# Towards High-level Theoretical Studies of Large Biodiesel Molecules: An ONIOM [QCISD(T)/CBS:DFT] Study of Hydrogen Abstraction Reactions of $C_nH_{2n+1}COOC_mH_{2m+1}$ + H

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ABSTRACT: Recent interests in biodiesel combustion urge the needs for theoretical chemical kinetics of large alkyl ester molecules. This is however computationally challenging for prevalent high-level

electronic structure theory based methods. The hydrogen abstraction reactions of alky esters $C_nH_{2n+1}COOC_mH_{2m+1}$ (n=1−5,9,15; m=1,2) by hydrogen radical were investigated by a computational technique based on a two-layer ONIOM method, employing a QCISD(T)/CBS method for the high layer and a DFT method for the low layer. The calculated energy barriers and heat of reactions by using the ONIOM method with a minimally required chemically active portion are in very good agreement with those obtained by using the widely accepted high-level QCISD(T)/CBS theory, as substantiated by that the computational errors are less than 0.1 kcal/mol for all the testing cases. The ONIOM[QCISD(T)/CBS:DFT] method provides a computationally accurate and affordable approach to high-level theoretical chemical kinetics of large biodiesel molecules.
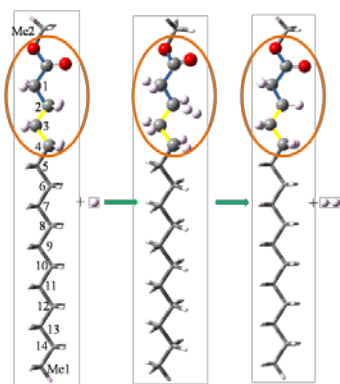
Key word: combustion, energy barrier, heat of reaction, *ab initio* kinetics, alkyl ester,

Introduction

Biofuels have been proposed as a viable solution to our contemporary challenges such as energy sustainability, energy security, and climate change. Biodiesel is one of the most widely used biofuels due to its many desirable advantages. Particularly, biodiesel can be produced from renewable, locally accessible feedstock. It is environment-friendly by holding the potential to reduce harmful emissions such as particulate matter and carbon monoxide[1-3]. Furthermore, biodiesel is economically feasible because it can replace or blend with petroleum-based diesel for direction utilization in diesel engines without or with only minor modifications to the engine and fueling system[4, 5]. Motivated by the practical significance of utilizing biodiesel, numerous studies have been conducted in recent years on its combustion chemical kinetics[6-8], with a particular interest in establishing accurate, detailed reaction mechanism[9-12] required by the CFD (computational fluid dynamics)-based computer-aided design of combustion energy conversion devices fueled with biodiesel.

The mechanism development for biodiesel faces grand challenges. First, biodiesel is a mixture of long-carbon-chain fatty acid alkyl esters with 12-20 carbon atoms and diverse molecular structures and hence distinct physiochemical properties. Consequently, most of the previous studies were focused on prototypical fuels whose molecules contain shorter carbon chains. These fuels are used as surrogates to mimic the combustion characteristics of real biodiesel. The representative surrogates are methyl butanoate (MB, $C_4H_9COOCH_3$)[13-17] and methyl decanoate (MD, $C_9H_{19}COOCH_3$)[18, 19]. Second, a detailed reaction mechanism for a surrogate fuel may consist of a few hundred or even thousand species and a few times more elementary reactions. Specifying accurate temperature(and pressure)-dependent reaction rate constants for such a large number of reactions is a formidable task, especially for the reactions and conditions that are difficult to explore experimentally albeit important for combustion chemistry.

Recent advances in theoretical chemical kinetics and electronic structure theory have enabled the prediction of reaction rate constants for relatively small molecules with the accuracy comparable to those of well-conducted experiments. For example, the high-pressure rate constant for a hydrogen

abstraction reaction, $RH + H \rightarrow R + H_2$, with a distinct energy barrier along the reaction coordinate, can be well defined by using the conventional transition state theory (TST)[20, 21]

$$k(T) = \frac{k_B T}{h} \frac{Q^\dagger}{Q_{RH} Q_H} e^{-V^\dagger / k_B T} \tag{1}$$

where $V^\dagger$ denotes the energy barrier height, $Q^\dagger$ the partition function, including vibrational, rotational and electronic factors, for the transition state, and $Q_{RH} Q_H$ the partition function per unit volume for the reactants. T, k_B and h are temperature, the Boltzmann constant and Planck constant, respectively. The barrier height and partition functions can be derived from the electronic structure calculation for the potential energy surface of $RH + H$.

The uncertainty of the theoretical rate constant significantly relies on that of the predicted barrier height. For example, an underestimation of $V^\dagger$ by 2 kcal/mol can cause an overshooting $k(T)$ by about a factor of 2 at a typical combustion temperatures, 1500K, and a factor of 7.5 at a typical ignition temperatures, 500K. It is recognized that the uncertainty also relies on other factors such as the tunneling effect[20, 22] at sufficiently low temperatures and torsional anharmonicity[23-25] of large molecules. Such large uncertainties in the rate constants, if used in a reaction mechanism, can cause the model prediction for combustion parameters, such as laminar flame speed and ignition delay time, to substantially deviate from the experimental measurement. A few theoretical methods have been demonstrated to be effective and accurate for organic molecules that are of interest to combustion chemistry[22]. The coupled cluster theory with single and double excitations and a quasiperturbative treatment of connected triple excitations [CCSD(T)] with an extrapolation to complete basis set (CBS) yields predictions of barrier height and reaction energy with uncertainties up to 1.1 kcal/mol[26]. The quadratic configuration interaction with singles doubles and perturbative inclusion of triples [QCISD(T)/CBS] is usually accurate to around 1.0 kcal/mol[27] in the prediction of barrier height and can be as accurate as 0.6 kcal/mol for thermochemistry with the inclusion of a bond additivity correction[28]. Unfortunately, none of these methods can be applied to a system with more than 10 non-

hydrogen atoms[22]. As a result, most reaction rate constants for MB were evaluated at lower levels of CBS-QB3[29] or B3LYP/6-31G(d,p)[30]. Only a few important reactions such as MB+H (OH, HO$_2$) were studied at the level of QCISD(T)/CBS[31]. Up to now, no high-level thermochemical and kinetic data are available for MD and larger esters except a few studies at the level of B3LYP/6-31G(d,p)[32, 33]. Clearly, there is an urgent need to develop methodologies for high-level chemical kinetics of larger biodiesel molecules.

In the present study, we aim to develop an two-layer ONIOM[34] (Our Own N-layered Integrated Molecular Orbital and Molecular Mechanics) method for high-level single point energy calculation by employing the high-level ab inito method, QCISD(T)/CBS, for the high layer and the B3LYP-favor density functional theory (DFT) method for the low layer. To the knowledge of the authors, the ONIOM-based methods have not been applied to study combustion chemical kinetics, which was mainly focused on relatively small molecules. We systematically tested the method by calculating the energy barriers and the heat of reactions of the hydrogen abstraction reactions of alkyl esters, $C_nH_{2n+1}COOC_mH_{2m+1}$ (n=1−5, m=1 or 2), by hydrogen radical, which are the crucial reactions in combustion of alkyl esters. The calculated ONIOM [QCISD(T)/CBS:DFT] energies were compared with the QCISD(T)/CBS energies. In addition, the method was tested for nonane (C$_9$H$_{20}$) for extending its applicability to study hydrocarbon molecules. The ONIOM method was subsequently applied to larger systems such as methyl decanoate (MD, n=9,m=1) and methyl heptadecanoate (n=15, m=1), whose molecular sizes are comparable to those dominant components in real biodiesel.

Computational Methods

The geometric structures and vibrational frequencies for stationary points on the PESs of $C_nH_{2n+1}COOC_mH_{2m+1}$ + H (n=1−5,9,15; m=1,2) were obtained via DFT employing the Becke three-

parameter functional and the Lee-Yang-Parr correlation functional (B3LYP) with the 6-311++G(d,p) basis set[35, 36]. This method is a compromise of computational accuracy and cost and has been widely used in combustion chemical kinetics. The connections of each saddle point to its local minima were examined by using the intrinsic reaction path calculations. Zero-point energy (ZPE) corrections were obtained from the B3LYP/6-311++G(d,p) vibrational frequencies.

For relatively small molecules, two high-level QCISD(T)/CBS methods are computationally affordable and used to produce benchmark data to validate the present ONIOM method. The first method, denoted by $[QCISD(T)/CBS]_1$ or $[QCISD(T)/CBS]_{TZ \to QZ}$, is based on the direct extrapolation of the QCISD(T) energies with correlation-consistent, polarized-valence, triple-ζ (cc-pVTZ, denoted by TZ) and quadruple-ζ (cc-pVQZ, denoted QZ) basis sets of Dunning[37, 38] to the complete basis set (CBS) limit[39].

$E[QCISD(T)/CBS]_1$

$= E[QCISD(T)/CBS]_{TZ \to QZ} = E[QCISD(T)/QZ]$

$+ \{E[QCISD(T)/QZ] - E[QCISD(T)/TZ]\} \times 0.6938$ (2)

However, this method is too computationally intensive for the studied reactions with $n \geq 3$. Instead, we used the alternative $[QCISD(T)/CBS]_2$ method[40]:

$E[QCISD(T)/CBS]_2$

$= E[QCISD(T)/CBS]_{DZ \to TZ} + \{E[MP2/CBS]_{TZ \to QZ}$

$- E[MP2/CBS]_{DZ \to TZ}\}$ (3)

where

$E[QCISD(T)/CBS]_{DZ \to TZ} = E[QCISD(T)/TZ]$

$+ \{E[QCISD(T)/TZ] - E[QCISD(T)/DZ]\} \times 0.4629$ (4)

and the calculation of $E[MP2/CBS]_{TZ \to QZ}$ and $E[MP2/CBS]_{DZ \to TZ}$ are the same to (2) and (4), respectively, except the QCISD(T) method is replaced by the MP2 method. The $[QCISD(T)/CBS]_2$ method avoids the most time-consuming QCISD(T)/QZ calculation and so are considerably more

computationally efficient. This method has been recently validated for C_4H_9O system[40] and will be further validated by $[QCISD(T)/CBS]_1$ in the present study for alkyl esters with n=0−2 and m=1, 2. However, the $[QCISD(T)/CBS]_2$ method becomes also computationally intensive due to the increasing computation load for the QCISD(T)/TZ calculation with the size of system. For the studied reactions with $n > 5$, the computationally demanding $[QCISD(T)/CBS]_2$ method has to be replaced by the present ONIOM method.
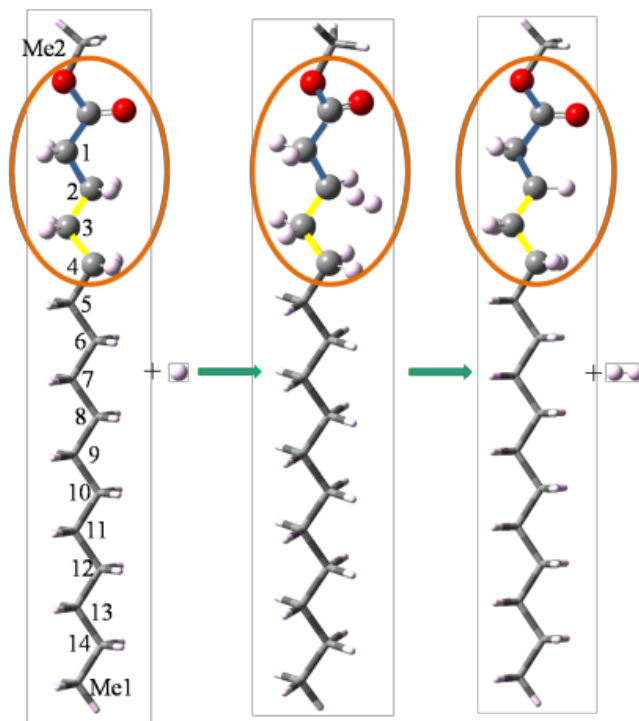
Fig.1 Illustration of an ONIOM/CAP(2,3) method for the reaction $C_{15}H_{31}COOCH_3 + H \rightarrow C_{13}H_{27}C \cdot HCH_2COOCH_3 + H_2$. The indices denote the sites for hydrogen abstraction, with 1-14 denoting the CH_2 groups from the closest to the farthest to the ester group, Me1 the methyl group in the alkyl chain, Me2 the methyl group connected to the ester group. CAP(2,3) denotes that the chemically active portion consists of the CH_2 (i.e. Index 2) group under attack by the H atom, the two neighboring CH_2 (i.e. Index 3 and 4) groups on the one side, and the CH_2 (i.e. Index 1), the carbonyl group C=O and the alkoxy O atom on the other side.

The present ONIOM method models a reaction system (denoted by R) by defining two layers within the structure, which are treated at different theoretical levels, as shown in Fig.1. The chemically active portion[34] (denoted by CAP) of the molecule is treated at the QCISD(T)/CBS level while the rest portion of the molecule is treated at the B3LYP/6-311++G(d,p) level. Since functional groups are always included in the same layer in the present study, using hydrogen atom as link atom to saturate the

dangling bonds is a satisfactory choice, as substantiated by our calculation results to be presented shortly in the next section. The CAP consists of the attacking H atom, the CH_2 (or CH_3) under attack, and the neighboring CH_2 (or CH_3, C=O, C−O) groups. In order to quantify the influence of the size of CAP on the calculation accuracy, we denote a CAP by two integers (N_1, N_2), where N_1 or N_2 is the number of the main-chain non-hydrogen atoms on the each side of the C atom whose H undergoes attack. Consequently, the total number of non-hydrogen atoms included in the CAP is N_1+N_2+1. For example, if CAP (2, 2) is specified to the reaction $C_{15}H_{31}COOCH_3$ + H → $CH_3CH_2C·H(CH_2)_{12}COOCH_3$ + H_2, corresponding to the hydrogen abstraction from the C atom of Index 13 shown in Fig. 1, the five non-hydrogen atoms included in the CAP consists of the C atom of Index 13, the C atoms of Index 11 and 12 on the one side, and the C atoms of Index 14 and Me1 on the other side. Exceptions exist when functional groups are involved in a reaction and will be explained in the following.

For the reaction $C_{15}H_{31}COOCH_3$ + H → $C_{13}H_{27}C·HCH_2COOCH_3$ + H_2 shown in Fig. 1, the H atom belonging to the C atom of Index 2 undergoes attack. If a CAP(2, 3) is specified to the ONIOM method, the CAP consists of the C atom of Index 2, two non-hydrogen atoms (i.e. the C atoms of Index 3 and 4) on the one side, and three non-hydrogen atoms (i.e. the C atom of Index 1, the carbonyl C atom and the alkoxy O atom) on the other side. In order to keep the integrity of the functional group, the carbonyl O atom is also included in the CAP, rendering a total number of seven non-hydrogen atoms in the CAP. It is noted that we always keep a functional group in the same layer in the present study. For example, if CAP(2, 2) is specified to the reaction shown in Fig. 1, the two O atoms must be also included in the CAP to keep the whole ester group undivided.

The ONIOM method approximates the energy of the system by the energy of the system at the low level with a correction for the difference between the high level and the low level for the CAP[34],

$$E^{ONIOM}[High:Low] = E^{Low}(R) + E^{High}(CAP) - E^{Low}(CAP) \qquad (5)$$

where the low level theory is always B3LYP/6-311++G(d,p) and the high level theory is QCISD(T) with the DZ or TZ basis sets. The ONIOM[QCISD(T)/CBS:DFT] energy is calculated by

$$E^{ONIOM}[QCISD(T)/CBS:DFT] = E^{ONIOM}[QCISD(T)/CBS:DFT]_{DZ \to TZ}$$

$$+ \{E^{ONIOM}[MP2/CBS:DFT]_{TZ \to QZ} - E^{ONIOM}[MP2/CBS:DFT]_{DZ \to TZ}\} \qquad (6)$$

where

$$E^{ONIOM}[QCISD(T)/CBS:DFT]_{DZ \to TZ} = E^{ONIOM}[QCISD(T)/TZ:DFT]$$

$$+ \{E^{ONIOM}[QCISD(T)/TZ:DFT] - E^{ONIOM}[QCISD(T)/DZ:DFT]\} \times 0.4629 \qquad (7)$$

$$E^{ONIOM}[MP2/CBS:DFT]_{TZ \to QZ} = E^{ONIOM}[MP2/QZ:DFT]$$

$$+ \{E^{ONIOM}[MP2/QZ:DFT] - E^{ONIOM}[MP2/TZ:DFT]\} \times 0.6938 \qquad (8)$$

$$E^{ONIOM}[MP2/CBS:DFT]_{DZ \to TZ} = E^{ONIOM}[MP2/TZ:DFT]$$

$$+ \{E^{ONIOM}[MP2/TZ:DFT] - E^{ONIOM}[MP2/DZ:DFT]\} \times 0.6938 \qquad (9)$$

The ZPE corrected energy barrier (EB) is calculated by the difference between $E^{ONIOM}[QCISD(T)/CBS:DFT]$ + ZPE of the transition state and that of the reactants. The ZPE corrected heat of reaction (HR) is calculated by the difference between $E^{ONIOM}[QCISD(T)/CBS:DFT]$ + ZPE of the products and that of the reactants. All the ZPE corrections are obtained at the B3LYP/6-311++G(d, p) level, as discussed above. In the present study, all the calculations were performed with the Gaussian 09 program package[34].

Results and Discussion

Validation and Comparison of [QCISD(T)/CBS]$_1$ and [QCISD(T)/CBS]$_2$

In the present study, [QCISD(T)/CBS]$_1$ was used to study the title reactions up to n=0−2 and m=1 and 2, and [QCISD(T)/CBS]$_2$ up to n=0−5 and m=1 and 2. In order to establish the benchmark data for the validation of the present ONIOM method, we first compared the [QCISD(T)/CBS]$_1$ and

[QCISD(T)/CBS]$_2$ energies for n=0−2 and m=1,2 and found they are in an excellent agreement. The discrepancies are less than 0.1 kcal/mol and independent of n and m, as shown in Table 1. Consequently, we can use the [QCISD(T)/CBS]$_2$ method to produce benchmark data for n=0−5 and m=1, 2 by assuming the small, size-independent discrepancies still hold for larger molecules with n=3−5. In the following discussion, all the ONIOM[QCISD(T)/CBS:DFT] energies will be compared with the [QCISD(T)/CBS]$_2$ energies.

For smaller ester molecules such as methyl formate (MF, i.e. n=0 and m=1), methyl acetate (MA, i.e. n=1 and m=1) and methyl butanoate (MB, i.e. n=3 and m=1), a few high-level theoretical data for the energy barriers of their hydrogen abstraction reactions by H radical are available in literature. the present calculation results show very good agreement with these data and the discrepancies are generally less than 0.4 kcal/mol, as shown in Table S1 in the Supporting Information.

It is noted that Zhang et al.[41] recently studied the *ab initio* chemical kinetics of the hydrogen abstraction reactions of MB by hydrogen and hydroxyl radicals. The potential energy surfaces were obtained at the level of [QCISD(T)/CBS]$_2$//B3LYP/6-311++G(d,p). The calculated energy barriers agree excellently with Liu et al.'s[31] results at the CCSD(T)/CBS//B3LYP/6-311++G(d,p). The calculated rate constants agree well with available theoretical and experimental data of high quality. These results substantiate the applicability of the present approach to the chemical kinetics of biodiesel molecules.

Reactions	EB (kcal/mol)		HR (kcal/mol)	
	[QCISD(T)/CBS]$_1$	[QCISD(T)/CBS]$_2$	[QCISD(T)/CBS]$_1$	[QCISD(T)/CBS]$_2$
H+HCOOCH$_3$→H$_2$+HCOOCH$_2$	11.02	10.94	-4.83	-4.93
H+HCOOCH$_2$CH$_3$→H$_2$+HCOOCHCH$_3$	8.72	8.65	-6.70	-6.73
H+HCOOCH$_2$CH$_3$→H$_2$+HCOOCH$_2$CH$_2$	11.68	11.61	-2.08	-2.14
H+CH$_3$COOCH$_3$→H$_2$+CH$_2$COOCH$_3$	10.18	10.10	-5.69	-5.71

$H+CH_3COOCH_3 \rightarrow H_2+CH_3COOCH_2$	10.60	10.52	-5.27	-5.37
$H+CH_3COOCH_2CH_3 \rightarrow H_2+CH_2COOCH_2CH_3$	10.10	10.03	-5.75	-5.77
$H+CH_3COOCH_2CH_3 \rightarrow H_2+CH_3COOCHCH_3$	8.35	8.27	-6.93	-6.96
$H+CH_3COOCH_2CH_3 \rightarrow H_2+CH_3COOCH_2CH_2$	11.50	11.43	-2.21	-2.28
$H+CH_3CH_2COOCH_3 \rightarrow H_2+CH_3CHCOOCH_3$	7.27	7.19	-10.88	-10.84
$H+CH_3CH_2COOCH_3 \rightarrow H_2+CH_2CH_2COOCH_3$	11.00	10.93	-3.02	-3.07
$H+CH_3CH_2COOCH_3 \rightarrow H_2+CH_3CH_2COOCH_2$	10.51	10.43	-5.35	-5.45

Table 1: The comparison of the calculation results by using the $[QCISD(T)/CBS]_1$ and $[QCISD(T)/CBS]_2$ methods.

Minimally required CAP (N₁, N₂) for C₅H₁₁COOCH₃ + H and C₉H₂₀ + H

The optimal CAP was systematically explored by thoroughly testing all the possible combinations of (N_1, N_2) in the reactions of $C_5H_{11}COOCH_3$ +H and C_9H_{20} + H, which are the largest systems studied by using the $[QCISD(T)/CBS]_2$ method in the present work. All the six possible sites on $C_5H_{11}COOCH_3$ for hydrogen abstraction were considered and the hydrogen abstraction of C_9H_{20} from the central CH_2 were considered. Fig.2a shows the difference between the energy barrier at the ONIOM[QCISD(T)/CBS:DFT] level, denoted by EB[ONIOM] for simplicity, and that at the $[QCISD(T)/CBS]_2$ level, denoted by EB[QCISD(T)/CBS], as a function of N_1 and N_2. For clarity, only N_1(and N_2) =1−4 are shown in the figure and more results for N_1(and N_2)=0, 5−7 can be found in Figure S1 of Supporting Information.

It is seen that, for all the tested CAP, EB[ONIOM] differs from EB[QCISD(T)/CBS] by less than 0.8 kcal/mol. Furthermore, all the relatively large differences occur for $N_1 \leq 1$ and $N_2 \leq 1$. If the CAP is larger than (2, 2), the energy difference can be as small as 0.1 kcal/mol or even less. Similarly, the difference of the heat of reaction at the two theoretical levels was calculated and shown in Fig.2b. Again, HR[ONIOM] agrees well with HR[QCISD(T)/CBS] for CAP(2, 2) and the larger CAPs, with the discrepancies being less than 0.1 kcal/mol. Relatively large discrepancies again occur for $N_1 \leq 1$ and N_2

≤ 1. These results suggest that CAP(2,2) is minimally required for the studied reactions and we believe

that CAP(2, 2) is sufficiently large for other similar systems. Furthermore, the results also substantiate

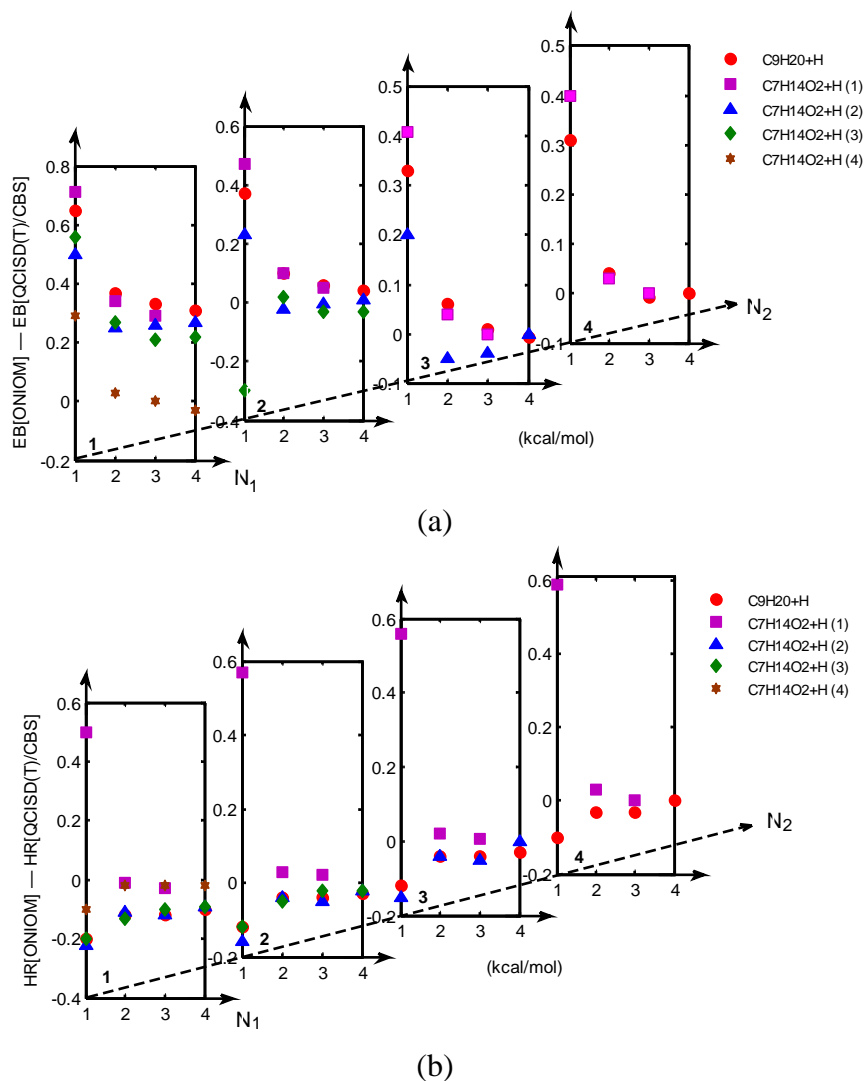the applicability of the present ONIOM method to hydrocarbon molecules.

Fig.2 (a) Variation of the difference of the calculated energy barriers, EB[ONIOM/CAP(N_1, N_2)] - EB[QCISD(T)/CBS], with N_1 and N_2, (b) Variation of the difference of the calculated heat of reaction, HR[ONIOM/CAP(N_1, N_2)] - HR[QCISD(T)/CBS] with N_1 and N_2, for the five reactions including C_9H_{20} + H → $C_4H_9C·HC_4H_9$ + H_2, $C_7H_{14}O_2$ + H → $C_4H_9C·HCOOCH_3$ + H_2 (1), $C_3H_7C·HCH_2COOCH_3$ + H_2 (2), $C_2H_5C·H(CH_2)_2COOCH_3$ + H_2 (3), $CH_3C·H(CH_2)_3COOCH_3$ + H_2 (4). Each two-dimensional plane represents a constant N_2 plane (N_2=1-4 from left to right).

$C_nH_{2n+1}COOC_mH_{2m+1}$ + H(n=1−5, m=1, 2) with the ONIOM/CAP(2, 2) or CAP(2, 3)

To further validate the preset ONIOM method, we calculated and compared the energy barriers and the heat of reaction for the reactions of $C_nH_{2n+1}COOC_mH_{2m+1}$ + H (n=1−5, m=1, 2) by using CAP(2, 2) or CAP(2, 3). The inclusion of CAP(2, 3) is for the situation that the alkoxy O atom should be included in the CAP to keep the ester group undivided. CAP(2,3) corresponds to the situation illustrated in Fig.1. It is seen that almost all the difference (absolute value) between EB[ONIOM] (or HR[ONIOM]) and EB[QCISD(T)/CBS] (or HR[QCISD(T)/CBS]) is less than 0.1 kcal/mol, as shown in Fig.3, substantiating again the accuracy of the present OINOM method. All the calculated energies can be found in Table 2. A few exception cases were found for the heat of reactions of the hydrogen abstraction reactions from the CH_2 (denoted by M in Fig.3) of the ethyl groups, yielding difference of less than 0.15 kcal/mol. Increasing the size of the CAP to include the whole ethyl group may reduce the difference to be within 0.1 kcal/mol.
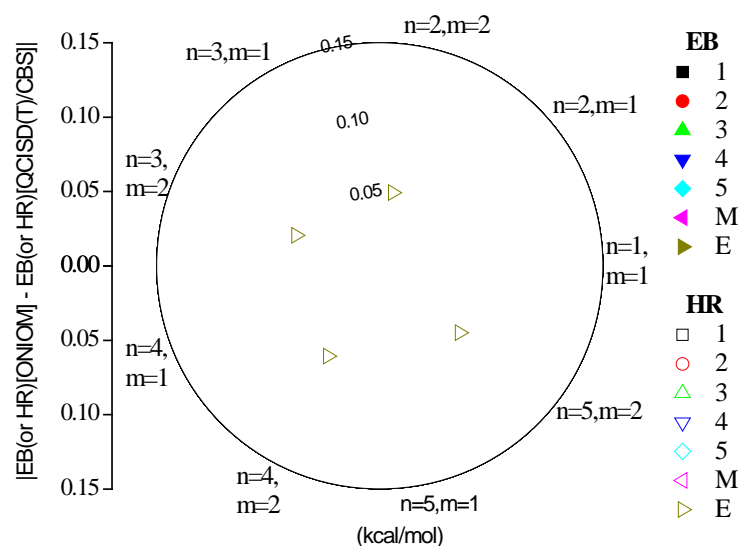
Fig.3 The difference of the calculated energy barriers, EB[ONIOM] - EB[QCISD(T)/CBS] (denoted by the solid symbols) or that of the calculated heat of reaction, HR[ONIOM]-HR[QCISD(T)/CBS] (denoted by the unfilled symbols), for the nine reactions of $C_nH_{2n+1}COOC_mH_{2m+1}$ + H (n=1−5, m=1, 2). The notations 1−5 denote the C atoms from the closest to the farthest to the ester group; M denotes the methyl group or the CH_2 in the ethyl group; and E denotes the CH_3 in the ethyl group.

Reactions	EB (kcal/mol)		HR (kcal/mol)	
	[QCISD(T)/CBS]₂	ONIOM	[QCISD(T)/CBS]₂	ONIOM

Reaction				
H+CH$_3$(CH$_2$)$_7$CH$_3$→H$_2$+CH$_3$(CH$_2$)$_3$CH(CH$_2$)$_3$CH$_3$	7.26	7.36	-5.87	-5.91
H+CH$_3$COOCH$_3$→H$_2$+CH$_2$COOCH$_3$	10.10	10.15	-5.71	-5.71
H+CH$_3$COOCH$_3$→H$_2$+CH$_3$COOCH$_2$	10.52	10.54	-5.37	-5.29
H+CH$_3$CH$_2$COOCH$_3$→H$_2$+CH$_3$CHCOOCH$_3$	7.19	7.21	-10.84	-10.80
H+CH$_3$CH$_2$COOCH$_3$→H$_2$+CH$_2$CH$_2$COOCH$_3$	10.93	10.89	-3.07	-3.13
H+CH$_3$CH$_2$COOCH$_3$→H$_2$+CH$_3$CH$_2$COOCH$_2$	10.43	10.40	-5.45	-5.51
H+CH$_3$COOCH$_2$CH$_3$→H$_2$+CH$_2$COOCH$_2$CH$_3$	10.03	10.10	-5.77	-5.77
H+CH$_3$COOCH$_2$CH$_3$→H$_2$+CH$_3$COOCHCH$_3$	8.27	8.29	-6.96	-6.82
H+CH$_3$COOCH$_2$CH$_3$→H$_2$+CH$_3$COOCH$_2$CH$_2$	11.43	11.40	-2.28	-2.33
H+CH$_3$CH$_2$CH$_2$COOCH$_3$→H$_2$+CH$_3$CH$_2$CHCOOCH$_3$	7.10	7.14	-10.19	-10.16
H+CH$_3$CH$_2$CH$_2$COOCH$_3$→H$_2$+CH$_3$CHCH$_2$COOCH$_3$	8.29	8.26	-6.00	-6.05
H+CH$_3$CH$_2$CH$_2$COOCH$_3$→H$_2$+CH$_2$CH$_2$CH$_2$COOCH$_3$	10.20	10.22	-3.49	-3.55
H+CH$_3$CH$_2$CH$_2$COOCH$_3$→H$_2$+CH$_3$CH$_2$CH$_2$COOCH$_2$	10.37	10.40	-5.52	-5.45
H+CH$_3$CH$_2$COOCH$_2$CH$_3$→H$_2$+CH$_3$CHCOOCH$_2$CH$_3$	7.14	7.19	-10.83	-10.79
H+CH$_3$CH$_2$COOCH$_2$CH$_3$→H$_2$+CH$_2$CH$_2$COOCH$_2$CH$_3$	10.94	10.90	-3.09	-3.16
H+CH$_3$CH$_2$COOCH$_2$CH$_3$→H$_2$+CH$_3$CH$_2$COOCHCH$_3$	8.20	8.21	-6.97	-6.83
H+CH$_3$CH$_2$COOCH$_2$CH$_3$→H$_2$+CH$_3$CH$_2$COOCH$_2$CH$_2$	11.40	11.36	-2.29	-2.35
H+CH$_3$CH$_2$CH$_2$CH$_2$COOCH$_3$→H$_2$+CH$_3$CH$_2$CH$_2$CHCOOCH$_3$	7.05	7.12	-10.39	-10.36
H+CH$_3$CH$_2$CH$_2$CH$_2$COOCH$_3$→H$_2$+CH$_3$CH$_2$CHCH$_2$COOCH$_3$	8.20	8.16	-5.66	-5.71
H+CH$_3$CH$_2$CH$_2$CH$_2$COOCH$_3$→H$_2$+CH$_3$CHCH$_2$CH$_2$COOCH$_3$	7.54	7.56	-6.34	-6.40
H+CH$_3$CH$_2$CH$_2$CH$_2$COOCH$_3$→H$_2$+CH$_2$CH$_2$CH$_2$CH$_2$COOCH$_3$	10.26	10.30	-3.51	-3.52
H+CH$_3$CH$_2$CH$_2$CH$_2$COOCH$_3$→H$_2$+CH$_3$CH$_2$CH$_2$CH$_2$COOCH$_2$	10.35	10.38	-5.52	-5.45
H+CH$_3$CH$_2$CH$_2$COOCH$_2$CH$_3$→H$_2$+CH$_3$CH$_2$CHCOOCH$_2$CH$_3$	7.12	7.16	-10.24	-10.20
H+CH$_3$CH$_2$CH$_2$COOCH$_2$CH$_3$→H$_2$+CH$_3$CHCH$_2$COOCH$_2$CH$_3$	8.32	8.27	-5.99	-6.05
H+CH$_3$CH$_2$CH$_2$COOCH$_2$CH$_3$→H$_2$+CH$_2$CH$_2$CH$_2$COOCH$_2$CH$_3$	10.21	10.23	-3.51	-3.58
H+CH$_3$CH$_2$CH$_2$COOCH$_2$CH$_3$→H$_2$+CH$_3$CH$_2$CH$_2$COOCHCH$_3$	8.25	8.27	-6.91	-6.78
H+CH$_3$CH$_2$CH$_2$COOCH$_2$CH$_3$→H$_2$+CH$_3$CH$_2$CH$_2$COOCH$_2$CH$_2$	11.41	11.38	-2.27	-2.34
H+CH$_3$CH$_2$CH$_2$CH$_2$CH$_2$COOCH$_3$→H$_2$+CH$_3$CH$_2$CH$_2$CH$_2$CHCOOCH$_3$	7.05	7.15	-10.29	-10.26
H+ CH$_3$CH$_2$CH$_2$CH$_2$CH$_2$COOCH$_3$→H$_2$+CH$_3$CH$_2$CH$_2$CHCH$_2$COOCH$_3$	8.20	8.20	-5.65	-5.70

H+ CH$_3$CH$_2$CH$_2$CH$_2$CH$_2$COOCH$_3$→H$_2$+CH$_3$CH$_2$CHCH$_2$CH$_2$COOCH$_3$	7.47	7.49	-5.92	-5.97
H+ CH$_3$CH$_2$CH$_2$CH$_2$CH$_2$COOCH$_3$→H$_2$+CH$_3$CHCH$_2$CH$_2$CH$_2$COOCH$_3$	7.69	7.72	-6.28	-6.30
H+ CH$_3$CH$_2$CH$_2$CH$_2$CH$_2$COOCH$_3$→H$_2$+CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$COOCH$_3$	10.13	10.17	-3.56	-3.59
H+ CH$_3$CH$_2$CH$_2$CH$_2$CH$_2$COOCH$_3$→H$_2$+CH$_3$CH$_2$CH$_2$CH$_2$CH$_2$COOCH$_2$	10.38	10.41	-5.32	-5.25
H+CH$_3$CH$_2$CH$_2$CH$_2$COOCH$_2$CH$_3$→H$_2$+CH$_3$CH$_2$CH$_2$CHCOOCH$_2$CH$_3$	7.05	7.12	-10.39	-10.34
H+ CH$_3$CH$_2$CH$_2$CH$_2$COOCH$_2$CH$_3$→H$_2$+CH$_3$CH$_2$CHCH$_2$COOCH$_2$CH$_3$	8.20	8.16	-5.62	-5.69
H+ CH$_3$CH$_2$CH$_2$CH$_2$COOCH$_2$CH$_3$→H$_2$+CH$_3$CHCH$_2$CH$_2$COOCH$_2$CH$_3$	7.50	7.52	-6.34	-6.40
H+ CH$_3$CH$_2$CH$_2$CH$_2$COOCH$_2$CH$_3$→H$_2$+CH$_2$CH$_2$CH$_2$CH$_2$COOCH$_2$CH$_3$	10.25	10.29	-3.51	-3.53
H+ CH$_3$CH$_2$CH$_2$CH$_2$COOCH$_2$CH$_3$→H$_2$+CH$_3$CH$_2$CH$_2$CH$_2$COOCHCH$_3$	8.23	8.26	-6.93	-6.79
H+ CH$_3$CH$_2$CH$_2$CH$_2$COOCH$_2$CH$_3$→H$_2$+CH$_3$CH$_2$CH$_2$CH$_2$COOCH$_2$CH$_2$	11.36	11.32	-2.34	-2.41

Table 2: The calculated EB and HR for with C$_n$H$_{2n+1}$COOC$_m$H$_{2m+1}$ + H (n=1–5, m=1, 2) with the ONIOM/CAP(2, 2) or CAP(2, 3) and [QCISD(T)/CBS]$_2$ methods.

ONIOM Energies of C$_n$H$_{2n+1}$COOC$_m$H$_{2m+1}$ + H (n=9, 15, m=1)

Finally, we applied the present method to the larger systems of C$_n$H$_{2n+1}$COOC$_m$H$_{2m+1}$ + H (n=9, 15, m=1), which have never been studied by using high-level theories. All the calculated energies can be found in Tables 3 and 4. The calculated energy barriers are shown in Fig.4a and those for (n=5, m=1) are also shown in the figure for comparison. It is seen that the hydrogen abstraction reactions from the two methyl groups, namely the one connected to the carbon chain (denoted by Me1) and the one connected to the ester group (denoted by Me2), have the highest energy barriers of about 10 kcal/mol. The energy barriers for the hydrogen abstraction from the other sites (refer to Fig.1), are around 7 kcal/mol. The results for heat of reaction are shown in Fig.4b. The heat of reaction is about -4 kcal/mol for Me1, -10 kcal/mol for the Site 1 (namely the CH$_2$ closest to the ester group), and -6 kcal/mol for other sites.

To the knowledge of the authors, there are no thermochemical and kinetic data for these large ester molecules by using higher level theoretical methods such as QCISD(T)/CBS or CCSD(T)/CBS. As a result, a direct validation of the calculated energy barriers and heat of reactions is not available in the

study. The consistent energies reported in Fig. 4 are believed to be reasonable and accurate since the ONIOM method has been extensively validated in the previous sections for smaller molecules.

It is noted that the group additivity method combined with Evans-Polanyi relations has been used in many studies to make reasonable estimations for heat of reactions and energy barriers. However the uncertainty of the estimations can be up to ± 2.0 kcal/mol[42], which is not satisfactory for high-level chemical kinetics, as discussed in the introduction. A linear correlation for the energy barriers (EB, kcal/mol) and heat of reactions (HR, kcal/mol), EB = $0.844 \times$HR + 15.013, was found for the reactions $C_nH_{2n+1}COOCH_3 + H \rightarrow C_nH_{2n+1}COOC \cdot H_2 + H_2$ (n=0-5, 9, 15) and the Evans-Polanyi plot is shown in Figure S2 in Supporting Information. Detailed investigation on the existence of linear Evan-Polanyi relations for other similar reactions of alkyl esters merits future study. We believe that the present method is of value to provide accurate theoretical data for developing and validating the group contribution based approaches for large molecules.

Another important issue for the present ONIOM method is the computation load. For the ONIOM[QCISD(T)/CBS:DFT] and QCISD(T)/CBS methods used in the present study, most of the computation time is spent on the QCISD(T)/cc-pVTZ calculation, as seen in Table S2 in Supporting Information. In the present ONIOM calculations with CAP(2, 2) or CAP(2, 3), the number of non-hydrogen atoms included in the high layer is 5-7, which does not necessarily increase with the size of molecules. Therefore, the computation load of the present ONIOM method remains to be equivalent to that of QCISD(T)/cc-pVTZ for a system containing 5-7 non-hydrogen atoms. Since the QCISD(T)/cc-pVTZ calculation for reactions containing more than 9 non-hydrogen atoms is generally not feasible, such reactions can be studied by using the present ONIOM method.

(a)

(b)
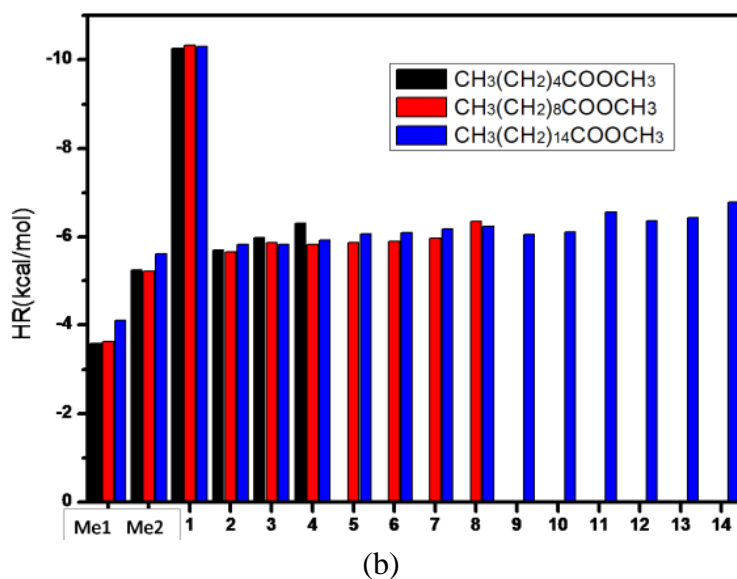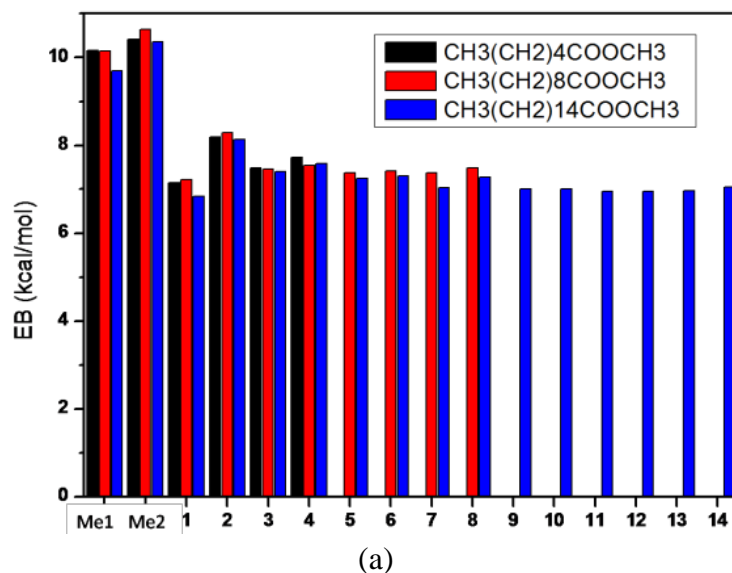
Fig.4 (a)The predicted energy barrier, EB[ONIOM/CAP(2, 2)] and (b) the predicted heat of reaction, HR[ONIOM/CAP(2, 2)] for the reactions $C_nH_{2n+1}COOC_mH_{2m+1} + H$ (n=9, 15, m=1) with various hydrogen abstraction sites (refer to Fig. 1). The reactions with (n=5, m=1) are shown for comparison.

Reactions	EB(kcal/mol)	HR(kcal/mol)
$H+CH_3(CH_2)_8COOCH_3 \rightarrow H_2+CH_3(CH_2)_7CHCOOCH_3$	7.22	-10.33
$H+CH_3(CH_2)_8COOCH_3 \rightarrow H_2+CH_3(CH_2)_6CHCH_2COOCH_3$	8.29	-5.66
$H+CH_3(CH_2)_8COOCH_3 \rightarrow H_2+CH_3(CH_2)_5CH(CH_2)_2COOCH_3$	7.46	-5.86
$H+CH_3(CH_2)_8COOCH_3 \rightarrow H_2+CH_3(CH_2)_4CH(CH_2)_3COOCH_3$	7.54	-5.82
$H+CH_3(CH_2)_8COOCH_3 \rightarrow H_2+CH_3(CH_2)_3CH(CH_2)_4COOCH_3$	7.37	-5.87
$H+CH_3(CH_2)_8COOCH_3 \rightarrow H_2+CH_3(CH_2)_2CH(CH_2)_5COOCH_3$	7.42	-5.89

Reactions	EB(kcal/mol)	HR(kcal/mol)
H+CH$_3$(CH$_2$)$_8$COOCH$_3$→H$_2$+CH$_3$CH$_2$CH(CH$_2$)$_6$COOCH$_3$	7.38	-5.96
H+CH$_3$(CH$_2$)$_8$COOCH$_3$→H$_2$+CH$_3$CH(CH$_2$)$_7$COOCH$_3$	7.49	-6.35
H+CH$_3$(CH$_2$)$_8$COOCH$_3$→H$_2$+CH$_2$(CH$_2$)$_8$COOCH$_3$	10.14	-3.63
H+CH$_3$(CH$_2$)$_8$COOCH$_3$→H$_2$+CH$_3$(CH$_2$)$_8$COOCH$_2$	10.64	-5.21

Table 3: The calculated EB and HR for the H + methyl decanoate with the ONIOM method.

Reactions	EB(kcal/mol)	HR(kcal/mol)
H+CH$_3$(CH$_2$)$_{14}$COOCH$_3$→H$_2$+CH$_3$(CH$_2$)$_{13}$CHCOOCH$_3$	6.84	-10.31
H+CH$_3$(CH$_2$)$_{14}$COOCH$_3$→H$_2$+CH$_3$(CH$_2$)$_{12}$CHCH$_2$COOCH$_3$	8.13	-5.83
H+CH$_3$(CH$_2$)$_{14}$COOCH$_3$→H$_2$+CH$_3$(CH$_2$)$_{11}$CH(CH$_2$)$_2$COOCH$_3$	7.40	-5.83
H+CH$_3$(CH$_2$)$_{14}$COOCH$_3$→H$_2$+CH$_3$(CH$_2$)$_{10}$CH(CH$_2$)$_3$COOCH$_3$	7.59	-5.93
H+CH$_3$(CH$_2$)$_{14}$COOCH$_3$→H$_2$+CH$_3$(CH$_2$)$_9$CH(CH$_2$)$_4$COOCH$_3$	7.25	-6.06
H+CH$_3$(CH$_2$)$_{14}$COOCH$_3$→H$_2$+CH$_3$(CH$_2$)$_8$CH(CH$_2$)$_5$COOCH$_3$	7.30	-6.09
H+CH$_3$(CH$_2$)$_{14}$COOCH$_3$→H$_2$+CH$_3$(CH$_2$)$_7$CH(CH$_2$)$_6$COOCH$_3$	7.04	-6.18
H+CH$_3$(CH$_2$)$_{14}$COOCH$_3$→H$_2$+CH$_3$(CH$_2$)$_6$CH(CH$_2$)$_7$COOCH$_3$	7.27	-6.23
H+CH$_3$(CH$_2$)$_{14}$COOCH$_3$→H$_2$+ CH$_3$(CH$_2$)$_5$CH(CH$_2$)$_8$COOCH$_3$	7.01	-6.05
H+CH$_3$(CH$_2$)$_{14}$COOCH$_3$→H$_2$+ CH$_3$(CH$_2$)$_4$CH(CH$_2$)$_9$COOCH$_3$	7.01	-6.11
H+CH$_3$(CH$_2$)$_{14}$COOCH$_3$→H$_2$+ CH$_3$(CH$_2$)$_3$CH(CH$_2$)$_{10}$COOCH$_3$	6.95	-6.55
H+CH$_3$(CH$_2$)$_{14}$COOCH$_3$→H$_2$+ CH$_3$(CH$_2$)$_2$CH(CH$_2$)$_{11}$COOCH$_3$	6.95	-6.36
H+CH$_3$(CH$_2$)$_{14}$COOCH$_3$→H$_2$+ CH$_3$CH$_2$ CH(CH$_2$)$_{12}$COOCH$_3$	6.97	-6.43
H+CH$_3$(CH$_2$)$_{14}$COOCH$_3$→H$_2$+ CH$_3$CH(CH$_2$)$_{13}$COOCH$_3$	7.05	-6.78
H+CH$_3$(CH$_2$)$_{14}$COOCH$_3$→H$_2$+ CH$_2$ (CH$_2$)$_{14}$COOCH$_3$	9.70	-4.11
H+CH$_3$(CH$_2$)$_{14}$COOCH$_3$→H$_2$+ CH$_3$(CH$_2$)$_{14}$COOCH$_2$	10.36	-5.61

Table 4: The calculated EB and HR for the H + methyl hexadecanoate with the ONIOM method.

Conclusion

An ONIOM[QCISD(T)/CBS:DFT] method was proposed and systematically validated in the present computational work for the hydrogen abstraction reactions of alkyl esters C$_n$H$_{2n+1}$COOC$_m$H$_{2m+1}$ (n=1−5,9,15; m=1, 2) by hydrogen radical. Several important conclusions can be drawn from the work. First, the [QCISD(T)/CBS]$_2$ method via an extrapolation from cc-pVDZ, cc-pVTZ to CBS with a MP2-

based correction has been proved to be as accurate as the $[QCISD(T)/CBS]_1$ method, whose computational uncertainty is usually about 1.0 kcal/mol. Second, the chemically active portion (CAP) in the ONIOM method, consisting of at least two main-chain C (or O) atoms (on the each side) adjacent to the C atom whose H atom is under hydrogen abstraction, is minimally required to yield small computational errors of less than 0.1 kcal/mol, compared with the $[QCISD(T)/CBS]_2$ method. Third, the ONIOM method with a minimally required CAP is able to predict the energy barriers and heat of reactions for the studied reactions up to n=5 with less than 0.1 kcal/mol uncertainties for almost all the testing cases. Finally, the predictions for n=9 and 15 indicate that the energy barriers for the hydrogen abstraction from the methyl groups are about 10 kcal/mol and 7 kcal/mol for those from the other sites. The predicted heat of reaction is about -4 kcal/mol for the hydrogen abstraction from the methyl group in the alkyl chain, -10 kcal/mol for that from the CH_2 closest to the ester group, and -6 kcal/mol for those from other sites. The present method provides a computationally accurate and affordable approach to study the large hydrocarbons and alkyl esters that are of interest to combustion chemistry.

ASSOCIATED CONTENT

Supporting information: Optimized geometries at the B3LYP/6-311++G(d,p) level for all the stationary points on the potential energy surfaces.

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