The Infra-red Multiphoton-induced Decomposition of Silicon-containing Four-membered Rings. A New Source of Silaolefins

By Henry M. Frey, Annoula Kashoulis, Lee Mei Ling, Susan P. Lodge, Ivy M. Pidgeon, and Robin Walsh
(*Department of Chemistry, University of Reading, Whiteknights, Reading* RG6 2AD)

Summary The title process is shown to be a new source of 2-methyl-2-silapropene for which some relative rate constants are reported.

There is considerable current interest[1] in the reactions of silaethenes, but although quite a lot is now known about their chemistry, very little is known about the kinetics of their reactions.[2] One of the problems has been that the preferred source, pyrolysis of silacyclobutanes, requires high temperatures (>670 K), and thus the reactions have usually to be studied under these conditions.[2] There have been some attempts to generate 2-methyl-2-silapropene (2MSP) at room temperature using vacuum-u.v. photolysis of the cyclobutane precursor but these have led to a rather poor fractional recovery and much polymerisation.[3] We report a new and promising method for the generation of 2MSP by use of multi-photon i.r.-induced decomposition.

Two precursors were used, *viz.* 1,1-dimethylsilacyclobutane (DMSCB) and 1,1,3,3-tetramethyl-1,3-disilacyclobutane (TMDCB). The experiments were carried out using a tunable, pulsed Laser Applications CO_2 TEA laser operating at a peak power of *ca.* 5 MW, and a repetition rate of one pulse per two seconds. Pulse energies were measured on a pyroelectric joulemeter (Laser Applications) and the output-line wavelength calibrated with a spectrum analyser (Optical Engineering). The output-beam diameter was reduced by focussing with a 50 cm focal length gold surfaced concave mirror. Experiments were carried out in 10 cm path reaction cells with sodium chloride windows. These were placed beyond the focus such that the beam diameter was *ca.* 0·5 cm and estimated peak power densities were 25 MW cm^{-2}. Sufficient product yields, which were analysed by gas chromatography, could be obtained with about 20 shots.

In the first series of experiments TMDCB was chosen as the source in the hope that only reaction (1) might occur.

$$\text{TMDCB} \rightarrow 2\text{Me}_2\text{Si}{=}\text{CH}_2 \qquad (1)$$

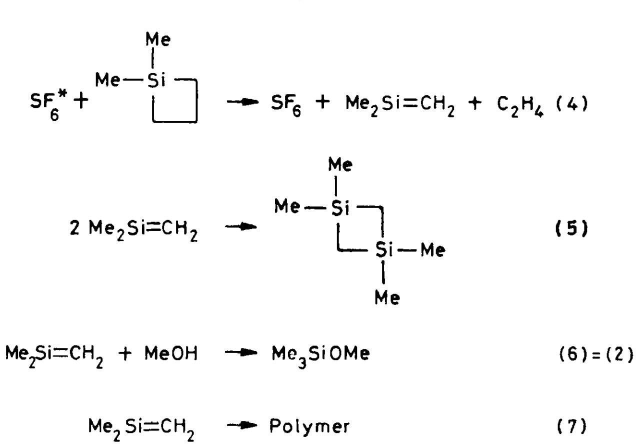
TMDCB at various pressures in the range 1—10 Torr was found to absorb the P24 line of the 10·4 μm CO_2 band but extensive decomposition resulted giving a large number of hydrocarbons, the most prominent of which was C_2H_4, as well as a whitish yellow polymer (which gradually built up inside the cell). In experiments with added methanol a new product, trimethylmethoxysilane, was formed indicating the transient presence in the reaction products of 2MSP which reacts by the known reaction (2).[1] Further

$$\text{Me}_2\text{Si}{=}\text{CH}_2 + \text{MeOH} \rightarrow \text{Me}_3\text{SiOMe} \qquad (2)$$

support for the presence of 2MSP is given by the formation of $(Me_3Si)_2NH$[1] when NH_3 is used as a trap instead of MeOH. The high yields of hydrocarbon, however, imply that other processes of decomposition apart from reaction (1) are occurring. This probably arises from the high vibrational energy content of TMDCB.

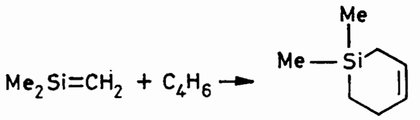
In the second series of experiments DMSCB was decomposed by SF_6 sensitization, using the P20 line of the 10·4 μm CO_2 band (DMSCB itself has no convenient i.r. band for direct absorption). By use of 2—3 Torr of SF_6 *ca.* 80% of the incident energy of *ca.* 1 J/shot was absorbed. 5—15 Torr of DMSCB was used and the major products in this case were ethene and TMDCB. Typically, *ca.* 0·5% decomposition per shot could be achieved under these conditions. Ethene was >90% of the observed hydrocarbon (CH_4 and C_2H_2 were minor products) and (80 ± 10)% of the silaolefin was recovered (*i.e.* [TMDCB]/[C_2H_4] = 0·40 ± 0·05). The remaining 20 ± 10% of silaolefin was presumed to result in polymer formation (which was again visually observed). Since this system appears to be relatively simple chemically we have embarked on a series of experiments to try to obtain rate constants for reactions of 2MSP. Thus far we have studied the system in the presence of added methanol and, separately, of added butadiene. In the methanol study partial pressures in the range 2—12 Torr were used (SF_6 = 3 Torr, DMSCB = 12 Torr) and the Me_3SiOMe product was monitored quantitatively. No other product (above the 5% level) was found apart from TMDCB. The ratio [Me_3SiOMe]/[TMDCB] increases monotonically with MeOH pressure to *ca.* 3·7 at [MeOH] = 12 Torr [in low (<20%) conversion experiments]. Experiments were carried out to show no sensitized MeOH decomposition occurred nor any reaction between 2MSP and Me_3SiOMe. Freshly cleaned cells were used to avoid the risk of surface effects through laser absorption by the polymer. In fact, a dirty cell filled with SF_6 and MeOH gave no observable product in a blank experiment.

These results suggest that the chemistry of these processes can be described by the reactions (3)—(7).



A major consideration is that of temperature equilibration in the system. We estimate peak temperatures in the beam to be possibly as high as 1500 K. However, a thermal distribution in the gas should be achieved in less than *ca.* 10^{-3} s (with an average temperature of 420 K). During this period reaction (4) will take place and 2MSP will be formed. The lifetime of 2MSP based on the published rate constant[4] for reaction (5) is *ca.* 0·1 s. Therefore temperature equilibration *in the gas itself* will be achieved long before steps (5) and (6) ensue. In addition, based on a thermal conductivity calculation, we estimate that most of the heat in the cell will have been conducted away prior to the onset of reactions (5) and (6). This was assumed to be the case and the kinetics of decay of 2MSP by reactions (5), (6), and (7) were solved by simple integration. A computer simulation of the complete set of shots in a given experiment could then be made for a chosen set of rate constants. The data could be fitted within experimental scatter (8 experiments) for k_6/k_7 = 0·013 ± 0·005. The polymerisation step (which was treated as diffusion controlled) showed considerable scatter. However, since this step had to be fitted to the 2MSP deficit, all the accumulated analytical errors were present.

Similar experiments with butadiene as trapping reagent gave $k_8/k_5 = (1{\cdot}1 \pm 0{\cdot}5) \times 10^{-4}$. Although k_5 has



(8)

apparently been measured to be $10^{6.55}$ dm^3 mol^{-1} s^{-1} (with no activation energy)[4] we have some doubts as to its reliability.[5] Nevertheless it is clear that reactions (6) and (8), which we believe to be homogeneous, in order to compete with reaction (5) must have activation energies only a little greater than that of (5) (perhaps by *ca.* 6 and 20 kJ mol^{-1}, respectively). This parallels recent measurements by Davidson and his co-workers on other reactions of 2MSP produced by pyrolysis of DMSCB.[2b] We plan to extend our measurements to these and other reactions of 2MSP.

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[1] L. E. Gusel'nikov and N. S. Nametkin, *Chem. Rev.*, 1979, **79**, 529 and references therein.

[2] Some kinetic work has appeared very recently: (a) P. John, B. G. Gowenlock, H. C. Low, and G. Peters, paper presented at the Chemical Society, Gas Kinetics Discussion Group Meeting, Keele, September 24th, 1979. (b) I. M. T. Davidson, C. E. Dean, and F. T. Lawrence, *J. Chem. Soc., Chem. Commun.*, 1981, 52.

[3] H. C. Low and P. John, *J. Organomet. Chem.*, 1980, **201**, 363.

[4] L. E. Gusel'nikov, K. S. Konobeyevsky, V. M. Vdovin, and N. S. Nametkin, *Dokl. Akad. Nauk SSSR*, 1977, **235**, 1086.

[5] R. Walsh, unpublished calculations.