



A theoretical kinetics study on low-temperature reactions of methyl acetate radicals with molecular oxygen

Qinghui Meng^{a,b}, Xudong Zhao^a, Lidong Zhang^{a,*}, Peng Zhang^{b,*}, Liusi Sheng^a

^a National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, PR China

^b Department of Mechanical Engineering, the Hong Kong Polytechnic University, Hong Kong, Hong Kong

ARTICLE INFO

Article history:

Received 8 January 2018

Revised 5 February 2018

Accepted 22 May 2018

Keywords:

Methyl acetate

RRKM

Master equation

Low-temperature oxidation

Biodiesel

ABSTRACT

Theoretical studies on the chemistry of methyl acetate radicals with molecular oxygen was conducted to get further understanding of biodiesel combustion. Reactions of the first oxygen addition to methyl acetate radicals has been investigated by high level quantum chemical methods, and rate constants were computed by using microcanonical variational transition state theory coupled with Rice–Ramsberger–Kassel–Marcus/Master-Equation theory. The calculated rate constants agree reasonably well with both theoretical and experimental results of chain-like alkoxy radicals. We considered each step in the oxidation process as a class of reaction, including all the possible reactions taking place, only the formation and re-dissociation of initial adducts are critical for the low temperature combustion of methyl acetate. The current study is an extension of kinetic data for such chain propagation reactions for methyl acetate oxidation in a wider pressure and temperature range, which can be used for the modeling study of low temperature oxidation of methyl esters.

© 2018 The Combustion Institute. Published by Elsevier Inc. All rights reserved.

1. Introduction

Biodiesel, as an environment friendly source of renewable energy, has been regarded as one of the most promising alternative fuels [1–3]. The main component of biodiesel is esters, which contain oxygen in their molecular structure and can be obtained from several types of oil, including soybean oil in the United States and rapeseed in Europe [4]. Esters are typically made of long (16–18) carbon atom chains and usually require very large detailed chemical kinetic models to precisely describe their oxidation. Compared with the combustion of fossil fuels, combustion of biodiesels could effectively reduce soot formation by suppressing its precursors in combustion processes [5], mitigating the climatic impact of fuel combustion. The detailed kinetic study of biodiesel is challenging both experimentally and theoretically because of the complexity and the size of the biodiesel components. As a result, surrogate molecules are widely used in kinetic studies to imitate the property of real biodiesel [6]. Some small molecules, such as methyl formate, methyl acetate (MA), methyl crotonate, and methyl butanoate (MB), which are usually chosen to investigate the chemical

kinetics of the characteristic ester moiety, have instead served as surrogates of biodiesels in combustion research [5,7–10].

MA is the simplest methyl ester with a chain only one carbon atom connected to the methyl ester group. And it is also an important reaction intermediate during the pyrolysis of biodiesel and a potential pollutant of the atmospheric degradation. Furthermore, association reactions of MA radicals and O₂ reaction represent an important model system to explore the kinetic consequences of the methyl ester radical oxidation; it contains many of the complexities of larger systems, yet is more feasible to detailed electronic structure calculations.

Regardless of the extensive research on developing elementary reactions for the high temperature oxidation and pyrolysis [11–13], only a few studies have been performed to promote the development of low-temperature combustion sub-mechanisms for methyl esters. It remains experimentally challenging to obtain reliable rate constants regarding biodiesel autoignition at low temperature due to the inherent complexity of chain reactions of ROO radicals formed by reactions between R with O₂. Low-temperature kinetics plays important role in the combustion of biofuel homogeneous charge compression ignition (HCCI) engines employing bio-fuels. Under normal HCCI conditions, the formation of combustion pollutants occur in a relatively low-temperature the formation of pollutants is believed to occur in the relatively low temperature regions of the combustion chamber. Thus, the low-temperature

* Corresponding authors.

E-mail addresses: zld@ustc.edu.cn (L. Zhang), pengzhang.zhang@polyu.edu.hk (P. Zhang).

oxidation processes is crucial in reducing NO_x and soot emissions and increasing combustion efficiency.

In the development of biodiesel reaction mechanisms, Dooley et al. [14] neglected the low-temperature oxidation of methyl ester peroxy radicals since its reactivity was assumed to be less relevant to a shock tube and rapid compression machine auto-ignition measurements. However, the rapid compression machine results suggested that reactions of O_2 addition to biodiesels have great influence on the combustion behavior at the low-to-intermediate temperature range (770–950 K). Recently, Zádor et al. [15] reviewed the low-temperature chemistry in an article and concluded that development of biofuel combustion modeling, given its potential significance, has been limited to the availability of detailed knowledge of dissociation and isomerization processes relevant to auto-ignition in oxygenated alkyl peroxy radicals.

Until recent years, researchers started to pay more attentions to the combustion mechanisms of the low-temperature oxidation of biodiesels. The first study of the low temperature oxidation of MA was performed by Dagaut et al. [16] in a jet-stirred reactor (JSR) at the temperature ranging from 800 to 1230 K and at the pressure of 10 atm. A comprehensive kinetic mechanism, largely based on the structure-reactivity of methyl acetate and related species including ethane, methanol, and dimethyl ether, was developed to interpret their experiments. The JSR results indicate that of the early reaction and the increase of CO formation are sensitive to the branching propagation reactions in low temperature oxidation of MA. A theoretical study of low-temperature oxidation of MB was conducted by Tao and Lin [17], in which reaction channels and thermochemistry of methyl ester peroxy radical decomposition has been analysed by the DFT method. Rate constants in the kinetic sub-mechanism were calculated by using the canonical transition state theory. However, the kinetic parameters for barrierless reactions of the O_2 addition to MB radicals, which are the entrance channels on the corresponding potential energy surface, were not considered. Jiao et al. [18] also investigated the auto-ignition of MB theoretically by employing the composite CBS-QB3 method, and their study focused on the quantum chemistry and kinetics of isomerization and decomposition reactions initiated by hydroperoxy methyl ester radicals formed in second O_2 addition reactions to MB peroxy radicals. The kinetic study of methyl acetate pyrolysis and oxidation was conducted experimentally and theoretically by Yang et al. [19]. Rate constants of the hydrogen abstraction and subsequent radical decomposition reactions for MA were calculated by high-level ab initio and RRKM master equation methods. The developed model by Yang et al. [19] was validated against experimental results from an atmospheric flow reactor and a low-pressure flat flame using molecular beam mass spectrometry. Deka and Mishra [20] developed a kinetic mechanism where the rate coefficient of the H-atom abstraction of MA by chlorine atoms was computed by using G2(MP2)//MPWB1K/6-31 + G(d,p) method and RRKM master equation analysis at 298 K. Tan et al. [21] also, respectively, conducted theoretical studies on the H-atom abstraction of MA initiated by free radicals (H, OH, HO_2 , CH_3 and O), whose predications were validated against available theoretical results reported previously [11,22].

Although the elementary reactions of the O_2 addition to MA radicals and the following isomerization and decomposition reactions of MA peroxy radicals are critical to determine the low-temperature auto-ignition, few studies has been done to focus on the sub-mechanism of low-temperature oxidation for MA. The ignition of MA is mainly initiated by hydrogen abstraction with free radicals to form one of two carbon centered radicals: $\cdot\text{CH}_2\text{COOCH}_3$ (denoted by MA2J) and $\text{CH}_3\text{COOCH}_2\cdot$ (denoted by MAMJ). The MA radicals can isomerize to each other via 1, 4-H shift. Under low temperature range, MA radicals can directly react with O_2 and then form peroxy radicals. These peroxy radicals can isomerize

to hydroperoxy alkyl radicals ($\cdot\text{QOOH}$), which in turn can decompose through concerted OH-loss or β -scission and can reverse to the peroxy radicals. The OH-loss and β -scission reactions involving $\cdot\text{QOOH}$ either propagate the radical chain reaction or lead to radical chain branching. These reactions have a great influence on the low-temperature combustion chemistry of MA. Compared with the analogous alkyl reaction systems, the present system is more complicated because of the presence of the oxygenated ester group.

In the manuscript, MA is recognized as a candidate methyl ester for surrogate formulation and is also considered as the starting point for the development of reaction rate rules and kinetic mechanism of other methyl esters. For the present work, we identified detailed reaction pathways for each radical and determined the potential energy surfaces (PES) by using highly accurate theoretical methods. Rate constants were subsequently calculated for dominant channels. Master equation analysis of the kinetics for barrierless reactions was performed to obtain accurate temperature- and pressure-dependent rate constants. Moreover, phenomenological rate coefficients and competing relationship among reaction pathways were provided for this system to develop the chemical kinetic modeling of low temperature oxidation of methyl esters. A detailed kinetic model of reactions of MA peroxy radicals and QOOH has been described in the present study which is also compared with MB peroxy radicals reported in early studies [17].

2. Theoretical methodology

2.1. Electronic structure calculations

The method of M06-2X/cc-pVTZ was employed in the geometry optimization and frequency analysis of stationary points on the MAOO potential energy surfaces [23]. Transition states possessing one and only one imaginary frequency were verified to correspond to desired reaction coordinates via visual inspections. For ambiguous cases, the intrinsic reaction path analysis was utilized to examine the connections of each saddle point to its local minima. Vibrational frequencies were scaled by a factor of 0.985 [24], and the zero-point energies (ZPE) were obtained at M06-2X/cc-pVTZ level. High level single-point energies of these species were corrected by using two high-level theories. The first one is the coupled-cluster singles and doubles with perturbative triples correction (CCSD(T)) theory implemented in Molpro package [25]. The single-point energies were obtained by restricted CCSD (T) with cc-pVXZ (X=D, T) basis sets [26]. The second is the explicitly-corrected CCSD(T)-F12 method [27] implementation in the same package [25]. The extrapolation of F12 correlation energies can be highly accurate even with just a DZ/TZ pair of basis sets [27]. Energy extrapolation to the complete basis set (CBS) limit was conducted with two-point extrapolation scheme [26,27]:

$$\begin{aligned} E[\text{CCSD(T)/CBS}]_{\text{DZ}\rightarrow\text{TZ}} &= E[\text{CCSD(T)/cc-pVTZ}] + \{E[\text{CCSD(T)/cc-pVTZ}] \\ &\quad - E[\text{CCSD(T)/cc-pVDZ}]\} \times 0.4629 \end{aligned} \quad (\text{E1})$$

$$\begin{aligned} E[\text{CCSD(T)-F12/CBS}]_{\text{DZ}\rightarrow\text{TZ}} &= E[\text{CCSD(T)-F12/cc-pVTZ}] + \{E[\text{CCSD(T)-F12/cc-pVTZ}] \\ &\quad - E[\text{CCSD(T)-F12/cc-pVDZ}]\} \times 0.4210 \end{aligned} \quad (\text{E2})$$

The molecular oxygen with triple ground state reacts like radicals in the entrance channel of O_2 addition reactions that are typically barrierless. Single reference methods failed to deal with this process. The multi-reference method CASSCF(7e,5o)/cc-pVDZ-F12 was employed for frequency calculations and the relaxed scan along the reaction coordinate. The frequencies of the initial formed

Download English Version:

<https://daneshyari.com/en/article/6593357>

Download Persian Version:

<https://daneshyari.com/article/6593357>

[Daneshyari.com](https://daneshyari.com)