

Time-resolved Studies of the Temperature Dependence of the Gas-phase Reactions of Methylsilylene with Silane and the Methylsilanes

Rosa Becerra,[†] H. Monty Frey, Ben P. Mason and Robin Walsh*

Department of Chemistry, University of Reading, Whiteknights, P.O. Box 224, Reading RG6 2AD, UK

The 193 nm laser flash photolysis of gas-phase 1,2-dimethyldisilane has been found to give a broad-band absorption in the wavelength range 454–515 nm, which is plausibly shown to be due to the transient species methylsilylene, MeSiH. By carrying out the title studies, the first direct kinetic studies of MeSiH, second-order rate constants have been obtained for reactions of MeSiH with SiH₄, MeSiH₃, Me₂SiH₂ and Me₃SiH, in the temperature range 360–580 K. The reactions are fast but show negative activation energies, increasing from –7.5 kJ mol^{–1} for SiH₄ to –18.4 kJ mol^{–1} for Me₃SiH. The data are interpreted as proceeding *via* an intermediate complex, whose rearrangement becomes rate-determining at higher temperatures. Comparisons of reactivity of MeSiH with those of other silylenes reveal the general pattern of methyl substituent effects of these complexes. In conjunction with *ab initio* theory (for the reaction of SiH₂ with SiH₄) these show that the electrophilic interaction probably precedes the nucleophilic interaction, although the latter is important in the rate-determining (second) step for the insertion reactions of both MeSiH and SiMe₂. Combination of MeSiH insertion rate constants with the reverse unimolecular decomposition rate constants of the product disilanes enable the calculation of an improved value of 202 ± 6 kJ mol^{–1} for Δ_rH°(MeSiH).

Silylenes are ubiquitous intermediates involved in the thermal and photochemical breakdown mechanisms of many organosilicon compounds.¹ This has given rise to a great deal of interest in the rates of reactions of silylenes.² In recent years time-resolved techniques have been used to measure gas-phase rate constants for reactions of silylene SiH₂ itself^{3–12} and dimethylsilylene, SiMe₂,^{13–17} as well as other silylenes such as phenylsilylene, PhSiH.¹⁸ These studies have shown silylenes to be very reactive species, but nevertheless revealed substantial differences in reactivity with different substrates and also with different substituents. Temperature variation studies carried out in our laboratory^{8,11,16,18} have also shown, in almost all cases, decreases in rate constants with increasing temperatures, implying negative activation energies. For the Si–H insertion reaction of SiXY:



an explanation has been offered in terms of intermediate complexes.^{11,16,18} For the prototype reaction of SiH₂ + SiH₄, *ab initio* calculations have revealed the existence of a shallow minimum corresponding to such an intermediate on the reaction potential-energy surface.¹¹

Amongst the silylenes so far studied, methylsilylene, MeSiH, is conspicuous by its absence. MeSiH is known to be formed in the pyrolyses of certain methyl-substituted disilanes,^{19–22} but although products of its reactions have been seen, no rate constants have yet been reported (there are only estimates based on interpolation²³). We have sought, therefore, to generate MeSiH and to initiate the study of its reactions by an investigation of the kinetics of its Si–H insertion process with silane and the methylsilanes. This will enable us to compare (i) the effect of single *vs.* double methyl substitution on silylene reactivity (ii) the effect of methyl *vs.* phenyl substitution. This study will also permit us to refine our understanding¹⁶ of the nature of the silylene Si–H insertion process in general. Additionally it will provide data which will allow a more reliable experimental estimate than

hitherto^{23,24} of the important thermochemical quantity Δ_rH°(MeSiH).

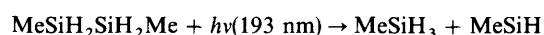
Experimental

The apparatus and equipment for these experiments has been described in detail elsewhere.^{13,25} Briefly, the reactive species was created by gas-phase photolysis using the 193 nm (ArF) line of a pulsed excimer laser (Oxford Lasers KX2). The intermediate was detected using a CW argon-ion probe laser (Spectra Physics, 2025) multipassed through the reaction zone to give an effective pathlength of up to 1.5 m. 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. Experiments were carried out in a variable temperature stainless-steel reactor with demountable windows.¹⁸

All silanes were carefully degassed prior to use. 1,2-dimethyldisilane (DMDS) was a gift from Professor E. Hennge. It was purified to *ca.* 94% by distillation with the main impurity (*ca.* 5%) 1,1-dimethyldisilane.²⁶ Methylsilane, MeSiH₃ (98.6%), and dimethylsilane, Me₂SiH₂ (99.6%) were prepared previously.⁹ Trimethylsilane, Me₃SiH (>99%) was obtained from Fluorochem and Monosilane (>99%) was from BOC (Electra II grade). Argon (>99.995%) was also obtained from BOC and sulfur hexafluoride, SF₆ (no GC-detectable impurities) was from Cambrian Gases. Pressures were measured by capacitance manometers (MKS, Baratron).

Generation and Characterisation of the Transient Intermediate

DMDS was used as the potential precursor to MeSiH on the grounds of the analogy between thermal and photolytic breakdown mechanisms of Si₂H₆⁵ and pentamethyldisilane.^{13–17} Thus, from thermal decomposition,²¹ we anticipated the occurrence of the process



Evidence has been obtained from end-product analysis studies²⁶ of the formation of Me₂SiHSiH₂Me and

[†] Present address: Instituto de Quimica-Fisica "Rocasolano", C.S.I.C., C/Serrano 119, 28006, Madrid, Spain.

$\text{Me}_3\text{SiH}_2\text{Me}$ from photolysis of DMDS in the presence of Me_2SiH_2 and Me_3SiH , respectively. These are the expected Si—H insertion products of MeSiH . When DMDS was photolysed at 193 nm absorption signals with lifetimes of *ca.* 5 μs were obtained in the wavelength region 450–520 nm. As found previously for phenylsilane,¹⁸ photolysis can lead to the formation of gas-borne dust, which results in probe-beam scattering. This dust tends to be prominent at low temperatures, high pressures and high laser fluences. Experiments were performed under conditions (<10 Torr† total pressure) to eliminate or minimize dust formation. The Spectrosil inlet window of the reactor was cleaned regularly to maintain good 193 nm transmission. Signals were accumulated and averaged (10–15 shots). Nevertheless, in practice, reliable data could not be obtained at room temperature. However, at temperatures of 80 °C and above, despite some scatter, the data appeared reliable. For a given reaction mixture, rate and absorption data showed no dependence on the number of shots, and laser intensity (60–110 mJ per pulse).

A set of runs was carried out at 357 K with a laser pulse energy of 83 ± 5 mJ, using 25 mTorr of DMDS diluted in 5 Torr of SF_6 with monitoring at each of the nine available wavelengths of the argon-ion laser (four runs at each wavelength). Signals decayed exponentially, with rate constants of $(2.0 \pm 0.3) \times 10^5 \text{ s}^{-1}$, independent of wavelength. The signal absorbances were recorded and averaged at a fixed time delay of 2.7 μs , corresponding to the onset of transient decay (Fig. 1). The absorption spectrum of MeSiH in an argon matrix reported by Maier *et al.*²⁷ is also shown, normalised so that the relative absorption maximum (at *ca.* 480 nm) is identical with that obtained here (at *ca.* 493 nm). Although the band is broad, the appearance of the two spectra is similar and the small displacement of the gas-phase spectrum to longer wavelengths is similar to that found for SiMe_2 .¹³ Many silylenes show broad band matrix-isolation spectrum with maxima in the 450–500 nm range.²⁸ These observations and the end-product studies offer strong evidence in favour of the attribution of the spectrum of Fig. 1 as that of MeSiH .

The absorption coefficient for MeSiH is not known, but on the assumption of a value similar to that for SiMe_2 ($1500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)¹³ we estimate initial MeSiH densities of *ca.* $5 \times 10^{13} \text{ cm}^{-3}$. These correspond to *ca.* 10% decomposition of DMDS in the irradiated zone. Since this zone is at most 6% of the total volume, depletion of DMDS is small even after 15 laser shots.

The presence of 5% of the 1,1-dimethyldisilane impurity in DMDS suggests the possible concomitant formation of small amounts of SiH_2 and SiMe_2 transients. End-product analyses²⁶ showed that the formation of these silylenes was negligible ($<3\%$ of MeSiH). These studies²⁶ (by GC) also showed that DMDS photolysis was relatively clean leading only to MeSiH_3 and 1,2,3-trimethyltrisilane (the insertion product of $\text{MeSiH} + \text{DMDS}$). The dust formation process is not clear.

Procedure for Kinetic Runs

Gas mixtures for photolysis were made up containing 25–85 mTorr of DMDS, 0–500 mTorr substrate together with inert diluent (Ar or SF_6) usually to 6 Torr total pressure and were studied under static conditions. The signal-averaged decay traces were processed by a non-linear least-squares program with sensible truncation to avoid initial perturbation by the photolysis laser spike and residual noise at low level signal

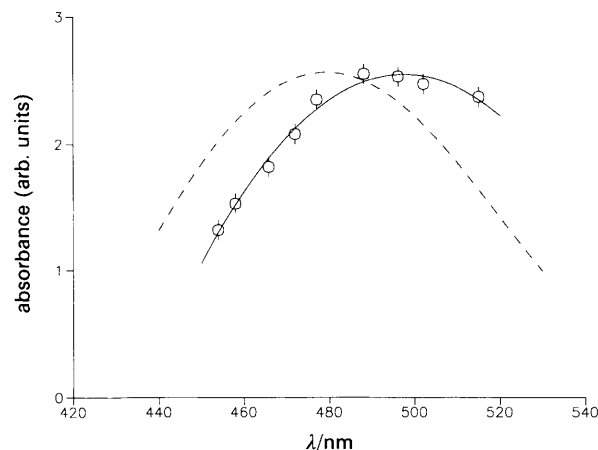


Fig. 1 Gas-phase spectrum of visible transient from DMDS photodecomposition (—). Matrix absorption spectra for comparison (---)

intensity (end of the decay). Within the tolerable noise level the decays were exponential. It should be added, however, that small deviations from a pure exponential form could have been lost in the noise. Thus small contributions from second-order decays or perturbations from secondary reactions might have escaped detection. However, we estimate that bimolecular self-reactions of MeSiH would occur at decay rates at least an order of magnitude slower than observed, even if taking place at the collision rate. Particularly noisy traces, generally associated with visible dust formation, were rejected. The first-order decay constants were measured over a suitable range of substrate pressures (with fixed precursor pressure) at constant total pressure in the usual way,^{3–18} to obtain second-order rate constants for each MeSiH reaction under investigation. Some examples of second-order plots are shown in Fig. 2.

Monitoring wavelengths of 457 and 477 nm were both routinely used during the course of these experiments. Both in the absence of substrates and in the presence of a given substrate, tests showed no effect of wavelength on rate data. Furthermore there was no effect of total pressure (in the range 1–100 Torr) or bath gas (Ar or SF_6) on measured rate constants within the normal scatter of the data.

Results

The reactions of MeSiH with SiH_4 , MeSiH_3 , Me_2SiH_2 and Me_3SiH were all studied. Reaction with Me_4Si was not investigated since previous work with SiH_2 ⁹ and SiMe_2 ¹³ showed it to be unreactive toward silylene insertion reactions. The present studies proved more difficult than earlier ones for SiH_2 ⁹ and SiMe_2 ,^{13,16} and suffered from the same problems encountered with PhSiH .¹⁸ This arose because of the combination of low sensitivity of detection for MeSiH (compared with SiH_2) combined with high reactivity of MeSiH (compared with SiMe_2) towards its precursor. This meant that reaction of MeSiH with DMDS was always a substantial fraction of the total decay. Limitations of time resolution, and interference of the laser spike meant that there was a practical upper limit for the decay constant of *ca.* $3.5 \times 10^5 \text{ s}^{-1}$. This restricted the range of possible substrate pressures which could be employed in practice. Nevertheless within some scatter, as illustrated in Fig. 2, linear second-order plots were obtained for the silanes investigated. The second-order rate constants with their uncertainties (one standard deviation) are shown in Table 1. The reaction of MeSiH with DMDS was too fast to be measured with reliability but values in the range $(0.85\text{--}3.0) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

† 1 Torr $\approx (101\,325/760)$ Pa.

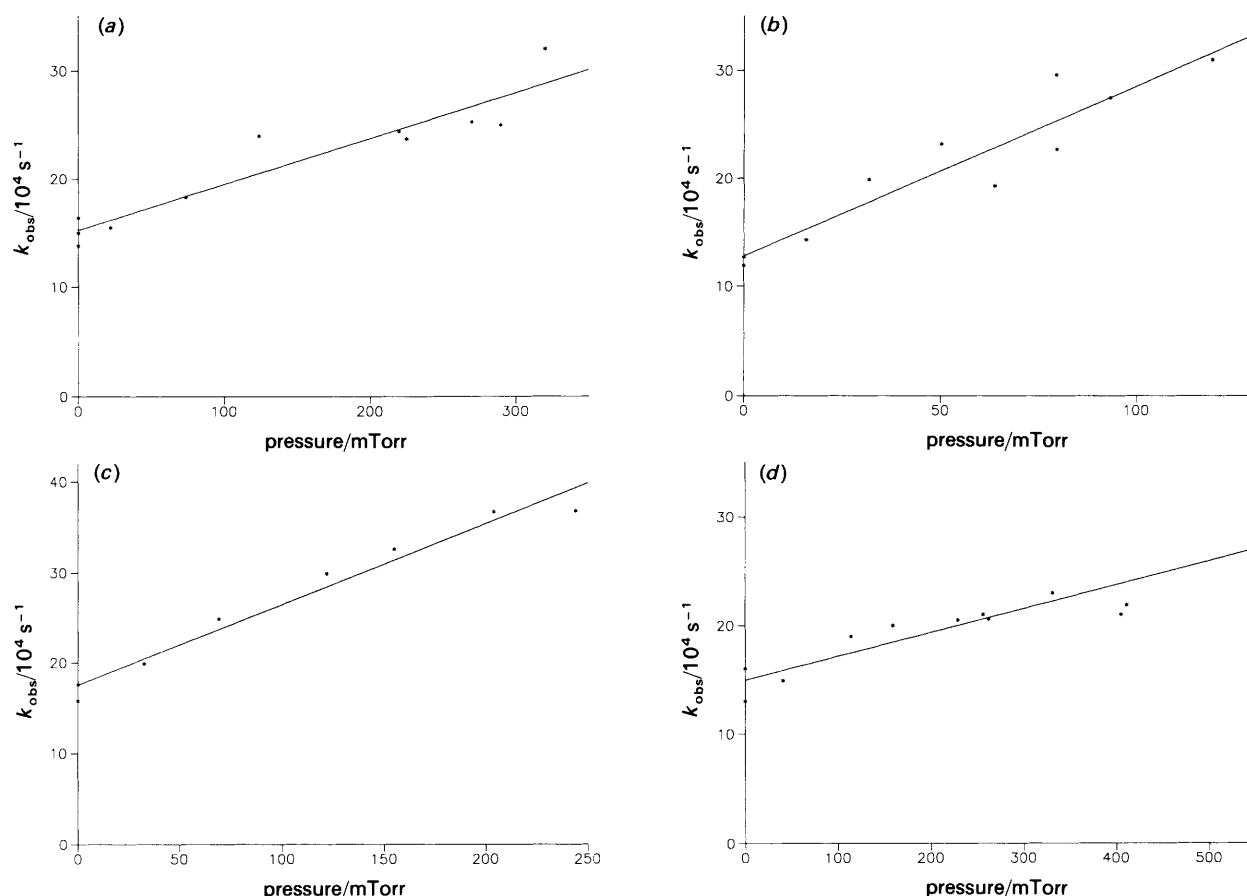


Fig. 2 Examples of second-order plots for reactions of MeSiH with silane and methylsilanes: (a) MeSiH + SiH₄ (497 K), (b) MeSiH + MeSiH₃ (412 K), (c) MeSiH + Me₂SiH₂ (452 K), (d) MeSiH + Me₃SiH (505 K)

were obtained, with an indication of decrease in magnitude with increasing temperature. Despite some attempts, room-temperature experiments with SiH₄ and the methylsilanes produced too much scatter to provide credible rate constants.

The data show a number of interesting features. First, the rate constants are all very high ($\geq 1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). Secondly, there is a clear trend towards lower values with increasing temperature, and thirdly there is a rate enhancement effect of methyl substituents in the substrate silane. This last point becomes clearer when rate constants are divided by L , the number of Si—H bonds. These points are brought out in Fig. 3 which show Arrhenius plots of the statistically corrected rate constants. It can be clearly seen that SiH₄ is the least reactive substrate and at lower temperatures the sequence of reactivity is Me₃SiH > Me₂SiH₂ > MeSiH₃ > SiH₄. Differences are less marked at high temperature and with the given level of uncertainty, the crossover between Me₃SiH and Me₂SiH₂ may be more apparent than real. Least-squares fitting of the rate constants

of Table 1 to the Arrhenius equation leads to the Arrhenius parameters shown in Table 2. The activation energies are all negative, but the variation with substrate is a bit erratic. There is a corresponding variability in the A factors. Since uncertainty in individual second-order rate constants tends to amplify errors in the Arrhenius parameters, it is probable that the single standard deviations of Table 2 underestimate the true errors. To explore the nature of the activation energy trends we have calculated another set of E_a values, by fitting the mid-range rate constants with an assumed A factor (per Si—H bond) of $10^{-12.4} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (average value). These values are shown in parentheses in Table 2. It is possible that more extended and precise data would reveal non-Arrhenius behaviour, as found for SiH₂ + SiH₄,¹¹ but insofar as the Arrhenius equation fits, these adjusted E_a values provide a more consistent variation than the apparent best-fit values. The magnitudes and trends, from -11 kJ mol^{-1} for SiH₄ to -15 kJ mol^{-1} for Me₃SiH, are very similar to those observed for PhSiH insertion reactions.¹⁸

Table 1 Second-order rate constants^a for MeSiH insertion reactions with silane and the methylsilanes

SiH ₄		MeSiH ₃		Me ₂ SiH ₂		Me ₃ SiH	
<i>T</i> /K	<i>k</i>	<i>T</i> /K	<i>k</i>	<i>T</i> /K	<i>k</i>	<i>T</i> /K	<i>k</i>
361	4.7 ± 0.8	370	7.4 ± 1.5	371	5.8 ± 1.1	359	7.8 ± 0.7
409	3.4 ± 0.4	412	6.7 ± 0.1	416	6.3 ± 0.9	412	3.3 ± 0.5
451	3.6 ± 0.5	450	2.7 ± 0.3	452	4.2 ± 0.3	446	2.2 ± 0.6
497	2.2 ± 0.3	509	2.4 ± 0.6	505	2.6 ± 0.1	505	1.15 ± 0.16
544	2.1 ± 0.2	576	1.51 ± 0.26	586	1.64 ± 0.17	543	1.02 ± 0.15

^a Units: $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Error limits are one standard deviation.

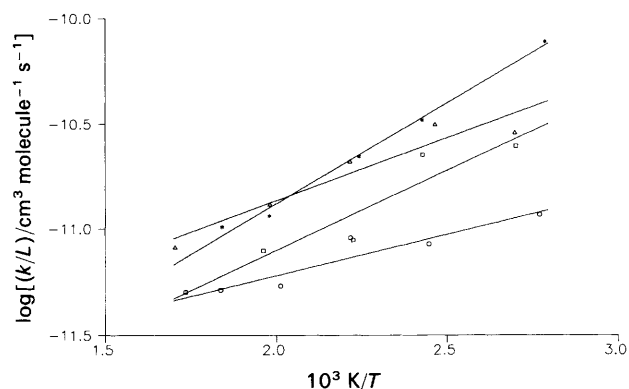


Fig. 3 Arrhenius plots for reactions of MeSiH with silane and the methylsilanes (per Si–H bond): *, Me₃SiH; △, Me₂SiH₂; □, MeSiH₃; ○, SiH₄

Table 2 Arrhenius parameters^a for MeSiH insertion reactions

substrate	log(A/cm ³ molecule ⁻¹ s ⁻¹)	E _a /kJ mol ⁻¹
SiH ₄	-11.4 ± 0.2 (-11.8)	-7.5 ± 1.7 (-10.9)
MeSiH ₃	-12.1 ± 0.3 (-11.9)	-14.5 ± 2.7 (-12.5)
Me ₂ SiH ₂	-11.8 ± 0.2 (-12.1)	-11.5 ± 2.1 (-14.3)
Me ₃ SiH	-12.8 ± 0.1 (-12.4)	-18.4 ± 0.9 (-14.9)

^a Error limits are one standard deviation (unweighted). See text for discussion of figures in parentheses.

Discussion

Comparison with other Silylenes

The rate measurements reported here are the first for MeSiH. The magnitudes of the rate constants show that the reactions of MeSiH are very fast, occurring at 1 in *ca.* 30 collisions even for the slowest example. They are *ca.* an order of magnitude greater than the interpolated estimates.²³ Although we were not able to measure room-temperature rate constants, the Arrhenius parameters (either observed or adjusted) imply values close to 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹. In order to examine these results in more detail the parameters obtained here have been used together with those of earlier studies^{9,11,16,18} to make a comparison of the reactivity of MeSiH with SiH₂, SiMe₂ and PhSiH. Tables 3 and 4 show these comparisons at low temperature (298 K) and high temperature (600 K), respectively. From the figures of these tables the following general points may be made:

(a) MeSiH is much closer in reactivity to SiH₂ than to SiMe₂. At 298 K, values of the ratio, $k(\text{SiH}_2)/k(\text{MeSiH})$, lie in the range *ca.* 1–5 whereas the ratio, $k(\text{MeSiH})/k(\text{SiMe}_2)$, has values in the range *ca.* 30–400. At 600 K, comparison is possible only for reaction with SiH₄, for which $k(\text{SiH}_2)/k(\text{MeSiH}) = 12$, and $k(\text{MeSiH})/k(\text{SiMe}_2) = 75$. It

Table 3 Comparison of silylene insertion constants^a at 298 K

silane	silylene			
	SiH ₂	SiMe ₂	MeSiH	PhSiH
SiH ₄	4.0	0.0020	0.81	0.51
MeSiH ₃	3.7	0.019	2.55	3.9
Me ₂ SiH ₂	3.3	0.055	1.69	2.1
Me ₃ SiH	2.5	0.045	2.78	3.9

^a Units: 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹.

Table 4 Comparison of silylene insertion rate constants^a at 600 K

silane	silylene			
	SiH ₂	SiMe ₂	MeSiH	PhSiH
SiH ₄	2.2 ^b	0.0024	0.179	0.120
MeSiH ₃	—	0.0046	0.133	0.31
Me ₂ SiH ₂	—	0.0060	0.164	0.32
Me ₃ SiH	—	0.0045	0.060	0.165

^a Units: 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹. ^b Extrapolated high-pressure value.

appears that MeSiH reactivity comes closer to the geometric mean of SiH₂ and SiMe₂ as temperature increases.

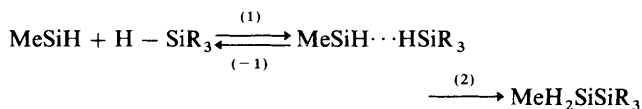
(b) PhSiH is slightly more reactive than MeSiH with the methylsilanes (factors of *ca.* 1.4 at 298 K and *ca.* 2.7 at 600 K) although less reactive with SiH₄ itself (factor of *ca.* 0.65 at both temperatures).

On the basis of the substantial rate decreases and generally negative activation energies we have previously proposed^{16,18} mechanisms involving intermediate complexes. We examine this again here in the light of the present results.

Intermediate-complex Mechanism

Although generalized treatments exist in the literature of reactions with negative activation energies,²⁹ we present here only an outline treatment as a preliminary to more detailed calculations.³⁰

The insertion processes may be generalised as follows:



where R ≡ H and/or Me. Step (1) may be viewed as a loose association of the methylsilylene with the substrate (the nature of the bonding is considered later). Step (2) involves the reorganisation of the intermediate complex, involving restriction of its motion *via* a much tighter transition state in which an H atom bridges two Si atoms, and migrates to give the product disilane. Since the experiments in the present work reveal only single exponential decays it is reasonable to presume a steady-state population of intermediate complexes (with implications of short lifetimes and shallow energy wells; a depth of ≤41 kJ mol⁻¹ was estimated previously¹⁶ for the complex in SiMe₂ + HSiMe₃). The observed second-order rate constants, are given by

$$k = k_1 k_2 / (k_{-1} + k_2) = k_1 / (1 + k_{-1}/k_2)$$

Since step (1) is a loose association process it seems reasonable to assume that it will have at most a weak temperature dependence, *i.e.* E_1 is approximately zero.¹⁶ This suggests that much of the temperature dependence is associated with k_{-1}/k_2 . The observed rate constants, k , are sufficiently high, however, that they approach the collisional rate especially at the lower temperatures which implies that at sufficiently low temperatures $k \approx k_1$ and k_{-1}/k_2 will be small, but as the temperature increases k_{-1}/k_2 becomes significant. In other words, the mechanism switches from one in which step (1) is mainly rate determining to one in which step (2) becomes rate determining over the temperature range of study. This is in contrast to the same analysis¹⁶ for the analogous SiMe₂ insertion reactions where step (2) is rate determining at all temperatures of study (300–600 K). Without a knowledge of the individual rate constants for this mechanism the analysis can only be carried forward with an assumption. If we take as

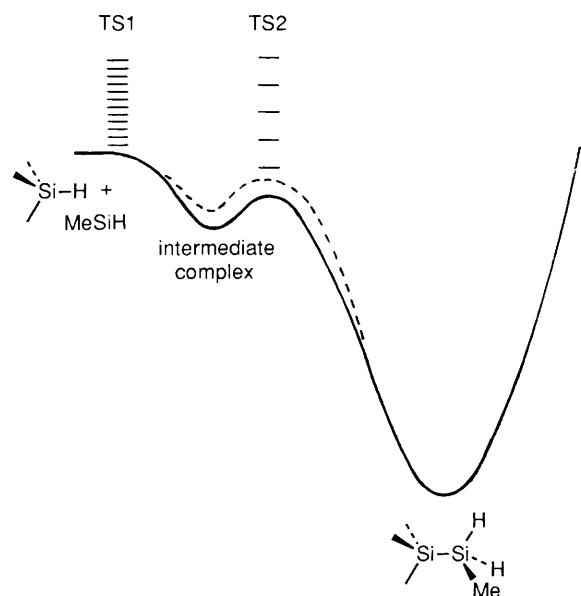


Fig. 4 Qualitative potential-energy surface for the MeSiH insertion process into an Si—H bond. The solid line represents the more facile process (Me₃SiH case). The dotted line is for the less facile process (SiH₄ case)

a hypothesis,[†]

$$k_1 = L \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

(where L is the path degeneracy)

then values for k_{-1}/k_2 can be calculated from observed values for k . These derived figures for k_{-1}/k_2 lie in the range 0.3–20, with the lowest values associated with MeSiH + Me₃SiH and the highest with MeSiH + SiH₄. The temperature dependences show some scatter but there is a significant increase with temperature which can be approximately generalised as

$$k_{-1}/k_2 \approx 10^{2.6} \exp[(E_2 - E_{-1})/RT]$$

The derived values for $E_2 - E_{-1}$ range from -12 kJ mol^{-1} (for MeSiH + SiH₄) to -17 kJ mol^{-1} (for MeSiH + Me₃SiH). These values represent the lowering of the secondary barrier [step (2)] compared with that for redissociation of the intermediate complex [step (–1)]. This is illustrated in Fig. 4 which shows a representative (qualitative) potential-energy surface for the reaction. The A factor ratio, $A_{-1}/A_2 = 10^{2.6}$, gives support to the view that the first transition state (TS1) is significantly looser in structure than the second (TS2). This finding is quite similar to that for the insertion reactions of SiMe₂.¹⁶

We may now rationalize the differences between the Si—H insertion reactions of MeSiH and SiMe₂ over the temperature range 300–600 K. For both silylenes their kinetic behaviour is determined by the relative propensities of the intermediate complexes to redissociate (k_{-1}) or rearrange (k_2). For all the insertion reactions of SiMe₂ redissociation of the complexes is more favourable than rearrangement, because the large entropic advantages outweigh the small energetic disadvantages. For the insertion reactions of MeSiH, the redissociation and rearrangement of the complexes are more closely competitive with one another. This is

Table 5 Activation energy differences for rearrangement (E_2) and redissociation (E_{-1}) of intermediate complexes in the Si—H insertion reactions of MeSiH^{a,b} and SiMe₂^{b,c}

substrate	$(E_2 - E_{-1})/\text{kJ mol}^{-1}$	
	MeSiH	SiMe ₂
SiH ₄	–12.6	–0.3
MeSiH ₃	–14.7	–6.0
Me ₂ SiH ₂	–16.7	–9.4
Me ₃ SiH	–17.3	–10.5

^a $(A_{-1}/A_2) = 10^{2.6}$. ^b Assumes $k_1 = L \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

^c $(A_{-1}/A_2) = 10^{3.3}$.

because the entropic advantage of redissociation is partially offset by the energetic disadvantage. The effect of energy is to favour rearrangement at lower temperatures. It also favours rearrangement of the complexes formed from the higher methyl-substituted substrate silanes.

This explanation may be refined by closer examination of the values for the activation energy differences $E_2 - E_{-1}$, derived by fitting the data to the complex mechanism. These are shown in Table 5. It can clearly be seen that for a given substrate molecule $|E_2 - E_{-1}|$ is larger for reactions of MeSiH than for those of SiMe₂. Although values for $|E_2 - E_{-1}|$ for reactions of SiH₂ are not yet available it seems reasonable to suppose that they will be larger again than for MeSiH reactions. This is because the reaction of SiH₂ + SiH₄ (the slowest per H insertion process⁹) is so fast, with only a slight decrease in rate over a 300 K temperature range,¹¹ that its rate seems little affected by the secondary barrier. In other words, for SiH₂ reactions, E_2 is probably so low compared with E_{-1} that step (1) is effectively rate determining up to 600 K. *Ab initio* calculations¹¹ support a potential surface in accord with this.

Table 5 also shows that for both MeSiH and SiMe₂, $|E_2 - E_{-1}|$ increases with methyl substitution on the substrate silane. Unfortunately E_2 and E_{-1} cannot be separated and thus we cannot say whether the effect of methyl substitution is to stabilise the complexes themselves or merely to facilitate their passage [via rearrangement step (2)] to final products. The differences $|E_2 - E_{-1}|$ are, however, still useful in helping to illuminate the picture we have presented earlier¹⁶ of the sequence of interactions occurring during the insertion process.

Nature of the Si—H Insertion Reaction

We have previously discussed the insertion process in terms of the coupling of electrophilic and nucleophilic interactions involved.^{9,16,18} Fig. 5(a) shows these basic interactions. Also shown is the summary of the effects of methyl-for-hydrogen substitution. Fig. 5(b) shows the geometry of the structure of the intermediate complex for the SiH₂ + SiH₄ reaction as derived by *ab initio* calculation.^{11†} From the bond lengths shown this suggests that in this structure H-transfer from SiH₄ to SiH₂ is significantly more advanced than Si—Si bond formation. It may be questionable whether there is any Si—Si interaction at all, in view of the high entropy requirement (structural looseness) of the intermediate. This implies that the electrophilic interaction precedes the nucleophilic to some extent, even though they are obviously coupled. This would tend to polarize the intermediate as indicated. The effects of methyl substitution can now be accounted for as

[†] A referee has pointed out that loose association reactions can have negative temperature dependences of *ca.* T^{-1} . This would have a small effect on the analysis presented here, without changing the significant conclusions.

[†] The geometry of the SiH₂ + SiH₄ complex reported in ref. 11 as provided by M. S. Gordon (personal communication).

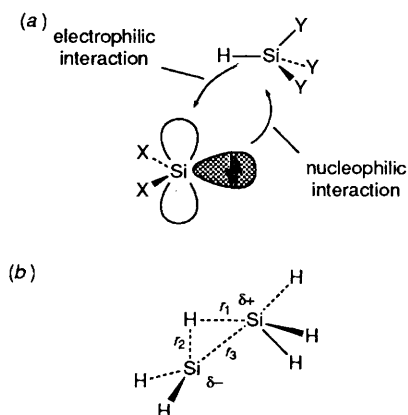


Fig. 5 (a) Electronic interactions involved in the silylene Si—H insertion process and the effects of Me-for-H substitution. Substitution at X retards rate, at Y enhances rate. (b) *Ab initio* structure of the intermediate complex (energy minimum) involved in the $\text{SiH}_2 + \text{SiH}_4$ insertion process: $r_1 = 2.046 \text{ \AA}$, $r_2 = 1.525 \text{ \AA}$, $r_3 = 2.470 \text{ \AA}$

follows. As we have argued previously,^{16,31,32} methyl groups are (weakly) electronegative when substituted on silicon centres. Thus they help draw off negative charge, but resist formation of positive charge at silicon centres. At first sight this might appear at odds with the observations. However, the silylenes are so electrophilic that we must presume they have little difficulty in accepting an electron pair regardless of substituent ($X = \text{H}$ or Me). The donor character of methyl silanes ($Y \equiv \text{Me}$) is also probably not affected significantly by methyl groups (Si—H bond dissociation energies are virtually constant in the methylsilanes and independent of methyl group substitution^{31,32}). It is the second, nucleophilic, stage where the methyl groups exert their influence. If the methyl groups are present in the silylene ($X \equiv \text{Me}$) then it will be more reluctant to donate its lone pair (thus destabilising the intermediate and second transition state). If the methyl groups are present on the silane ($Y \equiv \text{Me}$) then they will help draw off charge and facilitate acceptance of the lone pair (thus stabilising the intermediate and second transition state). Thus if the second stage becomes the rate-determining process (as with the SiMe_2 insertion) or at least rate-influencing (as with the MeSiH insertions) the methyl substituent effect in the silane becomes significant. This is exactly in accord with the effects observed.

We have previously discussed¹⁶ the alternative sequencing of nucleophilic and electrophilic interactions during the insertion process, favouring the process in which the nucleophilic interaction leads (without ruling out alternatives). The explanation offered here emerges largely as a result of the theoretically calculated structure and its implicit polarization. Nevertheless it appears fully compatible with our experimental findings. The effects of phenyl-for-methyl substitution in the silylene are very small and so are compatible with this explanation of the insertion process. The phenyl group, in spite of its increased size and different electronic character from methyl, clearly plays no special role. As stated earlier,¹⁸ there appears to be no special interaction (π -type or otherwise) with the empty or filled silylene orbitals.

Thermal Decompositions of Methylidisilanes which produce MeSiH and the Enthalpy of Formation of MeSiH

The kinetic data obtained for MeSiH may be used to examine the kinetics of the reverse reactions, *viz.* the thermal decompositions of methylidisilanes, by use of thermodynamic data connecting them and thus provide some yardstick for

Table 6 Calculation of A factors for some methyl-substituted disilane decompositions at 600 K.

reaction	ΔS^\ominus / $\text{JK}^{-1} \text{ mol}^{-1}$ ^a	$\log(A_f/\text{s}^{-1})$		
		calc.	obs.	ref.
$\text{MeSiH}_2\text{SiH}_3 \rightarrow \text{SiH}_4$ + MeSiH	125.4	13.81	14.14	19
$\text{MeSiH}_2\text{SiH}_2\text{Me} \rightarrow \text{MeSiH}_3$ + MeSiH	126.5	13.12	14.3	21
$\text{MeSiH}_2\text{SiHMe}_2 \rightarrow \text{Me}_2\text{SiH}_2$ + MeSiH	129.0	13.62	13.66	20
$\text{MeSiH}_2\text{SiMe}_3 \rightarrow \text{Me}_3\text{SiH}$ + MeSiH	142.6	13.29	13.81	22

^a S^\ominus values were taken from ref. 34 (methylsilanes and methylidisilanes) and from ref. 3 for MeSiH , by assuming the same values as for MeSH (isostructural principle³³).

comparison of results. This has been done previously using estimated rate data for MeSiH .²³ We have used our results in two ways. The first is to calculate the A factors for decomposition of selected methylidisilanes at a typical temperature of 600 K, *via* the entropy change ΔS^\ominus using the standard relationship,³³

$$\Delta S^\ominus = R \ln(A_f/A_r)$$

where A_f and A_r are the forward and reverse A factors. The results of these calculations (taking A_r values from Table 2) are shown in Table 6. This table shows that where comparison is possible, calculated A_f values are in tolerable agreement with observed, although for 1,2-DMDS, the discrepancy is rather large. Errors are probably experimental in origin, the uncertainties in the A_r values being of the order of $10^{\pm 0.4}$. The second treatment involves calculation, *via* the 'third-law' method, of ΔH^\ominus for the decomposition reactions shown in Table 7. This involves combining the absolute rate constant at 600 K, a temperature close to, or within the measurement range of both forward and reverse reactions, to obtain K_p , the equilibrium constant. This is then converted into ΔG^\ominus [*via* $\Delta G^\ominus = -RT \ln(K_p/p^\ominus)$] and thence into ΔH^\ominus (*via* $\Delta H^\ominus = \Delta G^\ominus + T\Delta S^\ominus$) using the ΔS^\ominus values of Table 6. Finally ΔH^\ominus is converted from its 600 K to 298 K value [*via* $\Delta H^\ominus(298 \text{ K}) = \Delta H^\ominus(600 \text{ K}) - \Delta C_p^\ominus \times 302 \text{ K}$]. The results are shown in Table 7. The $\Delta_f H^\ominus$ values for MeSiH are then derived, *via* Hess's law, by combination with the best available $\Delta_f H^\ominus$ values for the methylsilanes and methylidisilanes.²⁴ The resulting values shown in the last column of Table 7, give an average value of $\Delta_f H^\ominus(\text{MeSiH}) = 201.8 \text{ kJ mol}^{-1}$. This is surprisingly good agreement with the estimate of O'Neal *et al.*²³ ($201 \pm 8 \text{ kJ mol}^{-1}$) and our own earlier value²⁴ ($201 \pm 6 \text{ kJ mol}^{-1}$). This arises through a partial can-

Table 7 Calculation of enthalpy changes for some methyl-substituted disilane decompositions

reaction	$\Delta H^\ominus/\text{kJ mol}^{-1}$		$\Delta_f H^\ominus(\text{MeSiH})^b$ / kJ mol^{-1}
	600 K	298 K ^a	
$\text{MeSiH}_2\text{SiH}_3 \rightarrow \text{SiH}_4$ + MeSiH	217.4	221.1	205.2
$\text{MeSiH}_2\text{SiH}_2\text{Me} \rightarrow \text{MeSiH}_3$ + MeSiH	206.4	210.9	196.3
$\text{MeSiH}_2\text{SiHMe}_2 \rightarrow \text{Me}_2\text{SiH}_2$ + MeSiH	211.6 ^c	216.5	203.9

^a C_p^\ominus values (for temp. correction of ΔH^\ominus) taken from same sources as S^\ominus (see Table 6). ^b $\Delta_f H^\ominus$ for methylsilanes and methylidisilanes taken from ref. 24. ^c Kinetic data from ref. 22 used to calculate this figure.

cellation of a number of small differences in the calculation, compensating in part for the estimates (rather than measured values) of MeSiH rate constants on which the earlier values of $\Delta_f H^\ominus$ (MeSiH) are based. The present value, eliminates the assumptions of earlier values and is therefore more soundly based. However, experimental rate and thermodynamic uncertainties probably mean that it is realistic to retain the $\pm 6 \text{ kJ mol}^{-1}$ error limits of our earlier value.²⁴

We gratefully acknowledge the UK Rutherford Laser Loan Facility for use of the argon-ion laser. We thank the following: (i) Reading University Research Endowment Fund for the award of a studentship to B.P.M. (ii) the Royal Society for a fellowship to R.B. (iii) Professor Edwin Hengge (University of Graz) for the sample of DMDS. We would also like to thank Mark Blitz and Ivy Watts for assistance during the preliminary stages of this work.

References

- 1 P. P. Gaspar in *Reactive Intermediates*, ed. M. Jones, Jr. and R. A. Moss, New York, 1978, vol. 1, p. 229; 1981, vol. 2, p. 335; 1985, vol. 3, p. 333.
- 2 I. Safarik, V. Sandhu, E. M. Lown, O. P. Strausz and T. N. Bell, *Res. Chem. Int.*, 1990, **14**, 105.
- 3 G. Inoue and M. Suzuki, *Chem. Phys. Lett.*, 1985, **122**, 361.
- 4 J. M. Jasinski, *J. Phys. Chem.*, 1986, **90**, 555.
- 5 J. O. Chu, D. B. Beach and J. M. Jasinski, *J. Phys. Chem.*, 1987, **91**, 5340.
- 6 J. O. Chu and J. M. Jasinski, *J. Chem. Phys.*, 1988, **88**, 1678.
- 7 J. O. Chu, D. B. Beach, R. D. Estes and J. M. Jasinski, *Chem. Phys. Lett.*, 1988, **143**, 135.
- 8 J. E. Baggott, H. M. Frey, K. D. King, P. D. Lightfoot, R. Walsh and I. M. Watts, *J. Phys. Chem.*, 1988, **92**, 4025.
- 9 J. E. Baggott, H. M. Frey, P. D. Lightfoot, R. Walsh and I. M. Watts, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 27.
- 10 R. Becerra, H. M. Frey, B. P. Mason and R. Walsh, *Chem. Phys. Lett.*, 1991, **185**, 415.
- 11 R. Becerra, H. M. Frey, B. P. Mason, R. Walsh and M. S. Gordon, *J. Am. Chem. Soc.*, 1992, **114**, 2751.
- 12 T. R. Dietrich, S. Chiussi, M. Marek, A. Roth and F. J. Comes, *J. Phys. Chem.*, 1991, **95**, 9302.
- 13 J. E. Baggott, M. A. Blitz, H. M. Frey, P. D. Lightfoot and R. Walsh, *Chem. Phys. Lett.*, 1987, **135**, 39.
- 14 J. E. Baggott, M. A. Blitz, H. M. Frey, P. D. Lightfoot and R. Walsh, *J. Chem. Soc., Faraday Trans. 2*, 1988, **84**, 515.
- 15 J. E. Baggott, M. A. Blitz and P. D. Lightfoot, *Chem. Phys. Lett.*, 1989, **154**, 330.
- 16 J. E. Baggott, M. A. Blitz, H. M. Frey and R. Walsh, *J. Am. Chem. Soc.*, 1990, **112**, 8337.
- 17 J. E. Baggott, M. A. Blitz, H. M. Frey and R. Walsh, *Int. J. Chem. Kinet.*, 1992, **24**, 127.
- 18 M. A. Blitz, H. M. Frey, F. D. Tabbutt and R. Walsh, *J. Phys. Chem.*, 1990, **94**, 3294.
- 19 A. J. Vanderwielen, M. A. Ring and H. E. O'Neal, *J. Am. Chem. Soc.*, 1975, **97**, 993.
- 20 I. M. T. Davidson and J. I. Matthews, *J. Chem. Soc., Faraday Trans. 1*, 1976, **72**, 1403.
- 21 I. M. T. Davidson, K. J. Hughes and S. Ijadi-Maghsoodi, *Organometallics*, 1987, **6**, 639.
- 22 K. E. Nares, G. F. Licciardi, H. E. O'Neal and M. A. Ring, *Organometallics*, 1990, **9**, 2105.
- 23 H. E. O'Neal, M. A. Ring, W. H. Richardson and G. F. Licciardi, *Organometallics*, 1989, **8**, 1968.
- 24 G. Pilcher, M. L. P. Leitão, Y. Meng-Yan and R. Walsh, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 841.
- 25 J. E. Baggott, H. M. Frey, P. D. Lightfoot and R. Walsh, *J. Phys. Chem.*, 1987, **91**, 3386.
- 26 N. Al-Rubaiey and R. Walsh, unpublished results.
- 27 G. Maier, G. Mihm, H. P. Reisenauer and D. Littmann, *Chem. Ber.* 1984, **117**, 2369.
- 28 M. J. Michalczyk, M. J. Fink, D. J. De Young, C. W. Carlson, K. M. Welsh and R. West, *Silicon, Germanium, Tin and Lead Compounds*, 1986, **9**, 75.
- 29 M. Mozurkewich and S. W. Benson, *J. Phys. Chem.*, 1984, **88**, 6429.
- 30 R. Walsh, research in progress.
- 31 R. Walsh, *Acc. Chem. Res.*, 1981, **14**, 246.
- 32 R. Walsh, *Thermochemistry*, in *The Chemistry of Organic Silicon Compounds*, ed. S. Patai and Z. Rappoport, Wiley, New York, 1989, ch. 5, p. 371.
- 33 S. W. Benson, *Thermochemical Kinetics*, Wiley, New York, 2nd edn., 1976.
- 34 H. E. O'Neal and M. A. Ring, *J. Organomet. Chem.*, 1981, **213**, 419.
- 35 D. R. Stull, E. F. Westrum, Jr. and G. C. Sinke, *The Thermodynamics of Organic Compounds*, Wiley, New York, 1969.

Paper 2/04801I; Received 7th September, 1992