

Thermodynamic and Kinetic Studies on the SiH + XH₃ (X=N, P) Reactions

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Abstract: Based on the quantum chemical study of the silylidyne insertion reaction with NH₃ or PH₃, the general statistical thermodynamics and Eyring transition state theory with Wigner correction are used to compute the changes of thermodynamic functions, equilibrium constants, *A* factors and rate constants of the two reactions in the temperature range 200-2000K. The results show that both of these reactions are thermodynamically dominant at low temperatures and kinetically favored at higher temperatures. The comparison between these two reactions shows that the SiH reaction with NH₃ is more exothermic than SiH with PH₃, while the rate constant of SiH reaction with NH₃ is lower than that of SiH with PH₃ at the same temperature.

Keywords: Silylidyne insertion reaction, thermodynamic and kinetic studies.

Silicon chemistry has been attracted more attention because of its applications to the production of thin silicon films and the etching of silicon wafers in micro-electronics¹. Silylidyne (SiH), which plays an important role in plasma chemical vapor deposition (CVD) processes, has been investigated in experimental research²⁻⁵. The reaction mechanism of SiH insertion reaction with small molecules such as XH₃ (X=N, P) was recently studied by means of MØller-Plesset perturbation theory⁶. However, so far, the thermodynamic and kinetic quantities of SiH insertion reactions are very few and there are no available experimental data for these reactions. Therefore, in the present study, based on the results of quantum chemical study⁶, we have carried out the calculations of the thermodynamic and kinetic properties of SiH + XH₃ (X=N, P) reactions by means of general statistical thermodynamics and Eyring transition state theory with Wigner correction. It must be more suitable to judge the reactivity of these reactions not only from quantum chemical calculation but also from the thermodynamic and kinetic computation. It is hopeful that this study will provide a better understanding of the reactivity of SiH insertion reactions with XH₃ (X=N, P) molecules and would be helpful to the experimental research of SiH insertion reactions.

Computation methods

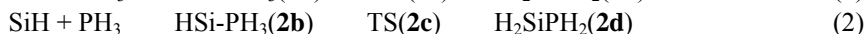
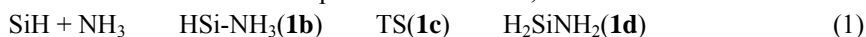
Standard *ab initio* molecular orbital calculations were performed using Gaussian 98

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program⁷. The structures studied in this study were optimized at mp2(fc)/6-31G(d,p) level in ref. 6. Frequency calculations were carried out at the same level which are scaled by a factor of 0.94 and given in **Table 1**. The electronic structure energies were obtained at mp2(fc)/6-31G(d,p) level and ZPE is obtained at the same level for correcting the zero-point energies. Furthermore, the general statistical thermodynamics (GST)⁸ and Eyring transition state theory (TST) with Wigner correction are used in the calculations of the thermodynamic and kinetic properties of both reactions⁹. The pressure is 1 atm and the temperature range is 200-2000K. All computations are accomplished using a locally developed program⁹⁻¹⁰.

Results and Discussion

The mechanism of SiH insertion reactions with NH₃ and PH₃ investigated by *ab initio* calculations at several levels is expressed as follows⁶,



The results with ZPE correction predict that there are two steps in each reaction in which the first step is a barrierless process while the second step is the determinant step for both reactions.

Table 1 Harmonic vibrational frequencies for stable molecules and transition states at the mp2(fc)/6-31G(d, p) level

Molecules	Harmonic frequencies(cm ⁻¹)
SiH	2009.2
NH ₃	1056.2, 1622.2, 1622.2, 3344.2, 3491.1, 3491.1
HSi-NH ₃ (1b)	164.8, 368.5, 529.2, 565.8, 856.9, 1220.2, 1597.0, 1598.8, 1966.5, 3327.4, 3464.7, 3468.1
TS(1c)	1494.4i, 496.9, 597.5, 610.4, 657.4, 878.5, 904.6, 1495.6, 1629.2, 2030.2, 3379.4, 3513.5
H ₂ SiNH ₂ (1d)	185.5, 447.8, 626.2, 759.5, 795.8, 884.7, 894.8, 1537.8, 2144.6, 2173.2, 3437.5, 3542.8
PH ₃	1013.1, 1112.6, 1112.6, 2381.4, 2396.4, 2396.4
HSi-PH ₃ (2b)	216.2, 318.6, 391.8, 399.7, 773.6, 1038.8, 1081.6, 1095.1, 1977.8, 2401.3, 2404.2, 2453.2
TS(2c)	79.3i, 189.1, 227.7, 342.8, 695.4, 995.2, 1058.6, 1159.1, 1896.5, 2009.1, 2382.1, 2402.3
H ₂ SiPH ₂ (2d)	165.1, 444.8, 475.6, 526.0, 732.4, 772.5, 905.7, 1072.3, 2156.6, 2181.3, 2376.2, 2382.8

The results of the thermodynamic function changes of SiH + NH₃→H₂SiNH₂ reaction are listed in **Table 2**.

It is shown that in the temperature range 200-2000 K, both the enthalpy changes ${}_rH_m^\ominus$ and the entropy changes ${}_rS_m^\ominus$ are negative, *i. e.*, it is an exothermic and of entropy decrease reaction. The Gibbs free energy changes ${}_rG_m^\ominus$ are negative when $T \leq 1600\text{K}$, positive when $T \geq 1800\text{K}$, indicating that the SiH insertion reaction with NH₃ is spontaneous only at lower temperatures $T \leq 1600\text{K}$. The higher the temperature, the smaller the equilibrium constant of this reaction, for $K(T)$ falls from 3.2×10^{45} at 200K to 0.16 at 2000K. Therefore, from the viewpoint of the equilibrium constant analysis, the SiH insertion reaction with NH₃ is thermodynamically dominant at lower temperatures.

Table 2 Thermodynamic and kinetic properties of SiH+NH₃ → H₂SiNH₂ reaction in 200-2000K

T/K	200	600	1000	1400	1600	1800	2000
${}_{r}H_m^\ominus$	-198.49	-197.51	-192.21	-186.36	-183.46	-180.59	-177.76
${}_{r}S_m^\ominus$	-121.24	-121.04	-114.34	-109.42	-107.48	-105.80	-104.31
${}_{r}G_m^\ominus$	-174.24	-124.89	-77.87	-33.17	-11.48	9.74	30.84
K(T)	.32E46	.74E11	.11E05	.17E02	.24E01	.52E00	.16E00
A	.33E13	.58E13	.91E13	.11E14	.12E14	.13E14	.14E14
k(T)/s ⁻¹	.69E-19	.92E02	.20E07	.16E09	.64E09	.19E10	.46E10
E _a	121.31	124.08	127.63	130.31	131.35	132.23	132.97
g	5.82	1.54	1.19	1.10	1.08	1.06	1.05

The calculated results of A factors and rate constants $k(T)$ of HSi-NH₃ → TS → H₂SiNH₂ are also given in **Table 2**. It is obvious that it takes place slowly below 600K at the rate constant $k(T) < 92 \text{ s}^{-1}$, however, with the increase of the temperature, $k(T)$ increases gradually which reaches $4.6 \times 10^9 \text{ s}^{-1}$ at 2000 K. Therefore, it is kinetically favored at higher temperatures. The A factors vary only slightly with the change of the temperature with $\log A$ equals about 13 ~ 14 in 200-2000 K. The activation energy E_a increases with increasing temperature, which confirms that E_a is a function related to the temperature.

The results of the thermodynamic properties of SiH + PH₃ → H₂SiPH₂ and the kinetic properties of HSi-PH₃ → TS → H₂SiPH₂ are given in **Table 3**.

Table 3 Thermodynamic and kinetic properties of SiH+PH₃ → H₂SiPH₂ reaction in 200-2000K

T/K	200	600	1000	1400	1600	1800	2000
${}_{r}H_m^\ominus$	-172.31	-170.60	-166.05	-161.16	-158.68	-156.19	-153.70
${}_{r}S_m^\ominus$	-123.76	-120.97	-115.19	-111.08	-109.43	-107.97	-106.65
${}_{r}G_m^\ominus$	-147.56	-98.02	-50.85	-5.64	16.41	38.15	59.60
K(T)	.34E39	.34E09	.45E03	.16E01	.29E00	.78E-01	.27E-01
A	.17E14	.29E14	.33E14	.35E14	.36E14	.36E14	.37E14
k(T)/s ⁻¹	.21E-06	.50E07	.26E10	.39E11	.92E11	.18E12	.30E12
E _a	76.30	77.70	78.55	79.19	79.44	79.64	79.82
g	1.04	1.00	1.00	1.00	1.00	1.00	1.00

Note: In **Tables 2** and **3**, ${}_{r}H_m^\ominus$, ${}_{r}G_m^\ominus$, E_a in the unit of kJ/mol and ${}_{r}S_m^\ominus$ in J/mol·K.

It is observed that in the temperature range 200-2000K, ${}_{r}H_m^\ominus < 0$ and ${}_{r}S_m^\ominus < 0$, i. e., it is exothermic and of entropy decrease. The changes of Gibbs free energy ${}_{r}G_m^\ominus$ are negative when $T \leq 1400$ K, while positive when $T \geq 1600$ K, which indicates that it is spontaneous at lower temperatures $T \leq 1400$ K. In 200-2000K, K(T) falls from 3.4×10^{39} to 0.027. Thus, it is thermodynamically dominant at lower temperatures. The kinetic results show that the rate constant increases from 2.1×10^{-7} to $3.0 \times 10^{11} \text{ s}^{-1}$ in 200-2000 K, which means that the higher the temperature, the faster the SiH reaction with PH₃. Therefore, it is kinetically dominant at higher temperatures. The A factors remain almost a constant with $\log A$ equals about 14 in 200-2000K. It is also noted that the activation energy E_a increases with the increasing temperature.

Since NH_3 and PH_3 have the same valence electronic structure, it is not surprising to note that the thermodynamic and kinetic properties of SiH with PH_3 reaction are similar to those of SiH with NH_3 . As seen above, both of the reactions are thermodynamically dominant in low temperature while kinetically favored in higher temperature. Although most of properties of the two reactions remain the similar changing regulations, they also demonstrate dissimilar changes in some features. The enthalpy changes of SiH reaction with NH_3 are larger than those of SiH with PH_3 while the rate constants of SiH reaction with NH_3 are lower than those of SiH with PH_3 at the same temperature.

Therefore, as it has been stated, the thermodynamic and kinetic properties are necessary to choose the proper reaction temperature since they cannot be predicted only by pure quantum chemical calculations. It is significant to discuss the effect of temperature on the equilibrium and rate constants in the practical production. Toward this object, it must be more suitable to determine the reactivity of chemical reactions combining all these theoretical calculations.

Acknowledgments

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