



Kinetic barriers, rate constants and branching ratios for unimolecular reactions of methyl octanoate peroxy radicals: A computational study of a mid-sized biodiesel fuel surrogate



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ABSTRACT

Towards the goal of establishing kinetic database for low-temperature combustion ($T < 1000$ K) of mid-sized biodiesel surrogates, the study uses quantum chemistry and statistical kinetic methods to investigate three primary unimolecular reaction pathways of methyl octanoate peroxy radicals, including dissociation, isomerization and concerted elimination. We calculate kinetic barriers and pressure-dependent rate constants at 500–1000 K. The comparison between our computed and previously estimated rate constants offers further insight into how transition state structures and molecular mechanics are correlated with reaction kinetics. In the branching ratio analysis, we investigate the proposed unimolecular reactions and factors affecting these kinetic characteristics. For the first time, the previously measured oxidation rates of methyl octanoate under the cool flame regime (560–1000 K) are computationally verified by kinetic modeling that reflects the contribution of the present submodel to an existing detailed mechanism of methyl octanoate. Consequently, the rate-of-production analysis reveals the significance of newly proposed reaction pathways.

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1. Introduction

Over the last decade or so, the use of biodiesel as a partial diesel substitute has continuously grown in global importance. In addition to their renewability and sustainability, biodiesel fuels offer reductions in particulate matters (PMs), carbon monoxide and hydrocarbons when blended in petroleum-based fuels in diesel engines [1–4]. One of the primary interests has therefore arisen in understanding complex chemistry of biodiesel combustion. Presently, fatty acid methyl esters (FAMES) are major components of commercial biodiesel. Their methyl ester structures that alter the important combustion phenomena, such as ignition characteristics, fuel-originated oxygenated species formation and soot precursor production, can be understood by means of kinetic modeling. Utilizing surrogate molecules or blends to build kinetic mechanisms that match the oxidation characteristics of real biodiesel fuels has been a common practice to overcome the computational burden without sacrificing the quality of solutions. In early studies, the choices of surrogate fuels started from small esters $C_{n \leq 5}$ including methyl formate [5–7], methyl acetate [8],

methyl butanoate [9–15] and methyl crotonate [12]. Later, intermediate esters, $C_{5 < n \leq 11}$, have been found to better represent a decrease in reactivity for a fuel below 1000 K (negative temperature coefficient, NTC) when compared with the kinetic modeling using small esters. The species of intermediate esters that have been analyzed are methyl hexanoate [16], methyl heptanoate [17], methyl octanoate [18], methyl octanoate [19–22], methyl decanoate [23–27] and methyl decenoate [28].

Low temperature (less than 1000 K) kinetics of hydrocarbons and biofuel molecule or surrogates have been increasingly studied [29–32] in recent years due to the developments of new combustion modes known as homogeneous charge compression ignition (HCCI) and low temperature combustion (LTC) diluted by exhaust gas recirculation (EGR) [33–36]. The first detailed kinetic mechanism for low temperature oxidation of biodiesel surrogate was proposed by Fisher et al. [9] for methyl butanoate, a widely used biodiesel surrogate. More recently, several studies further comprehensively explored pathways and kinetics for decompositions of methyl-ester peroxy radicals and hydroperoxy methyl-ester radicals in low temperature oxidation of methyl propanoate [37] and methyl butanoate [38–41].

Toward the goal of investigating low temperature combustion of large methyl esters, a couple of submechanisms have been proposed by analogy with existing rate constants from databases

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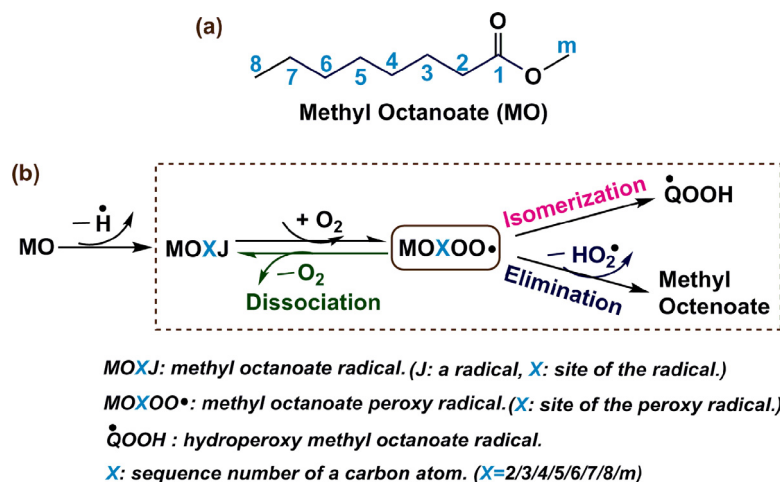


Fig. 1. (a) Structure of methyl octanoate (MO) and labels of the carbon atoms and (b) unimolecular reaction pathways of methyl octanoate peroxy radicals (in dash box) explored in the present study.

of hydrocarbon fuels. Togbé et al. [20] reported a submechanism for low temperature oxidation of methyl octanoate, in which rate constants of the reactions were derived from the mechanisms of C₄–C₁₀ alkanes and dimethylether proposed by Buda et al. [42] and Dagaut et al. [43], respectively. In addition, Herbinet et al. [27] constructed a submechanism for low temperature combustion of methyl decanoate and methyl decenoate, in which rate constants of the reactions were derived from the n-heptane and iso-octane mechanisms proposed by Curran et al. [44,45].

Very recently, the first experimental study that detected hydroperoxyalkyl radicals were carried out by Savee et al. [46] who investigated the oxidation of 1,3-cycloheptadiene. It is generally believed that methyl-ester peroxy radicals (ROO•), initiated by the reaction of fuel methyl-ester radicals and O₂, are one of the most crucial intermediates in the low-temperature oxidation process. These ROO• radicals can either dissociate back to original methyl-ester fuel radicals and O₂ or isomerize to hydroperoxy methyl-ester radicals (Q•OOH) via intramolecular hydrogen migration reactions.

Despite being computationally efficient, constructing mechanisms for biodiesel surrogates by adopting kinetic parameters from existing hydrocarbon fuel mechanisms inevitably sacrifices accuracy in assigning chemical kinetic and thermochemical parameters for reactions, particularly of methyl esters, due to its chemical complexity. Motivated by the need to establish chemical kinetic databases for low temperature combustion of methyl ester fuels, the present study uses quantum chemistry methods and statistical kinetic calculations to explore reaction pathways that dominate the low temperature oxidation of methyl octanoate. This molecule (see Fig. 1a) is an intermediate size biodiesel surrogate suitable for the use in predictions of low temperature combustion chemistry. We particularly focus on the primary unimolecular reactions of methyl octanoate peroxy radicals, including dissociation, isomerization and concerted elimination reactions, as shown in Fig. 1b. The findings of this study yield valuable insight into elementary reactions in methyl-ester fuel oxidation and contribute comprehensive information to facilitate building accurate kinetic modeling for biodiesel combustion chemistry.

2. Computational details

2.1. Quantum chemistry calculations

The electronic structure calculations are performed using the Gaussian 09 program [47]. Considering a compromise between the computational costs and calculation accuracy for such complex

molecular structures, the composite method, CBS-QB3 [48], is selected to calculate the potential energy surfaces (PES) for all unimolecular reactions of methyl octanoate peroxy radicals explored in the present study. Thermodynamic properties predicted by the CBS-QB3 method are able to reach “chemical accuracy” deviating from experimental data within ~1 kcal/mol. The molecular structures of reactants, products and intermediates are optimized and have no negative frequencies. Each transition state, except for those of barrierless reactions, has only one imaginary frequency with a correct vibrational mode. Unless otherwise stated, CBS-QB3 energies at 0 K are presented in this work.

Potential energy surfaces for internal rotations about single bonds in the investigated structures are calculated at the B3LYP/6-31G(d) level of theory with corresponding dihedral angles stepped in 10-degree increments. The computed torsional PESs are used to determine the lowest energy conformer and calculate the hindered rotor corrections in the rate constant calculations. In this study, the lowest energy conformer is used for each molecule. A cross examination method [39] through torsional PESs is used to identify the lowest energy conformers. In the proposed unimolecular reactions, the calculated torsional PESs of single bonds in methyl octanoate peroxy radicals and main transition states are presented in Figs. s8–s42 in the supporting information (SI) along with the averaged values of reduced moment of inertia.

Dissociation of a methyl octanoate peroxy radical (MOXOO•) to form a corresponding methyl octanoate radical (MOXJ) and O₂ is a barrierless process. Based on the generalized transition state theory (GTST) [49], we identify the position of the transition state along the minimum energy path (MEP) of each dissociation process that yields a minimum rate constant at a given temperature. To find the potential energy surface (PES) along the MEP, optimized geometries are obtained at various fixed lengths of the dissociating C–O bond in a methyl octanoate peroxy radical with a length interval of 0.05 Å. At each optimized geometry, a vibrational analysis ensures the orthogonality between a vibrational frequency and the MEP.

2.2. Rate constant calculations

The MultiWell program suit [50–52] is used to calculate the rate constants at the high pressure limit and in the fall-off region. Following the method of our previous study [39], the present work uses the canonical transition state theory (CTST) to calculate high pressure limited rate constants with Eckart tunneling corrections. 1-D decoupled hindered rotor corrections are included in the

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