

Theoretical Investigation on the Reactions of H with $(\text{CH}_3)_{4-n}\text{SiH}_n$ ($n = 1-4$)

ZHANG, Qing-Zhu*(张庆竹) ZHANG, Ji-Guo(张吉果) WANG, Shao-Kun(王少坤)
ZHANG, Miao(张苗) LIU, Chuan-Pu(刘传朴) GU, Yue-Shu(顾月姝)

Department of Chemistry, Shandong University, Jinan, Shandong 250100, China

The abstractions of H with $(\text{CH}_3)_{4-n}\text{SiH}_n$ ($n = 1-4$) have been investigated at high levels of *ab initio* molecule orbital theory. Geometries have been optimized at the MP-2 level with 6-31G(d) basis set, and G2MP2 level has been used for the final energy calculations. Theoretical analysis provided conclusive evidence that the main process occurring in each case is the abstraction of H from the Si—H bond leading to the formation of the H_2 and silyl radicals; the abstraction of H from C—H bond has higher barrier and is difficult to react in each case. The kinetics of the title reactions have been calculated with variational transition-state theory over the temperature range 200—1000 K, and the theoretical rate constants match well with the experimental values.

Keywords Reaction channel, variational transition state, tunneling effect, rate constants

Introduction

The reactions of H with silicon species play important roles in etching silicon surface.¹⁻³ Although many investigations of the reactions of H atoms with the silane and the methylsilanes have been reported,⁴⁻¹⁷ the values of the rate constants obtained cover a wide range, thus making it difficult to establish reactivity patterns. This conflict between results often appears to be associated with the different experimental methods employed. Another deficiency in the data available at present is that most work has been carried out only at room temperature, therefore few Arrhenius parameters have been reported. In this paper, we optimized the stationary point geometries and calculated their vibrational frequencies and energies. Based on this

information, we calculated the rate constants for the title reactions with variational transition-state theory (VTST) and tunneling method. The results of VTST calculations are compared with experimental values.

Computation and theory

Ab initio calculations have been carried out using Gaussian 94 programs. The geometries of reactants, transition states and products have been optimized at the UMP2 level with the standard 6-31G(d) basis set. The vibrational frequencies (scaled by 0.93) have been obtained at the same level in order to determine the nature of different stationary points and the zero-point-energy (ZPE) corrections. The intrinsic reaction coordinates (IRC) have been calculated, and the minimum energy paths (MEP) have been obtained at the same level. Then, a series of single-point energies have been calculated at the G2MP2 theory level.

Finally, the POLYRATE 7.8 program¹⁹ has been employed for calculating the rate constants. The rate constants of the title reactions have been calculated over the range of temperature 200—1000 K by using the variational transition-state theory, which is based on the electronic structure data on geometries, frequencies and energies calculated by *ab initio* along the MEP. In the calculation, we have considered the tunneling correction. Since the heavy-light-heavy mass-combination is not present in this hydrogen transfer reactions, the tunneling corrections have been calculated by using the centrifugal-dominant

* E-mail: guojz@icm.sdu.edu.cn

Received November 17, 2000; revised and accepted February 22, 2001.

Project supported by the Research Fund for the Doctoral Program of Higher Education of China.

small curvature semiclassical adiabatic ground-state (CD-SCSAG) method.²⁰

Results and discussion

Geometries and properties of various critical points along

reaction path

The optimized geometries of various stationary points are shown in Fig. 1. The corresponding frequencies and the energies are listed in Table 1 and Table 2, respectively.

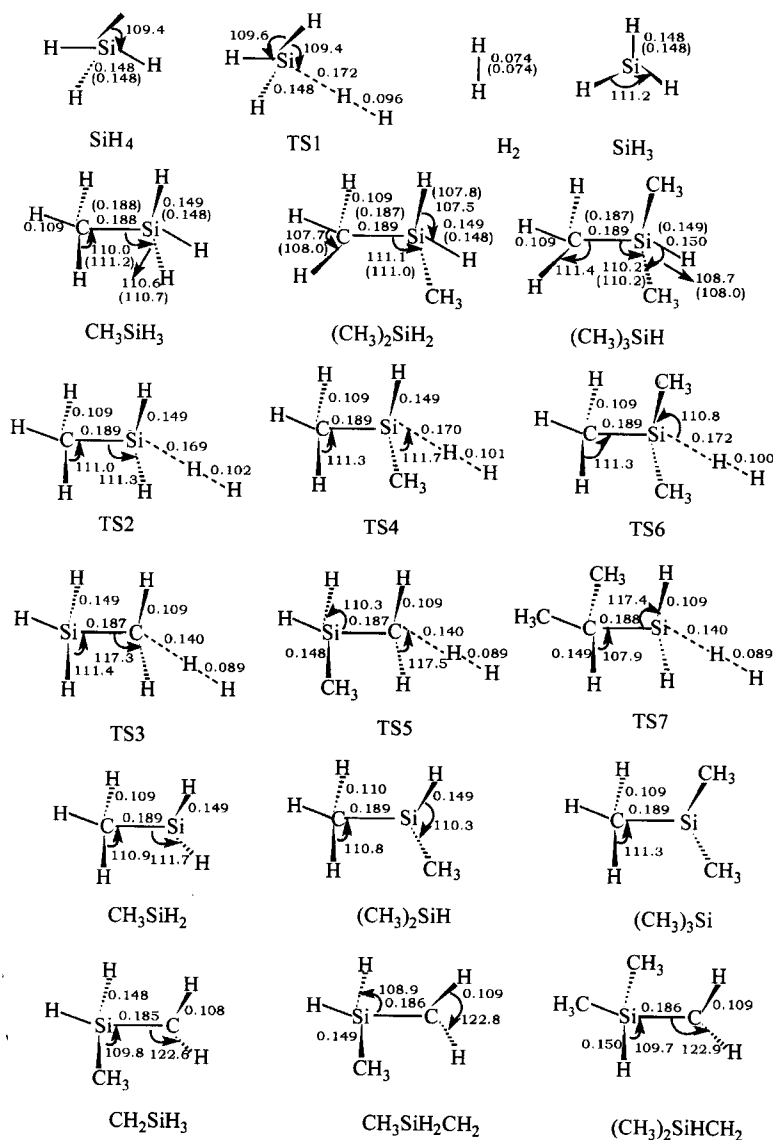


Fig. 1 Optimized geometries for the stationary points. The distance is in nm and the angle is in degree. The value in parenthesis is experimental one.^{21-22, 28-29}

a. H + SiH₄

The data show that the optimized geometries and vibrational frequencies of reactants and products are in good

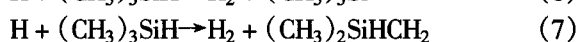
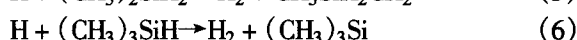
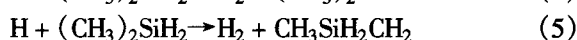
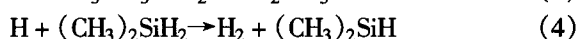
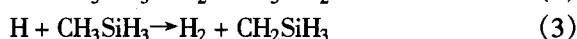
agreement with the experimental values. It might be inferred that the same accuracy could be expected for the calculated transition state geometries. By comparing the geometries of the reactant, product and transition state

Table 2 Total energy (hartree) and relative energy (kJ/mol)

Species	G2MP2	ΔE
SiH ₄ + H	-291.91553	0.00
CH ₃ SiH ₃ + H	-331.15307	0.00
(CH ₃) ₂ SiH ₂ + H	-370.39311	0.00
(CH ₃) ₃ SiH + H	-409.63265	0.00
TS1	-291.90716	21.97
TS2	-331.14531	20.38
TS3	-331.13947	35.69
TS4	-370.38484	21.71
TS5	-370.37329	52.01
TS6	-409.62534	19.20
TS7	-409.61581	44.22
SiH ₃ + H ₂	-291.94512	-77.78
CH ₃ SiH ₂ + H ₂	-331.17287	-52.01
CH ₂ SiH ₃ + H ₂	-331.15869	-14.77
(CH ₃) ₂ SiH + H ₂	-370.41086	-46.61
CH ₃ SiH ₂ CH ₂ + H ₂	-370.39535	-4.77
(CH ₃) ₃ Si + H ₂	-409.64929	-43.68
(CH ₃) ₂ SiHCH ₂ + H ₂	-409.63961	-18.28

b. H + (CH₃)_{4-n}SiH_n (*n* = 1—3)

As mentioned above, the direct hydrogen abstraction from (CH₃)_{4-n}SiH_n by H can occur via two channels; the abstractions from Si—H bond and from C—H bond, namely:



According to the Arrhenius parameters determined by Potzinger and coworker,²³ the rate constant of the reaction of H atoms with (CH₃)₄Si is $1.15 \times 10^{-16} \text{ cm}^3/\text{s}$ at 298 K. Considering the number of methyl groups in the various methylsilanes, the resultant rate constants of H abstraction from C—H bond account for 0.03, 0.02 and 0.01% of the experimental values for *n* = 1—3, respectively. So H atoms attack solely the Si—H bonds of the methylsilanes in the reaction of H with methylsilane.

In this work, the calculated barrier height of the hydrogen abstraction from Si—H bond of CH₃SiH₃ is 20.38 kJ/mol, while the calculated barrier height from C—H

bond is 35.69 kJ/mol. The corresponding reaction heats are -52.01 kJ/mol and -14.77 kJ/mol, respectively. The higher barrier makes the hydrogen abstraction from C—H bond more difficult than that from Si—H bond, so the hydrogen abstraction from Si—H bond is the sole channel. It agrees with the experimental results of Potzinger very well. Similar conclusions can be obtained from the reactions of the hydrogen abstraction from (CH₃)₂SiH₂ or (CH₃)₃SiH.

Rate constants

The potential energy of the minimum energy path V_{MEP} , and the ground-state vibrationally adiabatic potential energy V_{a}^{G} of the reaction of H with SiH₄ are plotted against the intrinsic reaction coordinate *s* as shown in Fig. 2, where MEP means the minimum energy path. It can be seen that the curves, V_{MEP} and V_{a}^{G} , are similar in shape, and this implies that the variational effect for the calculation of the rate constants would be small. The change trends of V_{MEP} and V_{a}^{G} against the intrinsic reaction coordinate *s* of the reactions of H with methylsilanes are similar to those of the reaction of H with SiH₄, so they will not be shown in this paper.

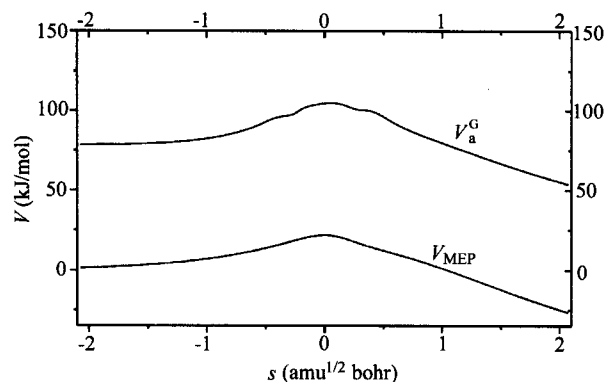


Fig. 2 The potential energy curve V_{MEP} and the vibrationally adiabatic ground-state potential energy curve V_{a}^{G} as a function of the intrinsic reaction coordinate *s*.

a. H + SiH₄

The reported experimental values of the reaction of H with SiH₄ are shown in Table 3. The front four values (Ref. 8,9,10,11) were determined before 1975 and are higher than recent experimental results probably because of the poor experimental conditions. Setting aside the

anomalously high values, we see that the remaining experimental rate constants fall within the range $2.0\text{--}4.6 \times 10^{-13} \text{ cm}^3/\text{s}$. It is interesting to note that all the recent results form three groups in the range of temperature 298–305 K. There are four values (Ref. 4, 15, 17, 6) from 2.0 to $2.8 \times 10^{-13} \text{ cm}^3/\text{s}$ in the first group. There are also four values (Ref. 12, 13, 14, 16) from 4.0 to $4.6 \times 10^{-13} \text{ cm}^3/\text{s}$ in the second group. There is only one value (Ref. 7) $3.4 \times 10^{-13} \text{ cm}^3/\text{s}$ in the third group that is just the average of all the values of the first and the second groups.

Table 3 Experimental results for $\text{H} + (\text{CH}_3)_{4-n}\text{SiH}_n$ ($n = 1\text{--}4$) (k , $10^{-13} \text{ cm}^3/\text{s}$)

T (K)	Rate	Ref.
	SiH ₄	
298	> 2.2	8
298	21 ± 7	9
298	26 ± 3	10
300	85 ± 34	11
300	4.6 ± 0.3	12
305	4.4 ± 1.0	13
298	4.4 ± 0.7	14
294–487	2.0 ± 0.1	4
293	2.2 ± 0.2	15
298	4.0	16
298	2.5 ± 0.5	17
298	2.8 ± 0.3	6
298	3.4 ± 0.3	7
	CH ₃ SiH ₃	
298	12.6 ± 3.8	9
298	11.5 ± 2.0	10
305	6.3 ± 1.2	13
298	3.8 ± 0.2	14
291	4.0 ± 0.1	4
298	3.9 ± 0.2	7
	(CH ₃) ₂ SiH ₂	
298	17.6 ± 4.8	9
298	4.1 ± 0.9	10
305	6.8 ± 1.3	13
298	2.8 ± 0.2	14
292	3.1 ± 0.1	4
298	3.9 ± 0.3	7
	(CH ₃) ₃ SiH	
298	15.9 ± 4.0	9
298	3.7 ± 1.0	10
305	5.8 ± 1.2	13
290	2.6 ± 0.1	4
298	2.7 ± 0.2	7

Table 4 gives the computational rate constants over the range of temperature 200–1000 K. Comparing the computational rate constants with the experimental values, it can be seen that our results agree with the experimental values of the first group very well. It is thought that the experimental results of the second group may be overestimated.

Table 5 shows other known theoretical results. Group A results were reported by Espinosa-Garcia and coworkers.²⁴ They constructed the potential energy surface of the reaction $\text{SiH}_4 + \text{H} \rightarrow \text{SiH}_3 + \text{H}_2$, and calculated the rate constants with variational transition-state theory and CD-SCSAG tunneling correction using this surface. In this work we use the “direct dynamics” method of variational transition-state theory, which is based on the information on geometries, frequencies and energies calculated by *ab initio* method along the minimum energy path. Compared with Espinosa-Garcia’s method, our method is easy and timesaving. Group B⁶ values were calculated from the Arrhenius equation $k(T) = 1.78 \times 10^{-10} \exp(-3820/RT)$ fitted by a series of experimental values. There are no direct experimental values when the temperature is higher than 500 K, so we think the values calculated from Arrhenius equation are the experimental values. Compared with the results in Table 5, our values and Espinosa-Garcia’s ones agree with the experimental values very well.

b. $\text{H} + (\text{CH}_3)_{4-n}\text{SiH}_n$ ($n = 1\text{--}3$)

The experimental rate constants of the reactions of H atoms with methylsilanes are also listed in Table 3. There is a clear separation between the earlier values and the later ones. The values of Hong,⁹ Cowfer¹⁰ and Auatin¹³ are earlier. The values of Worsdorfer,¹⁴ Potzinger⁴ and Arthur⁷ are later. The earlier values are much higher than the later ones. By comparing the values in Table 3 with those in Table 4, it can be seen that our computational values agree with the later experimental results very well.

c. Reactivity trends

The effect of the methyl substitution on the strength and reactivity is an interesting topic. The effect can be seen by evaluating k/n , the rate constant corrected for the reaction-path degeneracy, where n is the number of Si–H bonds. A plot of k/n versus n at 298 K is shown in Fig. 3. Our values show that methyl substitution leads

to a progressive increase in Si—H bond reactivity. The same trend is followed by the experimental values. Our computational k/n values agree with those of Arthur⁴ perfectly. The k/n values of Austin and coworkers¹³ are much higher than our computational values and other experimental results. The conclusion that the methyl substitution increases the reactivity of Si—H bond can be drawn

from the reactions of various atoms with SiH₄ and the methylsilanes. The ratios²⁵⁻²⁷ of the k/n values for (CH₃)₃SiH and SiH₄ at 298 K are 35, 2.8 and 4.6 for O, Cl and Br, respectively. Therefore the introduction of methyl groups enhances the reactivity of the Si—H bond to a similar extent for the H, O, Cl and Br reactions.

Table 4 CVT/CD-SCSAG rate constants (cm³/s)

<i>T</i> (K)	SiH ₄	CH ₃ SiH ₃	(CH ₃) ₂ SiH ₂	(CH ₃) ₃ SiH
200.00	5.13E-14	1.58E-14	9.13E-14	1.16E-13
298.00	2.15E-13	4.05E-13	2.79E-13	2.64E-13
300.00	2.21E-13	4.74E-13	2.86E-13	2.68E-13
350.00	4.23E-13	9.95E-13	4.88E-13	4.10E-13
400.00	7.50E-13	1.55E-12	7.95E-13	6.12E-13
450.00	1.24E-12	2.31E-12	1.23E-12	8.87E-13
500.00	1.92E-12	3.32E-12	1.81E-12	1.25E-12
550.00	2.83E-12	4.61E-12	2.57E-12	1.71E-12
600.00	4.01E-12	8.14E-12	3.52E-12	2.27E-12
700.00	7.23E-12	1.04E-11	6.08E-12	3.77E-12
800.00	1.18E-11	1.61E-11	9.60E-12	5.81E-12
900.00	1.78E-11	2.35E-11	1.42E-11	8.44E-12
1000.00	2.53E-11	3.25E-11	1.99E-11	1.17E-11

Table 5 Other known theoretical results for H + SiH₄ (cm³/s)

<i>T</i> (K)	Surface ^A	Expt. ^B
200	3.07 × 10 ⁻¹⁴	
250	8.80 × 10 ⁻¹⁴	
300	2.09 × 10 ⁻¹³	2.81 × 10 ⁻¹³
350	4.32 × 10 ⁻¹³	7.20 × 10 ⁻¹³
400	7.96 × 10 ⁻¹³	1.43 × 10 ⁻¹²
450	1.34 × 10 ⁻¹²	2.41 × 10 ⁻¹²
500	2.11 × 10 ⁻¹²	3.78 × 10 ⁻¹²
600	4.43 × 10 ⁻¹²	7.18 × 10 ⁻¹²
700	8.00 × 10 ⁻¹²	
1000	2.80 × 10 ⁻¹¹	

Conclusion

We have calculated the rate constants for the reactions of H with (CH₃)_{4-n}SiH_n ($n = 1-4$), using the "direct dynamics" method of variational transition-state theory. The results were found to be in agreement with the most recent experimental data. From the above studies the following conclusions can be drawn:

1. The hydrogen abstractions from Si—H bonds are

the sole channel for the reactions of H with (CH₃)_{4-n}SiH_n ($n = 1-3$).

2. The methyl substitution has an effect on the strength and reactivity of the Si—H bond in SiH₄.

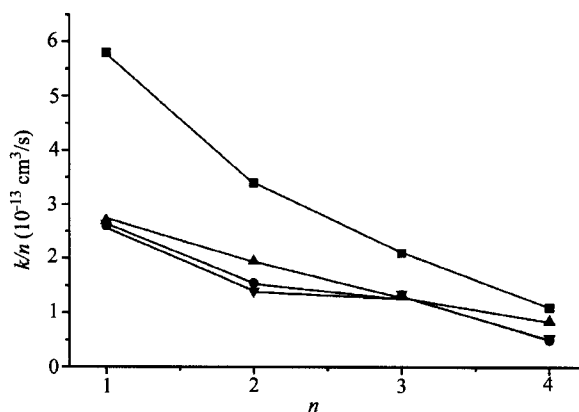


Fig. 3 Effect of methyl substitution on Si—H bond reactivity: ■ Ref. 13; ▲ Ref. 7; ▼ this work; ● Ref. 4.

References

- Gates, S. M.; Kunz R. R.; Greenlief, C. M. *Surf. Sci.*

- 1989, 207, 364.
- 2 Abrefah, J.; Olander, D. R. *Surf. Sci.* **1989**, 207, 291.
- 3 Lu, Z. H.; Griffiths, K.; Norton, P. R.; Sham, T. K. *Phys. Rev. Lett.* **1992**, 68, 1343.
- 4 Arthur, N. L.; Potzinger, P.; Reimann, B.; Steenberger, H. P. *J. Chem. Soc., Faraday Trans.* **1989**, 285, 1447.
- 5 Koshi, M.; Tamura, F.; Matsui, H. *Chem. Phys. Lett.* **1990**, 173, 235.
- 6 Goumri, A.; Yuan, W. J.; Ding, L.; Shi, Y.; Marshall, P. *Chem. Phys.* **1993**, 177, 233.
- 7 Arthur, N. L.; Miles, L. A. *Chem. Phys. Lett.* **1998**, 282, 192.
- 8 Moortgat, G. K. *Diss. Abstr.* **1970**, B31, 1879.
- 9 Hong, J. H.; *Thesis Ph. D.* University of Detroit, **1972**.
- 10 Cowfer, J. A.; Lynch, K. P.; Michael, J. V. *J. Phys. Chem.* **1975**, 79, 1139.
- 11 Choo, K. Y.; Gaspar, P. P.; Wolf, A. P. *J. Phys. Chem.* **1975**, 79, 1752.
- 12 Mihelcic, D.; Schubert, V.; Schindler, R. N.; Potzinger P. *J. Phys. Chem.* **1977**, 81, 1543.
- 13 Austin, E. R.; Lampe, F. W. *J. Phys. Chem.* **1977**, 81, 1134.
- 14 Worsdorfer, K.; Reimann, B.; Potzinger, P. *Z. Naturforsch.* **1983**, A 38, 896.
- 15 Koshi, M.; Tamura, F.; Matsui, H. *Phys. Chem. Lett.* **1990**, 173, 235.
- 16 Johnson, N. M.; Walker, J.; Stevens, K. S. *J. Appl. Phys.* **1991**, 69, 2631.
- 17 Loh, S. K.; Jasinski, J. M. *J. Chem. Phys.* **1991**, 95, 4914.
- 18 Curtiss, L. A.; Raghvachari, K.; Pople, J. A. *J. Chem. Phys.* **1993**, 98, 1293.
- 19 Steckler, R.; Chuang, Y. Y.; Fast, P. L.; Corchade, J. C.; Coitino, E. L.; Hu, W. -P.; Liu, Y. -P.; Lynch, G. C.; Nguyen, K.; Jackells, C. F.; Gu, M. Z.; Rossi, I.; Clayton, S.; Melissas, V.; Garrett, B. C.; Isaacson, A. D.; Truhlar, D. G. *POLYRATE* Version 7.8, University of Minnesota, Minneapolis, **1997**.
- 20 Liu, Y. P.; Lynch, G. C.; Truong, T. N.; Lu, D. H.; Truhlar, D. G.; Grett, B. C. *J. Am. Chem. Soc.* **1993**, 115, 2408.
- 21 Chase, M. W. Jr.; Davies, C. A.; Downey, J. R.; Frurip, D. J.; McDonaldand, R. A.; Syverud, A. N. *JANAF Thermochemical Tables* 3rd ed., National Bureau of Standards, Washington, D. C., **1985**, Vol.14.
- 22 Allen, W. D.; Shaefer, H. F. III *J. Chem. Phys.* **1986**, 108, 243.
- 23 Arthur, N. L.; Potzinger, P.; Reimann, B.; Steenberger, H. P. *J. Chem. Soc. Faraday Trans.* **1990**, 86, 1407.
- 24 Espinosa-Garcia, J.; Sanson, J.; Corchado, J. C. *J. Chem. Phys.* **1998**, 109, 466.
- 25 Ding, L.; Marshall, P. *J. Am. Chem. Soc.* **1992**, 114, 5754.
- 26 Ding, L.; Marshall, P. *J. Phys. Chem.* **1992**, 96, 2197.
- 27 Horie, O.; Taege, R.; Reimann, B.; Arthur, N. L.; Potzinger, P. *J. Phys. Chem.* **1991**, 95, 4393.
- 28 Almlof, J.; Faegri, K. Jr. *Theor. Chim. Acta* **1986**, 69, 438.
- 29 Lars, O.; Carl-Henrik, O.; Dieter, C. *J. Am. Chem. Soc.* **1995**, 117, 7460.

(E200011247 JIANG, X.H.; LING, J.)