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C₂H₃与CH₃F氢抽提反应机理与动力学性质

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摘要: 采用双水平直接动力学方法对C₂H₃与CH₃F氢抽提反应进行了研究. 在QCISD(T)/6-311++G(d, p)//B3LYP/6-311G(d, p)水平上, 计算的三个反应通道R1、R2和R3的能垒($\Delta E^\ddagger$)分别为43.2、43.9和44.1 kJ·mol⁻¹, 反应热为-38.2 kJ·mol⁻¹. 此外, 利用传统过渡态理论(TST)、正则变分过渡态理论(CVT)和包含小曲率隧道效应(SCT)的CVT, 分别计算了200–3000 K温度范围内反应的速率常数 k^{TST} 、 k^{CVT} 和 $k^{\text{CVT/SCT}}$. 结果表明: (1) 三个氢抽提反应通道的速率常数随温度的增加而增大, 其中变分效应的影响可以忽略, 隧道效应则在低温段影响显著; (2) R1反应是主反应通道, 但随着温度的升高, R2反应的竞争力增大, 而R3反应对总速率常数的影响很小.

关键词: C₂H₃; CH₃F; 氢抽提反应; QCISD(T)//B3LYP; 速率常数

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Mechanism and Kinetics of the Hydrogen Abstraction Reaction of C₂H₃ with CH₃F

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Abstract: A dual-level direct dynamics method was employed to study the hydrogen abstraction reaction of C₂H₃ with CH₃F. The calculated potential barriers ($\Delta E^\ddagger$) of reaction channels R1, R2, and R3 are 43.2, 43.9, and 44.1 kJ·mol⁻¹, respectively, and the reaction energy is -38.2 kJ·mol⁻¹ at the QCISD(T)/6-311++G(d, p)//B3LYP/6-311G(d, p) level. In addition, the rate constants of the reaction were evaluated by means of the conventional transition-state theory (TST) and canonical variational transition-state theory (CVT) with or without small curvature tunneling corrections (SCT) over a wide temperature range of 200–3000 K. The results indicate that the rate constants of the three hydrogen abstraction reaction channels exhibit a positive temperature dependence, in which the variational effect is negligible for all the channels, whereas the tunneling effect is considerable at lower temperatures. Moreover, the reaction R1 is the dominant channel. Reaction R2 competes kinetically with R1 as the temperature increases, whereas the contribution from R3 is small.

Key Words: C₂H₃; CH₃F; Hydrogen abstraction reaction; QCISD(T)//B3LYP; Rate constant

1 Introduction

Hydrofluorocarbons (HFCs) have been considered as new and potential refrigerant and flame suppressants due to the characters of efficiency, non-toxicity, and low global environ-

mental impact. The commercial productions of HFCs have come into widespread use in a variety of industrial applications as the interim replacements for the ozone-destroying chlorofluorocarbons (CFCs) and halon fire suppression agents.^{1,2} The re-

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search on the combustion property of HFCs has been receiving much attention recent years.³⁻¹⁶ As one of the most commonly used HFCs, the micro-reaction dynamics data of CH_3F are very helpful to better understand the reaction characters in flame and combustion chemistry and to estimate the atmosphere lifetime. On the other hand, unsaturated hydrocarbon radicals are regarded as key intermediates in hydrocarbon combustion processes and play an important role in the atmospheric chemistry. In this aspect, the vinyl radical C_2H_3 , the simplest alkenyl radical, is significant species in atmospheric environments. In fact, since CH_3F is widespread in atmosphere, CH_3F and C_2H_3 might coexist during the combustion processes. Hence, the reaction of C_2H_3 with CH_3F deserves our attention. Furthermore, the title reaction might influence the decay rate of the radical C_2H_3 and might further have an effect on the other chain reactions considered in the overall combustion processes. However, the task to study the reactive intermediate C_2H_3 is still challenging. The paucity of dynamics information is due to the extremely experimental difficulty in generating sufficient quantities of C_2H_3 radicals cleanly and the technique difficulty in detecting them sensitively at the quantum state level. Of course, in recent years, there has been limited progress in understanding some aspects of vinyl radical reaction. Certain experimental and theoretical investigations have been performed on the C_2H_3 reaction with different atoms, radicals, and molecules such as H ,^{17,18} N ,^{19,20} CH_3 ,²¹ O ,²² H_2 ,²³⁻²⁵ O_2 ,²⁶⁻³⁰ NO ,³¹⁻³³ NO_2 ,³⁴ C_2H_4 ,³⁵ C_3H_6 ,³⁶ C_2H_6 ,³⁷ HCOCN ,³⁸ etc. Nevertheless, in contrast to abundance of research on C_2H_3 radicals with other species, kinetic data on the reaction of C_2H_3 with CH_3F are sparse. Up to now, there have been no any direct kinetic measurement on the hydrogen abstraction reaction of C_2H_3 with CH_3F experimentally, and only one estimated value derived from an indirect source could be available in the literature³⁹. A comprehensive, detailed thermochemical and chemical kinetic mechanism study was performed by Burgess *et al.* for C_1 and C_2 fluorinated hydrocarbons. To some extent, this work was very important to understand the dynamic features of HFCs, especially to those reactions where no or incomplete kinetic data were available. As far as the title reaction was concerned, they presented a simple Arrhenius form $k=2.5 \times 10^{-13} \exp(-5184/T)$ (unit of k is $\text{cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$), which was helpful to instruct the future experimental study. However, this formula may have some uncertainties, because it was estimated by adjusting the activation energy (90% of the activation energy) and pre-exponential factor relative to a reference reaction of CH_3 with CH_3F in a narrow temperature range of 466–604 K. Therefore, it may not predict exactly the overall dynamic feature of the title reaction. Furthermore, the data provided from the limited temperature range are still far from covering the whole temperatures range of practical interest. To estimate the atmospheric lifetimes of such species, accurate data for the rate constants and their temperature dependence are still needed. In this paper, a dual-level

QCISD(T)/6-311++G(d, p)/B3LYP/6-311G(d, p) method was employed to study the hydrogen abstraction reaction of C_2H_3 with CH_3F , and the rate constants were calculated in the temperature range of 200–3000 K. The detailed dynamic study not only enriches the kinetic data in a wide temperature range, but also provides a theoretical prediction for the future experimental measurements.

2 Calculation methods

All of the electronic structure calculations were carried out employing the Gaussian 03 package.⁴⁰ The geometries and harmonic vibrational frequencies of all the stationary points (the reactants, transition states, and products) were calculated using B3LYP and MP2 methods in conjunction with the 6-311G(d, p), 6-311+G(d, p), and 6-311G(2df, 2p) basis sets. Some geometries were also calculated employing the high-level QCISD/6-311G(d, p) method. Based on a series of comparisons between the calculated methods and the basis sets, we chose B3LYP/6-311G(d, p) method to calculate the potential energy surface. Starting from the B3LYP/6-311G(d, p) saddle-point geometries, and going downhill to both the asymptotic reactant and product channels, we constructed the intrinsic reaction coordinate (IRC) with an even gradient step size of $0.02 (\text{amu})^{1/2} \cdot \text{Bohr}$. Each saddle point was confirmed to connect the designated reactants and products for all the channels. To improve the accuracy of the energy, single-point calculations for all the stationary points were carried out at the QCISD(T)/6-311++G(d, p), approximate QCISD(T)/6-311++G(3df, 2pd)⁴¹ [denoted as a-QCISD(T), which was evaluated *via* the relation a-QCISD(T)/6-311++G(3df, 2pd) $\approx$ QCISD(T)/6-311++G(d, p) + MP2/6-311++G(3df, 2pd) – MP2/6-311++G(d, p)], QCISD(T)/6-311++G(2df, 2p), CCSD(T)/6-311++G(d, p), and CCSD(T)/6-311++G(2df, 2p) levels using the B3LYP/6-311G(d, p) optimized geometries. As a reasonable compromise between the computational cost and accuracy, the dual-level QCISD(T)/6-311++G(d, p)/B3LYP/6-311G(d, p) method was chosen to refine the single point energies of the selected points along the minimum energy path (MEP). The potential energy curve was further refined with the interpolated single point energies (ISPE) method.⁴²

The level of variational transition-state theory employed in this paper was the canonical variational transition theory (CVT) with small curvature tunneling correction (SCT). The rate constants were calculated in the temperature range of 200–3000 K. All of the dynamics calculations were carried out using Polyrate 8.2 program.⁴³

3 Results and discussion

3.1 Stationary points

The geometries of the reactants, products, and the transition states optimized at the B3LYP/6-311G(d, p) level are displayed in Fig.1, including some geometric parameters calculated at the high-level QCISD/6-311G(d, p) and some available experimental data.^{44,45} More structural parameters obtained at the

Fig.1 Geometries of the reactants, products, and the transition states optimized at the B3LYP/6-311G(*d, p*) level

The data in bold are the theoretical values calculated at the high-level QCISD/6-311G(*d, p*); the data in parentheses are the experimental values which are taken from literature⁴⁴ for CH_3F and literature⁴⁵ for C_2H_4 . Bond lengths are in nm and bond angles are in degree.

MP2/6-311G(2*df, 2p*), MP2/6-311+G(*d, p*), MP2/6-311G(*d, p*), B3LYP/6-311G(2*df, 2p*), and B3LYP/6-311+G(*d, p*) levels can be found in Supporting Information Fig.S1. From Fig.1, we can see that the geometries optimized at the B3LYP/6-311G(*d, p*) level are close to those calculated at the high-level QCISD/6-311G(*d, p*), both are in agreement with the experimental values. Therefore, in this study, the reaction path was calculated mainly employing the B3LYP/6-311G(*d, p*) method. Four transition states were found, however, only the first three TS1, TS2, and TS3 will be discussed in detail later because the last transition state TS4 is exactly the same as the third TS3. The three channels are denoted by R1, R2, and R3, the rate con-

stants are labeled as k_1 , k_2 , and k_3 , respectively. For the three transition states, the breaking $C(4)-H(3)$ bonds are elongated by 18.8%, 18.3%, and 18.2% with regard to the $C-H$ equilibrium bond length of CH_3F at the B3LYP/6-311G(*d, p*) level, and the forming $C(2)-H(3)$ bonds are 28.8%, 29.5%, and 29.6% longer than the $C-H$ equilibrium bond length of C_2H_4 , respectively. Based on the active bond variational ratio, TS1, TS2, and TS3 are reactant-like transition states, and the title reaction should be the exothermic reaction.⁴⁶

The harmonic vibrational frequencies of all the stationary points at the B3LYP/6-311G(*d, p*) level as well as the experimental values^{44,47-49} are tabulated in Table 1. More values are

Table 1 Harmonic vibrational frequencies for the reactants, products, and the transition states involved in the reaction of C_2H_3 with CH_3F at the B3LYP/6-311G(*d, p*) level

Species	Method	Frequency/cm ⁻¹									
C_2H_3	B3LYP/6-311G(<i>d, p</i>)	712	820	921	1046	1391	1651	3038	3133	3236	
	expt. ⁴⁷		900	920	1200	1306					
CH_3F	B3LYP/6-311G(<i>d, p</i>)	1057	1190	1190	1485	1485	1498	3021	3100	3100	
	expt. ⁴⁴	1049	1182	1182	1464	1464	1467	2965	3006	3006	
C_2H_4	B3LYP/6-311G(<i>d, p</i>)	835	973	974	1066	1239	1380	1472	1692	3122	3137
	expt. ⁴⁸	826	943	949	1023	1236	1342	1444	1623	2989	3026
CH_2F	B3LYP/6-311G(<i>d, p</i>)	512	1173	1177	1472	3123	3282				
	expt. ⁴⁹		1163	1170							
TS1	B3LYP/6-311G(<i>d, p</i>)	68	92	258	282	516	539	863	916	965	1078
		1195	1310	1399	1447	1500	1659	3046	3080	3145	3161
TS2	B3LYP/6-311G(<i>d, p</i>)	28	84	204	240	510	546	868	922	960	1086
		1208	1316	1407	1431	1492	1657	3044	3078	3142	3151
TS3	B3LYP/6-311G(<i>d, p</i>)	11	106	143	319	494	546	875	921	959	1087
		1209	1324	1405	1432	1481	1657	3042	3080	3137	3153

listed in Supporting Information Table S1. It is obvious that the frequencies calculated at the B3LYP/6-311G(*d, p*) level agree with experimental values well. At the B3LYP/6-311G(*d, p*) level, the characters of the three saddle points are confirmed by normal mode analysis, which yield one and only one imaginary frequency with the values of 1576i, 1562i, and 1557i cm^{-1} , whose eigenvectors correspond to the stretching modes of the coupling between breaking and forming bonds. Since a large absolute value of the imaginary frequency means a narrow width of the potential barrier,^{50,51} which in turn benefits the tunneling effect, therefore, the quantum tunneling effect may be significant and plays a key role in the calculated rate constants for the title reaction system.

The reaction energies (ΔE) and classical potential barriers ($\Delta E^\ddagger$) calculated at different levels are listed in Table 2, including the proposed active energy³⁹ and the reaction enthalpy derived from the heats of formation^{44,52–54}. Note that the error limits of the reaction enthalpy were estimated by adding the maximum uncertainties of ΔH_f for the reference compounds. As seen in Table 2, although the reaction energies at different levels are all within the error margin of the estimated reaction enthalpy (-46.8 ± 16.4) $\text{kJ} \cdot \text{mol}^{-1}$, high-level single-point energy

Table 2 Potential barriers $\Delta E^\ddagger$ (in $\text{kJ} \cdot \text{mol}^{-1}$) and reaction energies ΔE (in $\text{kJ} \cdot \text{mol}^{-1}$) with the ZPE correction calculated at different levels for the reaction channels R1, R2 and R3

Method	$\Delta E^\ddagger(\text{R1})$	$\Delta E^\ddagger(\text{R2})$	$\Delta E^\ddagger(\text{R3})$	ΔE
MP2/6-311G(2df, 2p)	33.3	35.7	36.0	-50.7
MP2/6-311+G(<i>d, p</i>)	38.3	39.1	39.3	-45.4
MP2/6-311G(<i>d, p</i>)	36.1	38.1	38.5	-47.6
B3LYP/6-311G(2df, 2p)	27.5	29.1	29.3	-43.1
B3LYP/6-311+G(<i>d, p</i>)	31.6	32.0	32.2	-39.3
B3LYP/6-311G(<i>d, p</i>)	26.3	27.9	28.2	-42.5
QCISD/6-311G(<i>d, p</i>)	48.4			-41.2
MP2/6-311++G(<i>d, p</i>)//B3LYP/6-311G(<i>d, p</i>)	36.9	37.4	37.6	-38.9
MP2/6-311++G(3df, 2pd)//B3LYP/6-311G(<i>d, p</i>)	33.9	34.9	34.9	-41.6
QCISD(T)/6-311++G(<i>d, p</i>)//B3LYP/6-311G(<i>d, p</i>)	43.2	43.9	44.1	-38.2
QCISD(T)/6-311++G(<i>d, p</i>)//QCISD/6-311G(<i>d, p</i>)	43.2			-39.2
a-QCISD(T)/6-311++G(3df, 2pd)//B3LYP/6-311G(<i>d, p</i>)	40.2	41.4	41.4	-40.9
QCISD(T)/6-311++G(2df, 2p)//B3LYP/6-311G(<i>d, p</i>)	42.5	43.4	43.4	-40.4
CCSD(T)/6-311++G(<i>d, p</i>)//B3LYP/6-311G(<i>d, p</i>)	43.6	44.2	44.4	-38.5
CCSD(T)/6-311++G(2df, 2p)//B3LYP/6-311G(<i>d, p</i>)	42.8	43.6	43.7	-40.8
literature		43.1 ^a		-46.8 $\pm$ 16.4 ^b

^aThe activation energy reported in literature³⁹ is 90% of the activation energy for a hydrogen abstraction reaction of CH_3 with CH_3F ; ^bThe estimated enthalpy derived from the heats of formation of reactants and products (C_2H_3 : 300.0 ± 3.3) $\text{kJ} \cdot \text{mol}^{-1}$ in literature;⁵² CH_3F : (-232.6 ± 8.4) $\text{kJ} \cdot \text{mol}^{-1}$ in literature;⁵³ C_2H_4 : (52.4 ± 0.5) $\text{kJ} \cdot \text{mol}^{-1}$ in literature;⁴⁴ CH_2F : (-31.8 ± 4.2) $\text{kJ} \cdot \text{mol}^{-1}$ in literature⁵⁴)

calculations are still needed to get more accurate values, especially to the potential barriers. For this reason, the energies of all stationary points were further refined by the high-level QCISD(T)/6-311++G(*d, p*), a-QCISD(T)/6-311++G(3df, 2pd), QCISD(T)/6-311++G(2df, 2p), CCSD(T)/6-311++G(*d, p*), and CCSD(T)/6-311++G(2df, 2p) methods. It can be found that the reaction energies and the potential barriers obtained at the five higher levels are consistent with each other, which indicates the reliability of our calculations. In addition, to balance the computational cost and accuracy, the relatively cheaper QCISD(T)/6-311++G(*d, p*)/B3LYP/6-311G(*d, p*) dual-level method was used to study the potential energy surface and dynamics of the reaction. At this level, the potential barriers ($\Delta E^\ddagger$) of reaction R1, R2, and R3 are 43.2, 43.9, and 44.1 $\text{kJ} \cdot \text{mol}^{-1}$, and the reaction energy is -38.2 $\text{kJ} \cdot \text{mol}^{-1}$. This indicates that the title reaction is an exothermic reaction, which is consistent with the prediction mentioned above. On the other hand, we noted that the energy of TS1 is lower than those of TS2 and TS3. This fact may be resulted from the special geometry of TS1, because the distance 0.2712 nm between atoms H(7) and F(8) in TS1 is significantly less than 0.3452 nm between the corresponding atoms H(5) and F(8) in TS2, as shown in Fig.1. Clearly, the former is close to the sum of effective van der Waals radii of the hydrogen and fluorine atom (0.12 nm for hydrogen and 0.135 nm for fluorine),⁵⁵ illustrating existence of a weak intramolecular hydrogen bond in TS1, while no such weak hydrogen bond exists in the other two transition states TS2 and TS3. It has been previously demonstrated that an additional bonding interaction should reduce the energy of the species.⁵⁶ Therefore, we infer that the existence of hydrogen bond may influence the energies of the reaction. Similar characteristics have been reported in the hydrogen abstraction reaction from fluorinated alkanes.^{10,11,56}

3.2 Reaction path properties

Fig.2 shows the variations of bond distances of reaction R1 along the intrinsic reaction coordinate (*s*) at the B3LYP/6-311G(*d, p*) level. With the reaction going on, the distance between atoms C(4) and H(3) remains invariant until the *s* reaches $-1.20 \text{ amu}^{1/2} \cdot \text{Bohr}$, where it starts to elongate sharply. When $s = 1.50 \text{ amu}^{1/2} \cdot \text{Bohr}$, the bond distance of C(4)–H(3) reaches

Fig.2 Variations of bond distances of reaction R1 as functions of *s* at the B3LYP/6-311G(*d, p*) level

Fig.3 Classical potential energy curve (V_{MEP}), the ground-state vibrational adiabatic potential energy (V_a^G) and the zero-point energy curve (ZPE) of reaction R1 as functions of s at the QCISD(T)/6-311++G(d, p)/B3LYP/6-311G(d, p) level

0.19 nm, indicating that it is on the edge of broken. At the same time, the atoms C(2) and H(3) approach rapidly each other. When $s=1.50 \text{ amu}^{1/2} \cdot \text{Bohr}$, the bond distance of C(2)—H(3) is about 0.11 nm, which is close to the equilibrium bond length (0.1087 nm) of C—H radical.⁴⁵ In addition, the other bond lengths are almost unchanged over the entire reaction process. It demonstrates that the dissociation of the C(4)—H(3) bond and the formation of the C(2)—H(3) bond mainly take place in the region of $s=-1.20$ to $1.50 \text{ amu}^{1/2} \cdot \text{Bohr}$. The same conclusion can be drawn for the channels R2 and R3 (Fig.S2). These narrower active regions imply that the reaction owns narrower potential barrier width and more significant tunneling effect.

At the QCISD(T)/6-311++G(d, p)/B3LYP/6-311G(d, p) level, the classical potential energy curve (V_{MEP}), the ground-state vibrational adiabatic potential energy curve (V_a^G), and the zero-point energy curve (ZPE) of reaction R1 as functions of the intrinsic reaction coordinate are plotted in Fig.3, where $V_a^G(s)$ is defined as $V_a^G(s) = V_{\text{MEP}}(s) + \text{ZPE}(s)$. Seen from Fig.3, the ZPE curve is practically constant as s varies with only a gentle drop near the saddle point. This phenomenon is a usual characteristic for the hydrogen abstraction reaction.⁵⁷ In Fig.3, the two curves $V_{\text{MEP}}(s)$ and $V_a^G(s)$ are similar in shape, indicating that the variational effect may be small. The same conclusion can be drawn for R2 and R3 (Fig.S3). In addition, the curve $V_a^G(s)$ has a narrow width of the potential barrier, illuminating the significant quantum tunneling effect.

3.3 Rate constant calculations

Fig.4 Plots of the TST, CVT, and CVT/SCT rate constants versus T in 200–3000 K

(A) reaction R1; (B) reaction R2; (C) reaction R3

Table 3 CVT/SCT rate constants (in $\text{cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$) along with the literature data for the reaction of C₂H₃ with CH₃F in 200–3000 K

T/K	k_1	k_2	k_3	k	Reference ^a
200	4.48×10^{-19}	1.03×10^{-21}	1.32×10^{-22}	4.49×10^{-19}	
250	7.41×10^{-19}	1.29×10^{-20}	1.77×10^{-21}	7.58×10^{-19}	
298	1.32×10^{-18}	8.38×10^{-20}	1.17×10^{-20}	1.43×10^{-18}	
350	2.83×10^{-18}	4.47×10^{-19}	6.18×10^{-20}	3.40×10^{-18}	
400	6.83×10^{-18}	1.76×10^{-18}	2.36×10^{-19}	9.06×10^{-18}	
466	2.43×10^{-17}	8.19×10^{-18}	1.06×10^{-18}	3.46×10^{-17}	3.67×10^{-18}
500	4.61×10^{-17}	1.64×10^{-17}	2.07×10^{-18}	6.66×10^{-17}	7.83×10^{-18}
550	1.12×10^{-16}	4.08×10^{-17}	5.08×10^{-18}	1.63×10^{-16}	2.01×10^{-17}
604	2.69×10^{-16}	9.77×10^{-17}	1.20×10^{-17}	3.91×10^{-16}	4.67×10^{-17}
650	5.27×10^{-16}	1.90×10^{-16}	2.31×10^{-17}	7.63×10^{-16}	
700	1.03×10^{-15}	3.63×10^{-16}	4.41×10^{-17}	1.48×10^{-15}	
800	3.25×10^{-15}	1.11×10^{-15}	1.36×10^{-16}	4.63×10^{-15}	
900	8.52×10^{-15}	2.85×10^{-15}	3.50×10^{-16}	1.21×10^{-14}	
1000	1.94×10^{-14}	6.33×10^{-15}	7.87×10^{-16}	2.73×10^{-14}	
1100	3.94×10^{-14}	1.26×10^{-14}	1.59×10^{-15}	5.52×10^{-14}	
1200	7.33×10^{-14}	2.32×10^{-14}	2.96×10^{-15}	1.02×10^{-13}	
1300	1.27×10^{-13}	3.97×10^{-14}	5.14×10^{-15}	1.77×10^{-13}	
1400	2.08×10^{-13}	6.43×10^{-14}	8.44×10^{-15}	2.90×10^{-13}	
1600	4.87×10^{-13}	1.48×10^{-13}	1.99×10^{-14}	6.75×10^{-13}	
1800	9.91×10^{-13}	2.97×10^{-13}	4.09×10^{-14}	1.37×10^{-12}	
2000	1.82×10^{-12}	5.39×10^{-13}	7.57×10^{-14}	2.51×10^{-12}	
2200	3.08×10^{-12}	9.05×10^{-13}	1.30×10^{-13}	4.25×10^{-12}	
2500	6.07×10^{-12}	1.76×10^{-12}	2.59×10^{-13}	8.35×10^{-12}	
2800	1.08×10^{-11}	3.11×10^{-12}	4.68×10^{-13}	1.48×10^{-11}	
3000	1.51×10^{-11}	4.34×10^{-12}	6.62×10^{-13}	2.08×10^{-11}	

^a literature data³⁹ estimated from the simple Arrhenius form
 $k = 2.5 \times 10^{-13} \exp(-5184/T)$

In present study, the rate constants were evaluated using the canonical variational transition state theory with a small-curvature tunneling correction over a wide temperature range of 200–3000 K. The total rate constant k is the sum of individual rate constant of all channels, i.e., $k = k_1 + k_2 + k_3 + k_4 \approx k_1 + k_2 + 2k_3$.

The TST, CVT, and CVT/SCT rate constants over a wide temperature range of 200–3000 K are depicted in Fig.4. The CVT/SCT rate constants of k_1 , k_2 , k_3 , the total rate constant k including the literature values³⁹ are summarized in Table 3. As seen from Fig.4, the rate constants of the three hydrogen abstraction reaction channels exhibit positive temperature dependence over the entire process. The TST and CVT curves are quite close to each other in the temperature range, which means that the variational effect is small. However, the obvious separations between the CVT and CVT/SCT curves under

lower temperatures confirm the fact that the tunneling contribution of the title reaction is considerable in the lower temperature range. This is in accord with the above discussion. Comparing Fig.4(A), 4(B) with 4(C), we see that the tunneling effect of reaction R1 is more significant than those of R2 and R3. This accounts for why the CVT/SCT rate constants of k_1 are considerably larger than those of k_2 and k_3 in the lower temperature range of 200–350 K (in Table 3). From Table 3, we see that the calculated rate constants are somewhat higher than the literature values³⁹ in the temperature range of 466–604 K. However, as mentioned above, the simple Arrhenius form $k = 2.5 \times 10^{-13} \exp(-5184/T) \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ reported in the literature³⁹ may have some uncertainties, because it was an estimated formula, which took the pre-exponential factor and 90% of the activation energy of the analogous abstraction by CH_3 as its own A -factor and activation energy. Therefore, it may not predict exactly the dynamic feature of the title reaction. In addition, to get an overall insight to the reaction dynamics, the calculated rate constants in $\text{cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ were fitted into the following three-parameter expressions using the least-square method:

$$\begin{aligned} k_{\text{CVT/SCT}}(200\text{--}400 \text{ K}) &= 3.37 \times 10^{-21} T^{1.66} \exp(-989.26/T); \\ k_{\text{CVT/SCT}}(401\text{--}1400 \text{ K}) &= 5.27 \times 10^{-18} T^{2.01} \exp(-5320.54/T); \\ k_{\text{CVT/SCT}}(1401\text{--}3000 \text{ K}) &= 9.67 \times 10^{-15} T^{4.36} \exp(-9626.05/T). \end{aligned}$$

The detailed dynamic data in a wide temperature range could offer a theoretical prediction for the future experimental measurements.

The temperature dependence of the branching ratios of k_1/k , k_2/k , and k_3/k is presented in Fig.5. It is clear that the R1 channel is the dominant one in the whole temperature range. However, the R2 hydrogen abstraction channel will compete kinetically with the R1 as the temperatures increase. Especially, in the low temperature range of 200–550 K, the fraction of the branching ratio k_2/k elongates linearly from 0.2% to 25.0%. Compared with k_1/k and k_2/k , the branching ratio k_3/k is negligible. Consequently, although R1 hydrogen abstraction reaction is the dominant channel in the entire temperature range, the contribution from R2 channel should be taken into account for the calculation of the total rate constant as the temperatures in-

Fig.5 Temperature dependence of the branching ratios in 200–3000 K

crease. The contribution from R3 is relatively small.

4 Conclusions

A dual-level direct dynamics method was employed to investigate the hydrogen abstraction reaction of C_2H_3 with CH_3F . The following conclusions can be drawn.

(1) At the QCISD(T)/6-311++G(d, p)/B3LYP/6-311G(d, p) level, the potential barriers ($\Delta E^\ddagger$) of reaction channels R1, R2, and R3 are 43.2, 43.9, and 44.1 $\text{kJ} \cdot \text{mol}^{-1}$, respectively, and the reaction energy is $-38.2 \text{ kJ} \cdot \text{mol}^{-1}$.

(2) The rate constants of the three hydrogen abstraction reaction channels exhibit positive temperature dependence in the temperature region of 200–3000 K, in which the variational effect is negligible over the entire process, while the small-curvature tunneling effect is considerable under lower temperatures.

(3) The reaction R1 is the dominant channel, R2 will compete kinetically with R1 as temperature increases, while the contribution from R3 is small.

Supporting Information Available: Some information is available free of charge via the internet at <http://www.whxb.pku.edu.cn>.

References

- (1) Farman, J. D.; Gardiner, B. G.; Shanklin, J. D. *Nature* **1985**, *315*, 207. doi: 10.1038/315207a0
- (2) Solomon, S. *Nature* **1990**, *347*, 347.
- (3) Zhou, X.; Zhou, B. *Chin. J. Chem.* **2011**, *29*, 1335. doi: 10.1002/cjoc.201180251
- (4) Wang, L.; Zhao, Y.; Zhang, J.; Dai, Y.; Zhang, J. *Theor. Chem. Acc.* **2011**, *128*, 183. doi: 10.1007/s00214-010-0813-8
- (5) Han, W.; Kennedy, E. M.; Mackie, J. C.; Dlugogorski, B. Z. *Ind. Eng. Chem. Res.* **2010**, *49*, 8406. doi: 10.1021/ie100349x
- (6) Sun, H.; He, H.; Pan, Y.; Pan, X.; Li, Z.; Wang, R. *Chemical Physics Letters* **2008**, *450*, 186. doi: 10.1016/j.cplett.2007.11.003
- (7) Ali, M. A.; Rajakumar, B. *J. Mol. Struct. -Theochem* **2010**, *949*, 73. doi: 10.1016/j.theochem.2010.03.006
- (8) Gao, H.; Wang, Y.; Wan, S.; Liu, J.; Sun, C. J. *Mol. Struct. -Theochem* **2009**, *913*, 107. doi: 10.1016/j.theochem.2009.07.024
- (9) Zhang, L.; Li, S. J. *Mol. Struct. -Theochem* **2008**, *869*, 6. doi: 10.1016/j.theochem.2008.08.012
- (10) González-Lafont, À.; Lluch, J. M.; Varela-álvarez, A.; Sordo, J. A. *J. Phys. Chem. B* **2008**, *112*, 328. doi: 10.1021/jp075298v
- (11) Taghikhani, M.; Parsafar, G. A. *J. Phys. Chem. A* **2007**, *111*, 8095. doi: 10.1021/jp072403s
- (12) Yang, J.; Zhang, S. W.; Li, Q. S. *Chemical Journal of Chinese Universities* **2007**, *28*, 1975. [杨静, 张绍文, 李前树. 高等学校化学学报, **2007**, *28*, 1975.] doi: 10.3321/j.issn:0251-0790.2007.10.040
- (13) Zhang, L.; Li, S. J. *Mol. Struct. -Theochem* **2009**, *901*, 38. doi: 10.1016/j.theochem.2008.12.044

- (14) Song, C.; Tian, Z.; Li, Q.; He, T. *J. Mol. Struct. -Theochem* **2009**, *910*, 126. doi: 10.1016/j.theochem.2009.06.027
- (15) Han, W.; Kennedy, E. M.; Kundu, S. K.; Mackie J. C.; Adesina, A. A.; Dlugogorski, B. Z. *Journal of Fluorine Chemistry* **2010**, *131* (7), 751.
- (16) Han, W.; Kennedy, E. M.; Mackie J. C.; Dlugogorski, B. Z. *Journal of Hazardous Materials* **2010**, *180*, 181. doi: 10.1016/j.jhazmat.2010.04.011
- (17) Baulch, D. L.; Cobos, C. J.; Cox, R. A.; Esser, C.; Frank, P.; Just, T.; Kerr, J. A.; Pilling, M. J.; Troe, J.; Walker, R. W.; Warnatz, J. *J. Phys. Chem. Ref. Data* **1992**, *21*, 411. doi: 10.1063/1.555908
- (18) Monks, P. S.; Nesbitt, F. L.; Payne, W. A.; Scanlon, M.; Stief, L. J.; Shallcross, D. E. *J. Phys. Chem.* **1995**, *99* (47), 17151.
- (19) Payne, W. A.; Monks, P. S.; Nesbitt, F. L.; Stief, L. J. *J. Chem. Phys.* **1996**, *104*, 9808. doi: 10.1063/1.471740
- (20) Feng, C. J.; Zhang, W. C.; Du, B. N.; Mu, L. L. *J. Mol. Struct. -Theochem* **2007**, *847*, 79. doi: 10.1016/j.theochem.2007.09.001
- (21) Fahr, A.; Laufer, A. H.; Tardy, D. C. *J. Phys. Chem. A* **1999**, *103*, 8433.
- (22) Wang, X. L.; Yu, F.; Xie, D.; Liu, S. L.; Zhou, X. G. *Acta Chimica Sinica* **2008**, *66* (22), 2499. [王新磊, 于 锋, 谢丹, 刘世林, 周晓国. 化学学报, **2008**, *66* (22), 2499.]
- (23) Mebel, A. M.; Morokuma, K.; Lin, M. C. *J. Chem. Phys.* **1995**, *103* (9), 3440.
- (24) Knyazev, V. D.; Bencsura, Á.; Stoliarov, S. I.; Slagle, I. R. *J. Phys. Chem.* **1996**, *100*, 11346.
- (25) Li, Q. S.; Lu, R. H.; Wang, C. Y. *J. Mol. Struct. -Theochem* **2004**, *668*, 35. doi: 10.1016/j.theochem.2003.10.014
- (26) Mebel, A. M.; Diau, E. W. G.; Lin, M. C.; Morokuma, K. *J. Am. Chem. Soc.* **1996**, *118* (40), 9759.
- (27) Knyazev, V. D.; Slagle, I. R. *J. Phys. Chem.* **1995**, *99*, 2247.
- (28) Wang, H.; Liu, J. X.; Wang, B. S.; Kong, F. A. *Acta Phys.-Chim. Sin.* **2000**, *16* (8), 674. [王 惠, 刘建勋, 王宝山, 孔繁敖. 物理化学学报, **2000**, *16* (8), 674.] doi: 10.3866/PKU.WHXB20000801
- (29) Oguchi, T.; Sato, Y.; Matsui, H. *Chemical Physics Letters* **2009**, *472*, 181. doi: 10.1016/j.cplett.2009.03.012
- (30) Wang, L. C.; Wang, X.; Tian, A. M. *Acta Chimica Sinica* **2008**, *60* (3), 457. [李来才, 王 欣, 田安民, 化学学报, **2008**, *60* (3), 457.]
- (31) Benson, S. W. *Int. J. Chem. Kinet.* **1994**, *26*, 997. doi: 10.1002/kin.550261005
- (32) Boullart, W.; Nguyen, M. T.; Peeters, J. *J. Phys. Chem.* **1994**, *98* (33), 8036.
- (33) Feng, W. H.; Wang, B. S.; Wang, H.; Kong, F. A. *Acta Phys.-Chim. Sin.* **2000**, *16* (9), 776. [冯文辉, 王宝山, 王惠, 孔繁敖. 物理化学学报, **2000**, *16* (9), 776.] doi: 10.3866/PKU.WHXB20000903
- (34) Huang, C. S.; Zhu, Z. Q.; Ran, Q.; Chen, C. X.; Chen, Y. *Acta Phys.-Chim. Sin.* **2003**, *19* (1), 51. [黄存顺, 朱志强, 冉 琴, 陈从香, 陈 旸. 物理化学学报, **2003**, *19* (1), 51.] doi: 10.3866/PKU.WHXB20030112
- (35) Shestov, A. A.; Popov, K. V.; Slagle, I. R.; Knyazev, V. D. *Chemical Physics Letters* **2005**, *408*, 339. doi: 10.1016/j.cplett.2005.04.057
- (36) Goldsmith, C. F.; Ismail, H.; Abel, P. R.; Green, W. H. *Proceedings of the Combustion Institute* **2009**, *32*, 139. doi: 10.1016/j.proci.2008.06.142
- (37) Muszyńska, M.; Ratkiewicz, A.; Huynh, L. K.; Truong, T. N. *J. Phys. Chem. A* **2009**, *113*, 8327. doi: 10.1021/jp903762x
- (38) Feng, S.; Duan, W. Z.; Liu, Q.; Liu, F. L. *J. Mol. Struct. -Theochem* **2009**, *897*, 1. doi: 10.1016/j.theochem.2008.10.019
- (39) Burgess, D. R., Jr.; Zachariah, M. R.; Tsang, W.; Westmoreland, P. R. *Prog. Energy Combust. Sci.* **1996**, *21*, 453.
- (40) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; *et al.* *Gaussian 03*, Revision C.02; Gaussian Inc.: Wallingford, CT, 2004.
- (41) Thiesemann, H.; Clifford, E. P.; Taatjes, C. A.; Klippenstein, S. *J. J. Phys. Chem. A* **2001**, *105*, 5393.
- (42) Chuang, Y. Y.; Corchado, J. C.; Truhlar, D. G. *J. Phys. Chem. A* **1999**, *103*, 1140.
- (43) Chuang, Y. Y.; Corchado, J. C.; Fast, P. L.; *et al.* *Polyrate*, Version 8.2; University of Minnesota: Minneapolis, 1999.
- (44) *JANAF Thermochemical Tables*, 2nd ed.; Stull, D. R., Prohet, H. Eds. National Standard Reference Data Series N0 37, National Bureau of Standards, US Government, Printing Office: Washington, DC, 1971.
- (45) Duncan, J. L. *Mol. Phys.* **1974**, *28*, 1177. doi: 10.1080/00268977400102501
- (46) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334. doi: 10.1021/ja01607a027
- (47) Fahr, A.; Laufer, A. H. *J. Phys. Chem.* **1988**, *92* (29), 7229.
- (48) Ira, N. L. *Molecular Spectroscopy*; Wiley: New York, 1975.
- (49) Olleta, A. C.; Taccone, R. A. *J. Mol. Struct. -Theochem* **2000**, *507*, 25. doi: 10.1016/S0166-1280(99)00346-2
- (50) Liu, J. Y.; Li, Z. S.; Dai, Z. W.; Zhang, G.; Sun, C. C. *Chem. Phys.* **2004**, *296*, 43. doi: 10.1016/j.chemphys.2003.09.028
- (51) Zhang, Q. Z.; Zhang, R. Q.; Gu, Y. S. *J. Phys. Chem. A* **2004**, *108*, 1064. doi: 10.1021/jp036446u
- (52) Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98* (11), 2744.
- (53) Kolesov, V. P. *Russ. Chem. Rev.* **1978**, *47*, 1145.
- (54) Pickard, J. M.; Rodgers, A. S. *Int. J. Chem. Kinet.* **1983**, *15*, 569. doi: 10.1002/kin.550150607
- (55) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 260.
- (56) Martell, J. M.; Boyd, R. J. *J. Phys. Chem.* **1995**, *99*, 13402. doi: 10.1021/j100036a014
- (57) Garrett, B. C.; Truhlar, D. G. *J. Am. Chem. Soc.* **1979**, *101* (16), 4534.