predicted for DMSE[1] rather than with the electron diffraction value of 1.815 Å.[2] The 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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Table I. Internal Rotation Fine Structure[a] Observed for Several Transitions of Dimethylsilaethylene (DMSE)

trans	obsd, MHz	trans	obsd, MHz	trans	obsd, MHz
$4_{22} \rightarrow 4_{31}$	8002.586	$3_{12} \rightarrow 3_{21}$	8226.010	$2_{02} \rightarrow 2_{11}$	8413.286
	8002.755		8227.761		8414.519
	8003.202		8228.486		8415.662
	8003.592		8230.388		8417.467
	8005.688				
$2_{12} \rightarrow 2_{21}$	8827.380	$3_{22} \rightarrow 3_{31}$	9043.514	$0_{00} \rightarrow 1_{11}$	9129.760
	8829.922		9047.287		9130.658
	8833.588		9047.671		9131.892

[a] Many of the components exhibit additional partially resolved structure attributed to proton-proton hyperfine interactions.

high-temperature flow systems.[5] We judged DMSE to be too reactive[3] for these methods. Instead we based our experiment on the Mark II Flygare-Balle Fourier transform (FT) spectrometer,[6] modified to improve sensitivity, reliability, and ease of operation.[7] This type of spectrometer has been used to generate weakly bonded dimers and small clusters and observe their rotational spectra. In a typical operation, a carrier gas (Ar or "first run" neon, a Ne/He 70/30 mixture) at ~1 or 1.5 atm is seeded with a percent or so of cluster-forming species. The mixture is pulsed into an evacuated Fabry-Perot cavity through a supersonic nozzle (1 mm diameter). As the gas expands it cools to ~5 K. The cavity is a tuned element in the pulsed FT microwave spectrometer which detects the transitions of the polar species passing through the cavity.

A 3-cm length of 1.7 mm i.d. quartz tubing was attached to the outlet of the solenoid-activated valve (General Valve). The exit end of this extension was constricted to 0.6 mm i.d., and a heating coil was wound around 10-15 mm of that end, the inner length of bare tubing insulating the pulsed valve from the furnace. When operated at ambient temperature this device has little or no effect on S/N of the spectrometer, depending on the species observed. Carrier gas was saturated with the DMSCB precursor (Petrarch Systems, Inc.) by bubbling it through the liquid (bp 82 °C). It was then diluted with pure carrier. The furnace temperature was adjusted so that its operation reduced the intensity of a DMSCB transition at 8903 MHz to a tenth of its unheated value. With the furnace at ~1000 °C we observed the six transitions of DMSE listed in Table I. Because of the cooling in the expansion they are for the ground vibrational state.

The assignment of these transitions to DMSE is unamgibuous. They disappear when the temperature of the furnace is turned down. Their fine structure, with spacings of ~1 MHz, is that expected for the restricted internal rotation of the two equivalent methyl groups with a barrier of ~1 kcal/mol[8] in DMSE. The rotational constants are consistent with DMSE. The transitions found at 8004, 8831, and 9047 MHz were predicted by rotational constants from fitting the other (first) three transitions. The planar moment P_c from the rotational constants is small and very close to that for isobutylene,[9] 3.022 and 3.072 u Å^2, respectively. This strongly supports a planar dimethylethylenic skeleton for the species found. P_c is determined by mass out of the molecular plane[10] which should be the same in both cases (two protons in each of the methyl groups).[1,9]

The rotational constants obtained by fitting the approximate line centers of the six observed transitions are compared in Table II with those calculated for the DZ + d SCF theoretical structure (T), with an r(Si=C) of 1.692 Å, and for the electron diffraction structure (E). In the latter, we allowed for the high-temperature vibrational effects by reducing the r_g(Si=C) value of 1.83 Å to 1.815 Å and by using the theoretical values for the other distances.[2] DMSE is a near symmetric top. The C_2 dipole axis is the b-axis for T and the a-axis for E. The observed spectrum is fitted only as b-dipole transitions. Moreover, the fitted constants are systematically somewhat larger (15-50 MHz) than those for T and are much larger (130-300 MHz) than those for E. The microwave structure is incompatible with E and is actually somewhat more compact than T, the difference in A corresponding to an r(Si=C) smaller by 0.003 Å than predicted.

Table II. Comparison of Microwave Rotational Constants for DMSE with Those Predicted for the Theoretical and Electron Diffraction Structures

source	A, MHz	B, MHz	C, MHz	trans type
microwave[a]	6037.1	5896.9	3093.6	b-dipole
DZ + d SCF[1]	6025.98	5845.95	3078.89	b-dipole
electron diffraction[2,b]	5845.95	5583.95	2959.70	a-dipole

[a] Rigid rotor constants from transitions in Table I. [b] See text.

There are three main structural parameters in DMSE: r(Si=C), r(Si—C), and $\angle$(C—Si=C). Only the A and B rotational constants are independent, so the structure is underdetermined. However, the fine structure caused by internal rotation depends on the angle between the rotor and the inertial axes. Plans are underway to fit it and/or obtain spectra of isotopically substituted species to enable a more complete structure to be determined.

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Site Selectivity Studies on the Catalyzed Reaction of Isotopically Labeled MnRe(CO)$_{10}$ with ^{t}BuNC. Implications for Metal Dimer and Cluster Reactions

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In recent years a comprehensive understanding of the substitution reaction of monometallic transition-metal carbonyl complexes has emerged.[1] The same cannot be said for the substitution reactions of metal dimer and cluster carbonyl complexes in which the presence of a metal-metal bond permits a wider range of reaction mechanism and products.[2,3] This added complexity makes it possible for the site of ligand addition and loss to occur at the same or different metal atoms. For instance, the thermal reaction between MnRe(CO)$_{10}$ and L (L = PR$_3$,[4] P(OR)$_3$,[3,4] and RNC[5]) yields the Re-substituted derivative even though kinetic

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