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INVESTIGATION INTO BIO-AVIATION REACTION MECHANISMS USING QUANTUM MECHANICAL METHODS

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ABSTRACT

Using high level model chemistries the C-C and C-H bond dissociation energies for methyl butanoate molecule (MB) were estimated using the Gaussian 03 program at the CBS-QB3 level of calculations. This consequently located the weaker bonds more likely to break. Thermal decomposition of MB over the temperatures 500 to 2000 K was theoretically studied and the rate constants for these channels were calculated. Crucial reactions in combustion, among which there are reactions of the fuel molecule with flame reactive radicals OH and CH_3, were studied and the barrier heights for reactions including different hydrogen atoms transferring to the radicals were evaluated at the B3LYP/6-31+G(d,p) level of theory. The rate constants for these reactions are calculated over the temperatures 500 to 2000 K using the same level.

INTRODUCTION

The recent concerns over the disadvantages of fossil fuels for air transport, of which the most important concern their contribution to greenhouse gas emissions and their security of supply, have raised the need to look at alternative fuels as a new source of energy. To that end, potentially sustainable and environmentally friendly fuels are being considered. Bio-liquid-fuel derived from the so-called "3rd generation biomass" especially Algae is one of the alternatives with the advantage that it does not have the challenge of also being a source of humans' food or competing for land use with food production. Beside the fact that bio-fuels are renewable, research has also shown that diesel engines operating with bio-diesel produce less CO, unburned hydrocarbons and particulates [1]. Considering bio-fuel's low sulphur content there is also the possibility to use a catalyst without the issues of catalyst poisoning to remove NO_x from the engine exhaust. Moreover, the combustion of alternative bio-fuels can be considered to be carbon-neutral since their carbon content is derived from CO_2 which previously existed in the atmosphere.

A widely used bio-fuel is biodiesel which typically consists of mixtures of saturated and unsaturated methyl esters produced through a transesterification reaction between a lipid source and an alcohol. Fatty acid methyl esters with the general formula $R-C(O)O-CH_3$ (R is the alkyl group) with carbon chains of 12 to 22 atoms in length are the foremost constituents of biodiesel [2].

The combustion of fossil fuel based aviation fuels have been studied extensively over many years using a combination of experimental and theoretical studies [3]. However, the chemical structure of bio-fuels is considerably different in comparison to traditional ones and therefore there is much need of fundamental studies to generate the basic data with regard to the oxidation mechanism of the bio-diesel fuel. The bio-diesel fuels contain large oxygenated hydrocarbons and therefore from an experimental viewpoint it is difficult to study the combustion characteristics of such heavy molecules using classic techniques, and consequently a surrogate compound model which has the same chemical structural features as the real fuel is required. It has been shown [1] that methyl butanoate (MB) with the formula $CH_3CH_2CH_2C(O)OCH_3$ has the essential quality to be used as a model compound although it does not

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have the high molecular weight of a constituent component of the biodiesel fuel.

One of the initial studies on MB was carried out by Fisher et al. [4]. They developed the first detailed chemical kinetic model for the combustion of MB. Since then a number of experimental and theoretical studies have been carried out on MB using a developed reaction mechanism. Later Gail et al. [5] validated Fisher's MB oxidation reaction in a jet stirred reactor and an opposed-flow diffusion flame, resulting in some modification to the initial reaction mechanism. Metcalfe et al. [6] studied the oxidation of methyl butanoate and ethyl propanoate (EP) under high-temperature in a shock tube. They found the ignition of EP to be faster than that of MB, and also improved the existing chemical kinetic mechanisms.

In addition to the experimental studies a number of computations including molecular modeling studies have been carried out to investigate the different pathways of decompositions of MB at high temperatures. El-Nahas et al. [7] used a Complete Basis Set method to evaluate the properties of unimolecular and bimolecular reactions of MB. They used the Complete Basis Set method (CBS) for their calculations which is considered to be more accurate than other methods since it is a combination of different methods for its calculations. Huynh and Violi [8] also used a theoretical approach to estimate the rate constants for various decomposition channels. Recently Dooley et al. [1] used both an experimental and theoretical approach to study the auto-ignition of MB in a shock tube which resulted in a number of reactions to be added to the MB reaction mechanism. They found that the auto-ignition of MB follows an Arrhenius-like temperature dependence.

In order to predict the performance of biodiesel fuels in comparison to diesel fuels, understanding of the detailed fundamental chemistry of these alternative fuels during combustion process is vital. Quantum mechanics (QM) calculation is an effective method to provide these details. Based on classical mechanics, QM can present information on the kinetic pathways of long chain oxygenated hydrocarbons' combustion which due to their heavy molecular weight might be impossible to be obtained through experiments. To aid in this, the aim of this work is to provide more information on the thermo-chemistry and kinetics of the methyl butanoate unimolecular and bimolecular decomposition reactions over the range of temperature between 500-2000 K and compare it to previously published research data. Considering the C-C, C-H and C-O bonds and using the detailed QM computations, we have estimated the barrier heights for hydrogen abstraction reactions by the flame reactive radicals OH and CH_3.

COMPUTATIONAL METHODS

All quantum mechanical calculations were performed using the Gaussian 03 program [9]. The first step to obtain the required data is to optimise the structures of the reactants, products and the relevant transition states (TS). These optimised structures are then used to execute the thermochemistry calculations. Contributions to the thermochemical properties for the cited reaction ingredients are computed based on the vibrational, electronic, rotational and translational motions of the atoms in the molecules. Obviously the results obtained from these procedures will be dependent on the particular methods used.

In the present work the geometries of the reactant, products and transition states involved in the set of studied reactions were optimised using Density Functional Theory (DFT) at B3LYP level (Becke 3 parameter exchange, Lyp, Yang and Parr correlation). The basis set applied was 6-31+G(d,p) which is considered reliable to locate the minima on the potential energy surface [10]. These optimised geometries were followed by frequency calculations using the same theory and method, since as a matter of principle, the geometry and frequency computations should be run using identical methods. Contributions from these harmonic vibrational frequencies results in the final thermodynamic quantities of the reaction components. A scaling factor of 0.95 was applied to frequency calculations.

In an alternative attempt to calculate the bond dissociation energies, the Complete Basis Set method, CBS-QB3, is employed. CBS-QB3 is a combination of following methods and can predict molecular energies to around 4 kJ mol^{-1} accuracy [11].

- Geometry optimization and frequencies: B3LYP/6-311G(2d,p,d)
- Energy and CBS extrapolation: MP2/6-311G(3df,2df,2p)
- Energy: MP4(SDQ)/6-31(d(f),p)
- Energy: CCSD(T)/6-31G*

The high-pressure-limit rate constants for hydrogen abstraction reactions are estimated using transition state theory, as encapsulated in Equation (1) [12].

$$k(T) = \frac{k_b T}{h} \frac{Q_{TS}}{Q_r Q_{MB}} e^{-\Delta_+^+ G^o / RT} \tag{1}$$

Where $\Delta_+^+ G^o$ and Q (partition function) have been obtained from the Gaussian output. The calculations are done over the temperature rang 500-2000K. By fitting the results to an Arrhenius Equation, or modified Arrhenius equation, values for the rate coefficient parameters are obtained.

RESULTS AND DISCUSSION
Unimolecular Reactions

Bond dissociation energies are estimated using the CBS-QB3 level of calculations. Consequently these values show the weakest bonds more likely to break. Figure 1 presents the bond dissociation energies (kJ mol-1) for MB calculated in this work.

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(The red balls illustrate oxygen atoms while the big and small gray balls show carbon and hydrogen atoms respectively.)
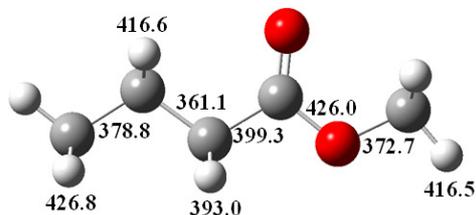

FIGURE 1. Calculated bond dissociation energies (kJ mol^{-1}) in MB.

Huynh and Violi [8] and earlier El-Nahas et al. [7] have also calculated these values using the same level. Recently Dooley et al. [1] estimated the bond enthalpies for MB, and provided the data in the form of NASA polynomials using Benson's group additivity method by employing the THERM software package [13]. The values obtained in all these works are listed in Table 1.

As shown in Figure 1, the C-C bonds are weaker than C-H ones hence it is more likely that for thermal degradation the paths along decomposition of C-C bonds be followed. The kinetic pathways for unimolecular dissociation reactions, which are among the initiation steps during the combustion process, were investigated in this work. These reactions involve the simple C-C and C-O bond fissions and since the products are both radicals they can in general be categorized as barrier-less processes (from the reverse radical recombination point of view), with no well defined transition state.

When defining the reactant and products along with an early guess for the possible TS structure, as an input for Gaussian to locate the real TS, the program starts investigating the highest barrier height along the specified reaction direction. If there is any such location Gaussian is capable of identifying it, otherwise there is none. There are five different channels for the simple C-O and C-C bond breaking of MB which proceeds toward producing radicals as shown in figure 2. The calculated enthalpies of reaction for them are presented in Table 2
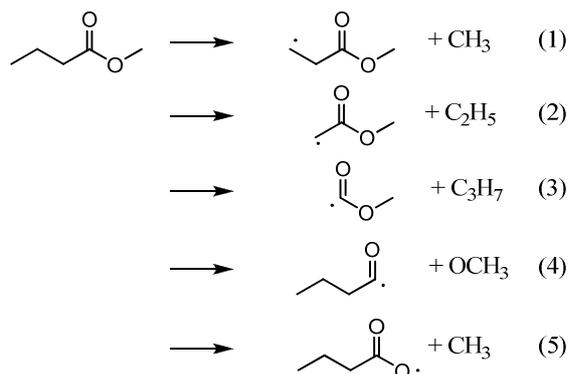

FIGURE 2. MB unimolecular C-C and C-O bond fissions.

Reaction	Enthalpy of Reaction
1	378.8
2	361.7
3	399.3
4	423.5
5	372.7

TABLE 2. Calculated reaction enthalpies (kJ mol^{-1}) for C-C and C-O bond fission in MB.

Additional Reactions

Bond Energies (kJ mol^{-1})

		This work	El-Nahas et al. [7]	Huynh and Violi [8]	Dooley et al. [1]
C-H bonds	H-CH$_2$CH$_2$C(O)CH$_3$	426.8	423	423	423.8
	H-CH(CH$_3$)CH$_2$C(O)OCH$_3$	416.6	413	413.0	412.1
	H-CH(C$_2$H$_5$)C(O)OCH$_3$	393.0	394	394.1	391.6
	CH$_3$CH$_2$CH$_2$C(O)OCH$_2$-H	416.5	414	410.0	418.4
C-C bonds	CH$_3$-CH$_2$CH$_2$C(O)OCH$_3$	378.8	373	372.8	372.0
	CH$_3$CH$_2$-CH$_2$C(O)OCH$_3$	361.1	353	353.1	356.5
	CH$_3$CH$_2$CH$_2$-C(O)OCH$_3$	399.3	391	391.2	373.2
C-O bonds	CH$_3$CH$_2$CH$_2$C(O)-OCH$_3$	426.0	424	423.8	415.1
	CH$_3$CH$_2$CH$_2$C(O)O-CH$_3$	372.7	364	364.0	363.2

TABLE 1. Predicted bond dissociation energies

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In the attempt to locate the transition state structures for the bond fissions, Gaussian found some other transition states which moved toward producing alternative products rather than the simple radicals. These reactions are listed below in figure 3, and the associated potential energy surfaces are shown in figure 4.
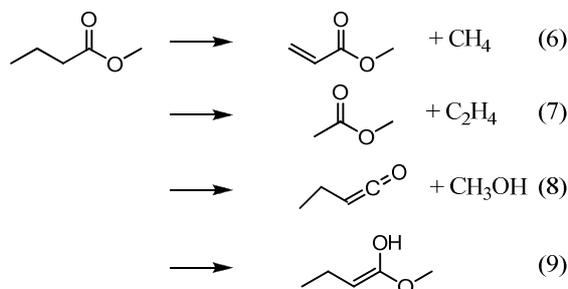

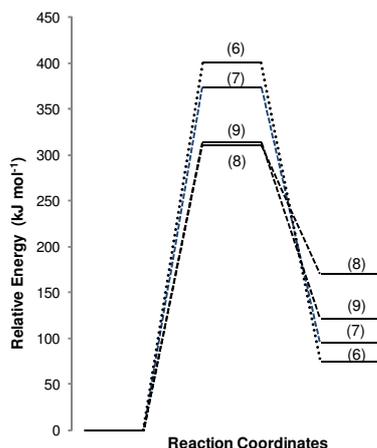FIGURE 3. MB alternative unimolecular reactions.

FIGURE 4. Potential energy surface for MB alternative unimolecular reactions.

In practice, all of these reactions are of minor importance. Reaction 6 can be discounted immediately as a consequence of the high energy barrier of over 400 kJ mol^{-1}. Reaction 7 produces methyl ethanoate (ME) and ethane, this reaction was identified in the ab-initio studies of El-Nahas et al. [7] who predicted a significantly lower energy barrier of 284.5 kJ mol^{-1}. However even with this much lower energy barrier, Metcalfe et al [6] estimated that this reaction accounted for less than 1% of the total MB decomposition rate in the experimental conditions they investigated. Reaction 8 was also identified by El-Nahas et al. [7], this time with a similar barrier within 3 kJ mol^{-1} of that obtained in this work. Reaction 9 is of a keto-enol type tautomerism, again the high barrier makes its practical relevance marginal.

BIMOLECULAR REACTIONS

Bimolecular decomposition reactions include hydrogen abstraction reactions by reactive radicals present in the system. Among the most important of these would be flame radicals such as OH, O, H and CH_3. The barrier heights for these reactions depend on the type of the transferring hydrogen atom and also the abstracting radical. There are four different channels for hydrogen migration to a radical in the MB molecule but the one with the lower barrier height is more likely to be proceeded under the combustion conditions.

We have taken hydrogen abstraction reactions by OH and CH_3 radicals into consideration to investigate their thermochemistry and kinetics. The reactive radicals can attack any of the hydrogen atoms in the MB molecule. The abstraction process moves toward the transition state and then the hydrogen atom is transferred to OH or CH_3 to produce an MB radical and H_2O or CH_4 respectively. Among the MB radicals produced, as expected, $CH_3CH_2CHC(O)OCH_3$ is found to be the most stable one. Different pathways of hydrogen abstraction by OH radical are shown in figure 5.
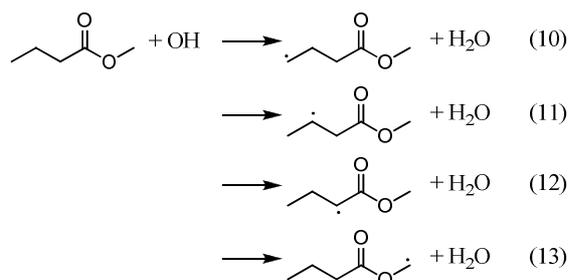

FIGURE 5. Hydrogen abstraction pathways by OH from MB.

The barrier heights for reactions (10) to (13) are estimated to be ~11.6, ~-5.1, ~7.8 and ~2.3 kJ mol^{-1} respectively. The barrier height reported by Huynh and Violi [8] for reaction (10) is 5 kcal mol^{-1} which reveals a significant difference with the value predicted in this work. Since the lowest barrier height was found for reaction (13) it is more likely that among the initiation reactions this reaction will occur rather than the others.

Figures 6 – 8 give Arrhenius plots showing the temperature dependence of the predicted rate coefficients, and also the equivalent expressions as used by Metcalf et al. [6]. A summary of the rate coefficient parameters is given in table 3.
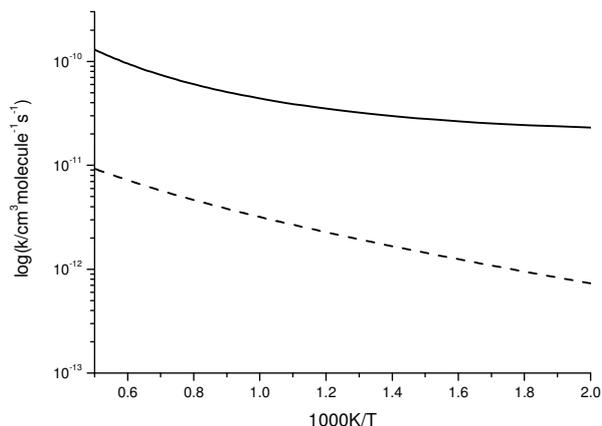
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FIGURE 6. Arrhenius plot of rate coefficient for reaction 10, solid line – this work, dashed line – Metcalf et al. [6].
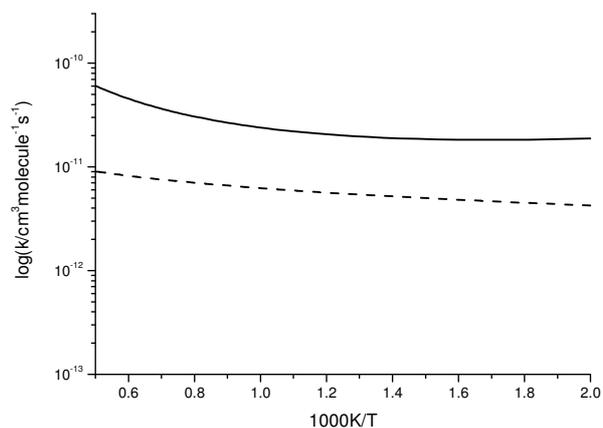

FIGURE 7. Arrhenius plot of rate coefficient for reaction 12, solid line – this work, dashed line – Metcalf et al. [6].
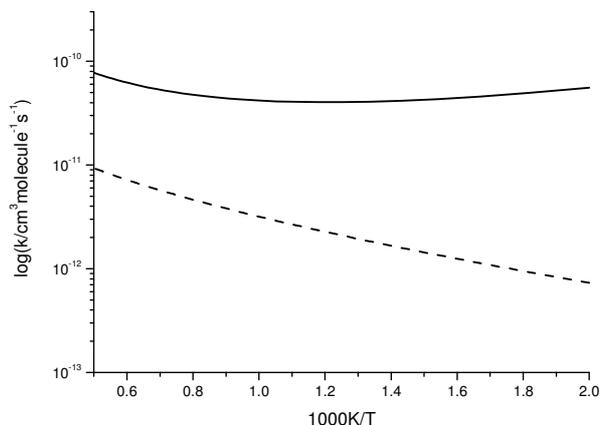

FIGURE 8. Arrhenius plot of rate coefficient for reaction 13, solid line – this work, dashed line – Metcalf et al. [6].

Reaction	This Work			Metcalfe et al. [6]		
	A	n	E	A	n	E
10	4.59×10^{-18}	2.2	-880	8.72×10^{-15}	0.97	800
12	6.27×10^{-19}	2.3	-1375	1.90×10^{-13}	0.51	-31.7
13	1.90×10^{-18}	2.2	-1801	8.72×10^{-15}	0.97	800

TABLE 3. Rate Coefficient Expressions for hydrogen abstraction by OH (cm^3molecule^{-1}s^{-1}).

In the case of hydrogen abstraction by methyl radicals, the reaction pathways are shown in figure 9. Figure 10 shows the details of the potential energy surface, and figures 11 to 13 give Arrhenius plots showing the temperature dependence of the predicted rate coefficients, and also the equivalent expressions as used by Metcalf et al. [6]. A summary of the rate coefficient parameters is given in table 4.
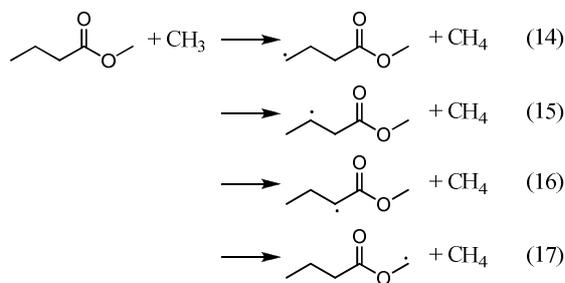

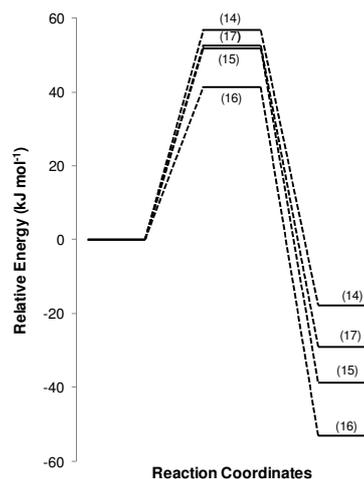**FIGURE 9.** Hydrogen abstraction pathways by CH_3 from MB.

FIGURE 10. Potential energy surface for MB reactions with CH_3.
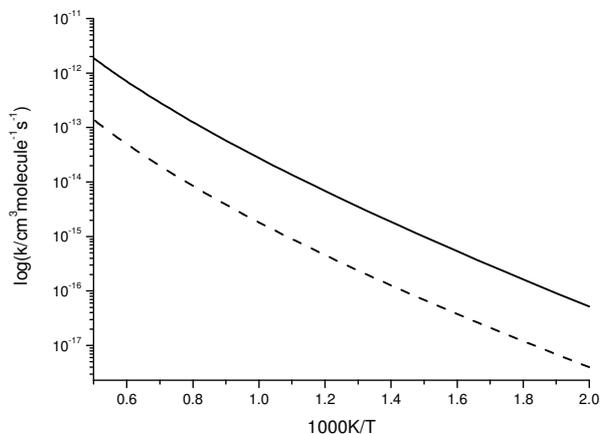
FIGURE 11. Arrhenius plot of rate coefficient for reaction 14, solid line – this work, dashed line – Metcalf et al. [6].
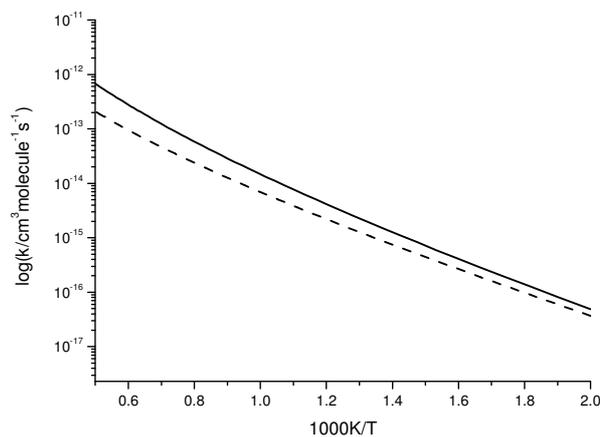

FIGURE 12. Arrhenius plot of rate coefficient for reaction 15, solid line – this work, dashed line – Metcalf et al. [6].
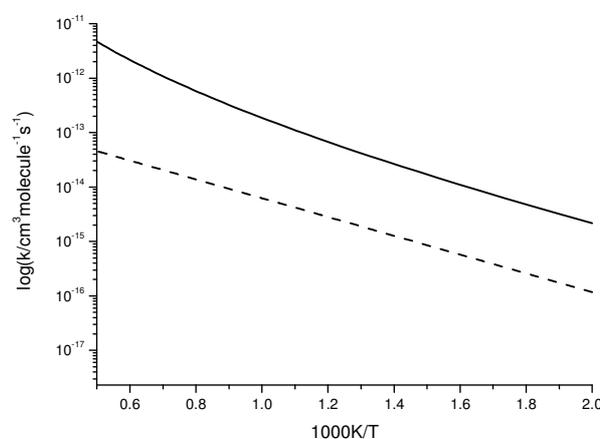

FIGURE 13. Arrhenius plot of rate coefficient for reaction 16, solid line – this work, dashed line – Metcalf et al. [6].

Reaction	This Work			Metcalfe et al. [6]		
	A	n	E	A	n	E
10	4.59×10^{-18}	2.2	-880	8.72×10^{-15}	0.97	800
12	6.27×10^{-19}	2.3	-1375	1.90×10^{-13}	0.51	-31.7
13	1.90×10^{-18}	2.2	-1801	8.72×10^{-15}	0.97	800

TABLE 4. Rate Coefficient Expressions for hydrogen abstraction by CH_3 ($cm^3 molecule^{-1}s^{-1}$).

The most striking aspect of the results shown from figures 6 to 12 is that apart from reaction 15, the predictions of the molecular modeling calculations performed in this work are all significantly faster than the rate coefficient expressions given in the kinetic model of Metcalfe et al. [6], typically by an order of magnitude, but in some instances more. These merit further investigation as if true would have significant implications for the predictions of the kinetic model.

CONCLUSIONS

Bond dissociation energies have been calculated for all the carbon-hydrogen, carbon-carbon, and carbon-oxygen single bonds within methyl butanoate. For the bimolecular reactions of methyl butanoate with OH and CH_3 radicals, transition state properties have been calculated, in terms of energy barriers and structures, from which high pressure limiting rate coefficient expressions have been calculated by the use of transition state theory. In virtually all cases investigated, these calculated expressions rate coefficient expressions are significantly faster than the equivalent rate coefficients used in the model of Metcalfe et al. [6]. This would have implications for the predicted reactivity of the methyl butanoate chemical kinetic model that warrant further investigation. However, it is not necessarily a surprise that there could be large differences between the current kinetic models and our predicted rate coefficient expressions, as none of the abstraction reactions within the current kinetic models are based on actual measurements with methyl butanoate, in all cases they make assumptions about the reactivity of the different hydrogen atoms in order to estimate rate coefficients for these processes.

ACKNOWLEDGEMENT

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