



Chemical kinetic modeling and shock tube study of methyl propanoate decomposition



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ABSTRACT

The unimolecular decomposition kinetics of methyl propanoate (MP), including the direct C–O/C–C bond fissions and molecular reaction channels, were studied by using high-level *ab initio* calculations and Rice–Ramsperger–Kassel–Marcus/master equation (RRKM/ME) theory. Four homolytic bond-fission and ten hydrogen transfer reactions of the MP unimolecular decomposition were identified. The phenomenological rate constants were determined using the RRKM/ME theory over a temperature range of 1000–2000 K and a pressure range of 0.01 atm to the high-pressure limit. At 1 atm, the branching ratios show that the dissociation reactions $MP \leftrightarrow \cdot CH_2C(=O)OCH_3 + CH_3$, $MP \leftrightarrow CH_3OC(=O) + C_2H_5$ and $MP \leftrightarrow CH_3CH_2C(=O)O\cdot + CH_3$ dominate MP pyrolysis over the temperature range of 1000–1500 K. Our calculated rate constants were adopted in a detailed kinetic model to reproduce the laser-absorption measured CO and CO₂ concentration time-histories during the pyrolysis of 0.2% MP/Ar in a shock tube from 1292–1551 K and at 1.6 atm. The updated mechanism accurately predicted the early-time CO and CO₂ formation over the entire temperature range. In particular, our mechanism well reproduced the CO₂ time-histories from the early-time formation to the final plateau level.

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1. Introduction

Biodiesel fuels consisting of long-chain alkyl esters (C₁₆–C₁₉) have gained significant attention as viable alternatives to petroleum-based fuels because of their renewability, low CO₂ emission and low sulfur content [1–4]. However, it is difficult to study the real biodiesel component experimentally and theoretically with such a complex molecular structure [3]. Methyl esters with (C₁–C₄) in the aliphatic chain were selected to understand the reaction kinetics of the ester moiety, which is the characteristic functional group of biodiesel fuels. Methyl formate (MF) [5–8], methyl acetate (MA) [7–10], and methyl butanoate (MB) [8,11–18] have been extensively investigated as a stepping stone to understanding their combustion behaviors. A systematic investigation of the combustion chemistry of these small surrogates is particularly helpful for elucidating the wide variety of distinct combustion properties of larger fuels. As a representative short-chain methyl ester, methyl propanoate (MP, CH₃CH₂C(=O)OCH₃)

is an important intermediate during the pyrolysis of biodiesel fuels [19]. The molecular structure of MP along with the atom numbering is depicted in Fig. 1.

The previous studies of MP mainly focused on the oxidation kinetics of the H-abstraction reactions by small radicals (H, OH, HO₂) [20,21–23] and the combustion measurements of flame speed and extinction, stable species concentrations and ignition delay times [8,24–26]. Tan et al. [27,28] recently performed *ab initio* calculations of (H, CH₃, O(³P), OH and HO₂) H-abstraction reactions of MP and the subsequent MP radical decompositions using high-level CCSD(T), MRSDCI and MRACPF2 methods. Felsmann et al. [29] developed a detailed MP mechanism by combining the MA sub-mechanism [9] with Tan's work [27,28], which was validated against the laminar low-pressure flame data ($\phi = 0.8$ and 1.5) and flame speed measurements in a spherically confined chamber (1–6 atm).

It is known that H-abstraction reactions dominate the MP consumption at low and intermediate temperatures. However, the unimolecular decomposition plays a significant role during the pyrolysis of MP at high temperatures. To our knowledge, little information is available in the literature on MP unimolecular decomposition.

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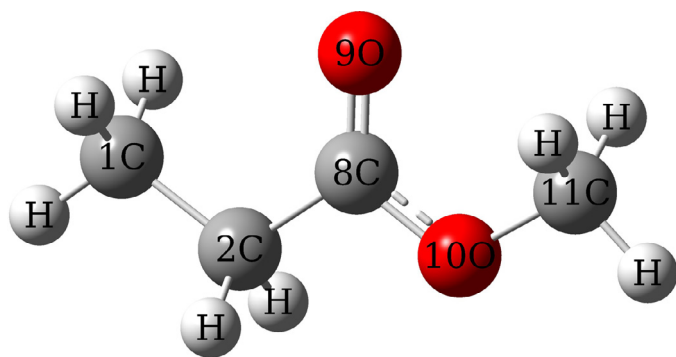


Fig. 1. The molecular structure of MP along with the atom numbering.

Farooq et al. [30] performed a comparative pyrolysis study of MP and EP (ethyl propanoate) in a shock tube from 1250–1750 K, at 1.5 atm and 1% fuel in argon. Due to the limited sensitivity of laser diagnostics in that work, the signal-to-noise ratios of the measured CO_2 and C_2H_4 data need further improvement. The high fuel concentration (1%) may also cause non-negligible uncertainties in laser-absorption diagnostics. Additionally, only the high-pressure limit rate constants of MP decomposition were used in the kinetic mechanism [30]. Hence, there is a need to refine the kinetic mechanism of MP decomposition by including the pressure-dependent rate constants. Zhao et al. [31] performed an experimental and modeling study of MP pyrolysis in a flow reactor and calculated the rate constants of five unimolecular decomposition pathways based on the potential energy profiles obtained at the CBS-APNO level. These rate constants were reported for a limited pressure range of 30–7600 Torr and temperature range of 1000–1500 K.

Hence, the research objectives of the current study include (1) providing a more complete picture of the unimolecular decomposition of MP, including its dissociation and molecular decomposition channels, using high-level *ab initio* methods CCSD(T)/cc-pVXZ (X=D, T, Q) in combination with Rice–Ramsperger–Kassel–Marcus/master equation (RRKM/ME) theory; (2) conducting shock-tube experiments of MP pyrolysis at a lower fuel concentration using more sensitive mid-infrared CO and CO_2 absorption diagnostics; and (3) analyzing and reproducing the shock tube species time-history data using an updated kinetic mechanism by adopting our new rate constants of MP unimolecular reactions into the Felsmann et al. [29] mechanism. Our study provides new insight into the accuracy and completeness of the MP kinetic mechanism relevant to the combustion feature of larger biofuels.

2. Experimental method

All the experiments were performed in the Stanford kinetics shock tube with a 14.13 cm inner diameter [32]. Gas temperatures and pressures behind reflected shock waves were calculated using standard normal-shock relations and the measured incident shock speed, with $\pm 1\%$ uncertainty in temperature over a test time of 1–2 ms. Liquid MP (> 99% pure, Sigma-Aldrich) was frozen and degassed three times to remove dissolved volatiles. All the test mixtures were manometrically prepared with argon as the bath gas in a stainless-steel mixing tank (40 L), heated uniformly to 50 °C, with an internal magnetically driven stirrer. A low fuel concentration (0.2% MP/Ar) was used to reduce the temperature variation during fuel pyrolysis to obtain more accurate experimental results. Side-wall pressures were measured by a Kistler 601B1 PZT located 2 cm from the shock tube end wall.

Species-specific, time-resolved and non-intrusive laser absorption spectroscopy was implemented for species monitoring behind reflected shock waves. CO and CO_2 were measured us-

ing two quantum cascade lasers (QCLs) near 4.6 μm and 4.2 μm , respectively. A fixed-wavelength direct-absorption strategy was used to detect the peak absorbance of the CO line centered at 2193.36 cm^{-1} [33] and achieved a ppm-level detection limit for CO at 1000–1800 K. The CO_2 diagnostic employed an external-cavity QCL to measure the peak absorbance of the fundamental vibration absorption line at 2390.52 cm^{-1} . The absorption coefficient of this CO_2 transition was experimentally characterized [34], providing a detection limit of 5 ppm for most high-temperature shock tube experiments. These two laser absorption diagnostics have been recently implemented in the shock tube chemical kinetics studies of methyl/ethyl esters [35–37] and ketones [38].

3. Computational method

The M06-2x hybrid exchange-correlation function within DFT [39] was used for geometry optimization with a 6-311++G(d,p) basis set in the Gaussian 09 program package [40]. The open-shell radicals were optimized with an unrestricted DFT, and the closed-shell molecules were described using a restricted DFT. To find the stationary point, the relaxed scans were performed at the DFT level to locate the global minimum of each species. The equilibrium structure and transition state (TS) were then confirmed by vibrational frequency analysis and characterized by all real frequencies and a single imaginary frequency, respectively. Intrinsic reaction coordinate (IRC) analysis [41,42] was performed to further ensure the TS was connected to the expected reactants and products. Harmonic vibrational frequencies and their corresponding zero-point energies were also calculated at the DFT-M06-2x level with the scale factor of 0.97, which was used to account for anharmonic effects [43]. To achieve more reliable energies for the geometries obtained at the DFT level, the CCSD(T) method with basis sets cc-pVXZ (X=D, T, Q) was applied to examine the MP molecular channels [44]. The CCSD(T) total energies were then extrapolated to the complete basis set (CBS) limit E_∞ with the following two-point extrapolation scheme [45]:

$$E(l_{max}) = E_\infty + \frac{B}{(l_{max} + 1)^4} \quad (1)$$

where l_{max} is the maximum angular momentum function found within the basis sets (e.g., for cc-pVXZ (X=D, T, Q), $l_{max} = 2, 3$ and 4), and B is the system-specific parameter. The CBS(D-T) was used to calculate the energies with the cc-pVDZ and cc-pVTZ basis sets in the Gaussian 09 program [40], and the CBS(T-Q) was used to calculate the energies with the cc-pVTZ and cc-pVQZ basis sets in the Molpro program [46]. In this work, the T_1 diagnostic values for reactant, transition states and products of MP molecular and bond-fission channels were calculated to gain insight into the significance of the multi-reference character. In general, the multi-reference wave function is only significant if the T_1 diagnostic value is greater than 0.02 for closed-shell species [47]. A recent theoretical study suggested that a higher T_1 diagnostic threshold (up to ~ 0.045) for the open-shell species may be acceptable [48].

The low-frequency torsional modes were treated as 1-D hindered rotors using the Pitzer–Gwinn-like approximation. The hindrance potentials of reactants and products were calculated at the M06-2x/6-311++G(d,p) level using the relaxed energy scan of the dihedral angle with an interval of 10°. For each transition state, the internal rotor scans were performed by freezing the atoms involved in the reaction coordinate and by taking into account the remaining torsional modes. The Cartesian coordinates of the optimized structures, frequencies, rotational constants and internal rotors are provided in the Supplementary material.

The multi-reference method CASPT2 was employed to study the barrierless reactions [49,50]. The active space (2e,2o) including bonding and anti-bonding (σ and σ^*) was chosen to describe the

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