Full Length Article

Kinetics of H abstraction and addition reactions of 2,4,4-trimethyl-1-pentene by OH radical

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1. Introduction

The chemical kinetic mechanisms of fuels are significant to deep comprehension of the basic combustion processes, which were proved to be powerful tools to the design and optimization of the advanced internal combustion engines. The kinetics of alkane have been quiet well investigated on oxidation, pyrolysis and combustion [1–5]. However, the kinetics of alkene are less well-known. Alkenes are also important components of practical fuels. In addition, they are key intermediates during decomposition of alcohols, ethers, alkenes and biofuels. The subsequent reactions have important impact on the final product distribution. More significantly, radicals addition to alkenes may lead to soot formation. Hydroxyl (OH), as one of the top vital radicals in combustion, dominated chain propagation, chain branching and chain termination processes at variable temperature ranges. Reactions with hydroxyl radical of alkenes play an important role in the combustion progress which leads to the acceleration of further decomposition.

Researches on alkenes with OH radicals are still limited. As for experimental investigations, Tully and Goldsmith [6] measured the rate coefficients for the reactions of propene with OH under various conditions. The kinetics of the reactions of propene and isoprene with OH radicals at low temperature were investigated by Spangenberg et al. [7] in a Laval nozzle expansion. The rate coefficients exhibited negative temperature dependence at low temperature. Recently, Badra et al. [8] detected the rate coefficients for the reactions of propene and five deuterated isotopes, including propene-1,1,2-D3, propene-1-D1, propene-3,3,3-D3, propene-1,1-D2 and propene-D6, with OH radicals in shock tube using OH laser diagnostic at the temperature range of 818 K–1460 K. The results showed that the allylic H abstraction channel is the most dominant channel while the OH addition reaction is negligible over the temperature range. These results are in line with the previous theoretical researches [9]. Vakhtin et al. [10] measured the rate coefficients of the reactions of ethylene, propene, and 1-butene with OH behind reflected shock waves under different conditions. Khaled et al. [11] performed a detailed experimental study on the reaction of longer chain alkenes, such as C4–C6 straight chain alkenes, with OH in shock tube with UV laser at 833–1377 K, 1.5 atm. As the results shown, longer straight chain alkenes have higher overall rate coefficients with OH, but the increase of rate coefficients with increasing chain length does not exhibit monotonicity.

As for theoretical kinetic study, recently, Huynh et al. [12] investigated the kinetics of enol formation from propene and OH. They found that H abstraction reactions with OH are dominant in propene reactions with OH.
consumption with the branching ratio of higher than 90%. More recently, Zador et al. [9] provided the detailed description of the different H abstraction channels of propene with OH and successfully reproduced the negative temperature dependence at low temperature. In addition, the results also showed that allylic H abstraction is favorable among all channels. Sgori et al. [13] adopted 9 computational methods to analyze the differences and similarities in the computed potential energy surfaces (PES) of the H abstraction from propene with OH, founding that the BHANDHLYP method shows more accuracy and efficiency. The BHANDHLYP method can closely reproduce the geometrical parameters of the CCSD-PES, especially at the maxima and minima. Besides, there are two possible allylic H abstraction channels, direct H and indirect H abstraction channel, while the latter involves a van der Waals pre-reactive complex. The indirect H abstraction channel with the conformation of reactant complex, the indirect H abstraction channel undergoes lower barrier, which facilitates the reaction. Sun and Law [14] studied the kinetics of H abstraction reactions of butene isomers with OH and found that the allylic H abstraction reaction is similar to propene which possesses both indirect and direct channels. In addition, there are two reaction conformers for 1-butene, skew and syn formers [15]. Their transition states are distinguishable at lower temperatures but almost the same at higher temperatures and can be ignored. Moreover, the allylic H abstraction channel is dominant, while the vinylic channel is subordinate. Greenwald et al. [16] investigated the kinetics of OH addition to isoprene at the temperature range of 30–500 K and found that OH addition to isoprene at this temperature range is dominant and the branching ratios of the four OH isoprene adduct isomers are relatively insensitive to temperature.

Current researches mainly focus on the description of the kinetics of reactions between small alkenes and OH, while studies on longer chain alkenes with OH are scarce in literatures. Disobutylene is one of the components of quaternary surrogates as a representative of highly branched alkenes. Until now, there are very limited researches on kinetic model of neat disobutylene, especially, theoretical studies. Metcalfe et al. [17] measured the ignition delay times of disobutylene isomers (both 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene) with shock tube at 1–4 atm, and for equivalence ratios of 0.25, 0.5, and 1.0. Hu et al. [18] measured the ignition delay times of disobutylene at wide initial conditions and optimized the Metcalfe model. In this paper, one of the disobutylene isomers (2,4,4-trimethyl-1-pentene (JC8H16)) with OH systems was examined through high-level quantum mechanical calculations and variational transition state theory [19]. The rate coefficients and branching ratios were obtained at the temperature range of 250–2000 K. The object of this work is to predict the accurate rate coefficients for longer chain alkenes kinetic mechanism, which can be used to make deeper understanding of alkenes combustion proceed and develop more accurate gasoline surrogate model.

2. Calculation method

2.1. Electronic structures

Achieving chemical accuracy by electronic structures calculations is computationally expensive, and the time consumption on rate coefficient calculation is governed almost entirely by the time required on calculating the gradients and Hessians during optimizing geometries. In addition, the accuracy of the rate coefficient mainly depends on the quality of the electronic structure. Therefore, it is necessary to choose a proper method to locate reliable transition-state geometries. For optimization of transition state geometry of allylic H abstraction reaction, several kinds of methods were conducted, namely ab initio HF [20,21], density functional theory (DFT) B3LYP [22–24] and BHANDHLYP [25]. The optimized transition state using HF method is not accurate. And it was found that the density functional theory B3LYP/6-311(d, p) cannot get a certain location for transition state the same as the result in Sun and Law’s [14] research. The transition state of the allylic H abstraction can be located at B3LYP/6-31G*, but cannot be located at B3LYP/6-311(d, p) level. In addition, BHANDHLYP can get a certain location for transition state. Therefore, there is transition state for allylic H abstraction and the B3LYP is not suitable to optimize geometries for this system. As to high-level theoretical procedures, as Henry et al. [26] proposed that MP2 method is not reliable for unsaturated radicals with high-spin contamination, since the contamination of wave functions for open-shell system due to contributions from higher spin states leads to erroneous single point energy. The coupled-cluster theory can reduce the contamination effectively resulting from its infinite order electron correction. However, it is too much time demanding on optimization of the geometries for 26-atom target system when using the coupled-cluster theory [27].

The BHANDHLYP/6-311(d, p) method using the Becke’s half and half nonlocal exchange with the Lee-Yang-Parr (LYP) [25] correlation functions and the split valence basis set, was applied to predict the transition state of primary allylic H abstraction. The forming O–H bond length is 1.337 Å while the cleaving C–H bond length is 1.203 Å, and the imaginary frequency for the stretching O–H bond is reasonable 1454i cm\(^{-1}\) compared with HF method. This method has been widely used to predict accurate transition state structures for H abstraction reactions of alkane, alkene and aldehyde by OH [14,28,29]. It has been proved that this method can capture similar geometries to that optimized using CCSD method. Therefore, optimized geometries and harmonic frequencies of the stationary points were calculated by the BHANDHLYP/6-311(d, p) method. In addition, the minimum energy path (MEP) was also predicted by BHANDHLYP/6-311(d, p) method. Furthermore, to increase the computational accuracy, the single point energy was determined by CCSD method with the split valence basis set which was augmented with diffuse and polarization functions, 6-311 + +G(d, p). In addition, a triple excitation was also considered at CCSD(T)/6-311 + +G(d,p) level. The T1 diagnostic of the CCSD(T)/6-311 + +G(d,p) calculations is less than 0.023 for transition states and radicals and less than 0.01 for stable species, which indicates that this energy calculation is reliable for JC8H16 + OH. In this work, all the electronic structures were calculated using the Gaussian09 [30] software.

2.2. Rate coefficients

The rate coefficients in this work were calculated using the canonical variational transition state theory (CVT) [19] compared with the conventional transition state theory (TST) [19,31]. The difference between two theories is the location of the dividing surface [19] at the reaction coordinate s along the reaction path. The generalized dividing surface is a hyperplane perpendicular to the MEP and intersecting it at that s. In TST theory, it is located at the saddle point (s = 0), while in CVT theory, the generalized transition state dividing surface is determined by the minimization of the state coefficient. Thus, the CVT rate constant \(k^{\text{CVT}}\), at temperature \(T\) is given by

\[
k^{\text{CVT}} = \min_s [k^{\text{GT}}(T,s)] = \min_s [\kappa(T) \frac{\sigma}{\beta h} Q^\text{GT}(T,s) \exp(-\beta V^\text{MEP}(s))]\tag{1}
\]

where, \(s\) is the distance along the reaction coordinate, \(s = 0\) indicates the location of the saddle point and \(s < 0\) and \(s > 0\) indicate the reactant and product side of the reaction path, respectively. \(\kappa(T)\) is the transmission coefficient to quantize the quantum mechanical tunneling effects. \(\sigma\) is the symmetry number, \(\beta\) and \(h\) are the Boltzmann factor and Planck constant, respectively. \(Q^\text{GT}(T,s)\) is the partition function of the generalized transition state, \(Q^\text{GT}(T)\) is the partition function of the reactants, \(V^\text{MEP}(s)\) is the potential energy on the MEP at \(s\) relative to overall zero of energy.

The rigid-rotor-harmonic-oscillator model (RRHO) was used to calculate the partition functions, \(Q^\text{GT}(T,s)\) and \(Q^\text{GT}(T)\), with corrections of internal rotations [32,33]. Specifically, the enharmonic rotations and vibrational partition functions were considered by statistical mechanics with the moments of frequencies and inertia at BHANDHLYP/6-311(d,
p) level scale by a factor of 0.935 [14]. This factor was used to compensate for the difference between calculated frequencies and experimental data.

All vibrations were treated as harmonic oscillators except low-frequency torsional models, such as the torsional motions of methyl group and OH group, specifically, the mode CH$_2$=C(CH$_3$)$_2$ CH(CH$_3$)$_3$. These torsional motions were treated as hindered internal rotors using the segmented reference Pitzer-Gwinn (SRPG) method [34]. This treatment had certain effect on the rate coefficients calculation and made the rate coefficients lower. However, the mode CH$_2$=C(CH$_3$)$_2$ CH(CH$_3$)$_3$ had little effect on the rate coefficients calculation. Therefore, this mode was still treated as harmonic oscillator. The SRPG model takes into account the contributions from each well when calculating the partition functions. In general, the partition function with SRPG hindered treatment is given by

$$Q_{SRP}^j = \sum_j Q_{jH}^i (\omega_j) Q_{SRC} (\omega_j)$$

where

$$Q_{jH}^i = \exp((-\beta U_j) Q_{jH}^i (\omega_j))$$

and

$$Q_{SRC} (\omega_j) = \left[\frac{1}{2\pi} \exp\left(-\beta W_j^L (\omega_j) / 2\right) \frac{1}{2\pi} \exp\left(-\beta W_j^R (\omega_j) / 2\right) \right]$$

with $j$ is the $j$th well. $U_j$ is the minimum energy of $j$th well at $\phi_j$ relative to the global minima energy. $Q_{jH}^i$ is the free rotor partition function. $W_j^L$ and $W_j^R$ are the left and right barrier heights located at $\phi_j^L$ and $\phi_j^R$, respectively. $Q_{jH}^i (\omega_j)$ and $Q_{SRC} (\omega_j)$ are the classical and quantum mechanical partition functions, respectively.

2.3. Quantum effects on reaction coordinate motion

The quantum mechanical effects, which are usually dominant by tunneling but also include nonclassical reflection, makes a big difference in rate coefficients calculation at low temperature. Thus, it should be treated properly and reasonably. The tunneling effects are more important if a particle has a small mass or if the barrier is narrower. For example, methyl and vinyl H abstraction reactions of JCaH$_{16}$ + OH, the barriers are narrower, as a consequence, more tunneling. The nonclassical reflection exists, when the energy is higher than the quantum threshold energy (the lowest energy at which it is possible to have tunneling). In general, the quantum mechanical effects are included through multiplying the rate constant by a transmission coefficient $\kappa(T)$. In this work, we adopted three very useful approaches to calculate $\kappa(T)$, namely the simplest one-dimensional Wigner correction [35] and the multi-dimensional zero-curvature tunneling method (ZCT) [21,36,37] and small-curvature tunneling (SCT) [38-40] methods, respectively.

The Wigner correction is expressed as

$$\kappa_W (T) = 1 + \frac{1}{\hbar^2} \left[ \frac{d^2}{dt^2} \right]$$

where $\hbar$ represents the reduced Planck constant and $\omega$ represents the imaginary frequency at the saddle point. There are several restrictions for this method to be valid. Tunneling must occur at the saddle point region of the potential energy surface, where the reaction path is well approximated as an inverted parabola, and the variability of transverse vibrational frequencies is not appreciable. In addition, the effect of the reaction path curvature must be neglected. Considering these reasons, the Wigner correction is justifiable at high temperature, where it is close to unity. It is usually found to be inaccurate when the assumptions of derivation are not satisfied.

The other two methods can generally provide more accurate and reliable results. The rate coefficients are estimated based on the semi-classically adiabatic ground-state assumption (SAG) [38]. The transmission coefficient $\kappa_{SAG}(T)$ is the ratio of the thermally averaged semi-classical transmission probability to the thermal averaged classical transmission probability, and determined by

$$\kappa_{SAG}(T) = \frac{\beta \int_0^\infty dE \text{exp} (-\beta E) P_{SAG}(E) \text{exp} (-\beta E_a)}{\beta \int_0^\infty dE \text{exp} (-\beta E)}$$

where $P_{SAG}(E)$ is the quantum transmission probability approximated in semi-classical method, and $V_{SAG}^a$ is the barrier of the ground-state adiabatic potential. The ZCT method has drawbacks that it takes MEP as tunneling path, neglecting the curvature coupling the motion along the reaction path. The tunneling effect is usually seriously underestimated. Compared with ZCT, the SCT includes the corner-cutting tunneling [41]. The corner cutting means that the tunneling path is shorter than the minimum energy path. In addition, the curvature of reaction path coupling the vibration modes is considered in the SCT method. Therefore, the more comprehensive SCT method can estimated the quantum effect more accurately.

As mentioned above, The $\kappa_{SAG}(T)$ is calculated on the adiabatic ground-state assumption. However, the generated transition state locates at the peak of the activation Gibbs free energy for CVT and at the saddle point for TST. The classical threshold energy of CVT has a different definition. Thus, the Eq. (5) should be revised. The multiplicative factor $\kappa_{TST/CAG}(T)$ [40] is adopted and the $\dagger$ means TST or CVT. The CAG means classical adiabatic ground-state.

$$\kappa_{TST/CAG}(T) = \exp[\beta (V_{TST} (s_{TST}) - V_a)]$$

$$\kappa_{CVT/CAG}(T) = \exp[\beta (V_{CVT} (s_{CVT}) (T) - V_a)]$$

All the quantum mechanical effect corrections and rate coefficient calculation are performed on the PolyRate [42] program package.  

2.4. Treatment of intermediates

The intermediates are treated in local equilibrium with the transition state. Consider a bimolecular gas-phase reaction of A with B, with a pre-reactive intermediate:

$$A + B \rightarrow AB \rightarrow AB \dagger \rightarrow P$$

where AB is an intermediate complex, $AB\dagger$ is the transition state, and P is the product. The reaction rate may be written as

$$\frac{d[P]}{dt} = k_{\text{unimol}} [A][B]$$

If the reactants A and B are in quasiequilibrium with the transition state, it may be reasonable to assume that they are also in local equilibrium with AB. In that case, we can also write

$$\frac{d[P]}{dt} = k_{\text{animal}} [AB]$$

where

$$k_{\text{animal}} = k_{\text{unimol}} / K$$

And K is the equilibrium constant for $A + B \rightarrow AB$.

3. Results and discussion

3.1. Stationary points of the potential energy surface (PES)

The conformational analysis of 2,4,4-trimethyl-1-pentene (JCaH$_{16}$) is performed by scanning the rotation on the CH$_2$=C(CH$_3$)$_2$CH(CH$_3$)$_3$ and CH$_2$=C(CH$_3$)$_2$CH(CH$_3$)$_3$ single bond. The potential energy surfaces are shown in Fig. 1, with torsion angle changing from 0° to 360°. As shown in Fig. 1(b), the rotation of CH$_2$=C(CH$_3$)$_2$CH(CH$_3$)$_3$ single bond. has no effect on the lowest energy conformer of the reactant. Therefore, there is no detail analysis on the scan of this single bond.
Two energy minima are found in a threefold torsional potential with an energy difference of 2.19 kcal/mol, as presented in Fig. 1(a). Moreover, the two conformers with C1 symmetry are named as A and B. The conformer A is a global energy minimum. Thus, in this work, the stationary points and transition state geometry searching and energy calculations are performed on the basis of the conformer A. Nevertheless, the other conformer and its corresponding transition state are not distinguishable at high temperature. Therefore, the results derived from conformer A can reasonably be a substitution of the other conformer.

As to H abstraction, 2,4,4-trimethyl-1-pentene contains nine primary alkylic (Rxn1), two secondary alkylic (Rxn2), two vinylic (Rxn3) and three primary alkylic (Rxn4) H atoms forming different octenyl radicals and H2O. The optimized geometries of H abstraction products are listed in Fig. 2. In addition, OH addition reactions form 2,4,4-trimethyl-2-pentanen and 2,4,4-trimethyl-1-pentanen adducts. MEP energies and the energies corrected by zero-point energies calculated at BHANDHLYP/6-311G(d, p) and CCSD(T)/6-311++G(d, p) methods are shown in Table 1. The CCSD(T) method predicts lower barrier than the BHANDHLYP method of about 1.5–2.0 kcal/mol. Considering the triple excitation, CCSD(T) method predicts more accurate energies. The vinylic H abstraction undergoes a decalescence of 0.55 kcal/mol at BHANDHLYP method and it is corrected at CCSD(T) method that the vinylic H abstraction forms JC8H15-C radical with an exothermicity of 5.09 kcal/mol. Fig. 3 presents the potential energy diagram of H abstraction and OH addition reactions calculated at CCSD(T)/6-311+ +G(d, p) level. The IRC calculation has been done of each channel and the TS certainly connected with either JC8H16+OH or its complex. Fig. 4 illustrates the optimized electronic structures of the transition states and the Van der Waals complexes, as well as the cleaving C–H bond length, forming O–H bond length and the C–C bond length. The Optimized geometries calculated at BHANDHLYP/6-311+G(d, p) level were shown in Table S1 in supplementary data.

As shown in Fig. 3, the allylic H abstraction undergoes both primary and secondary channel. As to primary channel, it involves the indirect channel via a reactant complex and the direct channel. For indirect channel, JC8H16 proceeds through the reactant complex RC4 with an energy of 3.17 kcal/mol lower than the entrance channel to the transition state with energy barrier of 2.79 kcal/mol, and then forms the Van der Waals product-complex PC 4 with a relative energy of −28.56 kcal/mol before the formation of JC8H15-D radical (P4). In addition, JC8H16 undergoes direct channel via TS4Dir with an energy barrier of 3.15 kcal/mol. The indirect channel is favored resulting from the lower barrier. Besides, the OH fragment orientations in TS4Ind is opposite to TS4Ind.

As to secondary channel, the JC8H16 directly proceeds through the transition state TS2 with a barrier height of 1.96 kcal/mol, 0.83 kcal/
the results showed both primary and secondary H abstraction optimized transition state structures are presented in Fig. 5. In this work, the latter possesses both secondary and primary allylic H.

It may undergo indirect channel. And interestingly, at the case of both existence of primary and secondary allylic H, such as in 2-C₈H₁₆ and JC₈H₁₅-6, indirect channel might only exist in primary allylic H abstraction.

In previous researches, The allylic H abstraction can be assumed with several possibilities: an indirect channel, a direct channel, a mixture of an indirect and direct channel. Szori et al. [13] reported that both indirect and direct channels exist in primary allylic H abstraction for propene+OH at QCISD(T)/6-311+G(3df, 2p)//CCSD/6-31G (d) level. In this work, the results showed both primary and secondary H abstraction may undergo indirect channel. And interestingly, at the case of both existence of primary and secondary allylic H, such as in 2-C₈H₁₆ and JC₈H₁₅-6, indirect channel might only exist in primary allylic H abstraction.


Table 1 Calculated energies of species involved in JC₈H₁₆ + OH reactions at BHANDHLYP/6-311G (d, p), CCSD(T)/6-311++G(d, p) level. The unit is kcal/mol. Rxn1, Rxn2, Rxn3, Rxn4, RxnA denote allylic, secondary allylic, vinylic, primary allylic H abstraction channels, and OH addition channels, respectively. Rxn4Ind and Rxn4Dir denote indirect and direct channels, respectively.

<table>
<thead>
<tr>
<th>Species</th>
<th>BHANDHLYP/6-311G(d, p)</th>
<th>BHANDHLYP/6-311G(d, p)</th>
<th>CCSD(T)/6-311++G(d, p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rxn1</td>
<td>RC₁</td>
<td>0.98</td>
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<td></td>
<td>TS₁</td>
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<td></td>
<td>P₁ + H₂O</td>
<td>−1.54</td>
<td>−8.09</td>
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<td></td>
<td>PC₁</td>
<td>0.75</td>
<td>−13.22</td>
</tr>
<tr>
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<td>TS₂</td>
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<td>3.32</td>
</tr>
<tr>
<td></td>
<td>P₂ + H₂O</td>
<td>−1.00</td>
<td>−23.20</td>
</tr>
<tr>
<td></td>
<td>PC₂</td>
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<td>Rxn3</td>
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<td></td>
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<tr>
<td></td>
<td>PC₄</td>
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<tr>
<td></td>
<td>PC₄</td>
<td>1.03</td>
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<td></td>
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mol lower than TS₄₆, and then forms the Van der Waals product-complex PC₂ with a relative energy of −27.64 kcal/mol before the formation of JC₈H₁₅-6, and JC₈H₁₅-7, then forms the Van der Waals product-complex PC₂ with a relative energy of −27.64 kcal/mol before the formation of JC₈H₁₅-6.
Regarding the structural parameters in different types of H abstraction, shown in Fig. 4, that cleaving C–H bond and forming O–H bond are 1.194 Å and 1.360 Å for the TS2, 1.203 Å and 1.337 Å for the TS4, 1.231 Å and 1.275 Å for the TS1, and 1.264 Å and 1.208 Å for the TS3, respectively, indicating that the transition state of allylic H abstraction occurs earlier than alkylic and vinylic H abstraction. Furthermore, the distance between roaming H atom with C might be in proportion to the barrier height of transition state.

In general, resulting from the larger exothermicity and lower transition state energy barrier, Rxn2 and Rxn4 are thermodynamically and kinetically more favorable than Rxn1 and Rxn3.

JC8H16 proceeds both H abstraction reactions and OH addition reactions, resulting from the existence of the C=C double bond. And it possesses two addition sites, the central (RxnA1) and terminal (RxnA2) carbon atoms, respectively. The potential energy of both channels are illustrated in Fig. 5. OH radicals first form Van der Waals complexes before them insert into both sites. As mentioned above, the primary allylic H abstraction has a mixture of a direct and indirect abstraction mechanism. Then one or two reactant complexes may exist for allylic H abstraction and OH addition [13], as shown in Fig. 6. For the addition channel A1, it has a slightly shallow well of $-2.31$ kcal/mol than that of H abstraction and the energy barrier of transition state (TSA1) is 0.95 kcal/mol, slightly higher than that of the entrance to RCA1. Just as presented in Fig. 6(b), there are two complexes formed. H abstraction possesses one with O close to C=C bond and OH addition possesses the other one with H close to C=C bond. For the addition channel A2, JC8H16 proceeds through a reactant complex (RCA2) then to the transition state (TSA2) with an energy 0.32 kcal/mol lower than that of the
entrance channel to \( \text{RC}_{A2} \). H abstraction and OH addition share a common reactant complex before the transition states, as illustrated in Fig. 6(a). The distinction between two channels may arise from the different OH orientation and insert sites. Besides, the transition state barrier for the OH addition to central carbon atom is slightly larger than to terminal carbon atom, suggesting a preference site for OH addition to be the terminal carbon atom for JC8H16.

Fig. 4 presented the optimized geometries of transition states and the reactant complexes for OH addition reactions. As to transition state, the OH radical is placed in the plane almost parallel to the plane of the carbon chain, with the oxygen atom above the attacking carbon atom at a distance of 2.125 Å for central carbon atom and slightly longer than that of terminal carbon atom (2.063 Å). In addition, the OH orientates the \( \text{C} = \text{C} \) double bond. Resulting from the early appearance of the transition state, the \( \text{C} = \text{C} \) double bond character is retained. The reactant complex of RxnA1 is similar to the transition state with OH radical lying further away from the carbon chain. For RxnA2, OH radical lies in a plane almost perpendicular to the carbon chain, with H tilted to the terminal carbon atom.

3.2. MEP and adiabatic ground-state energy

The MEP is defined to be the path of the steepest descent depending on the coordinate system down from the saddle point \( (s = 0) \) to the products side \( (s > 0) \) and to the reactants side \( (s < 0) \). Intrinsic reaction coordinate (IRC) calculation at BHANDHLYP/6-311G (d, p) level was performed to obtain MEP, offering how the electronic energy \( (V_{\text{MEP}}) \) evolves with \( s \). And the endpoints of the IRC were optimized to

Fig. 6. Model potential energy surfaces involving addition and allylic H abstraction. (a) two reaction paths with a single reactant complex; (b) two reaction paths with two separate reactant complexes.
the Van der Waals wells. The IRC calculations were performed using the Gaussian09 [30] software. The adiabatic ground-state potential energy $V_a^G$, which is the sum of $V_{MEP}$ and ZPE, is of great significance and should be calculated point by point. In GaussRate 2009-A package [43], the $V_{MEP}$ and $V_a^G$ can be calculated at the same time by calling Polyrate 2010-A and Gaussian 09 software, respectively. In this work, the Page-McIver method [32] was applied in GaussRate to predict the reaction path for H abstraction and OH addition reactions, in which second-
order algorithm is employed to describe the steepest descent path. 50 points were computed in each direction of saddle point at a gradient step size of 0.02 amu$^{1/2}$·Bohr. MEP and the adiabatic ground-state potential energy curve evaluated at BHANDHLYP/6-311G(d, p) level for H-atom abstraction and OH addition reactions are presented in Fig. 7. As shown in Fig. 7, for allylic H abstraction, the potential energy of secondary H abstraction channel is slightly lower than primary allylic H abstraction channel. The $V_{a\rightarrow 0}$ along the reaction coordinate of Rxn2 and Rxn4 are flatter than those of the allylic and vinylic H abstraction channels, resulting from the relative lower BDE of allylic C–H bonds. In addition, the flatter curves of Rxn2 and Rxn4 in reactant-side may cause a weaker tunneling effect on H abstraction. It is seen that several well-like curves are labeled in $V_{a\rightarrow 0}$ curve in Fig. 7(b) and (d). The existence of the wells results from the strong active force among fragments instead of the molecules. Thus, Those intermediates are not Van der Waals complexes presented in Fig. 4. Actually, for bimolecular reactions, the reactant and product locate at $s = \infty$, thus the real Van der Waals complexes are beyond the scanned $s$ region and distance from the saddle point.

For Rxn1, it possesses a reactant-well near saddle point of the $V_{a\rightarrow 0}$ curve. The existence of this well transfers the peaks of the curve from the saddle point to the left side of the reactant-well. At the product side, a shallow well-like curve locates at $s = -0.5$ amu$^{1/2}$·Bohr, which results in slope variation but fails to generate a local minima.

For Rxn3, the curve is the narrowest among all the H abstraction channels, which could lead to the strongest tunneling effect. Different from Rxn1, Rxn3 possesses a deeper reactant-well because of the stronger attractive force, but the curve still peaks near the saddle point with its $s$ slightly larger than zero. At the product side, a well occurs at the similar location as Rxn1. Just like the reactant side, the attractive force between products is stronger than that of Rxn1. It is noted that the depths of all the wells are less than 1 kcal/mol, thus the effect of the wells can be ignored.

As shown in the Fig. 7(b), the energies of the OH addition reactions are considerably lower than that of H abstractions. And both addition channels are flat near the saddle point, where the maximum $V_{a\rightarrow 0}$ is lower than zero. Especially for RxnA2, the transition state energy barrier is lower than that of reactant, leading to negative temperature dependence for the rate coefficients, particularly at low temperature.

3.3. Activation Gibbs free energy change

In conventional TST, the transition state is regarded as the saddle point of the MEP. The associated rate coefficients are always overestimated. The CVT method was adopted to obtain more reasonable rate coefficients, which takes into account both energetic and entropic effects. The transition state located where the corresponding activation Gibbs free energy change ($\Delta G$) is up to its maximum and the generalized rate coefficient achieves its minimum. The Gibbs free energy change is generalized to

$$\Delta G(T, s) = RT \left[ \beta V_{a\rightarrow 0}(s) - \ln \left( \frac{Q^{GT}(T, s)}{Q^{GT}(T) K^0} \right) \right]$$

(10)

where $K^0$ is the activation equilibrium constant. Obviously, the rate constant in CVT method is smaller than that in TST method.

Fig. 8 presents $\Delta G$ along the reaction coordinate ($s$) for allylic H abstraction reaction. And different color means different temperature. The results show that $\Delta G$ increases with temperature increasing. The peaks of $\Delta G$ ($s_{max}$) at 294–2000 K are expressed in the right axis of the coordinate which are slightly larger than zero, illustrating that the transition states locate at the product side near saddle point. In addition, as shown in Fig. 9, $s_{max}$ increases with the temperature increasing for H abstraction and OH addition reactions. It can be seen that the generalized transition states of H abstraction reactions are close to saddle point, even for Rxn2, limited to 0.08 amu$^{1/2}$·Angstrom. As to OH addition reactions, the $s_{max}$ changes at a wider span of $\sim 0.48$ amu$^{1/2}$·Angstrom. This might result from the flat MEP curves of OH addition reactions.

3.4. Rate coefficients

3.4.1. Quantum mechanical effect and variational effect

The quantum mechanical effects make a big difference in rate coefficients calculation at low temperature as shown in Fig. 10, which presents the rate coefficients calculated in unit of cm$^3$·molecule$^{-1}$·s$^{-1}$. For non allylic H abstraction reactions, the tunneling effect is considerable for the calculation of the rate coefficients at low temperature range, resulting from the high and narrow barriers. It has a significant effect on the rate coefficients and the rate coefficients increase by 5, 10 times under the correction of ZCT and SCT. The Wigner tunneling correction for conventional TST is just for informational purpose. The results just valid at high temperature. The ZCT transmission coefficient is lower than SCT. Because the ZCT neglects the curvature coupling the motion along the reaction path and ignores the corner-cutting tunneling. This method always seriously underestimates the tunneling effect. In comparison, the transmission coefficient of SCT is more accurate. Unusually, as to allylic H abstraction channels, the rate coefficients even drop at low and intermediate temperature when ZCT or SCT is adopted. Fig. 11 presents the correction factors of Rxn2, and the meanings of abbreviations are listed in its caption. One can factor the ground-state transmission coefficient into two parts. The first one refers to quantum mechanical effect (both tunneling effect and non-classical reflection effect). In the energy range of $V_{a\rightarrow 0} \leq E \leq 2V_{a\rightarrow 0} - E_0$ ($V_{a\rightarrow 0}$ denotes the maximum $V_{a\rightarrow 0}$ and $E_0$ denotes the quantum threshold energy), it is possible to have non-classical reflection, which can
reduces the rate coefficients. However, with the significant tunneling effect, the first factor is larger than unity. The second one refers to the effect of the displacement between transition state and the peaks of the adiabatic ground-state energy curve. And it is to give a relatively smaller correction factor. Therefore, the overall correction factor is lower than unity and results in an unusual decline in rate coefficient.

As to variational effect, it represents the effect of the displacement between transition state and saddle point, which gives rise to the

Fig. 10. TST and CVT rate coefficients with Wigner, ZCT and SCT tunneling corrections of all channels for JCdH16 + OH.
among H abstraction and OH addition. The much larger amount of the alkylic H atoms compared with secondary allylic H atoms can be expected to more than compensate for the higher barrier. Moreover, the rate coefficients of the alkylic and allylic H abstraction exhibit more than 10 times higher than that of vinylic H abstraction, due to the apparently lower barrier.

Comparison between the rate coefficients evaluated at CCSD(T)/6-311++G(d, p)//BHandHLYP/6-311(d, p) method with those of iso-butene, 1-butene, and neo-pentene is shown in Fig. 14. The alkylic, vinylic, secondary and primary allylic H abstraction channels and OH addition channels are compared with neo-pentane in Sivaramakrishnan et al. [44], 1-butene and isobutene in Sun and Law [14], 3-hexene in Yang et al. [45]. The experimental data were reported in Tully et al. [46]. It can be seen that reactions of the same category almost stay in the same magnitude. The rate coefficients of JC8H16 is within five times

**Fig. 13.** Branching ratio of the H abstraction and OH addition reactions.

<table>
<thead>
<tr>
<th>Temperature (1000/K)</th>
<th>Branching ratio</th>
<th>H ab</th>
<th>OH ad</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1.00</td>
<td>0.0</td>
<td>1.00</td>
</tr>
<tr>
<td>1.0</td>
<td>0.80</td>
<td>0.20</td>
<td>0.80</td>
</tr>
<tr>
<td>1.5</td>
<td>0.60</td>
<td>0.40</td>
<td>0.60</td>
</tr>
<tr>
<td>2.0</td>
<td>0.40</td>
<td>0.60</td>
<td>0.40</td>
</tr>
<tr>
<td>2.5</td>
<td>0.20</td>
<td>0.80</td>
<td>0.20</td>
</tr>
<tr>
<td>3.0</td>
<td>0.00</td>
<td>1.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

**Fig. 14.** Comparison between the rate coefficients of JC8H16 and isobutene, 1-butene, neo-pentene and 3-hexene with OH system.

---

**Fig. 12.** CVT/SCT rate coefficients for JC8H16 + OH of H abstraction and OH addition reactions.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Coefficient (cm³ molecule⁻¹ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JC8H16 Rxn1</td>
<td>1E-10</td>
</tr>
<tr>
<td>JC8H16 Rxn2</td>
<td>1E-12</td>
</tr>
<tr>
<td>JC8H16 Rxn3</td>
<td>1E-14</td>
</tr>
<tr>
<td>JC8H16 Rxn4</td>
<td>1E-16</td>
</tr>
</tbody>
</table>

**Fig. 11.** Correction factors for Rxn2Dir. CVT/CAG represents classical adiabatic ground-state correction. ZCT/notun and SCT/notun represent non-classical reflection effects. ZCT and SCT represent the quantum mechanical effects including both tunneling and non-classical reflection. CVT/CAG/ZCT represents classical adiabatic ground-state and ZCT quantum effect correction. CVT/CAG/SCT notun represents non-classical reflection effects including both tunneling and non-classical reflection. CVT/CAG/SCT represents classical adiabatic ground-state and SCT quantum effect correction.

**Fig. 10.** Correction factors for Rxn2DIR. CVT/CAG represents classical adiabatic ground-state correction. ZCT/notun and SCT/notun represent non-classical reflection effects. ZCT and SCT represent the quantum mechanical effects including both tunneling and non-classical reflection. CVT/CAG/ZCT represents classical adiabatic ground-state and ZCT quantum effect correction. CVT/CAG/SCT notun represents non-classical reflection effects including both tunneling and non-classical reflection. CVT/CAG/SCT represents classical adiabatic ground-state and SCT quantum effect correction.
of the compared ones. And the difference at lower temperature is resulting from more significant tunneling effect of small mass atoms. According to the similar methods of Sun and Law [14], as well as the good agreement of the rate coefficient in Sun and Law with the experimental data, the uncertainty of the rate coefficients in this work should be a factor of 5. In addition, the Arrhenius expressions (cm³·molecule⁻¹·s⁻¹) of the rate coefficients for all channels are presented for chemical reaction mechanism constructions.

\[
k_1 = 9.42 \times 10^{-24} T^{3.88} \exp(0.24/RT)
\]

(11)

\[
k_2 = 3.68 \times 10^{-24} T^{2.36} \exp(1.32/RT)
\]

(12)

\[
k_3 = 1.57 \times 10^{-25} T^{4.0} \exp(-1.43/RT)
\]

(13)

\[
k_{\text{ind}} = 6.12 \times 10^{-23} T^{2.8} \exp(1.04/RT)
\]

(14)

\[
k_{\text{AD}} = 9.54 \times 10^{-23} T^{3.26} \exp(0.39/RT)
\]

(15)

\[
k_{\text{A1}} = 6.72 \times 10^{-21} T^{2.8} \exp(2.75/RT)
\]

(16)

\[
k_{\text{A2}} = 7.70 \times 10^{-19} T^{2.8} \exp(2.18/RT)
\]

(17)

4. Conclusion

H abstraction and OH addition reactions with 2,4,4-trimethyl-1-pentene have been observed by quantum mechanical and variational transition state theory. The optimized geometries and harmonic frequencies of the stationary points were calculated by BHANDHLYP/6-311(d, p) method and scaled by 0.935. In addition, the minimum energy path (MEP) was predicted by BHANDHLYP/6-311(d, p). Furthermore, the more accurate energies were determined by CCSD(T) method augmented with diffuse and polarization functions, 6-311+ +G(d, p). Moreover, a triple excitation was considered. Rate coefficients were determined through transition state theory and canonical transition state theory with the Wigner, zero curvature and small curvature method for correction of the quantum mechanical tunneling effect.

\[
\text{C}_{2} \text{H}_{6} \text{e} \text{c}
\]

possesses both primary and secondary allylic H abstraction, but just the primary one can proceed via both indirect and direct channel. Moreover, resulting from the larger exothermicity and lower transition state energy barrier, Rxn2 and Rxn4 are thermodynamically and kinetically more favorable than Rxn1 and Rxn3.

The \( \text{C}_{2} \text{H}_{6} \text{e} + \text{OH} \) system is dominated by OH addition reactions under 500 K and dominated by H abstraction reactions above 1100 K. At the temperature range of 500–1100 K, the competitiveness of both reaction categories are comparable. The comparison between traditional and canonical transition state theory indicated that OH abstraction reactions exhibit strong variational effect while H abstraction reactions exhibit weak variational effect. In addition, the OH addition in terminal carbon atom proceed an indirect channel and its submerged barrier results in apparent negative temperature dependence at low temperature.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.fuel.2017.08.091.

Reference


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