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Thomas Panaget, Killyan Potier, Sébastien Batut, Amaury Lahccen, Yann Fenard, et al.. How ozone affects the product distribution inside cool flames of diethyl ether. Proceedings of the Combustion Institute, 2023, 39 (1), pp.325-333. 10.1016/j.proci.2022.08.081. hal-04243829

HAL Id: hal-04243829 https://hal.science/hal-04243829

Submitted on 16 Oct 2023

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How ozone affects the product distribution inside cool flames of diethyl ether

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Abstract

Cool flames of diethyl ether were stabilized and extensively studied in a stagnation plate burner. Two conditions were selected, enabling the assessment of the impact of ozone-seeding on the cool flame: In the first case, ozone was seeded to stabilize a lean cool flame with an equivalence ratio of 0.5, and in a second case a stoichiometric flame was stabilized without O3 addition. Excited formaldehyde chemiluminescence (CH2O*) was used to measure the cool flame position in the burner. Detailed temperature and mole fraction profiles of stable intermediates of the oxidation of diethyl ether were measured for both conditions. Relevant detailed kinetic models issued from the literature, respectively developed by Tran et al., [Tran et al., Proc. Comb. Inst. 2019, 37, 511-519] and Serinyel et al. [Serinyel et al., Combust. Flame 2018, 193, 453-462] were used in order to improve the understanding of the low temperature kinetics of this ether, as well as the effect of ozone on the species distribution after the cool flame. The Tran et al. model is able to correctly predict the cool flame position as well as its heat release in the lean case, but shows high discrepancy in the prediction of products formation, while the Serinyel et al. model shows a fair prediction of the cool flame products distribution. A numerical comparison between a stoichiometric flame, with and without ozone-seeding, was also performed in order to gain some insight into the ozone influence on the low temperature products distribution. Main results show that the RO radical decomposition is of particular importance in our conditions, which formation is directly linked to RO₂ bimolecular reactions, reinforcing the link between atmospheric chemistry and low temperature combustion.

Keywords: Diethyl ether; low temperature combustion; cool flame; Ozone-assisted combustion

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1. Introduction

From their discovery at the beginning of the 19th century [1] to their recent observation using the Flame Extinguishment Experiment in the International Space Station [2], cool flames raised many questions about their formation and specific chemistry. Their unique properties, that could lead to an improvement either in fuel conversion or pollutant emission reduction in compression ignition engines [3], motivates a research effort in this particular domain.

Ignition and stabilization of steady-state cool flames are particular challenges due to the high induction time of oxidation reactions in this temperature range, preventing radical branching. In this context, plasma- [4] and ozone-assisted [5] combustion enable the cool flame formation in lean conditions. Considering the complex chemistry of the plasma generation, O₃ has been intensively studied as its decomposition leads to the formation of a very reactive species, Ö. This species has been widely used to stabilize cool flames in lean conditions in counterflow [6], freely-propagating [7] or stagnation plate burner [8] configuration.

The effect of ozone addition on the low temperature oxidation product distribution was studied by Zhao *et al.* [9] and Liao *et al.* [10] respectively in a flow and a jet-stirred reactor, and using dimethyl ether as fuel. In addition to its influence on the temperature threshold at which the conversion of the fuel is initiated, ozone also possesses a high influence on the formation of some species, and especially on methyl formate, CH₃OCHO, in the case of dimethyl ether oxidation. Recently, our group [8] measured the distribution of products in an ozone-seeded cool flame of dimethyl ether, and observed the role of ozone in the direct addition of Ö on the fuel radical, CH₃OCH₂, to form CH₃OCH₂O radical and later on methyl formate.

While the influence of ozone on the low temperature kinetics has been widely studied with dimethyl ether in jet-stirred and flow reactors, direct comparisons of spontaneous and ozone-seeded cool flames of diethyl ether have never been investigated. Diethyl ether, $C_4H_{10}O$, is a potentially promising biofuel [11] as well as an excellent additive for homogeneous charge compression ignition engine [12]. Its low temperature oxidation has been widely studied in jet-stirred reactors [13–15] or rapid compression machine [16,17] but very rarely in recent studies of stabilized cool flames [18].

The aim of this work is to shed light on the effect of ozone on the kinetics of cool flames with help from reliable species measurements in two conditions: an ozone-seeded and a spontaneous cool flame, both stabilized in a stagnation plate burner. These experimental results demonstrate a few key points of the effect of ozone addition, and are compared to the predictions from two kinetic models from the literature. Kinetic modeling is then used to shed further light into the influence of ozone on the flame temperature, and the products distribution after the cool flame.

2. Experimental and computational methods

2.1 Stagnation plate burner

A stagnation plate burner was used in this study to stabilize ozone-seeded DEE/O₂ premixed flames, which was extensively described in a previous study using DME as fuel [8], therefore only a brief description is given here. The mixture was injected through a coaxial nozzle of an inner diameter of 10 mm, impinging a heated stagnation plate located at 13 mm above the burner. The plate temperature in this case was fixed at 700 K, the temperature distribution along the plate surface being homogeneous within +/-5%.

Liquid DEE (Sigma-Aldrich, $\geq 99.8\%$) was vaporized in the oxygen flow through a Controlled Evaporator Mixer (W-202-222-K, Bronkhorst). Ozone was generated using a BMT 803N ozone generator, and its inlet concentration was measured using a Teledyne API 452 ozone analyzer. Gas flow rates were controlled by mass flow controllers, liquid flow rate was controlled by a Coriolis flow controller (Bronkhorst). An ICCD Princeton PIMAX3 camera, equipped with a band-pass filter (396-450 nm) was used to collect the chemiluminescence signal of the cool flame.

Temperature profiles were measured using a 250 µm diameter type K thermocouple. Measurements were performed from the side, the tip of the thermocouple lying along the axis of the burner. Absence of catalytic effects on the thermocouple surface was verified by measuring the temperature profile from the bottom to the top and vice versa, yielding nearly identical temperature profiles, as shown in the Fig. S1 in the supplementary materials. The uncertainty is estimated to ± 25 K for the temperature and to $\pm 125 \,\mu m$ for the position, which corresponds to the maximum observed deviation between these two runs. Detailed major species mole fraction profiles were obtained by combining gas chromatography and quadrupole mass spectrometry techniques. Samples from the flame were extracted through a 250 um external diameter capillary. The capillary is placed perpendicular to the burner axis. An Agilent 6890 Gas Chromatograph (GC), equipped with a ShinCarbon ST micropacked column, flame ionization and thermal conductivity detectors, was used to analyze permanent gases and light hydrocarbons. A Bruker SCION 456-GC, equipped with a PoraBond Q column, FID and quadrupole detectors, was used for the identification and quantification of heavier hydrocarbons and oxygenated products. An Omnistar GSD 301 O2 Pfeiffer Vacuum mass spectrometer, equipped with a quadrupole analyser, was used to measure the ozone mole fraction profile. The ozone signal was measured at 48 m/z. Extra-signal at this m/z ratio coming from

O2, caused by the high ionization energy of the mass spectrometer (70 eV), was corrected using the O_2 mole fraction profile obtained by GC measurement. In order to limit the ozone decomposition and DEE reactivity, the injectors temperatures were fixed at 373 K, samples being injected at low pressures to avoid condensation. Calibrations were performed with different techniques according to the availability of the different species, respectively by using cold-gas mixtures and in-house, liquid or gaseous, prepared mixtures. The Effective Carbon Number (ECN) was used when the species were unavailable. Reported uncertainties are ± 5 or 10% for calibrated species, respectively with in-house and cold-gas mixtures, and ± 15% for species when the ECN was used. Carbon balance was verified in both conditions, leading to a maximum deviation of $\pm 13\%$ in the $\phi = 0.5$ case and $\pm 3\%$ in the $\phi = 1$ case.

2.2 Computational methods

Cool flames were simulated with multicomponent transport, using the impinging jet reactor class from Cantera [19]. Models from the literature developed by Tran *et al.* [15], including 749 species for 3570 reactions and a reduced version of the model from Serinyel *et al.* [13] including 193 species for 1243 reactions (reduction by Murakami *et al.* [18]), were used to simulate the experimental measurements, and shed light on the nature of the discrepancies observed. An ozone sub-mechanism from Foucher *et al.* [20] was also added in both mechanisms to describe the ozone decomposition.

Brute-force sensitivity analyses were performed on the first stage ignition delay, and the sensitivity coefficient on the reaction *i*, *Si*, was calculated as follows: $S_i = \ln (\tau_i^+/\tau_i^-) / \ln (2/0.5)$. τ_i^+ represents the first stage ignition delay time when the preexponential factor of the reaction *i* has been multiplied by a factor of two, and τ_i^- represents the first stage ignition delay time when the pre-exponential factor of the reaction *i* has been divided by a factor of two.

3. Results and discussion

3.1 Flame stabilization

Two experimental conditions, summarized in the Table 1, were selected for this study. In the fuel-lean condition, $\phi = 0.5$, an ozone concentration of 1.4% in the premixture was seeded to stabilize the cool flame. On the contrary, in the stoichiometric case, $\phi = 1$, the flame was stabilized without ozone. It should be noted that the lean cool flame could not be stabilized without ozone in the mixture. Further details on the experimental conditions are given in the Table S4 Supplementary Materials.

Table 1. Experimental conditions

Mixture	φ	α / s ⁻¹	x _{O3} / %
DEE/O ₂ /O ₃	0.5	50	1.4

DEE/O ₂	1.0	40	0		
$\alpha =$ Flow velocity / Burner-plate distance					

The chemiluminescence signal of excited formaldehyde formed in the cool flame, CH₂O*, was recorded. A grey-scaled raw image of the $\phi = 0.5$ flame is presented in the Fig. 1, where the burner exit and the plate can be identified using the light reflections of the cool flame. Abel-inversion of the CH₂O* signal is then used to measure the flame front position in the center of the burner, as previously presented [8].

3.2 Temperature profiles

Prior to cool flame heat release quantification, temperature profiles of both flames were measured. Experimental and numerical results using both models are shown in Fig. 2.



Fig. 1. CH_2O^* -chemiluminescence of the DEE/O₂/O₃ flame (the burner plate is represented with a white dashed line)



Fig. 2. Experimental and simulated temperature profiles

Maximum temperatures of 829 K and 753 K, respectively for the $\phi = 0.5$ and $\phi = 1$ case, were experimentally measured after the flame front. Achieving a good spatial resolution in the $\phi = 1$ experimental case is complex due to the short distance separating the flame from the plate. The Tran *et al.* model predicts a very similar temperature profile in both cases, and maximum temperatures roughly equal to 830 K. The predicted temperature profile is very close to the experimental measurements for the DEE/O₂/O₃ condition, whereas the flame temperature

is slightly overpredicted in the stoichiometric case. On the other hand, the Serinyel et al. model correctly predicts the maximum temperature in both cases within the uncertainty limit. The flame front position is however underestimated by the model, as well as the position at which the maximum temperature of the flame is reached. This discrepancy can originate from several causes, including the perturbation of the flame by the thermocouple, the kinetic model of DEE, and the physical model of impinging jets in Cantera. One can note, however, that the flame position, as inferred from CH2O* chemiluminescence imaging, is in good agreement with the measured increase of temperature. When comparing the simulated velocity profiles with both models, it can be observed that the stretched propagation speed is significantly higher in the case of the Serinyel et al. model, which is consistent with the fact that the flame front is predicted to be closer to the burner with this model. This suggests that further progress should be sought in the modeling of cool flame laminar burning velocities and the accurate description of stagnation plate burner experiments, which is however outside the scope of this work.

Increase in the heat release of the cool flame by ozone addition has been previously measured in a HCCI engine [20] and a stagnation plate burner [8], which is coherent with the results presented here. The differences observed here between the ozone-seeded and non-seeded flames will be discussed in details in the next section.

3.3 Structure of diethyl ether cool flames

A total of 16 stable species were detected and identified, but only 13 were quantified. Ethanol (C₂H₅OH) and ethyl formate (C₂H₅OCHO) were observed in both conditions, but could not be quantified. Ethyl acetate (C2H5OC(=O)CH3) was only observed in the ozone-seeded flame, and could also not be quantified. As suggested and detailed in a previous study [8], the sampling of mixtures in the pre-flame region can be perturbed by the presence of ozone. Its decomposition in the sampling capillary is an important process, however this previous work has demonstrated that only the pre-flame region measurements are affected, and this effect is negligible once ozone has decomposed in the flame. This hypothesis is supported by both experimental measurements and numerical simulations, showing that the ozone is totally converted after the flame, as shown in Fig. 3.

This effect was qualitatively described by simulation when studying the kinetics of DME/O₂/O₃ cool flame, and this experimental work now demonstrates it further. In Fig. 4 the DEE conversion through the flame is presented for the two conditions studied here, $\phi = 0.5$ and $\phi = 1$. As one can see, when comparing the position at which the fuel conversion starts in both cases, the DEE is partially converted in the sampling capillary in the fuel-lean, ozone-rich case (grey symbols in Fig. 4). However, in the

stoichiometric, ozone-less cool flame, pre-reactivity of the mixture is not observed, confirming the hypothesis that ozone decomposition in the capillary when approaching the flame is responsible for this phenomenon.



Fig. 3. Experimental ozone mole fraction profile (\blacklozenge) with simulated profiles with the Tran *et al.* model (dashed line) and the Serinyel *et al.* model (full line). $\blacklozenge = 0.5$, $x_{03} = 1.4\%$

Experimentally, 60% of the diethyl ether is converted in the $\phi = 0.5$ flame, 55% in the $\phi = 1$ flame. This is characteristic of the low temperature domain, where the fuel is only partially consumed. Interestingly, despite not being able to predict the correct position at which the fuel is oxidized, the Serinyel et al. model shows an excellent agreement with the experimental fuel mole fraction after the cool flame. On the other hand, the fuel conversion was overpredicted in both cases by the model from Tran et al., around 75% of the fuel being converted in both conditions. Considering the ability of the Serinyel et al. model to correctly predict the fuel mole fraction and temperature downstream from the cool flame, this model will be used further for the comparison between experimental and simulated results, as well as for the kinetic analysis. Comparison between experimental and simulated results with the Tran et al. model is presented in the Fig. S2 in the supplementary materials.



Fig. 4. DEE mole fraction profiles, $\phi = 0.5$, $x_{O3} = 1.4\%$ (\blacklozenge) and $\phi = 1$, $x_{O3} = 0\%$ (\blacklozenge), simulated results with the Tran *et al.* model (dashed line) and Serinyel *et al.* model (full line)

The mole fraction profiles of the reactants and products measured in both flames are pictured along with the predictions from the Serinyel *et al.* model in Fig. 5. In order to precisely qualify the effect of ozone on the cool flame using kinetic modeling, a cool flame at $\phi = 1$ seeded with an arbitrary fixed mole fraction of ozone equal to 1%, was also simulated and the results are also shown in the graphs, and will be discussed later in this section.

The major product measured in the cool flames is acetaldehyde, CH₃CHO, which mainly originates from the decomposition of the ketohydroperoxides, CH₃C(O)OCH(O₂H)CH₃, OCHCH₂OCH(O₂H)CH₃, as well as the decomposition of the RO radical, CH₃CH₂OCH(O)CH₃. Its mole fraction exceeds 4% in the $\phi = 1$ case. The Serinyel *et al.* model predicts fairly the amounts of acetaldehyde formed in both cases, with a slight overestimation especially in the stoichiometric case. Methanol, CH₃OH, is also measured as one of the main products of diethyl ether oxidation in the cool flame, its final mole fraction reaching 1% in $\phi = 1$ case. Its mole fraction is correctly reproduced by the model in the lean case, while an important discrepancy subsists in the stoichiometric case. The formation of 2-methyl-1,3dioxolane, C4H8O2-cy, is strongly underestimated by the Serinyel et al. model. This species is formed in both models by the decomposition of the following QOOH radical, CH3CHOCH2CH2OOH. Its mole fraction after the cool flame is higher in the $\phi = 1$ case, which can be mainly attributed to the higher initial mole fraction of the fuel. The formation of ethyl vinyl ether (EVE), C₂H₃OC₂H₅, is also strongly underestimated by the Serinyel et al. model. Interestingly, the experimentally measured mole fraction is slightly higher in the $\phi = 1$ case than in the $\phi = 0.5$ case, while the opposite trend is predicted by the model. EVE is formed by the decomposition of the $C_2H_5OCH(O\dot{O})CH_3$ and C₂H₅OCH(OOH)ĊH₂ radicals, leading in both cases to the formation of HO₂. The direct oxidation reaction of the fuel radical forming EVE is not present in the model, which could partially explain the underestimation of this species formation. Finally, the formation of acetic acid is accurately reproduced by the model in the fuel-lean case, but the observed increase in mole fraction in the stoichiometric case is not quantitatively predicted by the model. This suggests that some additional pathways towards this species might be missing.



Fig. 5. Mole fraction profiles at $\phi = 0.5$, $x_{O3} = 1.4\%$ (dark), $\phi = 1$, $x_{O3} = 0\%$ (red), experiments in diamonds, simulated results using the Serinyel *et al.* model (full lines for the comparison with experiments, dashed line for a $\phi = 1$ ozone-seeded case with $x_{O3} = 1\%$)

Concerning smaller species, the formation of C₂H₄ and C₂H₆ is slightly underestimated by the Serinyel *et al.* model, except for C₂H₄ in the $\phi = 1$ case. Interestingly, the CH₄ and CO mole fractions do not vary when comparing the $\phi = 0.5$ and $\phi = 1$ cases, and this trend is not captured by the model. CO₂ mole fraction is underestimated by the Serinyel *et al.* model, which is consistent with a previous study [13]. Finally, the O₂ conversion is fairly well reproduced by the Serinyel *et al.* model which is coherent with the diethyl ether conversion prediction shown in Fig. 4.

In order to gain further insight into the formation of the different species observed experimentally, as well as the effect of ozone on the reactivity, a reaction pathway analysis was performed in the cool flame, at 5% fuel conversion. At this low conversion rate, the kinetic analysis can precisely capture the initial stages of the cool flame. At this stage of conversion, the temperature is equal to 460 ± 5 K in the three cases, ϕ = 0.5 ($x_{03} = 1.4\%$), $\phi = 1$ ($x_{03} = 0\%$) and $\phi = 1$ ($x_{03} = 1\%$). Results are pictured in Fig. 6.

In every condition the H-abstraction reaction occurs preferentially on the α -position to the ether oxygen, which is consistent with previous studies [13,15]. In the lean ozone-seeded flame, i.e., $\phi = 0.5$, 91% of the H-abstraction reaction takes place with the OH radical, while it represents 75% of the Habstraction in the $\phi = 1$ case. The ozone decomposition upstream from the flame front, especially forming Ö, which will subsequently yield OH when reacting with DEE, can explain this difference. This is confirmed with the stoichiometric flame with $x_{O3} = 1\%$, where the branching ratio of the H-atom abstraction by the hydroxyl radical is increased in comparison with the same case without ozone. It is interesting to note that the CH₃OH mole fraction is two times higher in the $\phi = 1$ case, which is consistent with the fact that the H-abstraction on the fuel molecule by CH3O is promoted in the stoichiometric case, as visible in Fig. 6. It should also be stressed that the fuel mole fraction is not kept constant between the $\phi = 0.5$ and $\phi = 1$ cases, which can affect the formation of CH₃O and CH₃OH. One can also note that ozone addition in the stoichiometric case leads to increased formation of CH₃OH, while the branching ratio relative to H-atom abstraction by CH₃O is reduced, hinting at other, ozone-dependent, formation pathways for CH₃OH.

The fuel radical can add to molecular oxygen, O₂, to form a RO₂ radical. In low temperature oxidation conditions, it is expected that this radical undergoes an internal H-atom migration reaction to form a QOOH radical, the CH₃CHOCH(OOH)CH₃ radical being favored in these conditions. However, at very low fuel conversion, this pathway competes with the formation of the RO radical, that can be formed by reaction with HO₂ or with another RO₂ radical. In nondiluted conditions, *i.e.* conditions where the radical concentration is important, bimolecular reactions between radicals are more influent than in more diluted conditions, explaining this branching ratio in our experimental conditions. The Serinyel et al. model describes the following reactivity of this RO radical as the formation of CH₃CHO and CH₃CH₂O.

It was observed that during the low temperature oxidation of dimethyl ether, the β -scission of the CH₃OCH₂O radical mostly yielded methyl formate, CH₃OCHO [8]. In the case of diethyl ether, the same reaction sequence involves the CH₃CH₂OCH₂(\dot{O})CH₃ radical, which would not only decompose into acetaldehyde and CH₃CH₂O as predicted by the Serinyel *et al.* model, but into oxygenated species such as ethyl acetate and ethyl formate. A kinetic study from Orlando *et al.* [21] performed in atmospheric conditions supports this hypothesis. This could explain the slight overprediction of acetaldehyde by the Serinyel *et al.* model, as products from the RO decomposition will not majorly consist of acetaldehyde.

As explained previously, a cool flame was simulated at $\phi = 1$ with an initial mole fraction of ozone $x_{O3} = 1\%$ in order to better assess on the effect of ozone without changing the equivalence ratio or the fuel mole fraction. One can first note, from Fig. 5, that ozone has an impact on the flame position, which is slightly closer to the burner in the ozone-seeded case. as well as on the maximum flame temperature, which is increased by about 70 K with ozone-seeding. These effects have already been shown previously from experiments with DME [8]. This will also induce an increase of the fuel conversion through the cool flame of about ~ 12%, and impact the distribution of products. As can be seen in Fig. 5, the mole fractions of some products increase with ozone-seeding, as for example CH₃OH, CH₂O or CH₄. Interestingly, acetaldehyde, ethyl vinyl ether and 2-methyl-1,3dioxolane, which are relevant to the direct lowtemperature chain-branching sequence, are not impacted by the addition of ozone. Moreover, it can be observed that at a constant fuel mole fraction, the H-abstraction by OH is enhanced in the presence of ozone, because of the higher quantity of OH resulting from the conversion of atomic oxygen.

A brute force sensitivity analysis was performed on the first stage ignition delay at T = 600 K using the Serinyel *et al.* model for both cases, $\phi = 0.5$ and $\phi = 1$, and the 15 most sensitive reactions are presented in Fig. 7. Using the first ignition delay time as the target allows for better insight into the cool flame initiation. As expected, the most influent reaction in the case of the $\phi = 0.5$ flame is the decomposition of O₃, forming a Ö atom, which is known to strongly enhance the Habstraction of the fuel. As expected, this reaction is not influent in the $\phi = 1$ case as this particular flame was stabilized without ozone. The second most influent reaction in the $\phi = 0.5$ case is the isomerization of the O2OOOH, followed by other reactions of the low temperature chain branching sequence.



Fig. 7. Sensitivity analysis performed on the first stage ignition delay time at P = 1 atm, T = 600 K, and for both experimental conditions $\phi = 0.5$ ($x_{O3} = 1.4\%$) and $\phi = 1$ ($x_{O3} = 0\%$)

The most influent reaction in the $\phi = 1$ case is the decomposition of the ketohydroperoxide, leading to the formation of two radicals, thus enhancing the reactivity. The sensitivity coefficient of this reaction is lowered in the $\phi = 0.5$ case; which can be explained by the higher concentration of the OH radical due to the decomposition of O₃. The relative importance of the decomposition of the ketohydroperoxide in the formation of OH is therefore reduced. Interestingly, the bimolecular reaction $2 \text{ RO}_2 \rightarrow 2 \text{ RO} + \text{O}_2$ is seen to decrease the first stage ignition delay time, whereas the equivalent reaction had the opposite effect in the case of dimethyl ether [8]. This could be directly linked to the RO decomposition, which mainly undergoes a β -scission in the Serinyel *et al.* model. This suggests that other pathways [21] could be missing.



Fig. 6. Reaction pathway analysis in the cool flame at $\phi = 0.5$, $x_{03} = 1.4\%$ (**bold**), $\phi = 1$, $x_{03} = 0\%$ (*italic*), $\phi = 1$, $x_{03} = 1\%$ (<u>underlined</u>). Squared species correspond to species that were detected experimentally in this study.

4. Conclusion

The aim of this study was to investigate the impact of ozone-seeding on diethyl ether low temperature oxidation kinetics by means of stabilized cool flames in a stagnation plate burner. To that end, two cool flame conditions were selected, respectively at $\phi = 0.5$ with $x_{03} = 1.4\%$, and at $\phi = 1$ without ozone addition. Temperature and species mole fraction profiles were measured in both conditions, yielding useful experimental data. Two models from the literature, respectively from Serinyel *et al.* and Tran *et al.* were used in order to simulate the experimental results.

As expected, ozone plays an important role in the flame stabilization in the lean condition. Temperature measurements showed that the presence of ozone in the flame also slightly influences the cool flame heat release. The Serinyel *et al.* model correctly predicts this trend, which is not captured by the Tran *et al.* model. Ozone also slightly modifies the products distribution after the cool flame, as it increases the fuel conversion and constitutes an important source of OH radicals. Ozone addition also resulted in the formation of ethyl acetate, which was not detected when ozone was absent.

Concerning the species mole fractions, measurements show that acetic acid is formed in important quantities in the cool flame, especially at ϕ = 1. The Serinyel *et al.* model fails in quantitatively predicting the formation of this product, highlighting

possible missing reaction pathways. Reaction pathway analysis at low fuel conversion in the cool flame shows that the formation of RO radicals was of particular importance at the lowest temperatures, as observed previously in the case of dimethyl ether. These reactions, which are of minor importance in diluted conditions, are more influent in non-diluted conditions, i.e. in conditions where the radical concentrations are higher. The measurements globally showed that some oxygenated species were highly underestimated by both models, reinforcing the need of accurate calculations of low temperature specific reactions, such as the different RO decomposition pathways which need to be considered in the kinetic models.

5. Acknowledgements

This work is a contribution to the LabEx CaPPA project funded by the French National Agency under contract « ANR-11-LABX-0005-01 » and to the CPER research project CLIMIBIO funded by the French Ministère de l'Enseignement Supérieur et de la Recherche. The authors thank the Regional Council « Hauts-de-France » and the « European Regional Development Fund » for their financial support to these projects. The authors would also like to thank the technical staff from PC2A laboratory for the help in the construction of the burner.

6. Supplementary materials

Experimental evidence of the absence of catalytic effect at the surface of the thermocouple is presented in the Supplementary Material. Comparison between the experimental data, the model of Serinyel *et al.* and the model of Tran *et al.* is provided in the Supplementary Material. Tables presenting the experimental data points for both conditions shown in this paper are also given.

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