Contents lists available at ScienceDirect

Combustion and Flame

journal homepage: www.elsevier.com/locate/combustflame

Chemical interaction of dual-fuel mixtures in low-temperature oxidation, comparing *n*-pentane/dimethyl ether and *n*-pentane/ethanol

Hanfeng Jin^{a,b,1}, Julia Pieper^{a,1}, Christian Hemken^{a,c}, Eike Bräuer^a, Lena Ruwe^a, Katharina Kohse-Höinghaus^{a,*}

^a Department of Chemistry, Bielefeld University, Universitätsstraße 25, 33615 Bielefeld, Germany

^b Center for Clean Combustion Research, KAUST, Thuwal 23955-6900, Saudi Arabia

^c Physico Chemical Fundamentals of Combustion, RWTH Aachen University, Schinkelstraße 8, 52062 Aachen, Germany

ARTICLE INFO

Article history:

Received 12 January 2018

Revised 15 February 2018

Accepted 2 March 2018

Available online xxx

Keywords:

Dual-fuel strategy

Low-temperature oxidation

Chemical interaction

n-pentane

Dimethyl ether

Ethanol

El-MBMS

Flow reactor

ABSTRACT

With the aim to study potential cooperative effects in the low-temperature oxidation of dual-fuel combinations, we have investigated prototypical hydrocarbon (C_5H_{12}) / oxygenated (C_2H_6O) fuel mixtures by doping *n*-pentane with either dimethyl ether (DME) or ethanol (EtOH). Species measurements were performed in a flow reactor at an equivalence ratio of $\phi=0.7$, at a pressure of $p=970$ mbar, and in the temperature range of 450–930 K using electron ionization molecular-beam mass spectrometry (EI-MBMS). Series of different blending ratios were studied including the three pure fuels and mixtures of *n*-pentane containing 25% and 50% of C_2H_6O . Mole fractions and signals of a significant number of species with elemental composition $C_nH_{2n+x}O_y$ ($n=1-5$, $x=0-(n+2)$, $y=0-3$) were analyzed to characterize the behavior of the mixtures in comparison to that of the individual components. Not unexpectedly, the overall reactivity of *n*-pentane is decreased when doping with ethanol, while it is promoted by the addition of DME. Interestingly, the present experiments reveal synergistic interactions between *n*-pentane and DME, showing a stronger effect on the negative temperature coefficient (NTC) for the mixture than for each of the individual components. Reasons for this behavior were investigated and show several oxygenated intermediates to be involved in enhanced OH radical production. Conversely, ethanol is activated by the addition of *n*-pentane, again involving key OH radical reactions. Although the main focus here is on the experimental results, we have attempted, in a first approximation, to complement the experimental observations by simulations with recent kinetic models. Interesting differences were observed in this comparison for both, fuel consumption and intermediate species production. The inhibition effect of ethanol is not predicted fully, and the synergistic effect of DME is not captured satisfactorily. The exploratory analysis of the experimental results with current models suggests that deeper knowledge of the reaction chemistry in the low-temperature regime would be useful and might contribute to improved prediction of the low-temperature oxidation behavior for such fuel mixtures.

© 2018 The Combustion Institute. Published by Elsevier Inc. All rights reserved.

1. Introduction

Adverse effects on the environment and climate caused by the combustion of fossil fuels in conventional engines underline the need for more efficient and cleaner engine–fuel combinations [1,2]. Fuel additives as a component of intelligent fuel design can serve to control the ignition timing in advanced engine concepts using homogeneous charge compression ignition (HCCI), reactivity-

controlled compression ignition (RCCI), and stratified-charge compression ignition (SCCI), with the prospect of cleaner burning processes and higher thermal efficiencies [3,4]. However, the operation of such engine–fuel combinations must rely on the fundamental knowledge of the combustion chemistry that drives the low-temperature auto-ignition of fuel mixtures. Such low-temperature combustion (LTC) strategies can involve mixtures of high-cetane and high-octane fuels with their synergistic combustion characteristics to achieve high thermal efficiencies, and several approaches have been demonstrated, e.g. using primary reference fuels with additives to achieve efficient engine control and ignition timing [5,6]. High-cetane fuels usually auto-ignite early, showing typical low-temperature heat release (LTHR) and high-temperature heat release (HTHR) characteristics. The addition of high-octane fuels

* Corresponding author at: Department of Chemistry, Bielefeld University, Universitätsstraße 25, 33615 Bielefeld, Germany.

E-mail addresses: hanfeng.jin@kaust.edu.sa (H. Jin), kkh@uni-bielefeld.de (J. Pieper).

¹ They both contributed equally to this work.

suppresses the early LTHR, shifting more of the heat release from high-cetane fuels closer to the top dead center of engines, thereby improving the combustion efficiency in internal combustion engines.

Dual-fuel mixtures are a good basis to understand the chemistry of multi-component mixtures. In spite of its importance for practical applications in engines, however, detailed information regarding potential interactions between different fuel components in the LTC regime remains scarce. The auto-ignition of mixtures with simple molecular structures was investigated recently [7,8], including methane/dimethyl ether (DME) and propane/DME blends. These studies have profited from the numerous low-temperature oxidation investigations of light C_3 – C_4 alkanes [8–18] as a substantial basis to examine dual-fuel interactions. Regarding heavier alkanes, *n*-heptane/ethanol (EtOH) blends were investigated by Saisirirat et al. [19,20] under HCCI and jet-stirred reactor (JSR) conditions, with a noted impact of *n*-heptane on ethanol consumption between 600 and 700 K. Their work mainly focused on ignition delay times, however, and only a few intermediates were observed which could not illustrate the nature of the interaction between *n*-heptane and ethanol [19,20]. A challenge to fully understand such interactive effects for fuels of the size of *n*-heptane or *iso*-octane is the large number of isomeric structures that are formed in the low-temperature oxidation reactions via alkyl (R), peroxyalkyl (ROO), and hydroperoxyalkyl (QOOH) radicals. The identification and quantification of these radicals and their subsequent reaction products are often beyond the capability of commonly used diagnostic techniques. Furthermore, significant uncertainties exist in the pressure-dependent kinetic parameters of these reactions [21–25] which limit the further development of accurate kinetic models. As a reasonable compromise, we have therefore chosen *n*-pentane (C_5H_{12}), an alkane component in gasoline, as the primary fuel in this work to explore its interaction with fuel additives of different ignition reactivity.

As for lighter or heavier alkanes [8–18,21–25], a number of studies have been performed of the low-temperature oxidation of *n*-pentane, using rapid compression machine (RCM) [26–35], shock tube (ST) [34–36], and JSR [37–40] experiments. Most of the previous experimental work focused on the macroscopic auto-ignition behavior of *n*-pentane, with detailed speciation reported only in recent publications of Bugler et al. [39] and Rodriguez et al. [40]. Bugler et al. [39] have also developed a mechanism for the auto-ignition of pentane isomers which they examined against JSR data (500–1100 K, 1 and 10 atm) obtained by gas chromatography (GC), cavity ring-down spectroscopy (CRDS), and Fourier transform infrared spectroscopy (FTIR). Rodriguez et al. [40] complemented the atmospheric-pressure JSR experiments in the temperature range of Bugler et al. [39] with measurements using synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS). Their experiment successfully identified and separated contributions of different isomers, especially of saturated, unsaturated, and carbonyl hydroperoxides. These recent investigations support the choice of *n*-pentane as base fuel for the present work.

DME and ethanol have been selected as isomeric fuel additives of different reactivity in this study. They are considered as potential or widely applied biofuels that could reduce the emission of air pollutants [1,41,42]. DME has been used as a fuel additive or alternative fuel in compression ignition engines because of its excellent auto-ignition characteristics [43]. It has a high cetane number (CN = 55) and was found to be an excellent ignition improver for HCCI engines [44,45]. The present knowledge on these two isomeric fuels' low-temperature oxidation reactions is more detailed for DME than for ethanol. Experimental investigations, including ignition delay [7,46] and speciation [41,47–54] measurements in JSRs and flow reactors have laid an extensive foundation for DME's reaction kinetics. Quantum chemical calculations

were performed for both the first and second O_2 addition reactions, as well as the further reactions of the $CH_3OCH_2O_2$ (ROO) and CH_2OCH_2OOH (QOOH) intermediates [55]. The pressure-dependent description for these reactions is sensitive to the low-temperature oxidation of DME [56], which was well considered in the recently published DME models of Burke et al. [7] and Rodriguez et al. [57]. Very recently, Jiang et al. [58] determined ignition delay times of *n*-pentane/DME mixtures and their experimental results compared favorably to the pentane isomer model by Bugler et al. [35]. The situation for a detailed study including reactive intermediates of *n*-pentane/DME interactive mixture effects in the LTC regime attempted here should thus be considered favorable.

Ethanol is a commonly used additive to fossil transportation fuels. Different from DME, ethanol has a high research octane number (RON = 109 [59]) and displays single-stage ignition. Compared to ample studies on the high-temperature combustion of ethanol, its low-temperature oxidation chemistry has attracted lesser attention [51,60–63]. Haas et al. [61] and Herrmann et al. [51] studied the oxidation of pure ethanol in flow reactor conditions with somewhat different results. Very weak negative temperature coefficient (NTC) behavior might have been observed for the rich ethanol/ O_2 /Ar mixture by Herrmann et al. [51] as evident from their Fig. 3a, but not in the work of Haas et al. [61]. The model of Cancino et al. [60] also showed a slight NTC behavior in the reproduction of Herrmann et al.'s data [51], but no further studies confirmed these results. Recognizing these difficulties, ethanol auto-ignition has been investigated very recently for ST and RCM conditions by adding DME as a radical initiator [64].

Regarding this background, it is to be expected that *n*-pentane will exhibit different global NTC behavior when blended with either isomer of C_2H_6O , namely DME or ethanol. However, there is a lack of prior information on the detailed oxidation reactions and intermediate species mole fractions or on any potential interactions between the two fuels in such mixtures. We therefore provide speciation experiments in a flow reactor for both, the dual-fuel mixtures of *n*-pentane/DME and *n*-pentane/EtOH, at near-atmospheric pressure and in the temperature range of 450–930 K. The species composition along the reaction progress was analyzed using electron ionization molecular-beam mass spectrometry (EI-MBMS). The results for the mixtures were compared to the behavior of each individual fuel component. Temperature-resolved, extensive species information has thus been obtained systematically regarding synergistic or antagonistic effects between these fuels of different reactivity, and combined with an analysis of the detailed chemical oxidation pathways.

Although the main emphasis in the present work is on the experimental results, we have complemented the measured species data with initial simulations by two recent kinetic models. Specifically, we have used the model for pentanes of the Galway group [39] and the recent update of the Polimi mechanism [17]. Discrepancies between experiment and simulation were noted and are discussed in an attempt to improve the understanding of the low-temperature oxidation mechanisms for these mixtures including interactive effects.

2. Experimental and numerical approaches

2.1. Flow reactor experiment

The low-temperature oxidation reactions of *n*-pentane, DME, ethanol, and the respective dual-fuel mixtures were investigated in a flow reactor in the temperature regime of 450–930 K (step size $\Delta T = 5$ K), keeping several important parameters constant. The experiments were consistently performed at $\phi = 0.7$, 970 mbar, a total cold gas flow rate of 300 sccm (standard cubic centimeters per minute at 1 atm and 273.15 K), and an argon dilution of 90%.

Table 1Experimental conditions; γ is the fraction of *n*-pentane in the mixture: $\gamma = x_{C_5H_{12}}/(x_{C_5H_{12}} + x_d)$, *d*: DME or EtOH.

Fuel	Name	P (bar)	ϕ	γ	Gas flow rate (sccm), std. 273.15 K, 1 atm					
					Total	Ar	O ₂	C ₅ H ₁₂	DME	EtOH
<i>n</i> -Pentane (C ₅ H ₁₂)	P100	0.97	0.7		300.0	270.0	27.59	2.414		
Dimethyl ether (DME)	D100	0.97	0.7		300.0	270.0	24.32		5.676	
Ethanol (EtOH)	E100	0.97	0.7		300.0	270.0	24.32			5.676
C ₅ H ₁₂ /DME mixtures	PD75	0.97	0.7	0.75	300.0	270.0	27.18	2.114	0.705	
	PD50	0.97	0.7	0.50	300.0	270.0	26.61	1.694	1.694	
C ₅ H ₁₂ /EtOH mixtures	PE75	0.97	0.7	0.75	300.0	270.0	27.18	2.114		0.705
	PE50	0.97	0.7	0.50	300.0	270.0	26.61	1.694		1.694

A lean stoichiometry was chosen due to the importance of lean and efficient burning and of the influences of high amounts of oxygen for the formation of oxygenated species. Electron ionization molecular-beam mass spectrometry was employed to identify the species composition. A detailed description of the experimental set-up, including both the reactor and mass spectrometry technique, has been reported earlier [41,51,52] so that only some details of importance for the present experiment are given here.

The reactor is a fused silica tube with an inner diameter of 8 mm. Its total length is 1.4 m, with a heating area of 1.3 m that is divided into 8 independently regulated zones [65]. These are heated using an electrical furnace and are controlled by Ni-Cr/Ni thermocouples at the outside wall of the reactor. The exhaust gas from the reactor is extracted with a quartz nozzle (50 μ m orifice) at the reactor exit and guided *via* a copper skimmer and a two-stage differential pumping system into the ionization chamber of the mass spectrometer. Molecules are then ionized by a 17 eV electron beam and detected by their time of flight with a resolution of $m/\Delta m \approx 2200$, enabling the separation of hydrocarbon and oxygenated species of the same nominal mass.

The inlet conditions for the oxidation experiments are listed in Table 1 and address the three individual fuels as well as two sets each of *n*-pentane mixtures with DME or EtOH. *n*-Pentane ($\geq 99\%$) was supplied by ChemSolute, and ethanol ($\geq 99.96\%$) was provided by VWR Chemicals. Gases were obtained from Linde AG, including dimethyl ether ($\geq 99.9\%$), O₂ ($\geq 99.5\%$), and Ar ($\geq 99.996\%$). The fraction of *n*-pentane in the mixture is expressed as γ in Table 1. The delivery of *n*-pentane and ethanol relied on a dialysis pump (Protea PM-1000) providing flow rates in the μ l/min range with uncertainties of 1%. To prepare the respective mixtures, gases were metered by calibrated mass flow controllers (MKS Instruments, uncertainty $\sim 5\%$), and liquid fuels were vaporized, mixed with the gases, and then preheated to 423 K prior to the reactor inlet.

Quantitative species mole fractions were determined whenever possible according to the procedure by Schenk et al. [66] using Ar as the reference. Following that work, the ratio of the integrated ion signal of a species to a reference signal is proportional to the ratio of their mole fractions, weighted by an energy-dependent calibration factor that includes a number of relevant experimental parameters. Here, the calibration factors for major species (C₅H₁₂, DME, EtOH, O₂, H₂O, CO, and CO₂) were determined from calibration with cold-gas samples and using the C, H, and O element balances at high-temperature equilibrium conditions. Intermediates were calibrated by simulating the signal ("convolution" method in [66]). The resulting uncertainties of mole fractions for major species are typically within 15%, and those for intermediate species are within a factor of 2, depending on the available cross section information from the literature. In cases where electron ionization cross sections or calibration information was not available as for some of the detected oxygenated species, relative species profiles are reported in terms of signal intensities normalized by the respective fuel inlet mole fraction to facilitate the analysis of trends between the behavior of individual mixture components and the

mixtures. All experimental data reported in this work are provided in Supplementary Material 1 (SM1).

2.2. Numerical simulation

Simulations of the oxidation process in a laminar flow reactor have typically assumed a constant gas temperature or have relied on measured gas temperature profiles along the reactor, determined in non-reactive flows at identical reactor wall temperature [41,49,67]. Heat release in such reacting systems, typically approximated as negligible for highly diluted mixtures, is thus not considered, and consequently, negligible heat transfer between the reacting gas and the reactor wall is assumed, as no highly diluted conditions have been used here (10% reactive mixture). This limit may not be applicable for less diluted conditions, especially since temperature is a very sensitive parameter in the low-temperature oxidation process. An accurate physical model of a laminar flow reactor should consider mass convection, mass diffusion, heat release of the reacting gas, thermal conductivity, and thermal exchange with the wall of the reactor.

Since this work is mainly focused on reporting experimental results, we provide only a first approximation of model predictions for the investigated conditions. The simulation of the flow reactor using the OpenSMOKE++ package [68] follows procedures by Refs. [51,65]. A multi-zone approach was used, dividing the reactor into a pre-heating zone (14 cm), a reaction zone (111 cm), and a cooling zone (5 cm). A time-resolved non-isothermal solution was applied. The temperature profile of the non-reacting argon flow was measured along the reactor at different heating temperatures, and the heat transfer coefficient k for transfer between the heating furnace and the reacting gas through the flow reactor wall was evaluated by simulating a pure (non-reactive) argon flow. As a result, a coefficient of $k = 10 \text{ W m}^{-2} \text{ K}^{-1}$ was assigned for all reaction conditions. Details for the evaluation of k are provided together with the measured and simulated gas temperature profiles (Fig. S1) in Supplementary Material 2 (SM2). We acknowledge that this approach may reach its limits for the reactive mixtures with very temperature-sensitive chemistry, and suggest that the assumptions made here should be tested with more refined models in the future that might consider two-dimensional effects and changing heat transfer depending on reaction conditions.

For the initial simulation, two recent mechanisms were chosen to explore the interaction between *n*-pentane and dimethyl ether or ethanol. The mechanism by Bugler et al. [39], here called the NUIG model, provides a low-temperature oxidation pentane sub-mechanism, which was improved based on their previous model [35] and examined against ignition delay times and JSR experimental data. The DME and ethanol sub-mechanisms in the NUIG model were also comprehensively investigated in their former kinetic studies [7,49,62]. Also, we have chosen the long-term developing and regularly updated model by Ranzi et al. [17], here called Polimi model. Their recent improvements in the low-temperature oxidation chemistry were focused on the reaction of carbonyl-

hydroperoxides and peroxy radicals [17,21]. In any case, comparisons of our experimental data reported here with model simulations should be regarded as an initial exploration focused mainly on the trends observed for the mixtures, with the aim to detect substantial deviations between experiment and model that may serve to guide further model development.

3. Results and discussion

In this section, experimental results are presented for the dual-fuel mixtures and analyzed in consideration of those for the individual fuels. The main aim is to detect and contribute to understanding differences in reactivity and species formation in the low-temperature regime with *n*-pentane as the base fuel upon addition of each of the two oxygenated isomers. In addition, initial modeling is performed for the three individual fuels and the mixtures to examine, in particular, their capability to reproduce the trends in the low-temperature oxidation behavior. Generally, we will limit the model analysis to the NUIG model [39], with some additional results given for the Polimi model [17], especially to illustrate differences in the prediction for the fuel mixtures. A species list of the NUIG model with all species discussed in this work can be found in Table S1 in SM2 with formula, model name, nomenclature and structure.

Section 3.1 will present the conversion of the individual fuels and the dual-fuel combinations. Section 3.2 will provide more detailed insight into the reaction pathways for the different fuel components by reporting temperature-dependent profiles of intermediate species with an emphasis on the behavior of the fuel mixtures. Section 3.3 will conclude with selected aspects of the low-temperature chemistry of these dual-fuel combinations.

3.1. Reactivity of dual-fuel mixtures

Selected experimental results for the low-temperature oxidation of all individual fuels and fuel combinations listed in Table 1 are given in Fig. 1. It shows the consumption of fuel and O₂ as well as the formation of H₂O and permits a first inspection of the temperature-dependent oxidation behavior. All major species profiles are presented in Figs. S2–S8 in SM2 together with simulations with the NUIG and Polimi models. The profiles in Fig. 1 are presented with the same scale, and a thin broken line at 616 K, the temperature for the low-temperature minimum of *n*-pentane consumption, is included to facilitate comparison.

As expected, both *n*-pentane and DME show a two-stage oxidation behavior (*n*-pentane: 616 K and 830 K, DME: 550 K and additional ignition at 750 K not in the focus here), while the consumption of ethanol starts only above 750 K. The low-temperature minimum of the fuel mole fraction near 550 K for DME is significantly lower than for *n*-pentane at 616 K. These temperatures compare quite well with the results of Herrmann et al. [51] for DME and ethanol (see also the Supplemental Material of that paper), and of Bugler et al. [39] for *n*-pentane, considering the slightly different conditions in those studies. Increasing addition of DME to *n*-pentane increases the reactivity and shifts the minimum to temperatures below that for pure *n*-pentane. Ethanol/*n*-pentane mixtures show some low-temperature reaction already for PE50 as particularly evident from the H₂O mole fraction with a peak near 625 K, and further increasing reactivity for PE75, with minima shifted to higher temperatures than for pure *n*-pentane.

In Fig. 2, the interaction effects are visualized in more detail, showing only the fuel consumption curves including predictions with both models. The four panels (a–d) consider these effects with *n*-pentane as the base fuel to which increasing amounts of DME (a and c) and ethanol (b and d) are added. Every profile is

normalized by the inlet mole fraction of *n*-pentane in the specific mixture to ensure comparability between the measurements. The bottom two panels (e and f) take an inverse perspective, with DME and ethanol as the respective basis and a corresponding normalization. Because of the normalization, identical profiles would be expected if no mixture effects occurred.

The enhancement of the reactivity of *n*-pentane by DME in panels (a and c) in Fig. 2 is quite well reproduced by both models. The experimental profiles are slightly shifted toward lower temperatures and may indicate a small trend of increasing low-temperature fuel conversion (conversion = 1 – consumption) that is, however, within the experimental uncertainty. In the NTC region, some differences are seen in the shape of the experimental profiles with increasing DME addition, and the recovery of the fuel mole fraction toward the initial value near 750 K is less pronounced for the PD50 mixture. The NUIG model reproduces the shape of the profile excellently for the pure *n*-pentane condition and catches the trends for all conditions quite well. With shifts to lower temperatures by about 12 K for PD75 and 22 K for PD50 and an increase in low-temperature fuel conversion, it slightly overpredicts the effect of DME on the reactivity. With the Polimi model, the predictions are closer to the experimental results, with shifts by about 8 K and 16 K to lower temperatures and almost identical fuel consumption in this regime, and a slightly better representation of the profiles also at higher temperatures. A tendency toward predicting two peaks can be noted in the NTC region for both the PD75 and PD50 mixtures. This effect is seen also in the major species curves in Figs. S5 and S6 in SM2. The reason for this behavior seems to be related to the representation of heat transfer in the numerical simulation (see Section 2.2), since exploratory modeling results for these two neat fuels and their mixtures without considering the heat release of the reacting gases (Figs. S9–S12 in SM2) do not show this two-peak behavior. As explained above in Section 2.2, the present modeling results should be considered as a first approximation, awaiting a more full description of two-dimensional effects and changing heat release that is, however, beyond the present study with a mainly experimental focus.

As seen in Fig. 2b and d, the addition of ethanol significantly inhibits the consumption of *n*-pentane in contrast to the effect of DME. It shifts the consumption temperature to a higher region, narrows the temperature window of the NTC zone, and significantly reduces the maximum fuel conversion. Both models can well reproduce the *n*-pentane profile for the PE75 mixture but fail for PE50. The measured maximum conversion of *n*-pentane in PE50 is near 40%, while the NUIG model predicts only about 20% and the Polimi model shows only very weak low-temperature reaction.

Instead of focusing on *n*-pentane as the base fuel to which DME or ethanol is added, the opposite perspective is assumed in Fig. 2e and f which reports the consumption profiles for the oxygenated fuels. From this perspective, the addition of *n*-pentane inhibits the low-temperature behavior of DME but promotes that of ethanol. The strong effect evident from the experiments upon *n*-pentane addition to DME (Fig. 2e) is also reflected in the model predictions. The measured low-temperature consumption profiles are shifted to higher temperatures by 35 K for PD50 and 49 K for PD75. Both NUIG and Polimi models overestimate the reactivity of DME in the mixture conditions, and the NUIG model presents a wider temperature shift than the Polimi model. Also, differences are noted between experiment and model in the consumption around 725 K as a function of *n*-pentane addition, not well reflected in the NUIG model that apparently considers only weak interaction between both fuels and thus leads to negligible deviations between the PD75 and PD50 cases. The Polimi model results in a slightly better match with the experimental consumption curve in this region. A synergistic effect between DME and *n*-pentane is observed in the experiment, detecting somewhat higher conversion of these two

Fig. 1. Temperature-dependent species mole fraction profiles for Ar, fuel, O_2 , and H_2O for pure DME (D100), *n*-pentane (P100), and ethanol (E100) as well as for mixtures of either oxygenated fuel with 75% (PD75, PE75) and 50% (PD50, PE50) of *n*-pentane. The broken line at 616 K is drawn to guide the eye. The temperature plotted on the *x*-axis is the set temperature at the outside wall of the reactor.

active fuels in their mixtures than for each fuel individually. Trends in the two models differ in this respect.

The addition of *n*-pentane to ethanol enhances the ethanol reactivity in the low-temperature region (Fig. 2f). While inhibition of *n*-pentane consumption in this regime was already visible upon 50% ethanol addition (PE50, Fig. 2b,d), ethanol conversion in the PE50 mixture is negligible within the experimental uncertainty (therefore not included in Fig. 2f). A strong promotion tendency

of *n*-pentane is seen for the PE75 mixture that shows a maximum low-temperature ethanol conversion of 35%. One reason why the ethanol mole fraction could decrease would be a dilution effect by *n*-pentane; the total moles of the reacting gas can expand due to the oxidation of *n*-pentane, leading to a reduction of the ethanol mole fraction. To confirm the reaction of ethanol near 650 K, the result of a simulation with an assumed non-reactive ethanol species is provided in Fig. S13 in SM2 that shows the di-

Fig. 2. Reactivity for neat fuels and dual-fuel mixtures. Experimental fuel consumption mole fraction profiles (symbols) are given as a function of temperature, together with model simulations (lines). **Panels (a-d):** *n*-Pentane consumption profiles for pure *n*-pentane fuel and for mixtures containing 75% and 50% *n*-pentane with DME (a and c) or EtOH (b and d); each profile is normalized by the inlet mole fraction of *n*-pentane. Simulation results for (a and b) were obtained with the NUIG model [39] and for (c and d) with the Polimi model [17]. **Panels (e and f):** Consumption profiles for DME (e) and EtOH (f) for different inlet conditions; each profile is normalized by the respective inlet fuel mole fraction. Solid line: NUIG model, dashed line: Polimi model. The profile for PE50 is not shown in (f) because of negligible low-temperature chemistry behavior.

lution effect to be negligible compared to the chemical reaction. The experimental observations for *n*-pentane addition to ethanol are reasonably well predicted by both models (Fig. 2f).

For a deeper understanding of the low-temperature reaction behavior of the fuel mixtures in consideration of the detailed reactions of the individual components, intermediate species formation along the fuel decomposition and oxidation reaction pathways will be presented with a focus on the experimental data, including discussion of simulation trends with the NUIG model.

3.2. Intermediate species formation

In the following, we will discuss the formation of key intermediate species observed in the low-temperature oxidation of the dual-fuel mixtures in view of the reaction pathways of the individual fuel components. Although the general structure of these LTC pathways is quite well known, schematic diagrams for the fuel-specific reactions in this study are presented for *n*-pentane in Fig. 3 and for the two oxygenated fuels in Fig. 4. They are intended to facilitate identification of intermediate species discussed in the text by their mass and molecular structure (compare also Table S1 in SM2) as well as by an assigned code number.

The following discussion is organized along the reaction pathways of *n*-pentane and will present the experimentally observed species profiles for this base fuel and the dual-fuel mixtures regarding important classes of low-temperature intermediates and changes upon DME and ethanol addition. Simulation results with the NUIG model are included for orientation.

Starting with the fuel *n*-pentane (RH, **P1**), H-abstraction forms the fuel radicals (R, **P2**) and the subsequent first oxygen addition yields pentylperoxy radicals (ROO, **P3**), not detectable in the present experiment, however. ROO can either form hydroperoxypentanes (**P4**) by H-addition or alkenes (**P5**) by HO₂-elimination or isomerize to QOOH radicals (**P6**). Along the reaction progress, the first stable, and thus detectable species are hydroperoxypentanes (**P4**) and alkenes (**P5**), discussed in Section 3.2.1. After isomerization of ROO (**P3**) ↔ QOOH (**P6**), a second O₂-addition step can occur leading to O₂QOOH (**P7**) species. By OH-elimination the ketohydroperoxide (KHP, **P8**) is formed, which is the next stable and detectable intermediate, presented in Section 3.2.2, with consideration also of the ketohydroperoxide in the DME oxidation, hydroperoxymethyl formate (HPMF, **D8**). In Section 3.2.3, selected small oxygenated intermediates are provided including hydroperoxyalkanes, acids, and carbonyl compounds, accessible through further decomposition of the ketohydroperoxide,

Fig. 3. Reaction pathway diagram for *n*-pentane. Species code starts with P, the first figure denotes the step along the reaction progress, and isomers are distinguished by the second figure (e.g., **P2-3** identifies one of the three isomers of the fuel radical in the *n*-pentane oxidation). FAC: formic acid, AAL: acetaldehyde, FAL: formaldehyde.

and Section 3.2.4 reports information on some further detected intermediates.

3.2.1. Hydroperoxypentanes (P4) and pentenes (P5)

3.2.1.1. Hydroperoxypentanes ($C_5H_{12}O_2$, P4). Hydroperoxyalkanes are the products of ROO radicals via chain termination reactions, recognized as a competing channel to the $ROO \leftrightarrow QOOH$ isomerization [12]. The signal of the stable species detected at a mass-to-charge ratio of $m/z = 104$ with formula $C_5H_{12}O_2$ is therefore assigned here to hydroperoxypentanes (P4), without a possibility to discriminate between the **P4-1**, **P4-2**, and **P4-3** isomers in Fig. 3, however. Temperature-dependent $C_5H_{12}O_2$ profiles for the different conditions are provided in Fig. 5. The experimental profiles present the maximum for the base fuel *n*-pentane near 585 K in close agreement with the start of the fuel conversion. Small temperature shifts are observed when adding DME or ethanol to *n*-pentane. Modeling results, however, predict more important shifts, similarly to those observed for the *n*-pentane consumption profiles in Fig. 2. Quantification of hydroperoxypentanes (P4) was not possible because of lacking electron ionization cross sections, but the relative trends, namely higher conversion of $C_5H_{12} \rightarrow C_5H_{12}O_2$ in the mixtures, are evident from the observed signal intensities, normalized to the inlet *n*-pentane mole fraction. As an indication for the probable concentration range, a mole fraction of about 3×10^{-5} has been observed by Rodriguez et al.

[40] for the sum of hydroperoxypentanes in pure *n*-pentane oxidation under their lean JSR conditions. Hydroperoxypentane isomers (P4) are formed via the reaction of hydroperoxypentyl radicals ($C_5H_{11}O_2$, ROO, P3) and HO_2 . Thus, the formation of hydroperoxypentane (P4) is determined by the efficiency of the pentyl (P2) production in the reacting system. DME oxidation provides an enhanced amount of OH radicals already at lower temperatures, shifting hydroperoxypentane (P4) formation to lower temperatures and slightly increasing the amount. In contrast, ethanol reduces the production of hydroperoxypentanes (P4) and increases their formation temperature slightly. Particularly for the PE50 mixture, the signal is too weak to be detected in the experiment, thus only the modeling result is provided in Fig. 5. The NUIG model predictions show a slight tendency to overestimate the intensity of the influence of the oxygenated additive.

3.2.1.2. Pentenes (C_5H_{10} , P5). Temperature-dependent profiles for C_5H_{10} (P5) are given in Fig. 6; the mole fraction represents the sum of 1-pentene and 2-pentene, with the C_5H_{10} signal calibrated as 1-pentene (with calibration based on 2-pentene, the total mole fraction would be 4.9% higher). The profiles reveal both low-temperature reactions as well as high-temperature formation from the fuel radicals (R, P2). Temperature shifts in both regimes are negligible for DME addition and minor upon ethanol addition, a trend that is also well captured by the model. Mixtures containing

Fig. 4. Reaction pathway diagram for DME and ethanol. Species codes follow the same rules as in Fig. 3. FAC: formic acid, AAL: acetaldehyde, FAL: formaldehyde.

Fig. 5. Signal intensities (left axis, arbitrary units) of $C_5H_{12}O_2$, assigned to hydroperoxypentanes (**P4**), normalized by the different inlet mole fractions of *n*-pentane (symbols) and quantitative mole fractions (right axis) from NUIG model predictions (lines). (a) *n*-Pentane/DME, (b) *n*-pentane/EtOH. No experimental data of $C_5H_{12}O_2$ is observed in PE50 due to its low concentration, thus only the modeling result is provided.

75% *n*-pentane (PD75 and PE75) present similar pentene maxima to that in pure *n*-pentane (P100) oxidation, and reduction effects are only visible for the 50:50 mixtures (PD50 und PE50). Simulation results have been divided by a factor of 2 to fit the scale in Fig. 6 since the model over-predicts the mole fractions in all cases. For pure *n*-pentane oxidation, Bugler et al. [39] also show a tendency to over-predict especially 2-pentene concentrations under lean conditions at $\phi = 0.5$ and 1 atm.

3.2.2. Ketohydroperoxides (P8, D8)

3.2.2.1. Pentane ketohydroperoxide ($C_5H_{10}O_3$, P8). Figure 7 presents the signal intensity for $C_5H_{10}O_3$ (**P8**), normalized by the different *n*-pentane inlet conditions. Note again that all profiles should be identical because of this normalization if no mixture effects would occur. The observed signal can be ascribed to the sum of C_5 -ketohydroperoxide (**P8**), the three isomers of which have been identified by Rodriguez et al. [40]; from their SVUV-PIMS

Fig. 6. Experimental mole fractions (left axis) of pentenes (sum of C_5H_{10} , **P5**, symbols), normalized (in the *n*-pentane-containing mixtures) by the different *n*-pentane inlet mole fractions, and NUIG model predictions (right axis) for the sum of 1-pentene and 2-pentene (lines). (a) *n*-Pentane/DME, (b) *n*-pentane/EtOH. Please note that all simulation results have been divided by a factor of 2.

Fig. 7. Signal intensities (left axis, arbitrary units) for $C_5H_{10}O_3$ assigned to C_5 -ketohydroperoxides (**P8**), normalized by the different inlet mole fractions of *n*-pentane (symbols), and quantitative mole fractions (right axis) from NUIG model prediction (lines). (a) *n*-Pentane/DME, (b) *n*-pentane/EtOH.

study they reported a somewhat preferential formation of 3-hydroperoxy-pentanal (**P8-1**) and 1-hydroperoxy-3-pentanone (**P8-3**) over that of 2-hydroperoxy-4-pentanone (**P8-2**), which is kinetically favored, however, and provided mole fraction values of the order of 10^{-5} for the sum of the C_5 -ketohydroperoxides for pure *n*-pentane oxidation under lean JSR conditions. Quantification is not possible here because electron ionization cross sections are lacking. The addition of DME (Fig. 7a) reduces the formation temperature, in agreement with the observed tendencies for *n*-pentane consumption and hydroperoxypentane formation (see above). The model represents the relative profile shape reasonably well for the pure *n*-pentane (P100) case. For the mixtures investigated here, the model overestimates the influence of DME. The reason may be lacking low-temperature-related reactions of the mixtures, as e.g., $RO_2 + R'O_2 \rightarrow RO + R'O + O_2$ and H-abstraction of the RO_2 species of both fuels. With the addition of ethanol, the reactivity of the system is significantly reduced (Fig. 7b), and the profiles for the *n*-pentane/ethanol blends are shifted to higher temperature. The maximum signals decrease, in agreement with the lower consumption of *n*-pentane in Fig. 2b. The NUIG model can reproduce the tendencies for different conditions reasonably well, with the somewhat larger differences in the NTC region that were already evident in the fuel consumption profiles (Fig. 2b). For all five conditions, the experimental peak positions agree well with those for the hydroperoxypentanes (**P4**), as might be expected from the close relation of these species along the reaction pathway (Fig. 3), and those from the model again exhibit a larger spread in temperature.

3.2.2.2. DME ketohydroperoxide ($C_2H_4O_4$, HPMF, D8). The general formation path of the ketohydroperoxide of DME proceeds similar to that of the pentane ketohydroperoxide (compare Fig. 4). In their experiments focused on low-temperature oxidation of DME in a JSR, Moshhammer et al. [53,54] have identified the signal at $m/z = 92$ corresponding to the sum formula of $C_2H_4O_4$ as hydroperoxymethyl formate (HPMF, **D8**). In the present work, HPMF (**D8**) was only detected for pure DME conditions due to its significant fragmentation and correspondingly, low signal. CH_4O_3 at $m/z = 64$ was confirmed by Moshhammer et al. [53] to be a dominant fragment of HPMF (**D8**) by CO loss. They also performed theoretical calculations and assigned its structure as hydroxymethyl hydroperoxide ($HOCH_2OH$, **D9**), clarifying earlier results of Wang et al. [41], who had also reported strong signals at this mass but assumed the species to be either hydroxymethyl hydroperoxide (**D9**) or trihydroxymethane. For the PD75 and PD50 mixtures, we thus consider the signal at $m/z = 64$ to be representative of HPMF (**D8**) in light of the results of [53]. Figure 8 reports the results for $m/z = 92$ (HPMF, **D8**) in the pure DME case (see insert top left) and $m/z = 64$ (CH_4O_3 , **D9**) for pure DME and the PD75 and PD50 mixtures. The temperatures of the maxima for both signals agree, supporting the assumption that the signal at $m/z = 64$ can be used as an indicator for HPMF.

With the addition of a large amount of *n*-pentane, the concentration of HPMF (**D8**) decreases significantly, e.g., a reduction of 90% for PD50 which can be partly due to diluting and chemical effects. Further reasons can include the shift toward higher temperatures that could enhance the decomposition of such labile

Fig. 8. Signal intensities (symbols, left axis, arbitrary units) of $m/z=64$ (CH_4O_2 , **D9**) and (insert top left) of $m/z=92$ (HPMF, **D8**) for D100, together with quantitative mole fractions from NUIG model predictions for HPMF (lines, right axis). For D100 and $m/z=64$, both measured and modeled results are divided by a factor of 5. Profiles have been normalized by the different inlet mole fractions for DME.

3.2.3. Selected small oxygenated intermediates

3.2.3.1. *Hydroperoxymethane (CH_4O_2 , **P9-1**) and hydroperoxyethane ($\text{C}_2\text{H}_6\text{O}_2$, **P9-2**).* Unlike hydroperoxypentanes (**P4**) that were discussed before, smaller hydroperoxyalkanes are secondary oxidation products. Within the detection limit of the experiment of a few ppm, no quantifiable signals could be observed for hydroperoxybutane ($\text{C}_4\text{H}_{10}\text{O}_2$) and hydroperoxypropane ($\text{C}_3\text{H}_8\text{O}_2$). However, the smaller species hydroperoxymethane (CH_4O_2 , **P9-1**) and hydroperoxyethane ($\text{C}_2\text{H}_6\text{O}_2$, **P9-2**) could be found. Methyl and ethyl radicals are derived from the decomposition of C_5 -ketohydroperoxides (**P8**) and pentylperoxy radicals (ROO, **P3**), and their reactions with O_2 or HO_2 can lead to the formation of these smaller hydroperoxyalkanes. The profiles of CH_4O_2 (**P9-1**) and $\text{C}_2\text{H}_6\text{O}_2$ (**P9-2**) in Fig. 9 are normalized (in the n -pentane-containing mixtures) by the inlet mole fractions of n -pentane, and for the pure fuels, P100 shows higher conversion to these small hydroperoxyalkanes (**P9**) than DME.

Since doping with DME promotes the reactivity of the system and consequently, the formation of pentyl radicals (R, **P2**) and of typical intermediates derived from the fuel decomposition, it also enhances the formation of the hydroperoxyalkanes in Fig. 9a and c in the PD75 mixture. No significant further increase is observed with increased DME content for PD50, however. This behavior is different in the model for both, hydroperoxymethane (Fig. 9a and b) and hydroperoxyethane (Fig. 9c and d), especially for the formation of the latter in PD50. In the oxidation of DME, hydroperoxymethane (**P9-1**) is proposed to be formed along a sequence from the $\text{CH}_3\text{OCH}_2\text{OO}$ radical (the ROO of DME, **D3**) via methyl formate (**D4**) and methyl radicals [54,69]. For pure DME (D100), hydroperoxymethane (**P9-1**) is indeed experimentally observed as shown in Fig. 9a, but the NUIG model predicts only insignificant amounts. Similar observations were noted by Moshhammer et al. [54], who report a mole fraction for hydroperoxymethane of the order of 10^{-5} and point out large discrepancies between their DME JSR experiment and several models including the NUIG DME mech-

Fig. 9. Signal intensities (symbols, left axes, arbitrary units) of CH_4O_2 and $\text{C}_2\text{H}_6\text{O}_2$ assigned to hydroperoxymethane (**P9-1**) and hydroperoxyethane (**P9-2**), respectively, normalized (in the n -pentane-containing mixtures) by the different inlet mole fractions of n -pentane, and quantitative mole fractions from NUIG model predictions (lines, right axes). (a and c) n -Pentane/DME, (b and d) n -pentane/EtOH.

Fig. 10. Quantitative mole fractions of CH_2O_2 , calibrated as formic acid (HCOOH , **FAC**), normalized (in the *n*-pentane-containing mixtures) by the different *n*-pentane inlet mole fractions. Symbols: experiment (left axes); lines: NUIG model predictions (right axes). (a) *n*-Pentane/DME, (b) *n*-pentane/EtOH.

anism [7]. Ethanol can form neither of these hydroperoxyalkanes in its low-temperature reactions, so that in mixtures of *n*-pentane and ethanol they must be produced only from *n*-pentane. Their formation tendencies in P100, PE75, and PE50 (Fig. 9b and d) are similar to those of the hydroperoxypentanes (**P4**) (see Fig. 5b). The shift with ethanol to higher temperature is expected because of the decrease of the system in reactivity. The wider spread of the peak temperatures in the modeling results is similar to that shown before for the C_5 -ketohydroperoxides (**P8**). The NUIG model represents the observed tendencies for these mixtures reasonably well.

3.2.3.2. Formic acid (FAC). Acids are important intermediates in the fuel oxidation process and lead to the formation of CO , CO_2 , and esters. For the mixtures of *n*-pentane and DME, pentanoic, acetic, and formic acid are the most favorable products. Possible acid mass peaks, at $m/z = 102$, 60, and 46 respectively, were detected in this work by EI-MBMS. However, in their investigation of *n*-pentane oxidation with SVUV-PIMS, Rodriguez et al. [40] identified the peak of $m/z = 102$ as pentenylhydroperoxide, and their PIE curve did not indicate a slope at the ionization energy of pentanoic acid. The species of $m/z = 60$ was identified as acetic acid by GC in the *n*-pentane oxidation study of Bugler et al. [39]. Here, we would need to consider not only acetic acid for $m/z = 60$ but also methyl formate, since it dominates in the oxidation of DME [51]. With the used electron ionization, however, isomer identification was not possible. The signal at $m/z = 46$ (CH_2O_2) is likely to be formic acid (**FAC**) as there are no other reasonable isomers, and is therefore calibrated as formic acid in this experiment. It is a typical DME-derived intermediate. *n*-Pentane also forms formic acid (**FAC**), but not in a similar amount as DME. Thus, **FAC** is selected as a typical species here to represent the interaction of *n*-pentane and DME. Figure 10a shows the experimental results for pure *n*-pentane, DME, and their mixtures, together with model simulations, while the complementary mixtures with ethanol, for which no significant interaction is noted, are presented in Fig. 10b.

Large temperature shifts are seen along the replacement of *n*-pentane with DME that are quite well matched by the model and correspond approximately to the consumption maxima in Fig. 2. Trends for the mixtures in the low-temperature region are quite well captured by the NUIG model that over-predicts **FAC** for P100, however, and under-predicts it for D100. This could be explained by the lacking importance of a reaction producing formic acid as suggested by Wang et al. [70]. They showed that the isomerization reaction of $\text{OCH}_2\text{OCHO} \rightarrow \text{HOCH}_2\text{OCO}$ is predicted to be more dominant in most models than its reaction to form formic acid ($\text{OCH}_2\text{OCHO} \rightarrow \text{HCOOH} + \text{HCO}$) which has; however, a much lower energy barrier and should therefore be more dominant (see Fig. 3 of Ref. [70]). For the *n*-pentane/DME mixtures, the NUIG model re-

Fig. 11. Rate of production analysis of formic acid (HCOOH) for different inlet conditions modeled by the NUIG model at the temperatures of the respective maximum mole fraction (± 5 K) in the NTC zone.

veals two formation pathways of formic acid to yield major contributions as shown in the rate of production (ROP) analysis in Fig. 11, where the reaction suggested in Ref. [70] is not considered.

From the ROP in Fig. 11 it can be seen that the pathway involving acetaldehyde (CH_3CHO , **AAL**) is important in the *n*-pentane oxidation, while the HOCH_2O radical (**D12**) channel contributes for both fuels, but to a larger extent for DME oxidation. Over this channel, **FAC** is formed via the decomposition of HPMF (**D8**) for D100 (see Fig. 4), or the combination of OH and CH_2O via the intermediate radical of HOCH_2O for P100 (see Fig. 3). The formaldehyde pathway becomes more important with the addition of DME. However, the rate constant of this channel estimated in the NUIG model is much faster than that from the theoretical investigation of Xu et al. [71], and its influence might thus be overestimated.

3.2.3.3. Carbonyl compounds. Formaldehyde (**FAL**), acetaldehyde (**AAL**), and butanone are important intermediates in *n*-pentane oxidation [39]. **AAL** is mainly formed via the decomposition of 2-hydroperoxy-4-pentanone (**P8-2**), which is, however, not the major ketohydroperoxide isomer in the *n*-pentane oxidation according to Rodriguez et al. [40], who measured only **P8-1** and **P8-3** in their experiment. However, **P8-2** is quite important in the formation of methyl radicals and impacts the formation of hydroperoxymethane (**P9-1**), formaldehyde (**FAL**) and even OH radicals via its subsequent reactions. The mole fractions of acetaldehyde and formaldehyde, normalized (in the *n*-pentane-containing mixtures) by the inlet mole fraction of *n*-pentane, are given in Fig. 12; as stated before, changes observed are thus due to interactive effects in the mixtures.

As seen in Fig. 12a, the **AAL** mole fraction is not changed significantly upon blending with 25% DME, but it is notably reduced with 50% DME, while the model predicts a constant **AAL** mole fraction. With increasing ethanol addition (Fig. 12b), the pathway forming acetaldehyde from ethanol (compare Fig. 4) gains importance, as also seen in the ROP analysis in Fig. 13. Ethanol is ac-

Fig. 12. Quantitative mole fractions of (a and b) acetaldehyde (AAL) and (c and d) formaldehyde (FAL), normalized (in the *n*-pentane-containing mixtures) by the different *n*-pentane inlet mole fractions. Symbols: experimental measurements (left axes); lines: NUIG model predictions (right axes). (a and c) *n*-Pentane/DME, (b and d) *n*-pentane/EtOH.

Fig. 13. Contributions of the main pathways in the formation of acetaldehyde (CH_3CHO , AAL) and formaldehyde (CH_2O , FAL) for the different inlet conditions. The results were obtained with the NUIG model at the respective maximum AAL and FAL mole fractions (± 5 K) in the NTC zone. Abbreviations: $\text{C}_5\text{H}_9\text{O}_1\text{-2OOH-4}$ is 2-hydroperoxy-4-methyltetrahydrofuran, $\text{O}_2\text{C}_5\text{H}_{10}\text{OH23}$ the pentan-3-ol-2-peroxy radical, $\text{NC}_5\text{KET24O}$ (P10-2) the 2-pentanoxy-4-one radical, and $\text{sC}_2\text{H}_4\text{OH}$ (E2-3) the α -ethanol radical. (Compare also nomenclature and structures in Table S1 in SM2).

activated by OH provided by the *n*-pentane oxidation. The ethanol radical ($\text{sC}_2\text{H}_4\text{OH}$, E2-3) that consumes $\sim 70\%$ of ethanol is the precursor of acetaldehyde.

Formaldehyde (FAL) as a typical oxidation intermediate is formed by different reactions for the three investigated fuels. CH_3 radical reactions provide major contributions to FAL for *n*-pentane, while the decomposition of $\text{CH}_3\text{OCH}_2\text{OO}$ (ROO, D3) and $\text{CH}_2\text{OCH}_2\text{OOH}$ (QOOH, D6) radicals are the main formation reactions of formaldehyde (FAL) in the oxidation of DME. For ethanol, the formation of FAL involves pathways via the methyl and the $\text{O}_2\text{C}_2\text{H}_4\text{OH}$ (E3-1) radicals. Figure 12c and d shows the normalized mole fractions of formaldehyde for all mixtures. Opposite tendencies are observed. With DME addition, the mole fraction increases compared to P100, but PD75 and PD50 show nearly the same amount. With the addition of ethanol, the mole fraction is similar for P100 and PE75, but lower for PE50.

The behavior of acetaldehyde (AAL) and formaldehyde (FAL) could be roughly explained by the enhanced H-abstraction of C_5 -ketohydroperoxides (P8) according to the work of Ranzi et al. [17]. The common reaction pathway for the decomposition of ketohydroperoxide species is described as O-O scission and subsequent β -scission. Here, this reaction sequence would lead to the formation of acetaldehyde. However, the decomposition pathway by H-abstraction of the C_5 -ketohydroperoxide and subsequent β -scission proposed by Ranzi et al. [17] would lead to pentadiene and ketene. These recently proposed reaction classes are not included in the NUIG kinetic model, and their implementation could lead to a better prediction of acetaldehyde especially for PD50 compared to PD75 (see Fig. 12a). The ROP analysis for acetaldehyde (AAL) in Fig. 13 shows that $\text{NC}_5\text{KET24O}$ (P10-2) is the main pathway, with the caveat, however, that the used model does not include the competing channels. The ROP analysis for formaldehyde (FAL) in Fig. 13 shows another important formation channel from the $\text{CH}_3\text{COCH}_2\text{O}$ radical (via the acetonil radical) in the blends with ethanol. It is a product of the unimolecular decomposition of 2-hydroperoxy-4-pentanone (P8-2). Because of the reduced amount of OH by ethanol, it reduces the gen-

Fig. 14. Mole fractions of selected oxygenated and hydrocarbon intermediates at their respective maxima in the low-temperature regime (logarithmic scale); the mole fraction of each species is normalized by the inlet mole fraction of *n*-pentane for the respective condition. (a and d): experimental results; (b and e) predictions with the NUIG model; (c and f) predictions with the Polimi model.

eral efficiency of formaldehyde formation but favors the unimolecular decomposition of **P8-2**. The production of formaldehyde in the ethanol-containing blends is therefore altered to the reaction sequence 2-hydroperoxy-4-pentanone ($C_5H_{10}O_3$, **P8-2**) $\rightarrow$ 2-pentanoxy-4-one ($C_5H_9O_2$, **P10-2**) $\rightarrow$ CH_3COCH_2 (C_3H_5O , acetylonyl) $\rightarrow$ CH_3COCH_2O ($C_3H_5O_2$) $\rightarrow$ CH_2O (**FAL**), compare also Fig. 3.

3.2.4. Further intermediates

While the previous analysis has focused on the fuel decomposition schemes and small oxygenated species, a number of further intermediates has also been detected, and selected species are presented in Fig. 14, with experimental results in panels (a and d) and predictions with the NUIG and Polimi models in panels (b, e and c, f). Again, all mole fractions (in the *n*-pentane-containing mixtures) have been normalized by the inlet mole fraction of *n*-pentane for the respective conditions. The maximum values of all species in the NTC zone are grouped in order to illustrate the selectivity of *n*-pentane reaction pathways impacted by the addition of DME or ethanol. Please note that full temperature-dependent mole fraction profiles over the entire range from 450 to 900 K are provided, together with simulations with the NUIG model, in Figs.

S14–S21 in SM2. In general, the shapes of these profiles are reasonably well predicted. However, with an emphasis on the experiment and on the low-temperature reactions in the dual-fuel mixtures, we will limit the discussion here to some aspects in the LTC region. Due to the normalization, mole fraction values should agree if there were no interactive effects. Inspection of the patterns in Fig. 14 reveals some important differences between experimental and modeling results.

Figure 14a–c compares experiment and model predictions for selected oxygenated intermediates. Since acetic acid is the major acid produced in the oxidation of *n*-pentane [39], it is identified as the dominant isomer of $C_2H_4O_2$ in P100, PE75, and PE50. However, methyl formate is the oxidation product of DME with the formula of $C_2H_4O_2$ [51,54], which is also observed in this experiment. Therefore, with the addition of DME, methyl formate becomes the major isomer of $C_2H_4O_2$. However, due to lacking EI cross sections of methyl formate, $C_2H_4O_2$ has been calibrated as acetic acid in all experiments. Hydroxyacetaldehyde would be another isomer, but there is no known pathway how it could be formed and it seems kinetically unlikely. Compared to the modeling results, this species is well-predicted by the Polimi model but highly under-predicted by NUIG model. Bugler et al. [39] also

Fig. 15. Schematic diagram of the major reaction cycles of (a) *n*-pentane, (b) DME, and (c) ethanol in the low-temperature oxidation of fuel blends. Solid thick arrows: reactions that produce OH radicals; solid thin arrows: H-abstraction reactions of the respective fuel; thick dashed arrows: reactions that promote the chain branching cycle; solid light-grey arrows: fictitious chain branching pathways of ethanol; thin dashed arrows: other products during the oxidation procedure. Abbreviations: KHP: ketohydroperoxide of *n*-pentane, HPMF: hydroperoxymethyl formate.

reported the under-prediction of their measurement of $C_2H_4O_2$ in the oxidation of *n*-pentane in a JSR.

The further species in Fig. 14a–c are single oxygenated species of the sum formula $C_nH_{2n}O$ that can be assigned to cyclic ethers, aldehydes, and ketones, and $C_nH_{2n-2}O$ that are probably ketenes. CH_2O can only be formaldehyde, C_2H_2O obviously is ketene, and C_3H_4O has been calibrated as methyl ketene. According to previous analysis with GC, CRDS, and FTIR [39], C_2H_4O was separated for oxirane and acetaldehyde, but is here calibrated only as acetaldehyde due to missing distinction of isomers. In Ref. [39], C_3H_6O was identified as propanal, acetone, 2-methyloxirane, and oxetane, here it is calibrated as acetone. In general, aldehyde compounds could be produced from the decomposition of the C_5 -hydroperoxides or ketohydroperoxides by breaking the O–OH bond in the hydroperoxy group. Cyclic ethers are usually formed via the reactions of QOOH radicals. Looking at the tendencies in Fig. 14a–c in both experimental and modeling results, identical selectivity is observed in both experiment and Polimi model predictions among different $C_nH_{2n}O$ and $C_nH_{2n-2}O$ species under different inlet condition except for PE50. The NUIG model predictions for CH_2O , C_2H_4O and C_3H_6O are closer to the experimental values than those for the other shown species, with substantial deviations especially for C_2H_2O (ketene) and $C_2H_4O_2$ (acetic acid), see also Figs. S14 and S17 in SM2.

Figure 14d–f presents the experimental and modeling results for selected alkanes and alkenes. Pentene (C_5H_{10} , calibrated as 1-pentene), propene (C_3H_6), and ethene (C_2H_4) are major intermediates. Both models well predict the formation of pentene and ethene, but under-predict the formation of butene (C_4H_8 , here calibrated as 1-butene) and propene. A uniform selectivity can be found among these species in different conditions in Fig. 14d–f, except for ethane (C_2H_6), for which experiment and model reveal opposite tendencies with the addition of DME and ethanol. As observed in the formation of hydroperoxymethane (Fig. 9), the methyl radical formed in the decomposition of DME undergoes the recombination to ethane, but not the reaction with O_2 . Since ethane is under-predicted by a factor of 100 in P100, a significant difference can be observed by the addition of DME for the modeling result, but not in the experiment.

3.3. Selected aspects influencing the reactivity

To inspect the reactivity of the dual-fuel mixtures further, the known major low-temperature oxidation cycles for the three individual fuels are shown schematically in Fig. 15. For all cycles, the solid thick arrows show reactions that produce OH radicals, while the solid thin arrows indicate OH-consumption. To obtain the maximum of OH being produced from one complete cycle, the solid

thick arrows after the second O_2 addition (behind O_2QOOH) need to be considered as all other reactions producing OH before this step lead to a termination of the cycle.

As seen in Fig. 15a for *n*-pentane, the two-step O_2 addition reaction sequence from the fuel could yield three OH radicals (solid thick arrows after O_2QOOH), while it consumes only one OH radical in its pentyl radical production process via H-abstraction reactions (solid thin arrow). The α -step is the most important *n*-pentane consumption reaction, which may be in strong competition in the fuel blends or with other primary intermediates during the reaction process.

OH is the dominant initial radical for the recurrence of the branching process of DME. As shown in Fig. 15b, a maximum of two OH radicals could be produced through one cycle (solid thick arrows after O_2QOOH), while also only one OH is consumed by the DME radical formation (solid thin arrow). However, in the α -step, a strong competition from *n*-pentane impacts the consumption of OH radicals. When the more reactive fuel DME is added to *n*-pentane, OH radicals could be produced at lower temperatures, thus promoting the system's reactivity. However, the maximum conversion of *n*-pentane keeps almost the same with the addition of DME (compare Fig. 2a), which means that the consumption of OH radicals by *n*-pentane does not significantly increase. This may be due to the similar concentration of OH radicals at identical equivalence ratio, or *n*-pentane taking advantage over DME in the competition of OH radical reactions.

Figure 15c shows the reactions of ethanol in the low-temperature region. The light-grey arrows indicate a fictitious second O_2 addition that cannot happen because of ethanol's molecular structure. Therefore, ethanol consumes one OH radical (solid thin arrow), and produces almost none in its reaction recurrence, as the ROO is very unlikely to be formed. Since ethanol plays the role of an OH radical consumer in *n*-pentane/ethanol mixtures, it sufficiently reduces the pool of active radicals and inhibits the general reactivity of the whole system.

As discussed above, the OH radical plays an important role in the H-abstraction of *n*-pentane, DME, and ethanol during the ignition progress in the low-temperature regime. H-abstraction reactions, especially with OH, are the first step turning RH (C_5H_{12} , DME, or EtOH) into the R radical. It is interesting to view the balance of OH and HO_2 , another prominent radical associated with low-temperature reactions. Fig. 16 shows the simulated mole fraction ratio of OH/ HO_2 for all fuel conditions. It is the ratio between the maxima of OH and HO_2 radicals along the flow reactor at each temperature point in the range of 475–750 K.

According to both, NUIG and Polimi models, the mole fraction of the OH radical is $\sim 10^{-8}$ in the NTC zone, and that of the HO_2 radical is $\sim 10^{-5}$ in that zone, corresponding to the high reactiv-

Fig. 16. Ratio of maximum mole fractions of OH and HO₂ radicals x_{OH}/x_{HO_2} along the flow reactor at each temperature point, predicted by the NUIG model for (a) the pure fuels, (b) the mixtures of *n*-pentane and DME, and (c) the mixtures of *n*-pentane and ethanol.

ity of OH in the H-abstraction reactions. For the neat fuels, the x_{OH}/x_{HO_2} ratio is highest for DME at very low temperatures of 480–580 K. After a slow but steady rise in this region, a steep increase occurs around 540 K, coincident with the DME low-temperature consumption maximum (see Fig. 2e). With rising temperature, the low-temperature kinetics slows down and chain-terminating reactions become of increasing importance. After a steep increase in OH production at about 560 K for *n*-pentane, approximately in the zone where low-temperature fuel consumption accelerates (see Fig. 2a), a plateau is reached that represents the competing reactions in the NTC region. Similar approximately constant values of the x_{OH}/x_{HO_2} ratio are also evident in the intermediate temperature range of about 570–670 K for DME and the *n*-pentane/DME mixtures in Fig. 16b. As discussed before, ethanol shows a much lower relative OH production in the low-temperature regime, with a rise of the x_{OH}/x_{HO_2} ratio only noted above 650 K with much lower values than for the other two fuels, and it should be remembered that no significant low-temperature fuel consumption was noted in this case (see Fig. 2f). Ethanol-containing mixtures with *n*-pentane exhibit a significantly increased OH production around 580 K for PE75 and 600 K for PE50, approximately near the respective start of fuel consumption; a plateau at higher temperatures up to 650 K can also be noted for these mixtures (Fig. 16c). The formation and consumption of OH radicals based on the reaction cycles in Fig. 15 can contribute to the understanding of the low-temperature system reactivity; more details on the efficiency of OH production following a similar analysis of Dames et al. [8] and Merchant et al. [18] for propane and propane/DME mixtures are also provided in Section S6 of SM2. They support the strong decrease in low-temperature reactivity for ethanol addition to *n*-pentane and show a small tendency of higher OH yield in the *n*-pentane/DME mixtures. It must be noted, however, that an assessment of the total OH production in the system may explain some features of the dual-fuel behavior, especially when systems with quite different low-temperature reactivity are considered. For the *n*-pentane/DME mixtures that show synergistic effects, these cannot be understood in terms of the OH balance alone but need to consider the formed fuel radicals and other early intermediates and their secondary reactions. For this reason, sensitivity analyses of OH were performed with the NUIG model for P100, PD75, and PD50 at 25% *n*-pentane conversion and are provided in Fig. 17.

The results also show the interaction of *n*-pentane and DME via the competition of the OH radical. In general, H-abstraction of *n*-pentane at the γ -site shows the highest negative coefficient, since for this radical it is most difficult to form new OH radicals in its further reactions. Upon DME addition, the abstraction reactions at the other two sites of *n*-pentane by OH radicals reduce their positive sensitivity or even turn to negative values. Second O₂-addition reactions have stronger sensitivities than the first O₂-addition step. The unimolecular decomposition reaction of the C₅-

Fig. 17. Sensitivity coefficient for OH to reaction rate pre-exponential factors at 25% *n*-pentane conversion (NUIG model). Abbreviations: NC₅KET24 is 2-hydroperoxy-4-pentanone (P8-2), NC₅KET24O is the 2-pentanoxy-4-one radical (P10-2), C₅H₁₀OOH2-4 is the 2-hydroperoxy-4-pentyl radical, C₅H₁₀OOH2-4O₂ is the 2-hydroperoxy-4-pentylperoxy radical, C₅H₁₀OOH3-1 is the 3-hydroperoxy-1-pentyl radical, C₅H₁₀OOH3-1O₂ is the 3-hydroperoxy-1-pentylperoxy radical, C₅H₁₁O₂-2 is the 2-pentylperoxy radical (P3-2), and C₅H₁₀-2 is 2-pentene (P5-2); compare also nomenclature and structures in Table S1 in SM2.

ketohydroperoxide (P8), forming one OH radical, becomes slightly less important with the doping of DME, whilst the H-abstraction reaction of DME and the decomposition of HPMF (D8) become very sensitive reactions for the mixture conditions, of increasing importance with higher DME fraction. Especially the formation and decomposition reactions of the ketohydroperoxide of the respective fuel are thus important pathways in the formation of OH radicals influencing the overall reactivity of the system.

4. Summary and perspectives

The low-temperature oxidation of mixtures of *n*-pentane with the oxygenated C₂H₆O fuel isomers dimethyl ether and ethanol, including that of the three individual fuels, was experimentally investigated in a flow reactor at an equivalence ratio of 0.7 and atmospheric pressure, covering the temperature range of 450–930 K. Electron ionization molecular-beam mass spectrometry was used to provide a detailed species overview under all conditions, with quantitative evaluation as mole fraction profiles whenever possible. In cases where only relative signal intensities could be provided, trends between the individual fuels and the mixtures could be identified. The overall reactivity of the fuels and their mixtures was discussed, considering the very different low-temperature behavior of the three individual fuels. To emphasize interactive effects of the C₂H₆O isomers in the blends with *n*-pentane, normalization on the *n*-pentane inlet mole fractions was performed.

Ethanol, as a fuel that exhibits only marginal low-temperature reactivity, is a significant consumer of active free radicals and thus inhibits the oxidation process in the mixtures, whilst the mixture of two reactive fuels, *n*-pentane and DME, presents noticeable synergistic effects where the maximum conversion of both *n*-pentane and DME is improved in the mixtures compared to the pure fuels.

For a deeper albeit preliminary understanding of the effects in the LTC of the dual-fuel mixtures, two current models, namely the NUIG and the Polimi models that can both be considered well examined for the individual fuels were adopted in simulations for all conditions. Both models were seen to perform reasonably well regarding the fuel consumption and major species formation for the individual fuels, but the predictions of temperature shifts and synergistic effects, especially in the oxidation behavior of the mixtures leave room for improvement. Such further developments can in part be considered for the simulation of two-dimensional effects and heat transfer in the flow reactor with more refined models than used in these preliminary predictions, especially in zones with very temperature-sensitive reactions.

The oxidation chemistry in the fuel mixtures was analyzed in more detail on the basis of the reaction pathways of the individual fuel components by following the sequence of initial fuel decomposition products and their further reactions by means of intermediate species profiles. Mole fractions of oxygenated intermediates as well as selected hydrocarbon species were presented with an emphasis on the zone of the initial fuel conversion and NTC region in the mixtures, and trends between experiment and model were compared, resulting in an overall somewhat diverse picture. While many trends seen in the experiments upon blending of *n*-pentane with either one of the two isomers are quite well reproduced by these preliminary simulations, the magnitude of the effects is not always correctly predicted, and large discrepancies are seen for some intermediates.

Regarding the reactivity of the system, the OH balance as well as the ratio of OH and HO₂, both important intermediates in the low-temperature oxidation zone, were inspected to assist understanding of some aspects of the interactions for the dual-fuel mixtures. The OH competition between *n*-pentane and ethanol, two fuels with very different low-temperature reactivity, seems simpler than between *n*-pentane and DME that both show low-temperature reactions with different production cycles of OH. Secondary products such as alkyl radicals could participate in this OH competition by enhancement of O₂ addition reactions that in turn can contribute to OH radical production. Because they are involved in the formation of OH radicals, acetaldehyde, hydroperoxyethane, and especially hydroperoxymethane, could also be considered as indicative species of the reactivity of the fuel mixture. Interactive effects between the reactive species provided in the fuel mixtures may result in a higher maximum conversion of both fuels than found for each of them individually.

The work presented here suggests several areas for further work. As seen in some cases, the nature of the isomer composition might change for the fuel blends, with C₂H₄O₂ as one example that should be predominantly acetic acid for *n*-pentane and methyl formate for DME oxidation. Isomer-resolved, quantitative species analysis over the critical temperature range between about 500 and 650 K for these dual-fuel mixtures is thus recommended as a further continuation of this work. It would be especially useful if it provided detailed data on first fuel decomposition products and highly oxygenated species. Furthermore, in spite of recent model development and ample knowledge on the oxidation of the three individual fuels in the literature, it seems that interactive effects cannot be fully captured and might need more accurate determination of critical reaction parameters in the low-temperature zone where the initial fuel consumption accelerates. Temperature dependences may need to be inspected with care. As one indicator

for such needs, it is interesting to note that the rate expressions for the H-abstraction reactions by OH for the three individual fuels exhibit important differences in both tested models. Since reliable predictions for the oxidation behavior of mixtures of alkane fuels with ethanol or DME – or more generally of hydrocarbon with oxygenated fuels – are highly desirable, we hope that the presented experimental dataset will contribute to the further improvement of models for such dual-fuel mixtures.

Acknowledgments

The authors wish to thank the Deutsche Forschungsgemeinschaft (DFG) for support of this work under contract KO1363/31-1. HJ is grateful for a fellowship of the Alexander von Humboldt (AvH) Foundation that supported his research period in Bielefeld. Helpful discussions with Dr. Luc-Sy Tran, now at Lille University, during his research period as an AvH Fellow in Bielefeld are gratefully acknowledged. Furthermore, the authors wish to thank Prof. Yiguang Ju, Princeton University, USA, for his profound and continuous interest in this work, for insightful discussions and for hosting HJ for a research stay in his group.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.combustflame.2018.03.003.

References

- [1] A.K. Agarwal, Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines, *Prog. Energy Combust. Sci.* 33 (2007) 233–271.
- [2] W. Leitner, J. Klankermayer, S. Pischinger, H. Pitsch, K. Kohse-Höinghaus, Advanced biofuels and beyond: chemistry solutions for propulsion and production, *Angew. Chem. Int. Ed.* 129 (2017) 5500–5544.
- [3] X. Lu, D. Han, Z. Huang, Fuel design and management for the control of advanced compression-ignition combustion modes, *Prog. Energy Combust. Sci.* 37 (2011) 741–783.
- [4] S. Kokjohn, R. Hanson, D. Splitter, J. Kaddatz, R. Reitz, Fuel reactivity controlled compression ignition (RCCI) combustion in light- and heavy-duty engines, *SAE Int. J. Fuels Lubr.* 4 (2011) pp. 2011–01–0357.
- [5] S. Saxena, I.D. Bedoya, Fundamental phenomena affecting low temperature combustion and HCCI engines, high load limits and strategies for extending these limits, *Prog. Energy Combust. Sci.* 39 (2013) 457–488.
- [6] B. Prabhakar, S. Jayaraman, R. Vander Wal, A. Boehman, Experimental studies of high efficiency combustion with fumigation of dimethyl ether and propane into diesel engine intake air, *J. Eng. Gas Turb. Power* 137 (2015) 41505.
- [7] U. Burke, K.P. Somers, P. O'Toole, C.M. Zinner, N. Marquet, G. Bourque, E.L. Petersen, W.K. Metcalfe, Z. Serinyel, H.J. Curran, An ignition delay and kinetic modeling study of methane, dimethyl ether, and their mixtures at high pressures, *Combust. Flame* 162 (2015) 315–330.
- [8] E.E. Dames, A.S. Rosen, B.W. Weber, C.W. Gao, C.-J. Sung, W.H. Green, A detailed combined experimental and theoretical study on dimethyl ether/propane blended oxidation, *Combust. Flame* 168 (2016) 310–330.
- [9] M. Cord, B. Husson, J.C. Lizardo Huerta, O. Herbinet, P.-A. Glaude, R. Fournet, B. Sirjean, F. Battin-Leclerc, M. Ruiz-Lopez, Z. Wang, M. Xie, Z. Cheng, F. Qi, Study of the low temperature oxidation of propane, *J. Phys. Chem. A* 116 (2012) 12214–12228.
- [10] M. Cord, B. Sirjean, R. Fournet, A. Tomlin, M. Ruiz-Lopez, F. Battin-Leclerc, Improvement of the modelling of the low-temperature oxidation of *n*-butane – Study of the primary reactions, *J. Phys. Chem. A* 116 (2012) 6142–6158.
- [11] C. Bahrini, P. Morajkar, C. Schoemaeker, O. Frottier, O. Herbinet, P.-A. Glaude, F. Battin-Leclerc, C. Fittschen, Experimental and modeling study of the oxidation of *n*-butane in a jet stirred reactor using cw-CRDS measurements, *Phys. Chem. Chem. Phys.* 15 (2013) 19686–19698.
- [12] F. Battin-Leclerc, O. Herbinet, P.-A. Glaude, R. Fournet, Z. Zhou, L. Deng, H. Guo, M. Xie, F. Qi, Experimental confirmation of the low-temperature oxidation scheme of alkanes, *Angew. Chem. Int. Ed.* 49 (2010) 3169–3172.
- [13] O. Herbinet, F. Battin-Leclerc, S. Bax, H. Le Gall, P.-A. Glaude, R. Fournet, Z. Zhou, L. Deng, H. Guo, M. Xie, F. Qi, Detailed product analysis during the low temperature oxidation of *n*-butane, *Phys. Chem. Chem. Phys.* 13 (2011) 296–308.
- [14] D. Healy, N.S. Donato, C.J. Aul, E.L. Petersen, C.M. Zinner, G. Bourque, H.J. Curran, *n*-Butane: ignition delay measurements at high pressure and detailed chemical kinetic simulations, *Combust. Flame* 157 (2010) 1526–1539.
- [15] D. Healy, D.M. Kalitan, C.J. Aul, E.L. Petersen, G. Bourque, H.J. Curran, Oxidation of C1–C5 alkane quaternary natural gas mixtures at high pressures, *Energy Fuels* 24 (2010) 1521–1528.

- [16] D. Healy, M.M. Kopp, N.L. Polley, E.L. Petersen, G. Bourque, H.J. Curran, Methane/*n*-butane ignition delay measurements at high pressure and detailed chemical kinetic simulations, *Energy Fuels* 24 (2010) 1617–1627.
- [17] E. Ranzi, A. Cuoci, A. Frassoldati, M. Pelucchi, T. Faravelli, New reaction classes in the kinetic modeling of low temperature oxidation of *n*-alkanes, *Combust. Flame* 162 (2015) 1679–1691.
- [18] S.S. Merchant, C.F. Goldsmith, A.G. Vandeputte, M.P. Burke, S.J. Klippenstein, W.H. Green, Understanding low-temperature first-stage ignition delay: Propane, *Combust. Flame* 162 (2015) 3658–3673.
- [19] P. Saisirirat, C. Togbé, S. Chanchaona, F. Foucher, C. Mounaim-Rousselle, P. Dagaut, Auto-ignition and combustion characteristics in HCCI and JSR using 1-butanol/*n*-heptane and ethanol/*n*-heptane blends, *Proc. Combust. Inst.* 33 (2011) 3007–3014.
- [20] P. Saisirirat, F. Foucher, S. Chanchaona, C. Mounaim-Rousselle, Spectroscopic measurements of low-temperature heat release for homogeneous combustion compression ignition (HCCI) *n*-heptane/alcohol mixture combustion, *Energy Fuels* 24 (2010) 5404–5409.
- [21] M. Pelucchi, M. Bissoli, C. Cavallotti, A. Cuoci, T. Faravelli, A. Frassoldati, E. Ranzi, A. Stagni, Improved kinetic model of the low-temperature oxidation of *n*-heptane, *Energy Fuels* 28 (2014) 7178–7193.
- [22] D.M.A. Karwat, S.W. Wagnon, M.S. Wooldridge, C.K. Westbrook, Low-temperature speciation and chemical kinetic studies of *n*-heptane, *Combust. Flame* 160 (2013) 2693–2706.
- [23] O. Herbinet, B. Husson, Z. Serinyel, M. Cord, V. Warth, R. Fournet, P.-A. Glaude, B. Sirjean, F. Battin-Leclerc, Z. Wang, M. Xie, Z. Cheng, F. Qi, Experimental and modeling investigation of the low-temperature oxidation of *n*-heptane, *Combust. Flame* 159 (2012) 3455–3471.
- [24] R. Di Sante, Measurements of the auto-ignition of *n*-heptane/toluene mixtures using a rapid compression machine, *Combust. Flame* 159 (2012) 55–63.
- [25] G.E. Bogin Jr., A. DeFilippo, J.Y. Chen, G. Chin, J. Luecke, M.A. Ratcliff, B.T. Zigler, A.M. Dean, Numerical and experimental investigation of *n*-heptane auto-ignition in the ignition quality tester (IQT), *Energy Fuels* 25 (2011) 5562–5572.
- [26] M. Ribaucour, R. Minetti, L.R. Sochet, H.J. Curran, W.J. Pitz, C.K. Westbrook, Ignition of isomers of pentane: an experimental and kinetic modeling study, *Proc. Combust. Inst.* 28 (2000) 1671–1678.
- [27] R. Minetti, A. Roubaud, E. Therssen, M. Ribaucour, L.R. Sochet, The chemistry of pre-ignition of *n*-pentane and 1-pentene, *Combust. Flame* 118 (1999) 213–220.
- [28] C.K. Westbrook, H.J. Curran, W.J. Pitz, J.F. Griffiths, C. Mohamed, S.K. Wo, The effects of pressure, temperature, and concentration on the reactivity of alkanes: experiments and modeling in a rapid compression machine, *Symp. (Int.) Combust.* 27 (1998) 371–378.
- [29] M. Ribaucour, R. Minetti, L.R. Sochet, Autoignition of *n*-pentane and 1-pentene: experimental data and kinetic modeling, *Symp. (Int.) Combust.* 27 (1998) 345–351.
- [30] J.F. Griffiths, P.A. Halford-Maw, C. Mohamed, Spontaneous ignition delays as a diagnostic of the propensity of alkanes to cause engine knock, *Combust. Flame* 111 (1997) 327–337.
- [31] R. Minetti, M. Ribaucour, M. Carlier, L.R. Sochet, Autoignition delays of a series of linear and branched chain alkanes in the intermediate range of temperature, *Combust. Sci. Technol.* 113–114 (1996) 179–192.
- [32] A. Cox, J.F. Griffiths, C. Mohamed, H.J. Curran, W.J. Pitz, C.K. Westbrook, Extents of alkane combustion during rapid compression leading to single- and two-stage ignition, *Symp. (Int.) Combust.* 26 (1996) 2685–2692.
- [33] J.F. Griffiths, P.A. Halford-Maw, D.J. Rose, Fundamental features of hydrocarbon autoignition in a rapid compression machine, *Combust. Flame* 95 (1993) 291–306.
- [34] B. Marks, O. Mathieu, R. Archuleta, E.L. Petersen, J. Bugler, A. Heufer, H. Curran, Ignition delay time measurements and modeling of *n*-pentane and *iso*-pentane at elevated pressures, 51st AIAA Aerospace Science Meeting (2013).
- [35] J. Bugler, B. Marks, O. Mathieu, R. Archuleta, A. Camou, C. Grégoire, K.A. Heufer, E.L. Petersen, H.J. Curran, An ignition delay time and chemical kinetic modeling study of the pentane isomers, *Combust. Flame* 163 (2016) 138–156.
- [36] V.P. Zhukov, V.A. Sechenov, A.Y. Starikovskii, Self-ignition of a lean mixture of *n*-pentane and air over a wide range of pressures, *Combust. Flame* 140 (2005) 196–203.
- [37] A. Chakir, M. Bellimam, J.C. Boettner, M. Cathonnet, Kinetic study of *n*-pentane oxidation, *Combust. Sci. Technol.* 77 (1991) 239–260.
- [38] V. Simon, Y. Simon, G. Scacchi, F. Baronnet, Étude expérimentale et modélisation des réactions d'oxydation du *n*-pentane et du cyclopentane, *Can. J. Chem.* 75 (1997) 575–584.
- [39] J. Bugler, A. Rodriguez, O. Herbinet, F. Battin-Leclerc, C. Togbé, G. Dayma, P. Dagaut, H.J. Curran, An experimental and modelling study of *n*-pentane oxidation in two jet-stirred reactors: The importance of pressure-dependent kinetics and new reaction pathways, *Proc. Combust. Inst.* 36 (2017) 441–448.
- [40] A. Rodriguez, O. Herbinet, Z. Wang, F. Qi, C. Fittschen, P.R. Westmoreland, F. Battin-Leclerc, Measuring hydroperoxide chain-branching agents during *n*-pentane low-temperature oxidation, *Proc. Combust. Inst.* 36 (2017) 333–342.
- [41] Z. Wang, X. Zhang, L. Xing, L. Zhang, F. Herrmann, K. Moshhammer, F. Qi, K. Kohse-Höinghaus, Experimental and kinetic modeling study of the low- and intermediate-temperature oxidation of dimethyl ether, *Combust. Flame* 162 (2015) 1113–1125.
- [42] K. Kohse-Höinghaus, P. Oßwald, T.A. Cool, T. Kasper, N. Hansen, F. Qi, C.K. Westbrook, P.R. Westmoreland, Biofuel combustion chemistry: from ethanol to biodiesel, *Angew. Chem. Int. Ed.* 49 (2010) 3572–3597.
- [43] W. Ying, Z. Longbao, Performance and emissions of a compression-ignition engine fueled with dimethyl ether and rapeseed oil blends, *Energy Fuels* 21 (2007) 1454–1458.
- [44] Y. Tsutsumi, K. Hoshina, A. Iijima, H. Shoji, Analysis of the combustion characteristics of a HCCI engine operating on DME and methane, *SAE Tech. Pap.* 2007-65-41 (2007).
- [45] M. Konno, Z. Chen, Ignition mechanisms of HCCI combustion process fueled with methane/DME composite fuel, *SAE Tech. Pap.* 2005-01-01 (2005).
- [46] U. Pfahl, K. Fieweger, G. Adomeit, Self-ignition of diesel-relevant hydrocarbon-air mixtures under engine conditions, *Symp. (Int.) Combust.* 26 (1996) 781–789.
- [47] N. Kurimoto, B. Brumfield, X. Yang, T. Wada, P. Diévert, G. Wysocki, Y. Ju, Quantitative measurements of HO₂/H₂O₂ and intermediate species in low and intermediate temperature oxidation of dimethyl ether, *Proc. Combust. Inst.* 35 (2015) 457–464.
- [48] P. Dagaut, C. Daly, J. Simmie, M. Cathonnet, The oxidation and ignition of dimethylether from low to high temperature (500–1600K): Experiments and kinetic modeling, *Symp. (Int.) Combust.* 27 (1998) 361–369.
- [49] H.J. Curran, S.L. Fischer, F.L. Dryer, The reaction kinetics of dimethyl ether. II: Low-temperature oxidation in flow reactors, *Int. J. Chem. Kinet.* 32 (2000) 741–759.
- [50] H. Guo, W. Sun, F.M. Haas, T. Farouk, F.L. Dryer, Y. Ju, Measurements of H₂O₂ in low temperature dimethyl ether oxidation, *Proc. Combust. Inst.* 34 (2013) 573–581.
- [51] F. Herrmann, B. Jochim, P. Oßwald, L. Cai, H. Pitsch, K. Kohse-Höinghaus, Experimental and numerical low-temperature oxidation study of ethanol and dimethyl ether, *Combust. Flame* 161 (2014) 384–397.
- [52] F. Herrmann, P. Oßwald, K. Kohse-Höinghaus, Mass spectrometric investigation of the low-temperature dimethyl ether oxidation in an atmospheric pressure laminar flow reactor, *Proc. Combust. Inst.* 34 (2013) 771–778.
- [53] K. Moshhammer, A.W. Jasper, D.M. Popolan-Vaida, A. Lucassen, P. Diévert, H. Selim, A.J. Eskola, C.A. Taatjes, S.R. Leone, S.M. Sarathy, Y. Ju, P. Dagaut, K. Kohse-Höinghaus, N. Hansen, Detection and identification of the keto-hydroperoxide (HOOCH₂OCHO) and other intermediates during low-temperature oxidation of dimethyl ether, *J. Phys. Chem. A* 119 (2015) 7361–7374.
- [54] K. Moshhammer, A.W. Jasper, D.M. Popolan-Vaida, Z. Wang, V.S. Bhavani Shankar, L. Ruwe, C.A. Taatjes, P. Dagaut, N. Hansen, Quantification of the keto-hydroperoxide (HOOCH₂OCHO) and other elusive intermediates during low-temperature oxidation of dimethyl ether, *J. Phys. Chem. A* 120 (2016) 7890–7901.
- [55] A.J. Eskola, S.A. Carr, R.J. Shannon, B. Wang, M.A. Blitz, M.J. Pilling, P.W. Seakins, S.H. Robertson, Analysis of the kinetics and yields of OH radical production from the CH₃OCH₂ + O₂ reaction in the temperature range 195–650 K: an experimental and computational study, *J. Phys. Chem. A* 118 (2014) 6773–6788.
- [56] A.S. Tomlin, E. Agbro, V. Nevrlý, J. Dlabka, M. Vašínek, Evaluation of combustion mechanisms using global uncertainty and sensitivity analyses: a case study for low-temperature dimethyl ether oxidation, *Int. J. Chem. Kinet.* 46 (2014) 662–682.
- [57] A. Rodriguez, O. Frotier, O. Herbinet, R. Fournet, R. Bounaceur, C. Fittschen, F. Battin-Leclerc, Experimental and modeling investigation of the low-temperature oxidation of dimethyl ether, *J. Phys. Chem. A* 119 (2015) 7905–7923.
- [58] X. Jiang, F. Deng, F. Yang, Y. Zhang, Z. Huang, High temperature ignition delay time of DME/*n*-pentane mixture under fuel lean condition, *Fuel* 191 (2017) 77–86.
- [59] M. Eyidogan, A.N. Ozsezen, M. Canakci, A. Turkcan, Impact of alcohol-gasoline fuel blends on the performance and combustion characteristics of an SI engine, *Fuel* 89 (2010) 2713–2720.
- [60] L.R. Cancino, M. Fikri, A.A.M. Oliveira, C. Schulz, Measurement and chemical kinetics modeling of shock-induced ignition of ethanol-air mixtures, *Energy Fuels* 24 (2010) 2830–2840.
- [61] F.M. Haas, M. Chaos, F.L. Dryer, Low and intermediate temperature oxidation of ethanol and ethanol-PRF blends: an experimental and modeling study, *Combust. Flame* 156 (2009) 2346–2350.
- [62] G. Mittal, S.M. Burke, V.A. Davies, B. Parajuli, W.K. Metcalfe, H.J. Curran, Autoignition of ethanol in a rapid compression machine, *Combust. Flame* 161 (2014) 1164–1171.
- [63] M.S. Graboski, R.L. McCormick, Combustion of fat and vegetable oil derived fuels in diesel engines, *Prog. Energy Combust. Sci.* 24 (1998) 125–164.
- [64] Y. Zhang, H. El-Merhubi, B. Lefort, L. Le Moyné, H.J. Curran, A. Kéromnès, Probing the low-temperature chemistry of ethanol via the addition of dimethyl ether, *Combust. Flame* 190 (2018) 74–86.
- [65] C. Hemken, U. Burke, K.-F. Lam, D.F. Davidson, R.K. Hanson, K.A. Heufer, K. Kohse-Höinghaus, Toward a better understanding of 2-butanone oxidation: detailed species measurements and kinetic modeling, *Combust. Flame* 184 (2017) 195–207.
- [66] M. Schenk, L. Leon, K. Moshhammer, P. Oßwald, T. Zeuch, L. Seidel, F. Mauss, K. Kohse-Höinghaus, Detailed mass spectrometric and modeling study of isomeric butene flames, *Combust. Flame* 160 (2013) 487–503.
- [67] L. Cai, A. Sudholt, D.J. Lee, F.N. Egolfopoulos, H. Pitsch, C.K. Westbrook, S.M. Sarathy, Chemical kinetic study of a novel lignocellulosic biofuel: Di-*n*-butyl ether oxidation in a laminar flow reactor and flames, *Combust. Flame* 161 (2014) 798–809.

- [68] A. Cuoci, A. Frassoldati, T. Faravelli, E. Ranzi, OpenSMOKE++: An object-oriented framework for the numerical modeling of reactive systems with detailed kinetic mechanisms, *Comput. Phys. Commun.* 192 (2015) 237–264.
- [69] S.L. Fischer, F.L. Dryer, H.J. Curran, The reaction kinetics of dimethyl ether. I: High-temperature pyrolysis and oxidation in flow reactors, *Int. J. Chem. Kinet.* 32 (2000) 713–740.
- [70] Z. Wang, X. Zhang, L. Xing, L. Zhang, F. Herrmann, K. Moshhammer, F. Qi, K. Kohse-Höinghaus, Experimental and kinetic modeling study of the low- and intermediate-temperature oxidation of dimethyl ether, *Combust. Flame* 162 (2015) 1113–1125.
- [71] S. Xu, R.S. Zhu, M.C. Lin, Ab initio study of the OH+CH₂O reaction: the effect of the OH••OCH₂ complex on the H-abstraction kinetics, *Int. J. Chem. Kinet.* 38 (2006) 322–326.