

# An experimental and detailed chemical kinetic investigation of the addition of C2 oxygenated species in rich ethylene premixed flames

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## Introduction

The continuous increase in energy consumption and concerns about fossil fuels availability, together with the current trends in novel IC engines development, call for further research on alternative fuels [1]. Ethanol is particularly attractive as an alternative fuel due to its soot and emissions reduction potential and is often found as an oxygenated additive compound in gasoline fuels [2]. Fundamental research on the oxidation of conventional fuel/alcohol blends has determined aldehydes, such as acetaldehyde, as important intermediate species. Aldehydes are products of partial/ incomplete combustion and, being stable intermediates they influence the combustion pathways. Additionally, studies on engines [3]-[4], have shown that, depending on the engine operating conditions, up to 4-27% of the exhaust hydrocarbons are acids, mainly acetic and propionic acid, which have also been recognised as contributors to acid rain formation. In the same scope, ethylene is of significant interest, as it is a key intermediate of the oxidation of higher alkanes, and a very reactive fuel as well. It is often used as a model fuel for soot studies [5]. Studies on flame structure, can in principle provide great insight on the fundamentals of the combustion process, by providing a rudimentary description of the flow-chemistry interaction encountered in real combustion applications, but giving high insight on the details of chemistry. Several relevant experiments have been carried out in the past by different research groups. Among them, Yakimov *et al.* [6] measured product species in a premixed laminar ethylene flame at low pressure, with and without the addition of ethanol. Results yielded a reduction of soot precursor species such as C<sub>3</sub>H<sub>3</sub> and C<sub>6</sub>H<sub>6</sub> and other intermediate species as well. The scope of the present study is to quantify the effect of oxygenated species additives on the structure of rich ethylene premixed flames. The kinetic scheme of NTUA [7]-[8], and the detailed kinetic model of UCL [9]-[14], are utilized and further analyzed, highlighting the reaction paths leading to species of interest, such as benzene toluene etc.

## Experimental Setup

All experiments have been conducted in the facilities of the UCL. Detailed description of the experimental setup can be found in [13]-[14] and only a brief description is provided herein. The experimental setup consists of a gas chromatographer (GC) coupled to a combustion chamber. Flames A and B were stabilized at 50 mbar whereas measurements in Flame C were

made at 75 mbar. The latter flame was found to be positioned too far from the burner at 50 mbar and subsequently had a tendency to blow off. A conical quartz probe allows sampling from the flame. The sampling position is controlled by moving the burner, thus altering the distance between the burner and the sampling probe. The compressed gases were introduced into the GC in which a chromatographic separation was achieved by using either a Molsieve 5A (H<sub>2</sub>, O<sub>2</sub> and CO) or a PORAPLOT Q (other hydrocarbons) column provided by Varian Inc. The quantification detection was carried out by both a Thermal Conductivity Detector (TCD) and Flame Ionization Detector (FID) previously calibrated by the procedure described in an earlier paper [13]. Flame temperatures were measured using Pt/PtRh10% coated thermocouples of 0.1 mm diameter, placed in front of the sampling probe, at a distance of 0.3-0.5 mm. Correction of radiation losses was carried out by the electrical compensation method. Standard deviation on temperature measurements is estimated to  $\pm 50$  K. The composition of the investigated flames is listed in Table 1. In flames A-C, the initial ethylene, as well as the initial oxygenated additive molar concentration, have been held constant, namely 0.25 and 0.08 respectively. The flames with no oxygenated additive *e.g.* flames D-E, have the same C/O and equivalence ratio with flame A respectively, to allow for a comparison in two directions.

Flame	X <sub>C<sub>2</sub>H<sub>4</sub></sub>	X <sub>C<sub>2</sub>H<sub>5</sub>OH</sub>	X <sub>CH<sub>3</sub>CHO</sub>	X <sub>CH<sub>3</sub>COOH</sub>	X <sub>O<sub>2</sub></sub>	X <sub>Ar</sub>	Mass flow rate (g/cm <sup>2</sup> s)	C/O	$\phi$	Pressure (mbar)
Flame A	0.25	0.08	-	-	0.4	0.27	2.835 10 <sup>-3</sup>	0.75	2.475	50
Flame B	0.25	-	0.08	-	0.4	0.27	2.822 10 <sup>-3</sup>	0.75	2.375	50
Flame C	0.25	-	-	0.08	0.36	0.31	2.954 10 <sup>-3</sup>	0.75	2.527	75
Flame D	0.30	-	-	-	0.40	0.30	2.746 10 <sup>-3</sup>	0.75	2.250	50
Flame E	0.33	-	-	-	0.40	0.27	2.716 10 <sup>-3</sup>	0.82	2.475	50

Table 1. Detailed setup of investigated flames

The molecular oxygen content is held constant in the acetaldehyde and the ethanol flame but is decreased in the acetic acid flame in order to maintain constant the C/O ratio. The diluent (Ar) content rises instead. Concentration profiles for the following species have been measured for all three flames: H<sub>2</sub>, O<sub>2</sub>, CO (carbon monoxide), CO<sub>2</sub> (carbon dioxide), H<sub>2</sub>O, C<sub>2</sub>H<sub>2</sub>+C<sub>2</sub>H<sub>4</sub> (acetylene + ethylene), CH<sub>4</sub> (methane), C<sub>2</sub>H<sub>6</sub> (ethane), C<sub>3</sub>H<sub>6</sub> (propene), C<sub>3</sub>H<sub>8</sub>, CH<sub>2</sub>CCH<sub>2</sub> (allene), CHCCH<sub>3</sub> (propyne), CH<sub>3</sub>CHO (acetaldehyde), CH<sub>3</sub>COOH (acetic acid), C<sub>2</sub>H<sub>5</sub>OH (ethanol), C<sub>4</sub>H<sub>4</sub> (vinylacetylene), C<sub>4</sub>H<sub>6</sub>, C<sub>4</sub>H<sub>2</sub>, C<sub>5</sub>H<sub>6</sub> (cyclopentadiene), C<sub>6</sub>H<sub>6</sub> (benzene), C<sub>7</sub>H<sub>8</sub> (toluene).

## Numerical approach

The detailed kinetic schemes of the two research groups have been utilized to compute the experimentally investigated flames. Both mechanisms have been extensively validated against speciation data from premixed flames of both small H/C and C1-C2 oxygenated species, *e.g.* for the NTUA mechanism see [7]-[8], for the UCL mechanism see [9]-[14]. Additionally, the UCL mechanism was developed in part to simulate experimental data coming from C<sub>6</sub>H<sub>6</sub> and C<sub>7</sub>H<sub>8</sub> flames [13]-[14]. All computations have been performed using the PREMIX code [15]. Reaction path analysis will be extensively utilized in order to scrutinize the controlling elementary steps and the combustion pathways of the three oxygenated additives among ethylene. Parts of the mechanism are identified for further modeling.

## Discussion

Identifying the effect of each oxygenated dopant on the formation of higher hydrocarbon species such as benzene is of great importance in the framework of achieving lower soot formation. The respective concentrations for each flame are depicted in figure 1. Comparison shows that Flame C *e.g.* the acetic acid flame, poses higher 20% concentration than the neat ethylene flame with the same C/O ratio, *e.g.* Flame D, and 60% higher than all other oxygenated flames. Computationally, the kinetic scheme of UCL predicts very well the trends experimentally observed. The kinetic scheme of NTUA yields satisfying results in all flames, but does not capture the increased formation in the acetic acid flame, erroneously predicting a slightly higher peak in the ethanol flame. In both mechanisms, the main benzene formation path is the one of vinylacetylene reaction with vinyl radical (R1). Further analysis of the benzene formation paths, highlights the importance of smaller hydrocarbon species. In particular, analyses of the UCL mechanism showed the significant role of the decomposition of acetic acid to ketene. Ketene decomposes to form great amounts of the ethyl radical, which in turn gives ethylene. Ethylene reacts to produce vinyl radical and acetylene. Vinylacetylene is then formed as a product of the reaction of the two latter species. This significantly enhances the  $C_4H_4 + C_2H_3$  benzene formation path, justifying also the increase in benzene levels. Another explanation of the higher benzene levels in the acetic acid flame is the delayed formation of radicals that can react with it and lead to its decomposition. This somewhat problematic performance of the NTUA mechanism is attributed to the ketene sub-mechanism. Benzene destruction to the phenyl radical follows the typical routes of H abstraction reactions with H, OH, and  $CH_3$  radicals and unimolecular decomposition at a ratio of about 4:1 for both mechanisms.

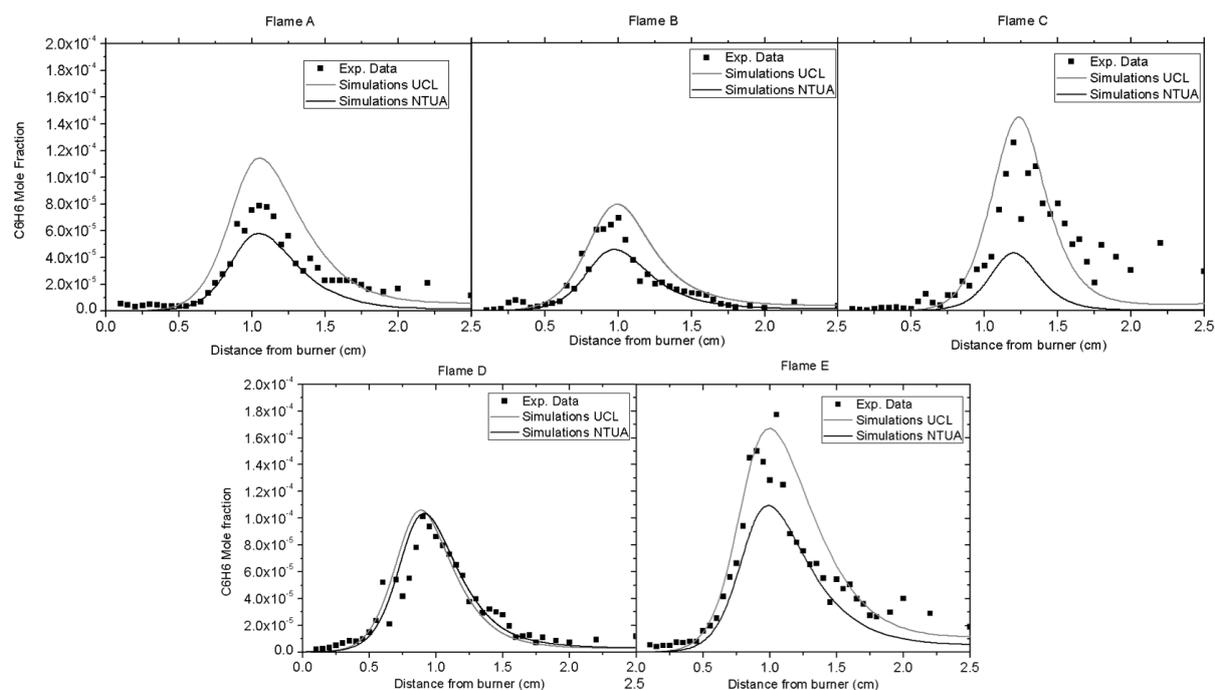
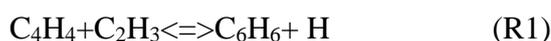


Fig. 1 Experimental and computational profiles of Benzene in all flames

## Conclusions

The present manuscript provides only a small part of the full study on the effect of the addition of oxygenated dopants to rich ethylene flames. Emphasis was given on the reaction paths leading to the formation of important species such as benzene. A complete reaction path analysis shedding light on the oxidation of each dopant and the synergies with the main fuel will be provided within the full paper. Overall, combined novel experimental measurements and numerical analyses were performed. Comparison between two detailed and well validated kinetic models for the combustion of small hydrocarbons was carried out. Results yielded good agreement for both mechanisms with some small discrepancies in peak levels and in reaction paths. Flames A and B seem to maintain an oxygenated character throughout the flame domain, causing also a decrease in the formation of certain species such as benzene, while at the same time the early shedding of CO<sub>2</sub> molecule in Flame C results in an apparent resemblance to an ethylene flame. The study recognizes the need for measurements of global combustion characteristics such as ignition time delay and flame velocity for purposes of further understanding.

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