

次甲基硅 SiH 与 HF 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 HF 反应计算的基础上, 运用统计热力学和 Wigner 校正的 Eyring 过渡态理论计算了该反应在 200 ~ 2000K 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。计算结果表明该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。该反应在研究的温度范围内是一放热、熵减少的反应, 反应的速率常数随温度的升高而增大, 且服从 Arrhenius 定律。

关键词: 次甲基硅插入反应 热力学及动力学性质
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Thermodynamic and Kinetic Studies on the Reaction of Silylidyne Insertion Into HF

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On the basis of quantum chemical study of the reaction of silylidyne insertion into HF, the statistical thermodynamics and Eyring transition state theory with Wigner correction are used to estimate the thermodynamic functions, the equilibrium constants, A factors and the rate constants of this reaction in temperature range from 200 to 2000K. The results of calculation show that the reaction of SiH insertion into HF is thermodynamically dominant at low temperature and kinetically favored at high temperature. The statistical thermodynamic calculation shows that this reaction is exothermic and of entropy decrease at 200 ~ 2000K. The kinetic calculation results indicate that this reaction obeys the Arrhenius rate law, and the rate constant of this reaction increases with increasing temperature.

Keywords: silylidyne insertion reaction thermodynamic and kinetic studies

0 Introduction

Silicon chemistry has been paid more attention because of its applications to the production of thin silicon films in micro-electronics. The fundamental significance of silicon chemistry in manufacturing

semiconductor materials has stimulated its extensive investigation^[1]. Silylidyne (SiH), as known to be the smallest silicon compound which plays an important role in plasma chemical vapor deposition (CVD) processes, has been experimentally investigated^[2-5]. The reaction mechanism of SiH insertion reaction with HF

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were studied by means of *ab initio* molecular orbital calculations incorporating electron correlation with Moller-plesset perturbation theory^[6]. However, so far, the thermodynamic and kinetic quantities of the insertion reaction of SiH into HF are few and there are no available experimental data for these reactions. Therefore, in the present study based on the theoretical mechanism study of reaction of SiH insertion into HF molecule, we have carried out the calculations of the thermodynamic and kinetic properties of SiH + HF reaction at different temperatures by means of the general statistical thermodynamics and Eyring transition state theory. Incorporating theoretical study of the mechanism of this reaction, it must be more suitable to judge the reactivity of this reaction from both *ab initio* molecular orbital calculation and thermodynamic and kinetic calculations. At present condition, since the direct experimental measurements of thermodynamic and kinetic properties for SiH + HF reaction are insufficient, it is hopeful that this study will provide a better understanding of the reactivity of reaction SiH insertion into HF molecule and would be helpful to the experimental research of this reaction.

1 Computation Method

The general statistical thermodynamics (GST)^[7] is used in the calculations of the thermodynamic functions and equilibrium constants, and Eyring transition state theory (TST) with Wigner correction is used to calculate A factors and rate constants at 101.325kPa and at temperature range from 200 to 2000K, an interval 200K. The rate constant is calculated using following equation,

$$k(T) = g(k_b/h) \exp(\Delta S_m^\ddagger / R - \Delta H_m^\ddagger / RT)$$

$$g = 1 + 1/24 (h\nu^\ddagger / k_b T)^2$$

Where g is the tunneling factor corrected by Wigner, k_b and h are Boltzmann's and Planck's constants respectively, R is the ideal gas constant, and $\nu^\ddagger$ is the imaginary frequency of the transition state, $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are standard mole enthalpy and entropy of activation for the system respectively. The optimized geometries of reactants, intermediate complexes, transi-

tion states and products of this reaction derived from ref. 6 are shown in Fig. 1. The energies of all species used as the electronic energy contribution are those in ref. 6 at 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 of all species required in the paper have been recalculated at (U) HF/6-31G(d) level by Gaussian 94 program^[8] which are listed in Table 1. All computations of the thermodynamic and kinetic quantities of SiH + HF reaction are accomplished using a locally developed program^[9-14].

Table 1 Harmonic Vibrational Frequencies

molecules	harmonic frequencies/cm ⁻¹
SiH	2183.1
HF	4355.9
HSi-FH(b)	103.5, 139.6, 387.6, 561.7, 2201.3, 4290.3
TS(c)	1753.1i, 494.8, 617.6, 694.3, 1602.5, 2250.1
H ₂ SiFH(d)	773.6, 886.4, 952.3, 1022.6, 2365.5, 2386.3

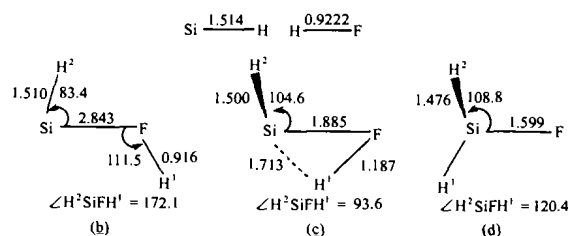
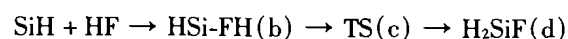


Fig. 1 Optimized structures of the reactants, intermediate complex, transition state TS, and product for the SiH reaction with HF molecule
Bond lengths are given in Å and angles in deg.

2 Results and Discussion

2.1 Entropies and Heat Capacities

The theoretical study of insertion reaction SiH into HF by standard *ab initio* molecular orbital calculations at several theoretical levels in ref 6, confirms that the reaction mechanism of SiH and HF reaction is as follows,



The thermodynamic data of the reactants, intermediate complex HSi-FH, transition state TS, and product H₂SiF of this reaction are shown in Table 2. From Table 2, it can be seen that the translational entropy St

Table 2 Thermodynamic Data of all Species in $\text{SiH} + \text{HF} \rightarrow \text{H}_2\text{SiF}$ Reaction in 200 ~ 2000K

T/K	200	400	600	800	1000	1200	1400	1600	1800	2000
SiH										
S_t	148.24	162.65	171.08	171.08	181.70	185.49	188.69	191.47	193.92	196.11
S_r	32.54	38.30	41.67	44.06	45.92	47.44	48.72	49.83	50.81	51.68
S_v	0.00	0.03	0.28	0.82	1.55	2.34	3.15	3.92	4.67	5.37
S_{total}	180.78	200.98	213.03	221.95	229.17	235.27	240.56	245.22	249.39	253.16
$C_{p,m}$	29.10	29.30	30.33	31.73	32.98	33.94	34.66	35.19	35.59	35.90
HF										
S_t	137.81	152.22	160.65	166.63	171.27	175.05	178.26	181.03	183.48	185.67
S_r	23.95	29.71	33.08	35.47	37.83	38.84	40.13	41.24	42.22	43.09
S_v	0.00	0.00	0.00	0.03	0.11	0.28	0.52	0.83	1.18	1.56
S_{total}	161.76	181.93	193.73	202.13	208.71	214.17	218.91	223.10	226.88	230.32
$C_{p,m}$	29.10	29.10	29.12	29.30	29.72	30.34	31.03	31.74	32.40	32.99
HSi-FH(b)										
S_t	154.77	169.18	177.61	183.59	188.23	192.02	195.22	197.99	200.44	202.63
S_r	83.88	92.53	97.59	101.17	103.96	106.23	108.15	109.82	111.29	112.60
S_v	22.37	40.68	53.30	63.02	71.06	77.98	84.09	89.58	94.57	99.13
S_{total}	261.02	302.39	328.50	347.78	363.24	376.22	387.46	398.39	406.30	414.36
$C_{p,m}$	55.84	62.88	65.90	68.25	70.32	72.13	73.69	75.03	76.15	77.08
TS(c)										
S_t	154.77	169.18	177.61	183.59	188.23	192.02	195.22	197.99	200.44	202.63
S_r	79.64	88.28	93.34	96.93	99.71	101.98	103.91	105.57	107.04	108.36
S_v	1.98	10.52	19.23	27.05	33.97	40.11	45.58	50.50	54.94	58.99
S_{total}	236.39	267.98	290.18	307.57	321.91	334.11	344.71	354.06	362.42	369.98
$C_{p,m}$	39.85	51.39	58.10	62.68	65.82	67.98	69.50	70.58	71.38	71.97
H₂SiF(d)										
S_t	154.77	169.18	177.61	183.59	188.23	192.02	195.22	197.99	200.44	202.63
S_r	72.52	81.17	86.22	89.81	92.59	94.87	96.79	98.46	99.92	101.24
S_v	0.43	5.82	13.82	21.83	29.29	36.10	42.29	47.91	53.05	57.77
S_{total}	227.72	256.17	277.65	295.23	310.11	322.99	334.30	344.36	353.41	361.64
$C_{p,m}$	35.53	48.20	57.79	64.33	68.94	72.20	74.53	76.23	77.50	78.46

Note: S and C_p in the unit of $\text{J}/(\text{mol} \cdot \text{K}^{-1})$

of HSi-FH, transition state TS, and H_2SiF are the same at the same temperature, while the translational entropy S_t of reactants SiH and HF are relatively smaller at the same temperature and the S_t values of SiH is larger than those of HF at the same temperature, because the value of S_t of a system depends on the pressure, temperature and the molecular weight of the molecule, and it is proportional to the molecular weight of the system. The rotational entropy S_r of HSi-FH, transition state TS, H_2SiF , SiH and HF decreases gradually according to this order with the decrease of the rotational inertia of these systems. The vibrational entropy S_v of these species changes as the same order as the rotational entropy in a large temperature range which can be confirmed by comparing the harmonic vibrational frequencies of these species in Table 1, and it is known

that the larger the frequency, the smaller the vibrational partitioning function, so the smaller the S_v value of the system. Therefore, the values of the total entropy S_{total} of these systems are in the order of $\text{HSi-FH} > \text{TS} > \text{H}_2\text{SiF} > \text{SiH} > \text{HF}$. Also as seen in Table 2, the values of molar heat capacity C_p of HSi-FH, transition state TS, H_2SiF differ slightly in the temperature range 200 ~ 2000K, while C_p of SiH is larger than that of HF molecule at the same temperature.

2.2 Thermodynamic Properties

It should be pointed out that in the discussion of the thermodynamic properties of this reaction, the thermodynamic function changes of ΔH , ΔG , ΔS and $K(T)$ of the overall reaction $\text{SiH} + \text{HF} \rightarrow \text{H}_2\text{SiF}$ are calculated and given in Table 3. In investigating the kinetic properties of the reaction, as it is shown in ref.

Table 3 Thermodynamic and Kinetic Properties of SiH + HF $\rightarrow$ H₂SiF Reaction in 200 ~ 2000K

T/K	200	400	600	800	1000	1200	1400	1600	1800	2000
ΔH	-246.78	-250.08	-251.18	-250.98	-249.99	-248.57	-246.88	-245.06	-243.18	-241.27
ΔS	-114.82	-126.75	-129.11	-128.85	-127.77	-126.47	-125.17	-123.95	-122.85	-121.84
ΔG	-223.82	-199.38	-173.72	-147.90	-122.23	-96.81	-71.65	-46.74	-22.06	2.41
$K(T)$	.28E59	.11E27	.13E16	.45E10	.24E07	.16E05	.47E03	.34E02	.44E01	.86
A	.58E12	.36E12	.34E12	.36E12	.39E12	.43E12	.46E12	.49E12	.52E12	.54E12
$k(t)/s^{-1}$	.72E01	.17E07	.90E08	.66E09	.23E10	.52E10	.97E10	.16E11	.28E11	.31E11
E_a	41.77	40.79	41.05	41.84	42.87	43.94	44.99	45.95	46.83	47.61
g	7.64	2.66	1.74	1.42	1.26	1.18	1.13	1.10	1.08	1.07

Note: ΔH , ΔG in the unit of $\text{kJ} \cdot \text{mol}^{-1}$ and ΔS in $\text{J}/(\text{mol} \cdot \text{K}^{-1})$. E_a is energy of activation including wigner correction.

6 that there are two steps in the reaction, the first step of SiH reaction with HF to obtain the intermediate complex HSi-FH is a non-barrier process which is the fast step of the reaction, so the second step is the determinant step of the overall reaction, thus the kinetic properties of the second step are calculated by Eyring transition state theory with Wigner correction which are also given in Table 3.

As it is shown in Table 3, in the temperature range 200 ~ 2000K, both the enthalpy changes ΔH and the entropy changes ΔS are negative, i. e., this reaction is exothermic and of an entropy decrease reaction. The Gibbs free energy changes ΔG are negative when $T \leq 1800\text{K}$, while positive when $T > 1800\text{K}$. This indicates that the insertion reaction of SiH into HF is spontaneous while $T \leq 1800\text{K}$. The equilibrium constant $K(T)$ of this reaction falls down quickly from 200 to 2000K, as it can be seen in Table 3, the higher the temperature, the smaller the equilibrium constant of the reaction. Therefore, from the viewpoint of the conversion coefficient analysis, it is shown that the SiH insertion reaction with HF is thermodynamically dominant at lower temperatures.

2.3 Kinetic Properties

For discussion of the kinetic properties of this reaction, the calculated A factors and rate constants $k(t)$ by using Eyring transition state theory(TST) with Wigner correction are given in Table 3. As it can be seen in Table 3, the insertion reaction of SiH into HF takes place slowly below 200K because of a small rate constant $k(t) < 7.3\text{s}^{-1}$. With the increase of the temperature, the rate constant increases gradually, and the higher the temperature, the faster the SiH reaction

with HF. Therefore, from the viewpoint of rate constant analysis, the SiH insertion reaction with HF is kinetically favored at high temperature. In Table 3, the A factors of this reaction vary only slightly with the change of the temperature, so this reaction obeys the Arrhenius rate law with that $\log A$ equals about 12 in 200 ~ 2000K. It is necessary to point out that the activation energy E_a obtained from the calculation with wigner correction for this reaction increases with increasing temperature. It is obvious that these thermodynamic and kinetic properties of the reaction cannot be predicted only by pure quantum chemical calculations. Therefore, it is of practical significance to discuss the changes of both equilibrium constant and rate constant with changes of temperature, furthermore, combining these two factors it is more suitable to choose the proper temperature for a certain reaction.

3 Conclusions

The principal conclusions emerging from the present study are as follows:

(1) In the temperature range 200 ~ 2000K, for SiH insertion reaction into HF, $\Delta H < 0$, $\Delta S < 0$, i. e., it is exothermic and of entropy decrease, and $\Delta G < 0$, so it is spontaneous only when $T \leq 1800\text{K}$.

(2) The higher the temperature, the faster the SiH insertion reaction into HF, and it is of the type of Arrhenius reactions.

(3) It is thermodynamically dominant at low temperatures and kinetically favored at higher temperatures. So it is important to consider both the rate constant and the conversion efficiency to choose the proper temperature for this reaction.

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