

Supporting Information

The direct and steady state rate constants of C_2H_6+X ($X=H, Cl, OH$): Influence of van der Waals well

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1. The van der Waals well, the direct free energy barrier (from the reactants to transition state) and the steady state free energy barrier (from the van der Waals well to transition state) for the C_2H_6+H , C_2H_6+Cl and C_2H_6+OH reactions in the temperature range of 250-1000 K.

Table S1. The van der Waals well, and the direct and steady state free energy barriers at different temperatures (kcal/mol)

T(K)	C_2H_6+H		C_2H_6+Cl		C_2H_6+OH		
	direct	well	steady state	direct	well	steady state	direct
250	11.29	-1.22	1.37	0.15	-3.32	5.17	1.85
300	12.15	-1.26	1.68	0.42	-3.39	5.90	2.51
400	13.53	-1.36	2.21	0.85	-3.45	7.26	3.81
500	14.75	-1.43	2.67	1.24	-3.44	8.17	4.73
600	16.19	-1.54	3.11	1.57	-3.39	9.05	5.66
800	18.22	-1.74	3.80	2.06	-3.38	10.45	7.07
1000	20.23	-1.91	4.28	2.37	-3.47	11.61	8.14

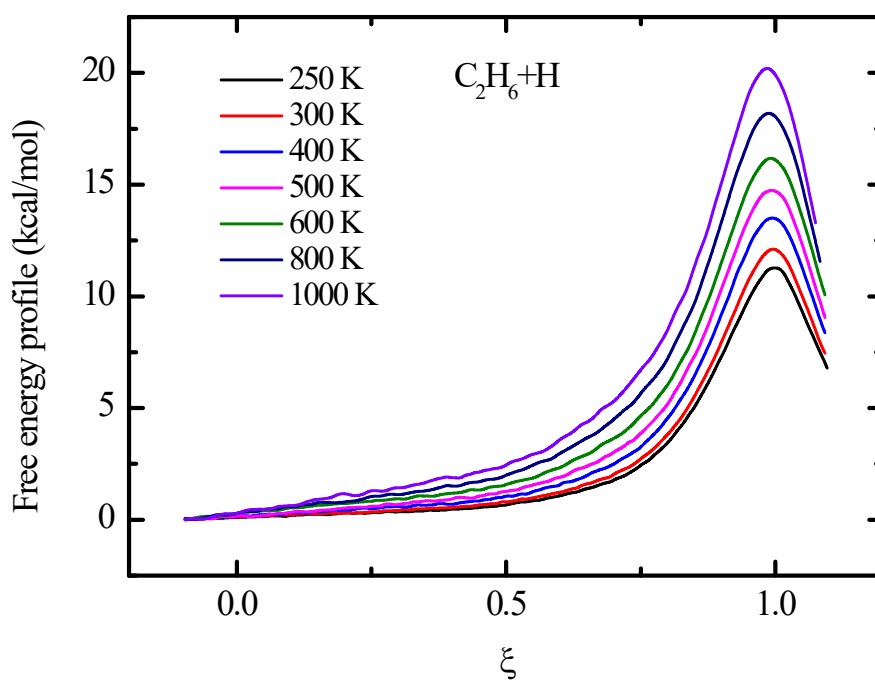


Fig. S1 Free energy profile for the C_2H_6+H reaction along the reaction path.

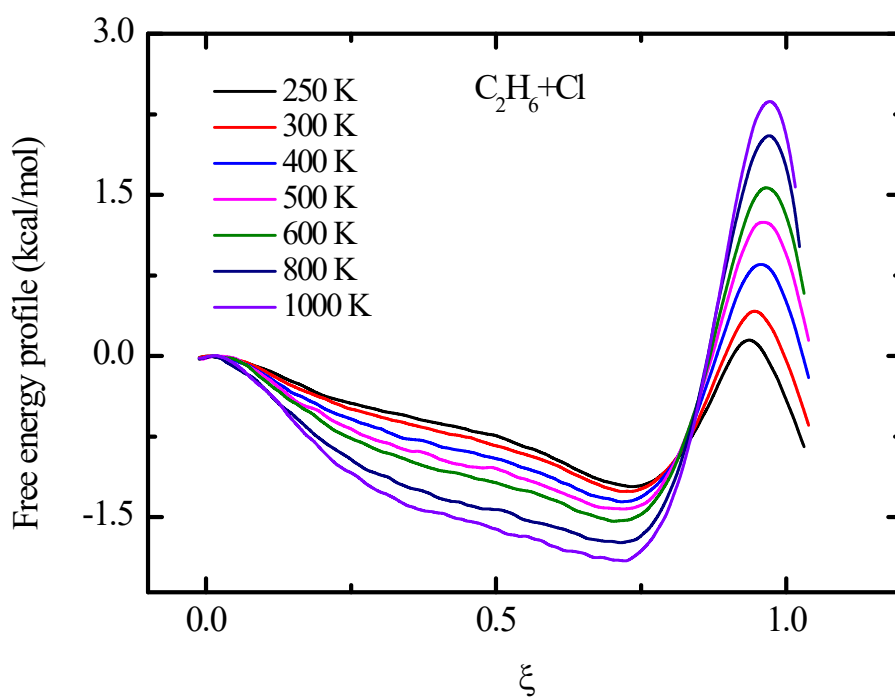


Fig. S2 Free energy profile for the $C_2H_6 + Cl$ reaction along the reaction path.

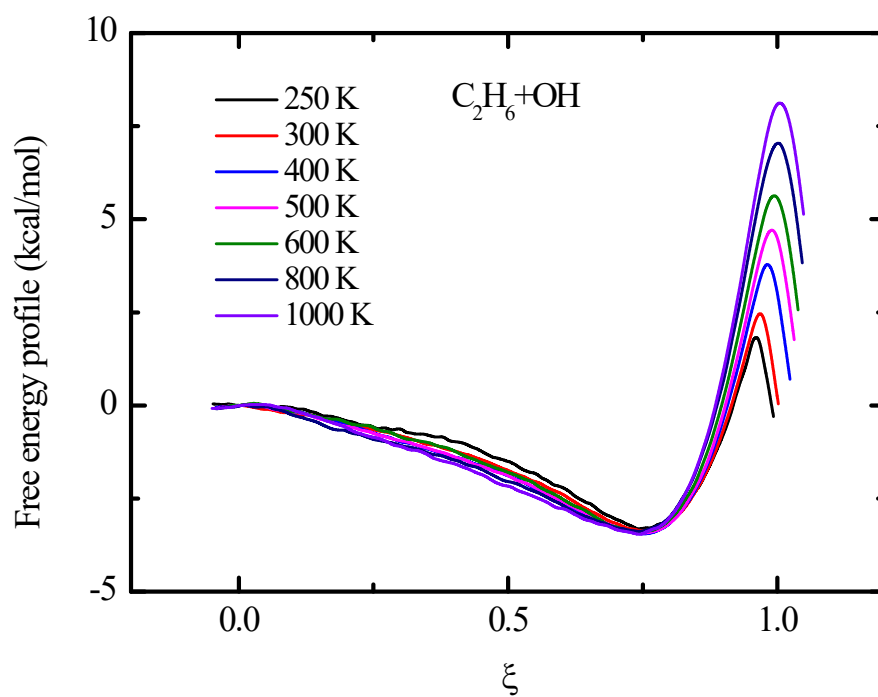


Fig. S3 Free energy profile for the $C_2H_6 + OH$ reaction along the reaction path.

2. For the classical transition state theory, the formulas of direct and steady state rate constants are given by

$$k_{\text{direct}} = \frac{k_{\text{B}}T}{h} \cdot e^{-[(G_{\text{TS}}-G_{\text{R}})/k_{\text{B}}T]} \quad (\text{S1})$$

$$k_{\text{steady}} = K \cdot k_2 = e^{-[(G_{\text{RC}}-G_{\text{R}})/k_{\text{B}}T]} \cdot \frac{k_{\text{B}}T}{h} \cdot e^{-[(G_{\text{TS}}-G_{\text{RC}})/k_{\text{B}}T]} = \frac{k_{\text{B}}T}{h} \cdot e^{-[(G_{\text{TS}}-G_{\text{R}})/k_{\text{B}}T]} = k_{\text{direct}} \quad (\text{S2})$$

where G_{R} , G_{RC} and G_{TS} represent the free energies of reactants, reactant complex and transition state, respectively.

It is clear that the direct and steady state rate constants are the same in the classical transition state theory without considering the tunneling effect.