次甲基硅 SiH 与 H₂X(X=O,S)反应的热力学及动力学性质研究

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在量子化学对 SiH 与 H₂O 和 H₂S 反应计算的基础上, 运用统计热力学和 Wigner 校正的 Eyring 过渡态理论, 计算了上述两反应在 200～2000 K 温度范围内的热力学函数、平衡常数、频率因子 A 和速率常数随温度的变化。计算结果表明, 两反应在低温下具有热力学优势, 而在高温下具有动力学优势。比较两反应的计算结果发现, 在相同的温度下, SiH 与 H₂O 反应比 SiH 与 H₂S 反应放热较多, 但速率常数却较小。SiH 与 H₂O 反应和前文报道的 SiH 与 HF 反应的比较表明, SiH 与 H₂O 反应放热较少, 而且在相同温度下, 速率常数也较小。

关键词:　　SiH　　H₂O　　H₂S　　热力学和动力学研究
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Thermodynamic and Kinetic Studies on the Reactions of SiH with H₂X (X = O, S)

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Based on the quantum chemical study of the SiH insertion reactions with H₂O and H₂S, the statistical thermodynamics and Eyring transition state theory with Wigner correction are employed to compute the thermodynamic functions, equilibrium constants, A factors and rate constants of the two reactions in the temperature range 200～ 2000 K. The calculated results show that the two reactions are thermodynamically dominant at low temperature and kinetically favored at high temperature. The reaction of SiH with H₂O is more exothermic than that of SiH with H₂S, while the rate constant of the former reaction is lower than that of the latter at the same temperature. Comparison of the SiH + H₂O reaction in the present study with the SiH + HF reaction in the previous study indicates that the reaction of SiH with H₂O is less exothermic than that of SiH with HF, and the rate constant of the former is relatively smaller than that of the latter at the same temperature.

Keywords:　　SiH　　H₂O　　H₂S　　thermodynamic and kinetic studies

0　Introduction

Silylidyne (SiH) is the smallest silicon compound and plays an important role in the plasma chemical vapor deposition　(CVD) processes. The reactions of silylidyne with small molecules have been investigated from both experimental[1~5] and theoretical viewpoints[6] . As far as we know, thermodynamic and kinetic data of these involving SiH reactions are not reported in

the literature, and so far there are no available experimental data for these reactions. Recently, based on the quantum mechanical study of the reactions of SiH with small molecules, we have carried out the thermodynamic and kinetic investigation on the reaction of SiH with HF molecule, which provided better understanding of the reactivity by discussing the influence of the temperature[7] . In the present study, we continue our thermodynamic and kinetic studies of the reactions of SiH with H₂O and H₂S molecules by means of general statistical thermodynamics and Eyring transition state theory with Wigner correction. Furthermore, we also intend to give the comparative discussion not only on the reactivity of the reactions of SiH with H₂O and H₂S based on the present study but also on the reactivity of the reactions of SiH with H₂O and HF based on the present and previous calculated results. It is hopeful that these studies will give more reliable results for the reactions of SiH with small molecules, which would be helpful for the experimental study of the SiH reactions.

1　Computational Method

The calculations have been carried out in the present study by general statistical thermodynamics (GST)[8] and Eyring transition state theory (TST) with Wigner correction at 101. 325 kPa and at temperature range from 200 to 2000 K. The equation for calculation

of rate constant is given in ref. 7. The optimized geometries of the intermediate complexes, transition states and products of the two reactions are shown in Fig. 1. The electronic structure energies of all species are those in ref. 6 at the MP4/6-311 + + G(d, p)// MP2/6-311 + + G(d, p) level in which ZPE correction is obtained at the HF/6-31G(d) level and scaled by a factor of 0. 9. The harmonic frequencies have been recalculated at the (U) HF/6-31G(d) level by Gaussian 98 program[9], which are listed in Table 1. All computations of the thermodynamic and kinetic quantities of the reactions of SiH with H₂O and H₂S are acc-

Table 1　Harmonic Vibrational Frequencies for Stable Molecules and Transition States at the (U)HF/6-31G(d) Level

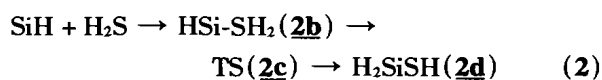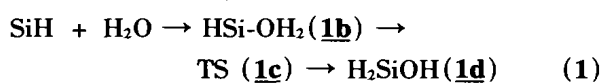| molecules	harmonic frequencies / cm^{-1}
SiH	2183. 1
H₂O	1826. 5, 4070. 5, 4188. 7
HSi-OH₂(**1b**)	133. 4, 250. 2, 461. 1, 522. 6, 826. 9, 1806. 5, 2147. 1, 4052. 8, 4166. 2
TS(**1c**)	1855. 5i, 531. 1, 646. 7, 757. 5, 944. 9, 1204. 6, 1625. 6, 2247. 1, 4031. 8
H₂SiOH(**1d**)	236. 1, 737. 1, 859. 6, 922. 0, 953. 3, 1019. 7, 2330. 6, 2389. 7, 4147. 4
H₂S	1367. 7, 2918. 5, 2930. 1
HSi-SH₂(**2b**)	141. 4, 144. 9, 411. 5, 433. 3, 745. 1, 1369. 3, 2159. 6, 2927. 7, 2943. 6
TS(**2c**)	1501. 9i, 256. 1, 508. 0, 602. 3, 898. 5, 1110. 9, 1453. 7, 2225. 8, 2926. 9
H₂SiSH(**2d**)	230. 1, 538. 9, 609. 4, 765. 3, 908. 8, 997. 9, 2357. 6, 2396. 1, 2904. 4
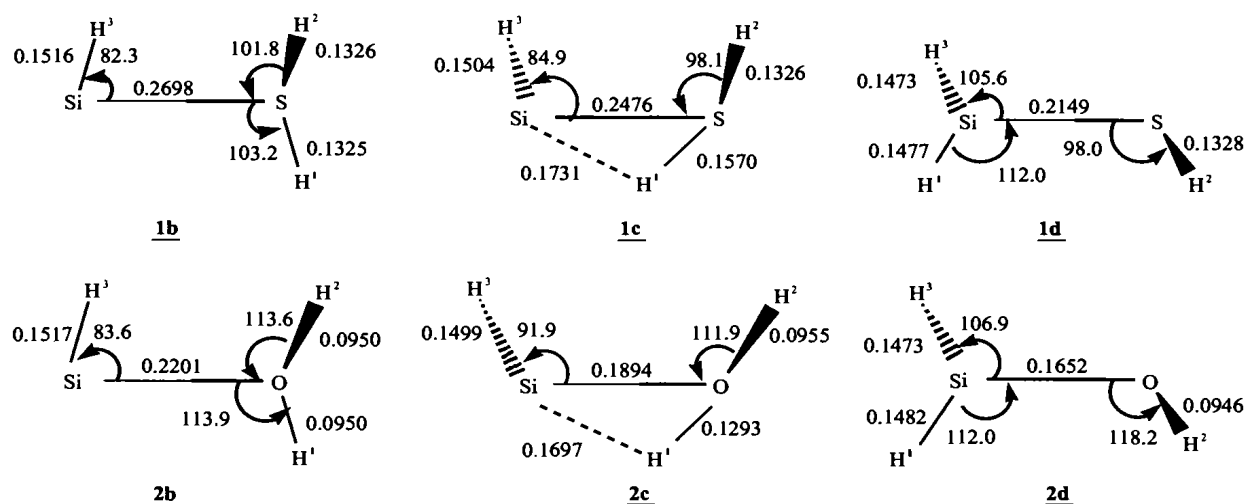
Fig. 1　Optimized structures of the intermediate complexes, transition states TS, and products for the SiH
reaction with H₂O and H₂S molecules
Bond lengths are given in nm and angles in degree.

omplished by using the program developed by us[10-12]. Although we do not claim quantitative accuracy for the absolute values of our thermodynamic and kinetic data, the comparison of our thermodynamic data with the results of Gaussian 98 shows that they are in good agreement, so our results should be reliable.

2 Results and Discussion

Theoretical study of the SiH insertion reactions with small molecules by standard ab initio molecular orbital calculations at several levels in ref. 6 confirms that the reaction mechanism of SiH and XH_2 ($X = O, S$) reactions are as follows,

$$SiH + H_2O \rightarrow HSi-OH_2(\underline{1b}) \rightarrow$$
$$TS (\underline{1c}) \rightarrow H_2SiOH(\underline{1d}) \qquad (1)$$
$$SiH + H_2S \rightarrow HSi-SH_2(\underline{2b}) \rightarrow$$
$$TS(\underline{2c}) \rightarrow H_2SiSH(\underline{2d}) \qquad (2)$$

It should be pointed out that in the present study, the thermodynamic function changes of $\Delta_rH_m^{\ominus}$, $\Delta_rG_m^{\ominus}$, $\Delta_rS_m^{\ominus}$ and $K(T)$ of the overall reaction are calculated for the above two reactions. When investigating the kinetic properties, we propose that because in each reaction there are two steps and the first step in which SiH reacts with H_2X ($X = O, S$) to give the intermediate complex $\underline{1b}$ or $\underline{2b}$ is a non-barrier process, so the second step is the determinant step of the overall reaction, thus the kinetic property of the second step of each reaction was calculated by Eyring transition state theory with Wigner correction. We will analyze the results for the reactions of SiH with H_2O and H_2S in subsection 1 and 2. Comparisons of the reactions of SiH with small molecules are made in subsection 3 and 4 respectively.

2.1 Results for SiH Insertion Reaction with H_2O

The results of thermodynamic function changes of the reaction $SiH + H_2O \rightarrow H_2SiOH$ are listed in Table 2. It is shown that in the temperature range 200 ~ 2000 K, both the enthalpy changes $\Delta_rH_m^{\ominus}$ and the entropy changes $\Delta_rS_m^{\ominus}$ are negative, i.e., the reaction is exothermic and of entropy decreasing. The Gibbs free energy changes $\Delta_rG_m^{\ominus}$ are negative when $T \leqslant 1800$ K, while positive when $T > 1800$ K, i.e., the reaction is spontaneous when $T \leqslant 1800$ K. The equilibrium constant $K(T)$ of this reaction fall quickly within temperature range 200 ~ 2000 K, i.e., the higher the temperature, the smaller the equilibrium constant of the reaction. Therefore, from the viewpoint of the conversion coefficient analysis, the SiH insertion reaction with H_2O is thermodynamically dominant at low temperature.

The calculated results of A factors and rate constants $k(T)$ are also given in Table 2, it is obvious that the SiH insertion reaction with H_2O takes place slowly below 200 K because of a small rate constant $k(T) < 0.73 \times 10^{-5}$ s^{-1}. With the increasing of the temperature, the rate constant increases gradually, and the higher the temperature, the larger the rate constant of the reaction. Therefore, from the viewpoint of rate constant analysis, it is kinetically favored at high temperature. The A factors of this reaction vary only slightly with the changing of the temperature, however, the activation energy E_a obtained from the calculation with Wigner correction increases with the increasing of the temperature.

2.2 Results of SiH Insertion Reaction with H_2S

Since H_2O and H_2S have the same valence elec-

Table 2 Thermodynamic and Kinetic Properties of SiH + H_2O → H_2SiOH Reaction in 200 ~ 2000 K

T / K	200	400	600	800	1000	1200	1400	1600	1800	2000
$\Delta_rH_m^{\ominus}$	−216.15	−218.35	−217.92	−216.20	−213.85	−211.18	−208.36	−205.50	−202.62	−199.75
$\Delta_rS_m^{\ominus}$	−166.48	−124.76	−124.01	−121.57	−118.96	−116.53	−114.36	−112.45	−110.75	−109.24
$\Delta_rG_m^{\ominus}$	−192.86	−168.44	−143.51	−118.94	−94.89	−71.35	−48.26	−25.58	−3.27	18.73
$K(T)$	2.3×10^{50}	9.9×10^{21}	3.1×10^{12}	5.8×10^{7}	9.0×10^{4}	1.3×10^{3}	63	6.8	1.2	0.32
A	1.6×10^{12}	9.9×10^{11}	9.7×10^{11}	1.1×10^{12}	1.2×10^{12}	1.4×10^{12}	1.5×10^{12}	1.6×10^{12}	1.7×10^{12}	1.8×10^{12}
$k(T)$ / s^{-1}	7.3×10^{-6}	2.9×10^{3}	1.8×10^{6}	4.6×10^{7}	3.4×10^{8}	1.3×10^{9}	3.4×10^{9}	7.3×10^{9}	1.3×10^{10}	2.1×10^{10}
E_a	66.37	65.36	65.81	66.88	68.15	69.42	70.62	71.70	72.66	73.52
g	8.43	2.86	1.83	1.46	1.30	1.20	1.15	1.12	1.09	1.07

tronic structure, it is not surprising to note that the thermodynamic and kinetic properties of the SiH insertion reaction with H_2S are similar to those of the SiH insertion reaction with H_2O. Table 3 shows the results of the thermodynamic properties of the reaction of SiH $+ H_2S \rightarrow H_2SiSH$ and the kinetic properties of the second step $HSi\text{-}SH_2 \rightarrow TS \rightarrow H_2SiSH$.

As it can be seen in Table 3, within the temperature range 200 ~ 2000 K, since $\Delta_r H_m^\ominus < 0$ and $\Delta_r S_m^\ominus < 0$, i. e., this reaction is exothermic and of entropy decreasing. The Gibbs free energy changes $\Delta_r G_m^\ominus$ are negative when $T \leqslant 1400$ K, while positive when $T > 1600$K. This indicates that it is spontaneous at low temperature when $T \leqslant 1400$ K, i. e., the higher the temperature, the smaller the equilibrium constant. Therefore, from the viewpoint of the thermodynamic aspect, the SiH insertion reaction with H_2S is thermodynamically dominant at low temperature.

The results of the kinetic properties of this reaction shows that the rate constant of the SiH insertion reaction with H_2S increases with the increasing of the temperature, i. e., the higher the temperature, the larger the rate constant and the faster the SiH reaction with H_2S. Thus, from the viewpoint of the rate constant aspect, it is kinetically favored at high temperature. In Table 5, the A factors remain almost a constant with $\log A$ equals about 13 within 200 ~ 2000 K, but the activation energy E_a obtained from the calculation with Wigner correction increases with the increasing of the temperature.

2. 3　Comparison Reactions between Two SiH + H₂O and SiH + H₂S

On the basis of the above analysis, it is shown that both of the SiH insertion reactions with H_2O and H_2S are exothermic and of entropy decreasing in the temperature range 200 ~ 2000 K. The two reactions are spontaneous at low temperature, while the SiH reactions with H_2O and H_2S are reversed at about 1800 K and 1400 K respectively. On the other hand, the rate constants and the activation energies of both reactions increase with the increasing of the temperature. As seen in Table 3 and 5, the values of g factors of the two reactions are relatively larger at low temperature, which gives the correction of the deficiency coming from Eyring transition state theory in which the tunneling effect is not included. In a word, SiH insertion reactions with both H_2O and H_2S are thermodynamically dominant in low temperature while they are kinetically favored in high temperature.

Although most of the properties of the two reactions remain the similar changing regularities, the SiH insertion reactions with H_2O and H_2S also demonstrate dissimilar changes in the features of the insertion reaction when the heavy atoms in H_2X drops from the first row to the second row in the same group(from O to S). The enthalpy change of the SiH reaction with H_2O is larger than that of the SiH reaction with H_2S at the same temperature, which means that the reaction of SiH with the second row hydride is less exothermic than that of the SiH with the first row hydride. This result supports the conclusion in ref. 6. The entropy change of the re-

Table 3　Thermodynamic and Kinetic Properties of SiH + H₂S → H₂SiSH Reaction in 200 ~ 2000 K

T / K	200	400	600	800	1000	1200	1400	1600	1800	2000
$\Delta_r H_m^\ominus$	− 182. 44	− 183. 78	− 182. 93	− 181. 18	− 179. 05	− 176. 73	− 174. 32	− 171. 85	− 169. 36	166. 86
$\Delta_r S_m^\ominus$	− 121. 02	− 126. 36	− 124. 72	− 122. 23	− 119. 86	− 117. 74	− 115. 88	− 114. 24	− 112. 77	− 111. 46
$\Delta_r G_m^\ominus$	− 158. 23	− 133. 24	− 108. 10	− 83. 40	− 59. 19	− 35. 44	− 12. 08	10. 93	33. 63	56. 05
$K(T)$	2.1×10^{41}	2.5×10^{17}	2.6×10^{9}	2.8×10^{5}	1.2×10^{3}	35	2. 8	0. 44	0. 11	3.4×10^{-2}
A	1.6×10^{12}	1.3×10^{12}	1.3×10^{12}	1.4×10^{12}	1.6×10^{12}	1.7×10^{12}	1.8×10^{12}	1.9×10^{12}	1.9×10^{12}	2.0×10^{12}
$k(T)$ / s⁻¹	1.3×10^{7}	3.8×10^{9}	2.4×10^{10}	6.2×10^{10}	1.1×10^{11}	17×10^{11}	2.4×10^{11}	3.0×10^{11}	3.7×10^{11}	4.3×10^{11}
E_a	19. 53	19. 30	19. 98	20. 95	21. 92	22. 80	23. 55	24. 18	24. 72	25. 18
g	5. 87	2. 22	1. 54	1. 30	1. 20	1. 14	1. 10	1. 07	1. 06	1. 05

Note: In tables 2 and 3, $\Delta_r H_m^\ominus$, $\Delta_r G_m^\ominus$ in the unit of kJ · mol⁻¹ and $\Delta_r S_m^\ominus$ in J · mol · K⁻¹. E_a is energy of activation including Wigner correction.

action of SiH with H_2O is smaller than that of SiH with H_2S, and the rate constant of the former reaction is much lower than that of the latter at the same temperature. The activation energy of SiH with H_2O is larger than that of SiH with H_2S, which can be confirmed by comparing the barrier heights of the two reaction pathways in ref. 6.

2.4 Comparison Reactions between Two SiH + H_2O and SiH + HF

On the basis of the results of the SiH insertion reactions with H_2O and HF, we could make the following remarks. As the heavy atom in the hydrides moves from left to right across the first row (from O to F), the reaction of the SiH with H_2O is less exothermic than that of the SiH with HF at the same temperature. At the low temperature, the rate constant of the reaction of SiH with H_2O is relatively smaller than that of SiH with HF, while the difference of the rate constants between the two reactions becomes smaller at the high temperature. According to the results by Eyring transition state theory (TST) with Wigner correction, the activation energy of the reaction of SiH with H_2O is larger than that of SiH with HF, which is in disagreement with the relative value of the barrier heights obtained by quantum chemical results in ref. 6. This indicates that the change of the temperature has different effect on different reactions, which cannot be predicted only by pure quantum mechanical calculations. Thus, it shows again that in order to give more reliable prediction of the reactivity of the reaction, the effect of the environmental temperature must be considered for discussing both the equilibrium constant and the rate constant of the reaction.

3 Conclusions

(1) Within the temperature range 200 ~ 2000 K, the SiH insertion reactions with H_2X (X = O, S) are exothermic and of entropy decreasing, and both reactions are spontaneous only at low temperature. The rate constants increase with the increasing of the tempera-

ture. The two reactions are thermodynamically dominant at low temperature and kinetically favored at high temperature, so it is important to consider both the rate constant and the conversion efficiency to choose the proper temperature for this kind of reaction.

(2) Comparison of the reactions of SiH + H_2X (X = O, S) shows that the reaction of SiH with H_2O is more exothermic than that of SiH with H_2S, while the rate constant of the former reaction is lower than that of the latter at the same temperature. Comparison of the SiH + H_2O with SiH + HF reactions indicates that the former is less exothermic than the latter, and the rate constant of the former is relatively smaller than that of the latter at the same temperature.

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