# A dramatic isotope effect in the reaction of ClSiH with trimethylsilane-1-d: experimental evidence for intermediate complexes in silylene Si-H(D) insertion reactions

Article

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# A Dramatic Isotope Effect in the Reaction of ClSiH with Trimethylsilane-1-d: Experimental Evidence for Intermediate Complexes in Silylene Si-H(D) Insertion Reactions

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**ABSTRACT:** A kinetic isotope effect ($k_D/k_H$) of 7.4 has been found for the reaction of chlorosilylene with trimethysilane (Me$_3$SiD vs Me$_3$SiH). Such a value can be accounted for by theoretical modelling, but only if an internal rearrangement of the initially form complex is included in the mechanism. This provides the first concrete evidence for such complexes.

The insertion reaction of silylenes into Si-H bonds is one of the fundamental and most widely studied reactions of silylenes.[1] The mechanism of this process is thought to involve weakly bound intermediate complexes.[2] The evidence for this comes largely from the interpretation of gas-phase kinetic studies, allied to theoretical (ab initio) calculations. The main arguments in favour of such complexes are the existence of low energy minima on the calculated potential energy surfaces[3] for such reactions and the experimental finding of negative activation energies[3,4]. Despite these arguments the experimental evidence may still be regarded as inconclusive. The complexes themselves have not been seen directly nor has any process unique to the complex itself been identified. We report here an experiment which provides unambiguous evidence of such a process.

The basis of our choice of this experiment was the prediction from ab initio calculations[5] that, in the reaction of ClSiH with Me$_3$SiH, not only does the reaction proceed via a complex, but the complex has a degenerate rearrangement process as shown in scheme 1 below, 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.
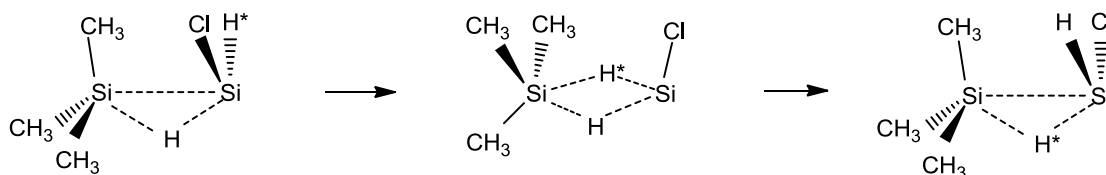
Scheme 1

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 (the complex has no known spectroscopic signature), its consequences should be detectable, since formation of the complex from its reactants is reversible, viz

$$ClSiH + Me_3SiH = Me_3SiH \cdot\cdot SiHCl$$
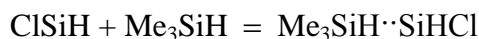
This fact is a necessary consequence of the low $A$ factor and negative activation energy found in our earlier kinetic study of this reaction.[5] Thus an investigation of the reaction of ClSiH + Me$_3$SiD should lead to H/D exchange and reveal the occurrence of the process

$$ClSiH + Me_3SiD \rightarrow Me_3SiH + ClSiD$$
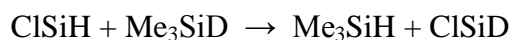
We report here studies of the kinetics of the gas phase reaction between ClSiH and Me$_3$SiD using laser flash photolysis. Details of the technique are given in our earlier review article.[2] ClSiH was made by excimer laser photolysis of 1-chlorosilacyclopent-3-ene[6] at 193 nm. ClSiH was monitored by means of a CW Argon Ion laser tuned to its known absorption at 457.9 nm.[6] Me$_3$SiD was prepared by standard means.[7] Experiments were carried out in a spectrosil quartz reaction vessel and signal decays (exponential) were collected and stored in a transient recorder. These yielded values for the pseudo first order rate constant, $k_{obs}$. A set of experiments was undertaken using different pressures of Me$_3$SiD. The results are shown in the Figure. The good linearity of the plot indicates that the reaction obeys second order kinetics. Also shown is the plot for ClSiH + Me$_3$SiH obtained previously.[5] The gradients of these plots yield values for the rate constants of $(1.395 \pm 0.052) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Me$_3$SiD) and $(1.876 \pm 0.065) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Me$_3$SiH), thus giving a kinetic isotope effect value of $k_D/k_H = 7.4 \pm 0.4$. Such a value is far in excess of the expectation of a value of less than one[8-10] for a direct insertion process (ie leading to Me$_3$SiSiClHD or

$Me_3SiSiClH_2$ in a single step). Only a mechanism change between the reactions of ClSiH with $Me_3SiH$ and $Me_3SiD$ can account for such a large value. Unfortunately we are not able to observe directly the formation of ClSiD with our detection system[11], but it is clear that a substantial additional pathway is needed to account for the disappearance of ClSiH in the reaction with $Me_3SiD$. One possibility can be eliminated, viz.

$$ClSiH + Me_3SiD \; = \; Me_3SiSiClHD^* \; \rightarrow \; Me_3SiH + ClSiD$$

where $Me_3SiSiClHD^*$ represents the vibrationally excited disilane product. If this process were to occur it would indicate that collisional stabilisation of the disilane product was incomplete and the measured rate constant would be pressure dependent. This has been checked experimentally and found not to be the case (as indeed it was also not the case for ClSiH + $Me_3SiH$ studied previously[5]). Only the rearrangement process involving the intermediate complex, predicted by calculation[5,12,13], would appear to offer an explanation. The full reaction mechanism is shown in scheme 2 below.
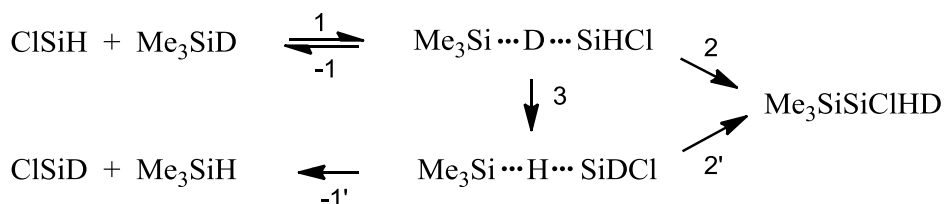
Scheme 2

In order to provide more concrete support for this mechanism we have undertaken theoretical calculations to investigate the isotope effect. This involved ab initio calculations (G3MP2B3 level) reported previously[5] followed by RRKM calculations[14] of the rate constants for rearrangement of the intermediate complex ($k_3$) relative to the rate constants for reaction to product ($k_2$) and to redissociation ($k_{-1}$), based on the structures and energies of transition states involved. The value of the isotope effect was obtained as the ratio of rate constants for ClSiH consumption with $Me_3SiH$ and with $Me_3SiD$. Of course the major difference in the latter case is the inclusion of the scrambling process which ceases to be degenerate with the inclusion of the D-label. The vibrational assignments of the species involved in this calculation as well as their energies were taken from the ab initio calculations

for both the H- or D- labelled species. Table 1 summarises the energy surface details and Table 2 the RRKM results.

Since the intermediate complex and rearrangement transition states are all more stable than the reactants a chemical activation version of RRKM theory was used in these calculations[14]. Table 2 shows that the isotope effect is dependent on the magnitude of the $A$ factor (and transition state structure) for redissociation of the complex, a quantity not available from theory. Values were selected based on an initial assumption that the association of ClSiH with $Me_3SiH$ (or $Me_3SiD$) was collision controlled. This gives the maximum possible value[15] for log $(A_{-1}/s^{-1})$ of 16.08 corresponding to $k_D/k_H = 9.27$. The table shows that $k_D/k_H$ decreases as log $(A_{-1}/s^{-1})$ decreases. For the latter a value of 15.90, corresponding to $k_D/k_H = 7.21$ gives a good fit to experiment. This corresponds to ca 66% collision efficiency in the initial, complex-forming reaction step. Since silylenes, in general, are very efficient at insertion into Si-H bonds[2] (when, unlike in this case, the initial association step is rate controlling) this is a reasonable result. In order to check further, the isotope effect was calculated in the absence of the scrambling process (step (3)), viz when the only pathway open to the complex (apart from redissociation, step (-1)) was rearrangement to form disilane product (step (2)). The value obtained for $k_D/k_H$, in these circumstances, was 0.73, in line with expectation for a normal insertion process[8-10], but clearly very different from experiment.

In summary, the large isotope effect found in this work, independent of pressure, can only be explained by a rearrangement process of an intermediate complex. This is the first experimental evidence for such a process and necessarily validates the existence of the complex in the Si-H insertion reaction. We have been able to reproduce the magnitude of this isotope effect by theoretical modelling. Further experiments are underway to extend these results to higher temperatures.

**AUTHOR INFORMATION**

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## REFERENCES and NOTES

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8.  Values in the range 0.3 to 0.9 for primary isotope effects are found for a variety of mechanistic processes[9], and an actual value of 0.9 obtained in the reaction of $SiMes_2$ + $Et_3SiH(D)$[10].

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10. Conlin, R. T.; Netto-Ferreira, J. C.; Zeng, S.; Scaiano, J. C. *Organometallics* **1990**, *9*, 1332.

11. Unlike ClSiH, ClSiD has no vibronic band coincident with any line of our Ar Ion Laser monitor.

12. Swihart and Carr[13] were the first to predict the possibility of such processes.

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15. Using microscopy reversibility and the calculated value of $\triangle S^o$ = -136.4 J $K^{-1}$ $mol^{-1}$ for forming the complex.
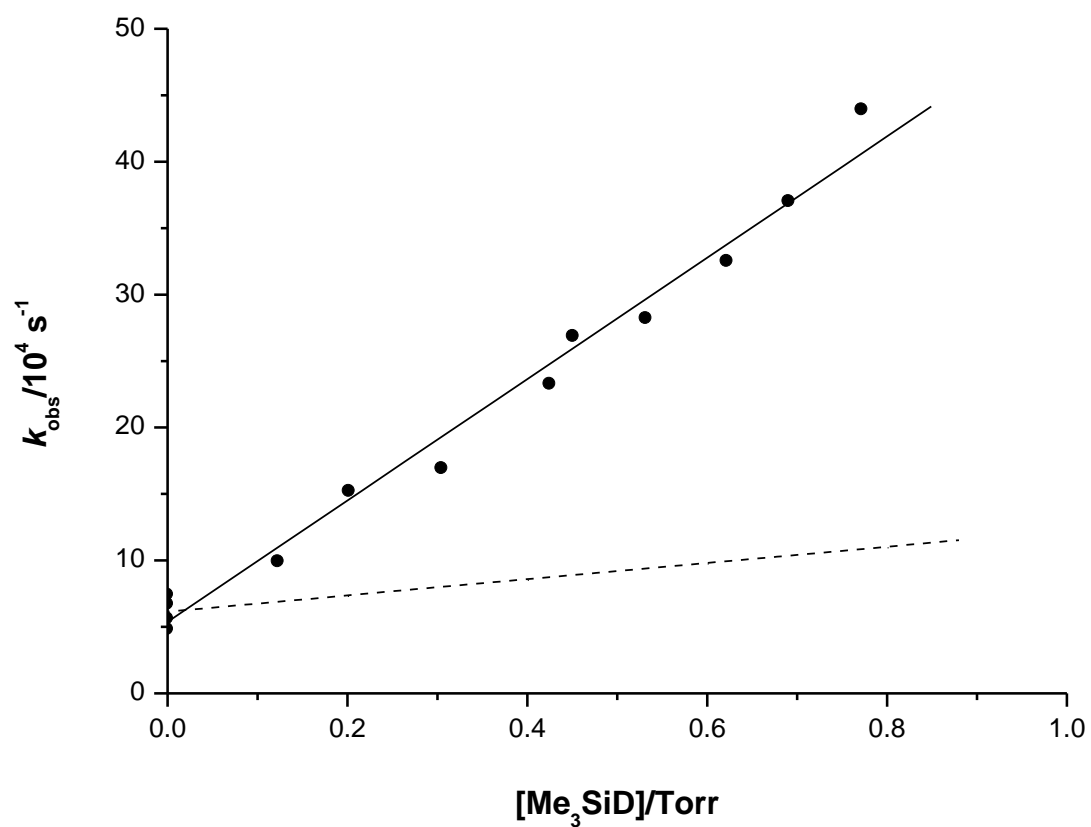
**Figure.** Second-order plot for reaction of ClSiH with $Me_3SiD$ in $SF_6$ (5 Torr) at 297 K. Dashed line shows fit to data for ClSiH + $Me_3SiH$ (ref. 5).

**Table 1. Ab initio calculation of energies of species involved in the reaction of ClSiH +Me₃SiH(D) at the G3MP2B3 level**

| Species | $E_0(H)$/kJ mol$^{-1}$ | $E_0(D)$/kJ mol$^{-1}$ |
|---------|------------------------|------------------------|
| ClSiH + Me₃SiH(D) | 0 | 0 |
| Complex (C1) | -36.90 | -36.64 |
| TS2[a] | -9.30 | -8.50 |
| TS3[b] | -21.90 | -21.27 |

[a]Transition state for step (2)    [b]Transition state for step (3)

**Table 2. RRKM calculations of the isotope effect based on the ab initio energy surface and different structures for redissociation of the intermediate complex**

| Quantity | Value | | |
|----------|-------|---|---|
| log $(A_{-1}$/s$^{-1})$[a] | 16.08[b] | 15.90[b] | 15.74[b] |
| $k_D/k_H$ | 9.27 | 7.21 | 5.45 |

[a]$A$ factor for redissociation of intermediate complex, step(-1)
[b]Values obtained after judicious modification of vibrational wavenumbers of transitional modes in TS(-1)

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