

## Theoretical Studies on $\text{CH}_3\text{SiH}_3 + \text{H} \rightarrow \text{CH}_3\text{SiH}_2 + \text{H}_2$ Reaction with the Variational Transitional State Theory

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**Abstract:** In this paper, the abstraction reaction of  $\text{CH}_3\text{SiH}_3$  with H has been studied by using the “direct dynamics” method of variational transition-state theory, which is based on the information on geometries, frequencies and energies calculated by *ab initio* along the minimum energy path. The rate constants of the title reaction were calculated for the range of temperature 298–1700 K. The rate constants calculated match well with the experimental values.

**Keywords:** Variational transition state, tunneling effect, rate constants.

### Introduction

The abstraction reaction between  $\text{CH}_3\text{SiH}_3$  and H plays an important role in silicon-containing species and has been the subject of many experimental studies<sup>1–6</sup>, but it has not been studied with the variational transition state theory. In this paper, the dynamics of the title reaction is investigated by using POLYRATE7.8 program obtained from Truhlar<sup>7</sup>. The theoretical rate constants for the title reaction are obtained over a wide range of temperature 298–1700 K.

### Theory and Methods

The generalized transition-state (GTS) theory rate constant is given by<sup>8</sup>

$$k^{GT}(T, s) = \frac{\sigma}{\beta h} \frac{Q^{GT}(T, s)}{\Phi^R(T)} \exp[-\beta V_{MEP}(s)] \quad (1)$$

where T is the temperature; s is the distance of GTS along the minimum energy path (MEP);  $\sigma$  is the symmetry factor<sup>9</sup> accounting for the possibility of two or more symmetry-related reaction paths;  $\beta$  is  $(k_B T)^{-1}$ ;  $k_B$  is Boltzmann's constant; h is the Planck's constant;  $\Phi^R(T)$  is the partition function per unit volume of the reactant;  $V_{MEP}(s)$  is the classical energy along MEP with its overall zero of energy at the reactant and  $Q^{GT}(T, s)$  is the partition function of GTS at s with the local zero of energy at  $V_{MEP}(s)$ . The canonical variational theory (CVT) rate constant  $k^{CVT}$  can be obtained by

variationally minimizing the generalized transition-state theory rate constant  $k^{\text{GT}}(\text{T},s)$  with respect to the position  $s$  of the GTS along the reaction path,

$$k^{\text{CVT}}(\text{T}) = k^{\text{GT}}(\text{T},s_*^{\text{CVT}}) = \min_s k^{\text{GT}}(\text{T},s) \quad (2)$$

The rate constants for the title reaction in the range of temperature 298-1700K were calculated by using the “direct dynamics” method of variational transition-state theory, which is based on the electronic structure data on geometries, frequencies and energies calculated by *ab initio* along MEP.

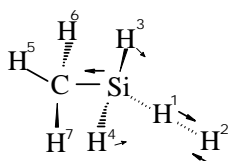
In the calculation, the Gaussian-94 and the POLYRATE programs were employed, the former for calculating the electronic structure data, the latter for calculating the rate constant.

## Results and Discussion

### *The geometries and properties of various critical points along reaction path*

The transition state for the title reaction and its imaginary vibrational mode are shown in **Figure 1**. This imaginary vibrational mode indicates that the transition state is on the reaction path and points at the products. **Table 1** shows the optimized geometries, frequencies (scaled by 0.93) and the energies for all species. The geometry optimizations and frequencies were performed at the UMP2(FULL)/6-311G(d,p) level. The energy was important to the rate constant, so in this paper the energy calculations were done at the high level QCISD(T)/6-311G(d,p).

**Figure 1** Transition state and its imaginary vibrational mode



The data in **Table 1** shows that the optimized geometries for the reactant and product are in good agreement with experimental values. By comparing the geometries of reactant, product and transition state in **Table 1**, it can be seen that the SiH<sup>1</sup> bond is elongated from 147.70 pm in reactant to 163.19 pm in transition state, the H<sup>1</sup>H<sup>2</sup> bond is shortened from 105.39 pm in transition state to 73.81 pm in product. The transition state has C<sub>s</sub> symmetry.

The **Table 2** gives the computational rate constants in the range of temperature 298-1700K. In the table,  $k^\ddagger$  and  $k^{\text{CVT}}$  denote the conventional transition-state theory (TST) rate constant and the canonical variational theory (CVT) rate constant, and the rate constants  $k^{\text{CVT}}$  corrected by MEPSAG (minimum energy path semiclassical adiabatic ground-state) and SCSAG (small curvature semiclassical adiabatic ground-state) transmission coefficient are expressed as  $k^{\text{CVT/MEPSAG}}$  and  $k^{\text{CVT/SCSAG}}$ , respectively.

**Table 1** The geometries, scaled frequencies and energies of various critical points along reaction path

Properties	Reactant	Transition state	Product	Expt. <sup>10</sup>	
Bond Length / pm	C-Si	187.43	187.42	187.95	187.5
	Si-H <sup>1</sup>	147.70	163.19	/	147.7
	H <sup>1</sup> -H <sup>2</sup>	/	105.39	73.81	
	Si-H <sup>3</sup>	147.70	147.74	147.82	
	C-H <sup>5</sup>	109.27	109.33	109.70	
Bond Angle / (°)	$\angle\text{SiH}^1\text{H}^2$	/	177.39	/	
	$\angle\text{H}^1\text{SiH}^3$	108.52	107.91	/	
	$\angle\text{H}^3\text{SiH}^4$	108.52	109.41	109.70	
	$\angle\text{CSiH}^3$	110.41	111.09	111.45	110-112
	$\angle\text{H}^5\text{CH}^6$	107.90	107.91	107.99	
Frequency/cm <sup>-1</sup>		2963	2965	H <sub>2</sub> 4219	
		2963	2959	CH <sub>3</sub> SiH <sub>2</sub> 2968	
		2874	2872	2953	
		2153	2153	2869	
		2153	2143	2148	
		2153	1372	2131	
		1374	1372	1370	
		1374	1226	1370	
		1228	1062	1222	
		937	981	909	
		937	965	845	
		920	915	816	
		845	844	666	
		845	836	549	
		670	670	495	
		487	562	171	
		487	499		
	183	301			
		167			
		142			
		1486i			
Energy/hartree	CH <sub>3</sub> SiH <sub>3</sub> -330.6283	-331.1176	CH <sub>3</sub> SiH <sub>2</sub> -329.9787		
	H -0.4998		H <sub>2</sub> -1.1683		

**The reaction rate constants****Table 2** Reaction rate constants (k/cm<sup>3</sup>·molecule<sup>-1</sup>·s<sup>-1</sup>)

T/K	k <sup>‡</sup>	k <sup>CVT</sup>	k <sup>CVT/MEPSAG</sup>	k <sup>CVT/SCSAG</sup>	k <sub>EXPT</sub> /10 <sup>-13*</sup>
298	4.27E-15	4.83E-17	1.92E-13	3.99E-13	3.9±0.2 <sup>1</sup>
800	4.80E-12	7.24E-13	3.71E-12	5.24E-12	
900	8.37E-12	1.49E-12	5.58E-12	7.51E-12	
1000	1.33E-11	2.72E-12	8.04E-12	1.04E-11	
1200	2.81E-11	1.70E-11	3.81E-11	4.64E-11	
1500	6.35E-11	4.03E-11	6.81E-11	7.82E-11	
1700	9.64E-11	6.26E-11	9.40E-11	1.05E-10	

\*other experimental rate constants: 4.0±0.1<sup>2</sup>(291K), 12.6±3.8<sup>3</sup>(298K), 11.5±2.0<sup>4</sup>(298K), 3.8±0.2<sup>5</sup>(298K), 6.3±1.2<sup>6</sup>(305K)

By comparing the data in **Table 2**, it can be seen that the tunneling effect is very obvious at room temperature, therefore, in calculating rate constants the tunneling effect must be

considered. At 298K,  $k^{\text{CVT/SCSAG}}=3.99\times 10^{-13}$ , which is in good agreement with the experimental values  $(4.0\pm 0.1)\times 10^{-13}$ ,  $(3.8\pm 0.2)\times 10^{-13}$  and  $(3.9\pm 0.2)\times 10^{-13}$ . By fitting the rate constants  $k^{\text{CVT/SCSAG}}$  in **Table 2** to the Arrhenius equation, the following rate-temperature relation formula can be obtained:

$$k^{\text{CVT/SCSAG}}=10^{8.24}\exp^{(-16.34\text{kJ/mol/RT})}$$

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