

in the NR mass spectrum of $\text{AlC}_2\text{H}_4^{*+}$ (Figure 5) we observe a weak but nevertheless clearly detectable signal at m/z 55, having the proper elemental composition (this is based on the exact elemental composition of the precursor ion which does not contain contribution from isobaric C_4H_7^+ species). The major decomposition pathways correspond to the formation of Al^+ (loss of C_2H_4) and $\text{C}_2\text{H}_4^{*+}$ (loss of Al). As already discussed above, there exist several variants for the formation of these ions. In view of the largely different energy requirements for the formation of the pairs $\text{Al}^+/\text{C}_2\text{H}_4$ versus $\text{C}_2\text{H}_4^{*+}/\text{Al}^+$, we presume that the $\text{C}_2\text{H}_4^{*+}$ signal originates from reionization of C_2H_4 generated from xenon-induced dissociation of AlC_2H_4^+ (note that the reaction $\text{AlC}_2\text{H}_4^+ \rightarrow \text{Al}^+ + \text{C}_2\text{H}_4$ gives rise to the base peak in the CA spectrum). We stress, however, that the NR spectrum shown in Figure 5 is compatible with the theoretically predicted¹⁷ existence of a solitary aluminum–ethylene complex. The relatively weak recovery signal observed in the NR of $\text{AlC}_2\text{H}_4^{*+}$ may be due to two factors: (i) The bond energy of the $\text{Al}/\text{C}_2\text{H}_4$ π -complex is, undoubtedly, significantly smaller^{16,17} than the bond energies of the AlCH_x species ($x = 2, 3$);⁹ relatively facile dissociation is expected to occur thus attenuating the flux of intact $(\text{Al}, \text{C}_2, \text{H}_4)$ species. (ii) In the case where the geometries of AlC_2H_4^+ and AlC_2H_4 differ, due to the vertical nature³ of the electron transfer in the NR experiment, the Franck–Condon factors will be small resulting in a smaller abundance of the survivor ions.²⁷ As the latter argument also applies to the $\text{HCAICH}_3^+/\text{HCAICH}_3$ system, the absence of a recovery signal in the NR spectrum of HCAICH_3^+ does not necessarily imply that neutral HCAICH_3 is not a minimum on the $(\text{Al}, \text{C}_2, \text{H}_4)$ potential energy surface.

(27) For further examples and a more detailed discussion of this aspect, see: Sülzle, D.; Terlouw, J. K.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 404.

Unfortunately, as this species is not included in the otherwise quite exhaustive theoretical study of Schaefer et al.,^{17a} no definitive conclusion is permitted for the time being.

Concluding Remarks

The present study provides experimental evidence that the neutral and ionic forms of AlCH_2 , AlCH_3 , $\text{Al}(\text{CH}_3)_2$, and AlC_2H_4 are stable species in the gas phase.²⁸ Quite remarkable is the finding that isomerization of AlCH_2 and AlCH_3 to their corresponding hydridoaluminum isomers HAICH_x ($x = 1, 2$) is negligible, if it takes place at all in gas-phase experiments. For the $(\text{Al}, \text{C}_2, \text{H}_4)$ system evidence for the existence of two non-interconverting ionic isomers is presented. One corresponds to the (aluminum/ethylene)⁺ complex AlC_2H_4^+ , which upon neutralization gives rise to a detectable recovery signal. The second isomer is assigned to the hitherto unknown HCAICH_3^+ ion; this isomer, however, could not be successfully neutralized to HCAICH_3 .

Acknowledgment. The support of our work by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the Gesellschaft von Freunden der Technischen Universität Berlin, and the Graduiertenkolleg Chemie Berlin is appreciated. R. Srinivas is indebted to the Deutscher Akademischer Austauschdienst (DAAD) for a visiting fellowship. We are grateful to Professor Helmut Vorbrüggen, Schering AG Berlin, for the supply of aluminum alkyl compounds, to Dr. Uwe Hartmann, Technische Universität Berlin, for technical assistance, and the reviewers for helpful comments. H.S. acknowledges the friendly criticism of his work by Professor Tino Gäumann, ETH Lausanne, to whom this article is dedicated on the occasion of his 65th birthday.

(28) For a recent, high-level ab initio MO study of AlCH , AlCH_2 , and AlCH_3 , see: Jin, S. Q.; Xie, Y.; Schaefer, H. F., III *Chem. Phys. Lett.* **1990**, *170*, 301.

Absolute Rate Constants for the Gas-Phase Si–H Insertion Reactions of Dimethylsilylene with Silane and the Methylsilanes in the Temperature Range 300–600 K

J. E. Baggott, M. A. Blitz, H. M. Frey, and R. Walsh*

Contribution from the Department of Chemistry, University of Reading, Whiteknights, P.O. Box 224, Reading, RG6 2AD, U.K. Received May 3, 1990

Abstract: The title reactions have been investigated by means of laser flash photolysis. Dimethylsilylene, SiMe_2 , was produced by 193-nm photolysis of pentamethyldisilane and detected via its visible absorption at 457.9 nm. Second-order rate constants were obtained for reactions of SiMe_2 with SiH_4 , MeSiH_3 , Me_2SiH_2 , and Me_3SiH . With the exception of SiH_4 , all the other rate constants decrease with increasing temperature. They represent a classic set of examples of reactions with negative activation energies, increasing to -11.2 ± 1.0 kJ mol⁻¹ for reaction with Me_3SiH . The substrate methyl substituent effect suggests the importance of the nucleophilic interaction in the rate-determining step. The measured A factors indicate tight structures for the activated complexes, consistent with kinetic measurements of the reverse reactions. A mechanism proceeding via an intermediate complex is shown to be consistent with the data, with entropy factors dominating the dynamics of the reaction pathway. A variational transition-state model (without an intermediate) is not thought to provide such a satisfactory explanation, although it cannot be ruled out.

Introduction

Grev and Schaeffer¹ have likened the role of the methyl substituent in silicon chemistry to that of hydrogen in traditional organic chemistry. Since silylenes, SiR_2 , are ubiquitous intermediates in organosilicon chemistry,^{2–4} playing the same central

role as free radicals in organic chemistry, one may legitimately claim that in terms of its importance dimethylsilylene, SiMe_2 , is the “methyl radical” of silicon chemistry.

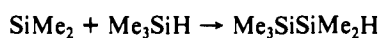
A great deal about the reactions and pattern of reactivity of SiMe_2 has been learned by careful pyrolytic and photolytic studies with end-product analysis. Experimental investigations in both

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

(3) Tang, Y.-N. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum: New York, 1982; Vol. 2, p 297.
(4) Davidson, I. M. T. *Annu. Rep. Prog. Chem., Sect. C* **1985**, *81*, 47.

gas and liquid phases indicate that SiMe_2 behaves rather like a singlet carbene in its reactions: it readily inserts into single bonds (eg Si-H, Si-OR,⁵ and O-H⁶) and adds stereospecifically across C=C bonds.⁷ Prior to 1987, kinetic studies were limited to relative rate constant measurements,^{5,8,9} although some attempts at estimation of absolute rate constants were made from the results of pyrolysis work by Davidson and Ostah.⁹ In the last 4 years, however, absolute rate investigations have begun to be carried out, employing the technique of time-resolved laser flash photolysis.^{10a,11-15} These investigations became possible only when a convenient optical absorption transition had been identified and characterized. This was first discovered by Drahnak, Michl, and West,¹⁶ who observed its electronic absorption [$\tilde{X}(^1A_1) \rightarrow \tilde{A}(^1B_1)_{\text{max}} = 450 \text{ nm}$] in an inert matrix. Despite some early controversy about this spectrum subsequent experimentation by West, Michl, and co-workers,¹⁷ and also the theoretical calculations of Grev and Schaeffer,¹ all support the original assignment.

In 1987 Gaspar and co-workers published their first kinetic studies of the reactions of SiMe_2 ^{10a} in solution (Gaspar's group had published earlier kinetic studies^{10b} of methylphenylsilylene reactions in solution.), while we published a gas-phase investigation of the reactions of SiMe_2 with SiH_4 and the methylsilanes.¹¹ Subsequent to this, other laboratories have measured rate constants for SiMe_2 reactions in solution^{12,13} while we have carried out further gas-phase investigations.^{14,15} In solution the findings are complicated by disagreements on the magnitudes of some rate constants, but in the gas phase, the picture emerges of a fast-reacting species, which nevertheless shows significant and interesting discrimination among reactive substrates. However, all of the studies so far reported have been carried out only at room temperature. Because of the utmost importance of a knowledge of energy barriers to understanding these processes, we have now embarked on studies of the temperature dependence of the rate constants of SiMe_2 reactions. Here we report our findings for the Si-H insertion reactions, the subjects of our original study.¹¹ The present work was given added impetus by the need to reconcile the earlier time-resolved results with rate data obtained from the decomposition reactions of certain selected methylated disilanes, which are the reverse of the SiMe_2 insertion reactions.¹⁸ We have, in fact, pointed out from the results of a kinetic study of pentamethyldisilane decomposition¹⁹ that the reaction



must have a negative activation energy and low A factor.

Experimental Section

(1) **Apparatus and Chemicals.** The apparatus for these experiments has been described in detail elsewhere.^{11,20} Briefly, a photolysis exciplex

(5) Gu, T. Y.; Weber, W. P. *J. Organomet. Chem.* **1980**, *195*, 29.

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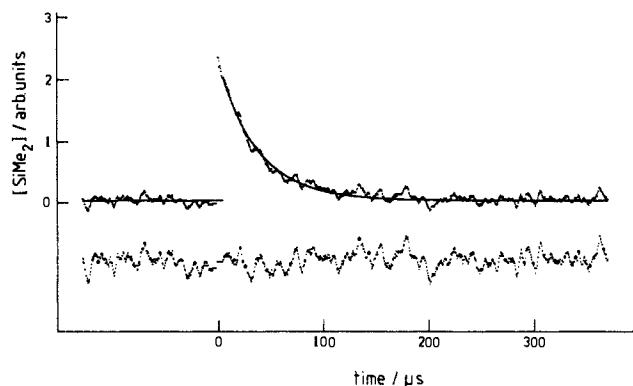
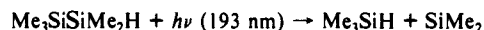


Figure 1. SiMe_2 transient absorption decay trace. Lower trace shows residual noise from exponential fit. Conditions: [PMDS] = 82 mTorr; [Me_3SiH] = 3.07 Torr; total pressure = 5 Torr; $T = 605 \text{ K}$.

laser (Oxford Lasers KX2) was used to irradiate gaseous reaction mixtures with pulses of 193-nm radiation at right angles to a CW Ar^+ laser probe beam. The reaction vessel consisted of a stainless steel T-shaped cell with a 3-cm inner tube diameter and demountable windows. The central portion was heated electrically and the temperature monitored with a chromel-alumel thermocouple. Preliminary measurements established that, over the reaction zone, temperature variation was $<5^\circ\text{C}$ at temperatures up to 300°C . The exciplex laser beam was defocused through a Spectrosil window to give fluences of $<20 \text{ mJ cm}^{-2}$. The probe beam, routinely operated on the 457.9-nm line, was multipassaged through the reaction zone to give an effective path length of ca. 1.4 m (40 passes). Light signals were captured by a dual photodiode/differential amplifier combination and stored in a transient recorder (Datalab DL910, 20-MHz resolution) interfaced to a BBC microcomputer.

All silanes were carefully degassed prior to use. Pentamethyldisilane, supplied by Professor J. Dunogues, was purified by preparative chromatography to $>99\%$. Methylsilane, MeSiH_3 (98.6%), and dimethylsilane, Me_2SiH_2 (99.6%), were prepared previously.⁹ Trimethylsilane, Me_3SiH ($>99\%$), was obtained from Fluorochem. Monosilane, SiH_4 , was from BOC (Electra II grade, $>99\%$) as was argon. Pressures were measured by capacitance manometers (MKS Baratron).

(ii) **Conditions, Precautions, and Transient Identification.** In all the experiments described here pentamethyldisilane, PMDS, was used as the source for SiMe_2 generation via its major photolytic breakdown reaction.¹¹



Pressures in the range 40–90 mTorr PDMS were found to generate sufficient SiMe_2 to obtain good signals (up to 4% absorbance) at the detection wavelength. Earlier evidence¹¹ showed that, in the absence of inert buffer gases, the transient absorption signals were characterized by a relatively slow buildup (time interval 20–30 μs) and decay. This behavior was pressure dependent at low pressures ($<1 \text{ Torr Ar}$) and probably arises from collisional deactivation of SiMe_2 formed initially with some excess vibrational energy (ca. 400 kJ mol^{-1} energy is available for distribution among the primary photoproducts Me_3SiH and SiMe_2). To avoid these complications Ar buffer gas pressures of at least 5 Torr were used.

At higher PMDS pressures ($>150 \text{ Torr}$) and high fluences ($>30 \text{ mJ cm}^{-2}$) gas-borne dust was formed. Since this was observed visually by probe beam scattering, it clearly represents an interference with signal and was therefore highly undesirable. In practice, at fluences of ca. $<20 \text{ mJ cm}^{-2}$ and lower PMDS pressures it appeared not to occur. Nevertheless, the Spectrosil photolysis laser inlet window required regular (daily) cleaning (with jeweler's rouge) to maintain good 193-nm transmission. Rate data were found to be independent of both the number of shots (up to 25) and exciplex laser energies (up to 90 mJ per pulse), suggesting no serious perturbations from aerosol particles or reaction products. The lack of any rate constant dependence of fluence also suggests no problem arising from multiphoton absorption.

SiMe_2 was detected and monitored via its known absorption band^{16,17} (see Introduction) by using the 457.9-nm Ar^+ laser line. The extinction coefficient is high (ca. $1500 \text{ M}^{-1} \text{ cm}^{-1}$ in 3-methylpentane glass at 77 K ¹⁶), permitting the generation of good signals with low noise. Previously, in room-temperature experiments,¹¹ we have shown that the gas-phase spectrum in the wavelength region of 458–515 nm matches closely

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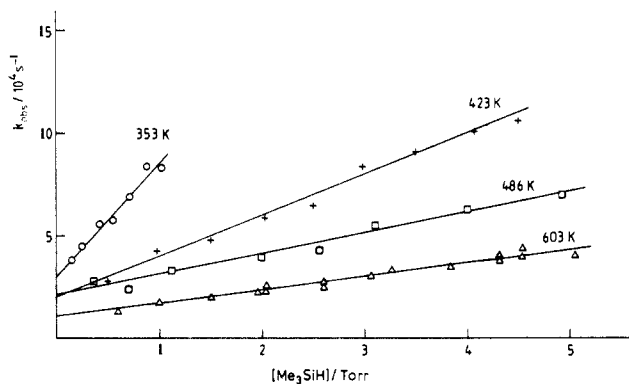


Figure 2. Dependence of exponential decay constants, k_{obs} , on substrate (Me_3SiH) pressure at several temperatures.

the matrix spectrum. In this work at higher temperatures, the SiMe_2 absorption signal at a given precursor pressure tended to decrease with temperature, possibly because of spectral broadening. Signal intensities were maintained by increasing precursor partial pressure. Signal decay rates, via reaction of SiMe_2 with PMDS, did not however increase at higher temperatures, thus indicating that the rate constant of this reaction must decrease as temperature increases.

The identification of this transient with SiMe_2 is further supported by our earlier gas chromatographic detection of the disilane and trisilane products of the SiMe_2 insertion reactions with methylsilanes and PMDS.^{11,21}

(iii) **Procedure for Kinetic Runs and General Considerations.** Appropriate gas mixtures (40–90 mTorr PMDS, up to 5 Torr substrate + Ar diluent to a fixed total pressure) were photolyzed. In a typical run, signals were accumulated over 15 laser shots at ca. 85 mJ per pulse. Although as much as 5% of the PMDS could be removed per laser shot under these conditions, only ca. 5% of the total sample volume was photolyzed. Thus, the PMDS precursor in the irradiated volume was replenished by diffusion between laser shots. A typical averaged decay trace is shown in Figure 1. The signal-averaged decay traces were analyzed by a nonlinear least-squares routine with sensible truncation to avoid any initial perturbation from the rise time. In the presence of substrate methylsilanes and SiH_4 , the traces were essentially exponential up to 95% absorbance decay. In the absence of added substrate, the decays showed some deviation from exponential at the higher temperatures (in contrast to the room-temperature studies¹¹). This phenomenon was suggestive of reactions of SiMe_2 with other photolysis-generated intermediates (or even dimerization of SiMe_2) under these conditions. Thus, experiments with pure PMDS were not included in the data analysis. The first-order rate constants, k_{obs} , obtained from the fitting procedure were studied as a function of substrate pressure at constant total pressure. In most experiments the total pressure was 5 Torr, but for the reactions with SiH_4 it was 10 Torr. About 10 different sets of values were obtained for each substrate at each temperature and these were plotted in the usual way^{10–15} to obtain second-order rate constants for each reaction of SiMe_2 under investigation. Some examples of second-order plots are shown in Figure 2.

Since SiH_4 and the methylsilanes are transparent to 193-nm radiation,²² there were no complications from reactant depletion, nor from product accumulation.

Results

The reactions of SiMe_2 with SiH_4 , MeSiH_3 , Me_2SiH_2 , and Me_3SiH were all studied. Reaction with Me_4Si was not investigated since previous work¹¹ had shown it to be unreactive toward SiMe_2 . For each substrate the reaction was carried out at each of five temperatures in the range 295–608 K. Some fluctuations in temperature occurred during the course of a given set of runs. This generally only amounted to a few degrees and was always within ± 5 K of the mean. The temperature dependences of the rate constants were such that this small variation of temperature was inconsequential. Good linear second-order plots such as those shown in Figure 2 were obtained for all the substrates. The second-order rate constants with their uncertainties are shown in Table I. The temperatures shown in this table are averages. The

Table I. Rate Constants for the Reactions of SiMe_2 with Monosilanes^a

T/K	$10^{13}k/\text{cm}^3$ molecule ⁻¹ s ⁻¹		T/K	$10^{13}k/\text{cm}^3$ molecule ⁻¹ s ⁻¹
SiH₄				
295	2.0 ± 0.3		491	2.07 ± 0.08
368	1.46 ± 0.16		602	2.44 ± 0.25
428	2.27 ± 0.07			
MeSiH₃				
295	19 ± 2		486	6.99 ± 0.38
363	13.2 ± 0.9		608	4.64 ± 0.31
430	7.29 ± 0.79			
Me₂SiH₂				
295	55 ± 5		485	9.39 ± 0.52
364	24.0 ± 1.5		596	6.03 ± 0.44
428	12.6 ± 1.7			
Me₃SiH				
295	45 ± 5		486	5.33 ± 0.45
353	16.6 ± 1.6		603	4.47 ± 0.31
423	8.54 ± 0.47			

^aSingle standard deviations quoted.

Table II. Arrhenius Parameters for SiMe_2 Insertion Reactions^a

substrate	$\log_{10}(A/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$	$E_a/\text{kJ mol}^{-1}$
SiH_4	-12.54 ± 0.16	+1.25 ± 1.23
MeSiH_3	-12.90 ± 0.09	-6.73 ± 0.68
Me_2SiH_2	-13.15 ± 0.05	-10.55 ± 0.38
Me_3SiH	-13.41 ± 0.14	-11.20 ± 1.03

^aSingle standard deviations quoted.

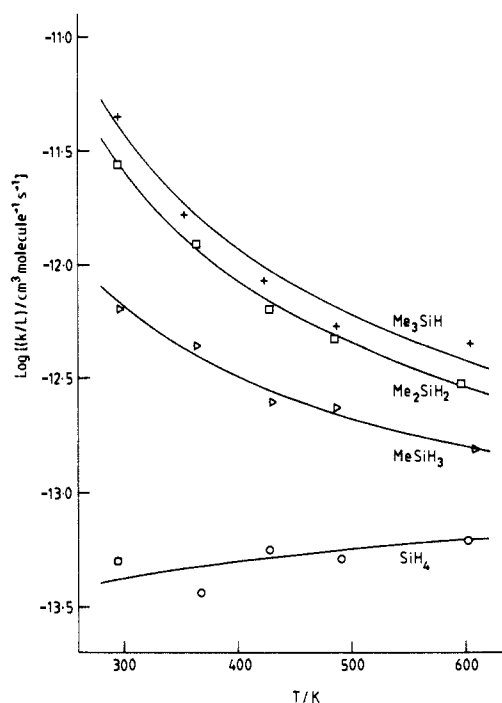


Figure 3. Dependence of rate constant per Si-H bond, k/L , on temperature for the SiMe_2 + methylsilane reactions.

room-temperature values are those obtained previously¹¹ in the quartz cell, but checks carried out in the present stainless steel vessel with a selected subset of runs showed excellent agreement with the earlier data.

The most striking feature of the data is that the rate constants, with the exception of those for SiH_4 , decrease with increasing temperature. The largest effect is for the case of reaction of SiMe_2 with Me_3SiH , for which the rate constant decreases by a factor of 10 over the ca. 300 K temperature range. The variation of rate constant with temperature increases with methyl substitution of the substrate silane, as illustrated in Figure 3. In this figure, the rate constants have been statistically corrected for the number

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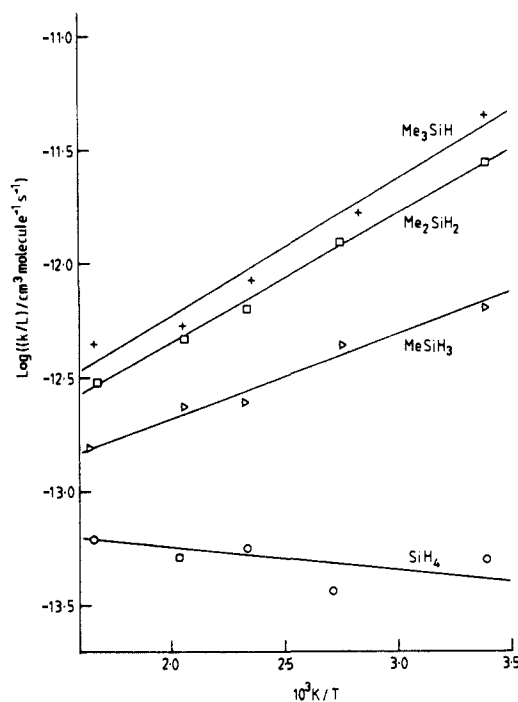


Figure 4. Arrhenius plots for reactions of SiMe_2 with the methylsilanes.

Table III. Comparison of Selected SiMe_2 Insertion Rate Constants (295 K)

reaction	phase	$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	ref
$\text{SiMe}_2 + \text{Me}_3\text{SiH}$	gas	$(4.5 \pm 0.5) \times 10^{-12}$	11, this work
$\text{SiMe}_2 + \text{Et}_3\text{SiH}$	solution	$(6.0 \pm 0.7) \times 10^{-12}$	12
$\text{SiMe}_2 + \text{Et}_3\text{SiH}$	solution	$(4.8 \pm 0.7) \times 10^{-12}$	13
$\text{SiMe}_2 + \text{Et}_3\text{SiH}$	solution	$(3.5 \pm 0.1) \times 10^{-16}$	10a

of Si-H bonds, L , available for insertion. The figure shows clearly that whereas the reactivity ordering of the methylsilanes is the same at all temperatures with Me_3SiH the most and SiH_4 the least reactive, the differences decrease as the temperature increases.

The temperature dependences expressed in Arrhenius form are displayed in Figure 4, and the derived Arrhenius parameters obtained by least-mean-squares fitting are given in Table II. The figures show clearly the systematic trend toward more negative activation energies with greater methyl substitution of the substrate silane. There is also a decrease in A factor with methyl substitution, but when statistically corrected for the number of Si-H bonds, an almost constant value of $\log(A/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ of $-13.30 (\pm 0.15)$ emerges. The Arrhenius plots also show a hint of curvature, which may reflect the failure of the data to conform to the Arrhenius equation, although this is only just beyond the error margins of the rate constants. Negative activation energies of similar magnitude have been found by us for the analogous insertion reactions of phenylsilylene, PhSiH_2 .²³

Discussion

(i) **Comparison with Other Data.** There has been no other direct gas-phase kinetic study of the reactions investigated here. However, since our earlier room-temperature study¹¹ there have been three ambient-temperature studies of the kinetics of SiMe_2 in dilute solution (cyclohexane or methylcyclohexane). These investigations all included data on the Si-H insertion reaction, which is shown in Table III together with our results. Although not strictly comparable, in that we have used Me_3SiH while the solution studies used Et_3SiH , there is no reason to believe that ethyl and methyl substituents should differ significantly in their influence. The close concordance of rate constants at 298 K between our work and the work of Shizuka et al.¹² and Levin et

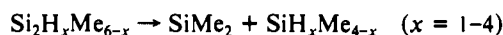
Table IV. Entropy Changes, Measured A Factors, and Calculated Reverse A Factors for Some Methyl-Substituted Disilane Decompositions

reaction	ΔS^\ddagger ^a	$\log(A_{\text{obs}}/\text{s}^{-1})$	$\log(A_{\text{rev}})$ ^b
$\text{H}_3\text{SiSiMe}_2\text{H} \rightarrow \text{SiH}_4 + \text{SiMe}_2$	125	13.12 ^c	-12.07
$\text{MeSiH}_2\text{SiMe}_2\text{H} \rightarrow \text{MeSiH}_3 + \text{SiMe}_2$	123	13.15 ^d	-11.96
$\text{Me}_2\text{SiHSiMe}_2\text{H} \rightarrow \text{Me}_2\text{SiH}_2 + \text{SiMe}_2$	134	13.17 ^e	-12.51
$\text{Me}_3\text{SiSiMe}_2\text{H} \rightarrow \text{Me}_3\text{SiH} + \text{SiMe}_2$	143	12.83 ^e	-13.30

^a Units of $\text{J K}^{-1} \text{ mol}^{-1}$; $T = 600 \text{ K}$. ^b Back-reaction A factor; units, $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. ^c Reference 24. ^d Reference 25. ^e Reference 19 (most recent value).

al.¹³ suggests no great differences between the gas phase and solution for this reaction. The difference with the solution studies of Gaspar et al.¹⁰ has been attributed¹³ to the possibility of complexation of the silylene with a reactant or product in Gaspar's studies. Levin et al.¹³ have shown that SiMe_2 complexes of O or N donor type react at greatly reduced rates compared with free SiMe_2 . However, modification of reactivity by other kinds of complexation has yet to be established. The major difference in the solution work of Gaspar¹⁰ was the SiMe_2 photolytic source, $(\text{PhMe}_2\text{Si})_2\text{SiMe}_2$ rather than $c\text{-(SiMe}_2)_6$ employed by the others.^{12,13} Until Gaspar's work is explained there must remain some doubts about the behavior of SiMe_2 in solution.

One doubt, however, that has been cleared up by these studies is the earlier suggested inconsistency (made by one of us¹⁸) between the rate constants of these SiMe_2 insertion reactions and the reverse reactions, viz. the decompositions of methyl-substituted disilanes:



Walsh¹⁸ pointed out that, in the event that SiMe_2 insertion reactions had zero or small positive activation energies, the directly measured room-temperature rate constants¹¹ implied a transition state sufficiently loose in structure that the A factors for the disilane decompositions must be ca. 10^{15} s^{-1} , considerably greater than measured. Subsequent further investigation of the kinetics of these disilane decompositions in both our own laboratories¹⁹ and those of O'Neal and Ring^{24,25} have produced Arrhenius parameters similar to those originally measured. This led us inevitably to conclude¹⁹ that, as originally suggested,¹⁸ the SiMe_2 insertion reactions must have the negative activation energies, which the present work has borne out.

The quantitative deductions from the disilane decompositions may be examined further. The Arrhenius A factors are shown in Table IV. When the A factors for these decompositions are combined with estimates¹⁸ of ΔS^\ddagger , values are obtained for A factors for the SiMe_2 insertion reactions in the range $10^{12.0}-10^{13.3} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, as shown in the table. The individual values, when compared to those measured here (Table II) show agreement for $\text{SiMe}_2 + \text{Me}_3\text{SiH}$ and differences up to a factor of 10 for $\text{SiMe}_2 + \text{MeSiH}_3$. Bearing in mind the errors involved in both the experimental data and the estimated thermodynamic functions, these differences are not large and indicate that the kinetic results for these SiMe_2 insertion reactions and the corresponding reverse unimolecular decompositions are now in moderately good agreement.

The activation energies of these decomposition reactions have been used by one of us²⁶ and others²⁷ to estimate $\Delta H_f^\circ(\text{SiMe}_2)$. Although the results obtained here bear on this question, the quantitative changes are insufficient to resolve current differences over $\Delta H_f^\circ(\text{SiMe}_2)$ and so this question is not explored further in the present paper.

In a very recent competitive rate study^{25,55} carried out at ca. 550 K and 500 Torr, Ring and O'Neal and co-workers have

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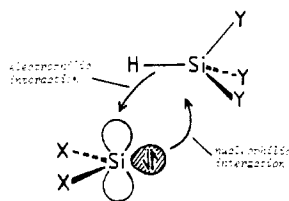
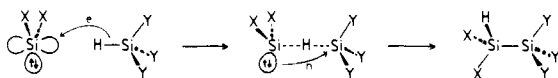


Figure 5. Important electronic interactions involved in the silylene insertion process into Si-H bonds.

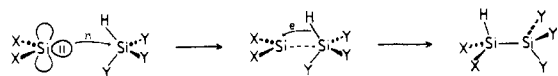
obtained relative rates of reaction of SiMe₂ with MeSiH₃ and SiH₄. The measurements gave values of ca. 8 for this rate constant ratio in contrast to our measurements for which a value of ca. 2.5 may be obtained (from the Arrhenius parameters of Table II). We are unable to offer any reason for this difference but plan to investigate it further.

(ii) **Nature of the Si-H Insertion Reaction.** The major finding of this work is that of the substantial rate decreases with temperature for SiMe₂ insertions into the Si-H bonds of methylsilanes. Also requiring explanation are the rate enhancements associated with increasing methyl substitution in the substrate silane. Furthermore, any coherent account of these processes must explain the much more discriminating behavior of SiMe₂ compared with SiH₂.²⁸ We have previously offered partial explanations^{19,23,28} for some of these observations, which we bring together here. Current theoretical ideas about the nature of the insertion process^{29,30} originating with Hoffmann³¹ are illustrated in Figure 5. The insertion process may be viewed as comprising an "electrophilic" stage with transfer of electron density from the Si-H bond into an empty p orbital in the silylene, and a "nucleophilic" stage with donation of the silylene lone pair to make the new Si-Si bond. Electron-withdrawing substituents (X) on the silylene will cause orbital contraction, thus disfavoring both the acceptor and donor character of the silylene. Electron-withdrawing substituents (Y) on the silane enhance the bond polarity Si^{δ+}-H^{δ-} by making the silicon more positively charged and thereby favoring the nucleophilic stage of the process. Since carbon is more electronegative than silicon, it is plausible that methyl substituents can function as weakly electron withdrawing groups. Some recent calculations of electrostatic charge densities³² appear to contradict this; however, evidence in support of the idea comes from bond dissociation energy values.^{32,33} Thus, if this idea is correct, SiMe₂ will have less extended empty p and lone-pair orbitals than SiH₂ and will require shorter range, closer contact with substrates for reaction to take place. Hence the lower reactivity of SiMe₂ compared with SiH₂.²⁸

To explain the methyl substituent effect in the silane requires the nucleophilic stage to contribute to the rate-determining step of the process. In principle there are three possibilities for the combination of these interactions: (a) a fully synchronous process in which both nucleophilic, n, and electrophilic, e, stages occur simultaneously; (b) a process led by the electrophilic, e, interaction, viz.



(c) a process led by the nucleophilic, n, interaction, viz.



In both processes b and c distinct, but different, intermediate

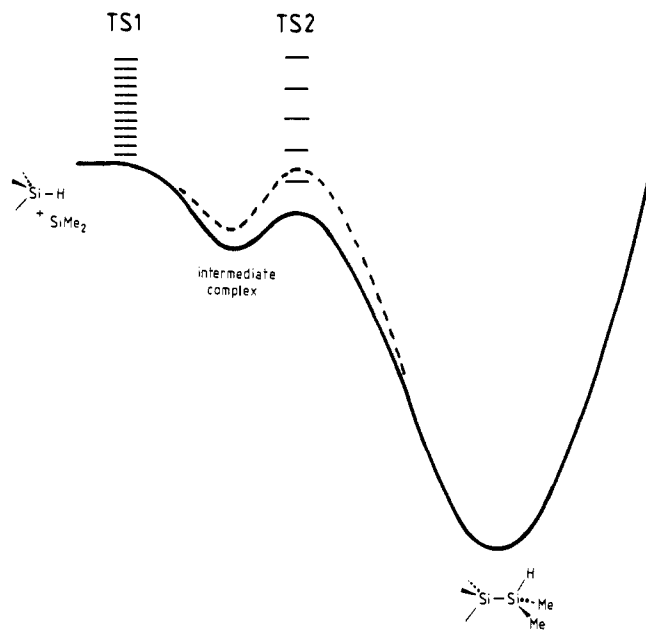


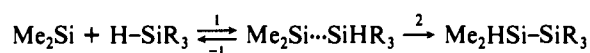
Figure 6. Qualitative potential energy surface for the SiMe₂ insertion process into an Si-H bond. The solid line represents the surface for the more facile isomerization of the intermediate complex (Me₃SiH case). The dotted line is for the less facile rearrangement of the complex (SiH₄ case).

complexes are involved. It is not easy to distinguish among these possibilities. Theoretical calculations on ¹CH₂ and ¹SiH₂ insertion into the H-H bond^{29,30} suggest an electrophilically led process, with a weak complex H₂Si...H₂ on the potential surface for the SiH₂ + H₂ reaction.³⁴ However, if process b were operative in the Si-H insertion process, the electrophilic stage is unlikely to be rate-determining since; if so, the process should be insensitive to the methyl substituent effect. This is because the Si-H bonds (which supply the electrons) have dissociation energies that are virtually constant and independent of methyl substitution.^{32,33} By elimination, therefore, the reaction would appear to require either process a or c. However (b) must still be considered possible provided the *second* stage is rate determining.

We have argued previously in favor of (c) for the reverse PMDS decomposition reaction on the grounds that a silylene donor-acceptor intermediate seems intrinsically more plausible than an H-bridged intermediate complex. Furthermore Beach et al.³⁵ recently found mass spectrometric evidence for the existence of an H₄Si...NH₃ adduct with a bond strength of ca. 25 kJ mol⁻¹. Thus, in the ensuing discussion we analyze the temperature dependences in terms of this mechanism while recognizing the other possibilities are not rigorously eliminated.

(iii) **The Intermediate-Complex Mechanism.** Generalized treatments for the explanation of negative activation energies (and curved Arrhenius plots) in terms of an intermediate complex exist in the literature.³⁶ Attempts at detailed transition-state modeling studies are underway³⁷ and therefore we limit the discussion here to a simplified outline treatment.

The process, for all the reactions investigated here, is



where R = H or Me.

Figure 6 shows a pictorial (qualitative) representation of the potential energy surface with an indication of the positions of the two transition states involved in the process. The observation of

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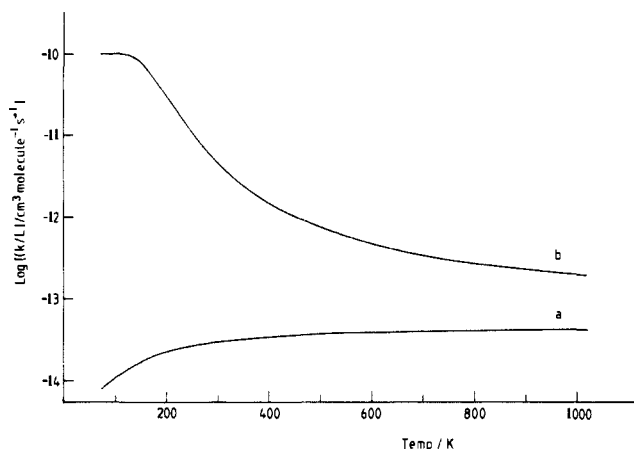


Figure 7. Temperature dependencies for the SiMe_2 insertion reaction, predicted by the simplified intermediate-complex model. Line a: high secondary barrier (SiH_4 case). Line b: low secondary barrier (Me_3SiH case).

single-exponential decays supports the assumption of a steady-state population of intermediate complexes. The observed (phenomenological) second-order rate constants, k , are given by

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

Since step 1 represents formation of the complex via association (encounter) of the silylene with substrate silane, it seems reasonable to assume that this will have at most a weak temperature dependence, i.e., E_1 is approximately zero.^{38,39} This suggests the major temperature dependence is associated with k_{-1}/k_2 . The implication is that k_{-1}/k_2 exceeds unity and is therefore the dominant term so that under most conditions, $k \approx k_1 k_2 / k_{-1}$, or in other words, step 2 is rate determining.

The measured A factors per Si-H bond are very similar in magnitude, i.e.

$$A = \frac{A_1 A_2}{A_{-1}} = L \times 10^{-13.3} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

This common value for the A factor quotient indicates a similar (tight) structure for transition state, TS2, for all the reactions. For step 1, although not mandatory, it seems reasonable to assume a similar loose structure for each reaction in view of the resemblances of the processes. If this is so, A_1 must have a value considerably greater than $10^{-11.35} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, since it cannot be less than the highest rate constant value measured (viz. that for $\text{SiMe}_2 + \text{Me}_3\text{SiH}$ at 295 K). The indications from Figure 3 are that at $T < 295 \text{ K}$ the rate constant for the $\text{SiMe}_2 + \text{Me}_3\text{SiH}$ reaction must rise to a significantly higher value than this limit. As a working hypothesis, therefore, we assume

$$A_1 = k_1 = 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

This permits the evaluation of values for the ratio k_{-1}/k_2 , which may be generalized as

$$\frac{k_2}{k_{-1}} \approx L \times 10^{-3.3} \exp[-(E_2 - E_{-1})/RT]$$

where $E_2 - E_{-1}$ values are identified with the measured activation energies in Table II. It is this ratio that determines the nature of the kinetics of this reaction. Under all conditions of the present measurements k_2/k_{-1} is small and considerably less than unity. This confirms step 2 as rate determining. For reaction of SiMe_2 with SiH_4 , k_2/k_{-1} will never exceed $10^{-2.7}$ at any temperature. For the other reactions, k_2/k_{-1} increases as T is reduced, so that the

possibility exists that step 1 could become rate determining at subambient temperatures. Figure 7 illustrates, in a semiquantitative way, these implications for the two extreme situations represented by the reactions of SiMe_2 with SiH_4 and with Me_3SiH over a wide range of temperature. The detection of a low-temperature limiting rate constant for $\text{SiMe}_2 + \text{Me}_3\text{SiH}$ (or the other methylsilanes) would provide a value for k_1 for the intermediate-complex mechanism and thereby shed further light on this mechanism.

The magnitude of the preexponential term, A_2/A_{-1} , in the expression for k_2/k_{-1} gives important clues about the nature of the two transition-state structures, TS1 and TS2. Expressed in terms of entropy

$$S^\ominus(\text{TS1}) - S^\ominus(\text{TS2}) = R \ln \left(\frac{A_{-1}}{A_2} \right) \approx 63 \text{ J K}^{-1} \text{ mol}^{-1}$$

This substantial value is a measure of the relative tightness of TS2 compared with TS1. Although more detailed calculations are underway,³⁷ it is clear that a substantial part of this entropy difference derives from (a) the loss of internal rotational motion, and (b) the tightening of low-frequency rocking modes in TS2 compared with TS1. For the reaction of SiMe_2 with SiH_4 , this tightness is the dominant effect on the value of k_2/k_{-1} . The energy term is negligible and so in this particular case the reaction may be said to be truly "entropy controlled". In the other cases the energy term partially offsets the unfavorable entropy of TS2, so that the lower barrier associated with TS2 means that intermediate complexes have an energetic advantage in proceeding to products (E_2) compared with reverting to reactants (E_{-1}). This advantage, however, can only overcome the entropy disadvantage at sufficiently low temperatures. Thus, the reaction of SiMe_2 with the methylsilanes while not entropy controlled, may still be said to be "entropy dominated".

Although this treatment is oversimplified, particularly in assuming a temperature-independent value for k_1 , a barrierless reaction, we believe that the substantial negative activation energies observed here offer strong support for this type of mechanism.^{40,41} There are, however, potentially other tests that could bear on this question. Low-temperature trapping of the complex, or even observation of a transient population, would provide the most direct evidence. While there is irrefutable evidence for such complex formation between silylenes and O, N, S, and P donors,⁴²⁻⁴⁵ there is, as yet, none for complexes of the type suggested here. This implies a relatively shallow well on the potential energy surface. An estimate of the maximum well depth can be obtained from the experimental observations. Biexponential decay kinetics are the signature of a significant population of transient complexes.¹⁵ Although decays were single exponential, a population of as much as 20% complexes might just have escaped detection (within the noise of the detection system). Such a population would place a limit on the value of the equilibrium constant, $k_{1,-1}$ ($=k_1/k_{-1}$) $< 150 \text{ atm}^{-1}$ at 353 K for the system



This means that the Gibbs free energy change ($-\Delta G^\ominus$) $\leq 14.7 \text{ kJ mol}^{-1}$. From standard vibrational assignment methods⁴⁶ and earlier calculated entropy values,¹⁸ we estimate $\Delta S^\ominus = -75 \pm 10 \text{ J K}^{-1} \text{ mol}^{-1}$. Thus:

(40) For alkyl radical recombination reactions, the strongest temperature dependence is that for the mutual reaction of two *tert*-butyl radicals, where a factor of ca. 3 decrease in the rate constant is observed between 300 and 650 K.⁴¹

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(38) Free-radical combination reactions are the most extensively studied class of such reactions. A recent review of experiments and theory for the CH_3 recombination reaction is given in ref 39.

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$$(-\Delta H^\ominus) = (-\Delta G^\ominus - T\Delta S^\ominus) \leq 41.3 (\pm 3.5) \text{ kJ mol}^{-1}$$

The negative enthalpy change, $-\Delta H^\ominus$, represents to a reasonable approximation the desired well depth. Since this is probably the most favorable case, the strength of binding of these intermediate complexes does not exceed $\sim 40 \text{ kJ mol}^{-1}$.

Another possible test concerns pressure dependence of the observed rate constant. We have not explored this question experimentally as yet. Use of lower pressures is made difficult in the present system because of the necessity of having a sufficient pressure to provide thermalized SiMe₂ from its energetic photochemical source (see Experimental Section). However, we may inquire, via theory, into the likelihood of pressure dependence in this system. An overall third-body-type pressure stabilization of the initially formed product disilanes seems exceedingly unlikely in view of their molecular size.^{47,48} However, a pressure dependence of a different kind associated with stabilization of intermediate complexes remains a possibility. A recent study of pyrene fluorescence quenching by Davis and Pilling⁴⁹ involving weak complex formation by association of large molecules provides an example not dissimilar from that discussed. The key to observation of a pressure dependence is whether the Boltzmann population of complexes exists substantially above the dissociation threshold of the complex. If so, the initially formed complexes can act as their own heat bath and further collisions will produce very little change in the population distribution. Otherwise a weak pressure dependence is possible. Detailed exploration of this possible pressure dependence will form part of our further theoretical investigations.³⁷

In summary, the evidence for the involvement of intermediate complexes is presently suggestive rather than conclusive. Further tests, both experimental and theoretical are required.

(iv) **Variational Transition-State Theory.** An alternative explanation for the negative activation energies is one based on a variational transition state.⁵⁰ A particular version of such a theory is one developed by Houk et al.⁵¹⁻⁵³ to account for kinetic data for the addition reactions of halocarbenes with alkenes. The theory is appropriate to association reactions that have zero or close to zero enthalpic barriers but may develop significant free energy

barriers due to the decrease in entropy occurring as the two molecules unite to form one. The location of the transition state (maximum in ΔG) is then determined by the point along the reaction coordinate at which the decrease in the ΔH term overcomes the increase in the $-T\Delta S$ term. Clearly since the magnitude of the $-T\Delta S$ term is temperature dependent, then so will be the location of the transition state. Higher temperatures will move the position of transition state further toward the product and result in a higher value for ΔG^\ddagger . Whether lower rate constants result depends on $\Delta G^\ddagger/T$. This in turn depends on intimate details of the potential surface and state density functions at different positions along it. Without ab initio calculations it is difficult to know whether this theory could be made to fit the present results. However, we can offer the following comments:

(a) The idea of an entropy-dominated barrier, characteristic of Houk's models is certainly not inconsistent with the measured rate constants and their temperature dependences.

(b) If the intermediate-complex mechanism were found to require the *second* step always to be rate determining, the distinction between it and this kind of model becomes academic. This is because in transition-state theory the only important features of the surface are those of the bottleneck to reaction (and of course the reactants). The existence of a potential well between reactants and the bottleneck does not affect the bottleneck and cannot be discerned from it.

(c) The differentiation between this idea and the intermediate-complex mechanism depends on detecting the well, either by a change of rate-determining process or other tests outlined in the previous section.

(d) We find the silane methyl substituent effect hard to accommodate to a monotonically decreasing potential surface. The increased rates at low temperatures for SiMe₂ + Me₃SiH compared with SiMe₂ + SiH₄ imply an increased attractive potential energy at long range for the former reaction. Since the overall enthalpy changes are all these insertion reactions are essentially identical (ca. 218 kJ mol^{-1}),²⁷ it is hard to see why the potential surfaces should differ *unless* there is some special, close-to-threshold, interaction, which disappears upon product formation. This, at present, seems the strongest argument against the simple variational transition-state model for this series of reactions.

In further publications we hope to report further progress in understanding the nature of the Si-H insertions reaction of SiMe₂,³⁷ as well as reactions of SiMe₂ with O donors and alkenes.⁵⁴

Acknowledgment. We thank the U.K. SERC for the award of a postgraduate studentship to M.A.B. We thank Jacques Dunoguès for samples of pentamethyldisilane. We also thank Mike Pilling for helpful discussion and Joe Jasinski and Ed O'Neal for prepublication manuscripts.

(47) Combination reactions of alkyl radicals larger than methyl show no pressure dependence.⁴¹ RRKM theory⁴⁸ leads to no expectation of any pressure dependences for SiMe₂ producing dissociations of methyl-substituted disilanes^{19,24,25} at the pressures and temperatures employed in the present study.

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