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# A theoretical investigation on Bell-Evans-Polanyi correlations for hydrogen abstraction reactions of large biodiesel molecules by H and OH radicals

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**Abstract:** High-accuracy prediction of activation energies and enthalpies of reaction is theoretically important while computationally challenging for accurately determining the kinetic parameters of chemical reactions in biodiesel combustion. In practice, the Bell-Evans-Polanyi (BEP) correlations between the activation energy and the enthalpy of reaction play an important role in fast estimation with acceptable accuracy. In the present study, the BEP correlations for hydrogen abstraction reactions of biodiesel surrogates by H and OH radicals were theoretically investigated by using high-level orbital-based and ONIOM-based methods. Reaction classes for these reactions were defined based on distinctive electron interactions due to the complex characteristics of esters. Linear BEP correlations were established for each reaction class and validated by the high-level calculations, with deviations being less than 0.90kcal/mol. The rate constants of some representative hydrogen abstraction reactions were calculated by using the BEP correlations and other approximate theories. These rate constants validate the BEP assumption of similar pre-exponential factors for the reactions in the same group, and they are found to agree reasonably well with the available data in literature. Furthermore, improved predictions to experimental data were obtained by using an existing kinetic model of methyl decanoate oxidation updated with the calculated rate constants. The present BEP correlations are believed to provide effective solutions to some kinetic issues of real biodiesel combustion.

**Key words:** Biodiesels, Activation energy, Bell-Evans-Polanyi correlations, Hydrogen abstraction reaction

## 1. Introduction

Biodiesel is regarded as one of the most potential fuel alternatives for its renewable and various feedstock, environmental benefits, and attractive combustion physicochemical properties [1-3]. It is typically constitutive of monoesters with 12-20 carbon atoms and derived from chemically reacting lipids with an alcohol through transesterification [4-7]. Biodiesels can be used in pure form or blended with petroleum diesels at any concentration in most injection pump diesel engines and fueling systems without any modifications [2, 6, 8]. Motivated by the practical interest of biodiesel usage, numerous investigations have been conducted on its combustion chemistry and emissions [9-15].

In a kinetics mechanism of biodiesel oxidation, the hydrogen abstraction reactions of biodiesel molecules by the H and OH radicals are critical chain propagation reactions at high temperatures and chain branching reactions at lower temperatures, which exert a great influence on the reactivity of target fuels [16, 17]. In addition, the hydrogen abstraction reactions from methyl esters by OH radicals play an important role in the formation of secondary organic aerosols under atmospheric condition [18-21]. Knowledge about the accurate kinetic parameters for these elementary reactions is essential to comprehend the combustion chemistry and atmospheric chemistry of esters.

The rate coefficients of reactions critically depend on their activation energies. For the reaction with a pronounced transition state, its high-pressure limit rate constant can be well calculated by using the conventional transition state theory [22-24]:

$$k(T) = \kappa \frac{k_B T}{h} \frac{Q_{TS}}{Q_R} \exp[-E_a/k_B T] \quad (1)$$

where  $E_a$  is the zero-point corrected activation energy,  $Q_{TS}$  and  $Q_R$  are the partition functions of the transition state and the same partition function per unit volume of the motionless reactants, and  $\kappa$ ,  $T$ ,  $k_B$  and  $h$  are the tunneling effect factor, the temperature, the Boltzmann constant, and the Planck constant, respectively. In fact, the tunneling effect, the torsional anharmonicity, and other factors affecting the pre-exponential factor vary insignificantly in a given reaction class, implying that the activation energy is the dominant parameter in

determining the rate constants.

1 Accurate energy determination is imperative for developing highly reliable combustion chemical kinetics.  
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3 For small- and medium-size molecules, the quadratic configuration interaction with singles, doubles and  
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5 perturbative inclusion of triple with the correlation-consistent, polarized-valence, triple- $\zeta$  (cc-pVTZ), and  
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7 quadruple- $\zeta$  (cc-pVQZ) basis sets constants with an extrapolation to complete basis set (CBS), predicts the  
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9 energy with uncertainties less than 1.0 kcal/mol. The prediction errors of QCISD(T)/CBS(T-Q) are believed to  
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11 be around 1.0 kcal/mol [25], which can be further decreased to 0.6 kcal/mol by using the bond additivity  
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13 correction. However, the QCISD(T)/CBS(T-Q) method is inapplicable to the large molecules (with more than  
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15 5-6 non-hydrogen atoms) due to its formidable computation load for the calculation with the cc-pVQZ basis  
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17 set. This limitation can be mitigated by using the QCISD(T)/CBS(D-T) method, where D denotes the  
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19 cc-pVDZ basis set, with a correction from MP2/CBS(T-Q), which enables the calculation for large molecules  
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21 with less than 9-10 non-hydrogen atoms while maintains the prediction accuracy. For the hydrogen abstraction  
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23 reactions of larger saturated and unsaturated biodiesel molecules by H radical, Zhang et al. [26, 27] developed  
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25 a two-layer ONIOM[QCISD(T)/CBS:DFT] method, whose accuracy was found to be within 0.15 kcal/mol  
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27 compared with the QCISD(T)/CBS methods.  
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40 Although the ONIOM[QCISD(T)/CBS:DFT] method is able to provide satisfactorily accurate  
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42 thermochemical data of large biodiesel molecules, there is scarcely available experimental data for direct  
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44 comparison. Accurate evaluation of thermochemical data from different sources would be beneficial for  
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46 studying biodiesel combustion. However, the large molecules and the oxygenated functional groups of  
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48 practical biodiesels make the experimental studies and higher-level calculations of activation energy difficult  
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50 in practice [26-28]. Consequently, many empirical methods [29-35] were developed for estimating activation  
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52 energies, among which the most widely used is the Bell-Evans-Polanyi (BEP) correlations [31, 32, 35]. In a  
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54 BEP correlation, a linear relation between the activation energy and reaction enthalpy of a given class of  
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reaction is given by

$$E_a = E_{a0} + \alpha\Delta H \quad (2)$$

where,  $E_{a0}$  is the activation energy of a reference reaction,  $E_a$  is the activation energy of a reaction from the same class, and  $\Delta H$  is the corresponding enthalpy difference of the two reactions. The constant  $\alpha$ , characterizing the location of transition state (TS) along the reaction coordinate, demonstrates that other factors such as tunneling factor and torsional anharmonicity are assumed identical for a given reaction class. From this perspective, activation energy is the only variable in determining kinetic parameters for a given reaction class.

In the past decades, the BEP correlations provide an efficient way to evaluate activation energies of many reaction classes and therefore facilitate building up complex reaction mechanisms [29, 36-40]. Sumathi et al. [41] summarized the BEP correlations of hydrogen abstractions within different  $\text{XOCH}_3$  ( $\text{X}=\text{H}, \text{CH}_3, \text{COH}, \text{COCH}_3, \text{OH}, \text{OCH}_3$ ) families by using group additivity methods. These correlations were verified by Akih-Kumgeh et al. [40] for the hydrogen abstraction reactions from the methoxy group of C1-C4 methyl esters, but the derivations at other reaction sites were as large as 2.0 kcal/mol. Sirjean et al. [42] showed that the BEP correlation for some cyclic compounds leads to significant deviations. Recently, the BEP correlations for the hydrogen abstraction reactions of alkanes [43] were used by Glaude et al. [39] and Herbinet et al. [37, 38] for developing detailed reaction mechanisms of oxidation of large methyl esters from C11 to C19, in which the activation energy of the hydrogen abstraction reactions from the  $\alpha$  position of the ester function group was taken as the same as the ones for tertiary H-atoms. Although the mechanisms predict well the reactivity of the biodiesel constituents and the mole fraction profiles of most reaction products, it was observed that the underestimated activation energies of some specific reactions in the oxidation of MD resulted in overestimated rate constants. This is because the rate constants of hydrogen abstraction reactions for reactive center surrounded by ester group are stabilized with strong conjugation effects, differing largely

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2 from those of the corresponding site on alkanes. Therefore, a detailed investigation on the BEP correlations for  
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4 biodiesel will benefit studying its thermochemistry and chemical kinetics.

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6 In the present work, we aimed to build up more accurate BEP correlations based on systematical  
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8 high-level quantum calculations of  $C_nH_{2n+1}COOCH_3 + H(OH)$ . Firstly, the high-level activation energies and  
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10 reaction enthalpies of  $C_nH_{2n+1}COOCH_3 + H(OH)$  ( $n=0-5$ ) were calculated at the  
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12 QCISD(T)/CBS//B3LYP/6-311++G(d, p) level. Secondly, reaction classes on base of the electron interactions  
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14 were defined to accord with the BEP assumptions. Finally, the BEP correlations were validated by comparing  
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16 with the available data of methyl decanoate [MD,  $CH_3(CH_2)_8COOCH_3$ ] and methyl hexadecanoate [MHex,  
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18  $CH_3(CH_2)_{14}COOCH_3$ ] [26]. Finally, we extend the above scope of study to include rate calculations to make  
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20 the present study directly useful for reaction mechanism developers. We noted that high-level rate calculations,  
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22 which requires to calculate the pre-exponential term of Eq. (1), would not only add a tremendous amount of  
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24 work to the present study but also make this paper to be out of focus. This is because the high-level  
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26 calculation of the pre-exponential term (entropy, in the thermodynamic perspective) for each reaction requires  
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28 the accurate treatment of torsional modes, which is quite difficult due to the torsional anharmonicity [44, 45].  
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30 Specifically, the one-to-one correspondence between a low frequency and a torsional mode is difficult to  
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32 identify; torsional modes could be coupled so that the one-dimensional hindered rotor treatment would  
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34 introduce a large error. The accurate treatment of torsional modes in the reactions involving large molecules is  
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36 an unsolved problem, which has drawn a lot of attention in the recent years. In the present study, we produced  
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38 rate constant data at three different levels of approximate theory. Although these rate constants were not  
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40 produced by using the state-of-the-art methods [46, 47], we believe they provide useful reference for reaction  
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42 mechanism developers and chemical kineticists.  
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## 57 **2. Theoretical Methodology**

### 58 **2.1 Computational methods**

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1 The Becke three-parameter functional and Lee-Yang-Parr correlation functional (B3LYP) with the  
 2 6-311++G(d, p) basis set [48, 49] were employed in the electronic structure optimization and the frequency  
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 4 calculations for all the stationary points on the potential energy surfaces of concern. The internal rotors along  
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 6 each single bonds were explicitly investigated at the B3LYP/6-311++G(d, p) level via relax scans with an  
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 8 increment of 10°, and the local minimum points were used for further refined optimization. All the  
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 10 connections between each saddle point and its minima were confirmed by the intrinsic reaction coordinate  
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 12 (IRC) calculation.  
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19 The quadratic configuration interaction with single and double excitation including perturbative inclusion  
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 21 of triples QCISD(T) with consistent polarized valence cc-pVXZ(X=D, T) basis sets, along with the  
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 23 second-order Møller–Plesset (MP2) method with cc-pVXZ(X=D, T, and Q) basis sets were used to calculate  
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 25 the single-point energies of C<sub>n</sub>H<sub>2n+1</sub>COOCH<sub>3</sub> (n=0-5). In order to achieve higher accuracy, the total energies  
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 27 were extrapolated to the complete basis set limit (CBS) by the following expressions [50]:  
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$$33 \text{E[QCISD(T)/CBS]} \\ 34 = \text{E[QCISD(T)/CBS]}_{\text{DZ} \rightarrow \text{TZ}} + \{ \text{E[MP2/CBS]}_{\text{TZ} \rightarrow \text{QZ}} - \text{E[MP2/CBS]}_{\text{DZ} \rightarrow \text{TZ}} \} \quad (3)$$

36 where

$$37 \text{E[QCISD(T)/CBS]}_{\text{DZ} \rightarrow \text{TZ}} \\ 38 = \text{E[QCISD(T)/TZ]} + \{ \text{E[QCISD(T)/TZ]} - \text{E[QCISD(T)/DZ]} \} \times 0.4629 \quad (4)$$

$$39 \text{E[MP2/CBS]}_{\text{TZ} \rightarrow \text{QZ}} = \text{E[MP2/QZ]} + \{ \text{E[MP2/QZ]} - \text{E[MP2/TZ]} \} \times 0.6938 \quad (5)$$

$$40 \text{E[MP2/CBS]}_{\text{DZ} \rightarrow \text{TZ}} = \text{E[MP2/TZ]} + \{ \text{E[MP2/TZ]} - \text{E[MP2/DZ]} \} \times 0.4629 \quad (6)$$

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 47 The QCISD(T)/CBS method utilized herein have a comparable accuracy with the QCISD(T)/CBS(T-Q)  
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 49 method, which is obtained by replacing MP2 in (5) with QCISD(T), and the deviations are less than 0.1  
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 51 kcal/mol. Such a good accuracy has also been verified for n-butanol (C<sub>4</sub>H<sub>9</sub>O) system [28] and for the  
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 53 hydrogen abstraction reactions of methyl butanoate [MB, CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>COOCH<sub>3</sub>] by H and OH radicals [51].  
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 59 The QCISD(T)/CBS method (3) avoids the computationally expensive QCISD(T)/QZ calculations and  
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 61 thereby can be used in systems with 9-10 non-hydrogen atoms, beyond which the method again becomes  
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1 computationally formidable and should be replaced by the ONIOM[QCISD(T)/CBS:DFT] method to be  
 2 delineated below.  
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5 The ONIOM energy of a reaction system (denoted by R) was obtained by using the low-level energy of  
 6 the system with the correction for the energy difference of chemically active portion (CAP) between the high  
 7 level and the low level:  
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$$10 E^{\text{ONIOM}}[\text{High: Low}] = E^{\text{Low}}(\text{R}) + [E^{\text{High}}(\text{CAP}) - E^{\text{Low}}(\text{CAP})] \quad (8)$$

11 Using the B3LYP/6-311++G(d,p) method for the low level and the QCISD(T)/CBS method (3) for the high  
 12 level, we have the ONIOM[QCISD(T)/CBS:DFT] energy given by  
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$$15 E^{\text{ONIOM}}[\text{QCISD(T)CBS: DFT}] \\
 16 = E^{\text{ONIOM}}[\text{QCISD(T)/CBS: DFT}]_{\text{DZ} \rightarrow \text{TZ}} \\
 17 + \{E^{\text{ONIOM}}[\text{MP2/CBS: DFT}]_{\text{TZ} \rightarrow \text{QZ}} - E^{\text{ONIOM}}[\text{MP2/CBS: DFT}]_{\text{DZ} \rightarrow \text{TZ}}\} \quad (9)$$

18 where

$$19 E^{\text{ONIOM}}[\text{QCISD(T)/CBS: DFT}]_{\text{DZ} \rightarrow \text{TZ}} \\
 20 = E^{\text{ONIOM}}[\text{QCISD(T)/TZ: DFT}] \\
 21 + \{E^{\text{ONIOM}}[\text{QCISD(T)/TZ: DFT}] - E^{\text{ONIOM}}[\text{QCISD(T)/DZ: DFT}]\} \times 0.4629 \quad (10)$$

$$22 E^{\text{ONIOM}}[\text{MP2/CBS: DFT}]_{\text{TZ} \rightarrow \text{QZ}} \\
 23 = E^{\text{ONIOM}}[\text{MP2/QZ: DFT}] \\
 24 + \{E^{\text{ONIOM}}[\text{MP2/QZ: DFT}] - E^{\text{ONIOM}}[\text{MP2/TZ: DFT}]\} \times 0.6938 \quad (11)$$

$$25 E^{\text{ONIOM}}[\text{MP2/CBS: DFT}]_{\text{DZ} \rightarrow \text{TZ}} \\
 26 = E^{\text{ONIOM}}[\text{MP2/TZ: DFT}] \\
 27 + \{E^{\text{ONIOM}}[\text{MP2/TZ: DFT}] - E^{\text{ONIOM}}[\text{MP2/DZ: DFT}]\} \times 0.4629 \quad (12)$$

28 For methyl decanoate [MD,  $\text{CH}_3(\text{CH}_2)_8\text{COOCH}_3$ ] + OH, the two-layer ONIOM method proposed by  
 29 Zhang et al.[26] was used to calculate the single point energies. More details of the ONIOM method for  
 30 energy calculations and relevant technical issues have been given in previous literatures [26, 27]. All  
 31 electronic structures were performed using the Gaussian 09 program [52].  
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## 46 2.2 Generic categorization of reaction classes for BEP correlations

47 In the derivation of BEP correlations, the pre-exponential factor and the TS locations on the PES  
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coordinate are assumed to be identical for all the reactions belonging to a specific class. The ester functional group has a great influence on its neighboring groups, and its strong  $\pi$ -resonance effect makes it different from other radicals. In order to accord with the assumption of the BEP correlations, the classification of analogous reactions was performed for  $C_nH_{2n+1}COOCH_3$  ( $n=0-5$ ) + H and  $C_nH_{2n+1}COOCH_3$  ( $n=0-5$ ) + OH, respectively. For  $C_nH_{2n+1}COOCH_3$  ( $n=0-5$ ) + H, the analogous reaction groups are based on the conjugation effect of ester moiety around the active site. Furthermore, the hydrogen bonding occurs in  $C_nH_{2n+1}COOCH_3$  ( $n=0-5$ ) + OH and must be considered in the classification. More details and justification of the classification of the reaction classes will be given in the following section.

### 3. Results and discussion

To facilitate the presentation and discussion of the present results, we named the sequence of reaction channels, the transition states, and the products by the location of reaction sites, as seen in Fig. 1. Each reaction channel corresponds to the abstraction site from 1-(or  $\alpha$ -), 2-(or  $\beta$ -), 3-(or  $\gamma$ -), ..., m1- and m2-site H atoms, leading to the P(n+1)-1, ..., P(n+1)-m1 and P(n+1)-m2 radicals, respectively. Such a nomenclature is consistent with previous literatures [26, 51].

#### 3.1 Hydrogen abstraction reactions of H + $C_nH_{2n+1}COOCH_3$ ( $n=0-5$ )

##### 3.1.1 Reaction characteristics

Energetically favorable reaction pathways at different sites have been investigated on the PES of H +  $C_nH_{2n+1}COOCH_3$  ( $n=0-5$ ) at the QCISD(T)/CBS level, as shown in Fig. 2. The thermal energetics of H +  $C_nH_{2n+1}COOCH_3$  ( $n=0-5$ ) and methyl butanoate [MB,  $CH_3(CH_2)_2COOCH_3$ ] + OH obtained by Zhang et al. [26, 51] at the QCISD(T)/CBS//B3LYP/6-311++G(d, p) level, were quoted in present study. It is evident that, in these exothermic reactions, a stronger H-H bond is formed at the expense of the weaker C-H bond of methyl esters. Consequently, an increase in the negative enthalpy change is accompanied with a decrease in the

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activation energy, which accord with the BEP principle expectedly. Among these reaction channels, the hydrogen abstraction from the 1-site of methyl esters is the most energetically favorable channel with the lowest  $E_a$ , and the hydrogen abstraction from the m2-site is the least one. It is also observed that the thermal energetics of the abstraction reactions from the m2-site are almost identical for different methyl esters. Similarly, the hydrogen abstraction from the 1-site have comparable  $E_a$  and  $\Delta H$  for different methyl esters. Furthermore, the  $E_a$  of hydrogen abstraction from the internal sites of larger methyl esters show a propinquity trend, which is mainly attributed to the diminishing effect of the ester moiety.

The characteristics of the reactions under investigation is exemplified by the case of n=5, namely, the methyl hexanoate [MH,  $\text{CH}_3(\text{CH}_2)_4\text{COOCH}_3$ ] + H system, and the optimized geometries of the products are shown in Fig. 3. It is seen that the six products have different configurations from MH. This is because that the orbitals of radicals generated from the hydrogen abstraction reactions of MH at the six carbon sites change from sp<sup>3</sup> hybridization to sp<sup>2</sup> hybridization. The singly occupied molecular orbital C1 p of P6-1 and C2 p of P6-2, which are perpendicular to the plane COO, are adjacent to the carbonyl C=O bond and form an extended  $\pi$ -resonance structure with the C=O  $\pi$ -orbital. Likewise, the stabilization of P6-m2 also involves an extended  $\pi$ -resonance consisting of singly occupied p orbital of Cm2, the filled p orbital on the O atom, and the C=O  $\pi$ -orbital. As for other sites, the products out of COO plane are dominantly stabilized by the  $\sigma$ - $\pi$  hyper-conjugation to ester functional groups, and the interaction around is similar to that of alkanes. As a summary, the effect of C=O around the reactive center plays an important role in reaction reactivity than the farther active sites.

### 3.1.2 BEP correlations

All the hydrogen abstraction reactions of  $\text{C}_n\text{H}_{2n+1}\text{COOCH}_3$  + H can be categorized into three reaction classes in terms of the position of reactive center with respect to the ester moiety: (1) at the  $\alpha$ -site as the first class, denoted by  $\alpha$ , (2) at the m2-site as the second class, denoted by m2, (3) at the rest hydrocarbonyl sites as the

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third class, denoted by *H*. The present BEP correlations of different reaction classes and those reported previously [41, 43] are displayed in Fig. 4. It can be seen that linear correlations between  $E_{as}$  and  $\Delta H$ s are well established for a given reaction class:

$$E_a = 13.63 + 0.63\Delta H \text{ kcal/mol} \quad [\alpha] \quad (r^2=0.99) \quad (13)$$

$$E_a = 15.80 + 0.99\Delta H \text{ kcal/mol} \quad [M2] \quad (r^2=0.99) \quad (14)$$

$$E_a = 13.78 + 0.99\Delta H \text{ kcal/mol} \quad [H] \quad (r^2=0.97) \quad (15)$$

Some scattering points tend to gather together on each line due to the increased similarity of reactive center with increasing the length of the aliphatic chain. Take the  $\alpha$  group as an example, only one point, belonging to the methyl acetate, is separated from the other points respectively standing for methyl propionate, methyl butanoate, methyl valerate, and methyl hexanoate. These points seem to gather together, implying that they have comparable activation energy and enthalpy change. When the aliphatic chain consists of 3 carbon atoms at least, the properties of different ester radicals with the active site located at the  $\alpha$  position of the ester functionality become relatively comparable. The phenomenon was also observed in the *H* and *m2* groups. With a longer carbon chain, the discrepancies among the same reaction group decrease and thus thermal energetics became more comparable.

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The BEP correlation proposed by Sumathi et al. [41] for oxygenated compounds  $\text{CH}_3\text{OX}$  with varying substituent X, such as H,  $\text{CH}_3$ ,  $\text{C(O)H}$ ,  $\text{C(O)CH}_3$ , OH, and  $\text{OCH}_3$ , has a similar trend (i.e. a similar slope of the BEP line) with Eq. (15), but it is higher than the one of H group by a factor of 1.5. Similarly, Dean et al. [43] considered the hydrogen abstraction reactions of alkanes as one reaction class, and its BEP correlation is given by

$$E_a = 9.43 + 0.65\Delta H \text{ (kcal/mol)} \quad (16)$$

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which is widely used in the development of biodiesel mechanisms. However, its value is significantly lower

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2 than the present calculated results, leading to overestimated rate constants by a factor 1.7 at 650K in the  
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4 oxidation of large methyl esters from C11 to C19 [38].

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6 It is known that the effect of ester functional group surrounding reactive center diminishes rapidly with  
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8 the distance away from the group. When radical sites of large methyl esters are far away from its functionality,  
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10 those radicals have similar electron interactions as those of alkanes, indicating that the Eq. (16) is comparable  
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12 with Eq. (15) to some extent. However, the effect of the ester functionality makes Eq. (16) is not equivalent to  
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14 Eq. (15). To quantify the difference of the activation energy between the *H* group of esters and corresponding  
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16 alkanes caused by the ester moiety, an average factor was obtained by comparing constants parameter in Eq.  
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18 (16) to those in Eq. (15). Likewise, we further obtained the factors of hydrogen abstraction reactions of methyl  
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20 esters by O, H and CH<sub>3</sub> radicals by using the same method. The factor is 1.36, 1.29 and 1.40 for hydrogen  
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22 abstraction from terminal C atom of methyl propionate by O, CH<sub>3</sub> and H, respectively [53]. The advantage of  
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24 using these factors is to estimate  $E_a$ s of hydrogen abstraction reactions of methyl esters from another  
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26 perspective, when there is no accurate data of ester for reference. Provided hydrogen abstraction reactions of  
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28 methyl esters have similar electron interactions with the ones of alkanes, their activation energies can be  
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30 obtained by the BEP correlations for alkanes with a correction factor listed above. This method was employed  
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32 in the energy calculations to be discussed shortly in the next section.

### 3.2 Hydrogen abstraction reactions of OH + C<sub>n</sub>H<sub>2n+1</sub>COOCH<sub>3</sub> (n=0-5)

#### 3.2.1 Reaction characteristics

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Hydrogen abstraction reactions of C<sub>n</sub>H<sub>2n+1</sub>COOCH<sub>3</sub> (n=0-5) + OH are an overall exothermic process, in which the H atom in OH radicals can interact with each atom of an ester functional group, forming a hydrogen-bonding reactant complex (RC) through a barrierless reaction. The present thermal energetics of C<sub>n</sub>H<sub>2n+1</sub>COOCH<sub>3</sub> (n=0-5) + OH together with other high-level calculation results from the literature are shown in Table 1. It should be noted that the  $E_a$  is the activation energy from the RC to the corresponding TS.

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2 Most of the previous high-level calculations were focused on small methyl molecules [11, 53-56]. The  
3  $E_{as}$  at the QCISD(T)/CBS level in this work are comparable with those obtained at the CCSD(T)/CBS(T-Q)  
4 level by Jørgensen et al. [56] and at the CCSD(T)/CBS(D-T) level by Mendes et al. [11] Tan et al. [53, 55]  
5 employed the multi-reference method to examine the multi-configurational characteristics of the hydrogen  
6 abstraction reactions of small methyl esters, from which the thermal energetics obtained with the present  
7 QCISD(T)/CBS method deviates by 0.50 kcal/mol.  
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16 The energetically favorable channels on PESs of  $C_nH_{2n+1}COOCH_3$  ( $n=0-5$ ) + OH were constructed at  
17 the QCISD(T)/CBS level, as shown in Fig. 5. All these reactions consist of reactant complexes except for the  
18 one at the  $m1$  site of methyl hexanoate [ $n=5$ ,  $CH_3(CH_2)_4COOCH_3$ ], which was also observed in large methyl  
19 esters such as MD. Among all the reaction channels, the hydrogen abstraction reaction from the  $\beta$ -site of  
20 methyl esters has the lowest  $E_a$  due to a strong H-bond interaction, while the reactions at the  $\alpha$ -site of methyl  
21 esters have relatively higher  $E_{as}$ .  
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33 Comparing with the reaction pathways of methyl esters + H, the variation of  $E_a$  and  $\Delta H$  of methyl esters  
34 + OH seems to be “non-monotonic” and contradicts with the BEP principle that the more stable products are  
35 formed via the lower TS. The BEP principle was once believed to not hold for most oxygenated organics +  
36 OH, because their  $E_{as}$  depend on not only the bond length but also the H-bonding interaction, which affects  
37 the TS energy but not the product energy. Consequently, the seemingly contradictory observations from Fig. 5  
38 can be explained by that hydrogen abstraction reactions at the  $\alpha$ -site have higher  $E_{as}$  than those at the  $\beta$ -site  
39 due to the stronger H-bonding interaction, and that the product P $n-1$  is more stable by the stronger  
40  $\pi$ -conjugation effect. Therefore, appropriate classifications based on geometrical and energetic parameters are  
41 essential to establish the BEP correlations for methyl esters + OH systems.  
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58 The present calculation results are exemplified by the MH + OH system. The most stable conformers  
59 with the lowest energies of the corresponding complexes and TSs are displayed in Fig. 6. All the TS structures  
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except TS6-m1 are ring-like and have a hydrogen bond. Unlike the other TSs, TS6-1 is stabilized by the H-bonding involving the carbonyl oxygen O atom. TS6-2 is more stable by the H-bonding interaction with the O atom on the alkoxy group, which results in the most energetically favorable pathway. The distance between the H atom of OH and the O atom of the ester moiety ( $d_{\text{H}\cdots\text{O}}$ ) is a measure of the strength of the interaction of hydrogen bonding, which influences the corresponding  $E_a$ . As an example,  $d_{\text{H}\cdots\text{O}}$  (2.116 Å) in TS6-2 is larger than that (2.251 Å) in TS6-1.

The defined  $L$  parameter [57] was used to evaluate the position of TSs on the reaction coordinates, indicating a connection between reactivity and structure:

$$L = \frac{\delta r(\text{CH})}{\delta r(\text{OH})} \quad (17)$$

where  $\delta r(\text{CH})$  represents the bond-length variation of the C-H bond from TS to the corresponding reactant, and  $\delta r(\text{OH})$  represents the bond-length variation of the O-H bond from TS to the corresponding product. The calculated  $L$  parameters for all the reaction channels are shown in Table 2. It can be seen that all the  $L$  parameters are less than 1, indicating the TS structures are more product-like than reactant-like. The comparable  $L$  parameters of reactions at the m2-site also explains the similar reactivity behavior among different carbon chains. The result that the larger  $L$  parameter renders the lower activation energy of TS accords with the behavior observed in the PESs.

### 3.2.2 BEP correlations

Categorizations of hydrogen abstraction reactions for BEP correlations are based on the orbital theory and internal interaction, as discussed above. For  $\text{C}_n\text{H}_{2n+1}\text{COOCH}_3 + \text{OH}$ , the whole reaction system was classified into four reaction classes in terms of the active site position: (1) hydrogen abstractions at the  $\alpha$ -site with H-bond in TSs as the first class, denoted by  $\alpha'$ , (2) hydrogen abstractions at the m2-site with H-bond in TSs as the second class, denoted by  $m2'$ , (3) hydrogen abstractions at 2- and farther hydrocarbonyl sites with

H-bond in TSs as the third class, denoted by  $H'$ , (4) hydrogen abstractions without H-bond in TSs actually at the  $m1$  sites of methyl esters with the aliphatic chain larger than 5 C-atoms as the fourth class, denoted by  $m1'$ .

The BEP correlations for the four reaction classes within distinct methyl esters are shown in Fig. 7, again showing linear relations between  $E_{as}$  and  $\Delta Hs$  for a given reaction class:

$$E_a = 15.18 + 0.43\Delta H \text{ kcal/mol} \quad [\alpha'] \quad (r^2 = 0.83) \quad (18)$$

$$E_a = 14.22 + 0.45\Delta H \text{ kcal/mol} \quad [m2'] \quad (r^2 = 0.99) \quad (19)$$

$$E_a = 17.12 + 0.68\Delta H \text{ kcal/mol} \quad [H'] \quad (r^2 = 0.92) \quad (20)$$

$$E_a = 13.48 + 0.67\Delta H \text{ kcal/mol} \quad [m1'] \quad (r^2 = 1.00) \quad (21)$$

Similar energetics scattering points gathered together on each line due to the increased similarity of reactive center with increasing the aliphatic chain, especially for the  $m2'$  group. The characteristics of the abstraction reaction from the methyl ester becomes more similar when its carbon chain increases. To be specific, all the scattering points except those for the hydrogen abstraction of methyl formate are relatively comparable with about 0.1kcal/mol deviation for both activation energy and entropy change. It is noted that the TS of the favorable hydrogen abstractions at the  $m1$ -site does not involve an H bond for larger methyl esters than MH. Only one point representing TS6-5 belongs to the  $m1'$  group in current work, thus its BEP correlation is unavailable by fitting. As discussed above, hydrogen abstraction reactions in the  $m1'$  group have similar electron interaction with the corresponding alkanes. Thus, the BEP correlation of  $m1'$  group was constructed by using the BEP correlation of Dean et al. [43] with the scaled factor of 1.36 discussed above.

### 3.3 Validation of BEP correlations for larger methyl esters

In order to examine the proposed BEP correlations specific for methyl esters, we compared the estimated  $E_{as}$  with the existing high-level data reported in the literature [26]. The estimated  $E_{as}$  using the BEP correlations and the calculated  $E_{as}$  by the two-layer ONIOM method for methyl decanoate [MD,

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$\text{CH}_3(\text{CH}_2)_8\text{COOCH}_3] + \text{H}$ , methyl hexadecanoate [ $\text{MHex}$ ,  $\text{CH}_3(\text{CH}_2)_{14}\text{COOCH}_3] + \text{H}$ , and  $\text{MD} + \text{OH}$  are summarized in Table 3. Due to the lack of thermochemical data of  $\text{MD} + \text{OH}$  in the literature, its data was calculated by the ONIOM method [26]. The most competitive reaction channel for hydrogen abstraction reactions are those from the  $\alpha$  group by H radical, while the reaction in  $m2$  group is the less competitive reaction pathway.  $E_{as}$  of reactions in  $H$  group for different esters are very close with mean deviations being around 0.17 kcal/mol. Consequently, the defined reaction classes were justified through the direct calculation results of  $\text{MD} + \text{OH}$ . The  $E_a$  of hydrogen abstraction from the  $\beta$ -site is still higher than that at the  $\alpha$ -site, and the energetically favorable abstraction reaction at  $m1$ -site does not involve a hydrogen bond.

Absolute deviations between the estimated data and the calculated results of  $\text{MD} + \text{H}$ ,  $\text{MD} + \text{OH}$ , and  $\text{MHex} + \text{H}$  are shown in Fig. 8. For  $\alpha$  and  $m2$  group of  $\text{MD} + \text{H}$  and  $\text{MHex} + \text{H}$ , the estimated  $E_{as}$  were comparable with the literature available data with deviations being less than 0.15 kcal/mol. Among all the hydrogen reactions of  $\text{MD} + \text{H}$  and  $\text{MHex} + \text{H}$ , the maximum deviation of 0.78 kcal/mol occurs at the 9th site of  $\text{MHex}$ , and it is attributed to the stable conjugation effect of long aliphatic chain, which is lacking in  $\text{MH}$  to some extent.

As seen in Fig. 8, the absolute deviation of the  $\alpha'$  group in  $\text{MD} + \text{OH}$  is less than 0.2 kcal/mol. A larger difference of  $E_{as}$  between the BEP correlations and the literature available data occurs for the  $H'$  group and is attributed to the slightly different TSs dominated by the position and the strength of the H-bonds at different sites. As mentioned above, the resemblance of reactions in the  $H'$  group of the large ester molecules is strengthened. Thus, the deviations are within an acceptable range of 0.90 kcal/mol.

### 3.4 Application of BEP correlations in kinetic modelling

#### 3.4.1 Reaction rate constants

In this work, the rate constants were calculated by using three different levels of theoretical methods, as



1 explained in the following. Method 1 is given below in the Eq. (22) based on the assumption of the  
2 Bell-Evans-Polanyi correlations that the pre-exponential factor is a constant for the same group, of which the  
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4 calculated rate constants of main reactions is displayed in Tables S1 and S2.  
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7  
8 Fig. 9 illustrates the calculated rate constants of the hydrogen abstraction reaction by H atoms at the  
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10  $\alpha$ -site of MH based on the derived BEP correlations, and the rate constants of Chi et al. [58] are also shown for  
11  
12 comparison. Chi et al. [58] have reported the rate constants of hydrogen abstraction reactions of MH by H  
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14 atom by employing the generalized energy-based fragmentation (GEBF) method. The rate constants in the  
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16 present work were calculated by  
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$$19 \quad k_{MH}(T) = k_{MB}(T)e^{(E_{a,MH}-E_{a,MB})/RT} \quad (22)$$

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21  
22 where the  $k_{MB}$  for the hydrogen abstraction of MB has been calculated by the Zhang et al. [51] and the  
23  
24 corresponding activation energy  $E_{a,MB}$  is 7.10 kcal/mol obtained at the QCISD(T)/CBS level. The relevant  
25  
26  $E_{a,MH}$  is 7.00 kcal/mol calculated by using the GEBF method. As shown in Fig. 9, the rate constant in this  
27  
28 work agrees excellently with that of Chi et al. [58] at temperature below 1500K and is higher than that of Chi  
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30 et al. [58] by a factor of 3 at high temperatures.  
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40 Sarathy et al. [59] have developed a kinetic model for MD pyrolysis, where the kinetic parameters of  
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42 hydrogen abstraction reactions were evaluated by an Evans-Polanyi correlation for alkanes. The rate constant  
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44  $k_{MD}$  in the present work is obtained by  
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46

$$47 \quad k_{MD}(T) = k_{MB}(T)e^{(E_{a,MD}-E_{a,MB})/RT} \quad (23)$$

48  
49 where the  $E_{a,MD}$  is 7.22 kcal/mol calculated by the ONIOM method. Fig. 9 shows the rate constant of hydrogen  
50  
51 abstraction reactions by H atoms at  $\alpha$ -site of MD in this work and that of Sarathy et al. [59] for comparison. It  
52  
53 is seen that the rate constant of Sarathy et al. [59] is larger than the present result by a factor of 6 at 600K and  
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55 a factor of 2 at 1000K. A similar trend has been observed by Herbinet et al. [38] that the kinetic parameter  
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calculated by using Evans-Polanyi correlations for alkanes is often overestimated because the C-H bond energy at the  $\alpha$ -site of ester group is lower than that a tertiary H atom.

Method 2 calculates the pre-exponential factor for each reaction by treating all the internal degrees of freedom as vibrational ones, namely harmonic oscillators. No torsional mode was considered in this method. The rate constant displayed in Tables S3 and S4 were calculated by using the MESS code [60]. Method 3 calculates the pre-exponential factor by multiplying a factor to the rate constant obtained by Method 2 so as to account for the torsional modes. This factor was obtained by dividing the high-level rate constants of MB+H (OH) [51] to the corresponding data predicted by Method 2. Apparently, this factor is a function of temperature. The rate constants generated by Method 3 are displayed in Tables S5 and S6.

It should be also noted that the presence of the shallow pre-reaction well in reactions abstracted by OH radicals is critical for the rate constants at a relatively low temperature, say below 300K. In addition, the pre-reaction complex was also identified to be about 6 kcal/mol lower than the reactants and is kinetically unimportant at sufficiently high temperature reactions [11, 51]. In the present work, we considered a range of temperature from 500K to 2500K and therefore neglected the influence of the shallow well.

In addition, the rate constants of representative abstraction reactions calculated by Method 2 were shown in Figs. S1-S6 in order to verify the assumption that the pre-exponential factor is the same in the same group. As shown in Figure S1, the rate constants of reactions abstracted by H radicals from the  $\alpha$ -group agree well with each other due to the similar energy barriers and pre-exponential factors. Such a good agreement can also be observed in Fig.S2. The rate constants of selected reactions abstracted by H radicals of the  $H$ -group is depicted in the Fig. S3, in which those with comparable energy barriers agrees well with each other and imply the similarity of pre-exponential factors. Similarly, the rate constants of some reactions abstracted by OH radicals of the  $\alpha'$ -group, the  $m2'$ -group and the  $H'$ -group were displayed in Fig. S4, Fig. S5 and Fig. S6, respectively. All of them substantiate again that the BEP assumption of similar pre-exponential factors is valid

for reactions in the same group.

### 3.4.2 Kinetic modelling of MD pyrolysis

To illustrate the important role of a correct BEP correlation in kinetic modelling, we investigated the pyrolysis of MD in a flow reactor at the pressure of 30 Torr [61], in which its products has been identified by using the synchrotron vacuum ultraviolet photoionization mass spectrometry. In order to emphasize the effect of kinetic parameters of the hydrogen abstractions in kinetic modelling, only the rate constants of hydrogen abstraction in Sarathy et al.'s model [59] was replaced by the calculated results in the present work. Fig. 10 shows the simulation results from Sarathy et al.'s original model [59], the present model updated with new rate constants, and the experimental data [61] for several mole fractions. The simulation of the experiment was performed with the measured temperature profiles as input parameters and using the Plug Flow Reactor (PFR) module in the CHEMKIN-PRO software [62]. It is seen that the kinetic parameters of hydrogen reactions have a great influence on the simulated mole fractions. The simulated mole fractions based on the present rate constants are lower than those based on Sarathy et al.'s model [59], and the present model has better agreement with the experiment. More modelling comparison for other reaction system merits future studies.

## 4. Concluding remarks

In the present work, the BEP correlations for practical biodiesel components were established and systematically validated for their hydrogen abstraction reactions by H and OH radicals. Imperative categorizations by molecular orbital theory and interaction analysis were proposed to enable such correlation by approximately fixing the pre-exponential factor for a specific reaction class. And the applicability of the categorizations was verified by the direct calculation results at the QCISD(T)/CBS level. For hydrogen abstraction reactions of methyl esters by H atom, three reaction classes were categorized by the ester moiety effect and conjugation types. The predicted  $E_a$ s by the BEP correlations show excellent agreement with available calculation results of large methyl esters + H, and the deviations are less than 0.78 kcal/mol. For

1 hydrogen abstraction reactions of methyl esters by OH radical, all the reactions were categorized into four  
2 classes based on the ester moiety effect, conjugation types, and H-bonding interaction. The MD + OH system  
3 was calculated with the ONIOM[QCISD(T):DFT] method, and the estimated  $E_{as}$  by the BEP correlations  
4 agree with the calculated resulted within 0.90 kcal/mol. Based on the BEP correlations, the calculated rate  
5 constants and kinetic modelling all show improved results compared with the previous works. In summary, the  
6 BEP correlations in the present work provide a balanced method for accurately estimating thermochemical  
7 data of biodiesel molecules with significantly reduced computation load. These BEP correlations will  
8 significantly facilitate the development of kinetic models for practical biodiesels.  
9

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Table 1. The EBs and HRs of OH + C<sub>n</sub>H<sub>2n+1</sub>COOCH<sub>3</sub> (n=0-5)

Reactions	EB <sup>a</sup>	EB(ref.)	HR <sup>a</sup>	HR(ref.)
HO+HCOOCH <sub>3</sub> →H <sub>2</sub> O+COOCH <sub>3</sub>	4.27	3.8 <sup>b</sup>	-19.91	-18.3 <sup>b</sup>
HO+HCOOCH <sub>3</sub> →H <sub>2</sub> O+HCOOCH <sub>2</sub>	5.72	6.1 <sup>b</sup>	-19.49	-18.7 <sup>b</sup>
HO+CH <sub>3</sub> COOCH <sub>3</sub> →H <sub>2</sub> O+CH <sub>2</sub> COOCH <sub>3</sub>	6.40	6.6 <sup>c</sup> , 6.84 <sup>d</sup>	-20.27	-20.1 <sup>c</sup> , -19.77 <sup>d</sup>
HO+CH <sub>3</sub> COOCH <sub>3</sub> →H <sub>2</sub> O+CH <sub>3</sub> COOCH <sub>2</sub>	5.35	5.3 <sup>c</sup> , 5.62 <sup>d</sup>	-19.97	-19.8 <sup>c</sup> , -18.16 <sup>d</sup>
HO+CH <sub>3</sub> CH <sub>2</sub> COOCH <sub>3</sub> →H <sub>2</sub> O+CH <sub>3</sub> CHCOOCH <sub>3</sub>	4.21	3.8 <sup>c</sup> , 4.2 <sup>e</sup>	-25.44	-24.7 <sup>c</sup> , -24.50 <sup>e</sup>
HO+CH <sub>3</sub> CH <sub>2</sub> COOCH <sub>3</sub> →H <sub>2</sub> O+CH <sub>2</sub> CH <sub>2</sub> COOCH <sub>3</sub>	5.31	4.5 <sup>c</sup> , 5.61 <sup>e</sup>	-17.71	-16.7 <sup>c</sup> , -16.79 <sup>e</sup>
HO+CH <sub>3</sub> CH <sub>2</sub> COOCH <sub>3</sub> →H <sub>2</sub> O+CH <sub>2</sub> CH <sub>3</sub> COOCH <sub>2</sub>	5.28	4.9 <sup>c</sup> , 5.67 <sup>e</sup>	-20.13	-19.1 <sup>c</sup> , -18.24 <sup>e</sup>
HO+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> COOCH <sub>3</sub> →H <sub>2</sub> O+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CHCOOCH <sub>3</sub>	4.35		-25.02	
HO+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> COOCH <sub>3</sub> →H <sub>2</sub> O+CH <sub>3</sub> CH <sub>2</sub> CHCH <sub>2</sub> COOCH <sub>3</sub>	3.04		-20.35	
HO+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> COOCH <sub>3</sub> →H <sub>2</sub> O+CH <sub>3</sub> CH(CH <sub>2</sub> ) <sub>2</sub> COOCH <sub>3</sub>	3.44		-20.94	
HO+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> COOCH <sub>3</sub> →H <sub>2</sub> O+CH <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> COOCH <sub>3</sub>	4.68		-18.11	
HO+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> COOCH <sub>3</sub> →H <sub>2</sub> O+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> COOCH <sub>2</sub>	5.21		-20.08	
HO+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> COOCH <sub>3</sub> →H <sub>2</sub> O+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CHCOOCH <sub>3</sub>	4.25		-25.04	
HO+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> COOCH <sub>3</sub> →H <sub>2</sub> O+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CHCH <sub>2</sub> COOCH <sub>3</sub>	2.97		-20.37	
HO+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> COOCH <sub>3</sub> →H <sub>2</sub> O+CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>2</sub> ) <sub>2</sub> COOCH <sub>3</sub>	3.02		-20.69	
HO+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> COOCH <sub>3</sub> →H <sub>2</sub> O+CH <sub>3</sub> CH(CH <sub>2</sub> ) <sub>3</sub> COOCH <sub>3</sub>	3.03		-20.94	
HO+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> COOCH <sub>3</sub> →H <sub>2</sub> O+CH <sub>2</sub> (CH <sub>2</sub> ) <sub>4</sub> COOCH <sub>3</sub>	1.66		-18.21	
HO+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> COOCH <sub>3</sub> →H <sub>2</sub> O+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> COOCH <sub>2</sub>	5.20		-20.10	

<sup>a</sup>QCISD(T)/CBS extrapolation energies in present work, <sup>b</sup>QCISD(T)/6-311++G(2d,2p) results of Tan et al. [54], <sup>c</sup>RSDCI+DS/CBS(D-T) results of Tan et al. [53,55], <sup>d</sup>CCSD(T)/CBS(T-Q) results of Jørgensen et al. [56], <sup>e</sup>CCSD(T)/CBS(D-T)/ results of Mendes et al. [11]. Unit: kcal/mol

Table 2. *L* parameters obtained at the B3LYP/6-311++G(d, p) level for hydrogen abstraction reactions of methyl esters + OH<sup>a</sup>.

	n=0	n=1	n=2	n=4	n=5
m1-site		0.28	0.35	0.29	0.35
m2-site	0.30	0.29	0.27	0.26	0.26
1-site	0.06		0.15	0.15	0.15
2-site				0.34	0.33
3-site				0.16	0.16
4-site				none	0.17

<sup>a</sup>The blank item indicates that no reactions occur at the active site.

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Table 3. The EBs and HRs of MD + H, MHex + H, and MD + OH.

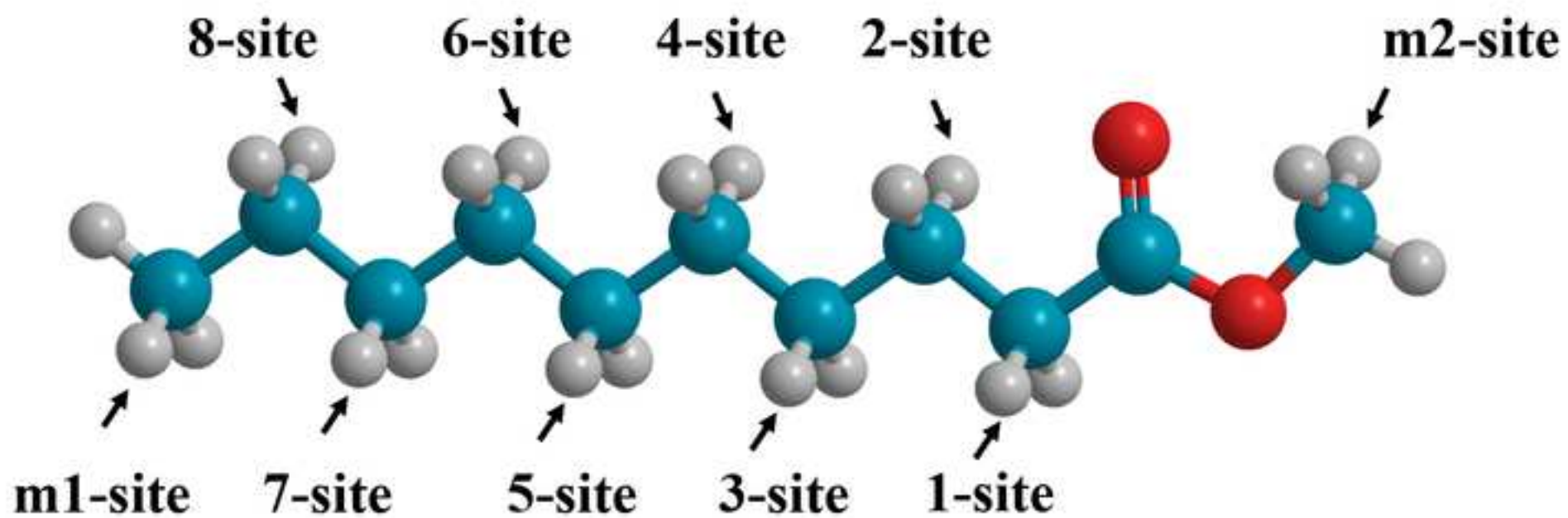
Reactions	HR <sup>a</sup>	EB <sup>a</sup>	EB <sup>b</sup>
H+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> COOCH <sub>3</sub> →H <sub>2</sub> +CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> CHCOOCH <sub>3</sub>	-10.33	7.22	7.12
H+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> COOCH <sub>3</sub> →H <sub>2</sub> +CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CHCH <sub>2</sub> COOCH <sub>3</sub>	-5.66	8.29	8.18
H+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> COOCH <sub>3</sub> →H <sub>2</sub> +CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CH(CH <sub>2</sub> ) <sub>2</sub> COOCH <sub>3</sub>	-5.86	7.46	7.98
H+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> COOCH <sub>3</sub> →H <sub>2</sub> +CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH(CH <sub>2</sub> ) <sub>3</sub> COOCH <sub>3</sub>	-5.82	7.54	8.02
H+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> COOCH <sub>3</sub> →H <sub>2</sub> +CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH(CH <sub>2</sub> ) <sub>4</sub> COOCH <sub>3</sub>	-5.87	7.37	7.97
H+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> COOCH <sub>3</sub> →H <sub>2</sub> +CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH(CH <sub>2</sub> ) <sub>5</sub> COOCH <sub>3</sub>	-5.89	7.42	7.95
H+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> COOCH <sub>3</sub> →H <sub>2</sub> +CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>2</sub> ) <sub>6</sub> COOCH <sub>3</sub>	-5.96	7.38	7.88
H+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> COOCH <sub>3</sub> →H <sub>2</sub> +CH <sub>3</sub> CH(CH <sub>2</sub> ) <sub>7</sub> COOCH <sub>3</sub>	-6.35	7.49	7.49
H+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> COOCH <sub>3</sub> →H <sub>2</sub> +CH <sub>2</sub> (CH <sub>2</sub> ) <sub>8</sub> COOCH <sub>3</sub>	-3.63	10.14	10.19
H+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> COOCH <sub>3</sub> →H <sub>2</sub> +CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> COOCH <sub>2</sub>	-5.21	10.64	10.64
H+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> COOCH <sub>3</sub> →H <sub>2</sub> +CH <sub>3</sub> (CH <sub>2</sub> ) <sub>13</sub> CHCOOCH <sub>3</sub>	-10.31	6.84	7.13
H+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> COOCH <sub>3</sub> →H <sub>2</sub> +CH <sub>3</sub> (CH <sub>2</sub> ) <sub>12</sub> CHCH <sub>2</sub> COOCH <sub>3</sub>	-5.83	8.13	8.00
H+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> COOCH <sub>3</sub> →H <sub>2</sub> +CH <sub>3</sub> (CH <sub>2</sub> ) <sub>12</sub> CH(CH <sub>2</sub> ) <sub>2</sub> COOCH <sub>3</sub>	-5.83	7.40	8.00
H+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> COOCH <sub>3</sub> →H <sub>2</sub> +CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> CH(CH <sub>2</sub> ) <sub>3</sub> COOCH <sub>3</sub>	-5.93	7.59	7.91
H+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> COOCH <sub>3</sub> →H <sub>2</sub> +CH <sub>3</sub> (CH <sub>2</sub> ) <sub>9</sub> CH(CH <sub>2</sub> ) <sub>4</sub> COOCH <sub>3</sub>	-6.06	7.25	7.78
H+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> COOCH <sub>3</sub> →H <sub>2</sub> +CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> CH(CH <sub>2</sub> ) <sub>5</sub> COOCH <sub>3</sub>	-6.09	7.30	7.75
H+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> COOCH <sub>3</sub> →H <sub>2</sub> +CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> CH(CH <sub>2</sub> ) <sub>6</sub> COOCH <sub>3</sub>	-6.18	7.04	7.66
H+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> COOCH <sub>3</sub> →H <sub>2</sub> +CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CH(CH <sub>2</sub> ) <sub>7</sub> COOCH <sub>3</sub>	-6.23	7.27	7.61
H+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> COOCH <sub>3</sub> →H <sub>2</sub> +CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CH(CH <sub>2</sub> ) <sub>8</sub> COOCH <sub>3</sub>	-6.05	7.01	7.79
H+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> COOCH <sub>3</sub> →H <sub>2</sub> +CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH(CH <sub>2</sub> ) <sub>9</sub> COOCH <sub>3</sub>	-6.11	7.01	7.73

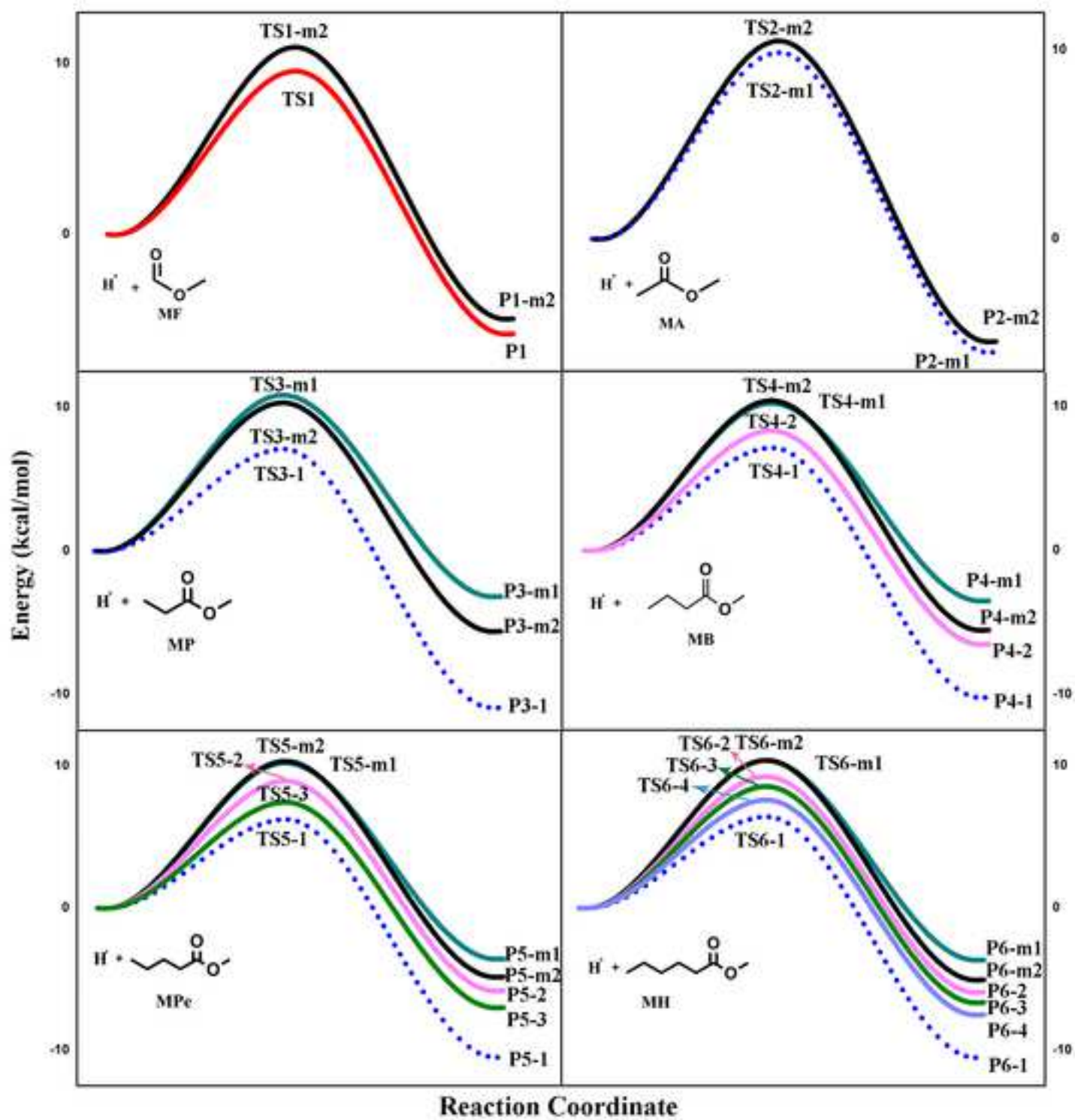
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Table 3. Continued

Reactions	HR <sup>a</sup>	EB <sup>a</sup>	EB <sup>b</sup>
H+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> COOCH <sub>3</sub> →H <sub>2</sub> +CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH(CH <sub>2</sub> ) <sub>10</sub> COOCH <sub>3</sub>	-6.55	6.95	7.29
H+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> COOCH <sub>3</sub> →H <sub>2</sub> +CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH(CH <sub>2</sub> ) <sub>11</sub> COOCH <sub>3</sub>	-6.36	6.95	7.48
H+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> COOCH <sub>3</sub> →H <sub>2</sub> +CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>2</sub> ) <sub>12</sub> COOCH <sub>3</sub>	-6.43	6.97	7.41
H+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> COOCH <sub>3</sub> →H <sub>2</sub> +CH <sub>3</sub> CH(CH <sub>2</sub> ) <sub>13</sub> COOCH <sub>3</sub>	-6.78	7.05	7.07
H+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> COOCH <sub>3</sub> →H <sub>2</sub> +CH <sub>2</sub> (CH <sub>2</sub> ) <sub>14</sub> COOCH <sub>3</sub>	-4.11	9.70	9.71
H+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> COOCH <sub>3</sub> →H <sub>2</sub> +CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> COOCH <sub>2</sub>	-5.61	10.36	10.25
HO+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> COOCH <sub>3</sub> →H <sub>2</sub> O+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> CHCOOCH <sub>3</sub>	-25.38	4.49	4.17
HO+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> COOCH <sub>3</sub> →H <sub>2</sub> O+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CHCH <sub>2</sub> COOCH <sub>3</sub>	-19.87	3.81	3.65
HO+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> COOCH <sub>3</sub> →H <sub>2</sub> O+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CH(CH <sub>2</sub> ) <sub>2</sub> COOCH <sub>3</sub>	-20.89	3.16	3.00
HO+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> COOCH <sub>3</sub> →H <sub>2</sub> O+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH(CH <sub>2</sub> ) <sub>3</sub> COOCH <sub>3</sub>	-20.86	2.18	3.02
HO+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> COOCH <sub>3</sub> →H <sub>2</sub> O+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH(CH <sub>2</sub> ) <sub>4</sub> COOCH <sub>3</sub>	-20.95	3.26	2.96
HO+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> COOCH <sub>3</sub> →H <sub>2</sub> O+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH(CH <sub>2</sub> ) <sub>5</sub> COOCH <sub>3</sub>	-21.10	3.61	2.86
HO+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> COOCH <sub>3</sub> →H <sub>2</sub> O+CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>2</sub> ) <sub>6</sub> COOCH <sub>3</sub>	-21.14	3.21	2.83
HO+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> COOCH <sub>3</sub> →H <sub>2</sub> O+CH <sub>3</sub> CH(CH <sub>2</sub> ) <sub>7</sub> COOCH <sub>3</sub>	-21.24	3.19	2.76
HO+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> COOCH <sub>3</sub> →H <sub>2</sub> O+CH <sub>2</sub> (CH <sub>2</sub> ) <sub>8</sub> COOCH <sub>3</sub>	-18.88	1.20	0.83
HO+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> COOCH <sub>3</sub> →H <sub>2</sub> O+CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> COOCH <sub>2</sub>	-20.84	5.37	4.93

<sup>a</sup>the calculated results of MD + H and MHex + H by Zhang et al. [26] with the ONIOM method, the calculated results of MD + OH with the ONIOM method [26] in this work. <sup>b</sup>the calculated results by corresponding BEP correlations in present work. Unit: kcal/mol





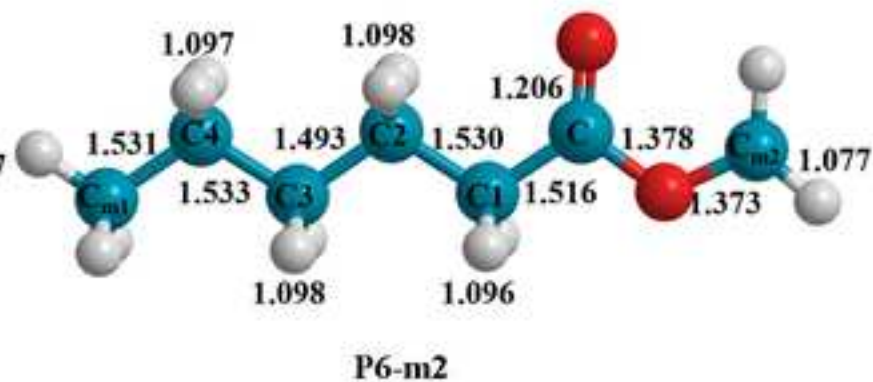
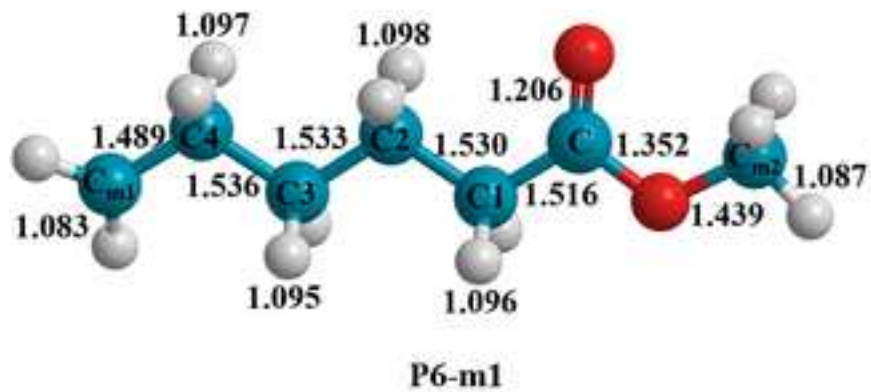
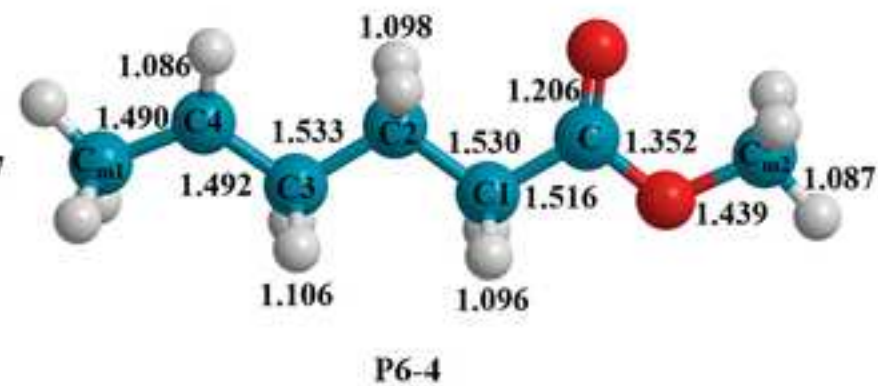
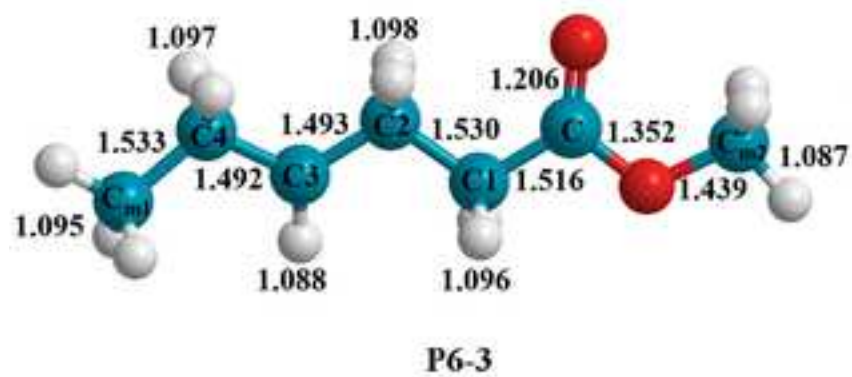
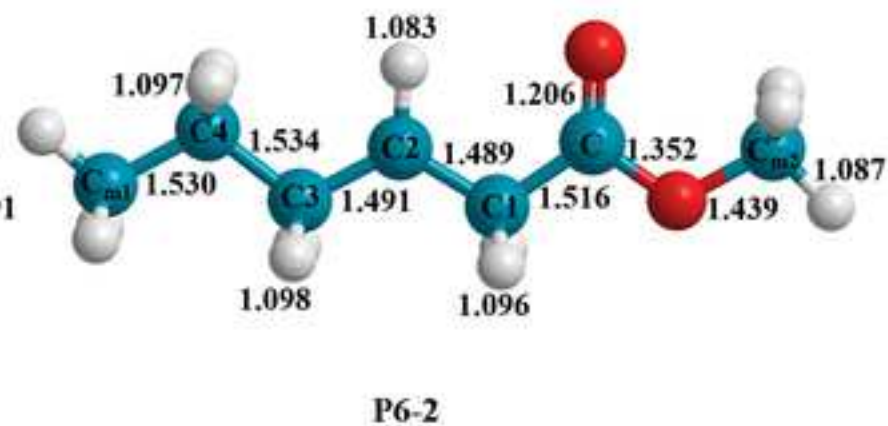
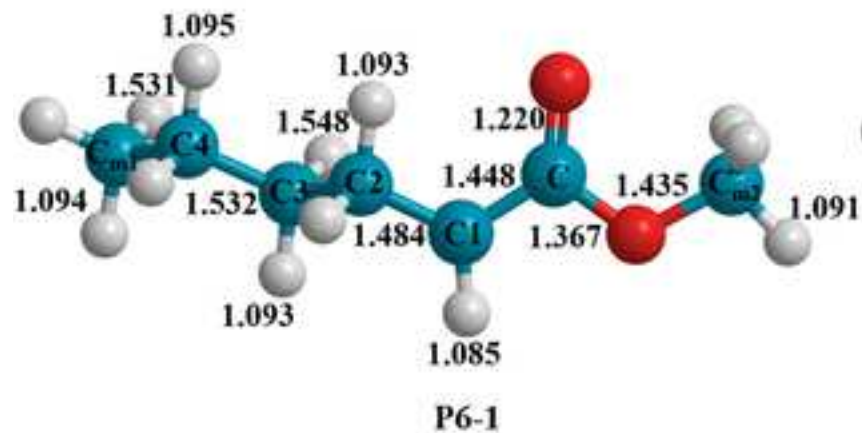


Figure 4 The BEP correlations of different reaction classes in  $C_nH_{2n+1}COOCH_3 + H$  ( $n=0-5$ ). For illustration, previous BEP correlations for oxygenated compounds [41] and

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