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Structure of Low Pressure Methyl 3-Hexenoate and Methyl Hexanoate/n-Heptane flames studied by Molecular Beam Mass Spectrometry

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Abstract

Mole fraction profiles of the species in a premixed methyl 3-hexenoate/oxygen/argon and methyl hexanoate/n-heptane flames stabilized on a McKenna burner at 15 and 20 torr are acquired using flame sampling molecular-beam mass spectrometry with vacuum ultraviolet photoionization. Influence of the studied flames composition on concentrations of different flame intermediates have been investigated.

Introduction

Alternative fuels on the basis of oxygenates cause an increasing interest because of a need in reducing of raw oil consumption and search for renewable energy sources for power engineering and transportation. An important feature of these fuels is their production from plant raw materials including uneatable (for people) biomass. Recently there is a special interest in biofuels which are methyl and ethyl esters produced from vegetable oils and animal fat by reesterification. Main features of these fuels are approximately the same density, viscosity and cetane number as those of conventional diesel fuels. It makes possible their application as individual fuels or in mixture with conventional ones without modification of the existing engines. Besides, in various studies it was demonstrated that under certain conditions a replacement of conventional fuel for biodiesel resulted in decrease in emissions of CO and NO_x in internal combustion engines [1, 2].

But investigation of biodiesel fuels by most of scientific methods is hindered because of their complex molecular structure and high molecular weight. Besides, the mechanisms for combustion biodiesel components are too complex and their use for modeling is very expensive.

Understanding of the combustion mechanism for biofuels actually reduces to study of influence of an ester group on the combustion process. Therefore, it is usual to study more light esters with shorter carbon chain. In particular some papers on experimental investigations of the structure of laminar flames of esters with chain length up to C₆ [3].

The objective of present research is to measure the structure of light methyl esters which were not studied earlier. The structure of stoichiometric and rich flames of methyl 3-hexenoate and mixture of methyl hexanoate with heptane was measured at low pressure. The first two flames were studied to reveal the influence of double C=C bond on the combustion mechanism. The last flame is a model fuel for a mixture of conventional and biodiesel fuels.



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Approach

Structure of stoichiometric ($\phi = 1.0$) and fuel rich ($\phi = 1.3$) methyl 3-hexenoate flames stabilized at a pressure of 15 torr, and one stoichiometric flame of methyl hexanoate/n-heptane mixture (with molar ratio 1:1) stabilized at 20 torr has been studied in this work. Molar compositions of studied flames were (fuel/O₂/Ar): 0.05/0.45/0.5 and 0.063/0.437/0.5 for a two methyl 3-hexenoate flames correspondingly and 0.044/0.455/0.5 for flame of methyl hexanoate/n-heptane fuel mixture. The total flow rate of the gas mixture through the burner was maintained constant and equal to 3 SLM in all flames. The flow rates of the fresh mixture components are set by mass flow controllers (MKS Instruments Inc.). The syringe pump ISCO. Inc. is used to feed the gas mixture with the liquid fuel.

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 [4]. 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.

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.

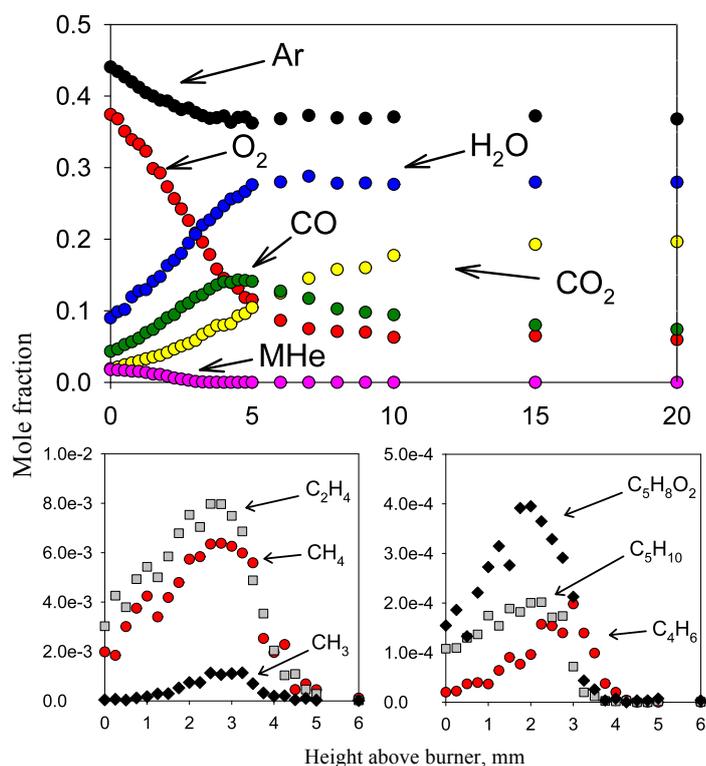


Fig.1. Mole fraction profiles of different species measured in a flame of methyl hexanoate/n-heptane fuel mixture.

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 $m/\Delta m \sim 4000$.

Results and Discussion

Implication of a high resolution mass-spectrometry technique allowed to achieve not only high accuracy of

experimental measurements, but also to separate mass peaks of different intermediates with the same m/z ratio. Mole fraction profiles of all major species: argon, oxygen, water, carbon monoxide, carbon dioxide, methyl 3-hexenoate, methyl hexanoate and n-heptane, were obtained in all studied flames. Also profiles of many different intermediates were measured, including the following species: methyl radical (CH_3), methane (CH_4), acetylene (C_2H_2), ethylene (C_2H_4), formaldehyde (CH_2O), ethane (C_2H_6), methanol (CH_3OH), propargyl radical (C_3H_3), allene (C_3H_4), propyne (C_3H_4), allyl radical (C_3H_5), ketene (CH_2CO), propene (C_3H_6), vinyl alcohol (CH_2CHOH), acetaldehyde (CH_3CHO), propane (C_3H_8), vinylacetylene (C_4H_4), butadiene (C_4H_6), 1-butene (C_4H_8), 1-pentene (C_5H_{10}), butanal ($\text{C}_4\text{H}_8\text{O}$), 1-hexene (C_6H_{12}), methyl acrylate ($\text{C}_4\text{H}_6\text{O}_2$), methyl propanoate ($\text{C}_4\text{H}_8\text{O}_2$), methyl 3-butenolate ($\text{C}_5\text{H}_8\text{O}_2$) and methyl butanoate ($\text{C}_5\text{H}_{10}\text{O}_2$).

Some of experimental results obtained in a flame of methyl hexanoate/n-heptane fuel mixture are presented on a Figure 1. Here can be seen mole fraction profiles of major stable species (top diagram), and also profiles of several light (left diagram) and heavy (right diagram) flame intermediates. The data obtained allows to analyze some specific details in combustion of these fuels and to make some preliminary conclusions about the reaction paths of their oxidation. This data is also important for validation of chemical kinetic mechanisms for methyl esters combustion, which are actively developing now.

Conclusion

A new data on mole fraction profiles of different species in a premixed methyl 3-hexenoate/oxygen/argon flames of stoichiometric and fuel-rich composition and one stoichiometric methyl hexanoate/n-heptane/oxygen/argon flame stabilized on a MacKenna burner at 15 torr and 20 torr are acquired using flame sampling molecular-beam mass spectrometry with vacuum ultraviolet photoionization. Differences in concentrations of several flame intermediates have been analyzed. The data obtained can be used for validation and testing of methyl hexanoate and methyl hexenoate combustion mechanisms.

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