

Shock tube/laser absorption studies of the decomposition of methyl formate

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Abstract

Reaction rate coefficients for the major high-temperature methyl formate (MF, CH₃OCHO) decomposition pathways, MF → CH₃OH + CO (1), MF → CH₂O + CH₂O (2), and MF → CH₄ + CO₂ (3), were directly measured in a shock tube using laser absorption of CO (4.6 μm), CH₂O (306 nm) and CH₄ (3.4 μm). Experimental conditions ranged from 1202 to 1607 K and 1.36 to 1.72 atm, with mixtures varying in initial fuel concentration from 0.1% to 3% MF diluted in argon. The decomposition rate coefficients were determined by monitoring the formation rate of each target species immediately behind the reflected shock waves and modeling the species time-histories with a detailed kinetic mechanism [12]. The three measured rate coefficients can be well-described using two-parameter Arrhenius expressions over the temperature range in the present study: $k_1 = 1.1 \times 10^{13} \exp(-29556/T, \text{K}) \text{ s}^{-1}$, $k_2 = 2.6 \times 10^{12} \exp(-32052/T, \text{K}) \text{ s}^{-1}$, and $k_3 = 4.4 \times 10^{11} \exp(-29078/T, \text{K}) \text{ s}^{-1}$, all thought to be near their high-pressure limits. Uncertainties in the k_1 , k_2 and k_3 measurements were estimated to be ±25%, ±35%, and ±40%, respectively. We believe that these are the first direct high-temperature rate measurements for MF decomposition and all are in excellent agreement with the Dooley et al. [12] mechanism. In addition, by also monitoring methanol (CH₃OH) and MF concentration histories using a tunable CO₂ gas laser operating at 9.67 and 9.23 μm, respectively, all the major oxygen-carrying molecules were quantitatively detected in the reaction system. An oxygen balance analysis during MF decomposition shows that the multi-wavelength laser absorption strategy used in this study was able to track more than 97% of the initial oxygen atoms in the fuel. © 2012 The Combustion Institute. Published by Elsevier Inc. All rights reserved.

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1. Introduction

Biodiesel, typically derived from a variety of vegetable oils, animal fats [1], and algae [2], is

one of the sustainable alternatives to fossil fuels. It is an oxygenated, diesel-like fuel consisting primarily of fatty acid methyl esters (FAMEs). Methyl formate (MF), CH₃OCHO is the simplest methyl ester, and its study assists in understanding the effects of oxygenated chemical structure that are characteristic of biodiesel fuels on reactivity and pollutant formation. MF has also been found to be a byproduct of the oxidation of several proposed fuel alternatives and additives, such as

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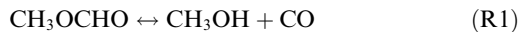
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dimethyl ether (DME), dimethoxymethane and 1,2-dimethoxyethane [3–5]. A fundamental study of MF kinetics is thus of immediate interest to fuel modelers.

The earliest study of MF pyrolysis was done by Steacie [6] who proposed that the dominant decomposition channel was to CO and CH₃OH (methanol). This pathway was confirmed by shock tube studies of Davis [7] showing the presence of methanol as a decomposition product of MF. Jain and Murwaha [8] observed the formation of CH₂O, H₂, and CO during MF pyrolysis at 760 K, reporting that the decomposition process is molecular and does not involve free radical reactions. Pereira and Isolani [9] detected large amounts of CH₃OH and CO together with smaller amounts of CH₄, CO₂ and C₃H₆, by studying the multiphoton gas-phase dissociation of MF.

In order to understand the observations of previous experimental studies, Francisco [10] performed an *ab initio* study of the decomposition pathways of MF, concluding that in addition to the most favorable decomposition of MF into CH₃OH and CO, other channels, such as decomposition to CH₂O, and to CH₄ and CO₂, are competitive in the gas phase. By studying the fuel-rich oxidation of MF in low-pressure burner-stabilized flames, Westbrook et al. [11] proposed a detailed sub-mechanism for MF oxidation that could reproduce the measured major species such as CO, H₂O and CO₂ in the flame. Very recently, Dooley et al. [12] have developed a comprehensive oxidation model for MF based on the experimental data from a flow reactor (3 atm and 0.5% fuel at 900 and 975 K), shock tube ignition delays (2.7, 5.4 and 9.2 atm, 1275–1935 K, 0.5% and 2.5% fuel), and laminar burning velocities (atmospheric pressure). The rate coefficients for the MF decomposition reactions were estimated from chemical group theory, and the A-factors were adjusted to fit the pyrolysis data at 975 K from flow reactor experiments. Metcalfe et al. [13] also investigated the energetics and kinetics of MF decomposition by high-level *ab initio* calculations and presented high-pressure-limit rate coefficients for the three major decomposition channels. Significant discrepancies of these three major decomposition rates were found between the Dooley et al. [12] mechanism and the calculations by Metcalfe et al. [13]. A subsequent study in low-pressure flames (22–30 Torr) by Dooley et al. [14] used the measured methanol profiles to test the chemical kinetic descriptions of MF decomposition. According to the authors, however, the most significant uncertainties in the kinetic model are in the rate coefficients describing the concerted elimination reactions of MF. Therefore, reliable rate measurements for MF decomposition are required to reach definite conclusions on this reaction system.

In this study, we have used a multi-wavelength laser absorption strategy to measure multiple species time-histories during MF pyrolysis in a shock tube. These target data enable the first direct high-temperature (>1200 K) measurements of the rate coefficients of MF decomposition, including the three major channels:



The measurements of CO, CH₄, and CH₂O time-histories were performed behind reflected shock waves at pressures between 1.36 and 1.72 atm, temperatures between 1202 and 1607 K, and with fuel concentration varying from 0.1% to 3%. The experiments were designed to maintain strong sensitivity (based on the Dooley et al. [12] mechanism) to the rate coefficients of interest. In addition, by also monitoring MF, methanol, and CO₂, together with CO, CH₄ and CH₂O, a detailed accounting of the oxygen balance in the MF pyrolysis system was achieved.

2. Experimental methods

2.1. Shock tube facility

All the experiments were performed in a high-purity stainless-steel shock tube with 15.24 cm inner diameter. The driven section has a length/diameter (*L/D*) ratio of 70, and is separated from the helium-filled driver section (with an *L/D* of 30) by a polycarbonate diaphragm. Properly executed, reflected shock wave experiments can generate stationary, spatially-uniform test gas mixtures under near-constant-volume conditions with near-instantaneous steps in temperature and pressure. Reflected shock temperatures and pressures were calculated using standard normal-shock relations and the measured incident shock speed (extrapolated to the end wall), with an uncertainty in temperature of ±1% over the highly-uniform test time of 1–2 ms. Further details about the shock tube can be found in [15]. Laser absorption and side-wall pressure measurements (using a Kistler 601B1 PZT) were made 2 cm from the shock tube end wall.

Research grade argon (99.999% pure, Praxair Inc.) was used without further purification. Methyl formate (>99% pure, Sigma–Aldrich) was frozen and degassed 3–5 times to remove dissolved volatiles before the mixtures were prepared. All test mixtures were manometrically prepared in a turbo-pumped stainless-steel mixing tank (14 L) with a magnetically driven stirrer. Between experiments, the shock tube driven section and mixing manifold were turbo-pumped

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