

# Direct dynamics study on the hydrogen abstraction reaction of CH<sub>3</sub>CH<sub>2</sub>F with O(<sup>3</sup>P)

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## Abstract

A direct dynamics method is employed to study three channels of the hydrogen abstraction reaction of CH<sub>3</sub>CH<sub>2</sub>F with O(<sup>3</sup>P) based on the potential surface calculated at the QCISD(T)/6-311G(d,p)//MP2(full)/6-311G(d,p) dual-level. The calculated potential barriers are 11.08 kcal/mol for the  $\alpha$ -H abstraction channel, 14.39 and 14.08 kcal/mol for the two channels associated with the  $\beta$ -H abstraction. The rate constants of the reactions are evaluated by means of the canonical variational transition-state theory (CVT) with small-curvature tunneling (SCT) correction in the temperature range of 200–3000 K. The dynamics calculations indicate that the variational effect is small for all the channels, and the tunneling effect is considerable in the lower temperature range for the calculation of the rate constants. At 298 K, the rate constants of  $\alpha$ -H and  $\beta$ -H abstraction reactions are  $5.22 \times 10^{-17}$ ,  $1.30 \times 10^{-19}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, and when up to about 1250 K, the values are  $5.10 \times 10^{-13}$ ,  $5.22 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, respectively. It is shown that at the lower temperature the main reaction process is the  $\alpha$ -H abstraction, while  $\beta$ -H abstraction will compete kinetically with the  $\alpha$ -H abstraction as the temperature increases.

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**Keywords:** CH<sub>3</sub>CH<sub>2</sub>F; Hydrogen abstraction reaction; QCISD(T)/MP2(full); Rate constant

## 1. Introduction

The well-documented catalytic activities of chlorofluorocarbons (CFCs) and halon fire suppression agents in the depletion of stratospheric ozone [1] lead to the severe restriction of their industrial use [2,3]. Therefore, the search for new flame suppressants, which are effective, nontoxic and of low global environmental impact, has sparked increased interest in the mechanisms of fire suppression and the development of predictive flame models [4–6]. Hydrofluorocarbons (HFCs), without the potential for ozone depletion due to the absence of chlorine or bromine atoms in their molecules, are widely used in industry as potential replacements for CFCs and halon fire suppression agents [7–10]. In order to model accurately the fire suppression capabilities of HFCs, some scholars have paid their attention to the hydrogen abstraction

reactions of HFCs with O(<sup>3</sup>P) [11], which is a significant reaction in environmental and combustion chemistry.

Experimentally, Shiina et al. [12] have measured the overall rate constants of the reactions of three fluoroethanes (CH<sub>3</sub>CH<sub>2</sub>F, CH<sub>2</sub>FCH<sub>2</sub>F, CH<sub>3</sub>CHF<sub>2</sub>) with O(<sup>3</sup>P) by laser flash photolysis, and proposed the corresponding simple Arrhenius form of the title reaction rate constants in a narrow temperature range of 1000–1250 K,  $k = 2.19 \times 10^{-9} (4.07) \exp[-(58.0 \pm 12.8)/RT]$ . Theoretically, some investigators have explored the combustion mechanism and the dynamic features of the reaction of CF<sub>3</sub>CHFCF<sub>3</sub> with O(<sup>3</sup>P) [13], CH<sub>3</sub>CHF<sub>2</sub> with O(<sup>3</sup>P) [14,15], and CHF<sub>3</sub> with O(<sup>3</sup>P) [16] using different computational methods. Although needs for high-quality thermochemical and kinetic data in the atmospheric chemistry and flame suppression communities are getting more and more urgent, only few work has been done on these systems near flame temperatures. The lack of relevant kinetic data is one of the problems limiting the application of fire suppression models for HFCs to interpreting its influence on combustion. To our knowledge, the reaction between CH<sub>3</sub>CH<sub>2</sub>F and O(<sup>3</sup>P) has not been reported.

To enrich the kinetic data in a wider temperature range, especially in combustion temperature, the direct dynamics study is carried out on the reaction of CH<sub>3</sub>CH<sub>2</sub>F with

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O(<sup>3</sup>P) in the present paper. The calculated results not only demonstrate the combustion mechanism of CH<sub>3</sub>CH<sub>2</sub>F in atmosphere, but also provide a theoretical prediction for the further experimental measurements of rate constant to design high-temperature combustion models and to develop predictive flame suppressants. Here, a dual-level direct dynamics method [17] QCISD(T)/6-311G(d,p)//MP2(full)/6-311G(d,p) is employed to reveal the reaction mechanism and to present the reaction potential energy surface (PES). Based on the ab initio calculation data, the rate constants of the reactions are calculated by using the conventional transition state theory (TST), the canonical variational transition-state theory (CVT) [18] with centrifugal-dominant small-curvature tunneling (SCT) [19] correction in the temperature range of 200–3000 K.

## 2. Computation methods

All of the electronic structure calculations are carried out with the Gaussian 98 package [20]. The optimized geometries, harmonic vibrational frequencies and zero-point energies (ZPE) for all the stationary points are calculated using the restricted or unrestricted second-order Møller–Plesset perturbation theory (MP2) method with the 6-311G(d,p) basis set, in which all the electrons are included in a correlation calculation. Starting from the MP2 saddle-point geometries, and going downhill to both the reactant and product channels, the minimum energy paths (MEPs) are constructed by the intrinsic reaction coordinate (IRC) method, with an even gradient step size of 0.05 (amu)<sup>1/2</sup> bohr. Each saddle point is confirmed to connect the designated reactants and products for all the channels. In order to gain more reliable potential energy surface (PES) information, single-point energies of all the stationary points and the selected points along the minimum energy path are refined at the QCISD(T)/6-311G(d,p) level of theory (quadratic configuration interaction with single and double substitutions and perturbative inclusion of connected triple substitutions) based on the MP2(full)/6-311G(d,p) optimized geometries.

The variational rate constants including the tunneling effect are calculated based on the ab initio results. The CVT rate constant for the temperature  $T$  is

$$k^{\text{CVT}}(T,s) = \min_s k^{\text{GT}}(T,s) \quad (1)$$

where

$$k^{\text{GT}}(T,s) = \frac{\sigma k_{\text{B}} T}{h} \frac{Q^{\text{GT}}(T,s)}{\Phi^{\text{R}}(T)} e^{-V_{\text{MEP}}(s)/k_{\text{B}} T} \quad (2)$$

in which,  $k^{\text{GT}}(T, s)$  is the generalized transition state theory rate constant at the dividing surface  $s$ ,  $\sigma$  is the symmetry factor accounting for the possibility of more than one symmetry-related reaction path,  $k_{\text{B}}$  is Boltzmann's constant,  $h$  is Planck's constant,  $\Phi^{\text{R}}(T)$  is the reactant partition function per unit volume,  $Q^{\text{GT}}(T, s)$  is the partition function of a generalized transition state, and  $V_{\text{MEP}}(s)$  is the potential on the MEP.

Finally, variational rate constant including the tunneling effect is

$$k(T) = \kappa(T)k^{\text{CVT}}(T) \quad (3)$$

where  $\kappa(T)$ , the quantum tunneling transmission coefficient, can be calculated by the small curvature tunneling method.

All the rate constants were calculated employing the Polyrate 8.2 program [21].

## 3. Results and discussion

For the reaction of CH<sub>3</sub>CH<sub>2</sub>F with O(<sup>3</sup>P), the hydrogen atom can be abstracted from the  $\alpha$ -position (CH<sub>2</sub>F group) and the  $\beta$ -position (CH<sub>3</sub> group). Because of the equivalent steric effect of H<sub>7</sub> and H<sub>8</sub> at  $\alpha$ -position (Fig. 1), we only focus on the H<sub>7</sub> abstraction reaction, denoted as R1, with transition state  $\alpha$ -TS1 and rate constant  $k_1$ . The two  $\beta$ -H atoms, H<sub>3</sub> and H<sub>4</sub>, are identical and different from the other  $\beta$ -H atom H<sub>5</sub>. We only investigate the H<sub>4</sub> abstraction reaction, namely R2b, with the transition state  $\beta$ -TS2b and rate constant  $k_{2b}$ . For the reaction occurred at H<sub>5</sub> position, similar to references [15,16], two transition states  $\beta$ -TS2a and  $\beta$ -TS2a' are found. Since their energy nearly degenerate with the discrepancy 0.07 kcal/mol, we only study the channel through the transition state  $\beta$ -TS2a, denoted as R2a, with the rate constant  $k_{2a}$ . Therefore, in present paper, only three reaction channels are considered:



Obviously, the total rate constant  $k$  should be  $2(k_1 + k_{2a} + k_{2b})$ .

### 3.1. Stationary points

Fig. 1 displays the optimized geometries of the reactants, transition states, and products at the MP2(full)/6-311G(d,p) level along with the available experimental data [22,23]. For CH<sub>3</sub>CH<sub>2</sub>F and OH, the theoretical bond lengths and bond angles are quite close to the corresponding experimental values with the largest deviations of 0.009 Å for C–F and 1.6° for FCH. It shows that the MP2(full)/6-311G(d,p) method is suitable for predicting these geometric parameters. In the  $\beta$ -H abstraction channels, the equilibrium geometries of the products CH<sub>2</sub>CH<sub>2</sub>F(1) and CH<sub>2</sub>CH<sub>2</sub>F(2) are very analogous, the CH<sub>2</sub>CH<sub>2</sub>F(1) structure might be seen as a result of methylene group rotation around the C–C bond axis by 47.8° with respect to CH<sub>2</sub>CH<sub>2</sub>F(2). The rotational barrier height is only 0.07 kcal/mol at the QCISD(T)/6-311G(d,p) level. At the MP2(full)/6-311G(d,p), MP2/6-311 + G(3df,2p), MP4/6-311(2df,p), and QCISD(T)/6-311G(d,p) levels of theory, the energies of CH<sub>2</sub>CH<sub>2</sub>F(1) are higher than that of CH<sub>2</sub>CH<sub>2</sub>F(2) by about 0.26, 0.12, 0.28, and 0.15 kcal/mol, respectively. It is because that CH<sub>2</sub>CH<sub>2</sub>F(1) with C<sub>s</sub> symmetry has the p-orbital on terminal C atom occupied by the unpaired electron, which is

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