

products with a *p*-MAP/*o*-MAP = 0.3 ratio (Isomers II). We have proposed that these products are formed from radicals escaping the primary cage but that are unable to percolate through the lattice and are forced to reencounter. The lifetime of this pair is determined either by decarbonylation (e_2) or by reencounter and reaction (c_2 , Scheme I), and the largest scavenging effects are observed on the yield of isomerization products and on the yields of oxides, which include the formation of phenylacetic acid (Oxides-II). The amplitude between the last two points in lines m and h of Figure 1a,d at pressures approaching 10^3 Torr reflects the fraction of radicals involved at this stage. Finally, at the end of the scavenging dynamics is the primary radical pair in the primary cage. The nonscavenging products remaining at high pressures (Isomers-I) come from reactions at the primary geminate site (supercage) and are characterized by *p*-MAP/*o*-MAP \approx 0.15 with $\langle S \rangle = 0.64$ and 0.48 at the highest oxygen pressures.

Although the dynamics of the radical pairs produced from photolysis of DBK in solution basically occurs in a succession of unresolvable steps, the conditions for time management in complex chemical and molecular dynamics not available in fluid media may be found in organized media such as zeolites.

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Experimental and Theoretical Evidence in Support of an Intermediate Complex in the Insertion Reaction of Silylene into Silane

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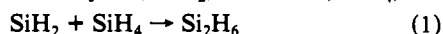
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The reaction between silylene, SiH_2 , and silane, SiH_4 , viz.



may reasonably be considered the prototype Si-H insertion process of silicon hydride chemistry. This reaction, which is also the second step in the thermolysis of silane¹ leading ultimately to solid silicon and silicon hydride deposition, is known to be fast. Experimental measurements of the rate constant²⁻⁴ show the reaction to proceed at close to the collisional limit. Theoretical calculations of the energy surface for the decomposition of Si_2H_6 show that it possesses no energy barrier at the threshold of dissociation,⁵ which suggests a zero barrier for reaction 1. The published kinetic studies of reaction 1²⁻⁴ have only been carried out at room temperature. We present here new experimental rate measurements of reaction 1 in the gas phase over the temperature range 296-658 K, supported by ab initio calculations which provide unambiguous evidence for a barrierless reaction and additionally suggest the

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Table I. Experimental Rate Constants for Reaction 1 at Different Temperatures (Bath Gas SF_6)

T/K	$10^{10}k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	
	$P = 10$ Torr	$P = \infty^a$
296	4.2	4.6 ± 0.3
363	3.3	3.9 ± 0.3
432	2.9	3.2 ± 0.3
488	1.90	2.6 ± 0.3
578	1.28	2.6 ± 0.4
658	0.72	2.2 ± 0.4

^a Obtained by extrapolation.

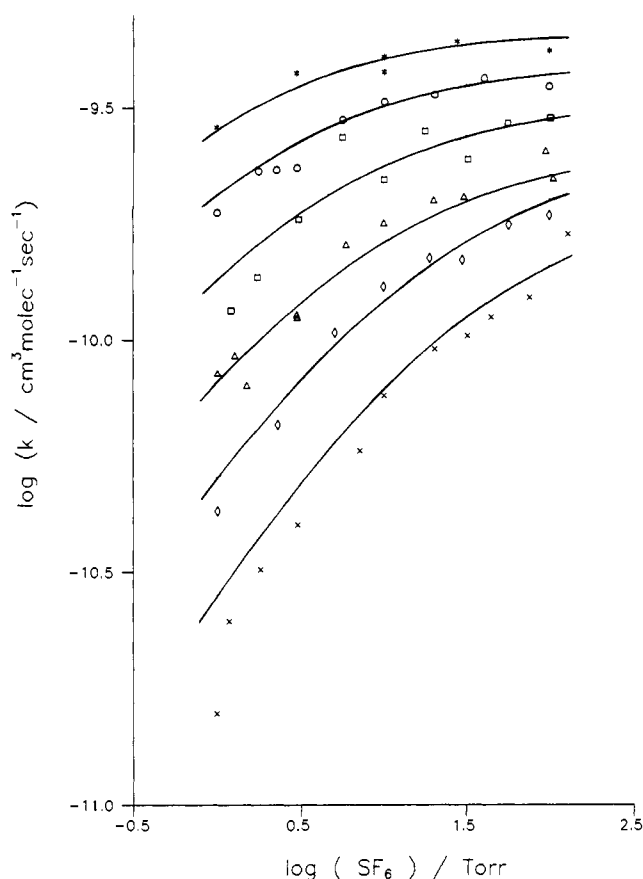


Figure 1. Pressure dependence of second-order rate constants for reaction 1 at different temperatures [\circ , 296 K; \square , 363 K; \triangle , 432 K; \diamond , 488 K; \times , 578 K; \times , 658 K]. Solid lines are variational RRKM theoretical fits.

existence of a weakly bound complex in the reaction potential entrance channel.

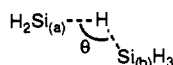
SiH_2 kinetic studies have been carried out by the laser flash photolysis technique, the details of which have been published previously.^{4,6} SiH_2 was created by photodecomposition of phenylsilane using the 193-nm ArF line of a pulsed excimer laser. SiH_2 was detected and monitored in real time by use of a single-mode dye laser tuned to a known (strong) vibration-rotation transition (17259.50 cm^{-1}) in the visible A \leftarrow X absorption band. Signal decays from 5-15 photolysis laser shots were averaged and found to give good first-order kinetic fits. Experiments were carried out with gas mixtures containing a few millitorr of phenylsilane, varying quantities of SiH_4 up to 100 mTorr, and inert diluent bath gas (SF_6 or Ar) at total pressures between 1 and 100 Torr. Second-order kinetics was confirmed by finding a linear pressure dependence of the pseudo-first-order decay constants on substrate SiH_4 pressures.

The reaction was studied at six temperatures in the range 298-653 K. Second-order rate constants were found to be pressure

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dependent at all temperatures, showing the typical variation corresponding to a third-body-mediated association. Table I shows the rate constants obtained in SF₆ at 10 Torr total pressure and at infinite pressure (obtained by extrapolation). We note that the rate constants at infinite pressure are close to the collisional limit (the Lennard-Jones collision number is estimated to be $4.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K) in support of a very loose type of transition state, although it should be added that there is a discrepancy of ca. a factor of 2 with Jasinski and Chu³ (at 298 K). Figure 1 shows the pressure-dependent rate constants as a function of temperature. For simplicity only the SF₆ data are shown. The rate constants in Ar showed similar trends but were smaller (as expected for a weaker collision partner). It is clear from the data that *k*_i decreases with increasing temperature. The average activation energy at the high-pressure limit is ca. -3 kJ mol⁻¹; however, the Arrhenius plot is slightly curved. RRKM calculations using a variational transition state have been carried out and fitted to these rate constants. These are also shown in Figure 1. To obtain reasonable fits it is necessary (i) to tighten the activated complex structure (increase the magnitude of low-frequency vibrations) with increasing temperature and (ii) to assume SF₆ removes an average of 10.8 kJ mol⁻¹ in a down collision ($\langle \Delta E \rangle_{\text{down}}$, stepladder model).

These results are qualitatively similar to earlier findings for the Si-H insertion reactions of SiMe₂,⁷ PhSiH,⁸ and MeSiH,⁹ where negative activation energies are also found. One possible explanation for these results is the occurrence of an intermediate complex in the pathway leading to products. This prompted us to re-examine the potential energy surface for reaction 1 using ab initio methods. Calculations of the geometry of the interacting SiH₂ + SiH₄ species during the reaction have been carried out at the MP2/6-31G(d,p)^{10,11} and the MP2/6-311G(d,p)^{10,12} levels of theory. A minimum energy configuration has been found at both levels of theory, corresponding to an intermediate complex of the type



With the smaller basis set, we find $\theta = 120.5^\circ$, with Si_(a)-H = 1.686 Å and Si_(b)-H = 1.569 Å. This C₁ structure has been verified to be a minimum on the potential energy surface by calculating and diagonalizing the matrix of energy second derivatives (Hessian) and demonstrating that the Hessian is positive definite. With the larger basis set, θ closes to 86.2° with the corresponding bond distances of 1.525 and 2.046 Å, respectively. At the latter level of theory (MP2/6-311G(d,p)), the complex is found to be 51.5 kJ mol⁻¹ lower in energy than separated SiH₂ + SiH₄ (not including zero-point vibrational corrections). This intermediate is separated from the global minimum (disilane) by a barrier of less than 6.5 kJ mol⁻¹. Thus, the energy required to move from the local minimum to disilane is well below that available from the reactants. This means that the surface in the region of the intermediate represents an extremely "shallow" minimum and should probably be thought of as rather flat. Although detailed dynamic calculations have yet to be performed, this is just the kind of potential surface likely to give rise to a reaction free energy bottleneck, the location of which will vary with system total energy (and therefore temperature), as supported by the kinetic findings.

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Origin of the Nonstereospecificity in the Ring Opening of Alkyl-Substituted Cyclobutenes

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The rule that photochemical ring opening in cyclobutenes occurs stereospecifically according to a disrotatory pathway¹ has recently been challenged by careful experimental work^{2a,3} in which a mixture of all possible diene isomers is obtained from the direct photolysis of alkyl-substituted cyclobutenes.² In particular, the direct photolysis³ (193 nm) of a single stereoisomer of 7-methylbicyclo[4.2.0]oct-7-ene (1) yields a mixture of cis,cis (c,c), cis,trans (c,t) and trans,cis (t,c) products (Scheme I). This example is a good candidate for a theoretical study because all possible products can be detected.

Using ab-initio CAS-SCF (complete active space) computations (using Gaussian 91⁴) at the 4-31G level, we have demonstrated that the occurrence of three products in the photochemistry of 1 can be rationalized via a reaction path that passes from the excited state to the ground state via three different transition points which correspond to conical intersections⁵ or touchings of the ground and excited states, shown as CI1, CI2, and CI3 in Figure 1 (CI is the parent butadiene). The three different conical intersections have almost equal energies and contain the same basic twisted tetradicaloid butadiene moiety (shaded) with all the

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