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Unusual Isotope Effect in the Reaction of Chlorosilylene with Trimethylsilane-*1-d*. Absolute Rate Studies and Quantum Chemical and Rice–Ramsperger–Kassel–Marcus Calculations Provide Strong Evidence for the Involvement of an Intermediate Complex

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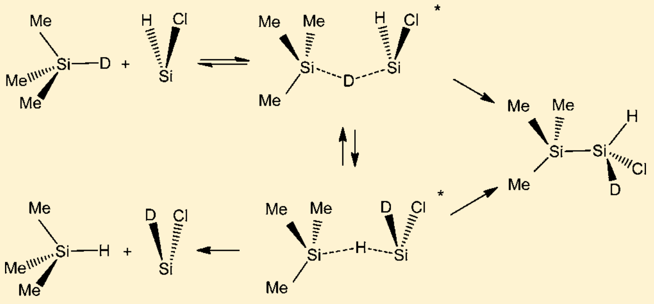
Supporting Information

ABSTRACT: Time-resolved studies of chlorosilylene, ClSiH, generated by the 193 nm laser flash photolysis of 1-chloro-1-silacyclopent-3-ene, have been carried out to obtain rate constants for its bimolecular reaction with trimethylsilane-*1-d*, Me_3SiD, in the gas phase. The reaction was studied at total pressures up to 100 Torr (with and without added SF_6) over the temperature range of 295–407 K. The rate constants were found to be pressure independent and gave the following Arrhenius equation: $\log[(k/(\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1})] = (-13.22 \pm 0.15) + [(13.20 \pm 1.00)\ \text{kJ mol}^{-1}]/(RT \ln 10)$. When compared with previously published kinetic data for the reaction of ClSiH with Me_3SiH, kinetic isotope effects, k_D/k_H, in the range from 7.4 (297 K) to 6.4 (407 K) were obtained. These far exceed values of 0.4–0.5 estimated for a single-step insertion process. Quantum chemical calculations (G3MP2B3 level) confirm not only the involvement of an intermediate complex, but also the existence of a low-energy internal isomerization pathway which can scramble the D and H atom labels. By means of Rice–Ramsperger–Kassel–Marcus modeling and a necessary (but small) refinement of the energy surface, we have shown that this mechanism can reproduce closely the experimental isotope effects. These findings provide the first experimental evidence for the isomerization pathway and thereby offer the most concrete evidence to date for the existence of intermediate complexes in the insertion reactions of silylenes.



INTRODUCTION

Kinetic isotope effects (KIEs) are a well-established diagnostic for chemical mechanisms, the most widely exploited variety being that of D-for-H substitution.[1] Values of k_H/k_D are normally in excess of unity,[1] and values as high as 8 can be accommodated by classical transition-state theory.[2] Even higher values can be found at low temperatures,[3] where tunnel effects become important.[4] Values less than unity (inverse isotope effects) are much less common and indicate something unusual about a mechanism. Pressure-dependent, gas-phase, unimolecular reactions can show inverse isotope effects,[5] and we have found examples in reverse association reactions.[6] Some recent examples of inverse isotope effects in the range of 0.4–0.8 in the field of transition-metal oxidative elimination reactions have caused some excitement,[1d,7] as well as a predicted value of 0.37 for the cyclopropylcarbinyl radical rearrangement at 20 K, where D-for-H substitution at the exomethylene carbon appears to increase, rather than reduce, the tunneling rate.[8] Until the present, the insertion reactions of silylenes into Si–H bonds have not been considered likely to produce unusual KIE values. Indeed, Conlin et al.[9] have obtained a value for k_H/k_D of 1.11 ± 0.12 in a study of $SiMes_2$ with Et_3SiD and Et_3SiH in solution using direct laser monitoring of the transient silylene, and Weber and colleagues[10] measured a value of 1.32 ± 0.19 for the related reaction of $SiMe_2$ + $n\text{BuMe}_2\text{SiH(D)}$ in cyclohexane solution using end-product analysis.

Silylenes are important because they are implicated in the thermal and photochemical breakdown mechanisms of silanes and organosilanes[11] as well as being key intermediates in chemical vapor deposition (CVD).[12] The insertion process of silylenes into Si–H bonds leading to the formation of disilanes is one of the most fundamental and widely studied reactions of

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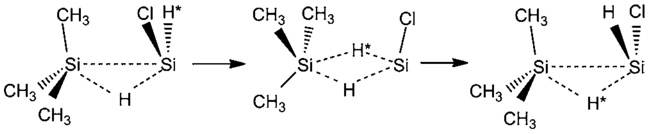
silylenes.[11] The mechanism of this process is thought to involve a weakly bound intermediate complex,[13−15] viz.

$$R_3SiH + SiXY \rightarrow R_3Si\cdots H\cdots SiXY \rightarrow R_3SiSiHXY$$

The first step consists of an association of the silylene with the substrate silane largely through interaction with the substrate H atom. The second step involves a rearrangement of the complex in which the silylene moiety straddles the Si−H bond in a relatively tight transition state before formally inserting into the bond. The evidence for this comes for the most part from the interpretation of gas-phase kinetic studies, allied with theoretical (ab initio) calculations. The theoretical argument in favor of such complexes is the existence of low-energy minima on the calculated potential energy surfaces[16−20] for these reactions, and the experimental evidence is the finding of negative activation energies,[16a−c,e,21] indicating the presence of low-energy secondary barriers which affect reaction rates. Despite these arguments, the experimental evidence may still be regarded as indirect. The complexes themselves have not been observed by any spectroscopic technique,[22−24] nor has any pathway unique to such a complex itself yet been identified. We report here an experiment, employing KIE measurements, which provides much stronger evidence of such a process.

Our choice for this experiment is based on findings from an earlier kinetic study of the reaction ClSiH + Me_3SiH.[16e] ClSiH reacts more slowly and selectively with silanes than does SiH_2,[16c] and the kinetic study of this reaction[16e] revealed a tight transition state ($A = 10^{-13.97}$ cm^3 molecule^{-1} s^{-1}) and significantly negative activation energy ($E_a = -12.6$ kJ mol^{-1}), indicating the strong likelihood of a complex. However, the significant finding was the prediction from quantum chemical calculations[16e] that not only does the reaction proceed via a complex, but the complex has a degenerate rearrangement process, indicated by the exchange of H and H* via a low-energy transition state in which both H atoms are coordinated to each Si atom as shown in Scheme 1. If correct, this indicates that the introduction of a D label would provide a means of lifting the degeneracy. Although the process cannot be observed directly, its consequences should be detectable since formation of the complex from its reactants is reversible, viz.

Scheme 1



$$ClSiH + Me_3SiH \rightleftharpoons Me_3SiH\cdots SiHCl$$

This fact is a necessary consequence of the low *A* factor and negative activation energy referred to above.[16e] Thus, the reaction of ClSiH + Me_3SiD should lead to H/D exchange, and the result of this, allied with the reversibility of the first step, should provide a rapid sink pathway leading to formation of Me_3SiH + ClSiD. Provided the barrier to the complex rearrangement process is low enough, this extra pathway will lead to an enhanced rate for reaction of ClSiH with Me_3SiD compared with Me_3SiH. The calculated quantum chemical barrier[16e] suggests that this should be so, and the present study was undertaken to obtain experimental evidence for this.

Our preliminary findings,[25] limited to room temperature (295 K) and a pressure of 5 Torr, gave a value for k_D/k_H of 7.4 ± 0.4[26] (an inverse isotope effect of 0.135 ± 0.007). An approximate Rice−Ramsperger−Kassel−Marcus (RRKM) model showed that this was consistent with the quantum chemical energy surface. The questions that remain, however, include whether the k_D/k_H value is mainly entropic or enthalpic in origin and to what extent any intermediate complex is collisionally stabilized, thus opening up the possibility of a longer lived species. To these ends we have extended our measurements to cover the temperature range of 295−407 K and the pressure range of 5−100 Torr. We have also extended the range of our RRKM model to explore the effects of different barrier heights and well depths on the KIE predictions for this process and to see whether experiment can help refine further its energy surface.

EXPERIMENTAL SECTION

Rate Measurements. The apparatus and equipment for these studies have been described in detail previously.[16b,27] Only essential and brief details are therefore included here. ClSiH was produced by flash photolysis of 1-chlorosilacyclopent-3-ene (CSCP) using a Coherent Compex 100 exciplex laser operating at 193 nm (ArF fill). Photolysis laser pulses (energies ca. 50−70 mJ) were fired into a variable-temperature quartz reaction vessel with demountable windows at right angles to its main axis. ClSiH concentrations were monitored in real time by means of a Coherent Innova 90-5 argon ion laser. The monitoring laser beam was multipassed 36 times along the vessel axis, through the reaction zone, to give an effective absorption path length of ca. 1.5 m. A portion of the monitoring beam was split off before entering the vessel for reference purposes. The monitoring laser was tuned to the 457.9 nm line, coincident with the known transition $\tilde{A}^1A''(0,2,0) \leftarrow \tilde{X}^1A'(0,0,0)$ in the ClSiH vibronic band.[28] Light signals were measured by a dual photodiode/differential amplifier combination, and signal decays were stored in a transient recorder (Datalab DL 910) interfaced to a BBC microcomputer. This was used to average the decays of typically five photolysis laser shots (at a repetition rate of 1 Hz or less). 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 the first-order rate coefficients, k_{obsd}, for removal of ClSiH in the presence of a known partial pressure of Me_3SiD.

Gas mixtures for photolysis were made up containing 13−30 mTorr of the transient precursor, CSCP, and variable pressures of Me_3SiD. An inert diluent, SF_6, was added to give a total pressure of 5 Torr in most experiments. Pressure was measured with a capacitance manometer (MKS Baratron).

1-Chlorosilacyclopent-3-ene was prepared as described previously.[29] Me_3SiD was prepared by standard means.[30] Its purity was checked by IR (<1.2% Me_3SiH). Sulfur hexafluoride, SF_6 (no GC-detectable impurities), was from Cambrian Gases. All gases used in this work were deoxygenated thoroughly prior to use.

Quantum Chemical Calculations. The electronic structure calculations were performed with the Gaussian 03, revision C.02, software package.[31] The DFT calculations, including the finding and verification of stationary points, were done with the B3LYP functional[32] using the 6-31G(d) basis.[33] All the structures obtained were verified by examination of their Hessian matrix as minima (all frequencies real) or transition states (one imaginary frequency). The identities of transition states for particular reactions were established by B3LYP calculations along the minimum-energy paths (intrinsic reaction coordinate, IRC) connecting them with local minima. The standard G3(MP2)//B3LYP/6-31G(d)[34] method (denoted G3MP2B3 for short) was employed to determine final energies for all minimum-energy species and transition states of interest. For all stationary points, enthalpies, entropies, and Gibbs free energies at 298 K were also calculated using harmonic oscillator and rigid rotor models.

■ RESULTS

Kinetic Measurements. It was independently verified during preliminary experiments that, in a given reaction mixture, k_{obsd} values were not dependent on the exciplex laser energy (50−70 mJ/pulse routine variation) or number of photolysis shots. Because static gas mixtures were used, tests with up to 10 shots were carried out. The constancy of k_{obsd} (five shot averages) showed no effective depletion of reactants in any of the systems. The sensitivity of detection of ClSiH was high but decreased with increasing temperature. Precise concentrations of ClSiH are not known, but are not required since the decay kinetics were pseudo-first-order; a rough estimate would be somewhere within the range of 0.1−1.0 mTorr (ca. 10^{13} molecules cm^{-3}). Increasing quantities of precursor were required at higher temperatures. However, at any given temperature precursor pressures were kept fixed to ensure a constant (but fairly small) contribution to k_{obsd} values of decay by reaction of ClSiH with the precursor. A series of experiments were carried out at five temperatures in the range of 295−407 K. The temperatures and the temperature range were selected to match those of our earlier study of ClSiH with Me_3SiH.[16e] At each temperature, a number of runs (at least eight) at different Me_3SiD partial pressures were carried out. The results of these experiments are shown in Figure 1, which demonstrates the linear dependence of k_{obsd} on [Me_3SiD], as expected for second-order kinetics. The second-order rate constants, k_D, obtained by least-squares fitting to these plots, are given in Table 1. The error limits are single standard deviations. The total pressure in these experiments was 5 Torr, maintained by addition of SF_6. A few experiments with pressures up to 100 Torr (SF_6) gave no change in value of k_{obsd}, thus showing that the rate constants were not pressure dependent.

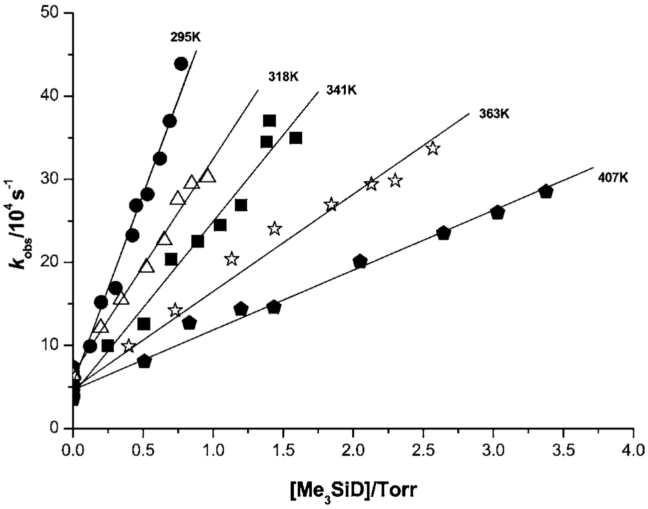


Figure 1. Second-order plots for the reaction of ClSiH + Me_3SiD at different temperatures (indicated).

Table 1. Experimental Second-Order Rate Constants for ClSiH + Me_3SiD (k_D) and ClSiH + Me_3SiH (k_H)[a]

T/K	k_D/(10^{-12} cm^3 molecule^{-1} s^{-1})	T/K	k_H/(10^{-12} cm^3 molecule^{-1} s^{-1})	k_D/k_H
295	13.90 ± 0.53	297	1.876 ± 0.065	7.41 ± 0.38
318	8.52 ± 0.21	316	1.304 ± 0.041	6.53 ± 0.26
341	7.33 ± 0.31	344	1.128 ± 0.062[b]	6.49 ± 0.45
363	4.45 ± 0.17	368	0.657 ± 0.029	6.77 ± 0.40
407	3.05 ± 0.09	407	0.480 ± 0.013	6.35 ± 0.25

[a] From ref 16e. [b] Replaces earlier value;[16e] see the text.

Figure 2 shows an Arrhenius plot of the rate constants. The resulting equation is

$$\log[k_D/(\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1})] = (-13.22 \pm 0.15) + [(13.20 \pm 1.00)\ \text{kJ mol}^{-1}]/(RT \ln 10)$$

Uncertainties are again quoted as single standard deviations.

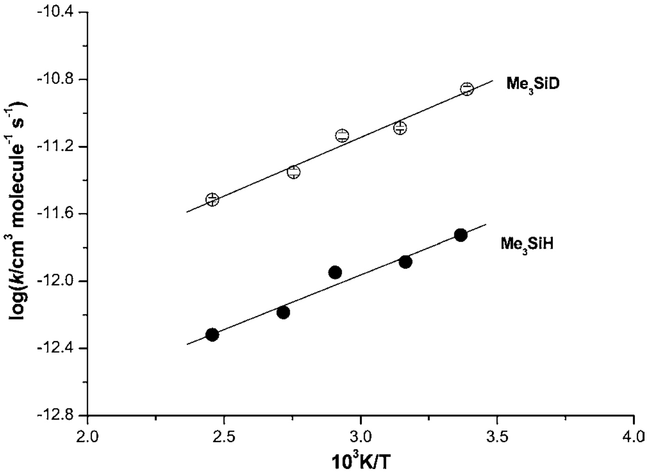


Figure 2. Arrhenius plots for ClSiH + Me_3SiD and ClSiH + Me_3SiH.

In addition to these experiments, the reaction between ClSiH and Me_3SiH was also reinvestigated at 344 K because the previous rate constant[16e] (7.03 × 10^{-13} cm^3 molecule^{-1} s^{-1}) was in poor agreement with the temperature trend of other values. The new second-order plot value (1.13 × 10^{-12} cm^3 molecule^{-1} s^{-1}) is shown in Table 1, and the revised Arrhenius plot is included in Figure 2. The revised Arrhenius parameters are given in Table 2. Also shown, for comparison purposes, are those obtained previously[16e] together with those for ClSiH + Me_3SiD and SiH_2 + Me_3SiH.[16c]

Table 2. Arrhenius Parameters for Chlorosilylene and Silylene Insertion Reactions with Me_3SiD/H

reaction	log[A/(cm^3 molecule^{-1} s^{-1})]	E_a/(kJ mol^{-1})	ref
ClSiH + Me_3SiD	−13.22 ± 0.15	−13.20 ± 1.00	this work
ClSiH + Me_3SiH	−13.90 ± 0.21	−12.43 ± 1.36	this work
ClSiH + Me_3SiH	−13.97 ± 0.25	−12.57 ± 1.64	16e
SiH_2 + Me_3SiH	−10.37 ± 0.10	−4.65 ± 0.76	16c

The kinetic isotope effects were calculated as k_D/k_H[26] from the individual rate constants and are also shown in Table 1. Where temperatures of each study differed slightly, values were averaged (for modeling purposes (see later)). An Arrhenius-type plot of these gives

$$\log(A_D/A_H) = 0.67 \pm 0.09 \quad \text{and}$$

$$E_a(\text{D}) - E_a(\text{H}) = -1.02 \pm 0.56\ \text{kJ mol}^{-1}$$

Quantum Chemical Calculations. The results of these calculations have been reported previously for the ClSiH +

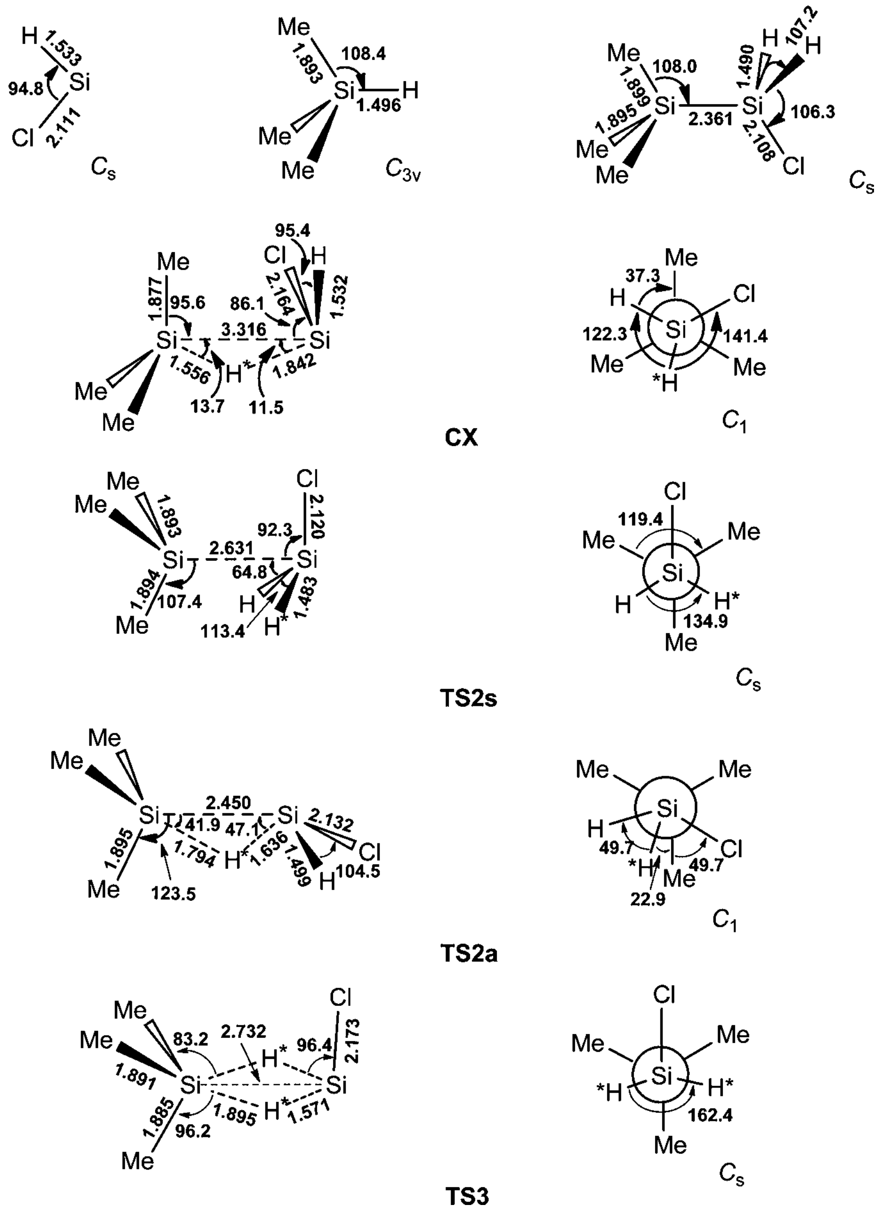


Figure 3. Molecular geometries of important species on the ClSiH + Me_3SiH potential energy surface at the G3MP2B3 level. Bond lengths are in angstroms and angles in degrees.

Table 3. Electronic Energies,[a] Enthalpies,[a] and Entropies[b] of the Complex, Transition States, and Product for Reaction of ClSiH + Me_3SiH/D Calculated at the G3MP2B3 Level

	ClSiH + Me_3SiH			ClSiH + Me_3SiD		
species	Δ*E*°(0 K)	Δ*H*°(298 K)	*S*°(298 K)	Δ*E*°(0 K)	Δ*H*°(298 K)	*S*°(298 K)
reactants	0	0	587.2	0	0	590.4
CX	−36.68	−36.11	461.8	−36.42	−35.85	465.0
TS2s	+10.83	+10.39	440.3	+11.60	+11.11	443.4
TS2a	−9.22	−11.24	432.3	−8.36	−10.45	434.8
TS3	−21.79	−23.71	430.9	−21.12	−23.18	433.1
product	−179.68	−180.50	441.1	−179.50	−180.31	444.6

[a] Values in kilojoules per mole. [b] Values in joules per kelvin per mole.

Me_3SiH reaction system,[16e] so only a brief summary is presented here. The calculations (G3MP2B3 level) reveal the presence of an intermediate complex as well as provide the structures of the separated reactants and product Me_3SiSiH_2Cl and several transition states. The structures are shown in Figure 3.[35] The complex (CX) has a structure in which the attached ClSiH moiety has a *syn* configuration to the Si−H bond in the substrate, but it is unsymmetrical (C_1 symmetry), so there are two (mirror image) minima. There are three transition states, TS2s and TS2a, which lead from the complex to the product, and TS3, which connects the two forms of the intermediate complex. TS2s, while retaining the *syn* configuration, has essentially transferred a H atom (H* in Figure 3) from the substrate to silylene so that it is now more symmetric (C_s) and rather resembles a radical pair, with the SiH_2Cl fragment in the process of inverting. This process is sufficiently energy demanding that TS2s has a positive energy relative to the reactants and cannot provide an accessible pathway for the rearrangement. TS2a has the ClSiH in an *anti* configuration and, although slightly unsymmetric, has a negative energy and therefore provides the lower energy route to the disilane product. TS3, not surprisingly, is of C_s symmetry, with the two bridging H atoms (both H* in Figure 3) almost coplanar with the two Si atoms. The energies and enthalpies of the stationary points are given in Table 3. Data for the ClSiH with both Me_3SiH and Me_3SiD are given to indicate the magnitude of the small differences arising from the inclusion of zero point and thermal energies in the two systems. The calculated energy surface is shown in Figure 4.

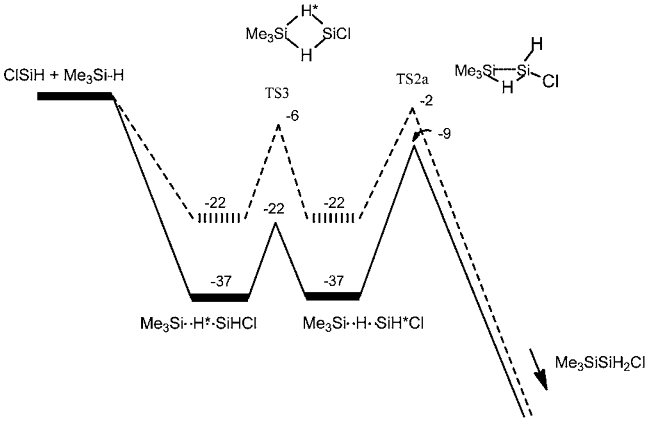


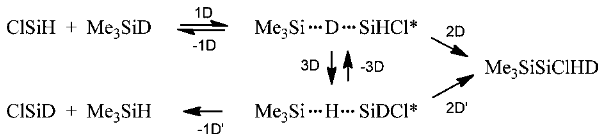
Figure 4. Potential energy surfaces for the reaction of ClSiH + Me_3SiH: solid line, calculated at the G3MP2B3 level; dashed line, calculated to fit the RRKM-calculated KIE. Energy values in kilojoules per mole.

RRKM Calculations. RRKM theory is conventionally used to calculate the pressure dependence of unimolecular dissociation reactions and their reverse association processes.[36] We have frequently used it in this context to model the pressure dependences of association reactions of silylenes.[6,16b,c,37] It can equally be used to model chemical activation systems, where intermediates are formed with excess energy and population distributions are different from those of thermal reactions. This is the case in the present reaction system. From the quantum chemical results the proposed mechanism is shown in Scheme 2. In this scheme $Me_3Si\cdots D\cdots SiHCl^*$ and $Me_3Si\cdots H\cdots SiDCl^*$ represent the energized species of the two forms of the intermediate complex. This mechanism does not include possible stabilization steps for the intermediates. A stationary state treatment of this mechanism (see the Supporting Information) leads to an expression for the overall second-order rate constant, k_D, of

$$k_D = k_{1D}/(2 + k_{-1D}/k_{3D}) \tag{1}$$

In the case of the reaction of ClSiH with Me_3SiH, already studied,[16e] the mechanism shown in Scheme 3 is simpler.

Scheme 2



Scheme 3

$$\mathrm{ClSiH + Me_3SiH \underset{-1H}{\overset{1H}{\rightleftharpoons}} Me_3Si\cdots H\cdots SiHCl^* \xrightarrow{2H} Me_3SiSiH_2Cl}$$

For this mechanism the steady-state analysis leads to an expression for the overall second-order rate constant of

$$k_H = k_{1H}/(1 + k_{-1H}/k_{2H}) \tag{2}$$

Thus, the KIE of interest here, viz., the comparison of second-order rate constants for the disappearance of ClSiH in the presence of Me_3SiD and Me_3SiH, is the following:

$$\mathrm{KIE} = \frac{k_D}{k_H} = \frac{k_{1D}}{k_{1H}}\,\frac{1 + k_{-1H}/k_{2H}}{2 + k_{-1D}/k_{3D}} \tag{3}$$

It seems reasonable to suppose, since step 1 in both systems is barrierless, that k_{1H} and k_{1D} will be close in magnitude and that to a good approximation[38]

$$\mathrm{KIE} = \frac{k_D}{k_H} = \frac{1 + k_{-1H}/k_{2H}}{2 + k_{-1D}/k_{3D}} \tag{4}$$

We have employed this expression in the calculations carried out here. The RRKM exercise was thus based on the unimolecular decomposition of the intermediate complexes via two or three channels. This required transition-state models for steps −1H, 2H, −1D, 3D, and also 2D since the latter would also be occurring in the ClSiH + Me_3SiD system. The vibrational assignments and geometries for TS(2H), TS(2D), and TS(3D) were taken from the quantum chemical calculations as were those for the reacting species, i.e., the complexes themselves ($Me_3Si\cdots H\cdots SiHCl$ and $Me_3Si\cdots D\cdots SiHCl$). Assignments for TS(−1H) and TS(−1D) were not available from the quantum chemical calculations since the processes are dissociative and without a specifically located energy maximum. They were therefore assigned empirically. First, values for the *A* factors, A_{-1}, were calculated at each temperature using $\ln(A_1/A_{-1}) = \Delta S^\circ_{1,-1}/R$.[39] Values for $\Delta S^\circ_{1,-1}$ were obtained from the quantum chemical calculations, and values for A_1 were assumed to be the same as those of the rate constants for the reaction of SiH_2 with Me_3SiH.[16c] This is justified on the grounds that SiH_2, unlike ClSiH, reacts very fast with Me_3SiH (at close to the collision rate), and calculations suggest that, for this reaction, formation of the intermediate complex $Me_3Si\cdots H\cdots SiH_2$, rather than its rearrangement, is the rate-determining step. With the resulting values for A_{-1}, the vibrational assignment of TS(−1) was obtained by adjusting the transitional mode wavenumber values to get a match for the entropy of activation, $\Delta S^{\ddagger}_{-1}$, using

$$A_{-1} = \frac{ekT}{h}e^{\Delta S^{\ddagger}_{-1}/R}$$

The values for $\log A_1$, $\log A_{-1}$ and $\Delta S^{\ddagger}_{-1}$ are shown in Table 4. The small temperature dependence of A_{-1} builds in variational behavior, a common feature of these reactions.[37] The vibrational assignments[40] for these transition states

Table 4. *A* Factors for Formation and *A* Factors and Entropies of Activation for Decomposition of the Intermediate Complexes in Step −1

quantity	*T* = 297 K	*T* = 317 K	*T* = 342 K	*T* = 365 K	*T* = 407 K
$\log[A_1/(\mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{s}^{-1})]$	−9.55	−9.60	−9.66	−9.71	−9.77
$\log(A_{-1}/\mathrm{s}^{-1})$	15.96	15.91	15.85	15.80	15.74
$\Delta S^{\ddagger}_{-1}/(\mathrm{J\ K^{-1}\ mol^{-1}})$	52.3	50.8	49.1	47.6	45.5

together with those for reaction steps 2 and 3 are given in the Supporting Information. As well as vibrational assignments, the TS models required values for E_0, i.e., critical energies for each channel and also a collisional deactivation model. For the latter we used a stepladder model with $\langle \Delta E \rangle_{\mathrm{down}} = 1000\ \mathrm{cm}^{-1}$. This follows previous practice when, as here, SF_6 is the bath gas. The minimum input energy of each complex corresponds to $E_0(-1)$, its redissociation energy. However, the complexes contain additional thermal energy. This was calculated as a distribution function using $f(E) = \rho(E) \exp[-(E - E_0(-1))/RT]$ where, at each energy level E above $E_0(-1)$, $\rho(E)$ corresponds to the species density of states (calculated by the RRKM program) and $f(E)$ is the resulting population (which was normalized by the program).

In the particular calculations undertaken, k values for each channel, and thereby KIE values, were obtained at each of the five temperatures of interest. This was carried out for several different E_0 scenarios. These included one with the original quantum chemical values of E_0 for each channel, as well as others with E_0 values modified to approach the conditions and results of the experiments. It should be noted that, for each set of calculations, E_0 values for the D and H species differ from one another because of their different zero point vibrational energies.

The first set of calculations, based on the quantum chemical energy surface, gave the KIE values shown in Table 5a. Since these do not match the experimental values of Table 3 and are furthermore pressure dependent, unlike experiment, we modified the E_0 values as follows:

(i) $E_0(-1)$ was reduced in magnitude to reduce the stabilization of the complex (which causes the pressure dependence effect).

(ii) $E_0(2\mathrm{H})$ was adjusted empirically to ensure an approximate value for $k_{2\mathrm{H}}/k_{-1\mathrm{H}}$ in the range from 0.004 to 0.007. This numerical range corresponds to that required to fit the rate constant values[16e] for ClSiH + Me$_3$SiH assuming step 1 occurs at close to the collision rate.

(iii) $E_0(3\mathrm{D})$ was adjusted empirically to ensure an approximate value for $k_{3\mathrm{D}}/k_{2\mathrm{H}}$ of ca. 7. This corresponds closely to the average measured isotope effect.

Table 5. RRKM Theory Calculated Values for $k_{\mathrm{D}}/k_{\mathrm{H}}$ (KIE) Using the Full Mechanism

P/Torr	*T* = 297 K	*T* = 317 K	*T* = 342 K	*T* = 365 K	*T* = 407 K
(a) Using Quantum Chemical Calculated Critical Energies[a]					
30	5.03	5.00	4.98	5.23	5.82
10	3.18	3.14	3.15	3.36	3.86
3	2.04	2.06	2.10	2.28	2.66
(b) Using Empirically Adjusted Critical Energies[b]					
30	8.02	7.46	6.93	6.24	5.52
10	7.89	7.47	6.99	6.34	5.72
3	7.08	6.77	6.39	5.79	5.32

[a]$E_0(-1)$[c] = 3066[d] (3044),[e] $E_0(2)$[c] = 2295[d] (2346),[e] and $E_0(3)$[c] = 1279.[e] [b]$E_0(-1)$[c] = 1866[d] (1844),[e] $E_0(2)$[c] = 1695[d] (1746),[e] and $E_0(3)$[c] = 1380.[e] [c]Values in inverse centimeters. [d]ClSiH + Me$_3$SiH. [e]ClSiH + Me$_3$SiD.

The $k_{\mathrm{D}}/k_{\mathrm{H}}$ values obtained with these modified E_0 values are shown in Table 5b. The altered E_0 values themselves are given in the footnotes. It is worth pointing out that while $E_0(-1)$ and $E_0(2)$ are reduced, $E_0(3)$ is increased slightly. Other combinations of E_0 values were tried, but the ones shown gave the optimal fit.

Additionally and to verify the importance of step 3, $k_{\mathrm{D}}/k_{\mathrm{H}}$ values were also calculated without step 3. The results are shown in Table 6.[41]

Table 6. RRKM Theory Calculated Values for $k_{\mathrm{D}}/k_{\mathrm{H}}$ (KIE) without Step 3[a]

P/Torr	*T* = 297 K	*T* = 317 K	*T* = 342 K	*T* = 365 K	*T* = 407 K
30	0.47	0.46	0.46	0.46	0.46
10	0.44	0.44	0.44	0.43	0.43
3	0.43	0.43	0.43	0.41	0.41

[a]Using a modified energy surface; see Table 5, footnote *b*.

■ DISCUSSION

Kinetic Findings and Comparisons. The main experimental objective of the present study was to measure the gas-phase rate constants and their temperature dependence for the reaction of ClSiH with Me$_3$SiD and thereby obtain $k_{\mathrm{D}}/k_{\mathrm{H}}$ and its temperature dependence by comparison with earlier data for ClSiH + Me$_3$SiH.[16e] This has been achieved over the temperature range of 295−407 K. This is the first reported gas-phase study of this isotope effect and its temperature dependence, as well as the first of any gas-phase study for a Si−D (Si−H) insertion reaction. The results, given in Tables 1 and 2, show that the rate constants for ClSiH + Me$_3$SiD decrease with increasing temperature similarly to those for ClSiH + Me$_3$SiH. The Arrhenius parameters for the two reactions are fairly similar, with *A* factors ca. 3 orders of magnitude lower than that for SiH$_2$ + Me$_3$SiH[16c] and activation energies significantly more negative than those for SiH$_2$ + Me$_3$SiH.[16c] These features indicate the strong likelihood of intermediate complexes in the present reaction system.

The $k_{\mathrm{D}}/k_{\mathrm{H}}$ value of ca. 7 is not only very large but almost constant with temperature (T), although it decreases slightly as T increases. Its value is significantly greater than the room temperature, solution values of 0.90 ± 0.10 for the reaction of SiMes$_2$ with Et$_3$SiD/Et$_3$SiH[9] or 0.76 ± 0.11 for the reaction of SiMe$_2$ with *n*BuMe$_2$SiH/*n*BuMe$_2$SiD.[10] Since a value of less than unity would be expected if the mechanism had been a straightforward (single-step) process,[1] this clearly shows that the present reaction has greater complexity.

The small temperature dependence of $k_{\mathrm{D}}/k_{\mathrm{H}}$ suggests that the energy barriers to the rate-controlling steps for the Si−D and Si−H insertion processes differ by only 1.0 kJ mol^{-1}. While the energy difference is clearly small, it should not be taken too literally since, as we argue in this paper, the behavior of the intermediate species is that of a chemically activated, rather than thermal, intermediate. Similarly the *A* factor ratio, which would mean that $\Delta S^{\ddagger}_{\mathrm{D}} - \Delta S^{\ddagger}_{\mathrm{H}} = -13\ \mathrm{J\ K^{-1}\ mol^{-1}}$ in a purely thermal reaction, cannot be taken too literally.

The lack of a pressure dependence of the rate constants allows the elimination of one mechanistic possibility, viz.

$$\begin{tikzcd} \mathrm{ClSiH + Me_3SiD} \arrow[r, shift left] & \mathrm{Me_3SiSiClHD^*} \arrow[l, shift left] \arrow[r] \arrow[d, "+M"] & \mathrm{Me_3SiH + ClSiD} \\ & \mathrm{Me_3SiSiClHD} & \end{tikzcd}$$

where $Me_3SiSiClHD^*$ represents the vibrationally excited disilane product. If this process were to occur, it would indicate that collisional stabilization of the disilane product was incomplete and the measured rate constant would be pressure dependent. The same lack of pressure dependence was found for ClSiH + Me_3SiH studied previously.[16e]

Quantum Chemical Calculations and the Mechanism. The results obtained here for the energy surface and the intermediate species involved in the ClSiH + Me_3SiH reaction have been discussed in detail previously.[16e] In summary, the intermediate CX has a structure with the attacking ClSiH moiety in a *syn* conformation to the substrate Si−H bond, while the lower energy (favored) transition state (TS2a) has an *anti* conformation. What is new here are the details for TS3 and the isotopic differences. TS3 has a more symmetric C_s structure with an almost planar Si···H···Si···H··· ring, clearly showing the geometric equivalence of the H atoms originating from ClSiH and Me_3SiH. The low energy (−21.8 kJ mol^{-1}) and enthalpy (−23.7 kJ mol^{-1}) indicate its stability and capability to allow easy exchange of the H atoms in the ring. In our earlier paper,[16e] calculations of the energy surface for the similar reaction of ClSiH with $MeSiH_3$ (at the same G3MP2B3 level) revealed an equivalent TS3-like transition state with an energy of −6.5 kJ mol^{-1} and an enthalpy of −9.8 kJ mol^{-1}. These negative values indicate that exchange reactions are also potentially possible in that reaction system as well (and presumably also ClSiH + Me_2SiH_2). The differences in energy and enthalpy between the two systems show that these TS3-like transition states are stabilized by Me-for-H substitution in the substrate silane, thus making ClSiH + Me_3SiH/Me_3SiD a particularly favorable reaction system for achieving this exchange experimentally. The first theoretical evidence for such exchange processes was obtained by Swihart and Carr,[42] who found similar four-center transition states for exchange reactions of the type

$$\mathrm{ClSiH + SiH_{\mathit{n}}Cl_{4-\mathit{n}} \rightleftharpoons SiH_2 + SiH_{\mathit{n}-1}Cl_{5-\mathit{n}}}$$

$$\mathrm{ClSiH + SiH_{\mathit{n}}Cl_{4-\mathit{n}} \rightleftharpoons SiCl_2 + SiH_{\mathit{n}+1}Cl_{3-\mathit{n}}}$$

These processes were calculated to have energy barriers several kilocalories per mole above those for the insertion processes (G2 and/or G2MP2 level), suggesting that Cl atom substitution in the substrate silane may not be as effective at stabilizing these TS3-like transition states as Me group substitution. It should be noted, however, that the exchange processes in our system are H-for-H(D), whereas those found by Swihart and Carr[42] are H-for-Cl. Therefore, strict comparisons are not possible. Recent calculations by some of us[43] have shown that, in the ClSiH + H_2 reaction system, H-for-H exchange reactions are less energy demanding than H-for-Cl. This latter system may also not be a good guide because it is not accompanied by a Si−H insertion process. All this suggests that a search for experimental evidence for these processes in the ClSiH + chlorosilane systems might well be worthwhile to extend our knowledge of substituent effects on the exchange process discovered in the present work. There is clearly also more theoretical work to be done to help identify the factors which affect the stabilities of these transition states.

RRKM Calculations and the Kinetic Isotope Effect. Our objective was to reproduce the experimental value of k_D/k_H and its temperature dependence by means of RRKM calculations based on a plausible potential energy (PE) surface. Within the limitations of some approximations, this has been achieved. The starting point for the calculations was the quantum chemical PE surface. When this was used, it was quickly apparent that agreement with experiment was not achieved (Table 5a). The most striking difficulty was that although the k_D/k_H values were substantially larger than 1, they were significantly pressure dependent, in disagreement with experiment. An examination of the results showed this to arise from varying degrees of collisional stabilization of the complexes at different pressures up to a maximum value of 47% (ClSiH + Me_3SiH, 30 Torr, 297 K). Since this clearly depended on the energy well depth of the intermediate complex, we adjusted its value empirically, together with the values of the energy barriers via the two reaction channels. This was done by maintaining the same zero point energy differences between the D and H species (as obtained from the quantum chemical calculations). The resulting best fit values (Table 5b) are in reasonable agreement with experiment (Table 1) and only slightly pressure dependent. The maximum collisional stabilizations of complexes obtained from the calculations for these conditions were 7.3% (ClSiH + Me_3SiH system, 297 K) and 5.3% (ClSiH + Me_3SiD, 297 K). Although these are now quite small, it is possible that further refinement of the energy surface could improve agreement slightly. However, the rate constant eq 1, and therefore the k_D/k_H eq 4, involve several approximations arising from simplifications of the steady-state treatment of Scheme 2, such as treating the initial and secondary complexes as having the same entropy and kinetic constants, so we considered such refinement not worthwhile. Separate checks on the assumptions and approximations underlying eq 4 showed the values of Table 5b to be reliable within a maximum uncertainty of ±15%. Similar, i.e., relatively small, uncertainties surround the values of k_D/k_H (Table 6) calculated for the mechanism without the participation of step 3. Such uncertainties are negligible compared to the large differences between the values of Tables 5b and 6. It is therefore clear that a mechanism without an additional removal step, or steps, for the initially formed complex cannot account for the observed isotope effect. It is also clear, via the kinetic modeling, that the proposed mechanism is able to account for the observed isotope effect as well as its only very slight temperature dependence to a very good approximation.

The adjustments of energy barriers and the intermediate complex well depth required to model the isotope effect are depicted in the PE surface shown in Figure 4. The comparison with the quantum chemical PE surface shows a qualitatively similar pattern of barriers. In quantitative terms, the complex well depth is reduced by 14.3 kJ mol^{-1} (39%), the secondary barrier, $E_0(2)$, is reduced by 7.1 kJ mol^{-1} (26%), and the complex label-scrambling barrier, $E_0(3)$, is increased by 1.2 kJ mol^{-1} (8%). It is worth pointing out that the increase of $E_0(3)$ relative to $E_0(-1)$ and $E_0(2)$, is a necessary consequence of the very small temperature dependence of k_D/k_H. Indeed $E_0(3)$ cannot be too small or step 3 would cease to be the rate-controlling process for ClSiH + Me_3SiD. These necessary changes in the energy barrier values are not particularly large, and we regard the differences as lying within reasonable bounds of the accuracy of the G3MP2B3 method.

One further modeling assumption deserves comment, that is, the use of the values of A_1 (Table 4) corresponding to those of the rate constants for SiH_2 + Me_3SiH.[16c] We have justified this on the grounds that, in this reaction, the first step in the mechanism is rate determining. However, it is not known whether, despite this, the values for k_1 for ClSiH + Me_3SiH should be identical in magnitude with these. Two arguments suggest that they should be high. First, the bottleneck in the overall insertion reaction of ClSiH with Me_3SiH is, without doubt, the second step (from the Arrhenius parameters of Table 2). Secondly, we found that the use of lower values for A_{-1}, implying lower values for A_1, produced poorer agreement with measured isotope effect values (see the preliminary communication[25]). This supports the view that, in comparing the Si−H insertion behavior of ClSiH and SiH_2, the substantial reduction of reactivity brought about by the Cl-for-H substitution arises almost entirely in the second step of the reaction, viz., the rearrangement of the complex rather than its formation. A collision theory estimate of the value of the encounter rate constant is 5.87×10^{-10} cm^3 $molecule^{-1}$ s^{-1} (see the Supporting Information), so this suggests that ClSiH reacts with Me_3SiH at ca. 48% of the collision rate at 298 K.

SUMMARY AND CONCLUSION

We have measured a uniquely high value for the kinetic isotope effect, k_D/k_H, in the reaction of ClSiH with Me_3SiD (Me_3SiH). We have shown that its value cannot be accounted for by the normal insertion mechanism alone. Quantum chemical calculations reveal not only the presence of the intermediate complex, but an unusual scrambling mechanism of the complex, whose degeneracy is lifted by the use of the D label. RRKM calculations show that, after necessary but still relatively small changes in the values for the energy barriers involved, the values of k_D/k_H, including its temperature dependence, can be reproduced. One prediction, viz., that the exchange reaction should lead to the formation of ClSiD, we have not been able to verify, because (unfortunately) ClSiD is not detectable in our reaction system.[44] The possibility that rate enhancement in ClSiH + Me_3SiD could occur via chemically activated decomposition of the vibrationally excited disilane product is eliminated by the lack of the overall pressure dependence of the measured rate constants. These findings significantly increase our confidence in the involvement of intermediate complexes in the Si−H insertion reaction of silylenes.

ASSOCIATED CONTENT

Supporting Information

Derivation of eqs 1−3, full microscopic reversibility equation, values for the vibrational wavenumbers for the silylene adduct (intermediate complexes), TS(−1H), TS(2H), TS(−1D), TS(2D), and TS(3D), collision number parameters, and quantum chemical energies, imaginary wavenumbers, and atomic coordinates for all species. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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(40) A reviewer has pointed out that some of the low-wavenumber vibrations might more realistically be modeled as internal rotations. The only obvious potential internal rotations in the structures for TS2 and TS3 are those of the Me groups in the Me_3Si part of the molecules. However, since these are common to both transition states, we do not think the calculated isotope effects will be affected.

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(44) Unlike ClSiH, ClSiD has no vibronic band coincident with any line of our Ar ion laser monitor.