Kinetic studies of methyl acetate pyrolysis and oxidation in a flow reactor and a low-pressure flat flame using molecular-beam mass spectrometry

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Abstract

The combustion chemistry of methyl acetate (MA) pyrolysis and oxidation was studied experimentally in an atmospheric flow reactor and a low-pressure flat flame using molecular-beam mass spectrometry (MBMS). Rate constants such as H-abstraction of MA by O, H, OH, CH_3, and HO_2 radicals as well as MA radical decomposition were computed by high-level ab initio and RRKM master equation calculations. A new methyl acetate kinetic model was developed and compared to the experimental data along with other existing models. Two-dimensional direct numerical simulations were conducted and the results were used to validate the zero-dimensional prediction in a flow reactor. The MA pyrolysis results in the flow-reactor experiments showed that MA decomposition to $CH_3 + CH_3 + CO_2$ and $CH_3OH + CH_2CO$ are the dominant pathways, which is consistent with the theoretical prediction of the new model. In addition, a two-stage MA oxidation was observed between 800 K and 1050 K, suggesting the possible existence of low-temperature chemistry for MA oxidation. The low-pressure flame experiment at a rich condition suggested that MA has unique reaction pathways to form aldehydes, ketones, and acids. Comparison with previous kinetic models showed that the present model considerably improved the predictability of species-temperature histories in the flow reactor and successfully identifies the main reaction pathway of ketene and acetic acid in a low pressure flame for the first time.
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1. Introduction

Biodiesel has received significant attention as a renewable biofuel for transportation [1,2]. Biodiesel constituents, mainly methyl esters, have been intensively studied regarding their chemical

kinetics [3–7], ignition delays [8,9], flame structures, speeds, and extinction [10–13]. However, methyl ester kinetics in flames remain poorly predictable [10,11]. Small alkyl esters including methyl formate, acetate, and propanoate have very distinctive reactivity originating from their molecular structure [11], in which MA has the lowest reactivity [10,11]. As such, it is necessary to understand the uniqueness of MA kinetics.

Kinetic studies of MA are scarce and limited to flames and jet-stirred reactors (JSR) [12,14,15]. These experiments are not well-suited to examine the elementary fuel decomposition and oxidation pathways because the diffusion and mixing of existing radicals will bypass the slow fuel decomposition pathways involving H-abstraction reactions by radicals. In flames, the H-abstraction via radical diffusion from the flame zone plays a dominant role for fuel decomposition and oxidation. In JSR experiments kinetic studies of fuel decomposition and oxidation can be complicated by the issues of back-mixing and difference in local micro-mixing time. Recent experimental and theoretical results [16,17] show the branching ratio of MA decomposition and the rates of H-abstraction by radicals (e.g. OH) to be neither well-determined nor consistent. Moreover, few pressure-dependent MA radical decomposition reaction rates are available in the literature. Therefore, new theoretical and experimental studies are needed to characterize the kinetics of MA decomposition and oxidation. To bridge the gaps of knowledge, in this study the combustion kinetic of MA was investigated experimentally in an atmospheric flow reactor and a low-pressure flame using molecular-beam mass spectrometry (MBMS) to measure species profiles in fuel pyrolysis and oxidation. Additionally, high-level ab initio RRKM calculations were performed to provide the best prediction of key elementary reaction rates. A detailed kinetic model was developed and validated against the experimental data and compared to previous kinetic models. Important reaction pathways for fuel destruction and formation of intermediates and products were investigated.

2. Experimental methods

2.1. Flow-reactor experiments

The pyrolysis and oxidation studies of MA were performed in an atmospheric flow reactor coupled to an electron-impact (EI) MBMS at Princeton. Details of this system were described elsewhere [18]. The cylindrical quartz tube reactor (17 mm ID, 355 mm of length) was jacketed in copper sleeves and housed in a furnace. The reactor temperature was varied between 500 K and 1150 K and the gas temperature inside the reactor was measured. A uniform temperature profile (± 10 K) was maintained throughout the reactor. At the entrance of the flow reactor, a heating and expansion nozzle was used (2 mm ID) to achieve rapid heating of the mixture to the reactor temperature, with the residence time in the preheating zone less than 1% of the total time.

Helium, argon, and oxygen flow rates were controlled by mass flow controllers and premixed before the fuel vaporizer. MA was injected into the fuel vaporizer (500 K) by a syringe pump and fully mixed with the oxidizer stream before entering the preheating section. The mole fraction of MA was set to be 0.5% to ensure that the temperature rise is less than 30 K and the axial species diffusion flux is negligible. The experimental conditions are listed in Table 1.

Species profiles as a function of reactor temperature were quantified by EI-MBMS with a mass resolution of ~ 900. The mole fractions of main species such as MA, O_2, CH_4, CO, C_2H_6, C_2H_4, CH_3OH, and CO_2 in the flow reactor are derived from direct calibrations and uncertainties were estimated to be within 20%. For CH_2O and CH_2CO, the mole fraction was estimated based on their ionization cross sections provided by NIST electron-impact ionization cross section database. In the mass spectrum, CH_3OH and O_2, CO and C_2H_4 as well as CH_2O and C_2H_6 are partially separated at the same mass peak and the relative contribution of each species was derived by double Gaussian fitting. An example is shown in Supplemental Information (SI) I.

2.2. Low-pressure flame experiment

The low-pressure flame experiment was carried out in Bielefeld using an EI-MBMS instrument described previously in [19,20]. MA was evaporated at 400 mbar and 80 °C, using argon as carrier gas. A laminar premixed MA flame with a composition of MA/oxygen/argon (13.5 mol%/ 34.6 mol%/50 mol%), resulting in a stoichiometry of $\phi = 1.3$, and a respective cold gas velocity of 72.3 cm/s at 330 K was stabilized on a moveable water-cooled bronze McKenna-type burner with a matrix diameter of 64 mm. The gases were regulated by calibrated mass flow controllers (MKS) with an error less than 5% since gas conversion factors were applied.

Gas samples were extracted from the flame via a quartz cone (400 μm diameter, 25° opening angle) and expanded into the first pumping stage ($\sim 10^{-4}$ mbar), via a skimmer where reactions between the molecules are quenched immediately. The molecular beam entered the ionization region of the mass spectrometer ($\sim 10^{-6}$ mbar) and the sample was ionized by a pulsed EI source and detected by a reflectron time-of-flight MBMS with a mass resolution of ~ 4000.

Five ionization energies (10.5, 11.5, 12.5, 16.0, and 18.0 eV) were used to minimize fragmentation