Gas-Phase Kinetic Study of the Prototype Silylene Addition Reaction $SiH_2 + C_2H_4$ over the Temperature Range 298–595 K. An Example of a Third-Body Mediated Association

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Time-resolved studies of silylene, SiH₂, generated by laser flash photolysis of phenylsilane, have been carried out to obtain rate constants for its bimolecular reaction with ethene. The reaction was studied in the gas phase, over the pressure range 1–100 Torr (in SF₆ bath gas) at five temperatures in the range 298–595 K. The reaction of SiH₂ with C₂H₄ is pressure dependent, consistent with a third-body assisted association reaction to form silirane. While silirane was too labile to be detected, vinylsilane, another possible product, was ruled out by GC analysis. Extrapolation of the pressure dependent rate constants gave the Arrhenius equation: $\log(k^{\infty}/\text{cm}^3$ molecule⁻¹ s⁻¹) = (-9.97 ± 0.03) + (2.9 ± 0.2) kJ mol⁻¹/RT ln 10. These parameters are consistent with a fast, nearly collision-controlled, association process. RRKM modeling, based on a consistent transition state for silirane decomposition, gave a good fit to the pressure dependent curves. The calculations employed a weak collisional deactivation model and confirmed (within ±12 kJ mol⁻¹) the most recent theoretical value for ΔH°_{f} (silirane) of 124 kJ mol⁻¹. An enthalpy surface for the reaction highlights the importance of entropy, rather than enthalpy (or energy), in determining the breakdown pathway of silirane.

Introduction

Silylenes are widely recognized as important intermediates in silicon hydride and organosilicon chemistry.^{1.2} They exist as ground state singlets, and their characteristic reactions include insertions into Si—H, Si—OR, and O—H bonds and π -type addition across C=C and C=C bonds.^{1.2} Until 1985 mechanistic information on such reactions came *via* end-product analytical studies, and the magnitudes of rate constants for such processes were largely a matter of conjecture. Since that time, there have been a steadily increasing number of direct, time-resolved kinetic studies of silylene reactions leading to an accumulating data base of absolute rate constants.^{3,4}

For silylene (SiH₂) itself we have investigated the kinetics of the fundamental processes of insertion into H_2^5 and $SiH_4^{6,7}$ and extend our investigations here to the prototype addition reaction with ethene, C₂H₄. Recent studies by Inoue and Suzuki (IS)⁸ and by Chu, Beach, and Jasinski (CBJ)⁹ have shown that the reaction occurs at close to collision (gas-kinetic) rates at room temperature. IS⁸ reported a rate constant at 1 Torr total pressure (in helium) of 9.7×10^{-11} cm³ molecule⁻¹ s⁻¹ while CBJ⁹ additionally found a pressure dependence of the rate constant between 1 and 9.5 Torr (He bath gas). In preliminary studies at 298 K,¹⁰ we have confirmed the pressure dependence between 1 and 50 Torr in both Ar and SF_6 bath gases and obtained rate constants consistent with those of CBJ.9 We describe here the extension of these preliminary studies (a) to obtain the temperature dependence for the first time, (b) to try to model the pressure dependence over a wide temperature range, and (c) to learn more about the mechanism of the process.

Present information on the mechanism of the reaction is the following. It is well established that silylene additions to alkenes give, in the first step the three-membered ring siliranes via a stereospecific process.¹¹ Siliranes are generally rather labile compounds and appear to require a fairly high degree of substitution to be stabilized.^{12,13} The parent molecule, $H_2SiCH_2CH_2$, has not yet been isolated. Ab initio theoretical calculations¹⁴ of the reaction of SiH₂ with C₂H₄ indicate a reaction with no energy barrier, consistent with the high rate constants.^{8,9}

Kinetic studies of the addition reaction of $SiMe_2$ with alkenes, in our own laboratories,¹⁵ indicate that the rates are controlled by the electrophilic character of the silylene (with its empty p-orbital). Concurrently, similar studies have been carried out on the related reaction of SiH_2 with ethyne (acetylene).^{16,17}

Experimental Section

The apparatus and equipment for these studies have been described in detail previously.^{5,6} Only essential and brief details are therefore included here. SiH₂ was produced by the 193-nm flash photolysis of phenylsilane (PhSiH₃) using an Oxford Lasers KX2 ArF exciplex laser. SiH₂ concentrations were monitored in real time by means of a Coherent 699-21 single-mode dye laser pumped by an Innova 90-5 argon ion laser and operating with Rhodamine 6G. Experiments were carried out in a variable temperature stainless steel reaction vessel with demountable windows.¹⁸ The monitoring laser beam was multipassed between 32 and 48 times through the reaction zone to give an effective path length of up to 1.8 m.

The monitoring laser was tuned to $17259.50 \,\mathrm{cm^{-1}}$, corresponding to a known strong vibration-rotation transition^{5,19} in the SiH₂, $\tilde{A}(^1B_1) \leftarrow \tilde{X}(^1A_1)$ absorption band. Light signals were measured by a dual photodiode/differential amplifier combination, and signal decays were stored in a transient recorder (Datalab DL910) interfaced to a BBC microcomputer. This was used to average the decays of up to 20 photolysis laser shots (at a repetition rate of 1 or 2 Hz). The averaged decay traces were processed by fitting the data to an exponential form using a nonlinear least squares package. This analysis provided the values for first order rate coefficients, k_{obs} , for removal of SiH₂ in the presence of known partial pressures of substrate gas.

Gas mixtures for photolysis were made up, containing between 1 and 15 mTorr of phenylsilane, PhSiH₃, and 0–1200 mTorr of C_2H_4 together with inert diluent (SF₆) at total pressures between 1 and 100 Torr. Pressures were measured by capacitance manometers (MKS, Baratron). Gas chromatographic analysis of product mixtures was carried out using a Perkin-Elmer 8310 chromatograph equipped with a flame ionization detector. Porapak Q (4-m) and Porapak T (2-m) columns were used to separate the products.

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Figure 1. Second order kinetic plots showing the dependence of decay constants on ethene pressures: (a) (O) 298 K, (\bullet) 355 K, (\Box) 415 K, (b) (Δ) 515 K, (\times) 595 K.

All gases used in this work were thoroughly degassed prior to use. PhSiH₃ (99.9%) was obtained from Ventron-Alfa (Petrarch). C_2H_4 (99.8%) was obtained from Matheson and not further purified. Sulfur hexafluoride, SF₆ (no GC-detectable impurities), was from Cambrian Gases. For product identification purposes, a sample of vinylsilane (88%) was prepared by LiAlH₄ reduction of vinyltrichlorosilane (Aldrich).

Results

Preliminary experiments established that, for a given reaction mixture, decomposition decay constants, k_{obs} , were not dependent on the exciplex laser energy (ca. 50–150 mJ/pulse) or number of photolysis shots. Since static gas mixtures were used, tests with up to 30 shots were carried out. The constancy of k_{obs} (10 shot averages) showed no effective depletion of reactants. The sensitivity of detection of SiH₂ was very high but decreased with increasing temperature. Therefore increasing quantities of phenylsilane precursor were required at higher temperatures. For the purpose of rate constant measurement at a given temperature phenylsilane pressures were kept fixed. A series of experiments



Figure 2. Arrhenius plot of rate constants for SiH₂ + C₂H₄. Rate constants: (\bullet) obtained at 10 Torr; (O) extrapolated to $p = \infty$ (including estimated uncertainties).

TABLE 1: Experimental Second Order Rate Constants for SiH_2 Addition at Different Pressures (SF₆)

	$10^{10}k/cm^{3}$ mol	ecule ⁻¹ s ⁻¹
T/K	$P_T = 10 \text{ Torr}$	$P_T = \infty^a$
298	1.58 ± 0.03	3.5 ± 1.2
355	1.15 ± 0.02	3.0 ± 1.2
415	0.731 ± 0.017	2.5 ± 1.0
515	0.357 ± 0.005	2.2 ± 0.9
595	0.148 ± 0.007	1.9 ± 0.9

^a Obtained by extrapolation: see text.

was carried out at each of five temperatures in the range 298-595 K. At 10-Torr total pressure (SF₆ diluent), five or six runs (of 10-20 laser shots each) at different C_2H_4 partial pressures were carried out at each temperature. The results of these experiments are shown in Figure 1, which demonstrates the linear dependence of k_{obs} with C_2H_4 , expected for second order kinetics. The second order rate constants, obtained by least squares fitting to these plots are collected in Table 1. The error limits are single standard deviations. It is clear that rate constants decrease with increasing temperature. An Arrhenius plot of the (10-Torr) rate constants, shown in Figure 2, is somewhat curved, and therefore we do not record Arrhenius parameters.

In addition to these experiments, another set of runs was carried out at each temperature, in which the total pressure (SF_6) was varied in the range 1-100 Torr in order to test the pressure dependence of the second order rate constants. In these runs, the full second order plot was not obtained, but second order behavior was assumed, and the constants were obtained by assuming a linear dependence of k_{obs} on $[C_2H_4]$. In order to keep errors to a minimum sufficient C_2H_4 was used to ensure k_{obs} values in the range $(2-3) \times 10^5$ s⁻¹ where reaction with C₂H₄ was at least 75% of the total reaction. Allowance was made for reaction of SiH₂ with phenylsilane (measured directly for each pressure, but found to be pressure independent). The pressure range was dictated by practical considerations. At pressures above 50 Torr, signals were partially quenched, and below 1 Torr, pressure measurement uncertainties became significant. The results from these experiments, representing over 100 measurements of individual rate constants, are incorporated into Figure 3, which shows the pressure dependence of the rate constants at each temperature, in a loglog plot for convenience. The uncertainties in individual rate constants shown in the figure are probably $ca. \pm 10\%$, but are not indicated, in order not to complicate the diagram.



Figure 3. Pressure dependence of second order rate constants for $SiH_2 + C_2H_4$ at different temperatures: (*) 298 K; (\Box) 355 K; (×) 415 K; (\blacksquare) 515 K; (\blacktriangle) 595 K.

Several points are immediately evident from an examination of Figure 3. Rate constants decrease with increasing temperature at all pressures. Rate constants increase with increasing pressure, the extent of variation being greatest at the highest temperature. Although the pressure dependence tends toward a high pressure limit, this is not actually reached at the experimentally highest pressure. Extrapolation to the high pressure limit is discussed later. These effects are characteristic of a third-body mediated association reaction, as discussed earlier,¹⁰ and for this reason we have carried out RRKM modeling calculations, described in the next section.

A gas chromatographic search was carried out for reaction products in the room temperature photolysis studies. No peak could be found with a retention time appropriate for a C_2Si containing compound. In particular vinylsilane could be ruled out from a knowledge of the retention time of an authentic sample. Silirane itself, although almost certainly formed, is probably too labile to survive passage through the chromatograph.

RRKM Calculations

The pressure dependence of an association reaction corresponds exactly to that of the reverse unimolecular dissociation process provided there are no other perturbing reaction channels. Therefore we have carried out RRKM calculations of the pressure dependence of the silirane unimolecular decomposition, i.e.,

$$H_2Si < \bigcup_{CH_2}^{CH_2} \xrightarrow{-1} SiH_2 + H_2C = CH_2$$

Since the silirane molecule has not yet been isolated and its decomposition kinetics are unknown, we are forced to make estimates of the necessary parameters prior to carrying out calculations. Fortunately, there is sufficient information of reliable quality to be able to do this. The approach adopted was first to calculate the thermodynamic properties of silirane (not previously available), secondly to evaluate ΔS° and ΔH° for reaction -1,1 and finally to combine these with the Arrhenius parameters (at infinite pressure) for step 1 to obtain those for step -1.

The thermodynamic properties of silirane were calculated by the methods of statistical mechanics^{20,21} based on structural parameters²² and vibrational wavenumbers²³ given by Boatz and Gordon. The results of these calculations are given in the Appendix. The thermodynamic values of the entropy, S° , and

 TABLE 2: Calculated Thermodynamic and Kinetic Quantities for Reaction -1,1

	(i) The	rmodynan	nic Quantiti	es ^a	
			T/I	<u>د</u>	
		300	400	500	600
$\Delta S^{\circ}/J \text{ K}^{-1} \text{ mod}$ $\Delta H^{\circ}/kJ \text{ mod}^{-1}$	$\frac{1}{1}$	159.5 200.8	159.2 200.8	157.4 200.0	155.5 198.7
	(ii)	Kinetic C	uantities ^b		
			T/K		
	296	355	415	515	595
$log(A_{-1}/s^{-1})$ $E_{-1}/kJ mol^{-1}$	17.32 195.4	17.24 195.0	17.14 194.1	16.96 192.5	16.81 190.8

^a Standard state = 1 bar. ^b Obtained from thermodynamic quantities combined with those of A_1 and E_1 : see text.

the enthalpy function, $\Delta H^{\circ} - \Delta H^{\circ}_{298}$, were combined with those of SiH₂²⁴ and C₂H₄²⁵ in order to obtain ΔS° and $\Delta H^{\circ} - \Delta H^{\circ}_{298}$ for reaction -1,1. ΔH°_{298} was taken to be 201 kJ mol⁻¹ on the basis of the ab initio calculation of Boatz and Gordon.22,23 Theoretical calculations by Horner et al.26 also give closely similar results for the enthalpy of formation and strain enthalpy of silirane. The ΔH°_{298} value chosen here was found to provide a fit in our preliminary calculations¹⁰ in contrast to a much lower value (ca. 130 kJ mol-1) based on the kinetics of hexamethylsilirane decomposition.²⁷ This is discussed later, but it appears that this latter figure does not provide a good model. The values of ΔS° and ΔH° obtained at each temperature were used to relate the Arrhenius parameters for steps -1 and 1 via $\ln(A_{-1}/A_1) = \Delta S^{\circ}/R$ and $\Delta H^{\circ} = E_{-1} - E_1 + RT$. The numbers obtained are shown in Table 2. In order to calculate A_{-1} and E_{-1} (values shown) it is necessary to know the infinite pressure values for the Arrhenius parameters A_1 and E_1 for the association reaction. These come from the Arrhenius equation below, obtained by extrapolation of the pressure dependent rate constants of this work (see Table 1).

 $\log(k_1^{\infty}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = (-9.97 \pm 0.03) \pm (2.9 \pm 0.2 \text{ kJ mol}^{-1})/RT \ln 10$

Extrapolation of pressure dependent rate constants is a somewhat problematical business. Empirical schemes exist²⁸ as well as theoretically assisted procedures.²⁹ We have adopted the latter approach, allowing an initial, rough estimate of k_1^{∞} values (at each temperature) to provide the basis for a first attempt at the RRKM calculations. The pressure dependent ("fall-off") curves generated were then used to refine the k_1^{∞} values to the ones shown in Table 1. Fortunately, the extrapolations were relatively short (compared with the range of fall-off values). The k_1^{∞} values were further supported by studies of the reaction SiH₂ + C₂D₄.³⁰ Nevertheless we estimate that the k_1^{∞} values probably have associated uncertainties of $10^{\pm 0.15}$ or ca. 40% (from all sources). The Arrhenius plot of these values is included in Figure 2. It is worth noting that the negative value for E_1 means that the values for E_{-1} are less than those for $\Delta H^{\circ}_{-1,1}$.

The information required for the RRKM calculations was obtained as follows. The Arrhenius parameters of Table 2 were used in combination with the molecular wavenumbers of silirane,²³ grouped together for convenience, to assign the wavenumbers of the activated complex at each temperature of study. In this exercise the values for the low wavenumber ring modes associated with the SiH₂ group vibrations were lowered until a match was achieved with the entropy of activation and A factor in the usual way.³¹ Values for the other modes were left unchanged except for the C-C stretch. Whether precise values of all vibrational wavenumbers are correct is not important provided the entropy of activation is matched. Because of the apparent decrease in value of A_{-1} with temperature, which we believe to be correct,

 TABLE 3:
 Molecular and Transition-State Parameters for RRKM Calculations for Silirane Decomposition at 298 K

	silirane	silirane [‡]
$\tilde{\nu}/\mathrm{cm}^{-1}$	2960(4)	2960(4)
	2135(2)	2135(2)
	1410(2)	1410(2)
	1120(2)	1120(2)
	955(1)	1500(1)
	935(2)	935(2)
	875(1)	875(1)
	740(2)	740(2)
	676(1)	50(1)
	620(2)	40(1)
	473(1)	30(2)
	392(1)	
reacn coordinate:	620 cm ⁻¹	
I^+/I :	1	
path degeneracy:	1	
E_0 (critical energy):	186.6 kJ mol ⁻¹ (46.7 kcal mol ⁻¹)
collision no. Z_{LJ} :	4.64×10^{-10} cm	³ molecule ⁻¹ s ⁻¹ (SF ₆)

 TABLE 4: Temperature Dependent Parameters Used in RRKM Calculations for Silirane Decomposition

	T/K				
	298	355	415	515	595
transition state	50(1)	50(2)	50(2)	60(1)	62(1)
wavenumbers/cm ⁻¹	40(1)	39(1)	45(1)	54(1)	60(2)
	30(2)	30(1)	40(1)	50(2)	55(1)
$E_{\rm o}/\rm kJ~mol^{-1}$	186.6	185.4	184.1	182.0	179.9
$10^{10}Z_{LJ}/cm^3$ molecule ⁻¹ s ⁻¹	4.64	4.67	4.89	5.09	5.24

we have modified the activated complex (wavenumbers and critical energy) at each temperature in order to build in variational character, rather than use a temperature-averaged, fixedwavenumber complex. The details are shown in Tables 3 and 4. We have assumed that geometry changes in the decomposing silirane molecule do not lead to significant changes in overall moments of inertia and adiabatic rotational effects (angular momentum conservation problems). This is an approximation, in view of the loose activated complex structures, but we believe it will not lead to serious errors. However we have used a weak collisional (stepladder) model for collisional deactivation,³¹ since there is considerable evidence against the strong collision assumption.³² Initial fitting of our data to these calculations suggested a slightly less efficient collisional stabilization at high temperatures than at low. Average energy removal parameters, $\langle \Delta E \rangle_{\rm down}$, varied between 12.0 kJ mol⁻¹ (296 K) and 8.4 kJ mol⁻¹ (600 K). However in the final fitting we kept to a fixed value of 9.6 kJ mol⁻¹. This is close to the value found for SF_6 in the $SiH_2 + SiH_4$ insertion reaction.⁷

The results of our final calculations are shown as the full curves in Figure 3.

Discussion

General Comments, Comparisons, and the Nature of the Reaction Process. The results reported here represent the first comprehensive investigation of the pressure and temperature dependencies of the kinetics in the $SiH_2 + C_2H_4$ reaction system. In our preliminary study¹⁰ at room temperature we showed that our pressure dependent rate constants (in SF₆ and Ar) were consistent with those of CBJ⁹ (in He) provided different, but reasonable, collision efficiencies were assigned to each collision partner. The rate constant of IS⁸ (in 1 Torr, He), however, is a factor of *ca*. 3 higher than that of CBJ⁹ and inconsistent with our results. A reassuring aspect of our studies is that direct kinetic measurements of the rate constants of SiH₂ with PhSiH₃,⁶ Me₃-SiH,⁶ C₂H₂,^{16,17} and now C₂H₄ give values at 298 K which are in good agreement with relative rate studies carried out in our laboratory some 8 years ago.³³ Details of this are shown in Table

TABLE 5: Some Absolute and Relative Rate Constants for Reactions of SiH_2 at 298 K

substrate	$k_{\mathrm{rel}}{}^{a,b}$	$10^{10}k/cm^3$ molecule ⁻¹ s ⁻¹	k _{rei} c
PhSiH ₃ Me ₃ SiH C_2H_4 C_2H_2	$1.00 0.47 \pm 0.07 0.88 \pm 0.07 0.90 \pm 0.05$	$4.1 \pm 0.4^{d} 2.5 \pm 0.3^{d} 3.2 \pm 0.3^{e} 3.6 \pm 0.4^{f} $	$\begin{array}{c} 1.00 \\ 0.61 \pm 0.09 \\ 0.78 \pm 0.11 \\ 0.88 \pm 0.13 \end{array}$

^a Values obtained in 200 Torr of N_2 . ^b Reference 33. ^c Based on absolute values. ^d Reference 6. ^e This work (200 Torr of SF₆). ^f Reference 16 (200 Torr of Ar).

TABLE 6: Rate Constants $(10^{10} k/cm^3 molecule^{-1} s^{-1})$ for Addition of Methylene and Several Silylenes $({}^{1}A_1 States)$ at 298 K

species	CH ₂ ^a	SiH ₂ ^b	SiMe ₂ ^c	SiCl ₂ ^d
C ₂ H ₄	1.9 ^e	3.55	0.22	0.0013
C_2H_2	2.8 ^g	4.0*	0.46	0.00071
C_3H_6	2.5	3.4'	0.37	0.0038

^a Rate constants corrected for collisionally induced intersystem crossing (to ³B₁ state). ^b High pressure limiting values. ^c Reference 15. ^d Reference 37. ^e Reference 38. ^f This work. ^g Reference 39. ^h References 16 and 17. ⁱ Reference 40.

5. Since the reactions with C_2H_4 and C_2H_2 were close to their high pressure limits the differences of bath gas are not important.

Another possible comparison of our data is with a relative rate study of SiH₂ with SiH₄ and C₂H₄ carried out by Fisher and Lampe (FL)³⁴ using IR multiphoton decomposition of SiH₄ as the SiH₂ source. FL obtained values for k_1/k_2 of 0.19 (300 K), 0.27 (400 K), and 0.33 (500 K), where k_2 corresponds to the reaction

$$SiH_2 + SiH_4 \xrightarrow{2} Si_2H_6$$

Since FL attempted to take account of pressure effects, these values should correspond to the ratio of high pressure limiting rate constants. Combination of k_1^{∞} obtained in this study with k_2^{∞} values from our earlier work⁷ gives $k_1^{\infty}/k_2^{\infty} = 0.76$ (300 K), 0.75 (400 K), and 0.82 (500 K). Thus we disagree with the results of FL by significant factors of between 4.0 and 2.5. We note that the IR multiphoton method produces, at least initially, nonthermalized reactive species. In our studies and those of CBJ,9 vibrationally relaxed SiH₂ is being directly monitored. Another difference with FL^{34} concerns the reaction product of SiH_2 + C_2H_4 . FL claim the product to be vinylsilane, from comparison of the mass spectrum of the products with those of an authentic sample. Our GC evidence specifically rules this out, and moreover, the pressure dependence of our second order rate constants is not consistent with formation of vinylsilane in any but minute quantities. It seems to us at least plausible that the mass spectrum observed by FL could have been that of silirane itself which is, after all, isomeric with vinylsilane. Further evidence comes from the work of Rogers, Walker, Ring, and O'Neal (RWRO)³⁵ who studied the products of reaction 1 in a static reactor at 600 K and found no vinylsilane, although small yields were found in a stirred flow reactor (674-715 K) and in a single pulse shock tube (935-987 K). These results also tend to cast doubt on the apparent rearrangement of 1,1-dimethylsilirane to dimethylvinylsilane (at ca. 270 °C) claimed some 30 years ago by Skell and Goldstein.³⁶ Unless dimethyl substitution substantially affects the mechanism, we would expect the products of 1,1-dimethylsilirane decomposition to be $SiMe_2 + C_2H_4$.

The growing data base of absolute rate constants enables us to compare the reactivity of CH₂, SiH₂, SiMe₂, and SiCl₂ with prototype π -bonds. This is done in Table 6 which updates a previous comparison¹⁵ in two ways. The data for CH₂(¹A₁) have been specifically measured and corrected for nonreactive collisionally-induced intersystem crossing in the same studies,^{38,39} and



Figure 4. Approximate transition state structure for the addition of SiH_2 to C_2H_4 showing lone pair interactions.

those for SiH₂ represent limiting high pressure rate constants unlike the values previously quoted.¹⁵ So far as is known, the reactions of CH₂(¹A₁), SiMe₂, and SiCl₂ are pressure independent processes. The rate constants for CH₂ and SiH₂ are close to the collisional maximum. SiH₂ is about twice as reactive as CH₂ in accord with the simple idea of an electrophilic reaction in which the initial interaction is dominated by the size of the receptor orbital (3p for SiH₂, 2p for CH₂). Me and Cl substitution on the silylene deactivate it, probably by a mixture of electronic and steric effects, as discussed previously.¹⁵

The small negative activation energy for reaction of SiH₂ with C_2H_4 (-3 kJ mol⁻¹) is almost identical with that found for reaction with C_2H_2 ,¹⁷ which suggests that this reaction may be thought of as a normal association reaction, *i.e.* not one requiring the involvement of an intermediate (weak) complex such as that proposed for SiH₂ + SiH₄.⁷ Ab initio theoretical calculations¹⁴ support a barrierless reaction (C_s geometry) with no long range intermediate complex at the highest level of calculation (MP2/ 6-31G*//3-21G). The reaction may be described as an initial π attack ("electrophilic phase" donation of C=C π electrons into the Si 3p-orbital), followed by σ attack ("nucleophilic phase" donation of the silicon lone pair electrons into the C=C antibonding π^* orbital). Although the transition state is not specifically characterized, it is clearly close to the switching point between the two "phases" of the reaction. Figure 4 shows these

processes and gives an approximate indication of the geometry of the transition state.

RRKM Calculations and the Silirane Strain Enthalpy. The reasonable fit of the RRKM calculations to the pressure dependencies of the experimental rate constants lends weight to the conclusion that the reaction of SiH_2 with C_2H_4 is a simple third-body assisted association. The most uncertain parameter in the calculation is the critical energy (or activation energy) for silirane decomposition. The good fit obtained with the theoretically-based value^{22,23} gives an indication of its reliability. The other parameters in the calculation are not likely to be seriously in error. The A factor, A_{-1} , for silirane decomposition is almost certainly reliable within a factor of $10^{\pm 0.5}$, and consequently, the transition state wavenumber assignment cannot be significantly in error. The incorporation of variational character into the modeling of the transition state reflects the reality of transition state "tightening" as the temperature is increased. In fact the extremely loose nature of the transition state (even at the higher temperatures) is one of the important findings of this study and explains, in part, the significant pressure dependence of the association rate constants. The remaining uncertainty is that of the weak collisional stabilization model. This is based on reasonable average energy removal parameters for SF_6 . SF_6 was in fact chosen as the bath gas because of its relatively efficient collider characteristics (thus keeping this source of uncertainty to a minimum). Our conclusion is that the thermochemistry is approximately correct; i.e. the enthalpy of formation of silirane is close to 124 kJ mol⁻¹, the enthalpy of its decomposition is close to 201 kJ mol⁻¹, and its strain enthalpy is 167 kJ mol⁻¹ (based on Benson group additivity⁴¹ increments). It is doubtful if our data could be fitted if these figures were more than ± 12 kJ mol⁻¹ in error.

There remains an unresolved difficulty over the measurement by Berry⁴² of a value of ca. 130 kJ mol⁻¹ for the activation energy of hexamethylsilirane decomposition (giving SiMe₂ + C₂Me₄). To reconcile this much lower figure with our results, we would need to imply that methyl group substitution significantly increases the strain in silirane rings. There is no evidence for such an effect in cyclopropanes.³¹ However we have found some further support for this in studies of SiH₂ with propene⁴⁰ where pressure dependencies are consistent with an enthalpy of decomposition of 2-methylsilirane of ca. 160 kJ mol⁻¹, significantly less than for silirane itself. We plan to explore this point further.



Figure 5. Schematic enthalpy surface (298 K) for the reaction $SiH_2 + C_2H_4$.

TABLE 7: Enthalpies of Formation of Molecular Species Involved in the $SiH_2 + C_2H_4$ Reaction

species	$\Delta H_{\rm f}^{\rm o}/{\rm kJ}~{\rm mol}^{-1}$	ref
SiH ₂	273 ± 2	43
C ₂ H ₄	52.2 ± 1	25
Silirane	124 ± 12	see text
CH2=CHSiH3	79 ± 6	see text
CH ₃ CH=SiH ₂	155 ± 20	see text
CH ₃ SiH=CH ₂	117 ± 20	see text
•CH ₂ CH ₂ SiH ₂ •	323 ± 10	see text
•CH ₂ SiH ₂ CH ₂ •	307 ± 10	see text
CH ₃ CH ₂ SiH:	185 ± 6	see text

Reaction Thermochemistry and Mechanism. To assist further understanding of the reaction, we have used the methods of thermochemical kinetics⁴¹ in conjunction with the results of our modeling to obtain an enthalpy surface for reaction. Since vinylsilane formation is still controversial, we include vinylsilane and related isomers on this surface. The values for the formation enthalpies of individual species are given in Table 7. The silirane value comes from the theoretical calculations of Boatz and Gordon,^{22,23} confirmed in this study. The figure for vinylsilane is obtained from the enthalpy of formation of ethylsilane,⁴⁴ by assuming the same enthalpy of hydrogenation as for propene.45 The values for 2-methyl- and 1-methylsilenes are based on known methyl-for-hydrogen substitution increments^{41,46} starting from $\Delta H^{\circ}_{f}(H_2C=SiH_2) = 187 \text{ kJ mol}^{-1}$. This latter value is still somewhat uncertain,⁴⁶ but the figure used here is based on the calculated isomerization enthalpy⁴⁷ from CH₃SiH employing our most recent estimate⁴ of $\Delta H^{\circ}_{f}(CH_{3}SiH)$. The figures for the biradicals, 'CH2CH2SiH2' and 'CH2SiH2CH2' are based on recent values for bond dissociation enthalpies43,48,49 together with the usual assumption of noninteracting radical centers.⁴¹ The value for ethylsilylene is obtained from that for ethylsilane by assuming the same 1,1-dehydrogenation enthalpy as for methylsilane.^{4,50} The procedures are known to give reasonably reliable estimates, and the assessments are intended to be conservative. Where other (theoretical) values exist, 51,52 they are in reasonable agreement.

The enthalpy surface is shown in Figure 5. The surface reveals that potential isomerization reactions for silirane may have slightly lower barriers than its redissociation to $SiH_2 + C_2H_4$ (step -1). These energetic advantages however are small and could be zero within experimental error. Nevertheless, on energetic grounds isomerization should at least be competitive. The modeling of our measured pressure dependencies, supported by the nonobservation of vinylsilane, rules this out and also means that formation of the other C_2SiH_6 isomers is unlikely (even though their detection would be more difficult). The explanation for this probably lies in the differing magnitudes of the entropies of activation of the alternative pathways, as reflected in the A factors. Thus the present study shows that, for silirane redissociation with its loose transition state, $A_{-1} \approx 10^{17}$ s⁻¹ while the A factor for isomerization should lie in the range 1014-1015 s⁻¹ on the analogy of cyclopropane isomerization.^{31,53} This difference means that SiH₂ elimination from silirane should be favored by a factor of $\geq 10^2$ on entropy grounds, which clearly offsets any slight energetic disadvantage. The observation of vinylsilane as a high temperature product, by RWRO,35 can be explained as a pressure dependence effect. In a competitive situation, reactions with looser transition states (higher A factors) will show a greater degree of fall-off than those with tighter transition states (lower A factors).³¹ Thus since unimolecular fall-off increases with temperature, the relative probability of silirane isomerization to vinvisilane and also other isomers should increase.

One other channel deserves comment. There is considerable evidence for the involvement of analogues of ethylsilylene, CH₃CH₂SiH:, in high temperature substituted silirane rearrangements⁵⁴⁻⁵⁶ as well as of CH₃CH₂SiH: itself in silirane isomerization.^{35,57} Figure 5 shows that ethylsilylene is potentially accessible although unstable relative to silirane itself. Thus, if formed in the present study, it will rapidly revert back to silirane. We have found evidence for its mechanistic involvement in studies of $SiH_2 + C_2D_4$.³⁰ This will be reported in a future publication.

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Appendix

Previously unavailable, the thermodynamic functions of silirane have been calculated using the methods of statistical mechanics.^{20,21} The values tabulated below assume ideal gas behavior and are based on the theoretically calculated structural and vibrational information of Boatz and Gordon.^{22,23} The rigid rotor and harmonic oscillator approximations have been used. The values are quoted in calories, the traditional units of such tables (1 cal = 4.184 J).

T/K	S° ª	C° p ª	$-(G^{\circ}-H^{\circ}_{298})/T^{a}$	H° – H° ₂₉₈ ^b
100	51.15	8.34	75.82	-2.47
200	57.93	12.25	65.26	-1.47
298	63.83	17.71	63.82	0.00
300	63.94	17.82	63.82	0.04
400	69.77	22.75	64.59	2.07
500	75.29	26.67	66.18	4.55
600	80.43	29.80	68.13	7.38
700	85.23	32.37	70.24	10.49
800	89.69	34.52	72.39	13.84
900	93.87	36.35	74.55	17.39
1000	97.78	37.92	76.68	21.10

^a Units; cal K⁻¹ mol⁻¹. ^b Units: kcal mol⁻¹.

References and Notes

(1) Gaspar, P. P. In Reactive Intermediates; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1978 (Vol. 1, p 229), 1981 (Vol. 2, p 335), 1985 (Vol. 3, p 333).

- (2) Tang, Y. N. In Reactive Intermediates; Abramovitch, R. A., Ed.; Plenum: New York, 1982; Vol. 2, p 297.
- (3) Safarik, I.; Sandhu, V.; Lown, E. M.; Strausz, O. P.; Bell, T. N. Res. Chem. Int. 1990, 14, 105.
- (4) Becerra, R.; Frey, H. M.; Mason, B. P.; Walsh, R. J. Chem. Soc., Faraday Trans. 1993, 89, 411 and references therein.
- (5) Baggott, J. E.; Frey, H. M.; King, K. D.; Lightfoot, P. D.; Walsh, R.; Watts, I. M. J. Phys. Chem. 1988, 92, 4025.
- (6) Baggott, J. E.; Frey, H. M.; Lightfoot, P. D.; Walsh, R.; Watts, I. M. J. Chem. Soc., Faraday Trans. 1988, 86, 27.
- (7) Becerra, R.; Frey, H. M.; Mason, B. P.; Walsh, R.; Gordon, M. S. J. Am. Chem. Soc. 1992, 114, 2751.
 - (8) Inoue, G.; Suzuki, M. Chem. Phys. Lett. 1985, 122, 361.
- (9) Chu, J. O.; Beach, D. B.; Jasinski, J. M. J. Phys. Chem. 1987, 91, 5340
- (10) Al-Rubaiey, N.; Frey, H. M.; Mason, B. P.; McMahon, C.; Walsh, R. Chem. Phys. Lett. 1993, 204, 301.
- (11) Tortorelli, V. J.; Jones, M., Jr.; Wu, S.; Li, Z. Organometallics 1983, 2, 759

(12) See, for example: Seyferth, D.; Annarelli, D. C.; Vick, S. C.; Duncan,

- D. P. J. Organomet. Chem. 1980, 201, 179. (13) Boudjouk, P.; Black, E.; Kumarathasan, R. Organometallics 1991,
- 10. 2095
- (14) Anwari, F.; Gordon, M. S. Isr. J. Chem. 1983, 23, 129.
- (15) Baggott, J. E.; Blitz, M. A.; Frey, H. M.; Lightfoot, P. D.; Walsh, R. J. Chem. Soc., Faraday Trans. 2 1988, 84, 515.
- (16) Becerra, R.; Frey, H. M.; Mason, B. P.; Walsh, R. J. Chem. Soc., Chem. Commun. 1993, 1050.
 - (17) Becerra, R.; Walsh, R. Int. J. Chem. Kinet. 1994, 26, 45.
- (18) Blitz, M. A.; Frey, H. M.; Tabbutt, F. D.; Walsh, R. J. Phys. Chem. 1990, 94, 3294
- (19) Jasinski, J. M.; Chu, J. O. J. Chem. Phys. 1988, 88, 1678. (20) Pitzer, K. S.; Brewer, L. Thermodynamics, 2nd ed.; McGraw-Hill:
- New York, 1961; Chapter 27, p 419. (21) Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. The Thermodynamics
- of Organic Compounds; Wiley: New York, 1969.
- (22) Boatz, J. A.; Gordon, M. S. J. Phys. Chem. 1989, 93, 3025.
 (23) Boatz, J. A.; Gordon, M. S. Private communication.

(24) Fredin, L.; Hauge, P. H.; Kafafi, Z. H.; Margrave, J. L. J. Chem. Phys. 1985, 82, 3542.

(26) Horner, D. A.; Grev, R. S.; Schaefer, H. F., III. J. Am. Chem. Soc. **1992**, *114*, 2093. (27) Berry, D. H. Private communication.

- (28) Oref, I.; Rabinovitch, B. S. J. Phys. Chem. 1968, 72, 4488.
 (29) Troe, J. J. Phys. Chem. 1979, 83, 114.

- (30) Al-Rubaiey, N.; Walsh, R. Unpublished results.
 (31) Robinson, P. J.; Holbrook, K. A. Unimolecular Reactions; Wiley: New York, 1972.
- (32) Heymann, M.; Hippler, H.; Troe, J. J. Chem. Phys. 1984, 80, 1853.
 (33) Eley, C. D.; Rowe, M. C. A.; Walsh, R. Chem. Phys. Lett. 1986, 126, 153.
- (34) Fisher, J. R.; Lampe, F. W. J. Photochem. Photobiol. A, Chem. 1991, 58, 173.
- (35) Rogers, D. S.; Walker, K. L.; Ring, M. A.; O'Neal, H. E. Organometallics 1987, 6, 2313.
 - (36) Skell, P. S.; Goldstein, E. J. J. Am. Chem. Soc. 1964, 86, 1442.
- (37) Safarik, I.; Ruzsicska, B. P.; Jodhan, A.; Strausz, O. P.; Bell, T. N. Chem. Phys. Lett. 1985, 113, 71.
- (38) Hack, W.; Kock, M.; Wagener, R.; Wagner, H. Gg. Ber. Bunsen-Ges. Phys. Chem. 1989, 93, 165.
- (39) Hack, W.; Kock, M.; Wagner, H. Gg.; Wilms, A. Ber. Bunsen-Ges. Phys. Chem. 1988, 92, 674.
 (40) Al-Rubaiey, N.; Walsh, R. Unpublished results.
 (41) Benson, S. W. Thermochemical Kinetics, 2nd ed.; Wiley: New York,
- 1976.

- (42) Berry, D. H. Private communication.
 (43) Walsh, R. In Energetics of Organometallic Species; Martinho-Simoes, J.A., Ed.; NATO-AS1 series C, Vol 367; Kluwer: Dordrecht, The Netherlands, 1992; Chapter 11, p 171.
- (44) Gordon, M. S.; Boatz, J. A.; Walsh, R. J. Phys. Chem. 1989, 93, 1584
- (45) Pedley, J. B.; Rylance, J. Sussex-N.P.L. Computer analysed thermochemical data: organic and organometallic compounds; University of
- mochemical data: organic and organometatuc compounds, Ontoest, J.
 Sussex: Sussex, U.K., 1977.
 (46) Walsh, R. In Chemistry of organic silicon compounds; Patai, S.,
 Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 5, p 371.
 (47) Grev, R. S.; Scuseria, G. E.; Scheiner, A. C.; Schaefer, H. F., III;
 Gordon, M. S. J. Am. Chem. Soc. 1988, 110, 7337.
 (48) Seetula, J. A.; Feng, Y.; Gutman, D.; Seakins, P. W.; Pilling, M. J.

- (49) Schem. 1991, 95, 1658.
 (49) Seakins, P. W.; Pilling, M. J.; Niiranen, J. J.; Gutman, D.; Krasnoperov, L. N. J. Phys. Chem. 1992, 96, 9847.
- (50) Doncaster, A. M.; Walsh, R. J. Chem. Soc., Faraday Trans. 2 1986, 82, 707.

 - (51) Gordon, M. S. Chem. Phys. Lett. 1980, 76, 163.
 (52) Allendorf, M. D.; Melius, C. J. Phys. Chem. 1992, 96, 428.

 - (53) Frey, H. M.; Walsh, R. Chem. Rev. 1969, 69, 103.
 (54) Barton, T. J.; Tillman, N. J. Am. Chem. Soc. 1987, 109, 6711.
 - (55) Dickenson, A. P.; O'Neal, H. E., Ring, M. A. Organometallics 1991,
- 10, 3513.
- (56) Davidson, I. M. T. J. Organomet. Chem. 1992, 437, 1.
- (57) Erwin, J. W.; Ring, M. A., O'Neal, H. E. Int. J. Chem. Kinet. 1985, 17, 1067.