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A comparative study of the chemical kinetics of methyl and ethyl propanoate

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Abstract

High temperature pyrolysis of methyl propanoate (CH$_3$-CH$_2$-C(=O)O-CH$_3$) and ethyl propanoate (CH$_3$-CH$_2$-C(=O)O-CH$_2$-CH$_3$) was studied behind reflected shock waves at temperatures of 1250 – 1750 K and pressure of 1.5 atm. Species time-histories were recorded for CO, CO$_2$, C$_2$H$_4$, and H$_2$O using laser absorption methods over a test time of 1 millisecond. Pyrolysis of methyl propanoate (MP) appears to be faster than that of ethyl propanoate (EP) under the present experimental conditions, where CO and CO$_2$ reach their plateau values faster for MP at a specific temperature and fuel concentration. Higher plateau values are reached for CO in case of MP while the CO$_2$ levels are similar for the two ester fuels. Ethylene production is larger for EP due to the presence of six-centered ring elimination reaction that produces ethylene and propanoic acid. Very little H$_2$O is produced during MP pyrolysis in contrast with appreciable H$_2$O production from EP. Sensitivity and rate-of-production analyses were carried out to identify key reactions that affect the measured species profiles. Previous kinetic mechanisms of Yang et al. [1, 2] and Metcalf et al. [3, 4] were used as base models and then refined to propose a new MP/EP pyrolysis mechanism.

Keywords: methyl propanoate; ethyl propanoate; biodiesel; pyrolysis; shock tube.
1. Introduction

Global warming and the world’s dependence on oil as an energy source have intensified the need for more efficient energy systems and alternative sources of energy based on renewable energy technologies. The world’s energy needs will increase throughout this century, driven by population and economic growth. Meeting these needs will require both the development of new energy resources, especially carbon-free ones, and the efficient and environmentally responsible utilization of fossil fuels. These trends have led to an increasing interest in the production and utilization of biofuels, like bio-alcohol and biodiesel [5-7]. Although biodiesel is gradually replacing crude-oil-derived diesel fuel, particularly in European Union, the combustion chemistry of biodiesel is not completely understood [8]. Specifically, significant work is needed on the chemical kinetics of biodiesel combustion to accurately predict the relevant emissions such as CO, particulate matter, unburnt hydrocarbons, and NOx.

Biodiesel is typically composed of a mixture of saturated and unsaturated long-chain methyl and ethyl esters. There have been only a few studies [8-12] on the chemical kinetics of these large esters because of their low vapor pressure and chemical complexity. Short chain molecules containing the same ester functional groups are thus studied to help understand the kinetic behavior of the practical fuel. A number of studies, e.g., [2, 4, 13-22], have been carried out on the oxidation and pyrolysis of methyl butanoate MB, CH$_3$-CH$_2$-CH$_2$-C(=O)O-CH$_3$, because MB contains much of the essential chemical structure of its long-chain counterparts, i.e., the methyl ester moiety and a shorter, but similar alkyl chain. There are few previous studies on the kinetics of methyl propanoate MP, CH$_3$-CH$_2$-C(=O)O-CH$_3$, and ethyl propanoate EP, CH$_3$-CH$_2$-C(=O)O-CH$_2$-CH$_3$. The purpose of the current study is to better understand the chemical kinetic behavior of methyl and ethyl propanoate and suggest improvements to the biodiesel chemical kinetic mechanism.
Among previous studies carried out on ethyl propanoate (EP), Blades and Gilderson [23] studied its thermal decomposition and measured the rate constant for the six-centered molecular elimination reaction producing propanoic acid \( C_3H_5(C=O)OH \) and ethylene \( C_2H_4 \) over 780 – 875 K:

\[
C_2H_5(C=O)OC_2H_5 \rightarrow C_2H_5(C=O)OH + C_2H_4 \tag{R1}
\]

O’Neal and Benson [24] used transition state theory to calculate the activation energy of the same six-centered molecular elimination reaction of EP and found it to be in close agreement with the measured value of Blades and Gilderson [23]. Thermal decomposition of EP was also studied by Barnard et al. [25] over 913 – 1317 K using a single-pulse shock tube and their measured rate constant for the molecular elimination reaction was in good agreement with previous studies. Schwartz et al. [26] performed non-premixed flame experiments by doping methane/air with EP (and other \( C_5H_{10}O_2 \) isomers) and concluded that the six-centered molecular elimination reaction of EP plays a critical role in flame environments. Shock tube ignition delay times of EP and methyl butanoate were measured by Metcalfe et al. [4], who assembled a detailed chemical kinetic mechanism to show that ethyl propanoate has a faster reactivity than methyl butanoate, due largely to the fact that EP has the fast molecular elimination reaction (R1) while MB does not. Oxidation of EP in a jet-stirred reactor was used by Metcalfe et al. [3] to develop an improved chemical mechanism for ethyl propanoate. Walton et al. [22] and Yang et al. [2] made modifications to the EP mechanism of Metcalfe et al. [3, 4] to extend it to lower reaction temperatures for rapid compression machine and low-pressure laminar flame simulations. Metcalfe et al. [3] also identified the most important features of EP oxidation by carrying out a very thorough and insightful analysis of their EP oxidation mechanism. Recently, Dayma et al. [27] measured laminar burning velocities for \( C_4 \) – \( C_7 \) ethyl esters and subsequently proposed a new kinetic mechanism to describe the oxidation of the studied ethyl esters.

Hoare and Kamil [28] investigated the cool flame and ignition limits for methyl propanoate (MP) in a static reaction vessel, although no kinetic modeling was carried out. Carbon dioxide yields were measured
behind reflected shock waves by Farooq et al. [19] during thermal decomposition of MP, as well as methyl butanoate and methyl acetate, but kinetic modeling was carried out only for methyl butanoate. Yang et al. [1] developed kinetic reaction mechanisms for oxidation of MP and its corresponding unsaturated species, methyl propenoate, as well as an isomer of MP, ethyl acetate, and its unsaturated partner, vinyl acetate, to simulate low-pressure laminar flame structures for all four fuels. Very recently, Zhao et al. [29] reported species concentration measurement experiments and kinetic modeling of MP pyrolysis in a laminar flow reactor at low pressure (30 Torr) and temperatures ranging from 1000 to 1500K. The kinetic reaction mechanism proposed by Zhao et al. [29] was supplemented by original theoretical calculations of many important elementary reactions and thermochemical parameters, providing valuable new information.

Here, we present a detailed experimental study on the pyrolysis of methyl propanoate (MP) and ethyl propanoate (EP) behind reflected shock waves, using laser absorption methods to measure time-histories of four major product species: CO, CO$_2$, H$_2$O, and C$_2$H$_4$. The measurements are used to compare the reactivity of the two esters and the different decomposition pathways taken by MP and EP. Comparisons of the measured species profiles with chemical kinetic simulations are used to refine or correct the rate coefficients of key reactions. The present study has permitted us to focus on some individual reactions and reaction rates that are important in biodiesel fuel combustion but can be more directly studied in the absence of oxidizers. In particular, studying pyrolysis conditions makes it possible to use CO and CO$_2$ production as reaction pathway diagnostics, since in the absence of oxidizers these species are formed only from the alkyl ester moieties in MP and EP. This has practical implications because details of the production of CO and CO$_2$ from these structures have been identified [30] as important factors that influence the ability of alkyl ester fuels to reduce soot production in diesel engine combustion. These particular reactants, MP and EP, are structurally very similar, so the differences in their pyrolysis rates and product compositions are due entirely to the presence of either an ethyl or a methyl radical at the alkoxy site in these fuels. Since the MP/EP decomposition, H-abstraction, and
subsequent reactions producing CO, CO₂, H₂O, and C₂H₄ form a subset of the detailed biodiesel kinetic mechanism, this work will help improve the overall predictive capability of biodiesel combustion models.

2. Experimental Procedure

2.1 Shock Tube Facility

Experiments were performed in the reflected shock region of a high-purity, stainless steel, helium-driven shock tube at Stanford University. The driven section is 10.5 m long and the driver section 3.7 m long, with an inner diameter of 15.24 cm. This geometric configuration provided at least 2 ms of high-quality test time of uniform temperature and pressure for these studies. Laser absorption measurements were made at an axial location 2 cm from the end-wall. Test mixtures were prepared manometrically in a 40-liter stainless steel tank equipped with a magnetically-driven stirring vane. Between experiments, the shock tube and mixing assembly were turbo-pumped to approximately 6 μTorr. Reflected shock temperatures and pressures were determined from the incident shock speed (extrapolated to the end-wall) using standard normal shock relations, with an uncertainty of ±0.7% and ±1%, respectively. Methyl propanoate and ethyl propanoate were provided by Sigma-Aldrich at > 99% purity. Research grade (99.999%) Argon and Helium supplied by Praxair Inc. were used in the experiments.

2.2 Laser Absorption Measurements

Mid-IR quantum cascade laser absorption of CO: Carbon monoxide concentration time-histories were measured in the fundamental vibrational band of CO near 4.56 μm using a thermoelectrically-cooled quantum-cascade laser (from Alpes Lasers). The R(13) transition of the ν₁ vibrational band of CO was chosen due to its relatively high absorption strength and negligible interference from CO₂ and H₂O. The detection limit for this diagnostic is approximately 5 ppm for the conditions of these experiments. Further details about the CO
diagnostic can be found elsewhere [31]. Quantitative CO concentration (mole fraction, $X_{CO}$) profiles are generated from the raw traces of fractional absorption ($I/I_0$) using Beer-Lambert law, the measured line-strength ($S$), the path length $L$, and the measured line-shape function ($\phi$):

$$I/I_0 = \exp(-S \phi P_{total} X_{CO} L)$$  \hspace{1cm} (1)

**IR diode laser absorption of CO$_2$:** Absorption measurements of CO$_2$ were made using wavelength-modulation spectroscopy with second-harmonic detection (WMS-2f). A commercially available distributed feedback diode laser (from NanoPlus) emitting near 3633 cm$^{-1}$ was used. This diagnostic was developed and demonstrated previously [32, 33] for the measurement of CO$_2$ concentration and gas temperature in shock tube kinetic experiments. Quantitative CO$_2$ concentration profiles were generated by comparing the measured 1f-normalized WMS-2f signals with simulated values. The WMS strategy was preferred over direct absorption to achieve higher signal-to-noise ratios in these relatively low fuel concentration experiments. This diagnostic can be used to detect minimum CO$_2$ mole fraction of approximately 100 ppm at 1300 K and 2 atm.

**IR diode laser absorption of H$_2$O:** Water concentration time-histories were determined by measuring the absorption of 2551 nm light at the peak of an absorption feature in the $\nu_3$ fundamental vibrational band of H$_2$O using a distributed feedback diode laser (from NanoPlus). A nitrogen purging system was implemented along the laser transmission path to eliminate signal loss due to absorption by ambient water vapor. The detection limit for this diagnostic is less than 50 ppm at 1200 K and 2 atm. Further details on the H$_2$O detection system as well as H$_2$O line characterization can be found elsewhere [34, 35].

**CO$_2$ laser absorption of C$_2$H$_4$:** Ethylene mole fraction was measured by taking advantage of the fortuitous overlap of the P(14) line of the CO$_2$ gas laser at 10.532 $\mu$m with the strong ethylene absorption band near 10.6 $\mu$m. Experiments were also conducted at an off-line wavelength of 10.675 $\mu$m to correct for interference absorption from methyl/ethyl propanoate and other hydrocarbon intermediates. The detection limit for ethylene measurements is approximately 100 ppm at 1200 K and 2 atm. Experimental details of this
diagnostic and high-temperature absorption cross-sections of ethylene and related alkenes are discussed by Ren et al. [36] and Pilla et al. [37].

2.3 Modeling and Analysis

In recent years, significant effort has been put into steadily building a hierarchical family of chemical kinetic reaction mechanisms for combustion of small alkyl ester fuels. At each step in this process, a kinetic mechanism for a new alkyl ester fuel is built on an existing mechanism for smaller alkyl esters that can be produced during the consumption of the larger alkyl ester molecules. Beginning with the smallest alkyl ester fuels, methyl formate and ethyl formate [38], kinetic mechanisms have been extended to several other alkyl ester fuels as large as methyl butanoate [2], and further studies of methyl pentanoate, methyl hexanoate, and methyl 3-hexenoate are in progress. Kinetic mechanisms were produced during this process for the present fuels, MP [1] and EP [2, 22], including the important kinetic modeling studies of EP combustion by Metcalfe et al. [3, 4]. All of these kinetic mechanisms were validated for oxidation experiments in low-pressure premixed laminar flames and ignition in a shock tube or rapid compression machine. That mechanism [1, 2], which included oxidation mechanisms for both MP and EP, was then refined by upgrading its core C0 - C4 hydrocarbon mechanism from Curran et al. [39]. This is the preliminary mechanism that we used to compute pyrolysis histories to compare with the present experimental results.

Kinetic simulations of the present pyrolysis experiments, using this preliminary model, were found to be sensitive to some reactions, reaction rates, and reaction pathways that had not been tested in past studies of flame propagation and oxidative ignition. Some reaction rates were identified that required modification to properly describe the present experimental results. The ability to use CO and CO2 as reaction pathway diagnostics, due to the unique features of fuel pyrolysis conditions, provided important evidence of the shortcomings of this preliminary kinetic model. In the following sections, we illustrate some of these preliminary
model failures and describe the model modifications that were made, based on the simulations of the new experiments and sensitivity analysis.

Pyrolysis is an endothermic process that leads to temperature and pressure decreases after shock heating. The temperature decrease can be significant for high initial temperatures, high initial fuel concentrations, relatively large fuel molecules or any combination of these factors. Since the absorption coefficient is a temperature-dependent quantity, accounting for temperature change can be critical for accurate species time-history determinations. When significant temperature changes occur during the measurement time, it is necessary to use time-varying absorption coefficients for converting measured absorbance time-histories to accurate concentration time-histories. Since temperature time-histories were not measured in this study, these have been estimated from simulations using the Chemkin-Pro [40] solver with an adiabatic constraint and post-reflected shock temperature and pressure calculated from normal shock relations. Shock tubes are usually modeled as constant-volume (CV) although endothermicity can cause the shock tubes to deviate from the ideal CV behavior and tend towards the constant-pressure (CP) mode. As demonstrated previously [41, 42], although shock tubes do not exhibit pure CV or CP behavior in pyrolysis experiments, predictions of temperature and species time-history are relatively insensitive to the choice between these two gasdynamic models for dilute experiments. Figure 1 shows simulated temperature time-histories for 1% MP/Ar and 1% EP/Ar pyrolysis. After an elapsed time of 1 ms, the CP and CV gasdynamic models predict a temperature decrease of 120 ± 15 K for MP and 113 ± 13 K for EP. As expected, the temperature reduction is slightly larger using CV simulation. Although neglecting such decreases in temperature can cause a significant error in species time-history measurements, a ± 13 – 15 K uncertainty, resulting from using CP or CV model, contributes an error of no more than ± 7% for any of the species measured here. Additionally, temperature time-histories calculated using our kinetic mechanism and the Metcalfe et al. [3] mechanism are quite similar.
All experimental species profiles presented in subsequent sections are converted to mole fractions using simulated temperature profiles based on the CV model and the MP/EP kinetic mechanism of the current work.

The temperatures in Fig. 1 suggest that pyrolysis of MP is different qualitatively from pyrolysis of EP. The temperature decrease is much more abrupt for the 1% MP/99% Ar sample than for the 1% EP/99% Ar sample. The primary temperature drop takes place in a few microseconds for MP and the temperature remains nearly constant thereafter. The temperature decrease for the case of EP is much less abrupt and the temperature continues to decrease in the full 1000 µs time interval of the experimental observations.

In order to provide a framework for the discussions to follow for both the experimental and computational results, it is useful to present sample pyrolysis calculations for both fuels. The computed results, shown in Fig. 2, summarize the fuel, major intermediate species and product species mole fractions calculated using the final kinetic mechanism from the current study at a representative temperature of 1500 K. These calculations were carried out to a total elapsed time of 5 ms, long after the last experimental mole fraction measurements were made (1 ms). Similar to the temperature results shown in Fig. 1, in the case of MP pyrolysis, all of the species reach nearly constant levels in the first few microseconds, after which there are slow increases in the H₂, CO, CH₄, and C₂H₂ mole fractions and a barely perceptible decrease in the C₂H₄ level. In this sense, high-temperature pyrolysis of MP under the present conditions is comprised of a rapid first stage followed by a very long relaxation stage that leads to final chemical equilibrium. We computed this equilibrium independently for the same initial conditions (1500 K, 1.5 atm, 1% MP/Ar) and found the MP equilibrium to have a temperature of 1374 K and the only species with significant mole fractions at equilibrium were H₂ (26,710 ppm), CO (19,150 ppm), C₂H₂ (2,965 ppm), C₆H₆ (1,880 ppm), CH₄ (1,300 ppm), and C₂H₄ (130 ppm), in addition to Ar (947,780 ppm). In particular, the CO₂ mole fraction at equilibrium is about 0.001 ppm, although CO₂ is a major intermediate measured in the current experiments. Similarly, most but not all of the C₂H₄ produced in the first pyrolysis stage is ultimately consumed during the long relaxation stage. When we extended the time-dependent
pyrolysis problem of Fig. 1 and Fig. 2(a) to thousands of seconds of adiabatic elapsed time, the computed species levels and temperature eventually evolved to the corresponding values provided by the equilibrium calculation, but this relaxation time is very long compared to the 1000 µs of observation time from the current experiments.

EP pyrolysis also has a rapid first stage, followed by a much longer relaxation stage towards final equilibrium. However, in contrast with MP, EP clearly takes longer time for the first pyrolysis stage to be completed, and as we will demonstrate, its first reactive pyrolysis stage is more complex than that of MP, consisting of several distinct kinetic processes. As shown in Fig. 2(b), EP produces a greater variety of intermediate species, such as propanoic acid (C_3H_5COOH) and methyl ketene (CH_3CHCO) that are formed and then consumed with time scales longer than the initiation reactions but still much shorter than the long relaxation time to reach equilibrium. The final equilibrium conditions for EP are similar to those for MP, with H_2 (30,340 ppm), CO(19,030 ppm), C_2H_2 (2,970 ppm), C_6H_6 (3,340 ppm), CH_4 (1,900 ppm), and C_2H_4 (170 ppm) and a final equilibrium temperature of 1359 K. For EP, the most significant changes after about 5 ms are the steady but slow conversion of C_2H_4, CO_2 and H_2O to C_2H_2, H_2, and CO.

3. Results and Discussion

3.1 CO Measurements

Experimentally measured CO time-histories are shown in Fig. 3(a) and Fig. 3(b) at a variety of initial, post-shock temperatures (1259 – 1756 K) for the pyrolysis of 1% MP and 1% EP, respectively. In every experiment, for both MP and EP, CO production begins immediately at initial rates that increase with higher initial temperature. At the highest initial temperatures, CO production is immediately very fast, but that rapid production lasts for only a few microseconds, after which CO production becomes very slow. At lower temperatures, the initial rate of CO production is lower than at high temperatures but continues steadily.
throughout the observed experimental time window of about 1 ms. As the reflected shock temperature increases, the CO levels in the MP pyrolysis experiments appear to plateau to a unique value (~7800 ppm) at 1 ms. A similar trend was observed recently [20] in a study of MB pyrolysis, albeit with a higher CO plateau (~10,000 ppm). For EP pyrolysis, however, the CO values at 1 ms continue to increase gradually as the initial temperature increases and reach about 6200 ppm for the highest temperature studied (1756 K). Figure 3 also shows that more CO is produced at 1 ms from MP compared to EP at the same initial temperature.

As noted above, virtually all of the oxygen in each mixture is present at equilibrium as CO, at a level of about 1.9% or 19,000 ppm. Therefore, the CO levels shown in Fig. 3 for both MP and EP are snapshots in time of mole fractions that would continue to increase, albeit very slowly, to final values of about 19,000 ppm. There are clearly two characteristic times or stages for CO production under most of the present conditions, the first shown as a rapid growth of CO to values of approximately 5,000 – 8,000 ppm, followed by a very slow second stage in which the CO mole fraction increases to an equilibrium level of about 19,000 ppm. At the higher range of temperatures in the current shock tube pyrolysis experiments, the first of these two time stages is very rapid and is complete within the 1.0 ms observation time, but at the lower temperatures the first stage is not completed before the observational time limit. Based on the experimental curves in Fig. 3, the first reaction stage is completed within the available residence time for MP for temperatures above 1370 K and above 1500 K for EP. The temperature decreases shown in Fig. 1 are all associated with the first of these stages, as is the consumption of the fuel and any major intermediate species shown in Fig. 2.

A subset of experimental data from Fig. 3 are compared in Fig. 4 with kinetic simulations using the preliminary kinetic mechanism [1, 2]. For MP pyrolysis, the preliminary model overestimated CO production at all initial temperatures and predicted a surprisingly lower CO mole fraction at the highest initial temperature (1690 K) than at lower initial temperatures of 1591 K and 1415 K. For EP pyrolysis, the preliminary model underpredicted CO up to about 1560 K and overpredicted CO at higher temperatures. These computed results
indicated that the preliminary kinetic model couldn’t reproduce the major features of the fuel pyrolysis and required modifications. When the kinetic reaction mechanism was revised for both MP and EP as described in the kinetic modeling section below, the computed and experimental CO mole fractions exhibited better agreement, as shown in Fig. 5. We will return below to discuss further the comparisons between the experimental and final kinetic modeling results.

Figure 6 shows CO fractional yield, defined as the ratio of CO mole fraction at 1 millisecond to the initial fuel mole fraction, as a function of temperature for the two fuels. Fractional yields predicted by the preliminary and revised mechanisms are also shown. As noted previously, CO yield is larger for MP compared with EP at all temperatures. As the initial temperature increases, CO yield increases quite rapidly until a transition temperature value is reached, above which CO yield for MP does not change noticeably and increases very slowly for EP. The revised mechanism does a much better job of reproducing the measured yields compared with the preliminary model.

3.2 CO₂ Measurements

CO₂ experimental time-histories are shown in Fig. 7 in comparison with the revised/final kinetic mechanism over a range of initial temperatures (1259 – 1599 K) and nominal pressures of 1.25 – 1.5 atm for the pyrolysis of 1% methyl propanoate (MP) and 1% ethyl propanoate (EP), respectively. Experimental CO₂ production appears to be quite similar between the two fuels; at a specific temperature and elapsed time, the CO₂ levels from the two fuels are with 20 – 30% of each other. Comparison of the measured time-histories with simulations using the preliminary MP model (not shown here) indicated that the simulations overpredicted CO₂ at lower temperatures and underpredicted at temperatures higher than about 1400 K. For EP pyrolysis, the preliminary model (not shown) underpredicted CO₂ at all temperatures by factors of 4 – 13. Significant revisions to the preliminary kinetic mechanism were required to correct the CO₂ predictions. Following modifications in
the kinetic model, the revised model-computed CO₂ time-histories are summarized together with the experimental profiles in Fig. 7. The revised kinetic mechanism will be discussed in subsequent section.

Figure 8 shows CO₂ fractional yield, defined as the ratio of CO₂ mole fraction at 1 millisecond to the initial fuel mole fraction, as a function of temperature for the two fuels. Fractional yields predicted by the preliminary as well as revised mechanism are also plotted for comparison. The experimental CO₂ yields increase with increasing temperature and are quite similar for the two fuels. The preliminary kinetic mechanism underpredicted CO₂ yields by a big margin for EP pyrolysis. The revised kinetic mechanism predicts much-improved yields for both fuels.

Computed equilibrium concentrations of CO₂ are extremely small (\( \sim 10^{-3} \) ppm) for both MP and EP pyrolysis, so virtually all of the oxygen atoms initially present in the ester moiety are eventually found as CO at equilibrium, and CO₂ production in the first stage of the present shock tube pyrolysis experiments is a temporary phenomenon that completely disappears at long times in the second stage of the pyrolysis.

### 3.3 Ethylene Measurements

Ethylene (C₂H₄) time-histories are shown in Fig. 9 over a range of initial temperatures (1354 – 1704 K) and nominal pressures of 1.5 – 1.7 atm for the pyrolysis of 1% methyl propanoate (MP) and 1% ethyl propanoate (EP), respectively. As expected, the presence of a second ethyl group in EP, compared with the single ethyl group in MP, leads to ethylene production during EP pyrolysis that is about twice the ethylene production during MP pyrolysis. Just after time zero, all of the EP decomposes to ethylene and propanoic acid. Ethylene mole fractions (\( \sim 10,000 \) ppm or 1%) are very close to the initial fuel mole fraction of EP, indicating that nearly every EP molecule immediately produces one C₂H₄ molecule. These higher ethylene levels in EP pyrolysis contribute to higher reactivity of EP compared with MP under oxidative conditions.
Chemical equilibrium calculations show that the eventual level of ethylene is very low (150 ppm). As already noted for CO₂, the levels of ethylene shown in Fig. 9 are artifacts of the fast initial decomposition of the fuel, produced in the first stage of the high-temperature pyrolysis. This ethylene is eventually consumed during the slow second stage of the pyrolysis of both MP and EP fuels. Extending the pyrolysis simulations far beyond the 1 ms observation time of the experiments, to 1000 seconds, confirmed that the slow relaxation reaction process does indeed lead to the adiabatic distribution of species produced by the equilibrium calculation.

Model predictions for C₂H₄ levels, using the revised kinetic mechanism, are also shown in Fig. 9 and exhibit good agreement with the experimental measurements. The kinetic model shows that the slow consumption of ethylene is due to H-atom abstraction from C₂H₄ by H and OH radicals. Concentrations of these radicals are higher as temperature increases, leading to a faster rate of C₂H₄ consumption as the pyrolysis temperature increases, as seen in Fig. 9.

### 3.4 H₂O Measurements

Laser absorption measurements carried out to detect H₂O during MP pyrolysis led to very weak signals indicating low water production from MP. The kinetic simulations predict only about 10 – 100 ppm of H₂O within the 1 ms observation time. On the other hand, large amounts of water are produced from EP and the experimental results are shown in Fig. 10 over a range of temperatures (1356 – 1729 K) and nominal pressure of about 1.7 atm for the pyrolysis of 1% EP/Ar. The H₂O production increases with increasing initial temperature and reaches a plateau value of about 4200 ppm for temperatures higher than 1500 K. Model predictions, based on the revised mechanism, are also shown in Fig. 10 and agree quite well with the experimental values. The kinetic mechanism shows that water is produced from H atom abstraction reactions from ethylene and propanoic acid by OH radicals under the present high-temperature pyrolysis conditions. Ethyl propanoate decomposes too rapidly at these conditions to produce water from OH reactions with EP. Figure 11 shows that
preliminary kinetic mechanism overpredicted water fractional yield, defined as the ratio of H₂O mole fraction at 1 millisecond to the initial EP mole fraction, at all values of the initial temperature. The revised mechanism, on the other hand, is in excellent agreement with the measured fractional yields.

4. Kinetic Modeling and Mechanism Improvements

Extensive sensitivity and reaction path analysis of MP and EP kinetic mechanisms were carried out, and a number of reactions were identified that were not particularly significant under oxidation conditions but had large sensitivities under pyrolysis conditions and considerable influence on computed mole fractions of the species measured in the present experiments. For some of these reactions, the existing rate expressions were quite uncertain. Kinetic sensitivities were calculated for both MP and EP pyrolysis at 1500K, showing the CO, CO₂, C₂H₄ and H₂O sensitivities in Figures 12 – 15, respectively. Water sensitivity is only shown for EP pyrolysis as very little H₂O is produced from MP, as discussed earlier. Sensitivity is defined here as the differential fractional change of species mole fraction divided by the differential fractional change in the reaction rate coefficient, at a given time. For each experimentally measured chemical species, there are relatively few elementary reactions to which the computed species concentrations are particularly sensitive.

4.1 Ethyl Propanoate (EP) Pyrolysis

Ethyl propanoate decomposes rapidly at the high temperatures of this study. As noted above, ethyl esters R₁(C=O)OC₂H₅ react rapidly via a six-centered molecular elimination of ethylene

\[ \text{R}_1(\text{C}=\text{O})\text{OC}_2\text{H}_5 \rightarrow \text{R}_1(\text{C}=\text{O})\text{OH} + \text{C}_2\text{H}_4 \quad (R1) \]

while the corresponding methyl ester R₁(C=O)OCH₃ does not have such a fast reaction. The rate of this reaction has been studied extensively and is quite well-established [23-25]. Under the present conditions, EP
decomposes over a period of just a few microseconds to produce propanoic acid $C_2H_5(C=O)OH$ and ethylene.

This is seen in Fig. 9(b) where the ethylene mole fraction in all of the 1% (i.e., 10,000 ppm) EP pyrolysis experiments and model calculations rises to 10,000 ppm almost instantaneously. This can also be seen in Fig. 14(b) where the early-time sensitivity of reaction R1 for $C_2H_4$ production is very large, but the sensitivity falls to zero very quickly as EP is entirely consumed. For this reason, H atom abstraction reactions with EP have effectively no influence or sensitivity on the present simulations or experiments. In addition, the established reaction rate expression for R1 is sufficiently accurate and has no significant sensitivity for the current results.

That is, large variations in the rate of reaction R1 would not change the computed results very much. The present EP experiments are thus almost equivalent to experiments in which EP is replaced by equivalent amounts of propanoic acid and ethylene, as discussed by Metcalfe et al. [3, 4]. At lower temperatures where the rate of R1 is slower, Metcalfe et al. noted that H atom abstraction reactions can consume significant fractions of EP, and this would also be true under lower temperature pyrolysis conditions, but the present experiments were carried out at sufficiently high temperatures that R1 accounts for all of the EP consumption.

Following fast initial decomposition of EP, propanoic acid $C_2H_5(C=O)OH$ then reacts primarily via H atom abstraction by H and OH with two major radical products:

\[
C_2H_5(C=O)OH + H \rightarrow CH_3CH(C=O)OH + H_2 \quad (R2)
\]

\[
C_2H_5(C=O)OH + H \rightarrow CH_2CH_2(C=O)OH + H_2 \quad (R3)
\]

\[
C_2H_5(C=O)OH + OH \rightarrow CH_3CH(C=O)OH + H_2O \quad (R4)
\]

\[
C_2H_5(C=O)OH + OH \rightarrow CH_2CH_2(C=O)OH + H_2O \quad (R5)
\]

Reactions R4 and R5 are major sources of water that is found as a significant product of EP pyrolysis, as seen in the sensitivity analysis for $H_2O$ in Fig. 15. The ratio of production of $CH_3CH(C=O)OH$ to that of $CH_2CH_2(C=O)OH$ has a significant effect on the relative production of CO and $C_2H_4$ in the present experiments,
which can be seen in the sensitivity analyses of Figs. 12(b) and 14(b). As observed by Metcalfe et al. [3, 4],
CH$_3$CH(C=O)OH, produced by reactions R2 and R4, is a resonantly stabilized radical which decomposes relatively slowly to produce either methyl ketene CH$_3$C=O and OH or propenoic acid C$_2$H$_3$COOH and H. Methyl ketene reacts quite slowly in these conditions, mostly via addition reactions of H and OH to the C=C double bond, producing relatively small amounts of ethyl radicals and then ethylene, while propenoic acid decomposes to produce vinyl radicals, CO and OH. Reactions R3 and R5 produce CH$_2$CH$_2$(C=O)OH which then decomposes rapidly via β-scission to produce ethylene and HOCO:

\[
\text{CH}_2\text{CH}_2(\text{C}=\text{O})\text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{HOCO} \quad \text{(R6)}
\]

This ethylene production is in addition to that formed immediately via reaction R1 and is responsible for the increase of ethylene levels above 10,000 ppm in Fig. 9(b).

Reaction path analysis for EP pyrolysis shows that the main channel responsible for CO formation is:

\[
\text{HOCO} \rightarrow \text{CO} + \text{OH} \quad \text{(R7)}
\]

The same reaction path analysis also shows that the closely related reaction R8 is the main source of CO$_2$ in the EP pyrolysis experiments:

\[
\text{HOCO} \rightarrow \text{CO}_2 + \text{H} \quad \text{(R8)}
\]

Thus reactions R3 and R5, followed by R6, lead to C$_2$H$_4$, CO and CO$_2$ production during EP pyrolysis, while reactions R2 and R4 produce CO and CO$_2$ but do not produce ethylene. Thus ethylene production rates following EP decomposition are sensitive to the ratio of (R2+R4)/(R3+R5); yet none of these reaction rates are very well established. Similarly, relative production of CO and CO$_2$ is very sensitive to the ratios of the rates of reactions R7 and R8.
One additional feature seen in Fig. 9(b) is that as the initial temperature increases from 1354 K to 1704 K, the rate of consumption of ethylene increases. Ethylene reacts primarily with H and OH to produce vinyl radicals and then acetylene, and this reaction sequence accelerates as the temperature increases, resulting in the more pronounced decrease in ethylene mole fractions at the highest temperatures. Reactions R7 and R8 produce the radical species that then react with ethylene, and reactions R7 and R8 proceed more rapidly as the temperature increases. All of these processes were illustrated together in Fig. 2(b), showing initial reactant, major intermediates, and the measured pyrolysis products for EP pyrolysis at an initial temperature of 1500 K. The EP level falls to zero in less than 10 microseconds, producing C$_2$H$_4$ and C$_2$H$_5$COOH in equal amounts of 10,000 ppm. Subsequent consumption of the propanoic acid is quite rapid but is not complete by the end of the experimental observation time of 1000 microseconds. Production of additional C$_2$H$_4$ as well as considerable levels of H$_2$ and lesser amounts of H$_2$O, CO, C$_2$H$_2$, CO$_2$ and CH$_3$CHCO can be seen from the consumption of propanoic acid. The calculations were extended to 5 ms in order to show more clearly the relative production of the different species. The slow onset of net consumption of ethylene can also be seen, beginning at about 2 ms. Eventually, based on further simulations carried to much longer times, as well as formal chemical equilibrium calculations, the C$_2$H$_4$, CO$_2$, H$_2$O, and methyl ketene (CH$_3$CHCO) all are consumed.

A conclusion that can be drawn from the equilibrium species concentrations is that the snapshot in time provided by the shock tube experiments shows, in most of the cases, a “frozen” mixture of intermediates and products. Once the initial reactive stage is completed, the evolution is then very slow. As noted above, at the lowest temperatures studied, the initial reactive stage is not completed before the end of the observation time window, and in some cases, there is no abrupt reactive stage at all.

4.2 Methyl Propanoate (MP) Pyrolysis
In the case of MP, unimolecular decomposition reactions of MP are quite fast at the temperatures of this study, but they do not dominate in the same manner as for EP. These reactions were written [1, 2] in the recombination direction with temperature independent rate constants, so the decomposition reaction rates were determined via detailed balance and the relevant thermochemistry of each set of reactants. Those reactions and rates were retained for the present study, and several of these reactions were found to contribute to MP decomposition at early times in the shock tube pyrolysis simulations. In declining order of their contribution to MP consumption, these are:

\[ \text{MP} \rightarrow \text{C}_2\text{H}_5 + \text{CH}_3\text{OCO} \]  \hspace{1cm} (R9)

\[ \text{MP} \rightarrow \text{CH}_2\text{COOCH}_3 + \text{CH}_3 \]  \hspace{1cm} (R10)

\[ \text{MP} \rightarrow \text{C}_2\text{H}_5\text{CO} + \text{CH}_3\text{O} \]  \hspace{1cm} (R11)

\[ \text{MP} \rightarrow \text{C}_2\text{H}_5\text{CO}_2 + \text{CH}_3 \]  \hspace{1cm} (R12)

Of these initiation reactions for MP, only reaction R12 leads to direct production of CO$_2$, and this reaction shows a negative sensitivity for CO production in Fig. 12(a). Two previous studies by Akih-Kumgeh and Bergthorson [43], using CBS QB3 theoretical method, and by Zhao et al. [29], using theoretical calculations at the CBS-APNO level, determined the rates of reactions R9 – R12. These reactions are written in the recombination direction in the current mechanism (see Table 1).

Since MP does not have the low activation energy molecular elimination that makes EP decomposition so fast, initiation of MP reaction is slower overall than that of EP. There is some time after the initiation where the kinetic model shows that H atom abstraction from MP is important. MP has three structurally distinct C-H bonds, and each supports H atom abstraction at a different rate. These include:

\[ \text{CH}_3\text{CH}_2(\text{C}=\text{O})\text{OCH}_3 + \text{H} \rightarrow \text{CH}_2\text{CH}_2(\text{C}=\text{O})\text{OCH}_3 + \text{H}_2 \]  \hspace{1cm} (R13)
as well as smaller contributions, under the present pyrolysis conditions, from H atom abstraction by OH and CH₃.

The radical CH₂CH₂(C=O)OCH₃ in reaction R13 then decomposes as:

CH₂CH₂(C=O)OCH₃ → C₂H₄ + CH₃OCO (R16)

The resonantly stable radical CH₃CH(C=O)OCH₃ from reaction R14 makes either methyl ketene and methoxy radicals or methyl propenoate and H:

CH₃CH(C=O)OCH₃ → CH₃CH=C=O + CH₃O (R17)

or

CH₃CH(C=O)OCH₃ → C₂H₃(C=O)OCH₃ + H (R18)

followed by

C₂H₃(C=O)OCH₃ → C₂H₅CO + CH₃O (R19)

and the third radical CH₃CH₂(C=O)OCH₂ from R15 decomposes via:

CH₃CH₂(C=O)OCH₂ → C₂H₅CO + CH₂O (R20)

Rate of production (ROP) analysis for MP pyrolysis indicates that CO is produced by the following reactions:

CH₃OCO → CH₃O + CO (R21)

C₂H₃CO → C₂H₅ + CO (R22)

C₂H₅CO → C₂H₅ + CO (R23)

HCO + M → H + CO + M (R24)

And CO₂ is produced primarily from CH₃OCO with small contribution coming from C₂H₅CO₂:

CH₃OCO → CH₃ + CO₂ (R25)
It was noted above for high-temperature EP pyrolysis that the HOCO radical provides a crucial branching function by having two decomposition reactions that produce either CO or CO₂. The same function is provided for MP pyrolysis by the CH₃OCO decomposition reactions R21 and R25. Decomposition reaction R9 of MP produces CH₃OCO immediately. More CH₃OCO is provided from H atom abstraction reaction R13 from MP, followed by the decomposition reaction R16. Reactions R21 and R25 both appear in the sensitivity plots, Fig. 12(a) and Fig. 13(a) for CO and CO₂, reinforcing the central role of CH₃OCO radical in MP pyrolysis.

Ethylene is produced from MP through R16 and the decomposition of ethyl:

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and Curran et al. [39] favored production of CO at 1500 K by a ratio of 9:1. However, both mechanisms had modeled only EP oxidation conditions, where the decomposition of HOCO has very little effect or sensitivity, in contrast with the present pyrolysis conditions. Barker et al. [47] used master equation approach with an excited HOCO* intermediate to see how the branching ratio of products (CO₂ + H or CO + OH) varies with temperature and pressure. The rates provided by Barker et al. [47] were modified slightly (~ 50%) to increase the CO₂/CO ratio. The modified rates, giving a ratio of CO₂/CO at 1500 K of about 1.9, are:

\[
\begin{align*}
\text{HOCO} & \rightarrow \text{CO} + \text{OH} \quad k = 2.2 \times 10^{26} \ T^{-5.12} \ \exp(-27570/RT) \ \text{cm}^3\text{mol}^{-1}\text{s}^{-1} \\
\text{HOCO} & \rightarrow \text{CO}_2 + \text{H} \quad k = 2.0 \times 10^{36} \ T^{-8.11} \ \exp(-29060/RT) \ \text{cm}^3\text{mol}^{-1}\text{s}^{-1}
\end{align*}
\]

As shown in Figs. 12(b), 14(b) and 15, the relative ratio of the production of CH₃CH(C=O)OH to CH₂CH₂(C=O)OH has significant sensitivities on the production of CO, C₂H₄ and H₂O in the pyrolysis of EP. For these reactions, we used the rate expressions from Metcalfe et al. [3, 4] in our preliminary mechanism but increased the rate of R3, producing CH₂CH₂(C=O)OH, by a factor of 2 and reduced the rate of R2, which produces CH₃CH(C=O)OH, by a factor of 2. Thus the ratio of k2/k3 was reduced by a factor of 4 to improve the predicted levels of the measured species. Finally, rates of decomposition of the resonantly stabilized radical CH₃CH(C=O)OH were modified slightly, with the rate of reaction producing methyl ketene and OH reduced by 10% and the rate of reaction producing propenoic acid and H was increased by 10%, both relative to rates taken from Metcalfe et al. [3, 4].

As discussed earlier, the decomposition of CH₃OCO plays a very critical role in controlling the CO₂/CO ratio during methyl propanoate (MP) pyrolysis. The CH₃OCO decomposition reactions R21 and R25 have been studied extensively [19, 30, 48, 49] using both theoretical and kinetic modeling approaches. In a recent shock tube and kinetic modeling study of the pyrolysis of several methyl esters, Farooq et al. [19] observed that the balance between these reactions strongly influenced the product ratio of CO₂/CO in pyrolysis of MB, and their
analysis suggested that the same reactions would be similarly important for pyrolysis of any methyl ester fuel. The present study is very consistent with this observation. In the current work, the only significant mechanism modification made to improve agreement between experimental and kinetic modeling results for MP pyrolysis was to correct an error that was found in the thermochemistry of the CH$_3$OCO radical. It appears that the number of internal rotors in the methyl formate species (the basis for the thermochemistry of its radical, CH$_3$OCO) was inadvertently assumed to be one rotor, rather than the correct number of two, and this led to a significant error in the equilibrium constant of CH$_3$OCO. In the current kinetic mechanism of MP/EP, the rates of CH$_3$OCO decompositions to produce CH$_3$ + CO$_2$ or CH$_3$O + CO, R21 and R25, are written in the addition direction, with the decomposition rates determined from the relevant equilibrium constants. The error in the number of rotors produced decomposition reaction rates that favored the production of CH$_3$O + CO. When the thermochemistry was corrected by Glaude [50], the two decomposition reactions of CH$_3$OCO strongly favored production of CH$_3$ + CO$_2$. The sensitivity of the computed results for CO and CO$_2$ is evident in Figs. 12(a) and 13(a), and this correction in the decomposition rates made significant improvements in the computed results for these species in MP pyrolysis. In particular, the corrected thermochemistry for CH$_3$OCO increased the rate of R25 by more than a factor of 5. Our final values of the rates of reactions R21 and R25 agree well with rates used in recent studies [19, 30, 48, 49]. Thermochemistry for species in kinetic reaction mechanisms can provide sensitivity in computed results that can be comparable to that of reaction rate parameters, but the documentation for thermochemical parameters such as bond energies, heats and entropies of formation, and specific heats is not generally available. Tables of thermochemical parameters, usually provided in NASA coefficient formats, are widely exchanged among kinetic modeling researchers, and it is very easy for errors like that described here to occur and then be propagated rapidly amongst modeling researchers. In addition to correcting the thermochemistry for CH$_3$OCO, the rates of the decomposition of MP were adjusted slightly to decrease the CO production or increase the CO$_2$/CO ratio. The rates of R9 and R12 were increased by 50% and the rates of R10 and R11 were reduced by 25%, all relative to rates taken from Yang et al. [1].
The above changes in the kinetic parameters produced the final mechanism that was used for the computations summarized in Figs. 1, 2, and 5-15. The revised reaction rates used in the final mechanism are summarized in Table 1. The specific reactions described in this section were found to be particularly sensitive and all of them had not been tested or refined by previous kinetic modeling studies that were based on oxidation experiments. Use of pyrolysis conditions made it possible to have sufficient sensitivity to them to suggest corrections in their reaction rates. Improved rates have been determined for them, but the real result of the present kinetic modeling is that further studies of these reactions would be desirable. Four of these reactions involve complex decompositions of CH$_3$OCO and HOCO, which proceed via excited intermediate adducts, and others involve branching ratios of hydrocarbon radicals, some involving resonantly stabilized reactants or products.

Recently, there has been an increased interest in the chemical kinetics community to carry out uncertainty analysis of reaction mechanisms and the use of global uncertainty analysis tools for theoretical kinetics studies [51-53]. Such involved methods are beyond the scope of current work. However, a simple estimation-based analysis was carried out to estimate the uncertainty in the proposed Arrhenius pre-exponential factors. If $f_k$ is the uncertainty factor of the rate coefficient, the uncertainty limits of the rate parameters are $A_kf_k$ and $A_k/f_k$. The uncertainty factors are given in Table 1 for the reactions modified in the current work. These uncertainty factors are obtained by considering the measurement uncertainty and the sensitivity of the measured species to these rate constants. As discussed earlier, the combination of rate constants proposed here provide improved predictions of the species measured during MP and EP pyrolysis. For the uncertainty analysis, one specific rate constant was varied till it provided improved prediction of the species most sensitive to that rate constant. Measured profiles of CO and CO$_2$ are very sensitive to HOCO and CH$_3$OCO decomposition and this leads to relatively small uncertainty factors for reactions R7, R8, R21 and R25. Other rate constants are assigned relatively large uncertainty factors due to complicated sensitivities of measured species.
to these reactions. However, for all reactions listed in Table 1, the assigned uncertainty factors are smaller than those in the original mechanisms.

5. Conclusions

Concentration time-histories of CO, CO$_2$, C$_2$H$_4$, and H$_2$O were measured using shock tube / laser absorption methods to study the high temperature pyrolysis of methyl propanoate (MP) and ethyl propanoate (EP). The measured species time-histories are used to elaborate the effect of structural difference (methyl vs ethyl) on the production of radical, intermediate, and product species. Both fuels exhibit a two-stage pyrolysis process – a rapid first stage followed by a long relaxation stage leading to equilibrium. The present experimental conditions and available test times target the first pyrolysis stage where MP decays faster than EP. The pyrolysis of EP is initiated entirely by the six-centered molecular elimination reaction (R1) that makes ethylene and propanoic acid. This is followed by H abstraction reactions of propanoic acid and eventually the formation of HOCO radical which determines the ratio of CO/CO$_2$ production. Updating the rate constants of HOCO decomposition pathways and H abstractions of propanoic acid led to much-improved agreement between the experimental species data and model predictions. The pyrolysis of MP, on the other hand, is controlled initially by unimolecular decomposition and H abstraction reactions of MP. These reactions produce the important CH$_3$OCO radical which controls CO/CO$_2$ production much like the HOCO radical in EP pyrolysis. The updated rate constant / thermochemistry for the decomposition of CH$_3$OCO resulted in excellent agreement between measured and simulated concentrations. We believe that the refined pyrolysis mechanism for MP/EP will be very useful for the development of a comprehensive and validated chemical kinetic mechanism for biodiesel combustion.
Acknowledgments

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Supplementary Material

The kinetic and thermodynamic files for the final mechanism are provided as supplementary material.
References


30
### Tables

Table 1: Rate constants used in the final MP/EP pyrolysis mechanism.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>A</th>
<th>n</th>
<th>E</th>
<th>$f_k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R2</td>
<td>$\text{C}_2\text{H}_3(\text{C}=\text{O})\text{OH} + \text{H} \rightarrow \text{CH}_3\text{CH}(\text{C}=\text{O})\text{OH} + \text{H}_2$</td>
<td>$6.25\times10^{13}$</td>
<td>0</td>
<td>7300</td>
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<tr>
<td>R3</td>
<td>$\text{C}_2\text{H}_3(\text{C}=\text{O})\text{OH} + \text{H} \rightarrow \text{CH}_2\text{CH}_2(\text{C}=\text{O})\text{OH} + \text{H}_2$</td>
<td>$2.60\times10^{06}$</td>
<td>2.54</td>
<td>6756</td>
</tr>
<tr>
<td>R7</td>
<td>$\text{HOCO} \rightarrow \text{CO} + \text{OH}$</td>
<td>$2.20\times10^{26}$</td>
<td>-5.12</td>
<td>27570</td>
</tr>
<tr>
<td>R8</td>
<td>$\text{HOCO} \rightarrow \text{CO}_2 + \text{H}$</td>
<td>$2.00\times10^{06}$</td>
<td>-8.11</td>
<td>29060</td>
</tr>
<tr>
<td>R9</td>
<td>$\text{C}_2\text{H}_5 + \text{CH}_3\text{OCO} \rightarrow \text{MP}$</td>
<td>$1.20\times10^{13}$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>R10</td>
<td>$\text{CH}_3\text{COOCH}_3 + \text{CH}_3 \rightarrow \text{MP}$</td>
<td>$7.50\times10^{12}$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>R11</td>
<td>$\text{C}_2\text{H}_5\text{CO} + \text{CH}_3 \rightarrow \text{MP}$</td>
<td>$6.00\times10^{13}$</td>
<td>0</td>
<td>0</td>
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<tr>
<td>R12</td>
<td>$\text{C}_2\text{H}_5\text{CO}_2 + \text{CH}_3 \rightarrow \text{MP}$</td>
<td>$1.50\times10^{13}$</td>
<td>0</td>
<td>0</td>
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<tr>
<td>R21</td>
<td>$\text{CH}_3\text{O} + \text{CO} \rightarrow \text{CH}_3\text{OCO}$</td>
<td>$1.55\times10^{06}$</td>
<td>2.02</td>
<td>5730</td>
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<tr>
<td>R25</td>
<td>$\text{CH}_3 + \text{CO}_2 \rightarrow \text{CH}_3\text{OCO}$</td>
<td>$4.76\times10^{07}$</td>
<td>1.54</td>
<td>34700</td>
</tr>
</tbody>
</table>

Notes:

(a) $k = A \times \exp(-E/RT)$, The units are in cm$^3$, mol, s, cal.
(b) MP = CH$_3$CH$_2$(C=O)CH$_3$
(c) $f_k$ is the uncertainty factor
(d) These rate constants are optimized over the measured temperature range (1250 – 1750 K)
Figure 1. Simulated temperature using the present kinetic mechanism with constant pressure (CP) and constant volume (CV) adiabatic constraints. Initial conditions: $T = 1500 \text{ K}$, $P = 1.5 \text{ atm}$.
Figure 2. Computed species mole fractions using the final MP/EP kinetic mechanism from current work for (a) 1% MP/Ar, (b) 1% EP/Ar. Initial conditions: $T = 1500$ K, $P = 1.5$ atm.
Figure 3. Measured CO mole fraction profiles during the pyrolysis of (a) 1% MP/Ar, (b) 1% EP/Ar. Reflected shock temperatures are shown, whereas reflected shock pressures range from 1.25 to 1.5 atm.
Figure 4. Comparison of measured CO profiles (solid lines) with simulations (dash lines) using the preliminary kinetic mechanism [1, 2]. Reflected shock temperatures are shown, whereas reflected shock pressures range from 1.25 to 1.5 atm.
Figure 5. Comparison of measured CO profiles (solid lines) with simulations (dash lines) using the final MP/EP kinetic mechanism from current work. Experimental conditions are same as in Fig. 4.
Figure 6. CO fractional yield (ratio of CO mole fraction at 1 ms to the initial fuel mole fraction) for 1% MP/Ar and 1% EP/Ar pyrolysis. Symbols (connected by solid lines) represent measurements, dashed lines are predictions using the preliminary mechanism, and dotted lines are predictions using the final mechanism.

Methyl propanoate

Ethyl propanoate
Figure 7. Comparison of measured CO profiles (solid lines) with simulations (dash lines) using the final MP/EP kinetic mechanism from current work. Reflected shock temperatures are shown, whereas reflected shock pressures range from 1.25 to 1.5 atm.
Figure 8. CO$_2$ fractional yield (ratio of CO$_2$ mole fraction at 1 ms to the initial fuel mole fraction) for 1% MP/Ar and 1% EP/Ar pyrolysis. Symbols (connected by solid lines) represent measurements, dashed lines are predictions using the preliminary mechanism, and dotted lines are predictions using the final mechanism.
Figure 9. Comparison of measured ethylene profiles (solid lines) with simulations (dash lines) using the final MP/EP kinetic mechanism from current work. Reflected shock temperatures are shown, whereas reflected shock pressures range from 1.5 to 1.7 atm.
Figure 10. Comparison of measured water profiles (solid lines) with simulations (dash lines) using the final MP/EP kinetic mechanism from current work. Reflected shock temperatures are shown, whereas reflected shock pressures range from 1.5 to 1.7 atm.
Figure 11. Water fractional yield (ratio of H$_2$O mole fraction at 1 ms to the initial fuel mole fraction) for 1% EP/Ar pyrolysis. Symbols (connected by solid lines) represent measurements, dashed line is the prediction using the preliminary mechanism, and dotted line is the prediction using the final mechanism.
Figure 12. CO sensitivity for (a) 1% MP/Ar, (b) 1% EP/Ar pyrolysis. Initial conditions: T = 1500 K, P = 1.5 atm.
Figure 13. \( \text{CO}_2 \) sensitivity for (a) 1\% MP/Ar, (b) 1\% EP/Ar pyrolysis. Initial conditions: \( T = 1500 \text{ K}, P = 1.5 \text{ atm.} \)
Figure 14. Ethylene sensitivity for (a) 1% MP/Ar, (b) 1% EP/Ar pyrolysis. Initial conditions: $T = 1500$ K, $P = 1.5$ atm.
Figure 15. H$_2$O sensitivity for 1% EP/Ar pyrolysis. Initial conditions: T = 1500 K, P = 1.5 atm.