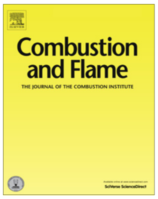
Combustion and Flame 161 (2014) 2270–2287

Contents lists available at ScienceDirect

Combustion and Flame

journal homepage: www.elsevier.com/locate/combustflame



Pathways, kinetics and thermochemistry of methyl-ester peroxy radical decomposition in the low-temperature oxidation of methyl butanoate: A computational study of a biodiesel fuel surrogate

Hairong Tao [a], Kuang C. Lin [b,*]

[a] College of Chemistry, Beijing Normal University, Beijing 100875, China
[b] Department of Mechanical and Electro-Mechanical Engineering, National Sun Yat-Sen University, Kaohsiung 80424, Taiwan

ARTICLE INFO

Article history:
Received 3 November 2013
Received in revised form 13 January 2014
Accepted 24 February 2014
Available online 18 March 2014

Keywords:
Low-temperature oxidation
Methyl butanoate
Methyl-ester peroxy radical
Hydroperoxy methyl-ester radical
Rate constant
Thermochemistry

ABSTRACT

A chemical kinetic submechanism proposed here is an essential prerequisite to model autoignition of methyl esters at low temperature region (less than ~900 K), where reactions of methyl-ester peroxy radicals (ROO$^\cdot$) and hydroperoxy methyl-ester radicals (Q$^\cdot$OOH) are crucial and relatively unexplored. The potential energy surfaces of the methyl butanoate peroxy radicals + O_2 systems are computed by the G3MP2B3 composite approach. 114 pathways are identified leading to the formation of key radicals in the ignition kernel such as OH and HO_2.

Particular attention is focused on: (1) intramolecular H-migration of ROO$^\cdot$, (2) unimolecular dissociations of ROO$^\cdot$ and Q$^\cdot$OOH and (3) reactions of ROO$^\cdot$ + HO_2. Using the canonical transition state theory, the high-pressure limit rate constants for reactions in the kinetic submechanism are calculated. Standard enthalpy of formation, entropy and heat capacities are evaluated for intermediates and products formed during combustion by means of the standard statistical mechanics formulae. The agreement and disagreement between our calculated kinetic parameters and previous estimates offer further insight into the uncertainty associated with theoretical estimation. We perform the branching ratio analysis for the competing channels between the reverse dissociation of ROO$^\cdot$ (ROO$^\cdot$ → R$^\cdot$ + O_2) and explored unimolecular reactions decomposing ROO$^\cdot$. Additionally, we also quantify the similarity and dissimilarity between the rate constants determined here and those previously calculated for normal alkanes. Finally, the effect of transition state size on the rate constants for the isomerizations of methyl-ester peroxy radicals is systematically analyzed.

1. Introduction

Biodiesel is an oxygenated, diesel-like fuel consisting of fatty acid alkyl esters (most commonly fatty acid methyl esters, or FAMEs) that are derived from oil fats [1] or algae [2]. When FAMEs are used as diesel fuels, methyl ester structures alter the evolution of important combustion phenomena, namely ignition characteristics, fuel-originated oxygenated species formation and soot precursor production. The fate of methyl ester is, therefore, of general interest in combustion chemistry [3–6]. Due to the complexity of biodiesel and the size of its constituent molecules, both direct experimental and detailed kinetic modeling studies have historically been limited. Simpler molecules such as methyl formate ($C_2H_4O_2$) [7–12], methyl butanoate ($C_5H_{10}O_2$) [13–29], methyl crotonate ($C_5H_8O_2$) [16,17,30], methyl hexanoate ($C_7H_{14}O_2$) [20,31], methyl hexenoate [32], methyl octanoate ($C_8H_{16}O_2$) [33,34], methyl decanoate ($C_{11}H_{22}O_2$) [25,35–42], and methyl decenoate ($C_{11}H_{20}O_2$) [43] have instead served as surrogates for studies of biodiesel combustion.

As extensively discussed in the recent reviews by Lai et al. [44] and Coniglio et al. [45], kinetic mechanisms for biodiesel have experienced a significant amount of recent development, primarily in the creation of surrogate models for small methyl esters with 1–4 carbon atoms (C_1—C_4) in their aliphatic main chains, towards larger esters with aliphatic main chains in $C_{n,n\geqslant 5}$. Methyl butanoate (MB, Fig. 1) that has received much attention in the literature was chronologically the first molecule considered as an acceptable biodiesel surrogate due to its richer combustion chemistry than methyl formate and yet simple structure suitable for a detailed theoretical analysis. Nevertheless, the absence of a negative

---

* Corresponding author. Address: 70 Lien-Hai Rd., Kaohsiung 80424, Taiwan. Fax: +886 7 525 4299.

E-mail address: kclin@umich.edu (K.C. Lin).

http://dx.doi.org/10.1016/j.combustflame.2014.02.012
0010-2180/© 2014 The Combustion Institute. Published by Elsevier Inc. All rights reserved.

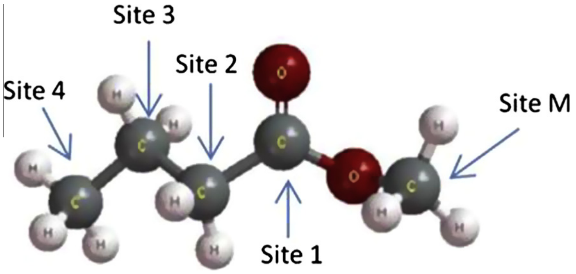


Fig. 1. Structure of methyl butanoate.

temperature coefficient (NTC) region in MB [16,18,19,29] suggests that aliphatic main chains of C_4-methyl esters are too short to exhibit the cool flame or NTC behavior of biodiesels. Recently, it has been recognized and generally accepted that such a deficiency has been overcome by the use of methyl esters with aliphatic main chains comprised of a carbon atom number greater than 5 [20]. Among mid-sized methyl esters mentioned above, mono-unsaturated methyl decenoate isomers ($C_{11}H_{20}O_2$) have yielded better characteristics than saturated methyl esters with aliphatic main chains of 5–11 carbon atoms in terms of reproducing the reactivity in the NTC region and tendency of soot formation [43]. Although methyl butanoate was determined to be not an ideal surrogate for biodiesels, it is regarded as a suitable model molecule for gaining insight into the oxidation chemistry of the methyl ester functional group.

While research has been extremely active on developing elementary reactions for high-temperature (>1000 K) oxidation and pyrolysis of methyl esters, relatively little work has been directed towards the development of kinetic mechanisms of low-temperature combustion for methyl esters due to its complexity in chemical reactions. Estimating reliable kinetic parameters regarding methyl ester autoignition at low-temperatures remains experimentally challenging due to the inherent complexity of chain reactions initiated by $ROO^{\cdot}$ radicals formed in reactions of initial fuel radicals $R^{\cdot}$ with O_2 [46]. Low-temperature kinetics, although complicated, has an important role in combustion of biofueled homogeneous charge compression ignition (HCCI), a relatively new concept for internal combustion engines [47]. This type of combustion happens at low temperature (<900 K) and hence holds for promise to reduce NO_x and soot emissions and increase thermal efficiency compared to conventional combustion engines. In a recent review article on low-temperature autoignition chemistry, Zádor et al. [46] concluded that progress in modeling biofuel combustion, given its potential significance, has been hampered by the nonavailability of detailed knowledge of dissociation and isomerization processes relevant to autoignition in oxygenated alkylperoxy radicals.

Only recently have researchers become increasingly concerned about reaction mechanisms for low-temperature combustion of oxygenated fuels [44–46]. The earliest study, by Fisher et al. [13], constructed the first detailed mechanism of methyl butanoate oxidation that consists of 279 species and 1259 reactions. The authors assigned rate constants for the $R^{\cdot} + O_2$ system by analogy with known rate constants from the propene [48] and propane [49,50] mechanisms. Thermodynamic properties were calculated using group and bond additivity methods and the statistical thermodynamics approach [51,52]. In the subsequent development of MB reaction mechanisms, Dooley et al. [18] omitted the low-temperature chemistry which describes the isomerization and dissociation of methyl-ester peroxy radicals due to the absence of low-temperature reactivity that was experimentally observed. However, their rapid compression machine results indicate that the reaction of fuel alkylester + O_2 ostensibly has an important role in slowing the reactivity at the low-to-intermediate temperature range (770–950 K).

In order to better understand low-temperature combustion of methyl butanoate, Hayes and Burgess [53] used G3MP2B3 calculations to systematically compute kinetic parameters for the isomerization of four methyl-ester peroxy radicals and quantify a reaction pathway for the early CO_2 formation involved in the decomposition of $CH_3CH_2CH(OO)C(=O)OC^{\cdot}H_2$. Their exploration of energetically preferred isomerization reactions constitutes a goal for future mechanism development and understanding of methyl ester oxidation.

Recently, Lin et al. [54] utilized a combined *n*-heptane [55] and methyl butanoate kinetic mechanism [13,56] to elucidate the influence of $ROO^{\cdot}$ radical decomposition on the ignition delay times of *n*-butane and MB. Their findings suggest the importance of a 5-membered transition state ring isomerization of $CH_3CH(OO^{\cdot})CH_2C(=O)OCH_3$ that favors a pathway leading to formation of HO_2 instead of OH, thus inhibiting NTC behavior. The effect of this unique pathway diminishes with the increase of alkyl chain length.

Towards the goal of developing kinetic models for large methyl esters, Herbinet et al. [43,57] have proposed kinetic mechanisms for methyl decanoate and methyl decenoate, respectively, including both low and high temperature combustion chemistries. The reaction rate constants and thermodynamic properties were derived from the *n*-heptane and iso-octane mechanisms by Curran et al. [55,58] using reaction class rate rules. The reactions involved in the low-temperature part of the mechanisms include: (1) addition of alkyl-ester radicals ($R^{\cdot}$) to O_2, (2) isomerization of $ROO^{\cdot}$ to $Q^{\cdot}OOH$, (3) C—O β-scission decomposition of $Q^{\cdot}OOH$ to unsaturated esters + HO_2, (4) decomposition of $Q^{\cdot}OOH$ to cyclic ethers + OH, (5) addition of $Q^{\cdot}OOH$ to O_2, and (6) isomerization of $^{\cdot}OOQOOH$ to ketohydroperoxide + OH. Although the mechanisms of C_{10} methyl esters were validated with the limited available experimental data of fuel oxidation, the authors suggested that future work should include refinement of the mechanisms, such as adding direct reaction of $ROO^{\cdot}$ to olefin + HO_2.

While rate constant properties for oxidative decompositions of methyl esters have not been systematically investigated, there is a need for continuous examination of methyl-ester peroxy radical pathways in the reactions of oxidized small methyl esters. In this paper, we present the results from our ongoing work on exploring oxidation reaction pathways, kinetics, and thermochemistry of methyl butanoate. A computational study, using quantum chemistry methods and statistical kinetic calculations, has been carried out to investigate isomerization and dissociation of methyl-ester peroxy and hydroperoxy methyl-ester radicals. The results of potential energy surfaces, rate constants, and thermodynamic data yield valuable insight into elementary reactions of methyl ester oxidation. In addition, the kinetic database of this study provides more information on a systematic generation of rate rules to estimate rate constants for oxidative decompositions of large methyl esters.

2. Computational details

In the present work, the proposed reaction pathways that contain 96 species and 125 reactions are based on the schematic mechanism developed in the literature [46] for low-temperature hydrocarbon oxidation and autoignition chemistry. Briefly, the decomposition of methyl-ester peroxy radicals is a chain propagation step which can be described by the reaction scheme given in Scheme 1. It is clearly seen that methyl-ester peroxy radicals + O_2 → $ROO^{\cdot}$ reactions lead to a very complex reaction system