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Structure of a Low Pressure Ethyl Pentanoate (Ethyl Valerate) Flame Studied by Flame Sampling Molecular Beam Mass Spectrometry with VUV Photoionization and Numerical Simulation

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Abstract

Mole fraction profiles of the species in a premixed ethyl pentanoate/oxygen/argon flame stabilized on a McKenna burner at 20 torr are acquired using flame sampling molecular-beam mass spectrometry with vacuum ultraviolet photoionization. The experimental results are compared with the results of numerical modeling using a chemical kinetic mechanism for ethyl pentanoate oxidation proposed in the literature.

Introduction

Biodiesel fuels and their blends with diesel fuel are of increasing interest as alternatives to petroleum-based transportation fuels not only because of reduction of consumption of petroleum, which is a source for diesel fuel production, but also because lower pollutant emissions (in particular, soot and polycyclic aromatic hydrocarbons - PAH) from Diesel engines are produced when biodiesel is added to diesel fuel or when biodiesel is used as an individual fuel. Therefore, the combustion chemistry of biodiesel fuels is of particular interest, because its understanding is vital for predicting operating performances of engines fueled by biodiesel. Most of the biodiesel are produced from soy, rapeseed or canola oils by transesterification with methanol or ethanol. Biodiesel fuels primarily consist of the same 5 major components: methyl (or ethyl) esters of palmic, stearic, oleinic, linoleic and linolenic acids in different proportions. Recent papers [1, 2] report the development of reaction kinetics mechanisms of these compounds, which are useful for studying biodiesel's ignition, combustion and engine emissions. However, the complexity of the molecular structure of biodiesel components and their low volatility makes it difficult to conduct gas-phase studies, which are helpful for developing kinetic mechanisms. As a consequence, the chemical kinetic models for combustion of the above-mentioned biodiesel components can be developed by the sequential upgrade of the combustion models starting from simple ethers. However, the development of these models is infeasible without the experimental data on combustion of surrogates of biodiesel components.

Ethyl esters obtained from the transesterification of triglycerides and bioethanol are now considered as more attractive than methyl esters that are derived by transesterification with methanol, which itself is mostly produced from syngas. Furthermore, exhaust analyses conducted on rapeseed oil methyl and ethyl esters showed that the emissions of NOx, CO, and smoke from the combustion of rapeseed oil ethyl ester were less harmful for the environment than that of rapeseed oil methyl ester [3].

Therefore, the combustion chemistry of ethyl esters is now of increasing interest.

Dayma et al. [4] contributed largely to improve our understanding of the combustion characteristics of ethyl pentanoate. They acquired new experimental data for its oxidation kinetics in a jet stirred reactor (concentration profiles of stable species were measured) and in a Spherical Combustion Chamber (Laminar Burning Velocities were determined). Dayma et al. [4] also proposed a new detailed kinetic reaction model (2719 reactions, 522 species) for ethyl pentanoate oxidation, which yielded good agreement with their measurement data.

However, combustion chemistry can differ significantly from the chemistry of oxidation in a reactor. Therefore, the aim of this work is to get insight into the chemical kinetics of ethyl pentanoate combustion using new experimental data on the structure of a premixed burner-stabilized low-pressure flame of ethyl pentanoate and the results of chemical kinetic modeling.

Approach

The structure of a stoichiometric premixed ethyl pentanoate/O_2/Ar flame is studied here. The flame was stabilized on a standard McKenna burner 60 mm in diameter at a pressure of 20 Torr. The total flow rate of the gas mixture through the burner is maintained constant and equal to 4 SLM.

Molecular beam mass spectrometry with photoionization by synchrotron VUV radiation was used for the flame study. The experimental setup is located at the Advanced Light Source (ALS) at the Lawrence Berkeley National Laboratory, CA, USA. The setup consists of a low-pressure combustion chamber (I), differentially pumped chamber (II) with molecular beam sampling system and photoionization chamber (III) with a reflectron time of flight mass spectrometer

Fig. 1. Schematic of the experimental setup.

(Fig. 1). Sampling was performed at different heights above the burner surface using a quartz conic probe with the opening angle of $40°$ and the orifice diameter 0.4 mm. To take the central part of the molecular beam a nickel skimmer was used. Its tip was located at 20 mm from the probe tip. The sample enters the ionization chamber, where the ionization of the gas under the influence of synchrotron radiation occur.

The flow rates of the fresh mixture components are set by mass flow controllers (MKS Instruments Inc.). To measure the pressure in the chamber I a capacitive manometer MKS Instruments Inc. is used; the pressure in the chamber I is adjusted by the valve from MKS Instruments Inc. controlled by the pressure gauge in chamber I. The syringe pump ISCO. Inc. is used to feed the gas mixture with the liquid fuel.

Ionizing synchrotron radiation was supplied from a storage ring with a particle energy 1900 MeV through an undulator with a Seya–Namioka monochromator (an average photon flux of 10^{14} s^{-1}). Higher-order harmonics were eliminated from the emission spectrum using a gas filter (He or Ar). The photon flux was measured by a silicon photodiode (SXUV-100, Intern. Radiation Detectors, Inc.) to normalize the ion signal. The resulting ions
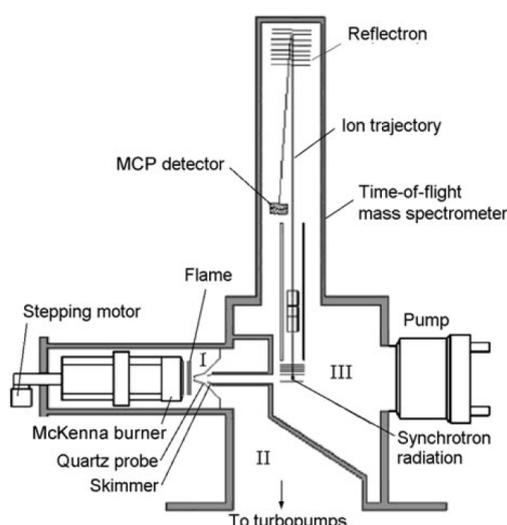
were analyzed using Kaesdorf reflectron time-of-flight mass spectrometer. The mass resolution of the mass spectrometer is m/Δm ~ 4000.

The ion signal intensities normalized to the photon flux were measured and plotted versus: (a) the distance from the burner to the tip of the probe at a constant photon energy (9, 9.5, 10, 10.4, 11.5, 12.3, 13.5, 14.35, 16.2, 16.65 eV); (b) the photon energy with the probe located at the center of the luminous zone. The first plots provide information on the spatial distribution of the species in the flame, and the second are photoionization efficiency curves needed to identify flame species. The error in the determination of the ionization energy did not exceed 0.05 eV.

Numerical simulation of the flame structure was performed using PREMIX code from the CHEMKIN II program suite. A detailed chemical kinetic reaction mechanism for ethyl pentanoate oxidation [4] was used for the modeling. The mechanism involves 522 species and 2719 reactions.

Results and Discussion

Figures 2 and 3 show as an example the screenshots of the window of the measurements control program. The window shown in Fig. 2 corresponds to the mode of the scanning of the distance from the burner surface at a fixed photon energy, and the window in Fig. 3 corresponds to the scanning mode of the photon energy at a fixed distance from the burner surface. In Figures 2 and 3, the abscissa is the time-of-flight of the ions to the detector, and the ordinate is the value, proportional to the distance from the burner surface to the tip of the probe (Fig. 2), and the photon energy (Fig. 3). Lighter color corresponds to a higher signal intensity.
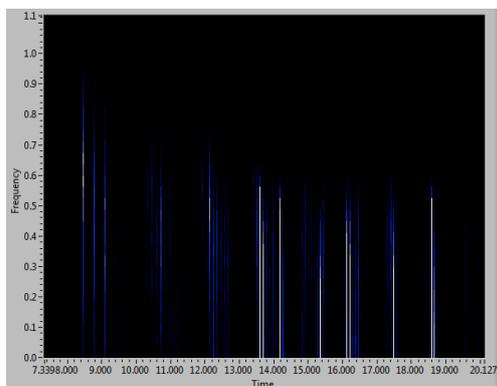

Fig. 2. Screenshot of the window of the measurements control program in the mode of scanning of the distance from the burner surface to the tip of the probe
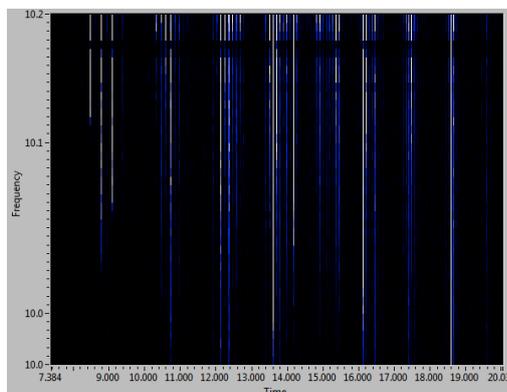

Fig. 3. Screenshot of the window of the measurements control program in the mode of photon energy scanning.

In the flame studied, the intensity profiles of the following species were measured: reagents (ethyl pentanoate, O_2), major products (CO, CO_2, H_2, H_2O), as well as a large number of intermediates such as methyl radical (CH_3), methane (CH_4), acetylene (C_2H_2), ethylene (C_2H_4), formaldehyde (CH_2O), methanol (CH_3OH), propyne (C_3H_4), ketene (C_2H_2O), propene (C_3H_6), acetaldehyde (C_2H_4O), propane (C_3H_8), vinyl acetylene (C_4H_4), 1,3-butadiene (C_4H_6), butene-2 and butene-1 (C_4H_6), acetone (C_3H_6O), pentene (C_5H_{10}) and others. The measurements results are compared with the results of numerical modeling. The mechanism used satisfactorily reproduces the measurement data. However, for some species the discrepancies between the experimental data and modeling results are observed.

Conclusion

Mole fraction profiles of the species in a premixed ethyl pentanoate/oxygen/argon flame stabilized on a MacKenna burner at 20 Torr are acquired using flame sampling molecular-beam mass spectrometry with vacuum ultraviolet photoionization. The experimental results are compared with the results of numerical modeling using a chemical kinetic mechanism for ethyl pentanoate oxidation proposed in the literature. The results obtained in this work could be used for development and validation of more complex models of combustion of biofuels based on ethyl esters.

References

[1] C.K.Westbrook, C.V. Naik, O. Herbinet, W.J. Pitz, M. Mehl, S.M. Sarathy, H.J. Curran, Combustion and Flame 158 (4) (2011) 742-755.

[2] J.Y.W. Lai, K.C. Lin, A. Violi, Progress in Energy and Combustion Science 37(1) (2011) 1-14.

[3] Makareviciene, V.; Janulis, P. Environmental effect of rapeseed oil ethyl ester. Renewable Energy 2003, 28 (15), 2395−2403.

[4] G. Dayma, F. Halter, F. Foucher, C. Togbé, C. Mounaim-Rousselle, P. Dagaut, Experimental and Detailed Kinetic Modeling Study of Ethyl Pentanoate (Ethyl Valerate) Oxidation in a Jet Stirred Reactor and Laminar Burning Velocities in a Spherical Combustion Chamber, Energy and Fuels, 2012, 26, 4735−4748.