**Photoionization Mass Spectrometry and Modeling Study of a
Low-Pressure Premixed Flame of Ethyl Pentanoate (Ethyl
Valerate)**

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Abstract

In order to get insight into the decomposition and high-temperature oxidation kinetics of ethyl pentanoate in combustion processes, a stoichiometric premixed burner-stabilized flame of ethyl pentanoate/O₂/Ar mixture at low pressure (20 torr) was investigated by molecular-beam mass spectrometry combined with single-photon ionization by vacuum ultraviolet radiation from the Advanced Light Source (ALS) in Berkeley, CA, USA. Mole fraction profiles of 43 species were measured in the flame and compared with those calculated using a detailed chemical kinetic mechanism proposed by Dayma et al. [Energy Fuels, 26 (2012) 4735-4748] for ethyl pentanoate oxidation. Although mole fraction profiles of major species and several intermediates were predicted quite accurately by the model, significant discrepancies between the measured and modeled peak mole fractions of many intermediates in the flame were observed. A kinetic analysis of the main reaction pathways of ethyl pentanoate oxidation was performed to trace the origins of these discrepancies. It was concluded that the reaction pathways responsible for consumption of primary radicals formed directly from the fuel molecule as well as of the products of successive β -scission reactions should be revised when developing a next-generation combustion model for ethyl pentanoate.

Keywords: biofuel, ethyl pentanoate, premixed flame, molecular-beam mass spectrometry, chemical kinetic modeling

1. Introduction

Biodiesel fuels are produced usually from soy, rapeseed, or canola oils by transesterification with methanol or ethanol [1] and primarily consist of the same 5 major components: methyl (or, respectively, ethyl) esters of palmitic, stearic, oleic, linoleic and linolenic acids in different proportions. The biofuels based on the ethyl esters (second-generation biofuels) are now considered as more attractive and preferable than those based on methyl esters (first-generation biofuels), because ethanol used for the esters production is also derived from biological raw materials, whereas methanol is mostly produced from syngas (coal). Furthermore, exhaust analyses conducted on rapeseed oil methyl and ethyl esters showed that the emissions of NO_x , CO, and smoke from the combustion of rapeseed oil ethyl ester were less harmful for the environment than that of rapeseed oil methyl ester [2]. Therefore, the combustion chemistry of ethyl esters is now of increasing interest.

However, the complexity of the molecular structure of biodiesel components and their low volatility make 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 small esters. The development and validation of these models is infeasible without experimental data on oxidation and combustion of surrogates of biodiesel components.

To date, the detailed kinetic mechanisms for small ethyl esters (ethyl formate, ethyl acetate, ethyl propionate) have been developed and validated against numerous experimental data [3-10]. The detailed kinetic mechanism of oxidation of ethyl

butanoate was developed on the basis of experimental data obtained in a shock tube [11] and in a laminar tubular plug flow reactor [12].

The next in order of the length of alkyl chain is ethyl pentanoate (ethyl valerate). Dayma et al. [13-14] contributed largely to improve our understanding of the oxidation and combustion mechanism of this ester. They studied its oxidation kinetics in a jet-stirred reactor (mole fractions of stable species in the range from 560 to 1160 K at 10 atm were measured) and measured the laminar burning velocities of ethyl pentanoate–air mixtures in the pressure range 1-5 atm in a spherical combustion chamber for equivalence ratios in the range 0.7–1.4. Dayma et al. [13] also proposed a new detailed kinetic reaction model (2719 reactions, 522 species) for ethyl pentanoate oxidation, which yielded good agreement with their measurement data.

The aim of this study is to extend the range of validation targets for ethyl pentanoate combustion modeling from the previously investigated low-temperature oxidation chemistry to detailed species measurements in the high-temperature regime. The data on the mole fractions of flame intermediates in burner-stabilized premixed flames of fuels are of prime importance for understanding their combustion chemistry. However, such data were reported only for ethyl esters of C₁-C₃ carboxylic acids [3–6]. Therefore, the objectives of this study are: (1) to report experimental mole fraction data of a low-pressure premixed flame of ethyl pentanoate (EPE), which are necessary for the development of a future model of biodiesel surrogates based on ethyl esters; (2) to validate a detailed chemical kinetic reaction mechanism for ethyl pentanoate oxidation, proposed previously by Dayma et al. [13], against new experimental data; and (3) to get insight into the kinetics of decomposition and

oxidation of ethyl pentanoate in the flame. However, it is beyond the scope of this contribution to present a newly updated chemically detailed model for the high- and low-temperature oxidation of EPE.

2. Experimental and modeling details

A burner-stabilized stoichiometric premixed flame of ethyl pentanoate was examined at low pressure conditions (20 torr) using a time-of-flight mass spectrometer with molecular beam flame sampling system and with photoionization by tunable vacuum ultraviolet (VUV) synchrotron radiation generated at the Advanced Light Source (ALS) of Lawrence Berkeley National Laboratory. Details on the experimental techniques used at the ALS have been presented in detail in previous publications [15–18].

A premixed laminar stoichiometric ($\phi = 1.0$) EPE/O₂/Ar flame was stabilized on a standard McKenna burner 60 mm in diameter. Using the ISCO 500D pump, the liquid fuel (EPE) was supplied into the vaporizer, the temperature of which was kept at 200°C. The fuel vapors together with argon were then supplied into the burner through a heated line. The temperature of the burner surface was maintained at 50°C using thermostated water flow. The cold-gas molecular composition was as follows: 50% Ar, 45.2% O₂, and 4.8% EPE ($C/O = 0.336$, $D = [O_2]/([O_2]+[Ar]) = 0.475$). The total flow rate of the gas mixture through the burner was maintained to be equal to 3 standard liters per minute.

Flame sampling was performed using a quartz conic probe with the opening angle of 40° and the orifice diameter of 0.35 mm. The sampled gas formed a

molecular beam. 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 entered the ionization chamber, where the ionization of the gas under the influence of synchrotron radiation occurred. The resulting photo-ions were analyzed using a custom-built reflectron time-of-flight mass spectrometer. The mass resolution of the mass spectrometer was $m/\Delta m \approx 1800$ for $m/z \approx 28$, which allowed us to separate some flame intermediates having very close m/z ratio but different number of C, H and O atoms (e.g. CO and C₂H₄, propene and ketene, etc.).

By moving the burner toward or away from the sampling cone tip, we performed measurements at different positions within the flame (burner scans). The ion signals were eventually converted into spatial profiles of the species mole fractions using a procedure described by Cool et al. [16], which was also used in our previous works [19, 20]. The uncertainty of determining the mole fraction of the flame reactants and major products (CO, CO₂, H₂O, H₂) was estimated to be $\pm 15\%$ of the maximum mole fraction values. For intermediate species calibrated directly, mole fractions were determined to be within an uncertainty of 20% (CH₄, C₂H₂, C₂H₄, C₄H₈). For other intermediates, especially those with unknown photoionization cross sections, the error could be as large as a factor of 2 or 3. Measurements were also performed at a fixed burner position for a range of photon energies to yield photoionization efficiency curves for flame species, which are useful for identifications of species of equal or near-equal masses.

Flame simulations were performed using the PREMIX code from the CHEMKIN-II package. Multi-component and thermal diffusion options were taken

into account in the calculations. A detailed chemical kinetic reaction mechanism for ethyl pentanoate oxidation [13] was used for the modeling. The mechanism involves 522 species and 2719 reactions. It was originally developed to predict the low-temperature chemistry of EPE at pressures 1-10 bar and especially the pressure-dependent radical-radical recombination reaction rates might not be accurately described to cover an extended pressure range from 20 Torr (26.7 mbar) to 1 bar.

3. Results and discussion

In total, 43 species were detected in the stoichiometric premixed flame of ethyl pentanoate and their mole fraction profiles determined. The species identified in the flame together with their ionization energies (IE) from reference data, the photon energies (E) used in the present experiments for measurements of their profiles and the photoionization cross sections (σ) used to determine the molecule-specific absolute mole fraction values are listed in Table 1. For some species photoionization cross-sections were unknown and they were estimated to be similar as for the species with analogous molecular structure.

Table 1. Species measured in the flame. m/z : mass-to-charge ratio, IE: ionization energy; E: photon energies used; σ : photoionization cross section (where needed).

m/z	Formula	Species	IE (eV)	E (eV)	σ (Mb)
2	H ₂	Hydrogen	15.43	16.2	-
15	CH ₃	Methyl radical	9.84	10.0	4.78
16	CH ₄	Methane	12.61	13.2	4.72
18	H ₂ O	Water	12.62	14.35	-
26	C ₂ H ₂	Acetylene	11.4	11.5	18.26
28	C ₂ H ₄	Ethylene	10.51	11	7.79
28	CO	Carbon monoxide	14.01	14.35	-

29	C ₂ H ₅	Ethyl radical	-	9.5	4.36
30	H ₂ CO	Formaldehyde	10.88	11.0	9.02
30	C ₂ H ₆	Ethane	11.52	12.3	13.29
32	CH ₃ OH	Methanol	10.84	11.0	3.33
32	O ₂	Oxygen	12.07	14.35	-
39	C ₃ H ₃	Propargyl	8.68	9.5	26.56
40	a-C ₃ H ₄	Allene	9.69	10	5.66
40	p-C ₃ H ₄	Propyne	10.36	10.5	18.9
40	Ar	Argon	15.76	16.2	-
41	C ₃ H ₅	Allyl	8.02	9.5	5.87
42	C ₃ H ₆	Propene	9.73	10.0	7.05
42	CH ₂ CO	Ketene	9.62	9.7	6.57
44	C ₂ H ₄ O	Acetaldehyde	10.23	10.5	6.69
44	C ₂ H ₃ OH	Ethenol		9.5	1.7
44	C ₃ H ₈	Propane	10.94	11.5	11.48
44	CO ₂	Carbon dioxide	13.78	14.35	18.21
46	CH ₂ O ₂	Formic acid	11.33	11.5	5.28
46	C ₂ H ₆ O	Dimethyl ether	10.03	10.5	8.22
46	C ₂ H ₅ OH	Ethanol	10.48	11.0	4.88
50	C ₄ H ₂	Diacetylene	10.17	11.0	25.79
52	C ₄ H ₄	Vinylacetylene	9.58	9.7	10
54	C ₄ H ₆	1,3-Butadiene	9.07	9.5	8.48
56	C ₄ H ₈	1-Butene	9.55	10	9.43
56	C ₄ H ₈	2-Butene	9.1	9.5	7.37
56	C ₃ H ₄ O	Methylketene	8.95	9.5	7.37
58	C ₃ H ₆ O	Acetone	9.7	10	7.71
58	C ₄ H ₁₀	n+i-Butane	10.53, 10.68	11	3.4
60	C ₃ H ₈ O	n-propanol	10.22	10.5	3.5
70	C ₅ H ₁₀	2-pentene	9.49	9.5	10
70	C ₅ H ₁₀	1-pentene	-	9.7	6.29
72	nC ₅ H ₁₂	n-pentane	10.28	11.0	12.75
72	C ₃ H ₄ O ₂	2-propenoic acid	10.60	11.0	10
84	C ₅ H ₈ O	Pental	-	9.5	2
100	C ₅ H ₈ O ₂	Ethyl-2-propenoate	-	10.5	4.66
114	C ₆ H ₁₀ O ₂	Ethyl-3-butenate	-	9.7	2
130	C ₇ H ₁₄ O ₂	Ethyl pentanoate	11.0	10.0	-

In Fig. 1, experimental mole fraction profiles of reactants and major flame products are represented and compared with the modeling results. Moreover, the temperature profile, which was used as input data for the flame simulations, is also plotted in this figure. The experimental temperature profile was derived from the temperature dependence of the sampling rate through the quartz nozzle, which was

determined by measuring the pressure in the chamber between the sampling cone and skimmer. The determination of a temperature profile in this way is a useful approximation for modeling MBMS data [21-23] that eliminates the need to shift simulated profiles. This approach requires, however, the temperature of exhaust gases in the vicinity of the sampling cone tip to be determined independently. We supposed this temperature to be within the range 1600-2100 K (typical temperature in final products of methyl esters in similar conditions [20]), and performed the flame structure simulations using the temperature profiles constructed on the assumption of different exhaust gas temperatures from the abovementioned range (using increment of 100 K). The calculations using the temperature profile with 1700 K in the post-flame zone provided the best fit to experimental data on mole fraction profiles of major flame species (see Fig. 1), as compared to the calculations using other temperature profiles (see Fig. 1S in the supplemental material). Fig. 1S also shows that variation of the post-flame temperature within the range 1600-2100 K did not result in any essential changes in the calculated mole fraction profiles of many intermediates. This allowed us to make a conclusion that the approach described above for determining the temperature profile and performing the flame simulations using this profile can be useful, at least in our flame conditions, for the kinetic mechanism validation. Uncertainty of this method of temperature determination is defined by an ambiguity of selection of the post-flame temperature and estimated to be ± 100 K in current conditions.

Fig. 1. Temperature profile and mole fraction profiles of reactants and main stable products in the flame. Symbols: experiment, lines: modeling.

As can be seen from Fig. 1, the mole fractions of the flame reactants (EPE, O₂, Ar) and the major flame products (CO, CO₂, H₂O, H₂) through the flame zone are reproduced by the model quite well. Deviations are within the experimental uncertainties. Post-flame mole fractions of the species predicted by the model also agree with the experimental data.

Figures 2 and 3 show experimental mole fraction profiles of intermediate hydrocarbons C_xH_y and oxygenates that were detected in the flame. Calculated mole fraction profiles of those species that are involved in the kinetic mechanism, are also plotted in these figures for comparison with the measurement data. Ethenol, dimethyl ether, pentanal and n-propanol were identified in the flame, but the model does not include the reactions involving these species, and therefore their calculated mole fraction profiles are not represented in Fig. 3.

Fig. 2. Mole fraction profiles of intermediate hydrocarbon species (C_xH_y) in the flame. Symbols: experiment, lines: modeling.

Fig. 3. Mole fraction profiles of oxygenated intermediates in the flame. Symbols: experiment, lines: modeling.

As can be seen from the Figs. 2 and 3, the model predicts the position of the mole fraction peaks quite accurately for the majority of the flame intermediates. It should be also noted that for many species the mechanism predicts their mole fraction in the vicinity of the burner surface to be significantly lower (close to zero) than the corresponding peak mole fractions. However, according to the measurements, the mole fraction near the burner is quite high and in some cases (C_2H_6 , acetaldehyde, 2-butene etc.) it is only slightly lower than the peak mole fraction of the species. The early formation of some of these intermediates (ethylene, propene, 2-butene, and acetaldehyde) close to the burner surface is related to the unimolecular decomposition of the different fuel radicals. The underestimation of acetaldehyde and C_3H_6 close to the burner surface by the model predictions in comparison to the experimental data, can be seen as evidence for the need to update the detailed chemistry in the models. It is also obvious that the oxidation of C_3H_6 to C_3H_5 , C_3H_4 , and C_3H_3 is not described accurately in the model calculations, as is the oxidation of 1-butene in the analogous reaction sequence for the C_4 species. The underprediction of ketene results from a not sufficient description of the acetaldehyde oxidation.

As is seen from Fig. 2, the model quite accurately (within experimental errors) predicts the peak mole fractions only for several C_xH_y species: CH_3 , C_2H_2 , C_2H_4 , C_2H_5 , 1,3-butadiene. However, for other hydrocarbons shown in Fig. 2 the predictions are beyond the measurement uncertainties. For some species, the discrepancy exceeds a factor of 8 (diacetylene, vinylacetylene, 1-pentene). For most of these species the model underpredicts the peak mole fractions. Overprediction can be seen only for ethane, 1-butene, iso- and n-butane, and for n-pentane.

However, the peak mole fractions of oxygenated hydrocarbons are reproduced by the model much better (Fig. 3). Significant discrepancies between the calculations and measurement data are observed only for ketene (underpredicted by ~8 times), ethanol (overpredicted by ~3 times), ethyl-3-butenate (overpredicted by ~10 times) and methylketene (underpredicted by several orders of magnitude).

Therefore, we come to a conclusion that despite some discrepancies the mechanism that we used adequately predicts peak mole fractions of oxygenated intermediates, but does not provide a good prediction of peak mole fractions of the majority of the C_xH_y intermediates. This observation can probably be explained by the fact that this model was developed based on the data for oxidation kinetics of EPE in a jet-stirred reactor [13], where the reactions involving peroxy compounds play more important role and therefore the chemistry of formation of oxygen-containing species is represented in the mechanism more thoroughly. Although this model was shown [13] to reproduce quite accurately the burning velocities of EPE/air mixtures in the range of equivalence ratios (0.7-1.4) and pressures (1-10 atm), our measurements showed that it is unable to predict the chemical structure of the low-pressure EPE flame accurately enough.

To trace the possible origins of the observed discrepancies, we performed a kinetic analysis of the main reaction pathways responsible for oxidation of ethyl pentanoate in the flame, as it was performed by Dayma et al. [13] for the jet-stirred reactor at 620 and 830 K.

The analysis for the flame conditions was performed in terms of the contributions (in percents) of the integrated rate of each individual reaction to the total

integrated rate of consumption of the selected species in the entire flame. An integrated reaction rate (mol/cm^3) was calculated in the same way as was done in previous works [20, 24, 25]:

$$\omega_i = \int_0^\infty \omega'_i dt = \int_0^\infty \frac{\omega'_i}{v} dx$$

where ω'_i is local rate of i^{th} reaction, $\text{mol}/(\text{cm}^3\text{s})$, v is local gas velocity (cm/s), x is distance from the burner (integration is carried out over the entire flame zone). To calculate the total integrated rate of consumption of a selected species, the summation was performed over all possible reactions associated with consumption of every species.

The routes of EPE oxidation in the flame, represented in Fig. 4, are shown with the percent values, representing contributions of the integrated rate of each pathway to the total integrated rate of consumption of the selected species in the entire flame. Detailed explanation of the nomenclature used in Fig. 4 is provided in the supplementary materials. According to the model, EPE is consumed mostly (95%) due to H-abstraction in the reactions with the main flame radicals (H, O, OH) to form six primary radicals, which are shown in the diagram as epeXj. Only 5 % of EPE is consumed due to molecular elimination of ethylene. The primary epeXj radical is consumed largely due to β - scission reactions (77%) and the reactions of O_2 addition (22%) yielding peroxy compounds (epeXOO). These latter could give then alkoxy compounds (epeXo) (52%), ethyl pentenoates (epeXd) (27%) or isomerize into hydroperoxy species (epeXOOHYj) (21%).

Fig. 4. Reaction pathways from the kinetic modeling of ethyl pentanoate combustion in the conditions considered.

However, according to previous findings, see e.g. [20], the contribution of the reactions with O_2 to esters consumption in the flames is negligible. Therefore, in the mechanism used in this work, the contribution of O_2 additions in the flame seems to be overestimated. We argue that this fact can then indeed explain the significant underestimation of C_xH_y hydrocarbon concentrations, which are basically the products of β -scission and recombination reactions. In order to improve the agreement between our experimental data and modeling results and therefore to check our assumption, we excluded from the mechanism the reactions of $epeXj$ radicals with oxygen, their products and related successive reactions, which are important only for low-temperature conditions. This modification, however, did not lead to any notable changes in the peak mole fractions of the species and their profiles despite the fact that the route $epeXj \rightarrow \beta$ -scissions products contributes now with 99% to the consumption of the $epeXj$ radicals (as compared with 77% in the original mechanism, Fig. 4).

Further analysis of the original mechanism (Fig.4) showed that the alkoxy radicals (epeXo) eventually undergo a unimolecular decomposition to form species that are similar to β -scission products. Moreover, ethyl pentenoates formed from peroxy compounds (epeXOO) are also involved in the reactions, which are specific for β -scission products. Therefore, excluding the route $\text{epeXj} + \text{O}_2 = \text{epeXOO}$ from the mechanism provides just direct conversion of epeXj radicals to β -scission products. Eventually, this modification to the mechanism does not result in any significant changes in the calculated mole fractions of the intermediates.

Thus, further work for the development of the mechanism should be focused on revising the pathways responsible for formation and consumption of the products of the β -scission reactions of epeXj radicals. In particular, the significant overprediction of the peak mole fraction of ethyl-3-butenate (Fig. 3) indicates the need of the abovementioned revisions of the mechanism. Moreover, the reactions involving the species such as ethenol, n-propanol, pentenal and dimethyl ether, which were identified in the flame and the peak mole fractions of which were measured to be as high as $\sim 10^{-4}$, should also be included to the future model.

Conclusions

A stoichiometric premixed flat flame of ethyl pentanoate/ O_2 /Ar mixture at low pressure (20 torr) was investigated by MBMS in combination with VUV photoionization at the ALS. Mole fraction profiles of over 40 species were measured and compared with the results of numerical simulations using a detailed chemical kinetic mechanism proposed by Dayma et al. [13]. This experimental work extends the

earlier work of Dayma et al. [13], who focused on the low-temperature regime, by providing species measurements during the high-temperature oxidation of EPE. Species such as ethenol, n-propanol, pentenal and dimethyl ether, which were not involved in the kinetic mechanism, were detected in the flame. Good agreement for major species and several intermediate species between the data of measurements and calculations was observed. However, underprediction of the peak mole fractions of many C_xH_y intermediates in the flame motivated us to trace the origins of these discrepancies by analyzing the routes of EPE oxidation in the flame. It was concluded that for further improvement of the model, particular attention should be paid to the reaction pathways determining the consumption of the products which are formed from epeXj radicals via β -scission. While it is beyond the scope of this work to present an updated chemically detailed model, the experimental results represented in this work give a detailed survey of the flame structure and can help to improve future kinetic models of ethyl pentanoate combustion.

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Figure captions:

Fig. 1: Temperature profile and mole fraction profiles of reactants and main stable products in the flame. Symbols: experiment, lines: modeling.

Fig. 2. Mole fraction profiles of intermediate hydrocarbon species (C_xH_y) in the flame. Symbols: experiment, lines: modeling.

Fig. 3. Mole fraction profiles of oxygenated intermediates in the flame. Symbols: experiment, lines: modeling.

Fig. 4. Reaction pathways from the kinetic modeling of ethyl pentanoate combustion in the conditions considered.

Fig 1

Fig 2

Fig 3

Fig 4