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Sub Topic: Reaction kinetics

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A high pressure jet-stirred reactor study of di-iso-pentyl ether and detailed kinetic modelling

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Abstract: In this study, the oxidation of di-iso-pentyl ether is investigated for the first time. Dilute mixtures (DIPEE/O_2/N_2) were oxidized in a jet-stirred reactor at 10 atm, between 450 and 1210 K and at a residence time of 0.7 s. Four mixtures were investigated with equivalence ratios of 0.5, 1, 2, and 4. In the low/intermediate temperature region, about 40 species were identified and quantified through FTIR and GC-FID-MS analyses. Given the quantified intermediates, it was observed that alkyl radicals such as iso-pentyl and iso-butyl radicals appear to be important intermediates in DIPEE oxidation. The most abundant oxygenated intermediates at low temperature include formaldehyde, iso-pentanal, acetaldehyde, and acetone which are reaching mole fractions greater than 100 ppm. Besides, species such as iso-butanal, isopentanoic acid, isoamyl formate, and isoamyl alcohol were also identified. DIPEE has very high reactivity (it starts to oxidize at 470 K) and exhibits two distinct zones of reactivity before the high-temperature zone, which can also be called as a double-cool flame. This behavior is due to the interactions caused by the low-temperature chemistry of the alkyl radicals within the cool flame regime. A detailed kinetic sub-mechanism for DIPEE oxidation was developed including detailed low-temperature chemistries of species like iso-pentanal and iso-butanal, based on our previous studies. While the kinetic mechanism predicts the experimental profiles reasonably well, there is room for improvement especially in assigning rate constants to the low-temperature reactions of the oxygenated species for which very few theoretically obtained or directly measured values exist.

***Keywords*:** di-iso-pentyl ether, jet-stirred reactor, oxidation, kinetics

1. Introduction

Recently, ethers caught the interest of the combustion community, since some of them have been proven to have suitable characteristics to be used as biofuels. Several studies have been published on these molecules; our team has put a great effort toward understanding the oxidation and pyrolysis behaviour of ethers, with systematic experimental and modelling studies [1-5]. In this context, the oxidation of di-iso-pentyl ether (DIPEE) is studied in a jet-stirred reactor, in the same experimental conditions as di-isopropyl, di-n-propyl, di-n-butyl and diethyl ethers, in order to have a direct comparison. All these ethers, except di-isopropyl ether, showed an important reactivity at low temperature (between 450 and 750 K).

To the best of our knowledge, there are no studies available on the combustion behaviour of DIPEE. Even if there are no proofs yet on its possible use as biofuel, it is worth understanding the oxidation behaviour of DIPEE, to add a further insight in studying the ethers.

2. Experimental set-up

Experiments were performed in a fused silica jet-stirred reactor (JSR). A detailed description of this setup can be found in [6], here only a brief summary will be given. The reactor is placed in a stainless-steel pressure resistant jacket, which allows experiments to be performed

up to 10 atm and it is heated by an electrical oven, enabling temperatures up to 1280 K. The temperature inside the reactor is continuously monitored by a Pt/Pt-Rh thermocouple, which can be moved along the reactor axis, allowing to check the homogeneity. The reactive mixtures are highly diluted in nitrogen, to prevent high heat release and ensure the stability of the temperature. Fuel and oxygen are brought separately to the reactor and only allowed to mix inside, in order to prevent premature reactions. All the experiments presented were performed at 10 atm, with a residence time of 0.7 s and an initial fuel concentration of 1000 ppm. A low-pressure sonic probe is used to freeze the reactions and collect samples of the reacting mixture.

Both online and offline analyses were performed on the collected samples. Online analyses were carried out by sending the sample through a heated line to a Fourier transform infrared (FTIR) spectrometer, which allows the quantification of H_2O, CO, CO_2, CH_2O and formic acid. Offline analyses were performed after storing the samples in Pyrex bulbs at around 85 mbar. Two gas chromatographs (GC) with a flame ionization detector (FID) were used: the first one is equipped with a CP-SIL 5CB column, coupled with a DB1 column, allowing the quantification of oxygenated compounds, while the second one uses a CP-Al_2O_3/KCl column in order to quantify hydrocarbons. The identification of the products is done by GC/MS on a Shimadzu GC2010 Plus, using electron impact as the ionization mode. Finally, H_2 and O_2 profiles were obtained through a GC-TCD (thermal conductivity detector), using a CP-CarboPLOT P7 column.

In this study, the main species that were quantified are DIPEE, H_2, H_2O, CO, CO_2, C_2H_4, CH_4, C_3H_6, isobutene, formaldehyde, acetone, isopentanal and isoamyl alcohol. Some other oxygenated species were also identified and quantified, such as isoamyl formate, isopentanoic acid and isobutyl formate. The carbon balance is checked for each sample and it was found to be maximum 20% for few conditions at low temperature where there may be some unidentified trace species.

3. Kinetic modelling

Similar to our previous studies, a sub-mechanism has been developed and integrated into the complete mechanism. In the DIPEE sub-mechanism the rate constants were adopted from the literature as follows:

- The hydrogen abstraction by OH radicals on the beta C-H site of the fuel is assumed from the calculations in [7, 8] for n-butanol; the H-abstraction by OH on the gamma site is taken from Cohen [9], similar to the tertiary carbon in an alkane. The same consideration was done for the delta sites, with the rate constant taken as the one of the primary site of an alkane. For the alpha site, the rate constant was taken as similar to di-n-propyl ether (DPE) [2].
- Similar considerations are made for the H-abstraction by H radicals on the gamma and delta sites. For the alpha and beta sites, similarly to DPE, the rate constants are taken respectively by Ogura [10] and by analogy to alkanes.
- Hydrogen abstraction by HO_2 and CH_3 radicals are taken by similar considerations, from Mendes [11] and Aguilera [12] and from Xu [13] respectively.
- Rate constants for the oxygen addition ($R+O_2 \rightleftharpoons RO_2$) are adopted from Goldsmith [14]. For the second O_2 addition, the rate constants are taken as half of that for the 1st addition.
- Beta-scission of the fuel radicals are taken as similar to DBE in our previous work [5], and for the QOOH radicals, these are adopted from the theoretical calculations of Villano et al. [15].
- Other reactions related to low-temperature reactivity are taken as similar to our previous works [2, 5].

- DIPEE unimolecular decompositions are taken by analogy from the works of Lizardo-Huerta [16] and of Cook et al. [17] but these do not play a role in these oxidation experiments.

The JSR simulations were carried out using the Perfectly Stirred Reactor (PSR) model in ChemkinPRO [18].

4. Results and discussion

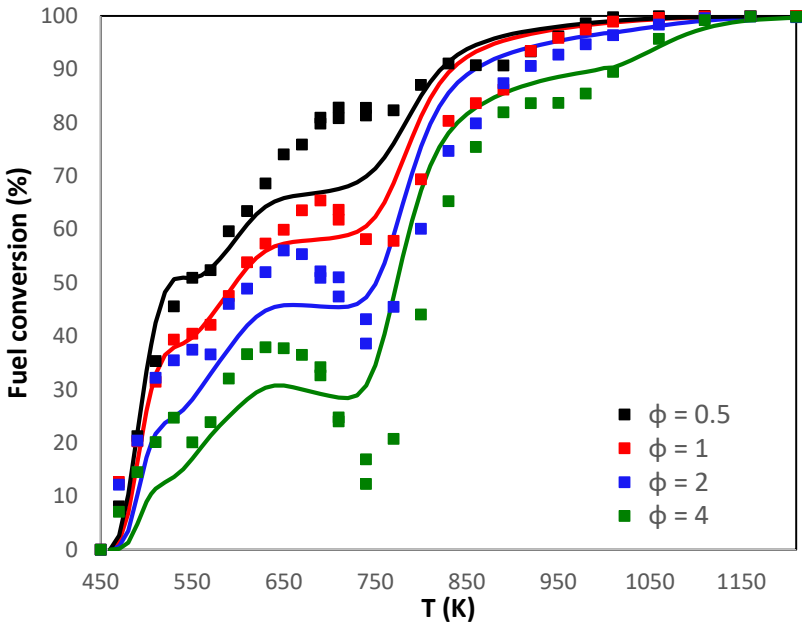

Figure 1. DIPEE fuel conversion for all equivalence ratios

DIPEE fuel conversions are reported in Figure 1. At all equivalence ratios, DIPEE is showing a strong low-temperature reactivity, which is then followed by an NTC region within a small temperature range. The NTC region starts at around 540 K, with the conversion (Figure 1) showing a small plateau up to 570 K. Then the reactivity increases again, until 650–690 K, depending on the equivalence ratio. After this point, a very strong decrease in reactivity is showed, especially for the richer mixtures, with an important drop in fuel conversion, up to 770 K. After this second cool flame regime, the reactivity increases again, reaching the high-temperature zone.

The mechanism is capable of predicting this double-cool flame regime, even if it is underestimating the reactivity at intermediate temperatures and especially under lean conditions. On the other hand, at higher temperatures, the model is slightly overpredicting the fuel consumption. These small inaccuracies are probably due to the rate constants which are mainly taken by analogies, leading to overprediction. In figures 4 to 6, molar fractions of some of the measured species are shown, along with the simulations, for three equivalence ratios, 0.5, 1 and 2. Representative uncertainty bars of 15% are added for all the experimental results. In general, the model is well reproducing the general tendencies of DIPEE and of its oxidation products.

Between the main products of DIPEE oxidation at low and intermediate temperature it is possible to find formaldehyde, iso-butene, acetone, isopentanoic acid, isoamyl formate and isoamyl alcohol. Formaldehyde is a typical marker of low-temperature reactivity and also for

DIPEE it is produced with a concentration up to 300 ppm. The mechanism is slightly over predicting the molar fractions, but it is capable of following the trend quite well.

Isoamyl formate is produced from the alpha-radical, which undergoes a first oxygen addition, then the RO_2 isomerizes through a 6-member transition state and β-scission of this QOOH, yields isoamyl formate, isobutene and an OH radical (Fig. 2). Both isobutene and isoamyl formate concentrations are well predicted in the intermediate temperature zone (650–750 K) for rich and stoichiometric mixtures, while isoamyl formate is still underpredicted in lean conditions. It may therefore be interesting to further analyse its production pathways, the assumed rate constants as well as the thermochemistry of RO_2 and QOOH species involved in its formation.

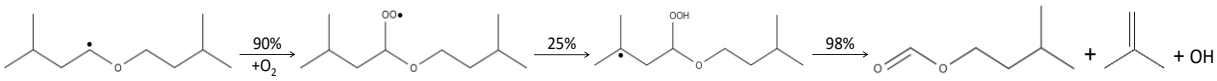

Figure 2. Reaction pathways leading to the formation of isoamyl formate (percentages are computed at 750 K for a stoichiometric mixture)

Isoamyl alcohol is produced through two main pathways (Figure 3), both starting with the gamma radical of the fuel, followed by addition to O_2 and $RO_2 \rightleftharpoons$ QOOH isomerisation through a 6-member transition state, followed by beta-scission. One of the products of this scission is the 3-methylbutyl radical, which undergoes O_2 addition and then form isoamyl alcohol through subsequent low-temperature pathways, as illustrated in Figure 3. Iso-pentanal mole fraction profiles are slightly underpredicted at lower temperatures and slightly overpredicted in the intermediate range. The opposite behavior is observed for isoamyl alcohol, meaning that the pathway leading to formaldehyde as a co-product should probably be more important in the intermediate temperature region. Finally, isopentanoic acid molar fractions are overall quite well predicted by the model. The maximum concentration (around 550 K) is well captured for rich and lean conditions, while it is underpredicted for the stoichiometric condition, even if the position of this peak is well simulated.

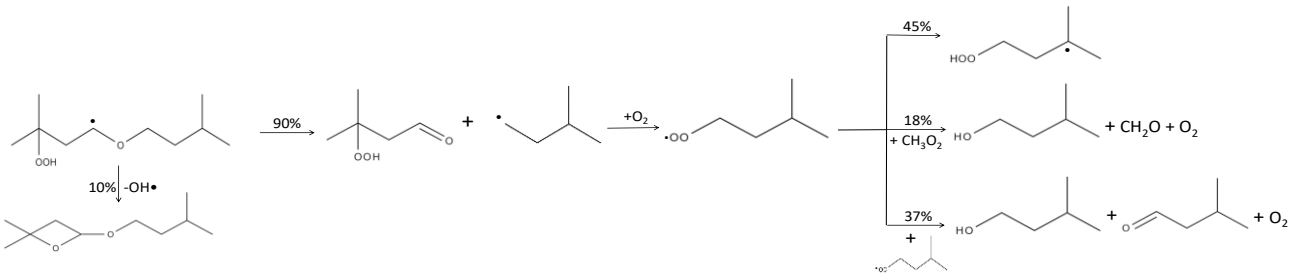

Figure 3. Reaction pathways leading to the formation of isoamyl alcohol (percentages are computed at 550 K for a stoichiometric mixture).

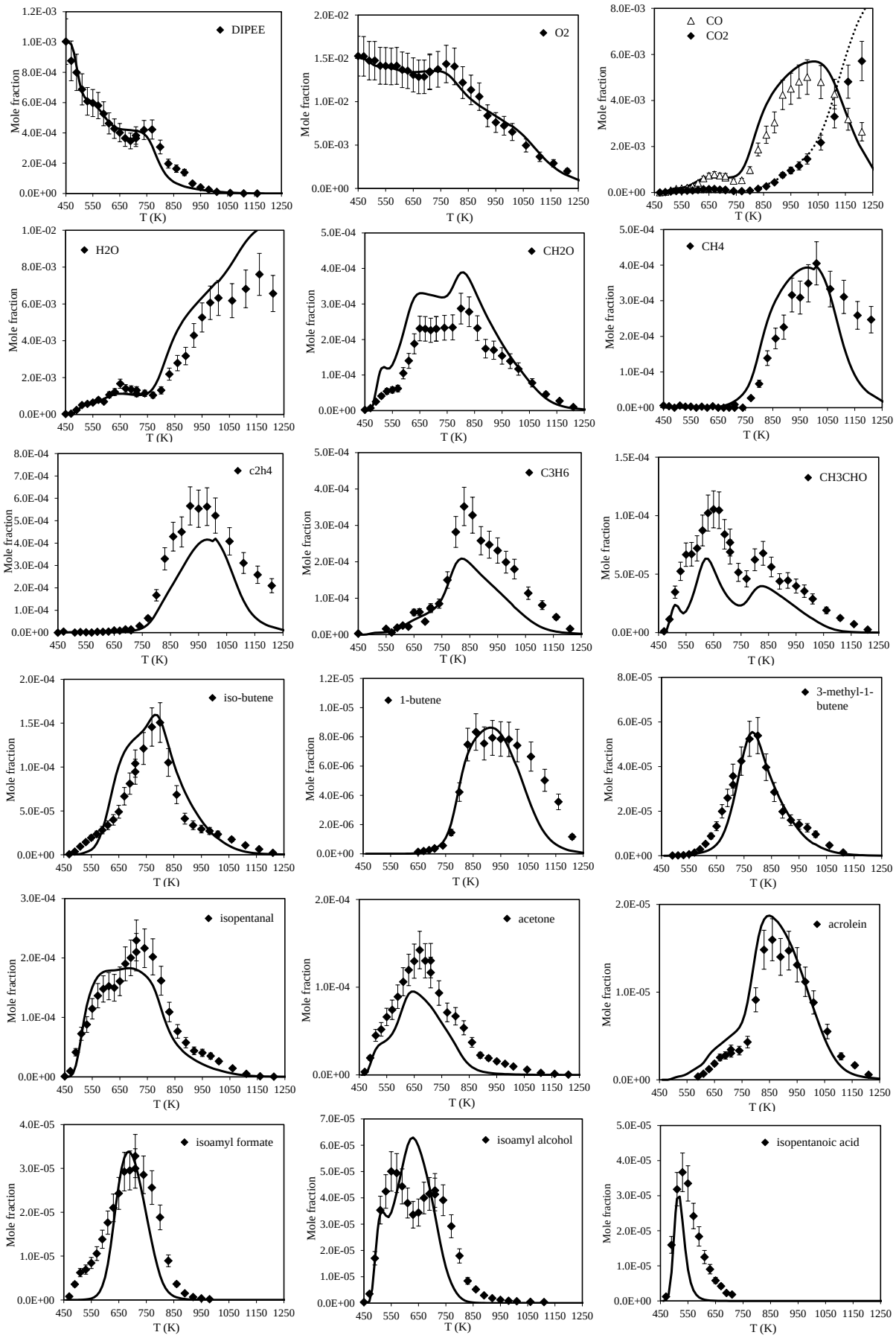

Figure 4. Mole fraction profiles as a function of the reactor temperature (points: experimental data, lines: simulations, p = 10 atm, τ = 0.7 s, φ = 1)

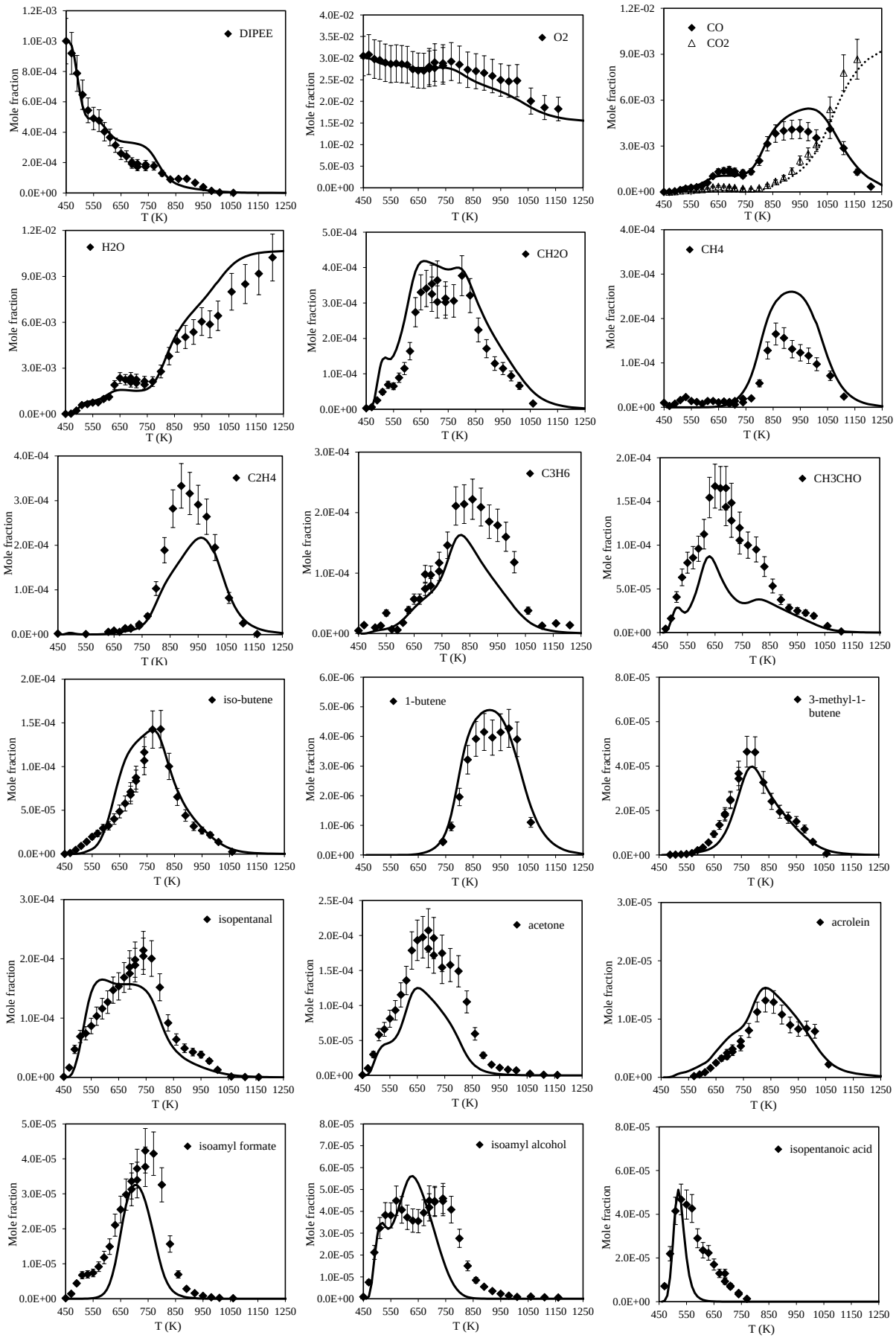

Figure 5. Mole fraction profiles as a function of the reactor temperature (points: experimental data, lines: simulations, p = 10 atm, τ = 0.7 s, φ = 0.5)

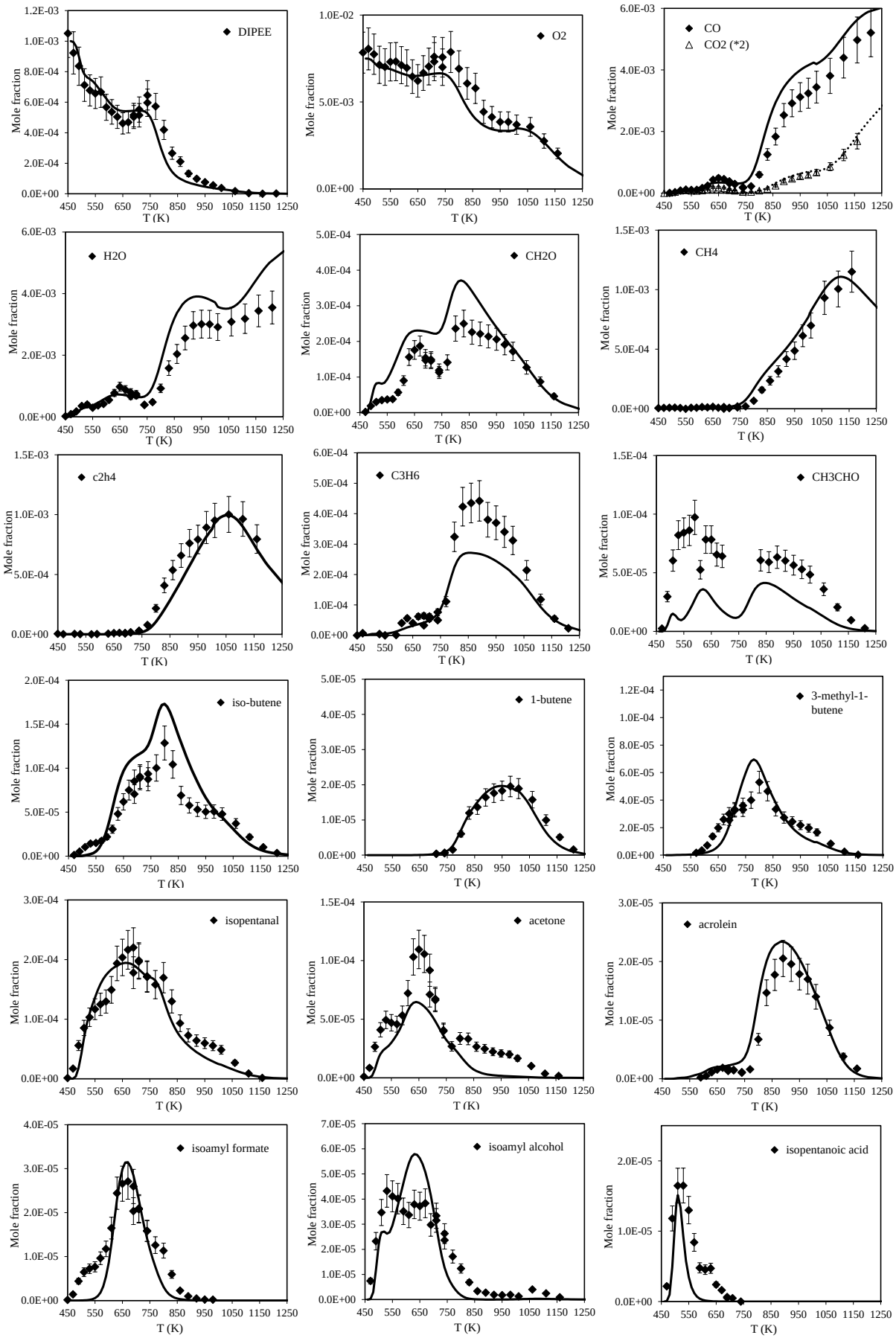

Figure 6. Mole fraction profiles as a function of the reactor temperature (points: experimental data, lines: simulations, p = 10 atm, τ = 0.7 s, φ = 2)

4.1 Reaction pathways

A reaction pathway analysis is performed and reported in Figure 7 for a stoichiometric mixture at 500 K. DIPEE can form four different radicals by H-abstraction, mainly by OH radicals. At this temperature, the most produced radical is the one where a hydrogen atom is removed from the carbon atom close to the oxygen.

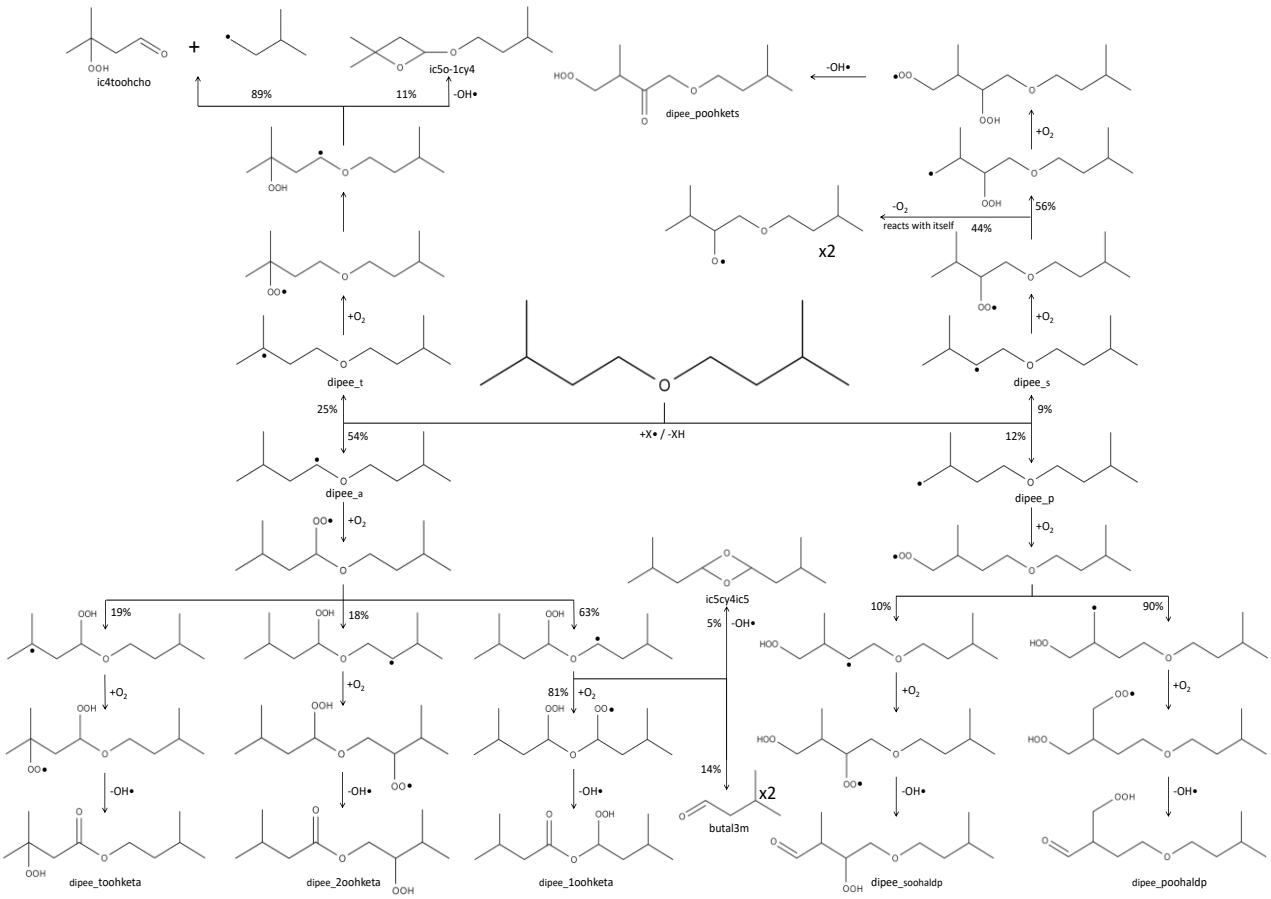

Figure 7. Reaction pathways for a stoichiometric mixture at 500 K.

At this low temperature, these fuel radicals undergo addition on O_2, forming the RO_2 radicals. Most of them then isomerize (internal hydrogen transfer), forming QOOH radicals, mostly via a 6-member transition state. A smaller flow rate goes through the reaction $RO_2+RO_2 \rightleftharpoons RO+RO+O_2$.

At 500 K, QOOH radicals mostly follow the reaction pathways leading to chain branching. A smaller flux undergoes β-scission or decomposes into a cyclic ether. A special case is the QOOH radical which is formed after the H-abstraction on the gamma site of DIPEE. Since no ketohydroperoxide can be formed, no second addition on O_2 happens and around 89% of the radicals goes through β-scission, while 11% forms the cyclic ether reported in the scheme.

4.2 Comparison to other ethers

It may be interesting to compare DIPEE behaviour to the other ethers studied before. The first direct comparison would be to DIPE, since it is the only other branched ether that was previously analysed in our group. Nevertheless, DIPE did not show any low temperature reactivity in the JSR, as can be clearly seen from the fuel conversion profile in Figure 8. It is then more interesting to compare isopentyl ether to the other ethers shown in Figure 8. Especially, DIPEE shows a profile which is very similar to the one obtained for dibutyl ether

(DBE) [5] in the low and intermediate temperature zone. Both these fuels display a double-cool flame regime, with the two NTC zones happening in the same ranges of temperatures.

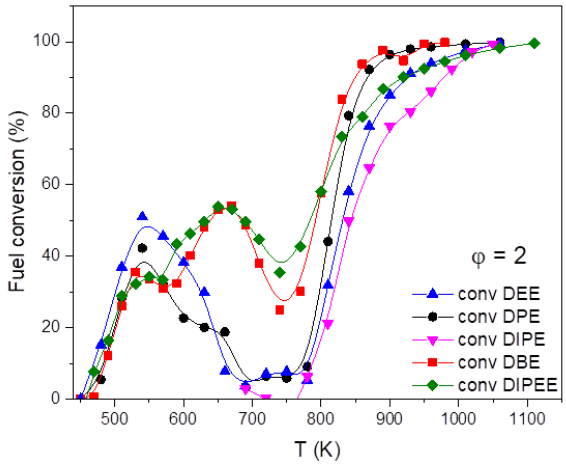

Figure 8. Comparison of DIPEE and other ethers fuel conversion profiles (p = 10 atm, τ = 0.7 s, φ = 2)

Considering the other ethers, DIPEE is more reactive than most of them in the intermediate temperature zone, where the NTC region of diethyl ether (DEE) and di-n-propyl ether (DPE) brings the fuel concentration back to almost its initial value, which is not the case for DIPEE at any temperature. This is due to the fact that, having a longer chain compared to DEE and DPE, DIPEE can form, even at these low temperatures, small radicals that have in turn their own low temperature reactivity. Similar considerations hold for DBE, which is why these two fuels have very similar conversion profiles.

5. Conclusions

This work focused on the oxidation of di-iso-pentyl ether in a jet stirred reactor, under comparable conditions with respect to the previous works on other ethers. This study is important in order to have a deeper understanding of the behaviour of this family of molecules, between which several have already been proven to have interesting characteristics as biofuels.

DIPEE shows an important low-temperature reactivity. At intermediate temperatures, it is the most reactive between the ethers that have been studied. Similarly to DBE, di-iso-pentyl ether is displaying a double-cool flame, with two zones where the reactivity stops increasing or even decreases significantly for rich mixtures.

Along with the experimental data, a new sub-mechanism has been developed and tested, giving overall good results. The mechanism is based on the previous works of our team on ethers and on analogies to alkanes for some reactions. There is therefore room for improvement in the choice of the rate constants to the most important reactions, especially in the low-to-intermediate temperature zone.

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