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Experimental and modeling studies of the oxidation of ethers and their blends

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Abbreviations

- BDE: Bond dissociation energy
- BP: Boiling point
- CEM: Controlled evaporator-mixer
- CHP: Carbonyl-hydroperoxide
- CHX: Cyclohexane
- CI: Compression ignition
- CN: Cetane number
- CPD: Cyclopentadiene
- CPT: Cyclopentane
- DBE: Di-n-butyl ether
- DCN: Derived cetane number
- DEE: Diethyl ether
- DHF: Dihydrofuran
- DHP: Dihydropyran
- DPE: Di-n-propyl ether
- FFA: Furfuryl alcohol
- FID: Flame ionization detector
- FTIR: Fourier transform infrared
- GC: Gas chromatograph
- GHG: Greenhouse gas
- GMFC: Gas mass flow controller
- HMF: Hydroxymethylfurfural
- HTR: High-temperature reactivity
- IDT: Ignition delay time
- IR: Infrared

- JSR: Jet-stirred reactor
- KHP: Ketohydroperoxide
- LHV: Lower heating value
- LMFC: Liquid mass flow controller
- LTR: Low-temperature reactivity
- MON: Motor octane number
- MS: Mass spectrometer
- MTHF: Methyltetrahydrofuran
- MW: Molecular weight
- NTC: Negative temperature coefficient
- PFR: Plug flow reactor
- RON: Research octane number
- SG: Specific gravity
- SI: Spark ignition
- TCD: Thermal conductivity detector
- THF: Tetrahydrofuran
- THP: Tetrahydropyran

1 Introduction

Contents

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The aim of this first chapter is to present the challenges and issues related to the production and usage of energy, particularly in the transport sector. It reveals the necessity of emphasizing the energy decarbonization and focuses on the role of biofuels development in realizing this transition.

1.1 Energy

It is well known that energy is essential for life on Earth, and population growth remains the main booster of global energy demand. During the two last centuries, the world population has significantly increased: from 1 billion people in 1800 to more than 8 billion in 2023 [\[1\]](#). This huge growth is consequently accompanied by a high rise in world primary energy consumption: from less than 6,000 TWh in 1800 to more than 180,000 TWh in 2023, as shown in Figure 1.1. This latter reveals also the evolution of energy sources in the global mix with time.

During the first half of the 19th century, the energy used across the world came mainly from burning traditional biomass (wood, crop waste, etc.). Then, the proportion of coal in the global energy mix showed an interesting rise, as a result of the Industrial Revolution. Later, more energy sources started to be used: oil (1870s) followed by natural gas and hydropower (1890s), nuclear energy and biofuels with other renewables (1960s), and finally solar and wind energies (around 1980). Fossil fuels (coal, oil, and natural gas) are currently dominating the global energy mix.

Hydroelectric, nuclear, and renewable energies were developed in response to the challenges posed by fossil fuels:

- Their accelerated depletion: if fossil fuels were used exclusively to meet global energy demand, they are projected to be exhausted by 2088 at the latest, according to [\[2\]](#).
- Their environmental impact: fossil fuels contribute to significant emissions of CO₂ – the most important greenhouse gas (GHG) – accounting recently for over 35 billion tons worldwide (see Figure 1.2).

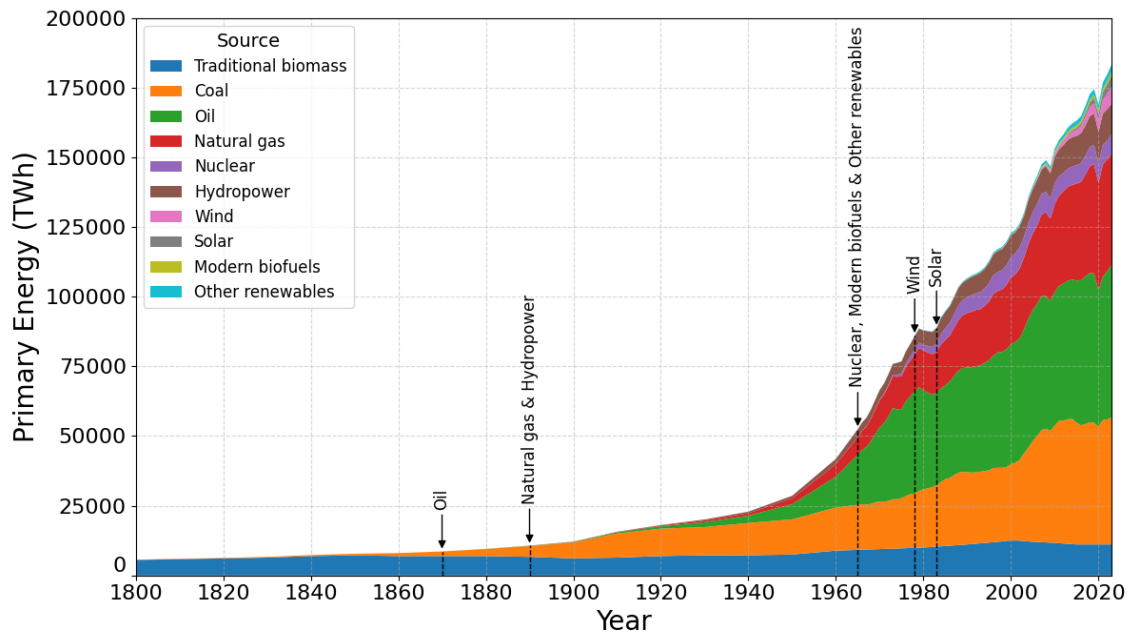


Figure 1.1: Evolution of annual global primary energy consumption by source from 1800 to 2023 (adapted from [3]). Each arrow marks the year of first appearance of its corresponding source.

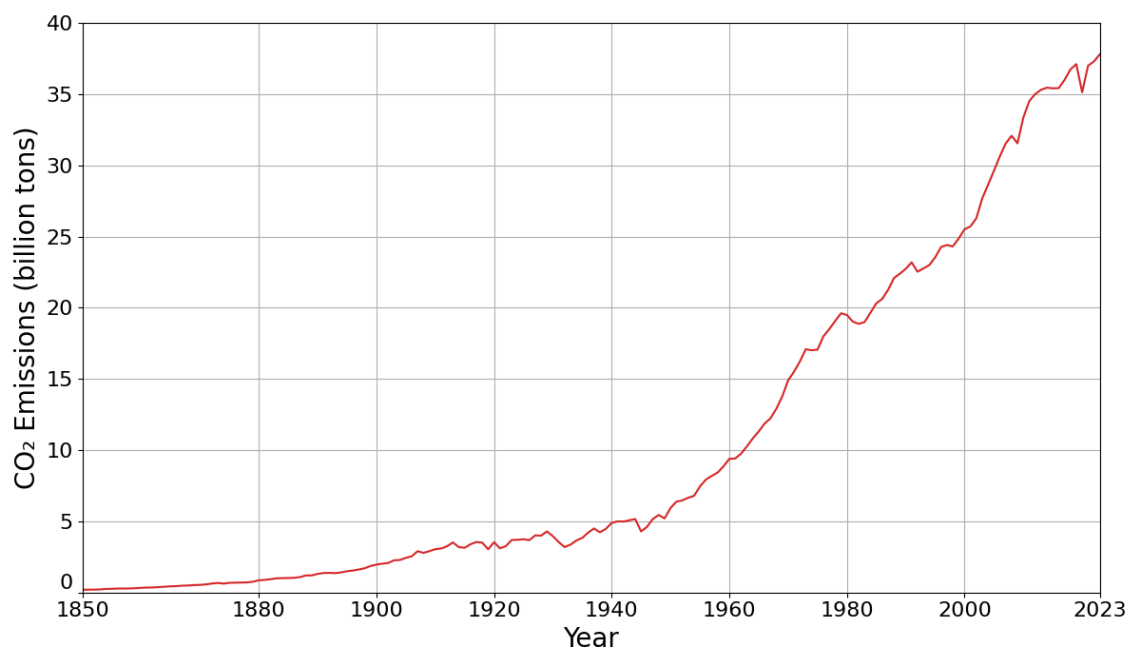


Figure 1.2: Evolution of annual global CO₂ emissions from fossil fuels from 1850 to 2023 (adapted from [4]).

Figure 1.2 traces the evolution of annual global CO₂ emitted by fossil fuels from 1850 to 2022. It lately shows a slight but sharp reduction in emissions, mainly due to travel restrictions imposed by the Covid-19 pandemic. However, this reduction was accompanied by a severe economic crisis, demonstrating that achieving a meaningful emission decrease cannot be reached by simply limiting transport [5].

1.2 Transport

Transport is one of the most energy-intensive sectors worldwide (representing about 30% of global energy use [6]), largely due to the rapid increase in the mobility of people and goods, driven certainly by the growing demand accompanying the aforementioned population expansion.

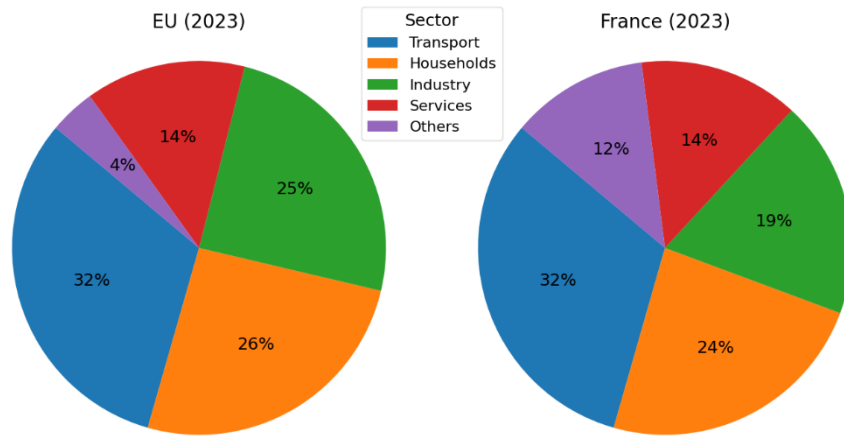


Figure 1.3: EU and France final energy consumption by sector in 2023 (adapted from [7,8]).

As shown in Figure 1.3, transport has been recently the most energy-consuming sector in the entire European Union (EU), and particularly in France, accounting for almost one-third of final energy consumption in both cases and surpassing households and industries.

Nowadays, transport is almost entirely powered by internal combustion engines running on liquid fuels derived from petroleum [5] [9,10]. It still contributes to almost the quarter of GHG emissions in the EU [7] and the world [11], even though combustion engines have recently become more efficient and less pollutant. Therefore, there is a growing need to boost the development of clean and renewable alternatives that offer similar efficiency to petroleum-derived liquid fuels.

Electrifying the transport grid or transitioning to gaseous hydrogen fuel could be a viable solution for light-duty passenger vehicles. However, due to the low energy density of both batteries and hydrogen compared to fossil-based liquid fuels, these latter remain the most efficient option for major transport modes, particularly for heavy-duty vehicles, ships and planes, that must be able to carry large loads and travel long distances without frequent refueling [12,13].

Moreover, we must consider that it is impossible to replace at once all the cars currently on the road. As a result, these vehicles will continue to have significant role in transport activities, at least in the recent future. However, to avoid the disaster of climate change and achieve the net-zero emissions by 2050 [14], a feasible solution for decarbonization must include the development of new low-carbon liquid fuels with physical and chemical properties similar to those made from petroleum [5]. The coexistence of low-carbon fuels and an electrified fleet has been identified as one of the most rapid and performant approaches for the reduction of CO₂ emissions [15].

In the present work, our scope will be limited to one of the most promising low-carbon fuels: “biofuels”.

1.3 Biofuels

Biofuels are fuels produced from biomass, especially plant-based materials. If the biomaterial used in their production is planted again, these fuels will have the major benefit of being both renewable and clean. In fact, although they release CO₂ after being burned similarly to fossil fuels, biofuels are considered carbon-neutral or low-carbon components because the plant sources used to create them have already captured CO₂ from the atmosphere through photosynthesis, and will continue to do so if they are replanted.

Biofuels can be classified based on their feedstock or production source into four various categories:

- First-generation or conventional biofuels: they come from food crops such as corn, sugarcane, and vegetable oils. Examples include bioethanol and biodiesel. While widely used, they are often criticized for competing with food production chains and causing land-use concerns.
- Second-generation or advanced biofuels: they are manufactured from waste biomaterials and non-edible sources, including lignocellulosic materials (e.g., straw, wood chips, etc.), to avoid competition with the food sector. They are more sustainable than first-generation biofuels but require more complex processing technologies.
- Third-generation biofuels: they are derived from algae or other micro-organisms that can be engineered to produce high yields of bio-oil. In addition to the benefit of not competing with food production, they offer high efficiency but remain costly and largely experimental.
- Fourth-generation biofuels: they are attributed to more advanced technologies such as genetically modified organisms or carbon capture and storage during production. These fuels aim to be carbon-negative, removing more CO₂ from the atmosphere than they emit. However, their development may involve unintended side effects, posing further risks to biodiversity and environment.

Unlike conventional fossil fuels, biofuels are characterized by the presence of oxygen in their composition with proportions ranging from 10 to 45 wt% [16]. Thus, a possible use of biofuels in internal combustion engines requires first in-depth knowledge of their combustion kinetics and of the nature and quantity of pollutants formed during their oxidation.

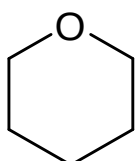
The presence of oxygen within the molecular structure of biofuels significantly limits the amount of carbon available for the formation of major soot precursors, such as ethylene and acetylene. However, the extent of this effect depends notably on the type of oxygen-containing functional group present. In this context, ethers have experimentally demonstrated a strong ability to reduce particulate emissions by chemically trapping C atoms in partially oxidized intermediates, such as small C₁–C₂ oxygenates [17–23]. In addition, their potential production pathways from lignocellulosic biomass place them among the promising biofuel candidates of the second-generation category [24–26].

1.4 Objectives

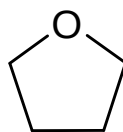
The oxidation of ethers has attracted the attention of researchers during the last few decades and has been the subject of many studies. Most of these studies have focused on ethers with linear chains [27–34]. Meanwhile, relatively few have addressed the combustion of those with cyclic chains and, to the best of our knowledge, no studies have discussed the interaction between these two types of ethers; especially between a linear ether highly reactive at low temperatures and another cyclic with a weak reactivity under same conditions.

Cyclic ethers are very important intermediates formed during the low-temperature oxidation of hydrocarbon fuels [35,36], and thereby they are key species in fully understanding this oxidation. Also, they play a crucial role in the development of second-generation biofuels, produced from non-edible lignocellulosic biomass [37,38]. Thus, studying the oxidation of cyclic ethers will help exploring the combustion of oxygenated biofuels, and subsequently boosting the transition to more clean and sustainable energy resources.

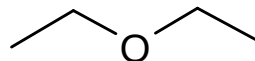
In this project, we plan to investigate the oxidation kinetics of two cyclic ethers, tetrahydropyran (THP) and tetrahydrofuran (THF), neat or in blend with linear ethers like diethyl ether (DEE). In fact, adding linear ethers makes it possible to trigger the reactivity of cyclic ethers at lower temperatures and to study the interaction between the chemistry of both types of ethers, as well as the reaction pathways of the radicals produced during such an oxidation, rarely studied in detail at low temperatures. The reaction pathways are elucidated by identification of the species formed during the oxidation and by detailed kinetic modeling.



THP



THF



DEE

This project hence has two aspects: experimental studies and kinetic modeling.

- The experiments are carried out in a jet-stirred reactor (JSR) able to operate in a wide range of temperature (T) [400–1300 K], pressure (p) [1–10 bar], equivalence ratio (ϕ) [0.1–4], and residence time (τ) [0.04–2 s]. Reactants, products, and oxidation intermediates are measured by chromatographic analyses and by infrared absorption.
- The kinetic modeling builds on previous studies conducted by our team at ICARE laboratory, especially those involving linear ethers, based on which relevant sub-mechanisms for cyclic ethers are developed in this work. The robustness of the core mechanism is also ensured through revisions and updates.

1.5 Outline

This work is presented in five chapters, subsequent to this introduction (**Chapter 1**).

The next chapter, **Chapter 2**, provides an overview of combustion, with a focus on both low- and high-temperature oxidation behaviors. Then, a section is dedicated to the production processes of cyclic ethers from lignocellulosic biomass. Finally, the key literature findings related to the combustion of the two particular cyclic ethers studied in the present work, THP and THF, are reviewed and summarized, after providing insights into their potential performance in existing engines.

Chapter 3 describes the experimental setup, the methodology followed, and the associated analytical techniques used throughout this PhD project, along with a brief discussion of measurement uncertainties. The chapter also presents the various experimental conditions tested in this study for THP and THF, with the latter investigated either as a neat fuel or blended with DEE.

In **Chapter 4**, the kinetic modeling aspect is addressed. The chapter first specifies and refines the mechanism chosen as the base for the new kinetic sub-mechanisms developed for THP and THF. It then presents the procedure followed to construct these two detailed sub-mechanisms from scratch, which are subsequently integrated into the base model. Finally, this chapter outlines the software tools used for all simulations performed in this work.

Chapter 5 first shows and discusses the performance of the updated core mechanism, followed by the results obtained for both THP and THF under various tested conditions. For each fuel, it compares the simulations predicted by our newly developed mechanism with the present experimental data and evaluates its performance against other mechanisms available in the literature. Thereafter, sensitivity and reaction pathway analyses are carried out using our mechanism to identify the key reactions governing the chemistry of each fuel. Moreover, the present mechanism is further tested and validated against previously reported data of THP and THF. In addition, these two ethers were evaluated and compared with other fuels investigated previously by our team under same experimental conditions. Finally, for the DEE/THF blends studied for the first time in this work, the experimental and numerical results are compared and briefly interpreted.

The last chapter, **Chapter 6**, concludes the present work and suggests some future perspectives.

2 Literature Review

Contents

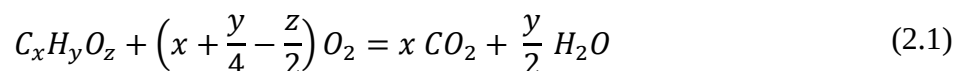
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This bibliographic chapter first presents an overview of combustion and then outlines the associated reaction mechanisms, covering both low- and high-temperature reaction classes. Subsequently, the chapter reviews the production methods of cyclic ethers as promising biofuel candidates, followed by a particular focus on the engine performance of the two cyclic ethers investigated in this work, THP and THF, in comparison with conventional fuels and linear ethers. Finally, a state-of-the-art review is provided on the combustion of both cyclic ethers.

2.1 Combustion

2.1.1 Overview

Combustion involves a complex network of elementary reactions that proceed through transient species, commonly known as reaction intermediates. However, the overall reaction between a fuel ($C_xH_yO_z$) and oxygen can be summarized by a single balanced equation:



While water and carbon dioxide are the final products of complete combustion, a variety of other species may also form without being fully oxidized depending on the operating conditions, further complicating the description of the reaction mechanism.

Several interrelated and overlapping phenomena can be identified in combustion, each governed by distinct chemical and physical processes. Among these phenomena, ignition and flame propagation are particularly important. Ignition refers to the critical transition of a fuel-oxidizer system from a slow to a rapid, self-sustaining chemical reaction. When the reacting mixture ignites spontaneously without any external energy source, the phenomenon is called

autoignition. Flame propagation, on the other hand, is the spread of a localized chemical reaction zone through a fuel-oxidizer system, sustained by the transport of heat and reactive species from reacted regions to adjacent unreacted regions.

Combustion phenomena are associated with key fuel-dependent characteristics, including chemical speciation, ignition delay time, and laminar flame speed. Numerous experimental setups have been developed to investigate and quantify these properties, such as jet-stirred reactors, plug-flow reactors, rapid compression machines, shock tubes, ... etc. These reactors offer an “ideal” environment in studying global and detailed fundamental combustion properties. Thanks to this diversity of tools, researchers have been able not only to develop efficient reaction mechanisms tailored to specific targets, but also to validate them against different types of data and across a wide range of conditions, including those relevant to more complex applications.

2.1.2 Reaction Mechanism

In parallel with the development of internal combustion engines, the oxidation of hydrocarbons has been extensively studied since the 19th century, with later attention shifting toward oxygenated fuels.

Until nearly the end of 19th century, the only oxidation process studied was the explosive combustion of hydrocarbons in flames [39,40]. With its high temperatures and extremely short timescales, this explosive pathway hindered the investigation of the real oxidation mechanism. Therefore, many research efforts [41–55] in the 20th century were directed toward the flameless slow oxidation of hydrocarbons, especially alkanes, in the gas phase at relatively low temperatures (200–600 °C), in parallel with ongoing studies on explosive combustion. Two distinct types of oxidation were thus discovered, each occurring within a specific temperature range: above ≈ 400 °C, dissociation reactions predominate; while below that temperature, the formation of reaction intermediates is more significant. These two regions are found to be not strictly continuous but separated by a zone in which the oxidation rate falls with increasing temperature.

Taking n-hexane as a representative example, Figure 2.1 illustrates the three different regimes that can be identified during the oxidation of alkanes (whether normal, branched, or cyclic) [56–60]: low-temperature reactivity (LTR), negative temperature coefficient (NTC), and high-temperature reactivity (HTR). Figure 2.2 summarizes the key reaction pathways responsible for these regimes, which are also characteristic of other hydrocarbons [61–64] and even oxygenated fuels [28,29] [31] [65–67], which are representative of biofuels expected to replace conventional hydrocarbon-based fossil fuels in future engines.

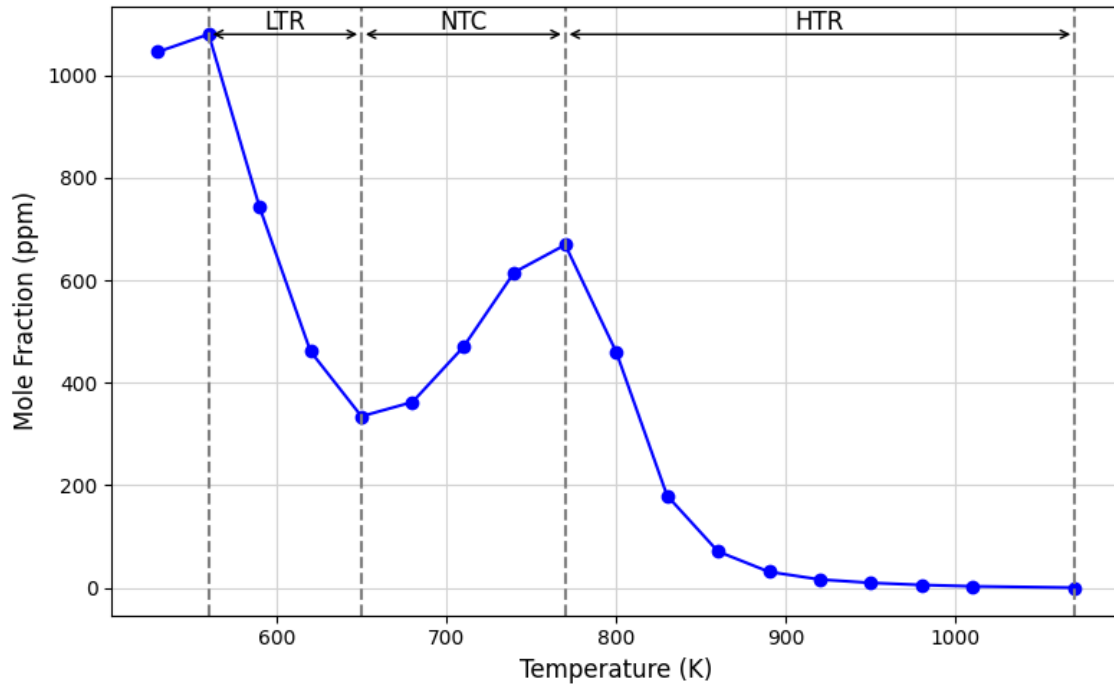


Figure 2.1: Mole fraction profile of n-hexane as a function of temperature during its oxidation in a JSR at $p = 10$ atm, $\tau = 0.7$ s, and $\phi = 0.5$ [68].

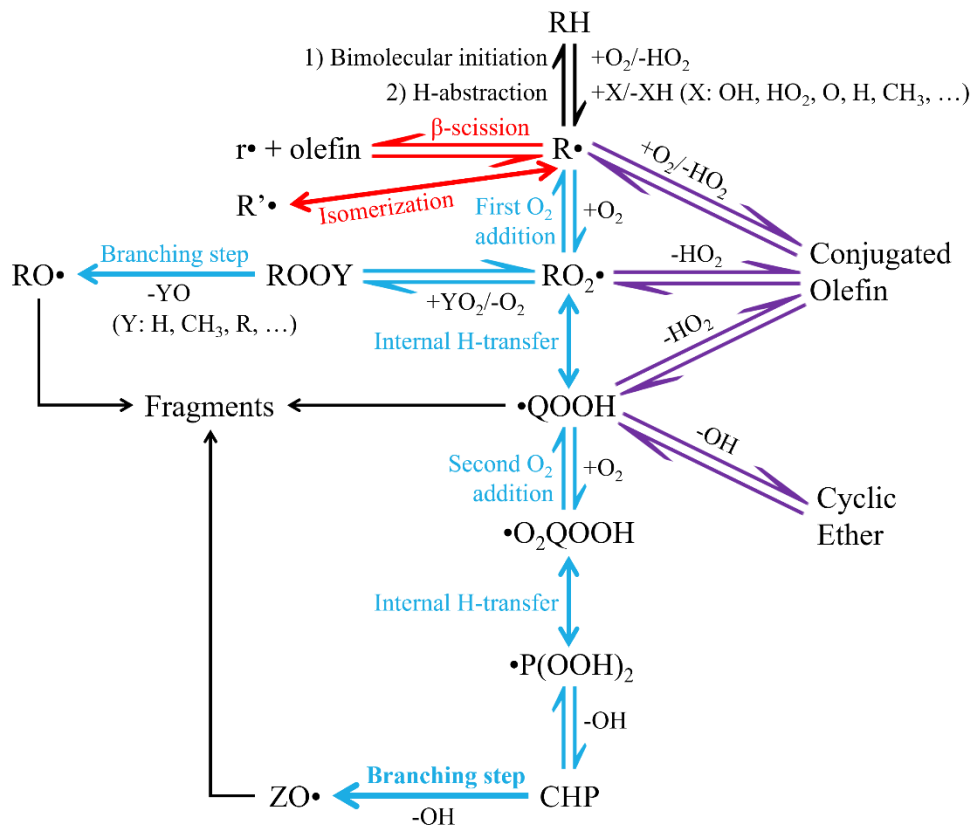
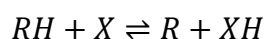
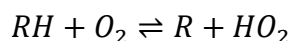


Figure 2.2: Simplified scheme of the primary mechanism of oxidation of alkanes, with the key reaction pathways of LTR, NTC, and HTR shown in blue, purple, and red, respectively.

The oxidation mechanism begins with an initiation step. An O_2 molecule of reaction medium can abstract a hydrogen atom from a fuel molecule (RH) to form an alkyl radical (R). Then, this reaction becomes negligible very quickly compared to the reactions of H-abstraction or metathesis, through which H is abstracted by small radicals (X: OH, HO_2 , H, O, CH_3 , ...) formed during the oxidation process. Both bimolecular initiation and H-abstraction reactions are shown in Figure 2.2 and presented below:

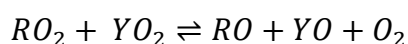


2.1.2.1 Low-temperature reactivity

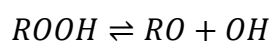
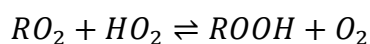
The low-temperature oxidation, also known as the cool flame regime, is generally characterized by slow reactivity and low exothermicity. Many families of species are involved in its complex chemistry, some of which are very unstable and difficult to measure or even detect. This makes the experimental study of this reactivity regime more challenging. However, a significant progress has been made with the development of advanced analytical techniques, like photo-ionization mass spectrometry by synchrotron radiation [69], making it possible to detect fragile species that are not observable with conventional measuring devices.

The LTR pattern, initially established for alkanes and later extended to other hydrocarbons and oxygenated fuels, has been described in many reviews over the years [70–77]. It starts with the addition of an O_2 molecule at the fuel radical site to produce a peroxyalkyl radical (RO_2) which can in turn react in several ways, mainly through:

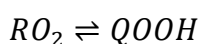
- A disproportionation reaction with another peroxyalkyl radical (YO_2) forming two alkoxy radicals (RO and YO) and a molecule of O_2 , proceeding through an unstable peroxide intermediate ($ROOY$) that quickly decomposes due to the weakness of its O–O bond. This reaction is commonly written in one step:



- A metathesis reaction with a hydroperoxyl radical (HO_2) – which can be considered as a particular case of the previous reaction, where $Y = H$ – leading to the formation of an unstable hydroperoxyalkyl molecule ($ROOH$), which then rapidly decomposes into an alkoxy radical (RO) and a hydroxyl radical:



- An isomerization reaction via internal H-transfer through a cyclic transition state to form a hydroperoxyalkyl radical ($QOOH$):



The rate of this last reaction depends on the size of the cyclic transition state involved. Small rings experience significant bond strain and therefore require high energy to form, while the cyclization energy decreases as the ring size increases. In contrast, increasing the ring size in the transition state leads to a greater loss of entropy, as internal rotations become increasingly

constrained. Consequently, the transition-state entropy decreases more significantly, resulting in a reduced pre-exponential factor. Thus, there is a trade-off between the reduction in activation energy and the accompanying loss of entropy. Considering these competing effects, the six-membered cyclic transition state is the most favorable, followed by the five-membered counterpart.

The QOOH radical then undergoes a second addition of O_2 at its radical site, forming an O_2QOOH radical. The isomerization of the latter by an internal transfer of an H atom forming a $P(OOH)_2$ radical, followed by the scission of its very weak O–OH bond, leads to the formation of an OH radical and an unstable carbonyl-hydroperoxide molecule (CHP). The decomposition of this species, again by the scission of the weak O–OH bond, releases a new OH radical. This sequence constitutes a chain-branching pathway: it leads, from one radical initiating the fuel metathesis reactions, to the production of two OH radicals which, in turn, further promote these reactions, resulting in an exponential increase in reactivity.

However, as illustrated in Figure 2.2, the reactions driving this chain-branching pathway are reversible, and the involved radical intermediates can follow competing side pathways, which are discussed below.

2.1.2.2 Zone of negative temperature coefficient

When the temperature increases ($T > \approx 650$ K, see Figure 2.1), a decrease in the overall reactivity is observed. This drop in reactivity is explained by the shift in equilibrium of the reactions of O_2 addition toward the reactants, which limits the formation of CHPs and inhibits the main chain-branching pathway responsible for the reactivity growth at low temperatures. Therefore, as shown in Figure 2.2, each of the radical intermediates (R, RO_2 , and QOOH) will primarily lead to the formation of another radical and a relatively stable compound: an HO_2 radical and an olefin, or an OH radical and a cyclic ether (in the case of QOOH).

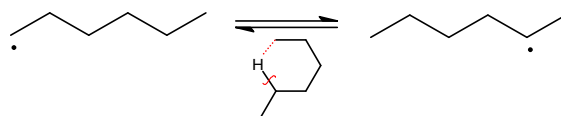
Although the highly reactive OH radicals can still be formed from QOOH radicals by propagation pathways, they are no longer dominant in the radical pool. Instead, the significantly less reactive HO_2 radicals become predominant. These radicals primarily undergo a disproportionation reaction to form hydrogen peroxide molecules (H_2O_2), which remain stable and inert within the NTC region. As a result, this reaction acts as a terminating step, effectively quenching the overall reactivity.

2.1.2.3 High-temperature reactivity

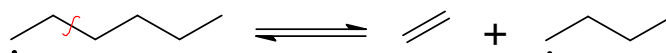
At higher temperatures ($T > \approx 770$ K, see Figure 2.1), H_2O_2 molecules begin to decompose, producing two OH radicals and thereby increasing the overall reactivity once again. At these temperatures, the isomerization and decomposition reactions of R radicals predominate over reactions with O_2 .

The isomerization reactions enable structural rearrangement of the radical via internal H-transfer through a cyclic transition state. Unless the transition state involves a five- or six-membered ring, these reactions are typically unable to compete with decomposition pathways and are considered negligible.

Here is an example of 1-hexyl radical isomerization involving a six-membered cyclic transition state:

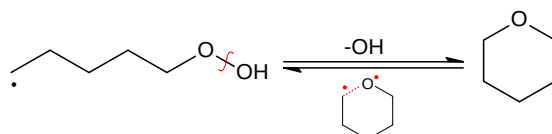


The R radicals mostly break down by β -scission reactions: a bond at the β -position relative to the radical site is broken and forms an unsaturation on the bond adjacent to the radical site, thus producing an alkene and a smaller alkyl radical or an H atom. The β -scission of 1-hexyl radical via C–C bond cleavage is presented here as an example:



2.2 Cyclic Ethers

We have already seen the importance of cyclic ethers as oxidation intermediates, whose formation pathways compete with the chain-branching channel and play a key role in the transition from low- to high-temperature chemistry through an NTC region. As an example, the reaction of formation of THP during n-pentane oxidation from the primary radical of 1-pentyl hydroperoxide is shown below:



In this section, we will discuss another crucial aspect of cyclic ethers; their potential to serve as second-generation biofuels, produced from lignocellulosic biomass. Since they represent the main biofuel candidates in this context and have the most stable cyclic arrangements, only cyclic ethers with five- and six-membered rings are considered in the present work. After reviewing the production routes of these heterocyclic compounds from lignocellulosic biomass, the scope then narrows down toward the two cyclic ethers investigated in this work, THP and THF, for which the key physicochemical properties are outlined, followed by a review of the state-of-the-art of their combustion studies.

2.2.1 Production Processes

Lignocellulosic biomass can be converted into biofuels through three principal pathways: gasification, pyrolysis, and hydrolysis [78].

According to Serrano-Ruiz and Dumesic [79], the main target of gasification and pyrolysis is the production of liquid hydrocarbons that resemble conventional fossil fuels in both composition and performance. However, gasification is generally considered economically viable only at large industrial scales, requiring significant capital investment and posing logistical challenges due to the low energy density of raw biomass and the associated costs of long-distance transport. On the other hand, pyrolysis, followed by catalytic upgrading (such as hydrodeoxygenation), presents a more decentralized and potentially cost-effective alternative. Despite this, the approach is hindered by low product selectivity, often resulting in complex mixtures rather than the desired fuel compounds.

In contrast, the hydrolysis route represents a more controlled and selective pathway. While Serrano-Ruiz and Dumesic [79] focus on the deoxygenation of the products of this route to target the production of hydrocarbon transportation fuels, Dahmen and Marquardt [80] discuss targeting that method toward the synthesis of specific oxygenated molecules, which can be engineered to meet defined physicochemical criteria relevant to engine performance and emission standards. These tailored compounds can function either as standalone biofuels or as high-performance blend components that enhance the quality and sustainability of fossil-based or other renewable fuel formulations.

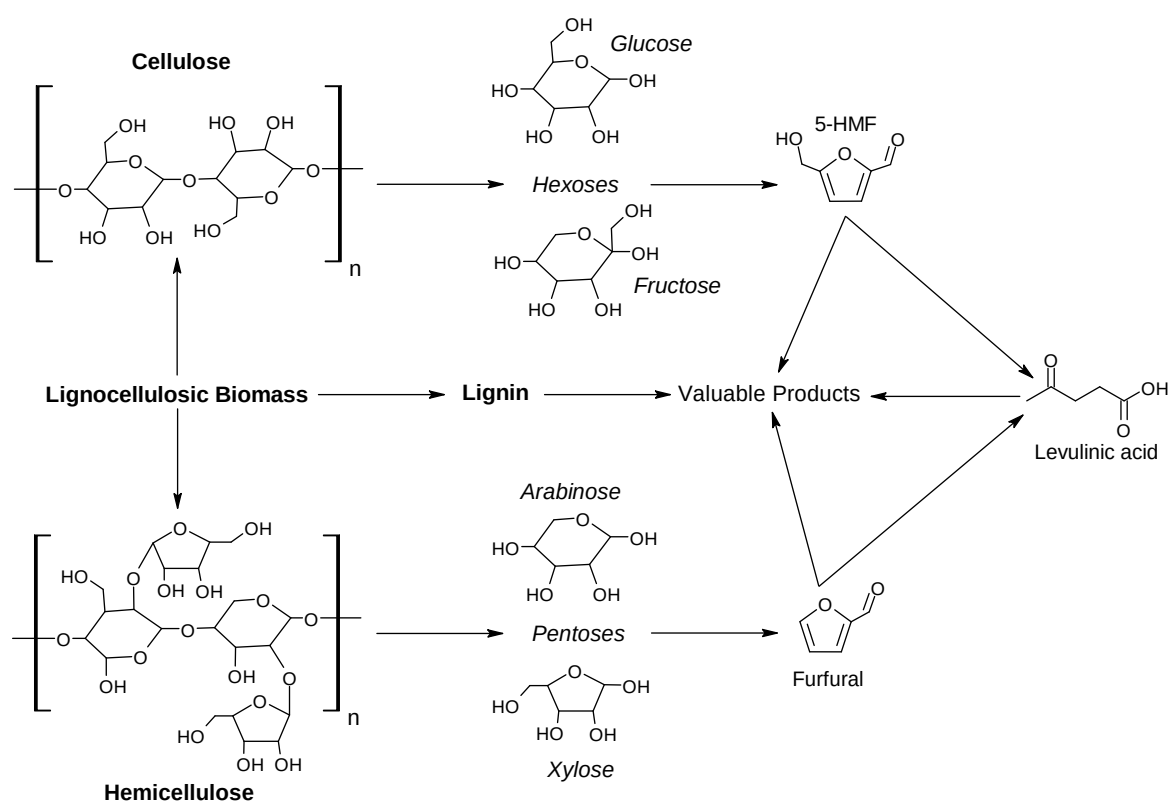


Figure 2.3: Simplified reaction pathways of lignocellulosic biomass hydrolysis (adapted from [81]).

As shown in Figure 2.3, lignocellulosic biomass is composed of three polymers: lignin, cellulose, and hemicellulose.

Lignin represents roughly 15–20 wt% of this biomass [82] and is characterized by a highly irregular polyaromatic network [83]. Its structural complexity, particularly the diversity of linkages between its units, makes its selective catalytic breakdown into specific monomers significantly challenging [84]. As a result, biomass conversion strategies in aqueous-phase catalytic systems tend to focus on cellulose and hemicellulose, which offer more straightforward processing routes due to their uniformity and higher accessibility [85]. However, lignin can still play a valuable role in biorefinery operations. It can be burned to supply heat or power for the overall process [86], or potentially serve as a feedstock for hydrogen production, offering a renewable route for the hydrogenation of sugar-derived intermediates [84].

Cellulose, the most abundant component of lignocellulose (40–50 wt%), is a linear chain of glucose units, while hemicellulose (25–35 wt%) is a branched amorphous polymer built from

a variety of pentoses (C_5 sugars) and hexoses (C_6 sugars) [79] [82]. To enable access to these carbohydrate fractions, chemical or mechanical pretreatments must be employed to break down the lignin matrix, which acts as a protective barrier. Subsequent hydrolysis, via enzymatic or acidic means, converts the polysaccharides into fermentable sugars. These sugar monomers must then be further transformed to produce biofuels [86].

Figure 2.3 shows clearly that cellulose and hemicellulose are characterized by the prominent presence of five- and six-membered heterocyclic rings in their core structures, based on THF and THP units. This structural feature enables their conversion into these cyclic ethers, while lignin can be transformed into distinct oxygenated compounds, but not cyclic ethers [87].

Cyclic ethers, especially those derived from THF, are found to be among the most promising second-generation biofuel candidates [24] [26]. Their synthesis starts with the depolymerization of the constituents of lignocellulosic biomass to produce – as shown in Figure 2.3 – sugars and subsequent dehydration products such as furfural, 5-(hydroxymethyl)furfural (5-HMF), and levulinic acid. These specific compounds are considered key platform chemicals for the production of cyclic ethers [25].

Furfural is a well-known commercial product derived from lignocellulosic biomass [25]. It is synthesized through the dehydration of pentoses ($C_5H_{10}O_5$), like arabinose and xylose, derived from hemicellulose (see Figure 2.3). This dehydration occurs in water at around 550 K with the presence of a strong acid [24] [88]. Then, furfural can be converted into THF-based compounds [88] through several processes, such as:

- Decarbonylation: producing furan, which can be hydrogenated to THF or can follow a Friedel-Crafts acylation then a reduction to form 2-ethyltetrahydrofuran [25].
- Hydrogenation: which yields tetrahydrofurfuryl alcohol and furfuryl alcohol (FFA). The hydrogenolysis of the latter is a common source of 2-methylfuran, whose hydrogenation yields 2-methyltetrahydrofuran (2-MTHF) [89,90]. Furthermore, FFA can undergo etherification with ethanol to form ethyl furfuryl ether, or sequential reduction and esterification to form ethyl tetrahydrofurfuryl ether [91].
- Reaction with acetone: leading to 2-n-butylfuran and 2-n-butyltetrahydrofuran after selective hydrogenation and dehydration [25].

5-HMF is synthesized through the dehydration of hexoses ($C_6H_{12}O_6$), like glucose and fructose, obtained from cellulose (see Figure 2.3). It can be transformed to 2,5-dimethylfuran [92], 2,5-dimethyltetrahydrofuran [93,94], or 2-ethylfuran such as during the aqueous-phase hydrogenolysis of glucose over different transition metal catalysts [95].

Another chemical platform is levulinic acid, which can be produced either by dehydration of 5-HMF or from furfural through FFA as an intermediate [93]. 2-MTHF can be produced from levulinic acid through catalytic hydrogenation, more efficiently than from furfural [26].

Similarly to THF, THP and its derivatives have also a promising role in the development of second-generation biofuels, as shown in [26] [80].

2.2.2 Combustion Performance

The combustion performance of a fuel depends on its physicochemical properties, such as boiling point (BP), density (ρ), and lower heating value (LHV). Designing fuel molecules to meet the specific requirements of internal combustion engines requires a fundamental understanding of the relationships between molecular structure and physicochemical properties, as well as their influence on engine performance. Although such relationships are complex and not yet fully elucidated for oxygenated biofuels, several general trends have emerged based on insights gained from conventional fossil fuels, as outlined in [80]. For instance, lower BP facilitates fuel vaporization and mixing with air, enhancing combustion efficiency, especially under cold-start conditions. Fuels with higher LHVs provide more energy per unit mass, contributing to better thermal efficiency, while higher densities increase the energy released per unit volume.

Two parameters are commonly used to assess the combustion performance of fuels in existing engines:

- The octane number, expressed either as the research octane number (RON) under mild conditions or the motor octane number (MON) under severe ones [96]: it measures the resistance of the fuel to autoignition, indicating its ability to avoid knocking and its suitability for use in spark ignition (SI) engines.
- The cetane number (CN), or the derived cetane number (DCN) serving as an estimate of CN [97,98]: it measures the tendency of fuel to auto-ignite, indicating its propensity to ignition and its suitability for use in compression ignition (CI) engines.

From their definitions, one can clearly see that the lower the RON or MON and the higher the DCN, the more easily the fuel ignites.

Table 1 compares the two cyclic ethers studied in this work, THF and THP, to conventional fuels, as well as to representative linear ethers, in terms of RON, DCN, and key physicochemical properties.

THF and THP exhibit low boiling points within the range of conventional gasoline components, while their relatively high densities are comparable to the heaviest fractions of diesel fuel. In terms of LHV, both cyclic ethers deliver approximately 75% of the energy content of typical gasoline and diesel fuels. In terms of engine compatibility, the RONs and DCNs of THF and THP indicate that their combustion behavior lies between that characteristic of SI and CI engines. However, with a RON relatively close to that of gasoline, THF appears better suited for SI engine applications. In contrast, with a DCN approaching that of diesel, THP seems more appropriate as a candidate fuel for CI engines. Although both cyclic ethers have not yet been fully characterized, their currently available data suggest that they possess particularly promising properties as blending components rather than standalone fuels for existing combustion systems: their use in conventional engines would require the addition of either an octane or a cetane improver.

On the other hand, linear ethers, such as DEE and DBE, have demonstrated significant cetane ratings and have thus emerged as strong candidates for CI applications. However, with very high DCNs combined with low boiling points and densities relative to conventional diesel, linear ethers are more practical as cetane-enhancing additives than as standalone diesel fuels.

Consequently, blends of linear and cyclic ethers exhibit substantial potential as compatible biofuels for existing CI engines. Investigating their oxidation behavior is therefore of particular interest, especially with regard to chemical kinetics and pollutant formation, which motivates the study of DEE/THF blends in this work.

Table 1: Key fuel properties of cyclic ethers (THP and THF) compared with conventional fuels and linear ethers [26] [80] [99–103] (--: unavailable).

Fuel	BP (°C)	ρ (g/mL)	LHV (kJ/g)	DCN	RON
THF	66	0.89	32.7	21.9	73
THP	88	0.88	34.0	38.2	52
Gasoline	30–200	0.71–0.77	44–46	--	85–100
Diesel	170–360	0.82–0.88	42–46	40–55	--
DEE	35	0.70	33.9	139	--
DBE	141	0.77	--	100	--

2.2.3 Tetrahydropyran

The first study on the combustion of THP was published in 1991 by Leppard [102], who used a test engine to explore the auto-ignition of THP at an equivalence ratio of 0.95 to 1, a temperature of 358 K, and a pressure of 60 kPa. Then, in 1997, Dagaut et al. [104] studied the ignition and oxidation of THP in a shock tube and in a JSR ($\tau = 0.5$ s) under a wide range of conditions: a pressure up to 10 atm, an equivalence ratio between 0.5 and 2, and a temperature range of 800–1700 K. They also developed a kinetic mechanism to perform simulations for their high-temperature experimental results. Labbe et al. [105] explored the flame chemistry of THP using vacuum-ultraviolet photoionization molecular-beam mass spectrometry and developed a corresponding kinetic mechanism. Their study was restricted to a laminar premixed flat flame of THP/O₂/Ar mixture at a low pressure of 20 Torr and under a fuel-rich condition ($\phi = 1.75$). Tran et al. [106] studied both pyrolysis and combustion of THP. They performed pyrolysis experiments using a tubular flow reactor for a constant THP molar flow rate of 1.68×10^{-4} mol.s⁻¹ with two different N₂ dilution factors (90% and 96%), at a pressure of 170 kPa and a temperature range of 913–1133 K. Then, they conducted combustion experiments in two premixed flat flame burners and in a shock tube. The first burner was operated at a low pressure of 50 Torr with 78% Ar with mixtures of $\phi = 1$ and 1.3. The second burner was used to measure the laminar burning velocities of THP/air mixtures using the heat flux method at

atmospheric pressure, three different inlet gas temperatures (298, 358, and 398 K) and an equivalence ratio range (0.55 to 1.5). Then, the shock tube was used to measure the ignition delay times of THP/O₂/Ar mixtures under a range of pressures (885–914 kPa), temperatures (1350–1613 K), and equivalence ratios (0.5–2). Finally, the authors developed a detailed kinetic mechanism suitable for the high-temperature oxidation and pyrolysis of THP.

While all the aforementioned studies focused only on the high-temperature oxidation of THP, the low-temperature reactions of this potential biofuel have been studied only recently, since 2017. Four distinct studies were published by: Rotavera et al. [107], Chen et al. [108], Telfah et al. [109], and Davis et al. [110]. Different flow reactors or reaction cells were employed across these studies, each coupled with one of the following analytical methods: multiplexed photoionization mass spectrometry, infrared laser absorption spectroscopy, and cavity ring-down spectroscopy. After determining the branching fractions of low-temperature chain-termination pathways ($R + O_2 \rightleftharpoons \text{unsaturated ring} + HO_2$) for THP and cyclohexane (CHX) at 10 and 1520 Torr from 500 to 700 K, Rotavera et al. [107] proved that these channels are more favored in THP due to its oxygen atom, and suggested that this effect might be generalized to other pathways competing with chain-branching routes at low temperatures. They also reported that, as temperature increases, the functional group in THP further promotes the ring opening of adjacent radicals. Chen et al. [108] measured the formation of OH and HO₂ radicals in the reactions of THP and CHX derived radicals with O₂ at 20 Torr within a temperature range of 500–750 K, and showed the possibility of comparing the low-temperature oxidation behavior of such analog fuels even without studying their detailed chemistry. Telfah et al. [109] detected tetrahydropyranyl peroxy radicals and associated the absence of those adjacent to the ether group (α -THPOO•) to their favored ring opening. Davis et al. [110] compared the photoionization spectra of ketohydroperoxides (KHPs) produced from THP and CHX, and revealed that the presence of ether group reduces the formation of KHPs in cyclic hydrocarbons.

Later, THP combustion was discussed in the comprehensive studies of Rotavera and Taatjes [77] and Tran et al. [26]. The former addressed the low-temperature chemistry of biofuels, covering THP and other cyclic ethers, while the latter investigated the combustion kinetics of cyclic ethers exclusively, including THP among the studied species.

More recently, low- and high-temperature chemistry of THP has been explored in detail:

- Zou et al. [111] used two JSRs (78 and 92 cm³) to study stoichiometric and lean THP oxidation between 450 and 900 K at atmospheric pressure, with a residence time of 4 s.
- Hartness et al. [112] conducted speciation and ignition delay time measurements for THP below 1000 K using a JSR (33.5 cm³) and two RCMs. The JSR experiments were carried out under stoichiometric conditions at a residence time of 4 s and a pressure of 1 bar, while the RCM studies covered pressures ranging from 5 to 20 bar and three equivalence ratios ($\phi = 0.5, 1, \text{ and } 2$).
- We studied the oxidation of THP in a JSR (42 cm³) at a high pressure of 10 atm, a residence time of 700 ms, an equivalence ratio range of 0.5–4, and a temperature range of 480–1260 K [113].
- Wang et al. [114] investigated THP pyrolysis and stoichiometric oxidation in an atmospheric-pressure JSR (102 cm³) between 733 and 1148 K, maintaining a constant liquid fuel flow rate of 0.0128 mL/min.

In each of these four studies, a detailed kinetic sub-mechanism was developed. These studies, along with all reported experimental investigations on THP oxidation, are listed in Table 2.

Table 2: Summary of experimental studies reported on the combustion of THP.

Reference	Apparatus	p (bar)	T (K)	ϕ
Leppard et al. [102]	TE	0.6	358	0.95–1
Dagaut et al. [104]	JSR	10	800–1100	0.5–2
	ST	2–5	1000–1700	0.5–2
Labbe et al. [105]	FFB	0.027	450–2500	1.75
Tran et al. [106]	FR	1.7	913–1133	∞
	FFB	0.067	600–2400	1, 1.3
	FFB	1	298, 358, 398*	0.55–1.5
	ST	8.85–9.14	1350–1613	0.5–2
Rotavera et al. [107]	FR	0.013, 2.03	500–700	--
Chen et al. [108]	RC	0.027	500–750	--
Telfah et al. [109]	RC	0.2	298	--
Davis et al. [110]	FR	0.013, 2.03	500–700	--
Zou et al. [111]	JSR	1	450–900	0.25–1
Hartness et al. [112]	JSR	1	500–900	1
	RCM	5–20	600–1000	0.5–2
Hoblos et al. [113]	JSR	10	480–1260	0.5–4
Wang et al. [114]	JSR	1	733–1148	1, ∞

TE: Test Engine; JSR: Jet-Stirred Reactor; ST: Shock Tube; FFB: Flat Flame Burner; FR: Flow Reactor; RC: Reaction Cell; RCM: Rapid Compression Machine; *: initial temperatures; --: unavailable.

2.2.4 Tetrahydrofuran

THF and the cyclic ethers of its family (e.g., furan and 2-MTHF) were the subjects of many previous studies in the combustion field. This could be clearly seen in the two aforementioned comprehensive researches established by Rotavera and Taatjes [77] and Tran et al. [26].

The pyrolysis of THF was extensively studied [115–118], as well as its oxidation and auto-ignition. First, Molera et al. [119] and Leppard [102] studied the oxidation of THF under static and engine conditions, respectively. Then, as with THP, Dagaut et al. [120] examined THF oxidation and auto-ignition under high pressure and temperature conditions using two different experimental apparatus: a JSR and a shock tube, and developed a kinetic mechanism to simulate their results. Kasper et al. [121] identified the reaction pathways of THF in low-pressure

premixed flat flames under stoichiometric and rich conditions. Uygun et al. [122] measured the ignition delay times of stoichiometric THF/air mixtures in a high-pressure shock tube within the temperature range of 691–1100 K. Tran et al. [123] studied the combustion chemistry of THF, at high temperatures and equivalence ratios ranging from 0.5 to 2, in low- and atmospheric-pressure laminar premixed flat flames as well as in a shock tube, and also developed a corresponding kinetic mechanism. To explore its low-temperature reactivity, Vanhove et al. [124] conducted an experimental study on THF auto-ignition and speciation in a rapid compression machine and a JSR, respectively. The former operated at pressures between 5 and 10 bar and under stoichiometric conditions, while the latter was maintained at atmospheric pressure and a constant residence time of 2 s, with equivalence ratios ranging from 0.5 to 2. Antonov et al. [125] reported an experimental study, combined with quantum chemistry, on the initial reactions involved in the low-temperature oxidation of THF, carried out in low- and high-pressure flow reactors. Giri et al. [126] studied the reactions of THF with OH radicals in a shock tube at pressures near 1.5 bar, and proposed theoretical rate constants for these reactions. The first and unique detailed kinetic sub-mechanism involving the low-temperature oxidation of THF was developed by Fenard et al. [127]. Following the same methodology used for THP, Telfah et al. [109] generated tetrahydrofuranyl peroxy radicals in a room-temperature gas-flow reaction cell and detected them using cavity-ring down spectroscopy. Using both experimental and theoretical approaches, Hansen et al. [128] identified and quantified the KHPs formed during the cool flame of a very lean THF mixture in a JSR operated at near-atmospheric pressure with a residence time of 2 s. Wu et al. [129] used a rapid compression machine to measure the ignition delay times of a stoichiometric mixture with 1 mol% THF at low-to-intermediate temperatures and a compressed gas pressure of 18 bar, then proposed a modified model to represent these data along with other previously reported experimental data. Belhadj et al. [130] characterized the cool-flame products of THF obtained in a JSR at a total of pressure of 10 atm, an equivalence ratio of 0.5, an initial fuel mole fraction of 5000 ppm, a mean residence time of 2 s, and a temperature range of 550–620 K. They detected twenty-four new fuel-related species, including KHPs and highly oxygenated molecules, then used the mechanism of Fenard et al. [127] to simulate their results. More recently, Do et al. [131] used a high-pressure shock tube to carry out the auto-ignition of various THF mixtures, and then compared the results with those of its cyclic hydrocarbon analog, cyclopentane (CPT). To simulate their data, they combined the mechanism of THF from Fenard et al. [127] with that of CPT from Lokachari et al. [132]. Finally, Sharma et al. [133] conducted an experimental and modeling study on the oxidation of THF in a JSR under conditions similar to those of the lean mixture investigated by Vanhove et al. [124], but using argon as the diluent instead of helium. All the previously presented experimental investigations on THF oxidation are summarized in Table 3.

Table 3: Summary of experimental studies reported on the combustion of THF.

Reference	Apparatus	p (bar)	T (K)	ϕ
Molera et al. [119]	SR	0.21	493	2.75
Leppard et al. [102]	TE	0.8, 12	400, 827	0.95–1
Dagaut et al. [120]	JSR	10	800–1100	0.5–1
	ST	2–5	1000–1800	0.5–2
Kasper et al. [121]	FFB	0.020–0.033	450–2500	1–1.75
Uygun et al. [122]	ST	20–50	691–1100	1
Tran et al. [123]	FFB	0.067	900–2400	0.7–1.3
	FFB	1	298, 358, 398*	0.55–1.6
	ST	8.5	1300–1700	0.5–2
Vanhove et al. [124]	RCM	5–10	640–900	1
	JSR	1	500–1000	0.5–2
Antonov et al. [125]	FR	0.013–2.6	400–700	--
Giri et al. [126]	ST	1.5	800–1340	--
Telfah et al. [109]	RC	0.2	298	--
Hansen et al. [128]	JSR	0.93	500–700	0.3
Wu et al. [129]	RCM	18	670–910	1
Belhadj et al. [130]	JSR	10	550–620	0.5
Do et al. [131]	ST	20	865–1700	0.44–2
Sharma et al. [133]	JSR	1	520–1020	0.5

SR: Static Reactor; TE: Test Engine; JSR: Jet-Stirred Reactor; ST: Shock Tube; FFB: Flat Flame Burner; RCM: Rapid Compression Machine; FR: Flow Reactor; RC: Reaction Cell; *: Initial temperatures; --: unavailable.

3 Experimental Study

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This chapter presents the apparatus, methodology, and analytical techniques used to conduct the experimental work of this study, along with the range of experimental conditions investigated. Also, the associated uncertainties are briefly discussed.

3.1 Setup and Equipment

Perfectly stirred reactors allow to conduct gas-phase kinetic studies on the oxidation and pyrolysis of a large variety of fuels. The main feature of such reactors is their excellent capability to create homogeneous reacting mixtures in terms of both chemical and physical properties. Moreover, when coupled with performant analytical techniques, these reactors enable the construction of accurate mole fraction profiles for the different reactant, intermediate, and produced species. Based on these profiles, researchers can develop detailed kinetic mechanisms for fuels of interest involving their low- and high-temperature chemistry.

In the present work, we used two spherical jet-stirred reactors (JSRs) of 42 and 34 cm³, designed by Dagaut et al. [134] and located in ICARE laboratory. A photograph of one of the reactors is shown in Figure 3.1. Each reactor is made of quartz to avoid any catalytic reactions on the wall, and equipped with four nozzles (having each a diameter of about 1 mm and an outlet in the equatorial plane) designed to provide perfect stirring for the injected reactants. The design of these injectors allows us to insert and move along the central vertical axis of reactor:

- A type S thermocouple (Pt/Pt-Rh 10%): used to continuously measure the temperature inside the reactor. This thermocouple is placed inside a thin wall fused silica tube to avoid any catalytic reactions that can occur on the metallic wires.
- A low-pressure sonic quartz probe: used to take samples from the reacting mixture after freezing the reactions in place preventing any further progress. Samples are then transmitted to distinct online and offline analytical devices.

The thermal and chemical homogeneity of the reacting mixture could be verified by measuring the temperature and taking samples at different positions inside the reactor, respectively. This also ensures the good repeatability of the experiments carried out in our reactor.

An electrical oven is used to heat the reactor, performing temperatures up to 1280 K, and a high dilution of the reactive mixtures by nitrogen is always done to prevent high heat release.



Figure 3.1: Photograph of a JSR used in this study [134].

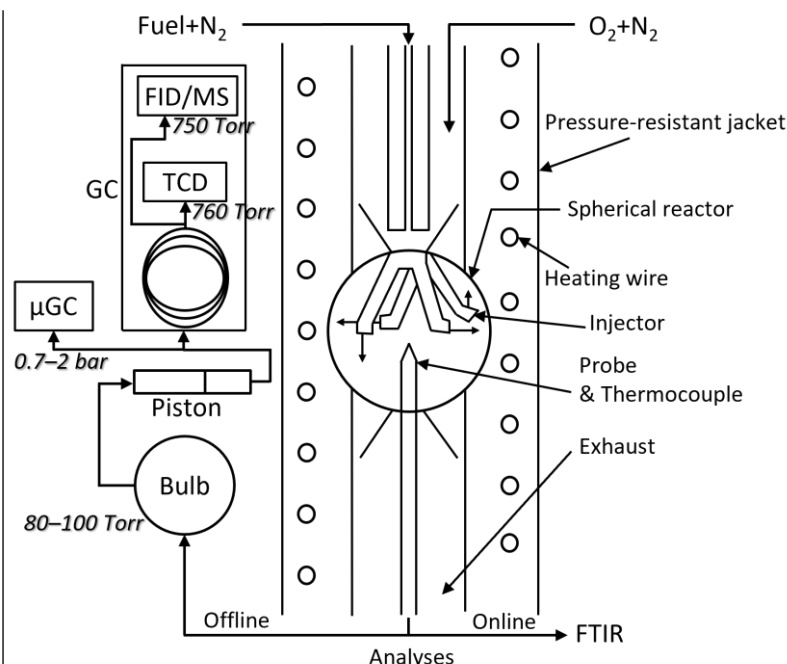


Figure 3.2: Schematic representation of the JSR setup and associated analytical instrumentation used in this work.

The additional characteristic of the JSRs used along this work is their abilities to carry out experiments up to 10 bar thanks to the usage of a stainless-steel pressure-resistant jacket. Placed inside this metallic vessel, the reactor can withstand high pressures due to the four holes drilled at the bottom of its outlet tube. In fact, the exhaust gases diffuse through the holes into the space between the reactor and vessel, leading to a pressure equilibrium between the interior and exterior of the reactor. The detailed schematic of our reactor system is illustrated in Figure 3.2.

3.2 Methodology and Conditions

As all the fuels studied in this work are initially in the liquid phase, their flow rate is regulated either by a liquid mass-flow controller (LMFC, Bronkhorst®) or by a high-performance liquid chromatography (HPLC) pump (Shimadzu LC-10ADVP). The fuel stream is first mixed with a small portion of the diluent flow to assist atomization. This auxiliary flow is accounted for in the total diluent flow and is regulated by a gas mass-flow controller (GMFC, Bronkhorst®). The resulting fuel/diluent mixture then passes through an evaporator to ensure complete vaporization of the fuel prior to the reactor entry. For experiments conducted with the LMFC, the mixing and evaporation steps are performed simultaneously using a controlled evaporator-mixer (CEM, Bronkhorst®), which can be directly coupled with both the LMFC and GMFC provided by the same manufacturer.

After vaporization, the fuel flow is delivered to the reactor through a capillary tube, while the oxygen flow is brought – with the primary diluent flow – in a separated stream (as shown in Figure 3.2) to avoid any premature reactions. Similar to the auxiliary diluent flow, the flow rates of primary diluent and oxygen are controlled by GMFCs, which are regularly calibrated and compatible with the required range for the experiments.

The fuels studied in this work are: THP, THF, and three different blends of DEE and THF. Neopentanal (also known as pivaldehyde) was also studied as a continuation of our team's previous work on the oxidation of pentanal isomers [65,66]. However, since it is not directly related to the context of this thesis, its tested conditions and obtained data are included in **Appendix F**. Table 4 summarizes the sources and key properties of the fuels tested in this study.

Table 4: Providers and properties of the fuels studied in this work.

Form tested	Fuel	CAS	Provider	Purity	MW (g/mol)	SG	BP (°C)
Neat	THF*, ¹	109-99-9	Sigma-Aldrich	≥99.9%	72.11	0.89	65–67
	THP	142-68-7	TCI	>98.0%	86.13	0.88	88
	Pivaldehyde	630-19-3	TCI	>95.0%	86.13	0.78	75
Blend	DEE*, ²	60-29-7	TCI	>99.5%	74.12	0.70	35
	THF*, ²	109-99-9	TCI	>99.5%	72.11	0.89	65

*Anhydrous; ¹Inhibitor-free; ²Stabilized with BHT; MW: Molecular weight; SG: Specific gravity; BP: Boiling point.

For fuel blends composed of distinct components, a specific preparation and handling procedure is followed. A blend (B) of two oxygenated fuels – DEE (C₄H₁₀O) and THF (C₄H₈O) in this work – can be treated as a single hypothetical oxygenated fuel (C_xH_yO_z), whose molecular composition is expressed as a function of those of its two components:

$$\begin{cases} x_B = x_{DEE} \times \chi_{DEE} + x_{THF} \times \chi_{THF} \\ y_B = y_{DEE} \times \chi_{DEE} + y_{THF} \times \chi_{THF} \\ z_B = z_{DEE} \times \chi_{DEE} + z_{THF} \times \chi_{THF} \end{cases} \quad (3.1)$$

Where χ is the mole fraction of each component in B, which can be readily determined from the targeted mole fractions (X) in the initial gaseous reacting mixture, as follows:

$$\begin{cases} \chi_{THF} = \frac{X_{THF}}{X_{DEE} + X_{THF}} \\ \chi_{DEE} = 1 - X_{THF} \end{cases} \quad (3.2)$$

In our study on DEE/THF blends, the purpose was to enhance the relatively weak low-temperature reactivity of THF by adding DEE, which demonstrated strong reactivity under the same operating conditions in our previous work [29]. For this reason, we fixed the initial mole fraction of THF and all other conditions to those we used in the stoichiometric oxidation of neat THF (taken as a reference), and we varied only the DEE content. This approach allows a direct comparison and reveals clearly the effect of DEE addition on THF reactivity.

The DEE/THF blends were prepared on a mass basis, with each component weighed using a digital balance. The desired mole fraction (χ) for each component in this blend was used to calculate the corresponding mass fraction (Z), based on the respective molecular weights (MW):

$$\begin{cases} \frac{Z_{DEE}}{Z_{THF}} = \frac{MW_{DEE}}{MW_{THF}} \times \frac{\chi_{DEE}}{\chi_{THF}} = a \\ Z_{DEE} + Z_{THF} = 1 \end{cases} \quad (3.3)$$

Thus:

$$\begin{cases} Z_{THF} = \frac{1}{1+a} \\ Z_{DEE} = \frac{a}{1+a} \end{cases} \quad (3.4)$$

Once the mass fractions of both fuels are determined, the desired blend can be prepared in three simple steps:

- Weighing a specified mass (m) of THF in a flask;
- Adding the corresponding mass of DEE ($a*m$) to the same flask;
- Sealing the flask and stirring or shaking for 15 to 20 min to ensure uniform mixing of the two fuel components.

For each prepared blend, the density was measured experimentally.

All the experiments done throughout this work were carried out at $p = 10$ bar. During each experiment, the residence time (τ) was kept constant. To fix it, the flow rates of reactants and diluent were decreased when increasing the reactor temperature (T), according to the following equation:

$$\tau = \frac{V}{Q} \times \frac{T_0}{T} \times \frac{p}{p_0} \quad (3.5)$$

Where T_0 and p_0 are respectively the room temperature and pressure, Q is the total volumetric flow rate, and V is the reactor volume. The experimental conditions tested in this work are listed in Table 5.

Table 5: List of experimental conditions studied and approximative number of species detected for each fuel tested in this work.

Fuels Studied	Initial Mole Fractions (%)			φ	T (K)	p (bar)	τ (s)	# Species Detected
	Fuel	O ₂	N ₂					
THP	0.080	1.400	98.520	0.400	480–1200	10	0.7	30–40
		0.700	99.220	0.800	570–1200			
		0.350	99.570	1.600	570–1250			
		0.175	99.745	3.200	570–1260			
	0.100	1.400	98.500	0.500	480–1250			
THF	0.085	1.100	98.815	0.425	570–1200	10	0.7	25–30
		0.550	99.365	0.850				
		0.367	99.548	1.275	660–1250			
		0.306	99.609	1.530	660–1260			
		0.275	99.640	1.700				
	0.100	0.550	99.350	1.000	550–1260			
		0.275	99.625	2.000	570–1260			
	0.500	5.500	94.000	0.500	480–1050	10	2.0	40
DEE/THF Blends	0.023/0.100	0.688	99.189	1.000	450–1200	10	0.7	30
	0.053/0.100	0.868	98.979					
	0.083/0.100	1.048	98.769					

3.3 Analytical Techniques

The reacting mixture was analyzed by extracting samples using a low-pressure sonic probe, as previously mentioned, and transmitting them for:

- Online analyses: performed through Fourier-transform infrared spectroscopy (FTIR). To avoid condensation, the Teflon line carrying the samples to the FTIR cell is heated and maintained at 150 °C.
- Offline analyses: performed with three different gas chromatographs (GCs) and one micro-gas chromatograph (μ GC). An extension of the aforementioned Teflon line allows for storing samples in 1 L Pyrex bulbs at room temperature and under a low pressure (80–100 Torr in this work), in order to prevent reinitiating chemical reactivity.

3.3.1 Fourier-Transform Infrared Spectroscopy

FTIR is an analytical method used to identify and quantify chemical species based on their response to exposure to infrared (IR) radiation. This light-matter interaction is usually expressed as a relationship between the amount of IR radiation absorbed by the species and its concentration (C) through a dimensionless parameter, the absorbance (A_b). This relationship is derived from the Beer-Lambert law and is represented by the following equation showing explicitly the proportionality “ $A_b \propto C$ ”:

$$\log_{10} \left(\frac{I_0}{I} \right) = A_b = \epsilon \times L \times C \quad (3.6)$$

Where I_0 and I are respectively the incident and transmitted intensities of the IR radiation, L is the length of the light path, and ϵ is the molar absorption coefficient of the species.

The FTIR spectrometer used in this work is the Thermo Nexus 670 with an optical path $L = 10$ m, a resolution of 0.5 cm^{-1} , and 32 scans per measure. The main quantified molecules using this spectrometer are water (H_2O), carbon monoxide (CO), carbon dioxide (CO_2), formaldehyde (CH_2O), methanol (CH_3OH), and carboxylic acids like formic acid (HCOOH) and acetic acid (CH_3COOH). Mole fractions of some hydrocarbons such as methane (CH_4), ethylene (C_2H_4), ethane (C_2H_6), propene (C_3H_6), and acetylene (C_2H_2) can be also measured by this instrument, but their values obtained from GCs are more accurate. GCs were used as well to quantify other hydrocarbons and oxygenated compounds, which exhibit similar absorption bands, leading to significant interferences that make their quantification by FTIR very difficult.

Quantifying a species using FTIR first requires calibration by injecting known amounts of this species into the cell and detecting its IR spectra. A quantification method is then developed using the associated software of the spectrometer – “*Quant Setup*”, in our case – to calibrate the measured mole fractions of the species against its actual values. The cell operating conditions must be recorded in that method. In this work, the conditions used were as follows: $p = 200$ mbar, $T = 146$ °C, and $L = 10$ m. To ensure accuracy, the method must avoid saturated peaks during the quantification of the desired species and account for potential interferences from peaks of other compounds.

3.3.2 Gas Chromatography

Gas chromatography is an analytical technique used to separate the different components of a gaseous mixture, called analyte. Its apparatus, GC, is constituted of the following parts:

- The sample injector: it is used to introduce the gaseous sample into an inert gas stream (such as He, Ar, or N₂), called carrier gas or mobile phase, which serves as a transporter for this sample.
- The column: it is the main part of GC, a kind of long tube packed with a stationary phase (a solid or liquid material). This material interacts differently with the distinct components of the analyte making them travelling through the column at different rates and thus leading to their separation; the higher the affinity of a molecule to the stationary phase, the longer it takes to elute from the column.
- The oven: it is used to heat the column in order to optimize the separation of species with a wide range of boiling points.
- The detector: it detects the separated chemicals as they elute from the column, generating signals proportional to their amounts. Three distinct types of detectors were used throughout this PhD work: thermal conductivity detector (TCD), flame ionization detector (FID), and mass spectrometer (MS). While the two former types are used for the quantification of species, the latter is needed for their identification:
 - TCD measures the change in the thermal conductivity of gases (like H₂ and O₂ in this work), as they pass over a heated sensing element, relative to that of the carrier gas (N₂ in our case). Any difference in conductivity shown by a gas is detected as a signal proportional to its amount.
 - FID ionizes each species eluted from the GC by burning it in a hydrogen flame and measures the current generated by the resulting ions, which is proportional to its amount.
 - MS ionizes and fragments the analyte molecules already separated by the GC. The resulting ions are then separated based on their mass-to-charge ratio (m/z). The mass spectrum obtained for each molecule provides detailed information about its composition, molecular weight, and structural features.
- The data system: it records the detector signals to produce a chromatogram, showing the separated components of the analyte in the form of peaks. The time at which a peak is observed is called the retention time, representing the characteristic travel time of the corresponding compound through the column. The area under the peak is used to quantify that compound. In fact, the mole fraction of the desired compound is calculated from its peak area through a conversion coefficient, which can be easily determined by injecting known amounts of the compound as pure standards, if available, or estimated through the effective carbon number method [\[135,136\]](#).

A μ GC is a miniaturized GC, designed with microfabricated components, such as microfluidic channels, microinjectors, and small-scale detectors. It allows not only for faster and more efficient analyses, but also for greater portability and lower power consumption. A new μ GC was only recently installed in our laboratory; it was calibrated and used for the concluding experiments. Table 6 shows the different GCs used during this work.

Table 6: Main characteristics of GCs used in this work.

GC	Column	Detector	Carrier Gas (flow or pressure)	Identified Species
Shimadzu QP2010-SE	“CP-SIL 5CB”: $L = 25$ m, $D_{\text{int}} = 0.32$ mm, $D_f = 1.2$ μm Coupled with “DB1”: $L = 30$ m, $D_{\text{int}} = 0.53$ mm, $D_f = 3$ μm	FID & MS	He (0.7 mL/min)	HCs & oxygenated compounds
	“CP-Al ₂ O ₃ /KCl”: $L = 50$ m, $D_{\text{int}} = 0.32$ mm, $D_f = 5$ μm		He (1.5 mL/min)	HCs mainly
Varian 3300	“CP-CarboPlot P7”: $L = 25$ m, $D_{\text{int}} = 0.32$ mm, $D_f = 1.2$ μm	TCD	N ₂ (15 mL/min)	H ₂ & O ₂
Micro GC Agilent 990	Module (A): “Molsieve 5Å” ($L = 10$ m) with Backflush	Catharometer (μTCD)	N ₂ (up to 30 psi)	(A): H ₂ , O ₂ , CH ₄ & CO
	Module (B): “PoraPLOT U” ($L = 10$ m)			(B): CO ₂ & C ₂ –C ₃ HCs

L: Length, D_{int} : internal diameter, D_f : film thickness of “stationary phase”, HCs: Hydrocarbons.

3.4 Measurement Uncertainty

The experimental results obtained in this work were used to validate and refine the kinetic mechanisms developed for the studied fuels. Therefore, it is crucial to assess the potential uncertainties associated with the measurements.

Several factors contribute to the uncertainties in JSR experiments. Temperature measurements, for instance, rely on a thermocouple and may have a typical uncertainty of ± 5 K. This margin arises not only from the instrument inherent precision but also from possible temperature gradients within the reactor. Another important source of uncertainty is the actual composition of the reacting mixture. Although all mass flow controllers are periodically calibrated, minor discrepancies may still arise, primarily due to variations in the voltage-to-flow conversion.

The determination of intermediate species concentrations introduces further uncertainty. For some species, direct calibration is possible, allowing for accurate quantification. However, for others, the response factor was approximated using the effective carbon number method [135,136], which introduces additional variability due to its lower precision.

Considering all these factors and given the element balances ($\pm 10\%$ for carbon in most samples of each experiment), the overall experimental uncertainty is estimated to be around $\pm 15\%$. An additional uncertainty is considered for the 800 ppm THP experiments due to the non-verified calibration of the liquid mass flow controller, thus a total representative uncertainty of $\pm 25\%$ is applied to the corresponding results.

4 Kinetic Modeling

Content

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Over the past few years, our team has investigated the oxidation kinetics of various linear and branched ethers, combining experimental measurements with modeling efforts to develop and improve the corresponding kinetic mechanisms. Following the same approach, and after outlining the adopted base mechanism and the refinement of its core, this chapter describes the development of the detailed kinetic model established in this work to capture the oxidation behavior of the two studied cyclic ethers, THP and THF (either neat or blended with DEE). While direct calculations of reaction rates and species thermochemistry would provide the most accurate predictions of reactivity, they are computationally expensive and time-consuming. Consequently, most reaction rate constants are estimated by analogy, as the limited literature on cyclic ethers does not allow for the computation of specific rates for every reaction. The procedures and software used to simulate the present results, along with various types of existing data, are also presented at the end of this chapter.

4.1 Base Mechanism

It is well known that the development of comprehensive kinetic mechanisms for fuel oxidation is performed in a hierarchical manner, beginning with the smallest molecular compounds and progressively extending to larger and more complex species. Accordingly, the construction of a kinetic model must start from well-established C_0 – C_2 bases, which include the fundamental reactions of the simplest species. The model can be then systematically expanded to integrate higher carbon-number sub-mechanisms, ensuring at each stage chemical consistency and reliability through validation against a wide range and type of experimental data. The robustness of the sub-mechanism of each species involved in the oxidation of a studied fuel, especially the common foundational bases, is therefore of paramount importance.

In this context, the C_0 – C_2 core mechanism of our team is revised and updated to provide a solid foundation for the kinetic model built in this study. The key modifications made relative to the mechanism version from which this work started are listed in **Appendix A**. In fact, testing that initial version against novel laminar flame speed data obtained for methanol and ethanol in the combustion chamber OPTIPRIME of our laboratory ICARE revealed large discrepancies, highlighting the need for refinement. The refinement process (simplified in Figure 4.1) was guided by sensitivity analyses, which identified the most sensitive reactions. By checking and comparing the reported rate constants of these reactions, key modifications were implemented. Further validation was then performed to ensure that the updated mechanism is not biased

toward the new data. Thus, additional laminar flame speeds from the literature were used to validate this mechanism, as well as ignition delay times and speciation profiles. Discrepancies identified in this broader comparison were again addressed through sensitivity analyses and subsequent adjustment of rate constants based on literature-reported values. This iterative procedure was repeated until achieving the best possible compromise that ensured good agreement between the mechanism and the diverse tested experimental datasets.

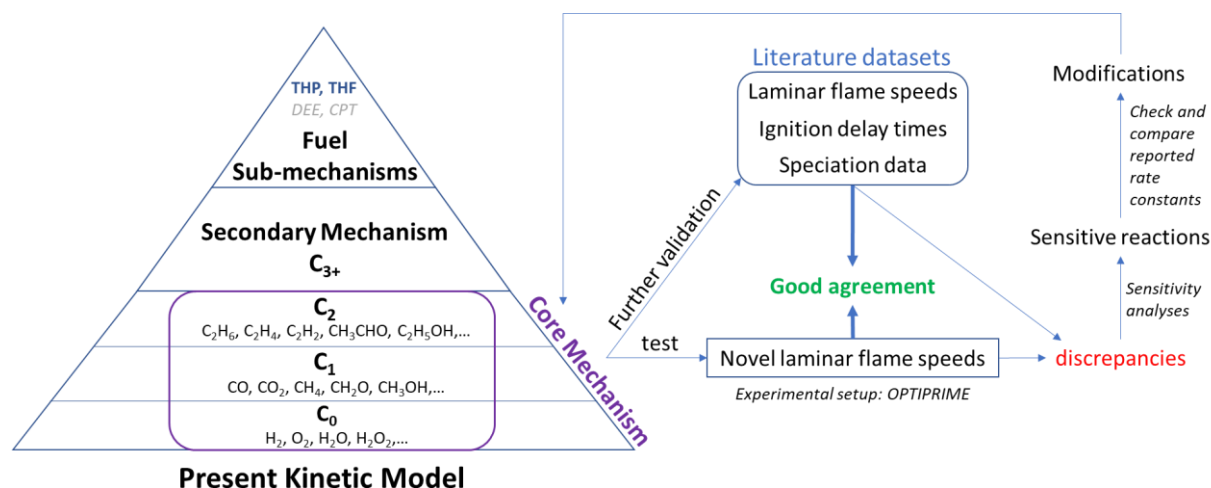


Figure 4.1: Schematic representation of the refinement process applied to the core mechanism in this work.

The base mechanism adopted in this work consists of the updated core combined with the C_3 – C_6 sub-mechanism of our previous work [65], which includes detailed chemistry for various compounds such as alcohols, aldehydes, and hydrocarbons. This sub-mechanism has shown good performance in several previous studies on different fuels, including cyclopentane [137], n-pentanal [66] and its isomers [65], as well as linear and branched ethers [29] [31] [33] [138].

4.2 Model Construction

As shown in **Chapter 2**, kinetic mechanisms for the high-temperature oxidation of both THP and THF were already available in the literature prior to this work. In contrast, no mechanisms had been proposed for the low-temperature oxidation of THP at that time, and only one existed for the LTR of THF. Due to this gap and the inability of existing mechanisms to accurately reproduce our experimental results, we developed our own cyclic ether sub-mechanisms from scratch. Nevertheless, the previous mechanisms still provided a valuable foundation for this development.

As the LTR of linear ethers had been extensively studied by our team and since the approach used to estimate their kinetic parameters had proven effective, we proceeded similarly with cyclic ethers in this work. Accordingly, the rate parameters of the low-temperature reactions were mainly estimated by analogy with those used for linear ethers, previously determined by analogy with alkanes. This analogy was based on the structural similarity between alkanes and ethers, with the latter differing only by the presence of an oxygen atom within the hydrocarbon chain. This functional group weakens the adjacent C–H and C–C bonds. The C–O bonds in ethers are also weaker than the corresponding C–C bonds in alkanes. These reductions in bond

dissociation energies (BDEs) increase the reactivity of ethers relative to their alkane analogs and were taken into account when estimating rate constants.

Detailed kinetic sub-mechanisms were developed during this thesis for THP and THF, covering both their low- and high-temperature oxidation. These sub-mechanisms were subsequently incorporated into the aforementioned base model. The DEE sub-mechanism, previously established by our team [29], was then integrated into the resulting kinetic model to simulate the experimental data of DEE/THF blends, investigated here for the first time. Additionally, our previous sub-mechanism of CPT [137] was included in order to extend the validation of the present mechanism to this species, as it shares similar oxidation behavior with THF.

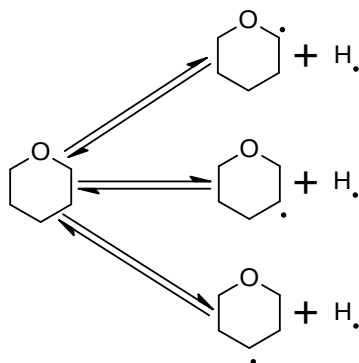
For each sub-mechanism developed in this work, the key reactions are listed by class in **Appendix B**, together with their rate constants, and the rationale behind the selected rate constants are presented in the next two sub-sections. The thermochemical properties of the newly introduced species were estimated using RMG [139], based on the group additivity method.

4.2.1 Tetrahydropyran

The THP sub-mechanism developed in this work was recently published [113]. In this sub-mechanism, the rate constants for fuel-specific reactions were adopted from the literature by analogy with similar reactions previously studied.

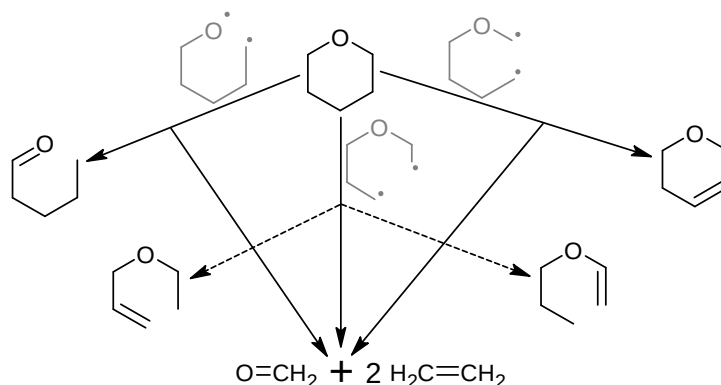
The two pericyclic reactions of THP studied by Lizardo-Huerta et al. [140] were considered in our work: the isomerization forming an alcohol (pent-4-en-1-ol) and the H₂ elimination yielding a cyclic biradical. This biradical will then undergo different pathways adopted from the work of Verdicchio et al. [118], who studied the analog biradical derived from THF, while the sub-mechanism of pent-4-en-1-ol was taken from our previous work [141].

A reverse rate constant of 10^{14} s^{-1} was attributed to each of the unimolecular initiation reactions of THP by C–H bond cleavage:



The rate constants for the fuel ring-opening reactions yielding n-pentanal and unsaturated ethers were estimated by analogy with the ring-opening of CHX producing 1-hexene from Sirjean et al. [142]. While only one ring-opening reaction exists for CHX, three different ring-opening reactions are possible for THP due to the presence of three distinct bond types (C–O, C–C at the β -position of ether group, and C–C at the γ -position). Thus, the pre-exponential factor used for each THP ring-opening reaction considered was taken equal to that used for CHX divided by 3. The rate constant for the decomposition reaction of THP producing formaldehyde and two

ethylene molecules was adopted by analogy with that of THF decomposition into formaldehyde and propene from Verdicchio et al. [118]. The aforementioned reactions are shown below:



Although all the previously mentioned unimolecular reactions of THF have a negligible effect under the oxidation conditions studied in this work, they were incorporated in our mechanism in order to simulate pyrolysis speciation data available in the literature.

Rate constants for bimolecular initiation reactions by O_2 and for reactions of hydrogen abstraction from fuel were estimated based on analogies with di-n-propyl ether (DPE) or THF for the α -C–H site and with CHX for the β and γ -C–H sites, as follows:

- For the α -site, the rate constants of bimolecular initiation by O_2 and of H-abstraction reactions by OH, HO_2 , O, CH_3 , CH_3O_2 , and C_2H_5 radicals were taken from Serinyel et al. [31], while the H-abstraction reactions by H, HCO, CH_2OH , and CH_3O were adopted from Fenard et al. [127].
- For the β - and γ -sites, rate constants were taken either from Zou et al. [59] or from Serinyel et al. [143] and were divided by 3 and 6 respectively. This is due to the fact that there are four equivalent C–H bonds at the β -position but only two at the γ -position, while twelve equivalent C–H bonds exist in CHX.

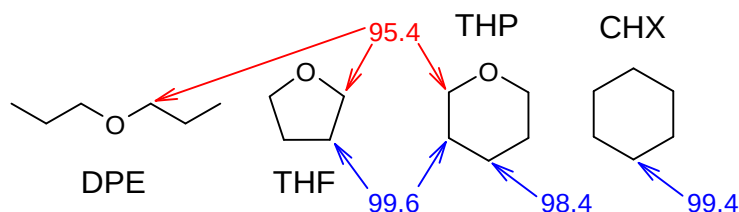


Figure 4.2: BDEs (in kcal/mol) calculated for C–H bonds adjacent to the ether group of DPE, THF, and THP (shown in red), and for other C–H bonds in THF and THP, as well as the C–H bond in CHX (shown in blue), based on thermochemical data obtained using the RMG group additivity method [139].

The choice of these analogies is supported by Figure 4.2, which shows that: the α -C–H bond in THP has the same BDE value as those in DPE and THF, while the β and γ -C–H bonds in THP have BDE values closer to that of the C–H bond in CHX. Figure 4.2 also confirms that the α -C–H is, as expected, the weakest C–H bond in THP, making the corresponding α -radical the most favored fuel radical.

A correction was applied for the H-abstraction reactions by OH radicals and H atoms; their pre-exponential factors were decreased by 50%. This correction was made to ensure the best

possible agreement between our model and the present experimental data, while maintaining reasonable estimates for the rate constants of these reactions (i.e., within the expected ranges based on relevant analogies), as shown in Figure 4.3.

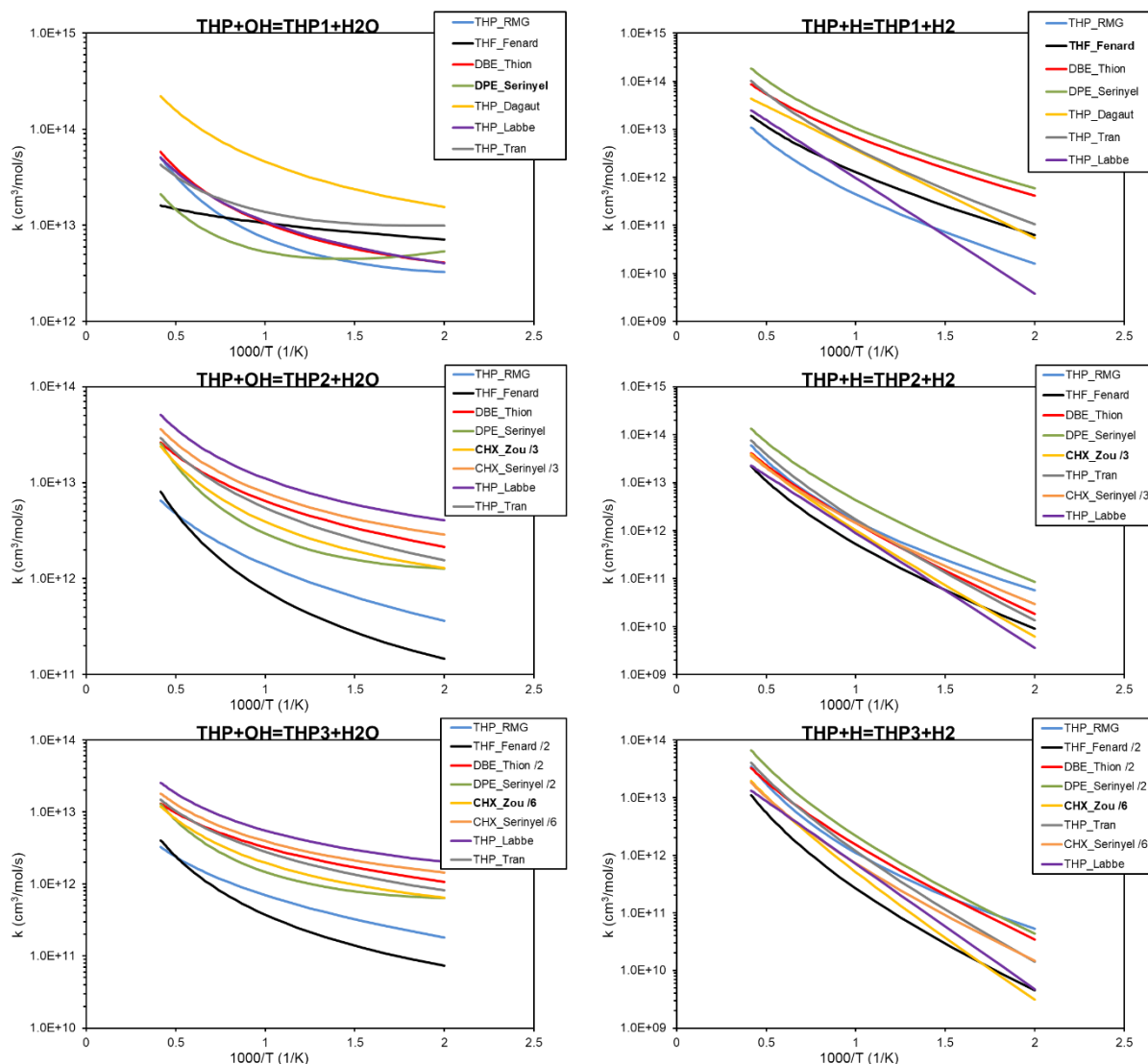
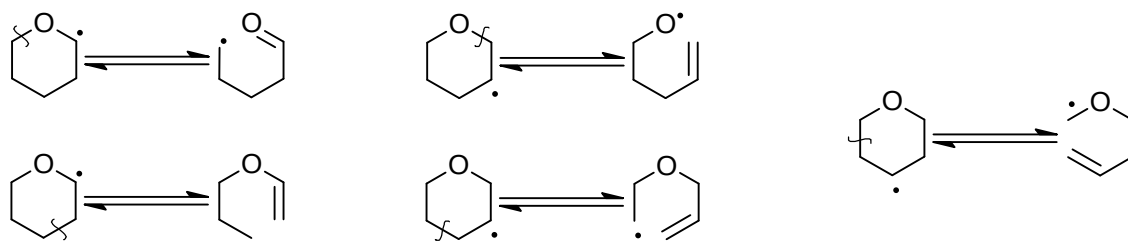


Figure 4.3: Rate constants of the H-abstraction reactions of THP by OH radicals and H atoms. THP1, THP2, and THP3 are the primary radicals of THP at α -, β -, and γ -positions of the ether group, respectively. The division of some rate constants by 2, 3, or 6 was done in order to account for the number of equivalent C–H bonds when making analogies between THP [104–106] [139], THF [127], DBE [33], DPE [31], and CHX [59] [143], depending on the site of the H abstracted. The references of the corrected rate constants used in this work are shown in bold.

In order to determine the rate constants for the β -scission reactions of fuel radicals involving ring-opening (shown just below), analogies were made with THF [127] and CHX [59] radicals.



Additional β -scission reactions were then incorporated to account for the consumption of the newly formed radicals resulting from the ring-opening of THP radicals.

The LTR of THP was also considered in this kinetic study. As an example, Figure 4.4 illustrates the main low-temperature reaction pathways of THP α -radical.

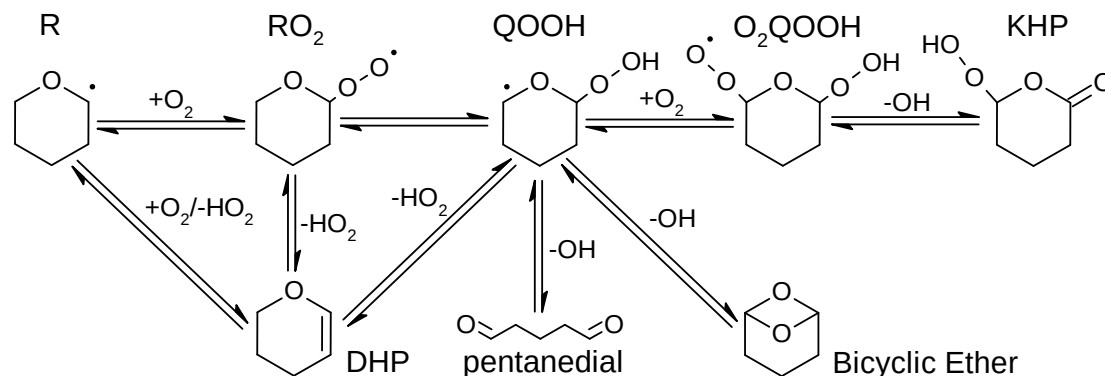


Figure 4.4: Main low-temperature reaction pathways of THP α -radical.

Rate constants for addition reactions of fuel radicals (R) to molecular oxygen (O_2) forming RO_2 radicals were taken from the work of Goldsmith et al. [144]. Same rate constants were also attributed to the addition reactions of QOOH radicals to O_2 , but they were divided by 2 to take into account the larger size of QOOH compared to R radicals. In fact, the presence of $-OOH$ group could have a steric effect on QOOH, making it more difficult for this radical to collide successfully with O_2 (i.e., in an orientation that leads to a reaction) and thus reducing the pre-exponential factor in the rate constant of such a reaction. For the reactions of R and O_2 producing dihydropyrans (DHPs) and HO_2 , the rate constant was brought from DeSain et al. [145] with a reduction of 50%. Only in the case of the fuel radical at the γ -position of the oxygen atom, the pre-exponential factor was then multiplied by 2 (thereby cancelling the reduction) to take into consideration the four equivalent C–H bonds present in the β -position of this radical.

The rate constants for the isomerization of RO_2 to QOOH and their decomposition (both RO_2 and QOOH) to DHPs and HO_2 , as well as for the formation of KHPs and cyclic ethers derived from THP (bicyclic ethers) were adopted from Villano et al. [146,147] in the same manner considered previously for di-n-butyl ether (DBE) [33]:

- For RO_2 isomerization to QOOH radicals, the activation energy proposed by the authors was reduced by 3 kcal.mol^{-1} only when the H atom to be transferred was at the α -position of the ether group.
- The rate constants for RO_2 /QOOH decomposition and cyclic ether formation were considered without any alteration.
- The activation energy of KHP formation was reduced by 3 kcal.mol^{-1} when the carbonyl group is formed at the α -position of the ether group to take into account the effect of the two oxygenated groups (hydroperoxy and ether groups) on the C–H bond dissociation energy.

To account for the four equivalent C–H bonds present at the α - and β -positions of the ether group, the pre-exponential factor of RO_2 isomerization and decomposition reactions was multiplied by 2 when the peroxy group is at the γ -position. After their formation, cyclic ethers

were consumed through H-abstraction reactions by OH, H, and HO₂ radicals. The rate constants of these reactions were adopted from our previous work [31]. Finally, for the reactions of KHP decomposition, the rate constants were adopted from the study of Vasudevan et al. [148].

4.2.2 Tetrahydrofuran

Based on our THP sub-mechanism, a sub-mechanism of THF was also developed in this work, covering both its low- and high-temperature oxidation.

Although their effect is negligible under the oxidation conditions studied in this work, the unimolecular reactions of THF were incorporated into our mechanism, as some influence the simulation of shock tube data from the literature presented later in this manuscript. The two pericyclic reactions of THF studied by Lizardo-Huerta et al. [140] were considered in our work: the isomerization forming but-3-en-1-ol and the H₂ elimination yielding the cyclic α - α biradical, obtained by elimination of an H atom from each one of the two carbon atoms adjacent to the ether group. This biradical will then undergo different pathways adopted from the work of Verdicchio et al. [118], while the sub-mechanism for but-3-en-1-ol was built by analogy to that of pent-4-en-1-ol used in our previous mechanism [141]. The rate constants for the ring-opening of THF via C–O and C–C bonds scission, yielding n-butanal and unsaturated ethers, were estimated by analogy with the ring-opening of CPT to 1-pentene present in our previous study [137]. While only one ring-opening reaction is possible in the case of CPT, three different reactions are possible in the case of THF due to the existence of three distinct types of bonds: the C–O bond, the C $_{\alpha}$ –C $_{\beta}$ bond at the β -position of the ether group, and the C $_{\beta}$ –C $_{\beta}$ bond at its γ -position. While THF has two C–O bonds and two C $_{\alpha}$ –C $_{\beta}$ bonds, it has only one C $_{\beta}$ –C $_{\beta}$ bond. In order to account for this, the rate pre-exponential term (A) used for C–O and C $_{\alpha}$ –C $_{\beta}$ homolysis was taken equal to the two-fifths of that of CPT (constituted of five identical C–C bonds), and the last one-fifth went for the A-term of the C $_{\beta}$ –C $_{\beta}$ homolysis. The rate constants for the decomposition reaction of THF producing propene and formaldehyde and that forming ethylene and acetaldehyde were adopted from the mechanism of Fenard et al. [127].

Rate constants for the β -scission reactions of THF radicals, accompanied by ring-opening, were also adopted from the work of Fenard et al. [127]. Subsequently, additional β -scission reactions were added to account for the consumption of the new radicals formed by the decomposition of THF radicals.

Rate constants for bimolecular initiation reactions by O₂ and for reactions of H-abstraction were adopted from our THP sub-mechanism without modification: the α - and β -radicals of THF were considered similar to those of THP, as the corresponding C–H bonds were shown to have the same BDE values in both fuels (see Figure 4.2). The same low-temperature chemistry considered for THP was also used for THF, showing again its good performance in predicting the reaction pathways followed by cyclic ethers under cool-flame conditions. In addition, key isomerization reactions, involving the internal transfer of an H atom from an acyl site through a six-membered cyclic transition state, were included for the radicals generated from the ring opening that follows the decomposition of THF-derived KHPs. The competition between these favored isomerization reactions and the β -scission pathways splits the reaction routes originating from KHP decomposition, as illustrated in Figure 4.5 for the three most abundant KHPs of THF.

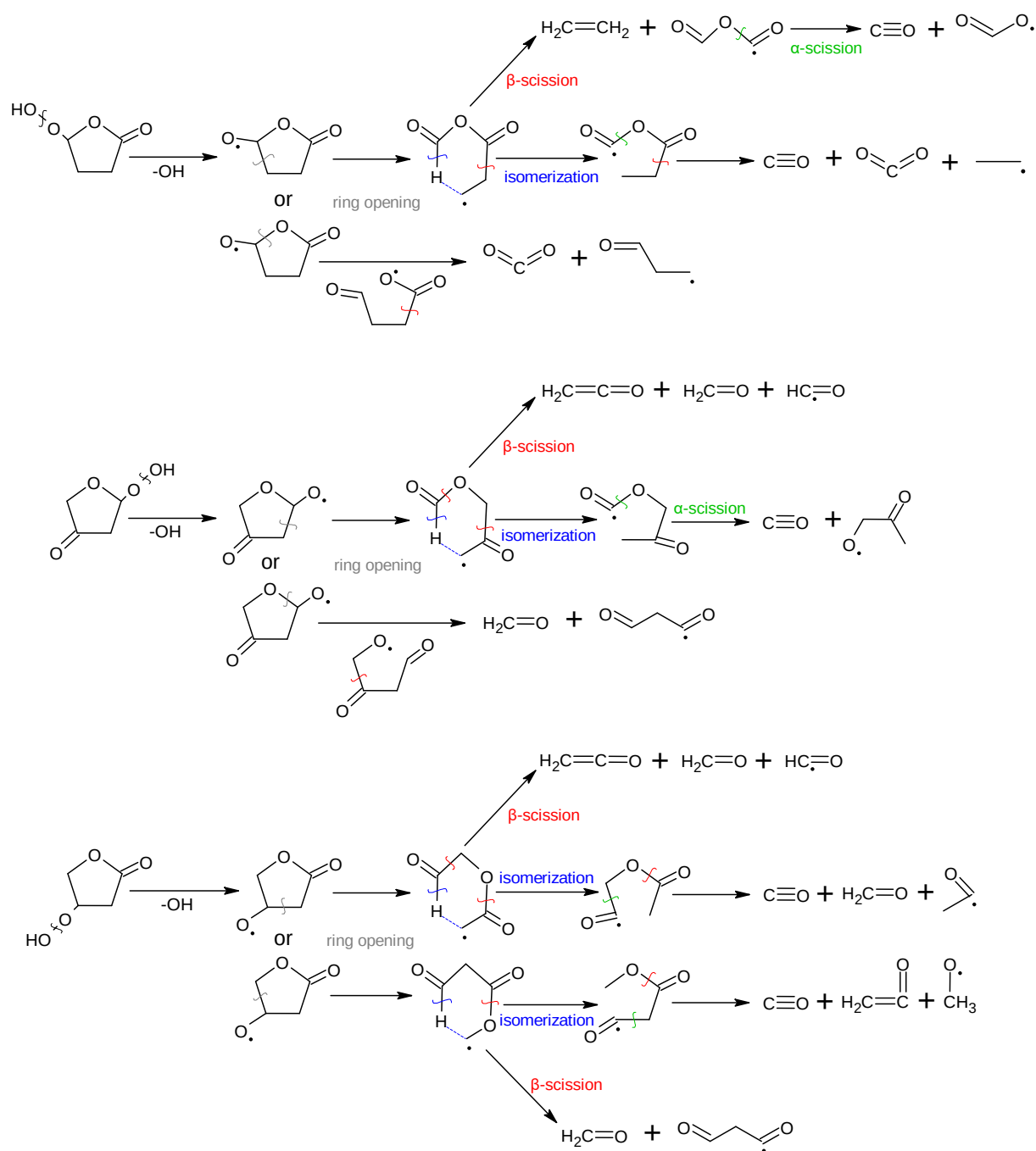


Figure 4.5: Reaction pathways of the three main KHPs derived from THF as considered in the present mechanism.

4.3 Simulations

All the simulations in this work were performed using the software Ansys Chemkin [149]. In this software, our experimental setup – the JSR – is modeled using the Perfectly Stirred Reactor (PSR) approach [150], which allows to simulate an isothermal open reactor operating under steady-state flow conditions. In this configuration, reactants are continuously fed into the reactor, where they react over a certain residence time. For the simulations, the following inputs must be specified: residence time (τ), temperature (T), pressure (p), and volume (V) of the

reactor. Since T varied between 450 and 1260 K in our experiments, a series of continuation steps was added to the model to compute the mole fractions of all species included in the mechanism over the experimental temperature range. Additionally, the initial composition of the gas mixture must be defined in the inlet section. Once all inputs are provided, the solver calculates the steady-state species mole fractions by solving the mass and energy conservation equations for the system.

The PSR model was also used alongside other Chemkin modules to simulate previously reported data, offering further validation for the kinetic model developed in this work and supporting the refinement for its core mechanism. Specifically, the PLUG [\[151\]](#), PREMIX [\[152\]](#), and SENKIN [\[153\]](#) codes were employed to simulate speciation data in tubular plug flow reactors, laminar flame speeds in isochoric combustion chambers, and ignition delay times in shock tubes, respectively.

A kinetic model is described in Chemkin using two input files: the mechanism file and the thermodynamic file.

The mechanism file consists of three blocks:

- Elements block: lists the atomic elements (C, H, O, N, Ar, and He in this work) that constitute the species.
- Species block: defines all chemical species participating in the reactions.
- Reactions block: contains the set of all elementary reactions included in the kinetic mechanism, each described by three parameters (A , n , E_a) for the rate constant, expressed in the modified Arrhenius form:

$$k(T) = A \times T^n \times e^{-\frac{E_a}{R \times T}} \quad (4.1)$$

Where R is the ideal gas constant, and the three Arrhenius parameters are defined as follows:

- A : the pre-exponential factor, its unit depends on the reaction order (“ $\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ ” for a second-order reaction).
- n : a dimensionless temperature exponent, used to account for deviations from simple Arrhenius behavior.
- E_a : the activation energy, representing the energy barrier that must be overcome for the reaction to proceed (expressed in $\text{cal} \cdot \text{mol}^{-1}$).

Some reactions exhibit pressure-dependent behavior, which can be represented either through the PLOG format (where separate Arrhenius parameters are specified at discrete pressures) or via Troe formalism [\[154\]](#), which introduces a more complex expression with additional parameters to describe fall-off behavior. Detailed descriptions of both methods, along with further relevant information, are available in Chemkin theory manual [\[155\]](#).

The thermodynamic data file specifies the thermochemical properties of species using NASA polynomial formalism [\[156\]](#). Each species is associated with two sets of seven polynomial coefficients: one for the low-temperature range (typically 300–1000 K) and another for the

high-temperature range (usually 1000–5000 K). These coefficients allow the calculation of enthalpy, entropy, and specific heat as functions of temperature.

With the thermodynamic data and the forward rate constants (k_f), Chemkin is able to compute the reverse rate constants (k_r) automatically through the equilibrium constants (K_{eq}), as follows:

$$k_r = \frac{k_f}{K_{eq}} \quad (4.2)$$

An additional transport file is needed when performing 1D laminar flame simulations using the PREMIX code, as it provides diffusion coefficients and other transport-related parameters.

5 Results and Discussion

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This chapter first shows and discusses the performance of the updated core mechanism on novel and existing data of methanol and ethanol. It then presents the results obtained for both THP and THF under various tested conditions. For each fuel, it compares the simulations predicted by our newly developed mechanism with the present experimental data and evaluates its performance against other mechanisms available in the literature. Thereafter, sensitivity and reaction pathway analyses are carried out using the present mechanism to identify the key reactions governing the chemistry of each fuel. Moreover, the present mechanism is further tested and validated against previously reported data of THP and THF. In addition, these two ethers were compared with other fuels previously tested by our team under identical conditions. Finally, for the DEE/THF blends studied for the first time in this work, the experimental and numerical results are compared and briefly interpreted.

5.1 Methanol and Ethanol

Contents

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5.1.1 Novel Laminar Flame Speeds

Novel laminar flame speed data, obtained for methanol and ethanol using the advanced experimental setup OPTIPRIME [157] developed in our laboratory ICARE, highlighted the need to revisit our C₀–C₂ core mechanism, which was accordingly updated during this work as mentioned in the previous chapter.

For the different mixtures studied, the laminar flame speed (S_u) is plotted as a function of the pressure (p) and temperature (T) in Figures 5.1–5.3: an axis (for each p_0) is added at the top of each graph to show the isentropic increase of T with p due to the compression of the fresh gases induced by the flame front propagation. The experimental data are shown as gray shaded bands representing the $\pm 5\%$ uncertainty. The transparency of the gray experimental traces and T -axes is decreased as p_0 increases to better distinguish between the distinct values of p_0 in the same graph. Black solid and dashed lines are added to the graphs to show simulations performed with the present core mechanism and its previous version (that served as the starting point for this thesis, and which significantly underpredicts almost all S_u data), respectively, highlighting the substantial improvement achieved in the core mechanism. In order to assess the performance of our mechanism relative to others, additional simulations (displayed with distinct colored lines) were carried out using various kinetic mechanisms from the literature. These mechanisms are listed in Table 7, indicating for each the number of species and reactions, and whether they have been tested against the methanol and/or ethanol data. The mechanism of Burke et al. [158], Mech15.34, was validated against various methanol data determined under engine relevant conditions, while that of Wang et al. [159], HPMech, was designed particularly for supercritical-pressure methanol oxidation. Mittal et al. [160] mechanism was proposed primarily for ethanol autoignition in a rapid compression machine, while that of Millán-Merino et al. [161] is a skeletal model suggested and validated for both premixed flame propagation and autoignition of ethanol. Finally, POLIMI C₁–C₃ [162] and AramcoMech3.0 [163] are multi-purpose mechanisms validated on different targets and for various fuels, including methanol and ethanol.

Table 7: Tested chemical kinetic mechanisms.

Mechanisms	#Species	#Reactions*	Fuels tested
Present work	56	471	CH ₃ OH, C ₂ H ₅ OH
Mech15.34 [158]	173	1011	CH ₃ OH
HPMech [159]	131	899	CH ₃ OH
Mittal et al. [160]	68	390	C ₂ H ₅ OH
Millán-Merino et al. [161]	34	69	C ₂ H ₅ OH
POLIMI C ₁ –C ₃ [162]	114	1999	CH ₃ OH, C ₂ H ₅ OH
AramcoMech3.0 [163]	581	3037	CH ₃ OH, C ₂ H ₅ OH

*Duplicate reactions were counted individually.

5.1.1.1 Methanol mixtures

Figure 5.1 shows the experimental and simulated plots $S_u = f(p)$ obtained for the methanol/air mixtures tested at $\phi = 0.7$, 1, and 1.4.

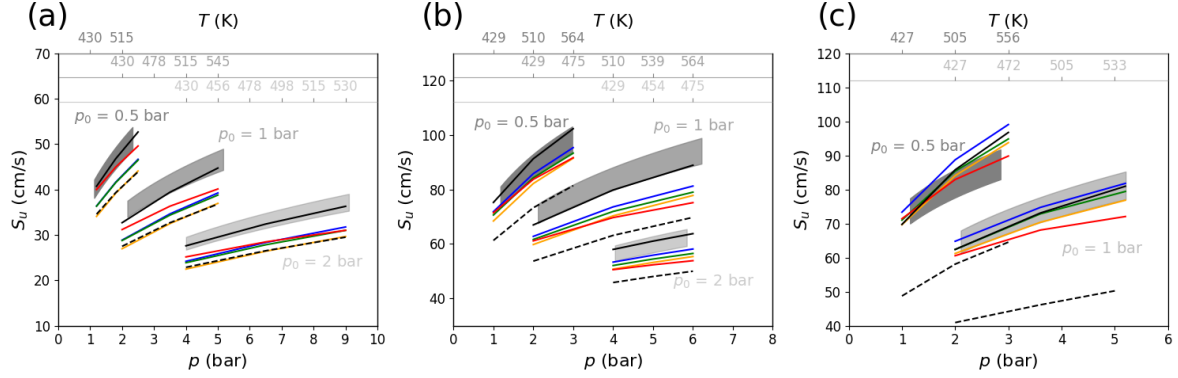


Figure 5.1: Methanol/air flame speed evolution as a function of pressure and temperature for $\phi = 0.7$ (a), 1 (b), and 1.4 (c). These mixtures were tested under the same initial temperature $T_0 = 358$ K. Thickened gray traces correspond to experimental results with their associated uncertainty ($\pm 5\%$). Lines correspond to simulations. Black: present core mechanism (solid) and its previous version (dashed); Green: Mech15.34 [158]; Red: HPMech [159]; Blue: POLIMI C₁-C₃ [162]; Orange: AramcoMech3.0 [163].

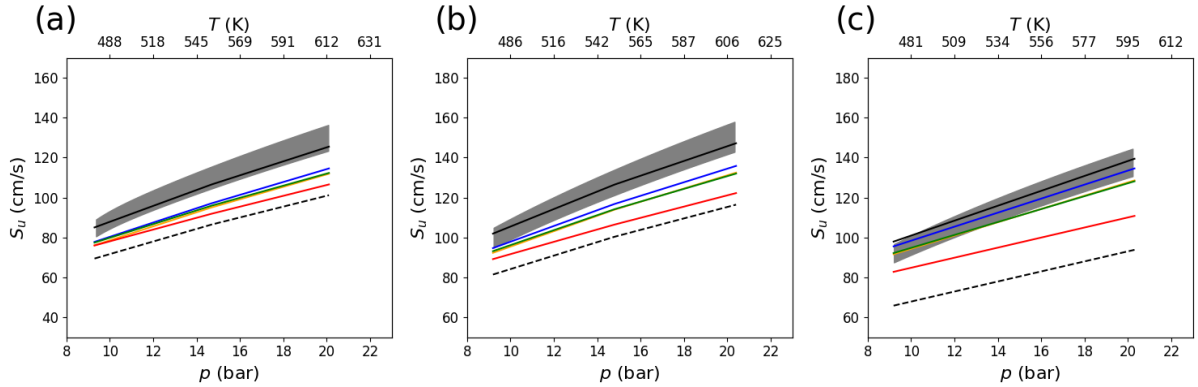


Figure 5.2: Methanol/O₂/He/Ar flame speed evolution as a function of pressure and temperature for $\phi = 0.85$ (a), 1 (b), and 1.36 (c). These mixtures were tested under the same initial pressure ($p_0 = 4$ bar) and temperature ($T_0 = 358$ K). Thickened gray traces correspond to experimental results with their associated uncertainty ($\pm 5\%$). Lines correspond to simulations. Black: present core mechanism (solid) and its previous version (dashed); Green: Mech15.34 [158]; Red: HPMech [159]; Blue: POLIMI C₁-C₃ [162]; Orange: AramcoMech3.0 [163].

Under both lean and stoichiometric conditions, the present mechanism gives the best prediction for the experimental data compared to the other mechanisms tested: the S_u simulated by our mechanism stays within the corresponding uncertainty range (or at the lowest limit of this range in the worst case). On the other hand, it can be seen that the literature mechanisms underpredict the experimental results for both lean and stoichiometric mixtures, although they (all except HPMech) show better predictions for the latter compared to the former.

When the mixture becomes rich, there is a good agreement between the experimental data and the S_u computed at $p_0 = 1$ bar with all mechanisms except HPMech. As for the lean and stoichiometric mixtures, the latter continues to underestimate the experimental data. However, at $p_0 = 0.5$ bar, it provides the best prediction, while the simulations from the other mechanisms

initially match the experimental trace but then tend to slightly overestimate the flame speed above a certain value of pressure and temperature (which varies from one mechanism to another), with POLIMI C₁-C₃ showing the highest overprediction.

Flame speeds of the methanol/O₂ mixtures, diluted in the He/Ar blend and tested at a high initial pressure $p_0 = 4$ bar, are presented in Figure 5.2, as functions of the pressure. The present mechanism predicts very well these experimental data for all equivalence ratios tested. However, the other mechanisms show again an underprediction for these data, which becomes less pronounced with the increase of ϕ for Mech15.34, AramcoMech3.0 (coinciding with the latter) and POLIMI C₁-C₃ (which becomes completely inside the uncertainty range at the rich condition).

5.1.1.2 Ethanol mixtures

Figure 5.3 exhibits the experimental and computed plots $S_u = f(p)$ obtained for the ethanol/air mixtures studied at $\phi = 0.7, 1$, and 1.2 . The present mechanism and that of Mittal show almost the same simulations for all these mixtures.

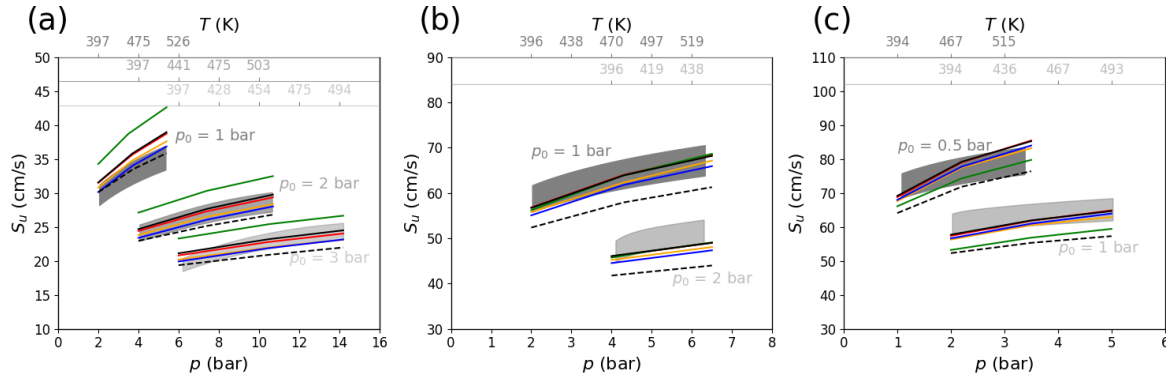


Figure 5.3: Ethanol/air flame speed evolution as a function of pressure and temperature for $\phi = 0.7$ (a), 1.0 (b), and 1.2 (c). These mixtures were tested under the same initial temperature $T_0 = 331$ K. Thickened gray traces correspond to experimental results with their associated uncertainty ($\pm 5\%$). Lines correspond to simulations. Black: present core mechanism (solid) and its previous version (dashed); Red: Mittal et al. [160]; Green: Millán-Merino et al. [161]; Blue: POLIMI C₁-C₃ [162]; Orange: AramcoMech3.0 [163].

For the fuel-lean mixture, S_u is overpredicted highly by the mechanism of Millán-Merino and slightly by the present mechanism and that of Mittal when $p_0 = 1$ bar, while AramcoMech3.0 and POLIMI C₁-C₃ are showing simulations near or at the upper limit of the experimental trace. Then, the discrepancies between the experimental results and the simulations decrease when p_0 increases to 2 and 3 bar. Thus, S_u becomes better predicted for these two initial pressures by all the mechanisms except for the skeletal mechanism of Millán-Merino, which continues to overestimate the experimental trace.

At the stoichiometric condition, all the simulations are in good agreement with the experimental data when $p_0 = 1$ bar, with our mechanism and those of Mittal and Millán-Merino showing the best estimation. When p_0 increases to 2 bar, the simulations underpredict the experimental data: the S_u computed remain at the lowest edge of the experimental trace, with POLIMI C₁-C₃ and AramcoMech3.0 showing the less accurate estimations (staying below the uncertainty range).

For the rich mixture, the mechanisms are showing generally good predictions at $p_0 = 0.5$ bar even though our mechanism and that of Mittal display a slight overprediction above a pressure close to 3 bar (similarly to what was seen for methanol under a similar condition). Only the skeletal mechanism shows an underestimation for the experimental trace when $p < 2$ bar, but then reveals a better prediction within this trace. When p_0 increases to 1 bar, we could see that, this time, all the mechanisms predict pretty well the experimental data except the skeletal model, which reveals relatively a significant underestimation.

5.1.2 Sensitivity Analyses

Sensitivity analyses are performed on the flow rate in order to identify the key reactions controlling the flame speed evolution for both methanol and ethanol. The analyses were carried out using the present mechanism, which showed the best prediction for the novel flame speed data obtained in our laboratory. Only the fourteen most sensitive reactions are considered for each condition. These reactions could be classified in two different groups based on their effect on the flame speed: those promoting S_u (having a sensitivity coefficient $S > 0$) and those inhibiting S_u (with $S < 0$). For each fuel, two equivalence ratios were considered with three different pressures and their corresponding temperatures. Similar to the results presented in the previous sub-section, sensitivities at a given equivalence ratio are described in terms of pressure only, as the associated temperature variation follows the same trend. While sensitivities of most reactions generally exhibit large variations with equivalence ratio, they change only slightly with pressure and temperature at a fixed equivalence ratio.

5.1.2.1 Methanol mixtures

Figure 5.4 (left) illustrates the sensitivity analyses done for methanol/air mixtures at $\phi = 0.7$ and 1.4. As far as promoting reactions are concerned, in any condition, and as expected, $\text{H} + \text{O}_2 \rightleftharpoons \text{O} + \text{OH}$ (R1) is the most positively sensitive reaction and its sensitivity significantly increases with ϕ . In the second place, appears the reaction $\text{CO} + \text{OH} \rightleftharpoons \text{CO}_2 + \text{H}$ (R2), which is highly sensitive at the lean condition but less sensitive as ϕ increases, and not sensitive when the mixture is rich. Although it consumes the highly reactive OH radicals, this reaction supplies H atoms to the chain-branching reaction R1. $\text{HCO} + \text{M} \rightleftharpoons \text{H} + \text{CO} + \text{M}$ (R3) comes thirdly in the promoting group, providing H to R1 and CO to R2, and shows decreasing sensitivity with increasing ϕ or p . Although it consumes H atoms, $\text{HO}_2 + \text{H} \rightleftharpoons 2\text{OH}$ (R4) has a positive sensitivity coefficient, as each H consumed generates two OH radicals. This coefficient increases with an increase in equivalence ratio, as the H atoms become more abundant at rich conditions. In addition, the two reactions $2\text{HO}_2 \rightleftharpoons \text{H}_2\text{O}_2 + \text{O}_2$ (R5) and $\text{H}_2\text{O}_2 (+\text{M}) \rightleftharpoons 2\text{OH} (+\text{M})$ (R6) appear among the promoting reactions with a sensitivity that decreases with the equivalence ratio, since HO_2 radicals and subsequently H_2O_2 molecules (produced from the HO_2 self-disproportionation) become less abundant. Moreover, $\text{OH} + \text{H}_2 \rightleftharpoons \text{H} + \text{H}_2\text{O}$ (R7) and $\text{CH}_3\text{OH} + \text{OH} \rightleftharpoons \text{CH}_3\text{O} + \text{H}_2\text{O}$ (R8) promote the reactivity but become less sensitive when increasing ϕ or p . Furthermore, two fuel-specific reactions appear in the promoting list at the rich condition: $\text{CH}_3\text{OH} + \text{HO}_2 \rightleftharpoons \text{CH}_2\text{OH} + \text{H}_2\text{O}_2$ (R9) and $\text{CH}_2\text{OH} + \text{O}_2 \rightleftharpoons \text{CH}_2\text{O} + \text{HO}_2$ (R10), which have an increasing sensitivity with the pressure rise.

On the other hand, $\text{HCO} + \text{O}_2 \rightleftharpoons \text{CO} + \text{HO}_2$ (R11), which competes with HCO dissociation (R3), is the most important negatively sensitive reaction (inhibiting overall reactivity) at lean conditions (given the abundance of O_2). However, as ϕ increases, the sensitivity of this reaction decreases while that of $\text{H}_2 + \text{O}_2 \rightleftharpoons \text{H} + \text{HO}_2$ (R12) increases. Thus, the latter reaction (occurring in the reverse direction as a terminating step) becomes the most inhibiting reaction at the rich condition for all pressures. In addition, the sensitivity of R11 also decreases as the pressure increases to be exceeded by those of the terminating reaction $\text{HO}_2 + \text{OH} \rightleftharpoons \text{H}_2\text{O} + \text{O}_2$ (R13) and the recombination $\text{H} + \text{O}_2 (+\text{M}) \rightleftharpoons \text{HO}_2 (+\text{M})$ (R14) (converting H into the less reactive HO_2) for $p > 2$ bar. The latter becomes less sensitive with the increase of ϕ (as O_2 concentration decreases) and disappears from the list at the rich condition, while a new recombination reaction appears: $\text{H} + \text{OH} + \text{M} \rightleftharpoons \text{H}_2\text{O} + \text{M}$ (R15), whose sensitivity coefficient increases with pressure. $\text{CH}_2\text{O} + \text{H} \rightleftharpoons \text{HCO} + \text{H}_2$ (R16) (becoming less sensitive when p increases) and $\text{HO}_2 + \text{O} \rightleftharpoons \text{OH} + \text{O}_2$ (R17) (becoming more sensitive when p increases) have an inhibiting effect on the reactivity as well. These two reactions disappear from the list when the mixture is rich, while two new inhibiting reactions appear (given the abundance of CH_3 radicals at rich conditions): $\text{CH}_3 + \text{OH} \rightleftharpoons \text{CH}_2\text{OH} + \text{H}$ (R18) and $\text{CH}_3 + \text{H} (+\text{M}) \rightleftharpoons \text{CH}_4 (+\text{M})$ (R19), the latter consuming H atoms to form stable methane molecules. Finally, the reaction $\text{HCO} + \text{H} \rightleftharpoons \text{CO} + \text{H}_2$ (R20) appears in the inhibiting group (as it both competes with R3 and consumes H) at the rich condition (due to the abundance of H atoms), with a sensitivity that decreases when the pressure increases.

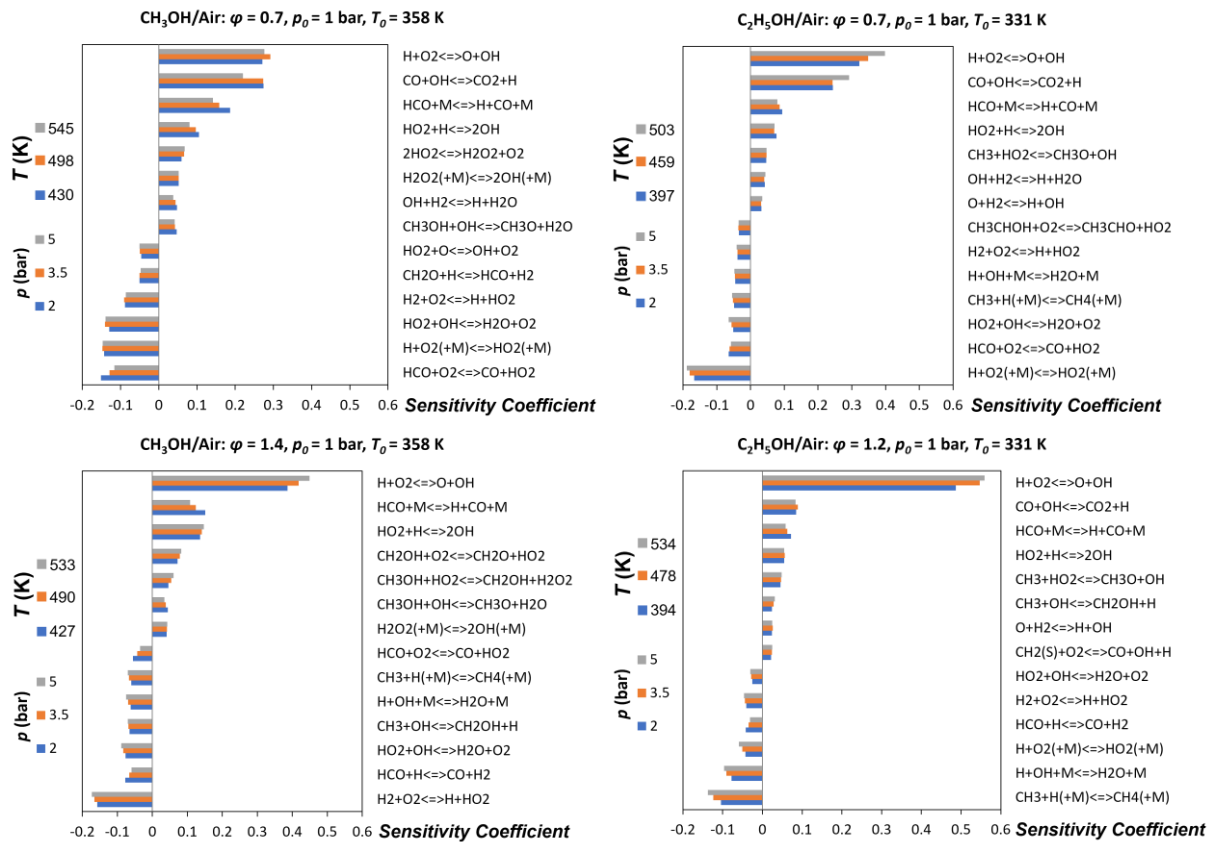


Figure 5.4: Sensitivity analyses on the flow rate performed using the present mechanism at two different equivalence ratios for: methanol/air (left) and ethanol/air (right) mixtures.

We can conclude that, despite the dominance of the reactions of syngas sub-mechanism on the list of the most sensitive reactions, the fuel-related reactions (R8–10 and R18) still have their impact on the flame speed, especially under rich conditions. These four reactions are: the H-abstraction of methanol by OH (forming CH₃O) and by HO₂ (forming CH₂OH), as well as the subsequent reactions of the latter with O₂ (producing formaldehyde and HO₂) and with H (producing CH₃ and OH). In addition, these sensitivity analyses provide insight into the discrepancies between previous mechanisms and the present one, which can explain their respective predictive performances and help future improvements. For instance, the underestimation of most present data by HPMech can be mainly attributed to a rate constant of R3 that is an order of magnitude lower than that used in the present mechanism. In contrast, the highest flame speeds predicted by POLIMI C₁-C₃ at $\varphi = 1.4$ arise from an $\approx 10\%$ increase in the pre-exponential factor of R1 relative to the present and other mechanisms: this small increase can have a significant effect on flame speed, especially under rich conditions, as the sensitivity of R1 strongly increases with equivalence ratio.

5.1.2.2 Ethanol mixtures

Figure 5.4 (right) exhibits the sensitivity analyses done for ethanol/air mixtures at $\varphi = 0.7$ and 1.2. The most sensitive reactions in this case are almost the same as for methanol, excluding those that were specific for the latter. However, additional reactions can be identified in the case of ethanol, such as: $\text{CH}_3 + \text{HO}_2 \rightleftharpoons \text{CH}_3\text{O} + \text{OH}$ (R21) which promotes reactivity by converting the less reactive HO₂ into OH, and $\text{CH}_3\text{CHOH} + \text{O}_2 \rightleftharpoons \text{CH}_3\text{CHO} + \text{HO}_2$ (R22) which inhibits reactivity by diverting the fuel radical away from direct production of reactive radicals. In fact, while the favored radical of methanol, CH₂OH, leads mainly to formaldehyde and subsequently to HCO chemistry, the dominant radical of ethanol, CH₃CHOH, produces primarily acetaldehyde, which in turn forms acyl radicals that undergo α -scission to yield CH₃ radicals. This difference explains the higher sensitivity of HCO reactions for methanol and, in contrast, the higher sensitivity of CH₃ reactions for ethanol. Finally, it is worth noting that R18 shows opposite sensitivity for ethanol when compared to methanol. It is negatively sensitive for methanol, as it proceeds in the reverse direction due to the abundance of its primary radicals CH₂OH, thus competing with R1 for H atoms. In contrast, it is positively sensitive for ethanol, as it occurs in the forward direction (due to CH₃ abundance), thereby producing H atoms for R1.

Therefore, apart from syngas chemistry, the evolution of ethanol flame speed depends mainly on methane sub-mechanism; only one reaction related to the fuel subset was seen in the list of most sensitive reactions: R22, the reaction of ethanol secondary radical (CH₃CHOH) with O₂ forming acetaldehyde and HO₂, but it appears in the list only at the lean condition (where O₂ is more concentrated) and as the lowest negatively sensitive reaction.

5.1.3 Further Validation

In order to validate its performance, the present mechanism was tested on different literature data of methanol and ethanol in this sub-section and showed good predictions for them. More validation plots are also available in **Appendix C**.

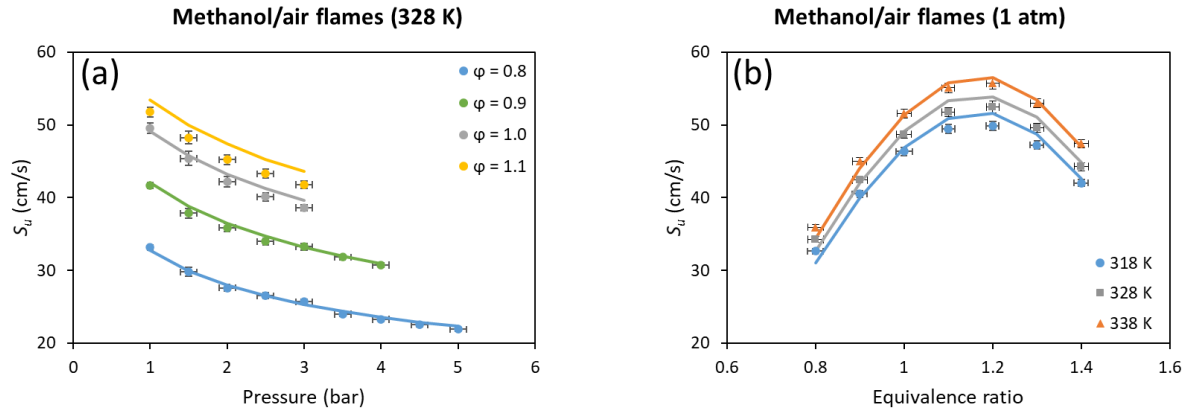


Figure 5.5: Laminar burning velocities of methanol/air flames as functions of pressure at 328 K (a) and as functions of equivalence ratio at 1 atm (b). Symbols: experiments (Raida et al. [164]), lines: simulations (this work).

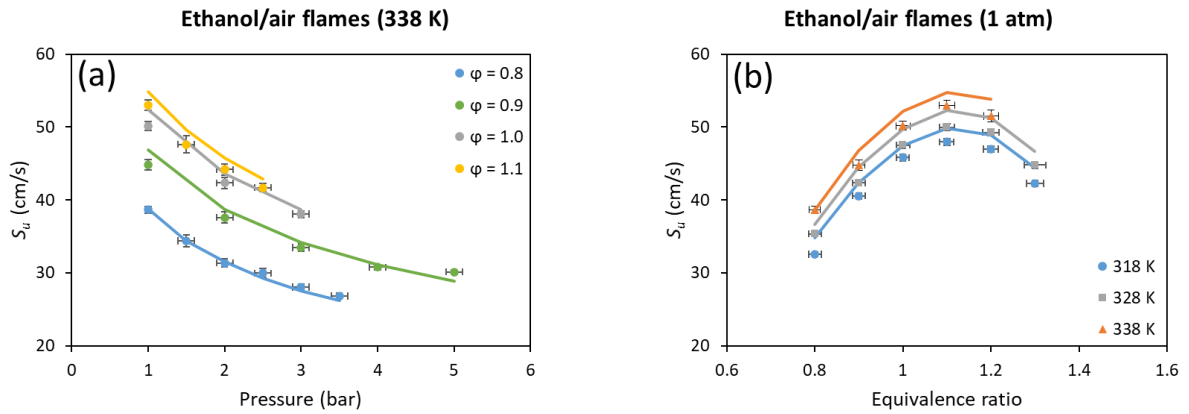


Figure 5.6: Laminar burning velocities of ethanol/air flames as functions of pressure at 338 K (a) and as functions of equivalence ratio at 1 atm (b). Symbols: experiments (Raida et al. [164]), lines: simulations (this work).

Figure 5.5a and Figure 5.6a show the good performance of our mechanism in predicting the evolution of laminar flame speed with the pressure for both fuels reported by Raida et al. [164], although it slightly overestimated them for the rich mixture $\phi = 1.1$. Furthermore, our mechanism presents well the evolution of flame speed with the equivalence ratio for methanol and ethanol (see Figure 5.5b and Figure 5.6b), even though it reveals a slight overprediction for the data of the latter fuel.

Figure 5.7 and Figure 5.8 show the experimental and simulated mole fraction profiles of species obtained at 10 atm under three different equivalence ratios from JSR oxidation of methanol [158] and ethanol [165], respectively. We could see that, although our mechanism underpredicts the mole fractions of both fuels under about 900 K, it becomes then in better agreement with them at higher temperatures.

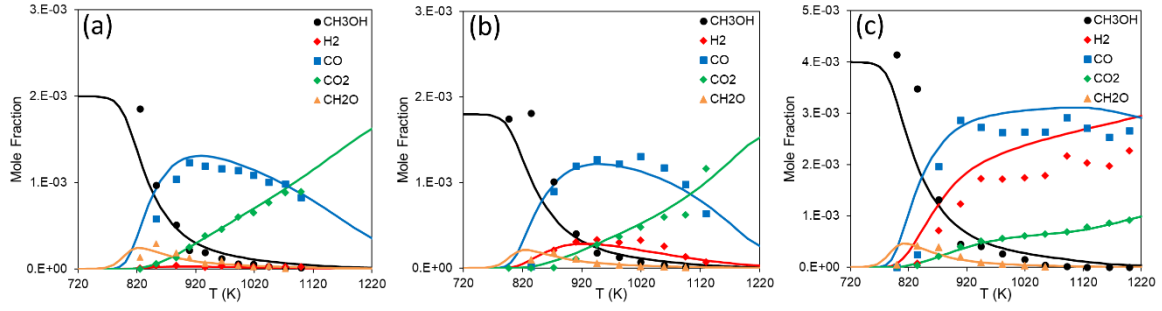


Figure 5.7: Experimental (symbols: Burke et al. [158]) and computed (lines: this work) mole fraction profiles of species obtained during the oxidation of methanol in a JSR at $p = 10$ atm, $\tau = 0.5$ s, and $\phi = 0.2$ (a) / 1 (b) / 2 (c).

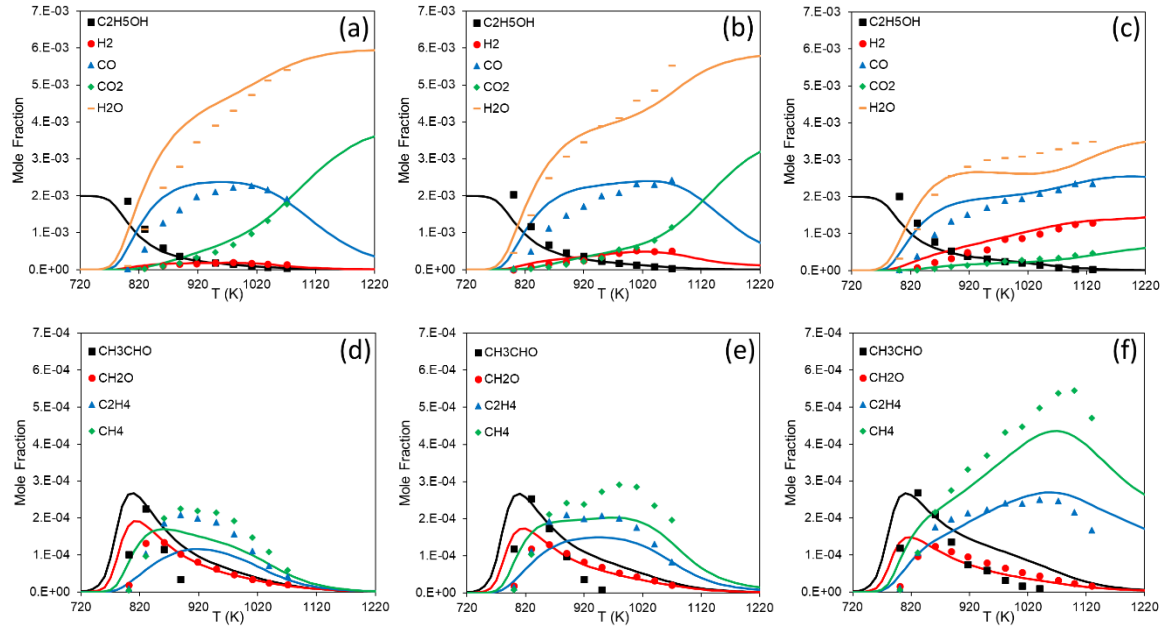


Figure 5.8: Experimental (symbols: Leplat et al. [165]) and computed (lines: this work) mole fraction profiles of species obtained during the oxidation of ethanol in a JSR at $p = 10$ atm, $\tau = 0.7$ s, and $\phi = 0.6$ (a,d) / 1 (b,e) / 2 (c,f).

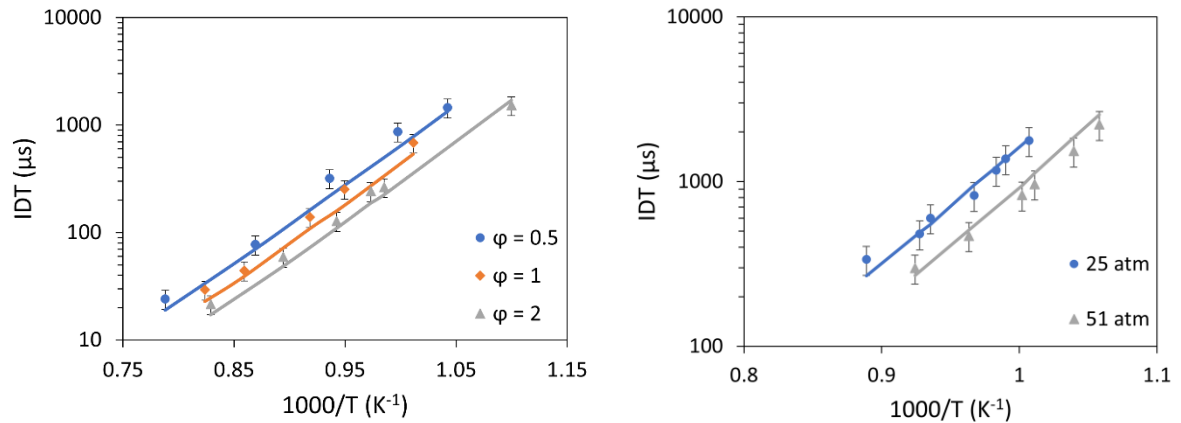


Figure 5.9: Experimental (symbols) ignition delay times measured in shock tubes for different methanol/air mixtures by Burke et al. [158] at 50 atm (left), and for stoichiometric ethanol/air mixtures by Mathieu et al. [166] at about 25 and 50 atm (right). Simulations (lines) were performed using the present core mechanism.

The mechanism also successfully reproduces the general trends of the mole fraction profiles with temperature and reasonably estimates their values for the different species formed during the oxidation of methanol and ethanol.

Finally, as shown in Figure 5.9, the present mechanism successfully captures the observed decrease in ignition delay time with increasing pressure and/or equivalence ratio, and accurately reproduces the measured values for different methanol/air [\[158\]](#) and ethanol/air [\[166\]](#) mixtures.

5.1.4 Conclusion

The core mechanism updated in this work was validated against novel laminar flame speeds of methanol/O₂ and ethanol/O₂ diluted mixtures measured at our laboratory ICARE over a large domain of conditions. It showed more accurate simulations than other performant mechanisms available in the literature.

Sensitivity analyses were performed using the present core mechanism for both fuels at lean and rich conditions. These analyses highlighted the importance of syngas and methane chemistry in controlling the laminar flame speed of methanol and ethanol. Some reactions specific to the former fuel show a notable effect on its flame speed, while those of the latter seem to have only a very small effect.

Finally, further validations were achieved with our mechanism, which shows good predictions for experimental data previously reported, including ignition delay times and JSR speciation data. Therefore, this mechanism proves its ability to serve as a robust core for future kinetic models, and particularly for the model developed as part of this thesis.

5.2 Tetrahydropyran

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5.2.1 Experimental Behavior

The oxidation of THP was studied in a JSR of 42 cm³ at a pressure of 10 bar and a constant residence time of 0.7 s. Experiments were conducted using an initial fuel mole fraction of 800 ppm across four different equivalence ratios ($\phi = 0.4, 0.8, 1.6$, and 3.2). The fuel conversion for these conditions is reported in Figure 5.10. Also, the oxidation of 1000 ppm THP was tested in a JSR of 34 cm³ at $\phi = 0.5$ under the same pressure and residence time conditions.

Before discussing the performance of our kinetic mechanism in reproducing the present data, it is important to observe the oxidation behavior of the fuel. As shown in Figure 5.11, the three classical zones of reactivity can be clearly identified for THP at $\phi = 0.4$: low-temperature reactivity (LTR), negative-temperature coefficient (NTC), and high-temperature reactivity (HTR). The LTR regime begins around 540 K and extends up to 660 K, during which slightly less than half of the initial THP is consumed. Then, a pronounced NTC region is observed over a temperature window of about 90 K, characterized by a marked decrease in reactivity and bringing the fuel mole fraction back to about 90% of its starting value. Finally, the HTR regime emerges, leading to the complete consumption of THP near 1100 K.

Figure 5.10 shows that, as the equivalence ratio increases, the LTR of THP becomes progressively less pronounced and both the LTR and NTC shift slightly in temperature: the onset of LTR is delayed, while that of NTC occurs earlier. A noticeably weaker HTR is observed at $\phi = 3.2$ compared to lower equivalence ratios. This behavior will be interpreted in the next sub-section.

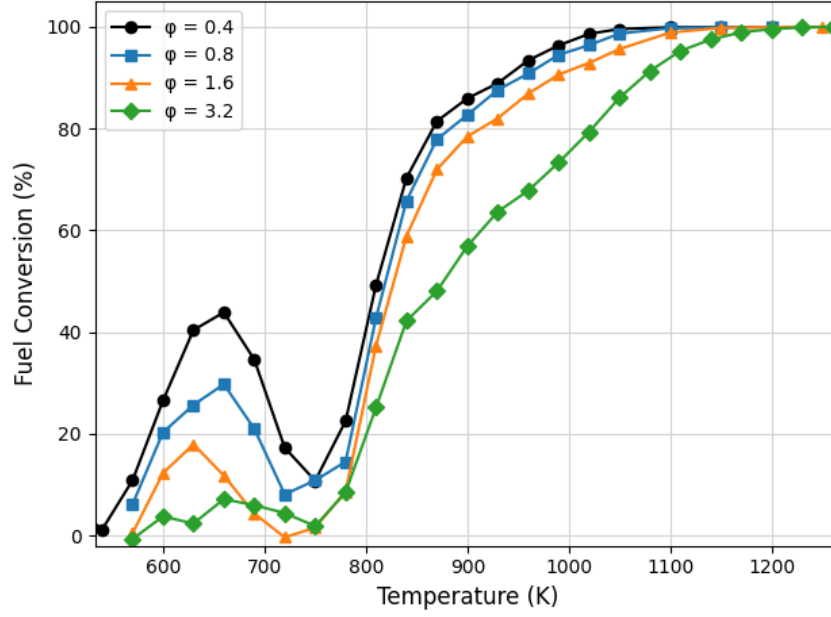


Figure 5.10: Fuel conversion of THP during its oxidation in a JSR as a function of temperature for all equivalence ratios studied at $p = 10$ bar, $\tau = 0.7$ s, $X_0(\text{fuel}) = 800$ ppm (lines are added to represent the trend).

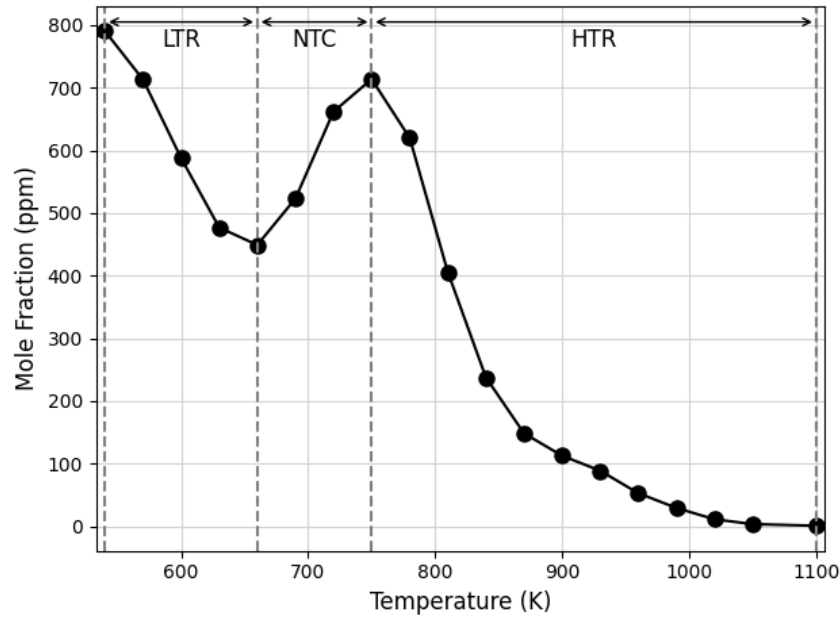


Figure 5.11: Mole fraction profile of THP during its oxidation in a JSR as a function of temperature at $\phi = 0.4$, $p = 10$ bar, $\tau = 0.7$ s, $X_0(\text{fuel}) = 800$ ppm (lines are added to represent the trend).

5.2.2 Mechanistic Interpretation

The comparison between the measured and predicted mole fractions of THP for all conditions is presented in Figure 5.12. This comparison is essential to assess whether the present mechanism accurately captures the distinct reactivity regimes observed experimentally, along with their corresponding temperature ranges. Starting with the leanest mixture, and accounting for the experimental uncertainty, it can be seen that our mechanism reproduces reasonably well

the evolution of the fuel mole fraction with temperature. However, it anticipates the onset of the NTC region (at 630 K, instead of 660 K). As a result, it interrupts the LTR phase slightly before its expected completion, leading to a modest overprediction (still within the uncertainty range) of the fuel mole fraction in the NTC regime. Additionally, the mechanism overestimates the HTR within a temperature window of about 120 K (880–1000 K). Although they persist at $\phi = 0.8$, the observed discrepancies are suppressed under rich conditions, falling entirely within the uncertainty range.

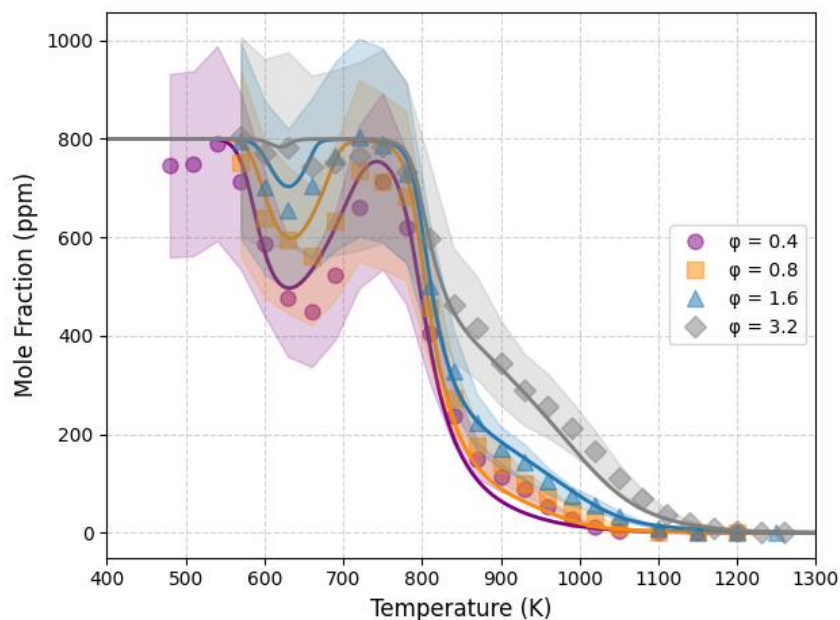
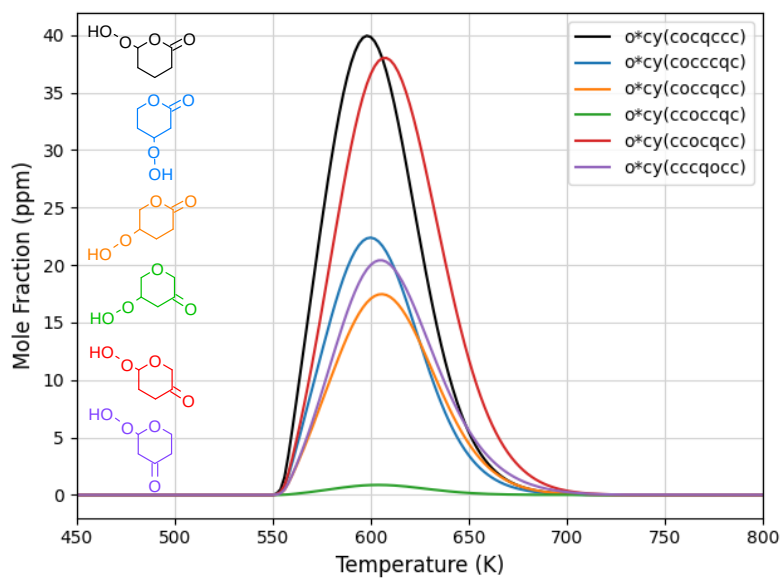
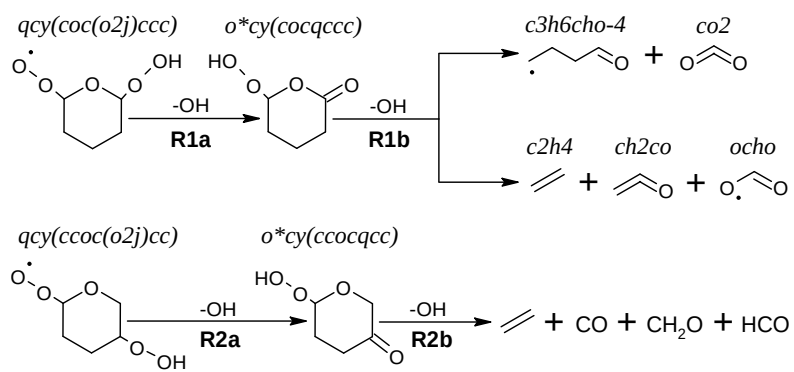


Figure 5.12 : Experimental (symbols) and simulated (lines) mole fraction profiles of THP during its oxidation in a JSR as a function of temperature for all equivalence ratios at $p = 10$ bar, $\tau = 0.7$ s, $X_0(\text{fuel}) = 800$ ppm (shaded areas are included to represent the measurement uncertainty of $\pm 25\%$).

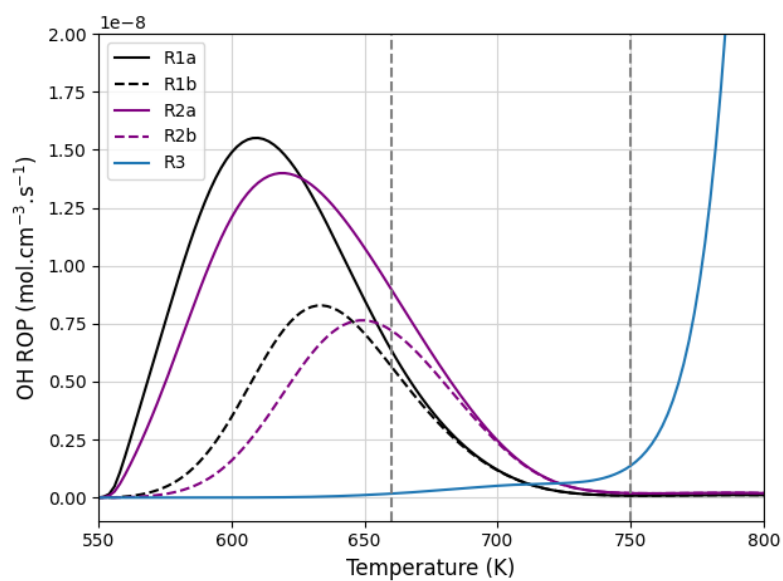
In order to gain deeper insight into the main reactions involved during THP oxidation, it is useful to analyze the reaction pathways leading to the formation of the highly reactive OH radicals, which are the primary drivers of global reactivity. The reactions responsible for the highest production of OH radicals vary across the different temperature regimes. At low temperatures, reactivity is primarily driven by the chain-branching pathways that generate OH radicals through the formation and decomposition of ketohydroperoxides (KHPs) derived from the fuel. The mole fraction profiles of these KHPs (as predicted by the present mechanism) are shown in Figure 5.13a, followed by the formation and decomposition reactions of the two most abundantly formed KHPs in Figure 5.13b. Figure 5.13c illustrates the rate of production (ROP) of OH radicals through the main reactions responsible for their formation in the low-to-intermediate temperature range. Initially, the formation of KHPs (R1a and R2a) drives the LTR, followed by their subsequent decomposition (R1b and R2b): the OH ROP of these reactions rises and then peaks successively within the LTR regime. It can be observed that OH production in this regime is primarily attributed to the formation and decomposition of the most abundant KHP, *o**cy(cocqccc), which is derived from the more abundant fuel α -radical. As the temperature increases, the OH ROP of these low-temperature reactions begins to decrease, leading to a drop in overall reactivity and the emergence of the NTC region. At higher temperatures, H_2O_2 decomposition (R3) becomes the main source of OH radicals, resulting in a renewed increase in reactivity that continues until complete fuel conversion.



(a)



(b)



(c)

Figure 5.13 : (a) Mole fraction profiles of KHPs derived from THP during its oxidation in a JSR, as predicted by the present mechanism at $\phi = 0.4$, $p = 10$ bar, $\tau = 0.7$ s, $X_o(\text{fuel}) = 800$ ppm; (b) Formation (R1a and R2a) and decomposition (R1b and R2b) reactions of the two mostly formed KHPs during this oxidation; (c) OH ROP analysis for these reactions, together with H_2O_2 decomposition into two OH radicals (R3) – the dashed vertical lines indicate the transition temperatures between the distinct reactivity zones as identified experimentally.

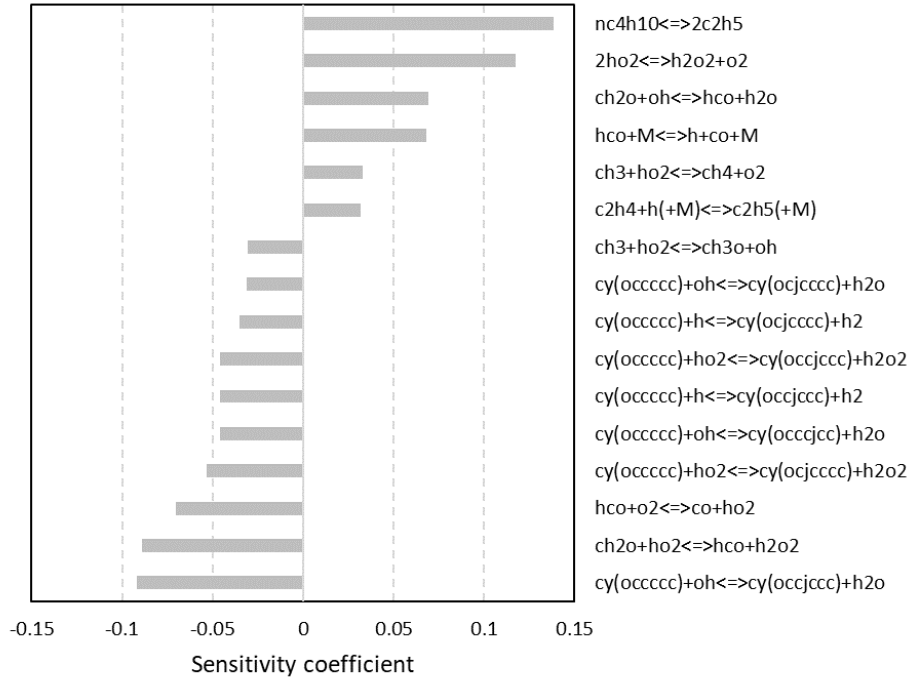


Figure 5.14: Sensitivity analysis performed on THP with the present mechanism for the richest mixture studied ($\phi = 3.2$, $p = 10$ bar, $\tau = 0.7$ s) at 900 K.

As previously mentioned, a noticeably weaker HTR is observed for THP under the richest condition compared to lower equivalence ratios. This behavior is well captured by the present mechanism, as shown in Figure 5.12. A sensitivity analysis, illustrated in Figure 5.14 and carried out on the fuel with the present mechanism at $\phi = 3.2$ and $T = 900$ K, highlights the critical role of the recombination of ethyl radicals into n-butane under such conditions. This reaction is identified as the most positively sensitive reaction with respect to the fuel, thereby tending to inhibit its overall reactivity. However, this analysis alone does not explain the high formation and accumulation of ethyl radicals that enable their recombination. A reaction pathway analysis performed later under same conditions provides further clarification.

5.2.3 Speciation Analysis

Figure 5.15 and Figures 5.16a–d present the mole fraction profiles of the various reactant, product, and intermediate species observed during the JSR oxidation of THP at all conditions studied. A representative error bar (or band) was added to the experimental profiles to account for the estimated measurement uncertainty discussed previously at the end of **Chapter 3**.

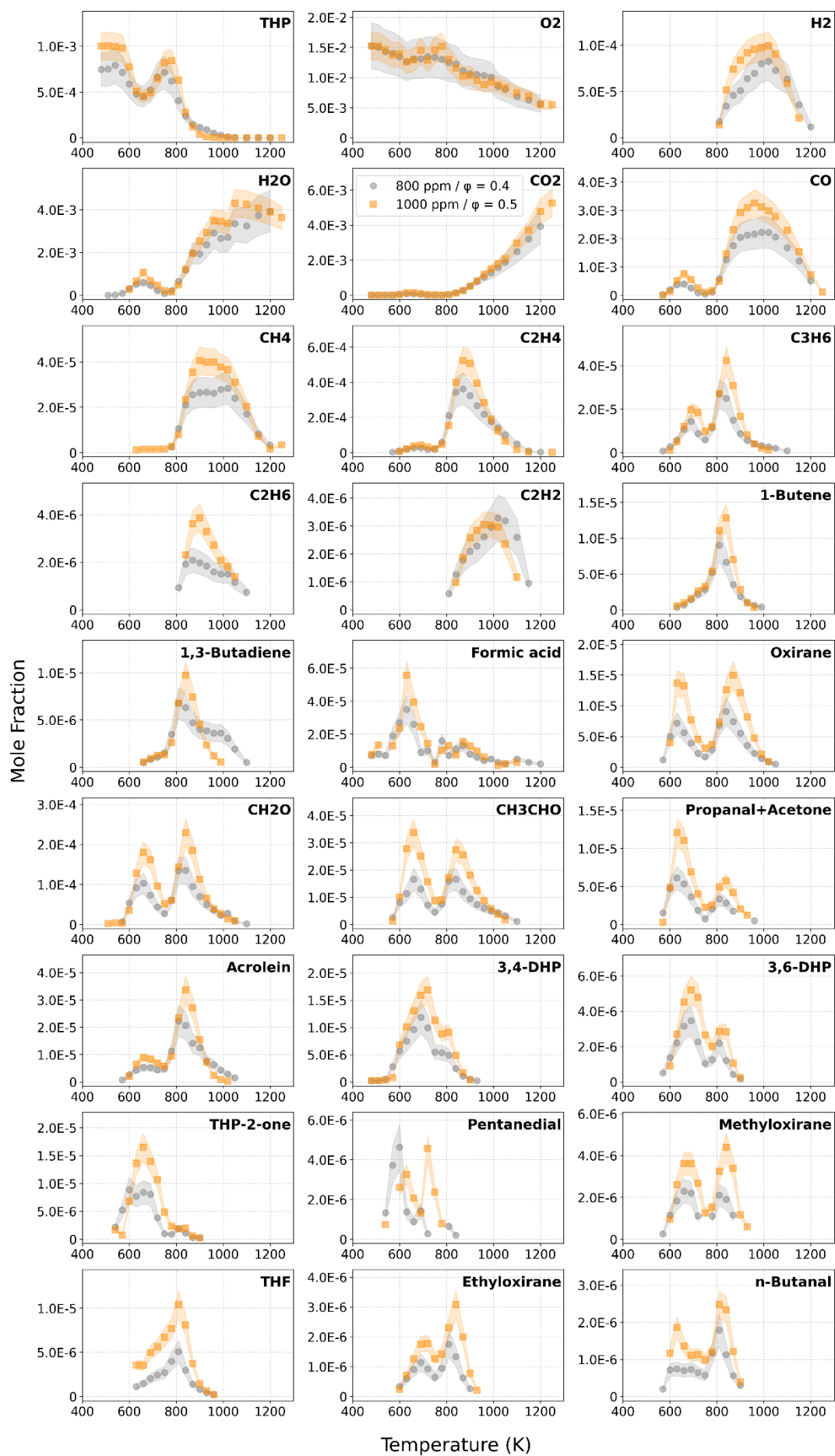


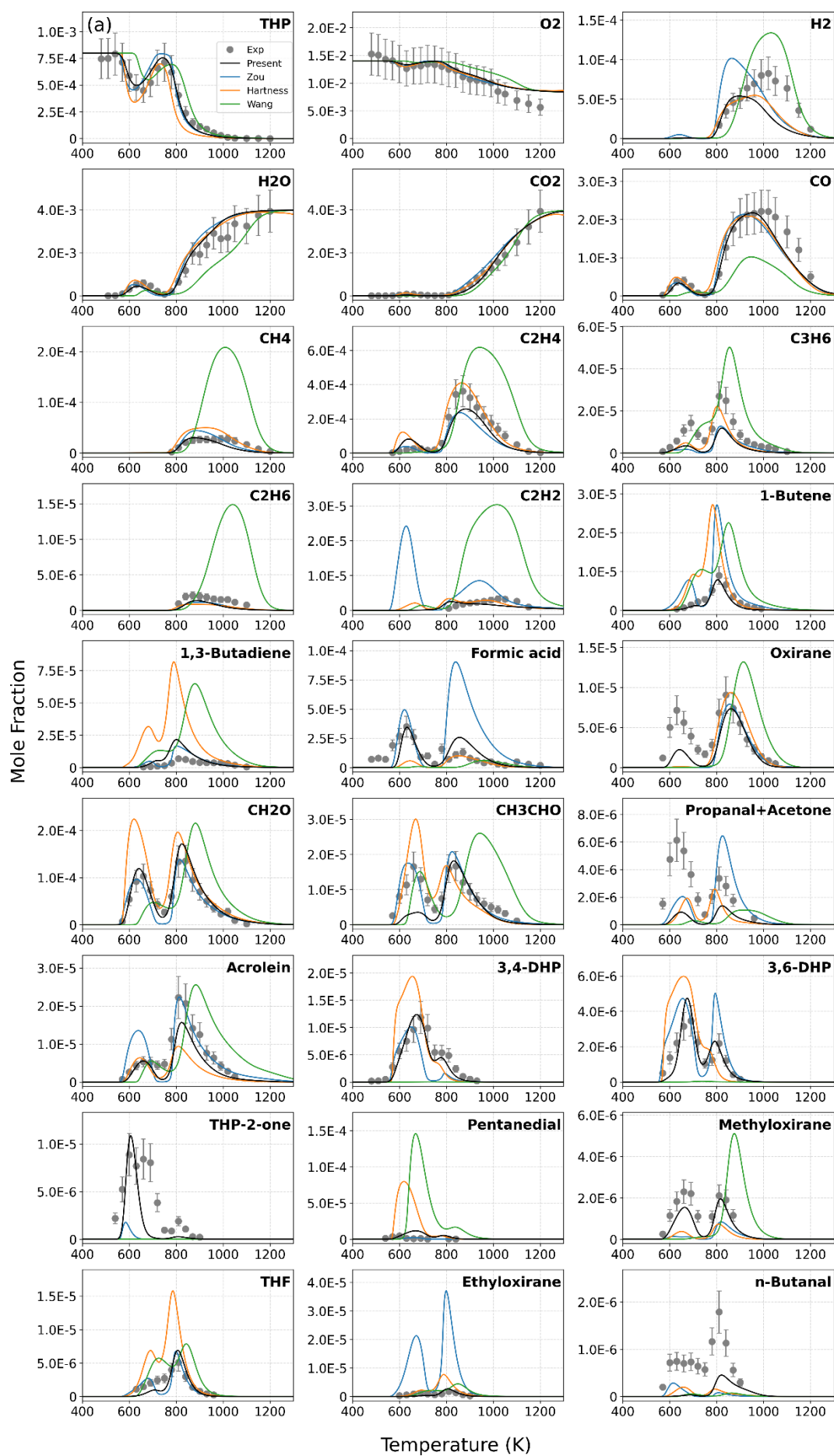
Figure 5.15: Mole fraction profiles of reactant, product, and intermediate species during THP oxidation in a JSR at $p = 10$ bar, $\tau = 0.7$ s, and: $X_0(\text{fuel}) = 800$ ppm / $\phi = 0.4$ (gray circles with shaded uncertainty bands of $\pm 25\%$); $X_0(\text{fuel}) = 1000$ ppm / $\phi = 0.5$ (orange squares with shaded uncertainty bands of $\pm 15\%$).

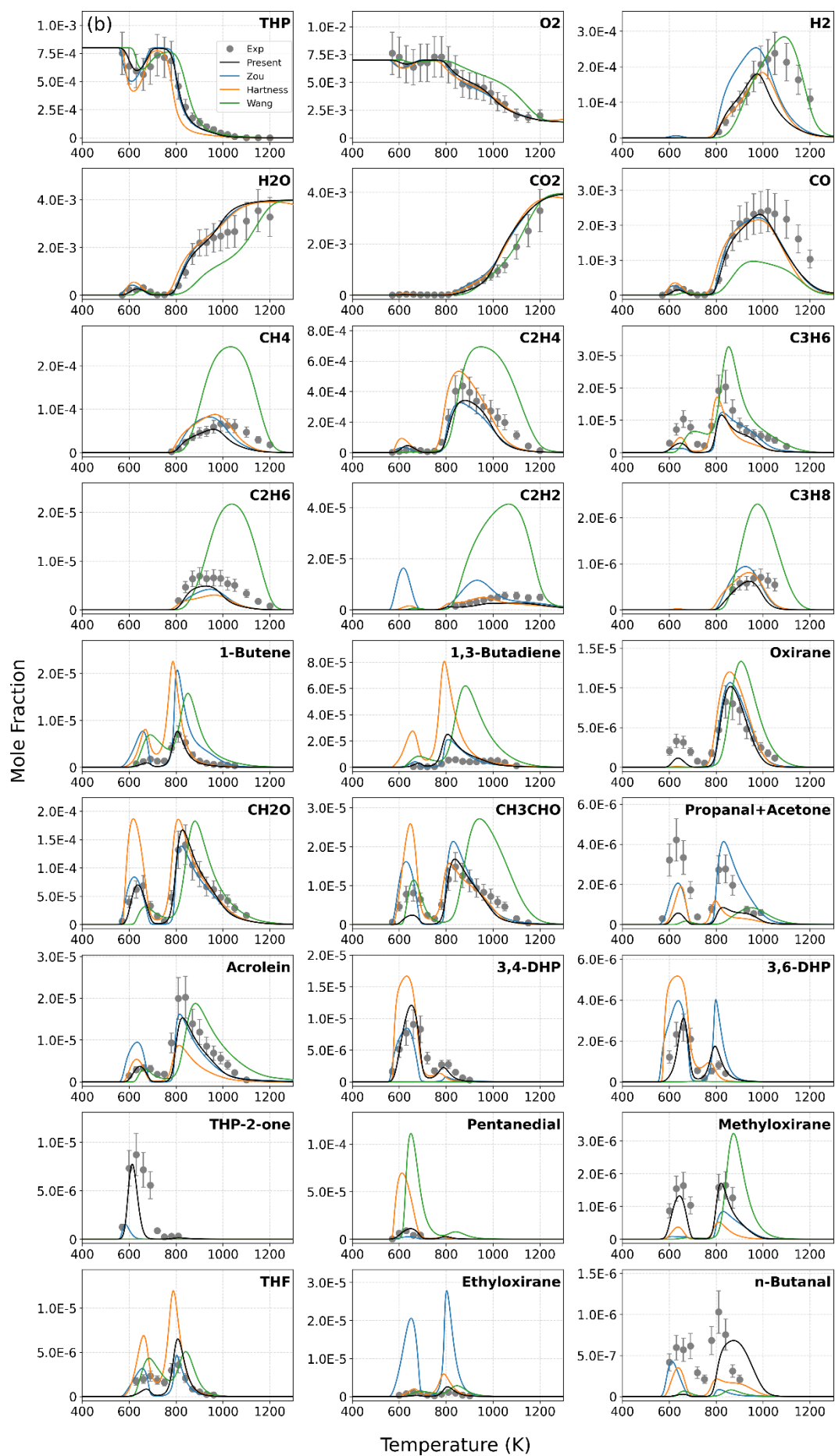
Apart from CO, CO₂, and H₂O, the most important oxygenated species formed during the oxidation of THP was the smallest aldehyde, formaldehyde, which is a typical marker of reactivity for many fuels. Other aldehydes and oxygenated compounds were also quantified: acetaldehyde, propanal (and/or acetone), acrolein, oxirane, formic acid, tetrahydropyran-2-one (THP-2-one), and the two possible mono-unsaturated derivatives of THP (3,4- and 3,6-dihydro-2H-pyran: 3,4-DHP and 3,6-DHP). All of these species were formed during both low- and high-temperature oxidation. Some traces of methyloxirane, ethyloxirane, THF, butanal, and pentanediol were as well detected. Ethylene was the most abundant in the set of hydrocarbons identified across all tested conditions, which also includes: methane, ethane, acetylene, propene, 1-butene, and 1,3-butadiene. Additionally, propane formation was observed starting from $\phi = 0.8$. Benzene, allene, and propyne were as well detected at high temperatures under rich conditions, with their mole fraction profiles at $\phi = 3.2$ shown in Figure 5.16d. Additional data on species detected at trace levels, as well as on species with uncertain identification and/or quantification, are provided in **Appendix D** (Fig. D4 and Fig. D5).

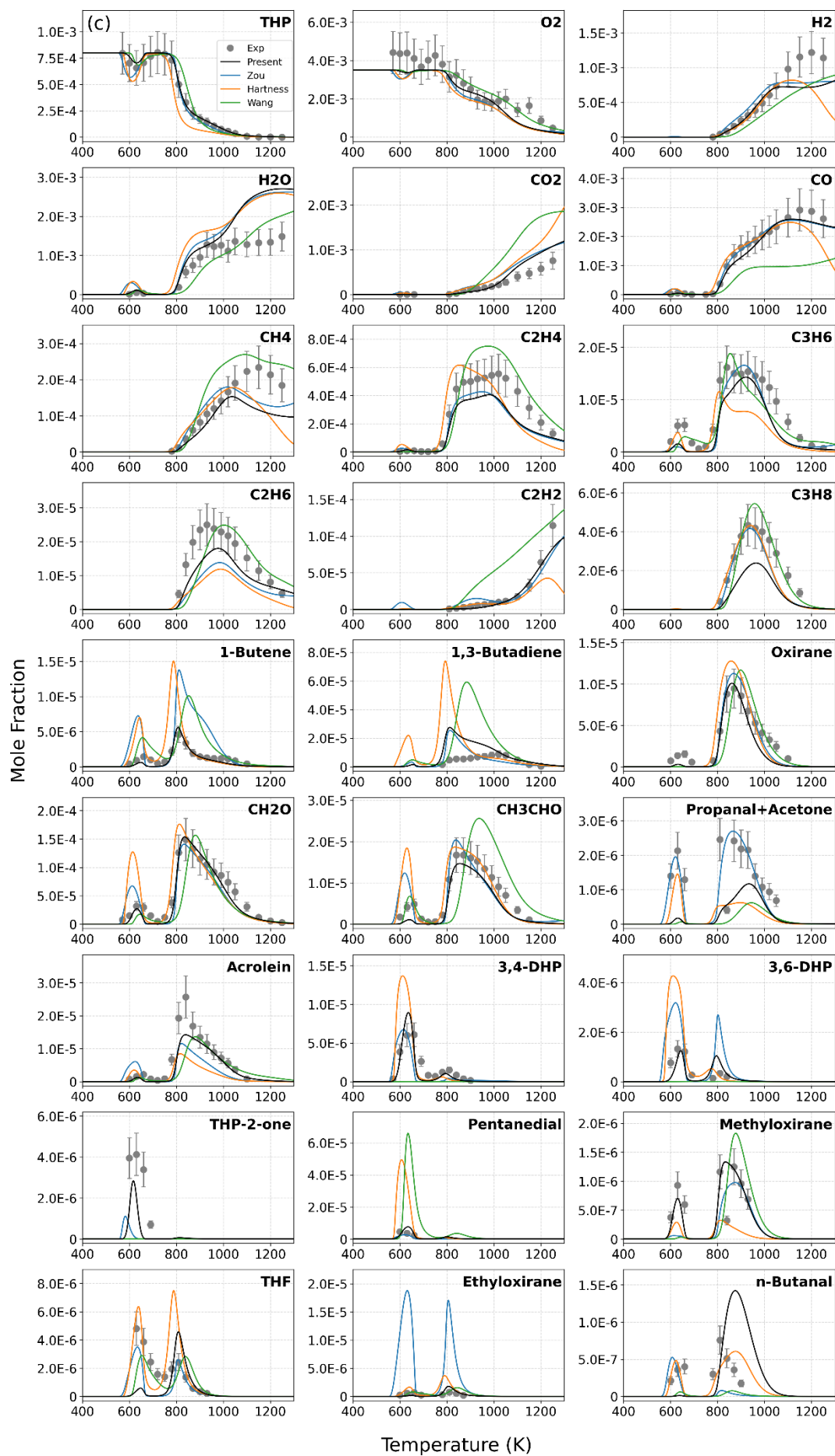
Figure 5.15 compares two conditions with identical pressure ($p = 10$ bar), residence time ($\tau = 0.7$ s), and initial O₂ mole fraction (≈ 14000 ppm) to illustrate the effect of the initial fuel mole fraction on overall reactivity. The initial fuel mole fraction was increased from 800 to 1000 ppm, corresponding to an equivalence ratio increase from 0.4 to 0.5. This change clearly results in stronger fuel reactivity, reflected by increased species production. In both cases, the fuel mole fraction reaches ≈ 500 ppm at the end of LTR, corresponding to a fuel conversion of 37.5% for $X_0(\text{fuel}) = 800$ ppm and 50% for $X_0(\text{fuel}) = 1000$ ppm.

Figures 5.16a–d show the simulated mole fraction profiles of the various species measured during THP oxidation at the distinct equivalence ratios tested. As noted for the fuel, the mechanism performs well in capturing the mole fractions of the different species. Nevertheless, some discrepancies remain, primarily in the absolute values, whereas the general trends are well captured. Because propanal and acetone co-elute during GC analysis, their individual contributions cannot be distinguished if both are present. In order to ensure consistency with the experimental data corresponding to their shared peak, the total mole fraction of both species combined was considered in the simulations.

Finally, it is worth noting that while the present mechanism successfully reproduces the mole fraction profiles of major LTR species like formaldehyde, it highly underpredicts the formation of relatively minor products associated with this reactivity, including acetaldehyde, oxirane, propene, and propanal/acetone. Therefore, further investigation is still required to propose a mechanistic explanation for their formation under low-temperature conditions.







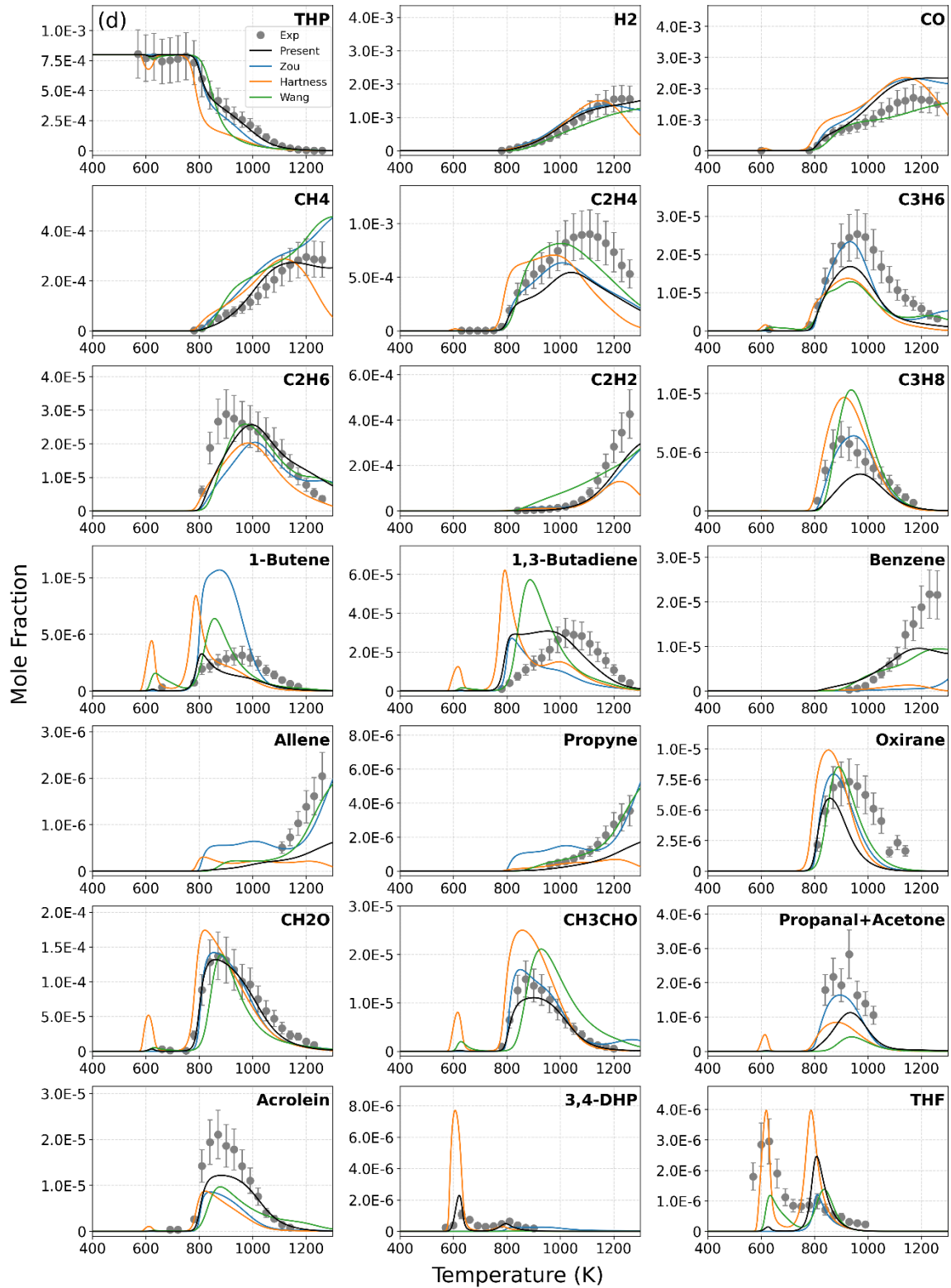


Figure 5.16: Experimental (symbols with error bars of $\pm 25\%$) and simulated (lines) mole fraction profiles of reactant, product, and intermediate species during THP oxidation in a JSR at $p = 10$ bar, $\tau = 0.7$ s, $X_0(\text{fuel}) = 800$ ppm, and: (a) $\phi = 0.4$; (b) $\phi = 0.8$; (c) $\phi = 1.6$; (d) $\phi = 3.2$. Black: present work; Blue: Zou et al. [111]; Orange: Hartness et al. [112]; Green: Wang et al. [114].

5.2.4 Mechanism Evaluation

Following the general assessment of the present mechanism against the experimental data obtained in this work, it is also valuable to evaluate its performance against other THP oxidation mechanisms. Accordingly, simulations from three recently published mechanisms [111,112] [114] are included for comparison in Figures 5.16a–d. The present mechanism provides globally the most accurate representation of the experimental fuel profiles across the various tested conditions, although the other mechanisms may outperform it within certain temperature ranges.

At the leanest condition, and relative to our mechanism, the mechanism of Zou et al. [111] predicts a stronger LTR that terminates at a slightly lower temperature, and a more pronounced NTC regime that results in full regeneration of the initial 800 ppm of THP. On the other hand, the mechanism of Hartness et al. [112] overestimates both the LTR and HTR, though it performs well in capturing the NTC behavior. While these two mechanisms predict correctly (like our mechanism) the onset of LTR (540–570 K), the mechanism of Wang et al. [114] estimates it at higher temperatures (600–630 K) and thereby shifts similarly the NTC region. This mechanism exhibits the weakest global reactivity among all mechanisms across almost the full temperature range, but it still manages to capture the fuel mole fraction within certain intermediate (690–780 K) and high (above 900 K) temperature intervals.

As the equivalence ratio increases, each mechanism continues to exhibit similar trends to those previously observed. However, Wang mechanism begins to show improved predictions for both the LTR and NTC zones, in line with their experimental weakening and the slight shift in their onset temperatures. At the richest condition ($\phi = 3.2$), only our mechanism succeeds in accurately representing the HTR. Hartness mechanism continues to highly overpredict this reactivity from its onset, while the mechanisms of Zou and Wang tend to overestimate it above 870 K.

Overall, all mechanisms (except that of Wang) reproduce similarly the final combustion products, while differences emerge primarily for intermediate and minor species across temperature and equivalence ratio ranges. The present mechanism generally provides the most accurate predictions for formaldehyde, formic acid, acrolein, fuel-specific species, minor cyclic ethers (oxirane, methyloxirane, ethyloxirane, and THF), and certain hydrocarbons (acetylene and 1-butene). Despite exhibiting the weakest overall reactivity, Wang mechanism significantly overpredicts the high-temperature formation of several species, particularly light hydrocarbons. In line with its overestimation of the LTR, Hartness mechanism predicts excessive production of most species during this regime. Although it provides predictions closest to the present mechanism, Zou mechanism shows – unexpectedly and unlike the others – very high formation of ethyloxirane across the entire temperature range and of acetylene at low temperatures. Finally, it is worth noting that the formation of propene and propanal/acetone is underpredicted at low temperatures, whereas that of 1,3-butadiene is overestimated at high temperatures by all mechanisms (with Hartness mechanism showing the largest overprediction).

5.2.5 Reaction Pathways

Reaction pathway analyses for THP oxidation are performed with the present mechanism at two distinct temperatures, 600 K (Figure 5.17) and 900 K (Figure 5.18), for the leanest and

richest conditions respectively, in order to see the most important reactions consuming the fuel in two very different temperature regimes (LTR and HTR). In both figures, the fuel is emphasized and the pathway carrying the largest flux is indicated by thicker arrows.

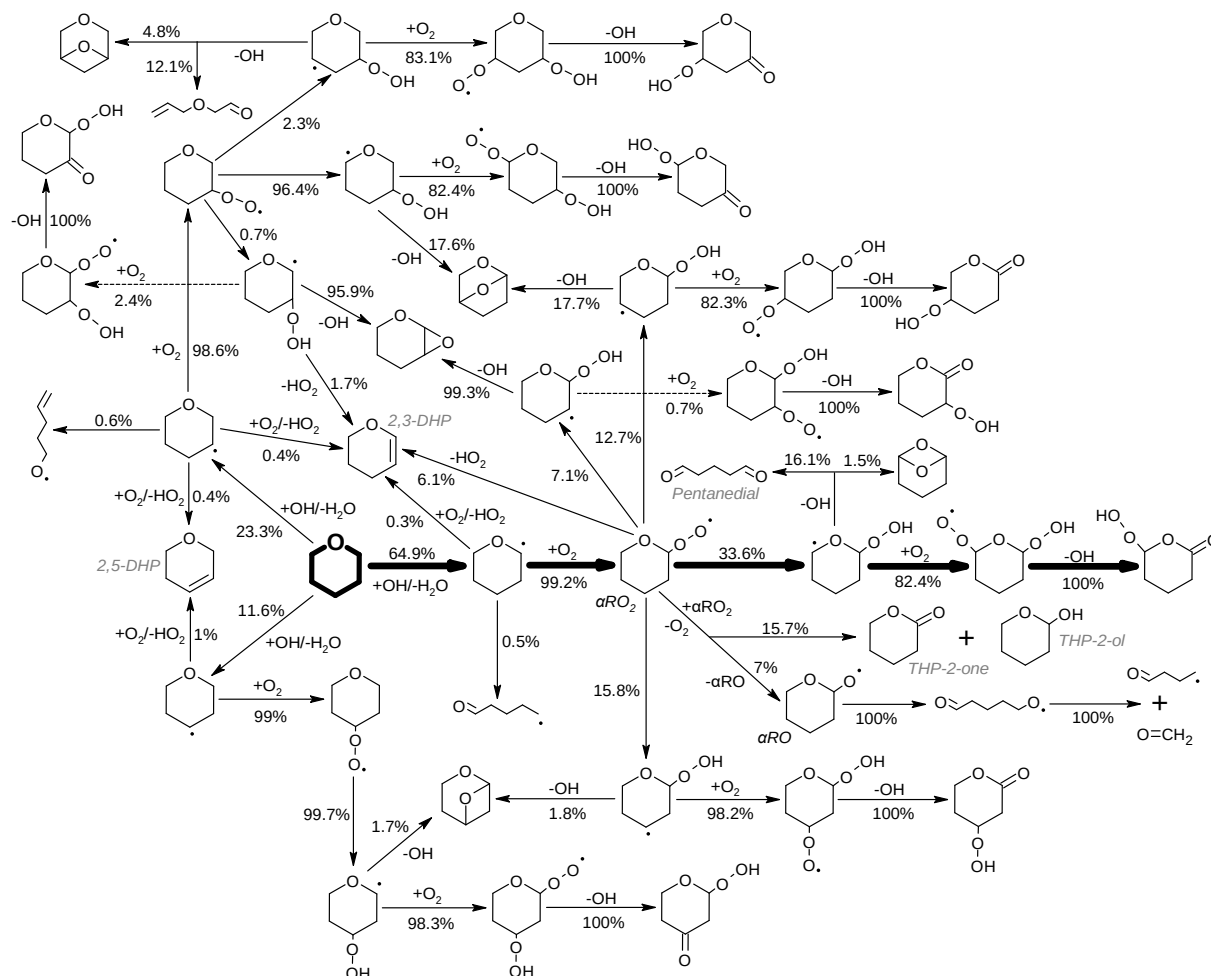


Figure 5.17: Reaction pathways during THP oxidation in a JSR at 600 K for the leanest mixture studied ($\phi = 0.4$, $p = 10$ bar, $\tau = 0.7$ s), as predicted by the present mechanism.

Based on the low-temperature reaction pathway analysis shown in Figure 5.17, all three possible radicals derived from the fuel are formed, with the α -radical being the most abundant. This is attributed to the presence of the ether oxygen, which weakens the adjacent C–H bonds, as previously discussed in **Chapter 4**. As it can be clearly seen, the fuel is consumed through H-abstraction reactions by OH radicals to form its primary radicals. Then, the most common reaction pathway followed by these radicals is the typical LTR pathway: a first addition to O_2 , followed by an internal isomerization, a second O_2 addition, and finally the formation of an OH radical and a keto-hydroperoxide. The latter rapidly decomposes into chain-branching fragments and another OH radical, thereby promoting overall reactivity. However, minor fluxes follow alternative low-temperature routes that compete with the dominant chain-branching channel. These pathways lead to the formation of unsaturated and bicyclic ethers derived from THP, as well as β -scission products such as pentanediol. Their growing contribution with temperature gives rise to the NTC regime. Additionally, a portion of the αRO_2 radical flux undergoes disproportionation reactions, yielding either THP-2-one and tetrahydropyran-2-ol (THP-2-ol; not identified experimentally, but may correspond to one of the small unidentified peaks) or two αRO radicals that subsequently decompose into smaller radicals and molecules.

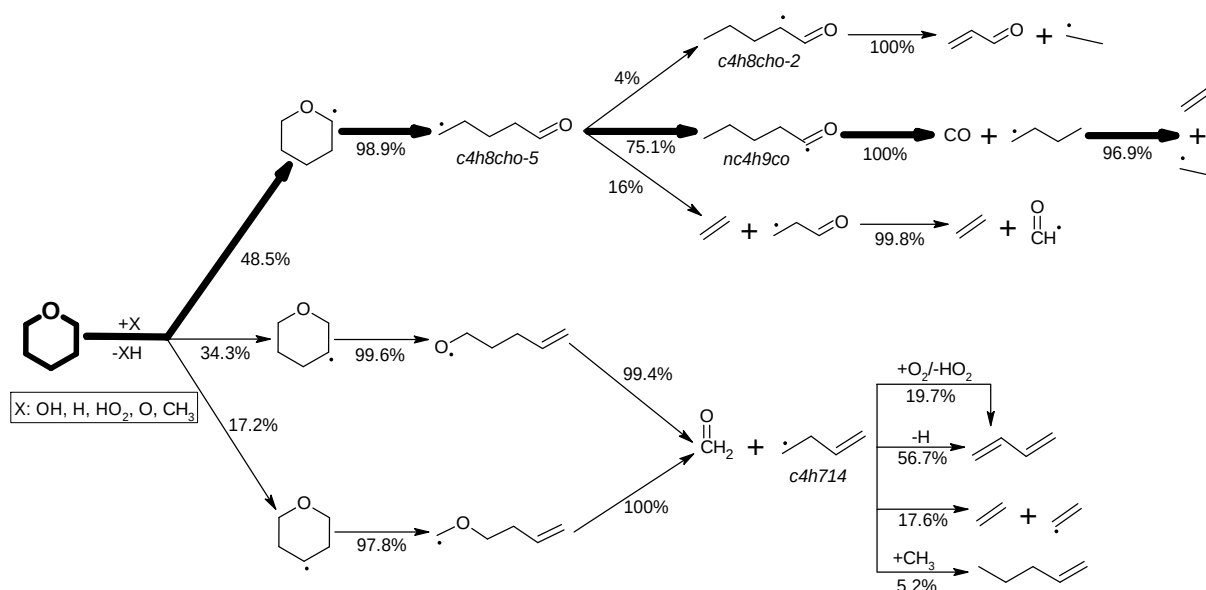


Figure 5.18: Main reaction pathways during THP oxidation in a JSR at 900 K for the richest mixture studied ($\phi = 3.2$, $p = 10$ bar, $\tau = 0.7$ s), as predicted by the present mechanism.

Considering the high-temperature reaction pathway analysis shown in Figure 5.18, the α -radical is still the most abundant fuel radical but the underlying reactions are different. Again, the fuel is consumed through H-abstraction reactions mostly by OH radicals but also by H, HO₂, O, and CH₃. Under such conditions, the fuel radicals dominantly undergo a β -scission reaction accompanied by ring opening. In their turn, the newly generated radicals undergo another β -scission but may also proceed through isomerization. However, such an isomerization reaction should be favored enough to compete with the β -scission, which is the case of the primary radical (c4h8cho-5) of n-pentanal formed from the ring-opening of the fuel α -radical. In fact, this radical can undergo a favorable isomerization via internal H-transfer, involving a six-membered transition state and the transfer of an aldehydic H, leading to the formation of the acyl radical (nc4h9co) of n-pentanal. Another isomerization is also possible through internal H-transfer with a five-membered transition state, resulting in the formation of the secondary radical (c4h8cho-2) of n-pentanal. However, this pathway is significantly less favored, with only 4% of c4h8cho-5 radicals following it. The nc4h9co radical fully decomposes through α -scission (decarbonylation) to form a 1-butyl radical, which mostly decomposes through β -scission into ethylene and an ethyl radical. Therefore, the most important reaction pathway of the most favored fuel α -radicals produces ethyl radicals, confirming the crucial inhibiting effect of their recombination (a chain-terminating step) on the global reactivity under present conditions.

Furthermore, the high-temperature pathways that lead to the formation of 1,3-butadiene can be identified. This species is the dominant product obtained from the pathways followed by both β - and γ -radicals of THP. Indeed, after two consecutive β -scission reactions, these radicals give formaldehyde and the primary radical (c4h714) of 1-butene. 1,3-Butadiene is then produced from this radical through β -scission involving C–H bond cleavage, and also via H-transfer to O₂ but to a lesser extent. Since the high-temperature formation of formaldehyde is accurately captured by our mechanism under all tested conditions, the overprediction of 1,3-butadiene is likely due to an overestimation of the branching ratio of C–H to C–C β -scission reactions of c4h714 radicals. This may also help explain, at least in part, the underprediction of ethylene at

high temperatures, as it is formed through the C–C β -scission of c4h714. Moreover, a minor flux (about 5%) of c4h714 combines with methyl radicals to form 1-pentene, in line with the traces of this species detected experimentally (see Fig. D5 in **Appendix D**).

Finally, it should be noted that the very small remaining flux (not shown in Figure 5.18) of each fuel radical, as well as other derived radicals like the 1-butyl radical, follows minor pathways. These radicals can still add to O₂, for example, before either eliminating an HO₂ radical to form an unsaturated compound or isomerizing and then decomposing. Nevertheless, these fluxes are negligible and have no real influence on the overall reactivity.

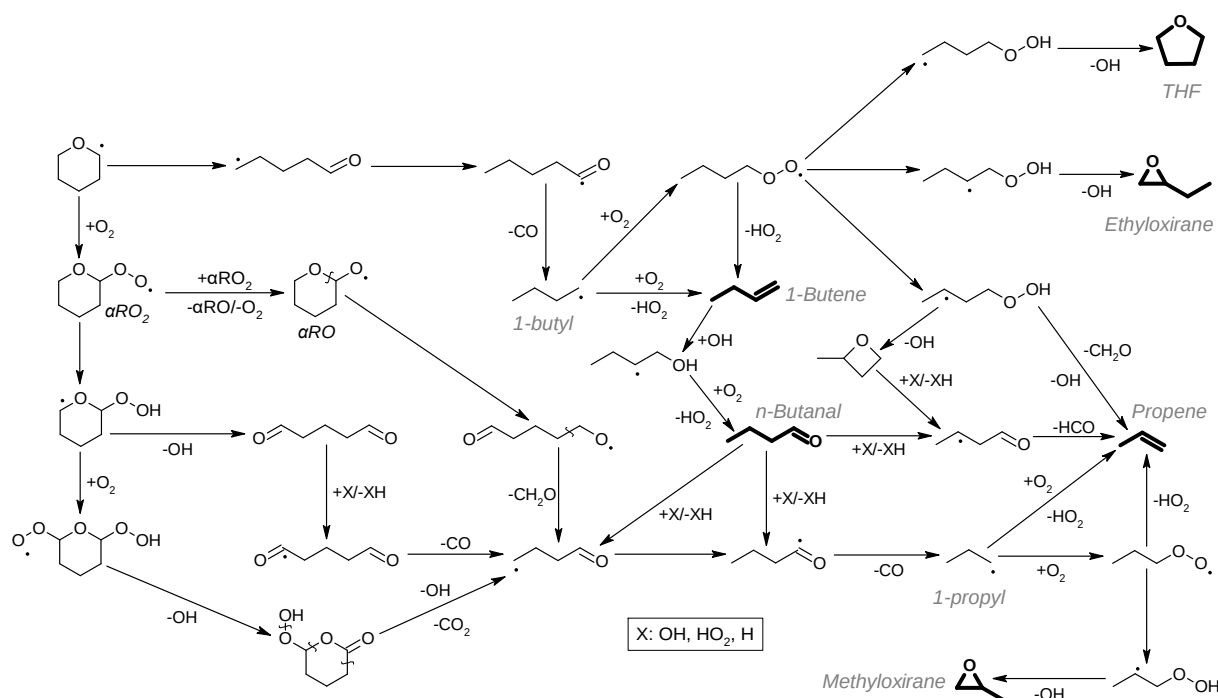


Figure 5.19: Formation of 1-propyl and 1-butyl radicals, along with some of their characteristic oxidation products (highlighted), via the main THP reaction pathways originating from its most favorable α -radical across various temperature ranges.

Figure 5.19 illustrates the crucial role of alkyl radicals in THP oxidation, specifically the 1-butyl and 1-propyl radicals formed via α -scission (decarbonylation) of acyl radicals. The depicted pathways reveal how these alkyl radicals participate in the oxidation process and elucidate the formation of several characteristic species, associated with their reaction routes and experimentally observed. Therefore, while it is well known that studying the oxidation of cyclic ethers is essential for fully understanding that of alkanes, we see here that the reverse is equally true.

While the discrepancies between simulations and experimental data indicate that further refinement of the THP sub-mechanism is still needed (based on accurate theoretical calculations, as previously mentioned in **Chapter 4**), some of these differences may also arise from C₃–C₄ sub-mechanism which may need to be revisited to ensure its robustness, particularly for propane and n-butane, similar to the validation performed for the C₀–C₂ core mechanism in this work. Therefore, achieving a more robust THP oxidation mechanism will require testing it against additional experimental data previously reported for these alkanes, in addition to THP. The following sub-section evaluates the present mechanism against various THP datasets

available in the literature, while a review of the C₃–C₄ sub-mechanism is beyond the scope of this work.

Unlike linear ethers such as DBE, where the involvement of 1-propyl and 1-butyl radicals leads to a double cool flame and NTC behavior [33], these alkyl radicals do not induce such behavior during the oxidation of THP. In fact, the reactivity regimes of these radicals occur within the same temperature ranges as THP itself, whereas the reactivity of DBE begins ≈ 100 K earlier. This difference explains why two distinct reactivity behaviors – the first from the fuel and the second from alkyl radicals – are observed for DBE but not for THP.

5.2.6 Further Validation

The present mechanism is further evaluated against experimental data available in the literature, including speciation from atmospheric-pressure oxidation in JSRs and pyrolysis in a plug flow reactor (PFR), as well as ignition delay time (IDT) measurements in a shock tube. Overall, the mechanism reproduces reasonably well the general trends of these datasets, though some discrepancies remain in the absolute values. We also compare our mechanism with the one originally developed for each dataset, to provide a more comprehensive assessment.

5.2.6.1 Atmospheric-pressure JSR oxidation of THP at lean conditions

Zou et al. [111] studied the oxidation of 5000 ppm THP in two different JSRs (78 and 92 cm³) at $\phi = 0.25$, atmospheric pressure, a residence time of 4 s, and using Ar and He as diluents, respectively. Figure 5.20 compares the mechanism developed in that study with the present mechanism in terms of their ability to reproduce the reported speciation data.

As previously observed under our tested conditions, Zou mechanism again exhibits slightly more pronounced LTR and NTC regimes compared to the present mechanism. However, when considering data from the two distinct JSRs, both mechanisms can be regarded as good representations of the LTR regime. In contrast, both tend to overpredict the fuel mole fraction in the NTC region and underestimate it in the intermediate-to-high temperature range. Our mechanism generally provides a better representation of fuel-specific products: dihydropyrans (DHPs), tetrahydropyranones (THPones), and pentanedial. For small oxygenated species (O₂, H₂O, H₂O₂, CO₂, CO, and CH₂O), both mechanisms perform similarly. However, notable differences arise for larger oxygenates: Zou mechanism better reproduces CH₂CO and acetaldehyde, whereas the present mechanism provides more accurate predictions for formic acid, oxirane, C₂H₅OOH, acrolein, and 2-butenal, particularly at low temperatures. Methanol mole fraction profiles differ notably between the two JSR datasets, with the present mechanism aligning better with one profile, while Zou mechanism reproduces the other more accurately. Finally, both mechanisms generally fail to capture the profiles of hydrocarbons and continue to underpredict propanal formation at low temperatures.

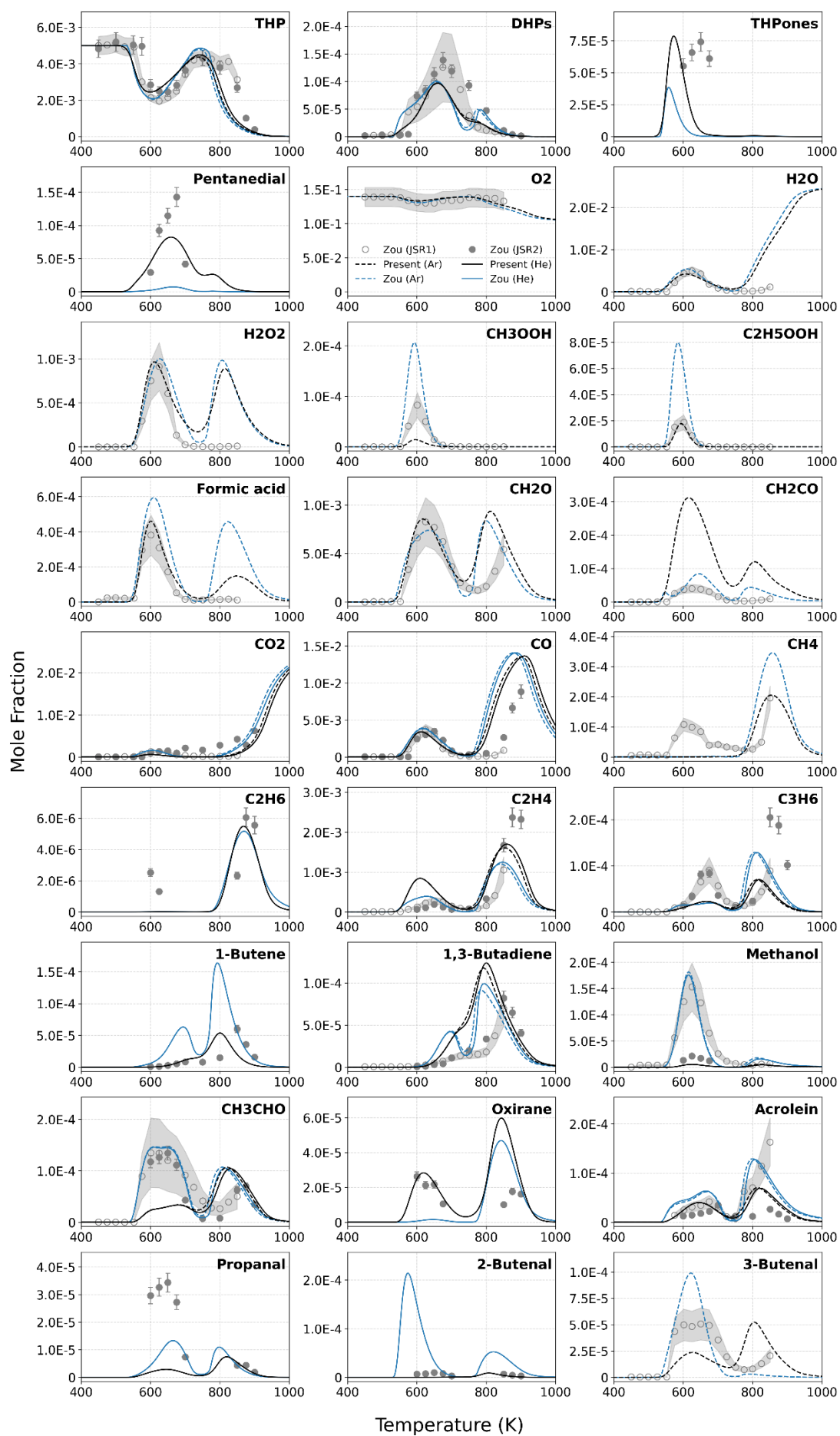


Figure 5.20: Experimental (symbols: Zou et al. [111]) and simulated (lines) mole fraction profiles of reactant, product, and intermediate species during THP oxidation in two JSRs (JSR1 and JSR2, with Ar and He as diluents, respectively) at $p \approx 1$ bar, $\tau = 4$ s, $X_0(\text{fuel}) = 5000$ ppm, and $\phi = 0.25$. JSR1 data: filled symbols with error bars and solid lines; JSR2 data: open symbols with shaded uncertainty bands and dashed lines.

5.2.6.2 Atmospheric-pressure JSR oxidation of THP at stoichiometric conditions

Both Hartness et al. [112] and Zou et al. [111] studied the stoichiometric oxidation of 5000 ppm THP in JSRs (33.5 and 92 cm³) at atmospheric pressure, with a residence time of 4 s, using N₂ and He as diluents, respectively. Although the conditions in both studies are similar, notable discrepancies between their speciation data are observed, highlighting the need for further experimental investigations to clarify the underlying causes and provide more reliable data for kinetic modeling. Figure 5.21 compares the mechanisms developed in these studies with the present mechanism in terms of their ability to reproduce the reported speciation data.

Relative to those of Hartness, the experimental data of Zou exhibit significantly weaker fuel reactivity throughout the tested temperature range, shifted to higher temperatures. Correspondingly, the measured species are formed in lower amounts, with profiles also shifted toward higher temperatures. Overall, all mechanisms predict fuel mole fractions more consistently with Hartness data than with those of Zou. While Hartness mechanism shifts the HTR onset toward lower temperatures, resulting in an overprediction of reactivity between 750 and 900 K, the present mechanism and that of Zou show good agreement in this regime. Although both Hartness and Zou mechanisms overpredict the LTR, they reproduce the NTC region more accurately. The present mechanism is the only one that shows a simulated fuel profile falling between the mole fractions obtained from the two datasets at low temperatures.

Regarding the various species formed, all mechanisms show generally similar or better agreement with Hartness data than with those of Zou, either in terms of absolute values, overall trends, or both. The present mechanism provides the best overall representation for most species: O₂, H₂, CH₄, C₂H₄, 1-butene, 2-butenal, 3,4-DHP, THPones, and the five minor cyclic ethers identified (oxirane, methyloxirane, ethyloxirane, 2-methyloxetane, and THF). In line with its overestimation of both LTR and HTR, Hartness mechanism predicts excessive production of several species during one or both of these regimes, including CH₄, C₂H₄, 1-butene, 3,4-DHP, pentanedial, 2-methyloxetane, and THF. Zou mechanism also tends to highly overpredict many species, especially at high temperatures, such as H₂, CH₄, 1-butene, acetone, ethyloxirane, 2-butenal, and 3,6-DHP.

Finally, as observed under previous conditions, both acetone and propanal are again underestimated at low temperatures, while the high-temperature formation of 1,3-butadiene remains overpredicted by all three mechanisms (with Hartness mechanism showing the largest overestimation).

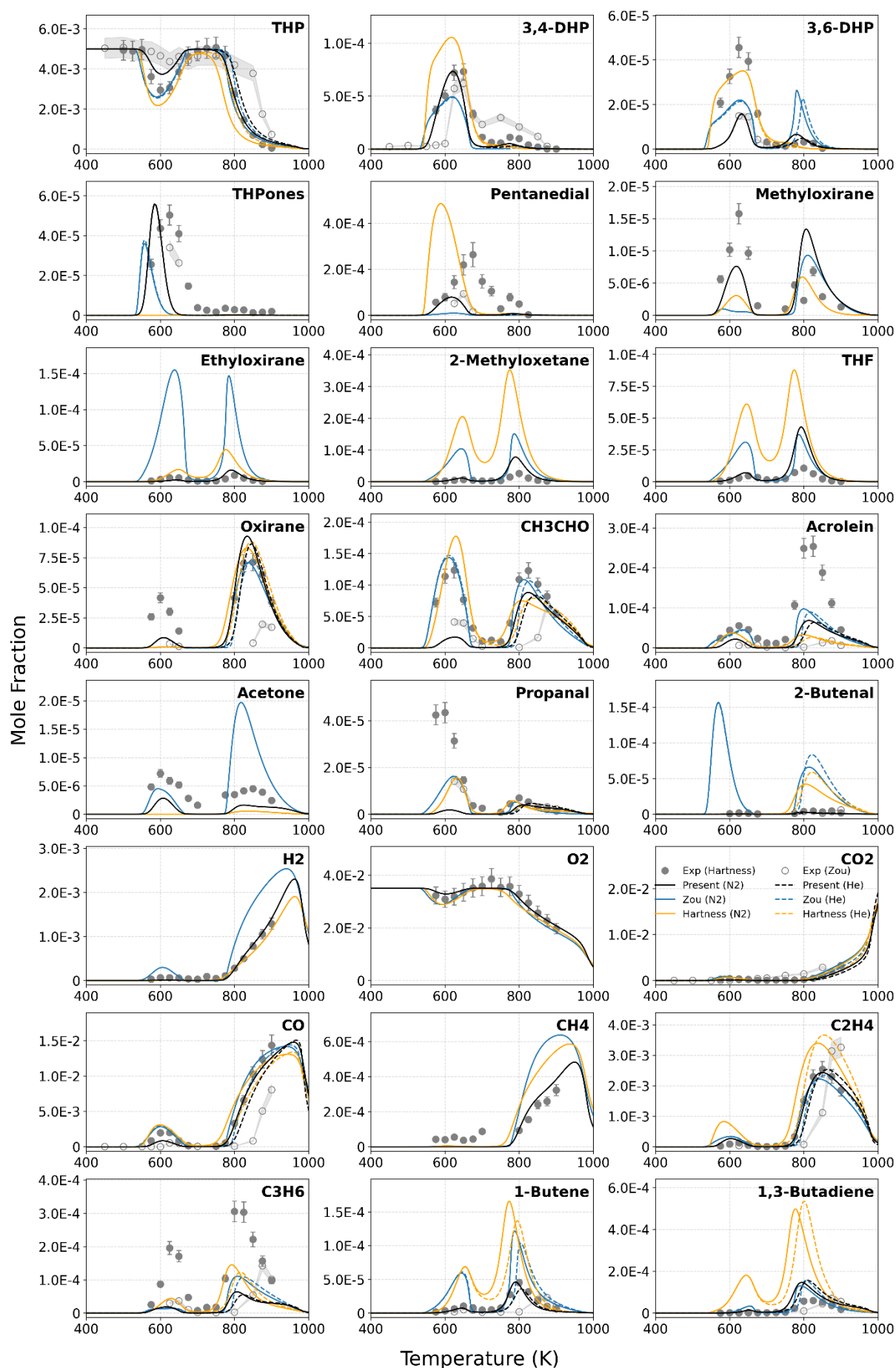


Figure 5.21: Experimental (symbols: Hartness et al. [112] and Zou et al. [111]) and simulated (lines) mole fraction profiles of reactant, product, and intermediate species during THP oxidation in JSRs at $p \approx 1$ bar, $\tau = 4$ s, $X_0(\text{fuel}) = 5000$ ppm, $\phi = 1$, and using N_2 and He as diluents, respectively. Hartness data: filled symbols with error bars and solid lines; Zou data: open symbols with shaded uncertainty bands and dashed lines.

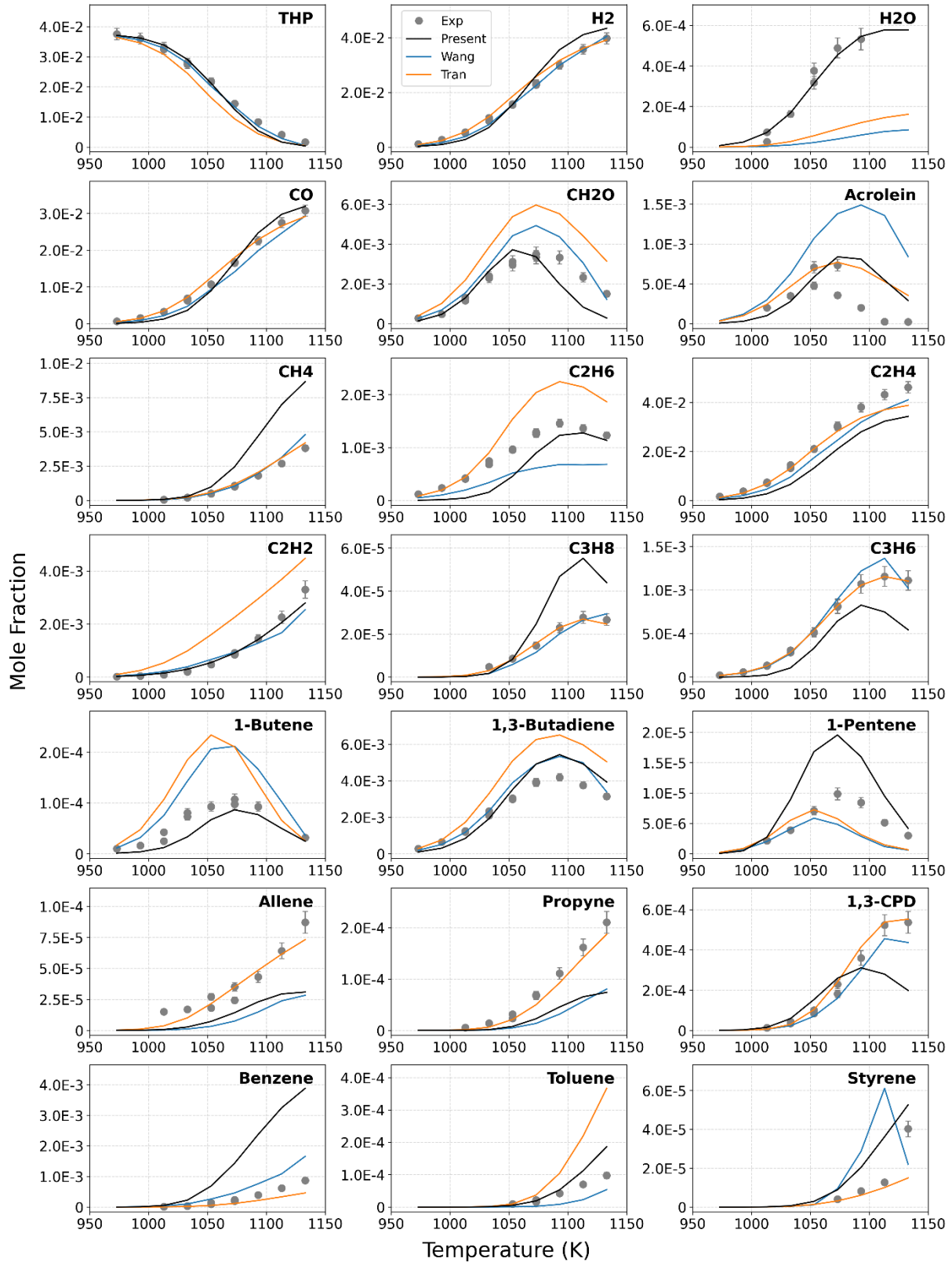


Figure 5.22: Experimental (symbols with error bars: Tran et al. [106]) and simulated (lines) mole fraction profiles of fuel and products during THP/N₂ ($\approx 4\%/96\%$) pyrolysis in a PFR at $p = 1.7$ bar. Black: present work; Blue: Wang et al. [114]; Orange: Tran et al. [106].

5.2.6.3 Pyrolysis of THP in a plug flow reactor

Figure 5.22 presents the experimental and simulated results for the pyrolysis of THP diluted with 96% N₂ in a PFR. the present mechanism accurately reproduces the fuel mole fraction profile, performing better than the mechanism originally developed by the authors (Tran et al. [106]) of that study to simulate the speciation data of this pyrolysis, along with other measurements. In fact, Tran mechanism overpredicts fuel reactivity across the entire tested temperature range, resulting in an overestimation of several species, including CH₂O, C₂H₂, 1-butene, and 1,3-butadiene, which are reasonably well captured by our mechanism. The recently published mechanism of Wang et al. [114], which also considered THP pyrolysis, shows closer agreement with our simulations for both the fuel and the aforementioned species (except 1-butene) compared to Tran mechanism. However, Tran mechanism interestingly provides the best agreement for the mole fraction profiles of most measured species, including light C₁–C₃ hydrocarbons (except for the overpredicted C₂H₂ and C₂H₆) and 1,3-cyclopentadiene (1,3-CPD). These species are also reproduced reasonably well by Wang mechanism, though to a lesser extent, except for allene and propyne, whose formation is underestimated by both our mechanism and that of Wang. Our mechanism additionally underpredicts the production of C₂H₄ and C₃H₆, while it overpredicts that of CH₄ and C₃H₈. For H₂ and CO, which are with C₂H₄ the most abundant products of THP pyrolysis, all three mechanisms show very good agreement with the experimental data. Water formation is well captured by our mechanism but underestimated by the other two. Finally, regarding aromatics, our mechanism tends to overestimate their formation (slightly for toluene and significantly for benzene), which begins above ≈ 1050 K. Although Tran mechanism provides the closest match for benzene and styrene, it highly overpredicts toluene production by up to a factor of four.

5.2.6.4 Ignition of THP in a shock tube

Figure 5.23 illustrates the predictive performance of the present mechanism against the IDTs of THP measured by Dagaut et al. [104] in a shock tube. Our mechanism captures well the observed increase in reactivity, whether due to rising pressure, decreasing equivalence ratio, or increasing initial fuel mole fraction. The mechanism also performs reasonably well in predicting the IDT values, although it tends to overpredict them at lower temperatures, with the largest deviation occurring in the lowest tested temperature range at the highest studied pressure ($p = 5$ bar). In contrast, at higher temperatures, the mechanism tends to underestimate IDTs for the lean mixtures, especially the one with the lowest initial fuel mole fraction (0.5% THP).

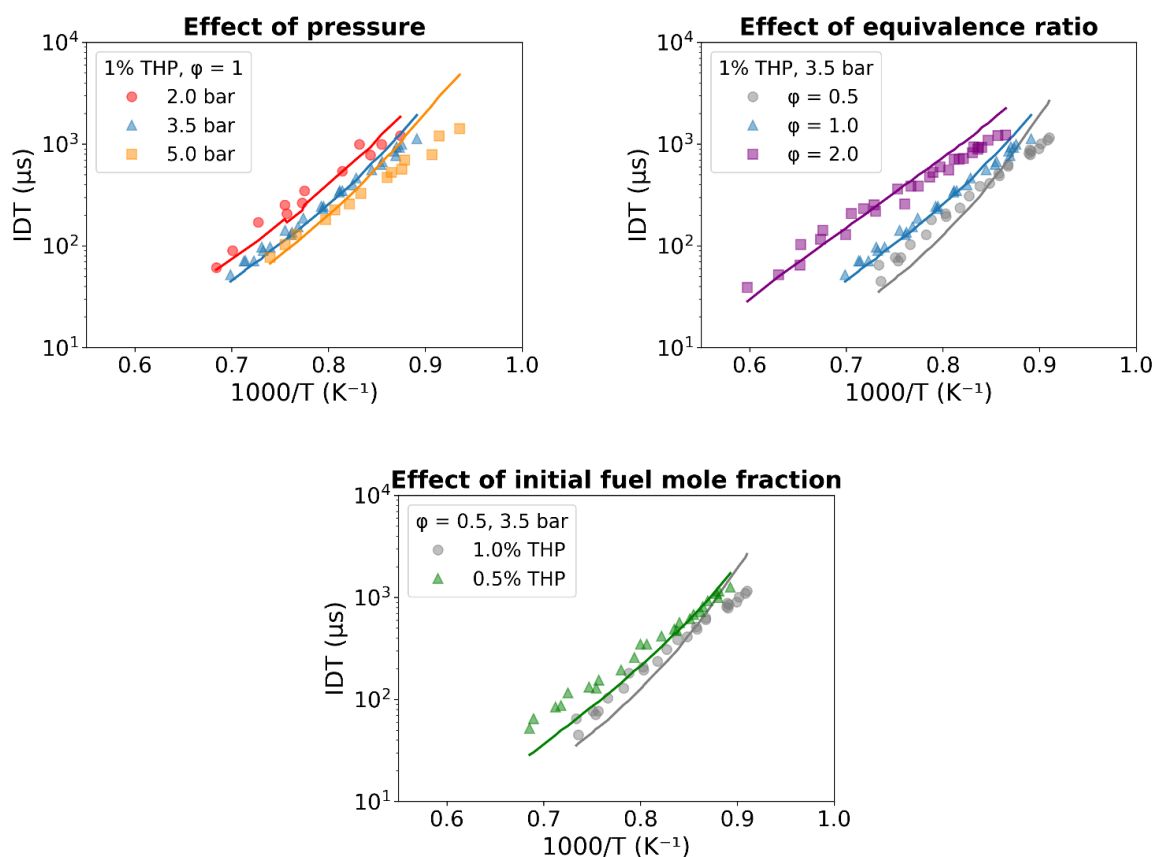


Figure 5.23: Ignition delay times of THP/O₂/Ar mixtures measured in a shock tube. Symbols: Experimental data (Dagaut et al. [104]); Lines: Simulations (Present work).

5.2.7 Conclusion

To sum up, the JSR oxidation of THP was studied at a high pressure of 10 bar over a wide range of conditions using both experimental and modeling approaches. The study covered the low- and high-temperature chemistry of THP, which exhibited the three typical reactivity zones (LTR, NTC, and HTR). In addition to the oxidation products and the common hydrocarbons (with ethylene as the most abundant) and oxygenated intermediates (with formaldehyde as the most abundant), four fuel-specific species were identified: 3,4-DHP, 3,6-DHP, THP-2-one, and pentanedial.

The present mechanism demonstrated strong performance in predicting the experimental data obtained in this work and, overall, outperformed existing literature mechanisms, despite some remaining discrepancies, leaving room for further refinement. These discrepancies can be attributed to uncertainties in the estimated rate constants of reactions and thermochemical data of species in the newly developed sub-mechanism of THP, for which advanced theoretical calculations are required to achieve better accuracy. Another source of discrepancies may arise from missing reactions specific to THP that have not yet been explored. Here, it is worth noting that a key drawback shared by all tested mechanisms is their failure to reproduce the formation of propanal/acetone and propene at low temperatures under lean conditions.

For the richest mixture ($\phi = 3.2$), the fuel showed a noticeably reduced HTR compared to mixtures with lower equivalence ratios. A sensitivity analysis performed on THP at $\phi = 3.2$ and

$T = 900$ K attributed this behavior to a crucial termination step under such conditions, namely the recombination of ethyl radicals. This explanation was subsequently confirmed by a reaction pathway analysis conducted at the same conditions. This pathway analysis also revealed the routes leading to the formation of 1,3-butadiene, suggesting that its overprediction by the present mechanism may stem from an overestimation of the branching ratio of C–H to C–C β -scission reactions of the primary radical of 1-butene.

As expected, the THP α -radical was identified as the most favored fuel radical regardless of the condition. Its reaction pathways reveal the involvement of alkyl radicals (i.e., 1-propyl and 1-butyl) and elucidate the formation of species characteristic of their oxidation. This illustrates the reciprocal contribution of cyclic ethers and alkanes to their respective oxidation, and indicates a potential need to revisit propane and n-butane sub-mechanisms, in addition to THP, when aiming to improve the present mechanism.

Finally, various literature data were used to further validate the present mechanism, which demonstrated good performance in representing experimental results compared to the mechanisms originally established to reproduce them. Nevertheless, more accurate atmospheric speciation measurements and additional data (including laminar flame speeds), along with further improvement of the present mechanism, are still required in order to complete this validation and to fully understand the oxidation kinetics of THP.

5.3 Tetrahydrofuran

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5.3.1 Experimental Behavior

The oxidation of THF was studied in a 42 cm³ JSR at a pressure of 10 bar and a constant residence time of 0.7 s. Experiments were conducted with an initial fuel mole fraction of 850 ppm across five different equivalence ratios ($\phi = 0.425, 0.85, 1.275, 1.53, \text{ and } 1.7$). The fuel conversion for these conditions is reported in Figure 5.24. In addition, the oxidation of 5000 ppm THF was tested in the same reactor at $\phi = 0.5$ under the same pressure but with a longer residence time of 2 s, in order to enhance the weak cool flame of THF and enable a more detailed examination. The results of this oxidation are used to further validate the kinetic mechanism developed in this work. Finally, the oxidation of 1000 ppm THF was investigated in a JSR of 34 cm³ at $p = 10$ bar and $\tau = 0.7$ s for two equivalence ratios ($\phi = 1$ and 2). The $\phi = 1$ results are used for additional mechanism validation. The $\phi = 2$ data are presented in **Appendix D** (Fig. D1), where they are compared with those of $\phi = 1.7$ mixture, studied using same initial mole fraction of oxygen but differing in that of fuel.

As with THP, the three classical reactivity regimes are also observed for THF. However, compared to THP under comparable lean conditions, THF exhibits much weaker LTR and NTC regimes, which become negligible or disappear under rich conditions (Figure 5.24). As shown in Figure 5.25, THF has a weak LTR regime at $\phi = 0.425$, starting around 570 K and extending up to 630 K, during which only 20% of the initial THF is consumed. This is followed by a weak NTC region, spanning a similar temperature window of 60 K, marked by a slight decrease in reactivity and the regeneration of less than 4% of the initial fuel. Finally, the HTR regime emerges, resulting in the complete consumption of THF near 1100 K.

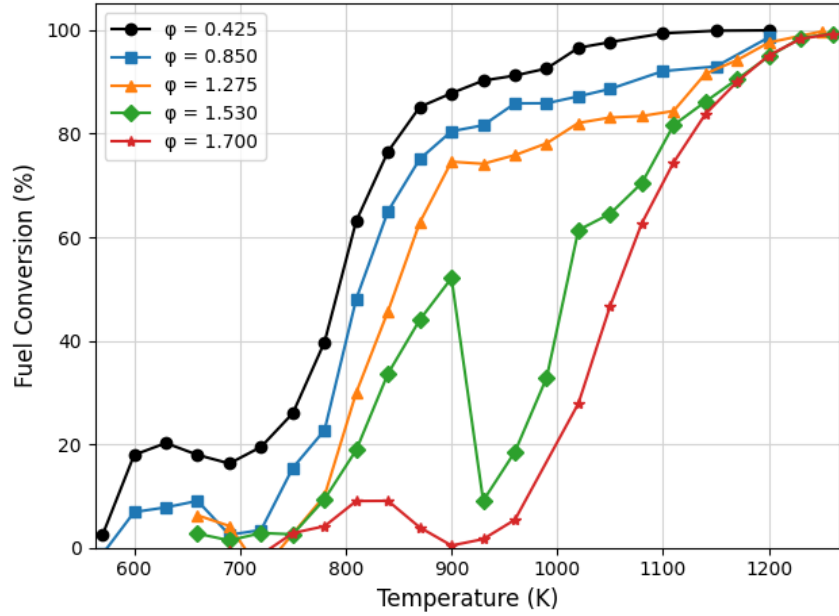


Figure 5.24: Conversion of THF during its oxidation in a JSR as a function of temperature for the five equivalence ratios studied at $p = 10$ bar, $\tau = 0.7$ s, $X_o(\text{fuel}) = 850$ ppm (lines are added to represent the trend).

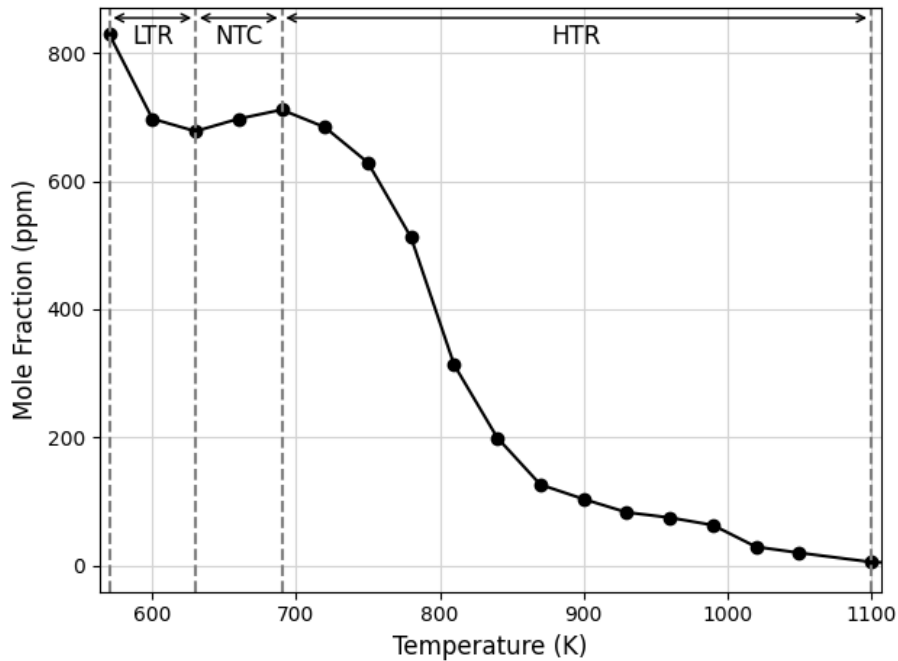


Figure 5.25: Mole fraction profile of THF during its oxidation in a JSR as a function of temperature at $\phi = 0.425$, $p = 10$ bar, $\tau = 0.7$ s, $X_o(\text{fuel}) = 850$ ppm (lines are added to represent the trend).

Figure 5.24 illustrates that, as the equivalence ratio increases, the HTR regime shifts toward higher temperatures. Moreover, unlike THP, the reactivity growth of THF slows significantly above 900 K, without truly ceasing. At $\phi = 1.53$, however, a sharp reactivity drop is observed between 900 and 930 K, after which reactivity is restored and proceeds until the fuel is fully consumed. When the equivalence ratio is further increased to $\phi = 1.7$, the reactivity decline becomes smoother, occurring at lower temperatures over a wider interval (of 60 K instead of

30 K); i.e., from 840 to 900 K. While a decrease in reactivity separating the LTR and HTR is common for many fuels and well known as NTC regime, a decrease in reactivity within the HTR phase is reported here for the first time in the case of THF, with no known precedents except for its hydrocarbon analog, CPT, under comparable conditions [167]. However, no similar behavior was observed at atmospheric pressure for either THF or CPT under rich conditions, as shown in the studies of Vanhove et al. [124] and Dayma et al. [137], respectively. Further discussion of this novel behavior is provided in the next sub-section, and the mole fraction profiles of THF and CPT obtained under same experimental conditions are compared in the following section.

5.3.2 Mechanistic Interpretation

The comparison between the measured and predicted mole fractions of THF at the five investigated equivalence ratios is presented in Figure 5.26. As was done for THP, we begin with this comparison to assess whether the present mechanism accurately captures the distinct reactivity regimes observed experimentally, along with their corresponding temperature ranges. Starting with the leanest mixture, and accounting for the experimental uncertainty, it can be seen that the present mechanism reproduces reasonably well the evolution of the fuel mole fraction with temperature. However, it shifts the onset of HTR by ≈ 50 K toward higher temperatures, therefore underpredicting reactivity between 720 and 820 K. This discrepancy diminishes as the equivalence ratio increases, disappearing entirely above $\phi = 0.85$. Nevertheless, an overprediction of reactivity appears at the end of the HTR above a temperature that varies between ≈ 1000 and 1050 K depending on the equivalence ratio. Additionally, the mechanism underestimates reactivity between 880 and 1020 K at $\phi = 1.275$. On the other hand, the mechanism reproduces well the sharp reactivity suppression at $\phi = 1.53$ between 900 and 930 K, although it shows a slight overprediction of reactivity below 900 K, ending with a narrow plateau just before the brutal drop. The mechanism also succeeds at $\phi = 1.7$ in capturing this drop at lower temperatures (but still sharp; between 870 and 900 K) and in showing less pronounced reactivity before the drop, but not sufficiently, resulting in a significant underestimation of the fuel mole fraction between 800 and 900 K.

The ability of the present mechanism to reproduce the similar reactivity decline observed for CPT under rich conditions is successfully validated in **Appendix E** (Fig. E2).

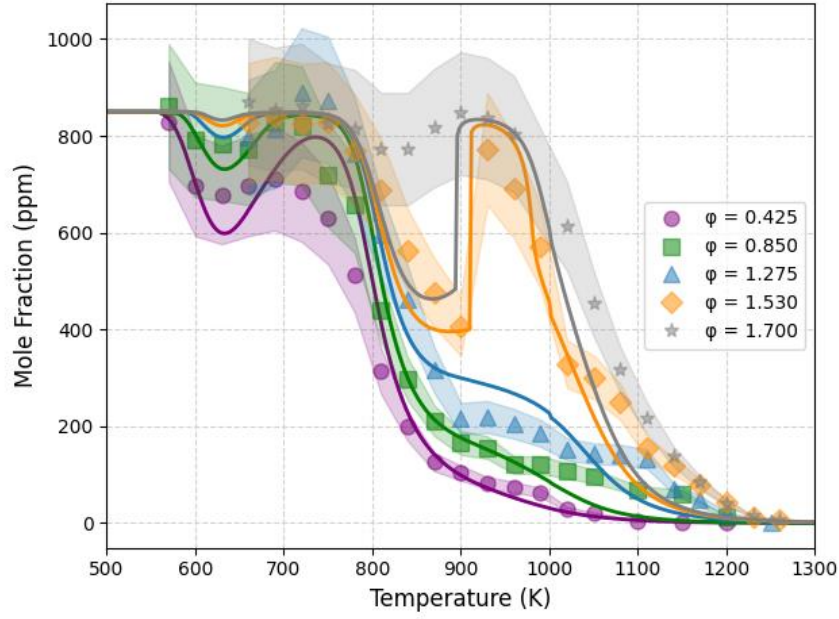


Figure 5.26: Experimental (symbols) and simulated (lines) mole fraction profiles of THF during its oxidation in a JSR as a function of temperature for the five equivalence ratios studied at $p = 10$ bar, $\tau = 0.7$ s, $X_O(\text{fuel}) = 850$ ppm (shaded areas are included to represent the measurement uncertainty of $\pm 15\%$).

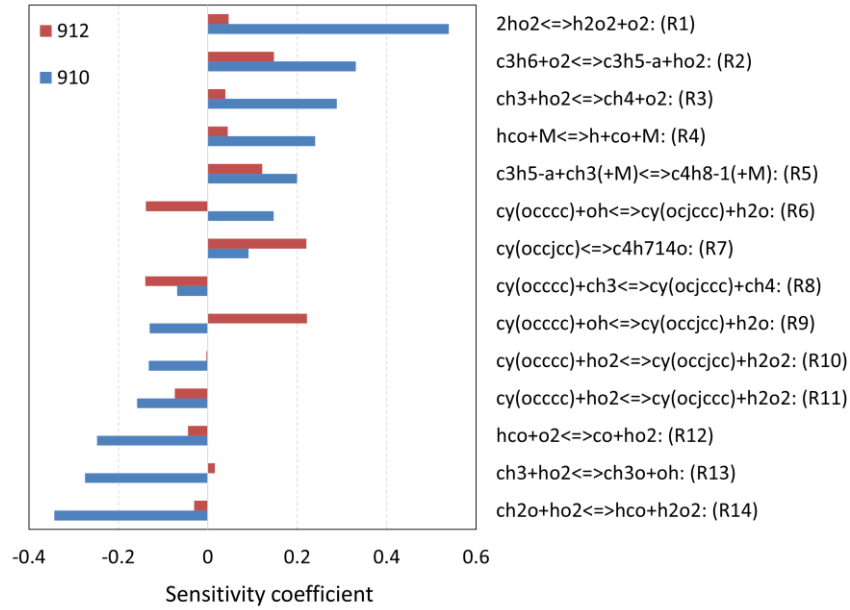


Figure 5.27: Sensitivity analysis performed on THF with the present mechanism for the rich mixture ($\phi = 1.53$, $p = 10$ bar, $\tau = 0.7$ s) at 910 and 912 K.

The present mechanism predicts the sharp suppression in reactivity observed for THF at $\phi = 1.53$ between 900 and 930 K to occur precisely between 910 and 912 K. In order to understand this interesting behavior, a sensitivity analysis is performed on the fuel at these two temperatures. This analysis, illustrated in Figure 5.27, highlights the importance of three key radicals (HO_2 , CH_3 , and $\text{C}_3\text{H}_5\text{-a}$), particularly through their mutual reactions. These reactions are the self-recombination of HO_2 radicals (R1), the reactions of allyl ($\text{C}_3\text{H}_5\text{-a}$) radicals with HO_2 (R2) and CH_3 (R5) radicals, and the reactions of CH_3 with HO_2 radicals (R3 and R13).

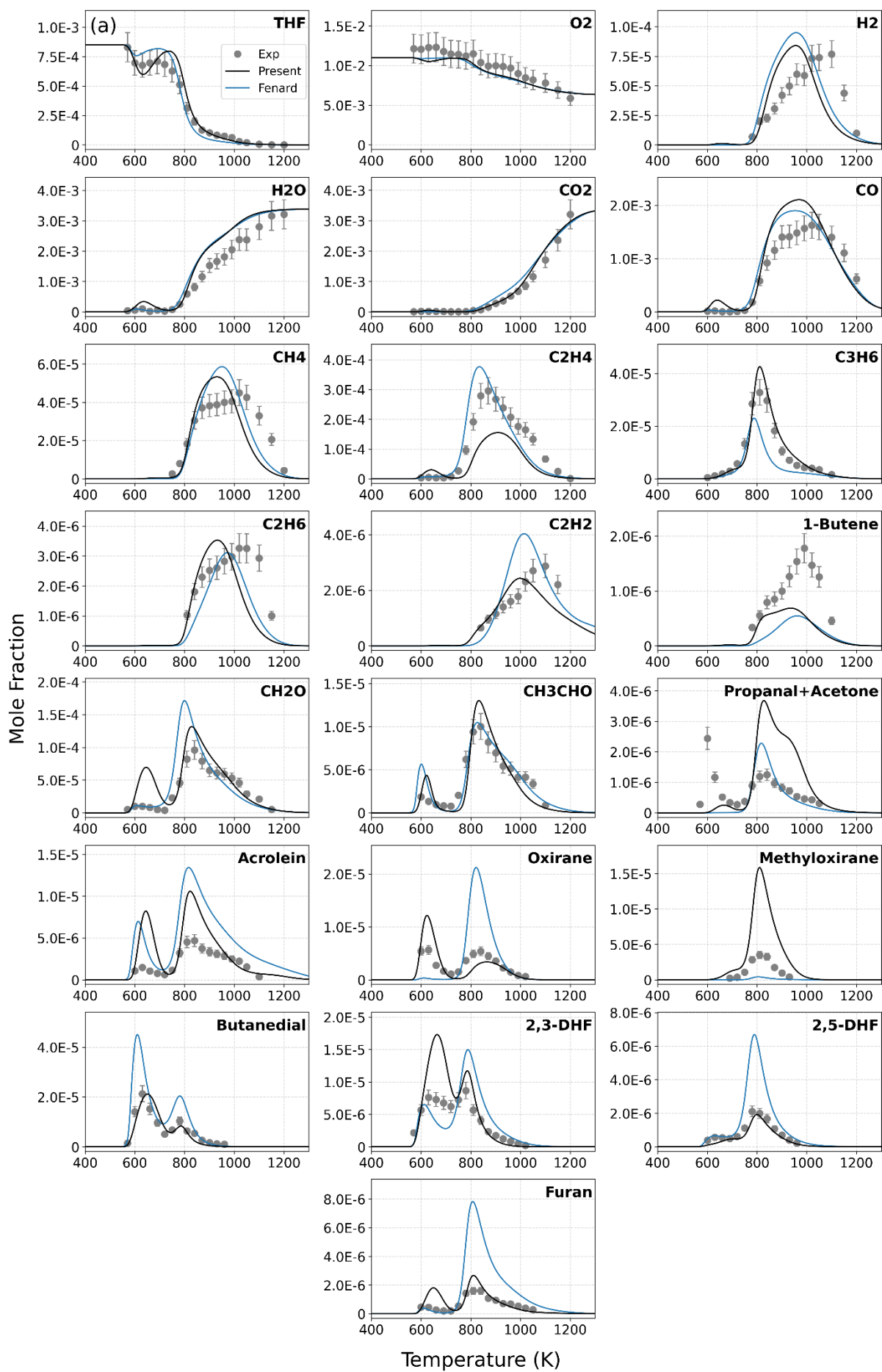
At 910 K, all of these reactions strongly inhibit overall reactivity. The only exception is reaction R13, in which CH_3 and HO_2 form CH_3O and highly reactive OH radicals, thereby promoting reactivity. Although R1 inhibits reactivity, it produces H_2O_2 that subsequently decomposes into two OH radicals; the most important chain-branching reaction at intermediate temperatures that marks the transition from the NTC to the HTR regime. In contrast, R2, R3, and R5 lead to the formation of relatively stable molecules (propene, methane, and 1-butene, respectively). Thus, these reactions are most likely the ones responsible for the observed drop in reactivity. Like R13, the H-abstraction reactions of THF (R10 and R11) and CH_2O (R14) by HO_2 radicals are also among the most sensitive promoting reactions. The HCO radicals formed from the latter reaction of CH_2O primarily undergo unimolecular decomposition (R4) or reaction with O_2 to form CO and HO_2 radicals (R12): the former inhibits reactivity, while the latter promotes it.

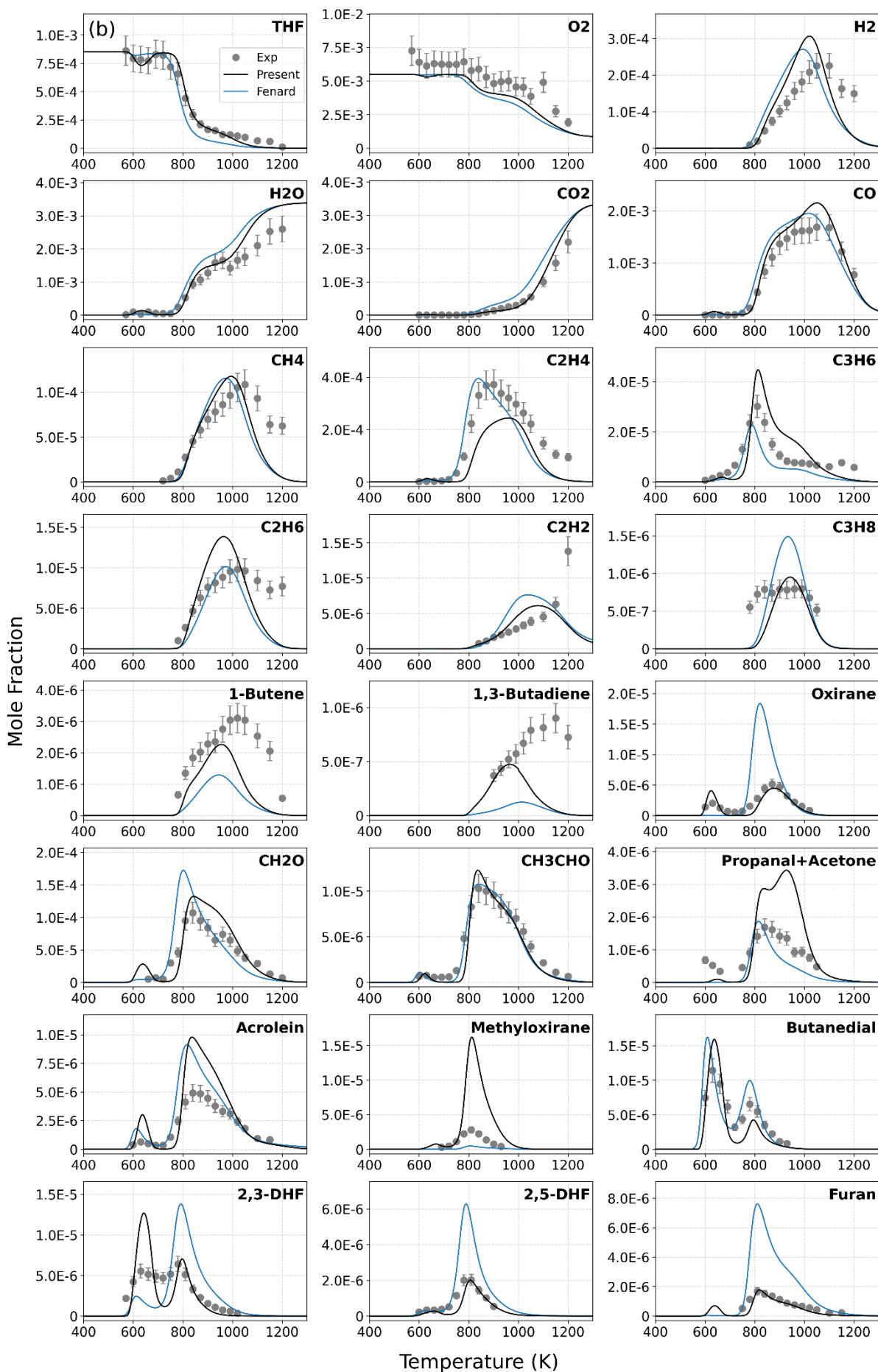
When the temperature increases to 912 K, all of the aforementioned reactions continue to affect reactivity in the same direction but with much lower sensitivity, consistent with the sharp suppression of reactivity and the associated depletion of the radical pool (especially HO_2). Only R13 shifts from negative to slightly positive sensitivity. On the other hand, as the fuel becomes more abundant, its H-abstraction reactions by OH (R6 and R9) and CH_3 (R8) radicals, together with the ring-opening of its β -radical (R7), become more sensitive. Their effects on global reactivity are as follows: R8 promotes reactivity, R7 inhibits it, R6 shows a promoting effect at 910 K but acts as an inhibitor at 912 K, while R9 exhibits the opposite trend to R6. As these two latter H-abstraction reactions are expected to be the main fuel-consuming pathways, the reversal in their sensitivities provides further evidence of the observed reactivity decline.

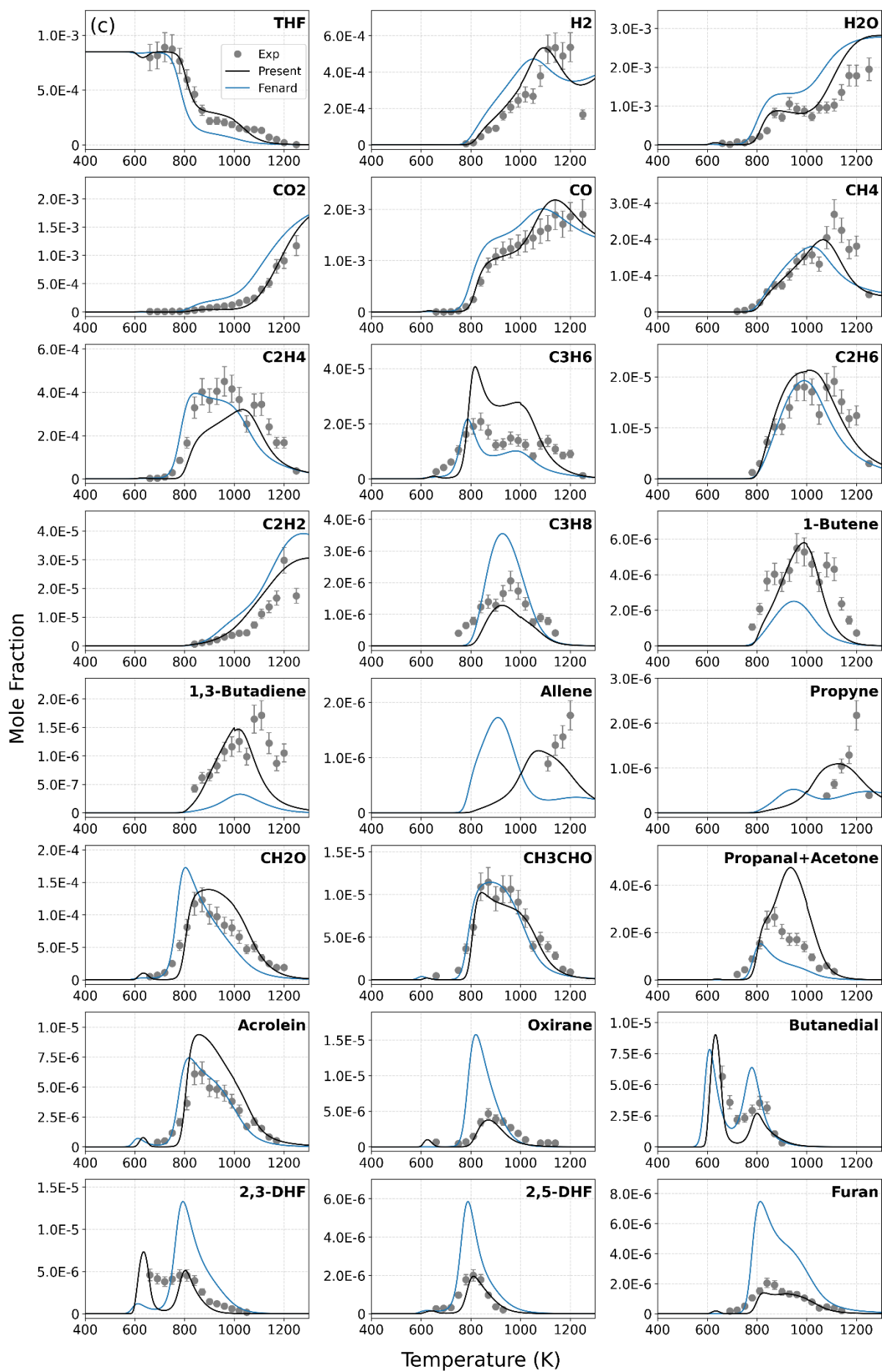
This sensitivity analysis provides an initial mechanistic insight into the novel kinetic behavior of THF. However, it does not capture the complete picture, and a detailed reaction pathway analysis is performed later to achieve deeper understanding of this behavior.

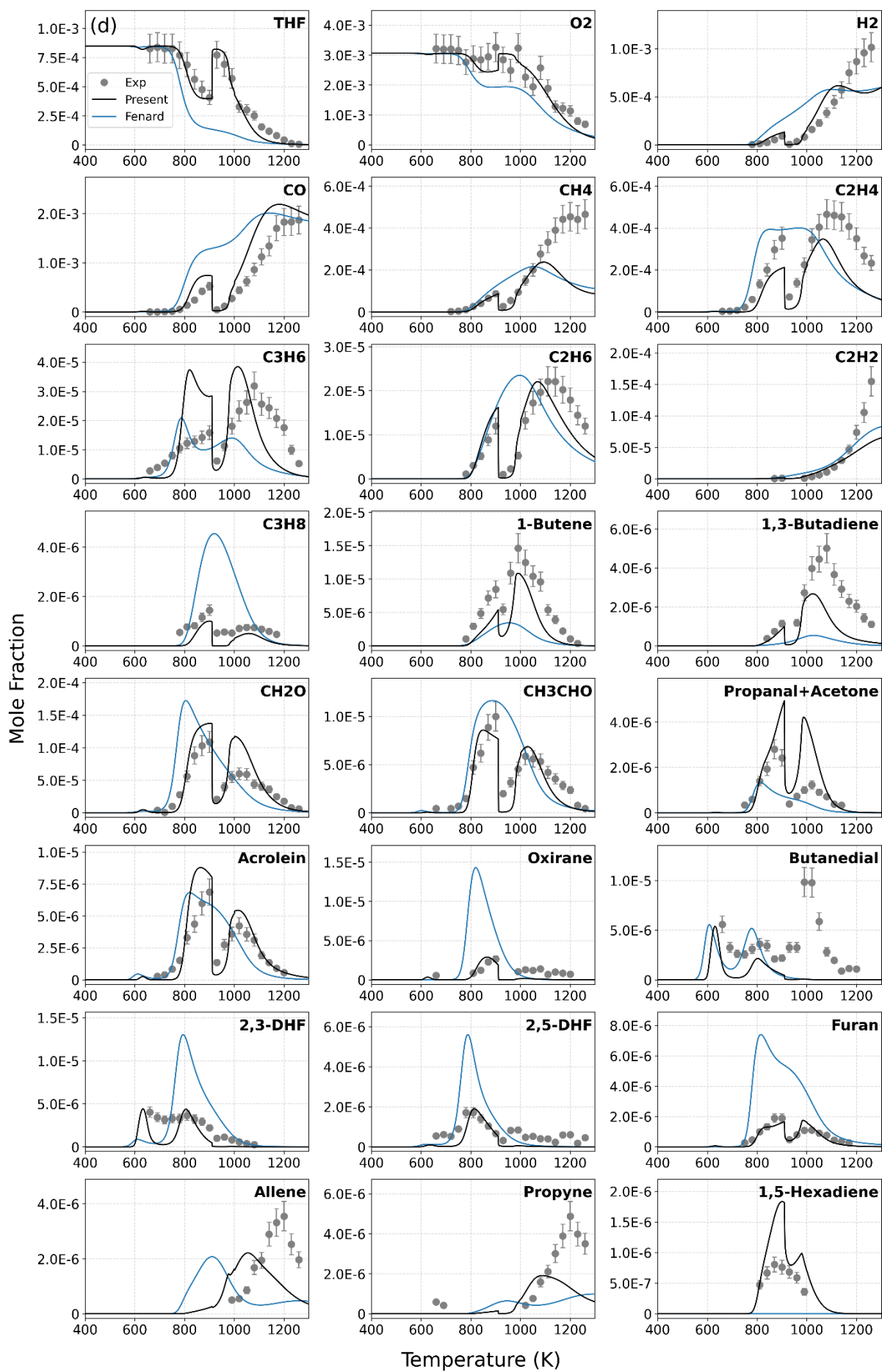
5.3.3 Speciation Analysis

Figures 5.28a–e present the measured and simulated mole fraction profiles of the various reactant, product, and intermediate species observed during the JSR oxidation of THF at the five equivalence ratios investigated with the initial fuel mole fraction of 850 ppm. A representative error bar was added to the experimental profiles to account for the estimated measurement uncertainty of $\pm 15\%$. Apart from CO, CO_2 , and H_2O , the most important oxygenated species formed during the oxidation of THF is formaldehyde (≈ 100 ppm maximum) in the HTR regime, as for THP. In the weak LTR regime, however, the most significant compound is a THF-specific product, butanedial (≈ 20 ppm maximum). Other fuel-specific species are also quantified: furan, 2,3- and 2,5-dihydrofuran (2,3-DHF and 2,5-DHF), in addition to the oxygenates common to THP: oxirane, acetaldehyde, acrolein, and propanal/acetone. All of these species were formed during both low- and high-temperature oxidation of THF. Methyloxirane was as well detected but only at high temperatures. Ethylene is the most abundant in the set of hydrocarbons identified across all tested conditions, which also includes: methane (formed in amounts comparable to ethylene at the richest conditions), ethane, acetylene, propane, propene, 1-butene, and 1,3-butadiene. Traces of allene, propyne, and 1,5-hexadiene were as well detected at high temperatures under rich conditions. Additional data on species detected at trace levels, as well as on species with uncertain identification and/or quantification are provided in **Appendix D** (Fig. D1).









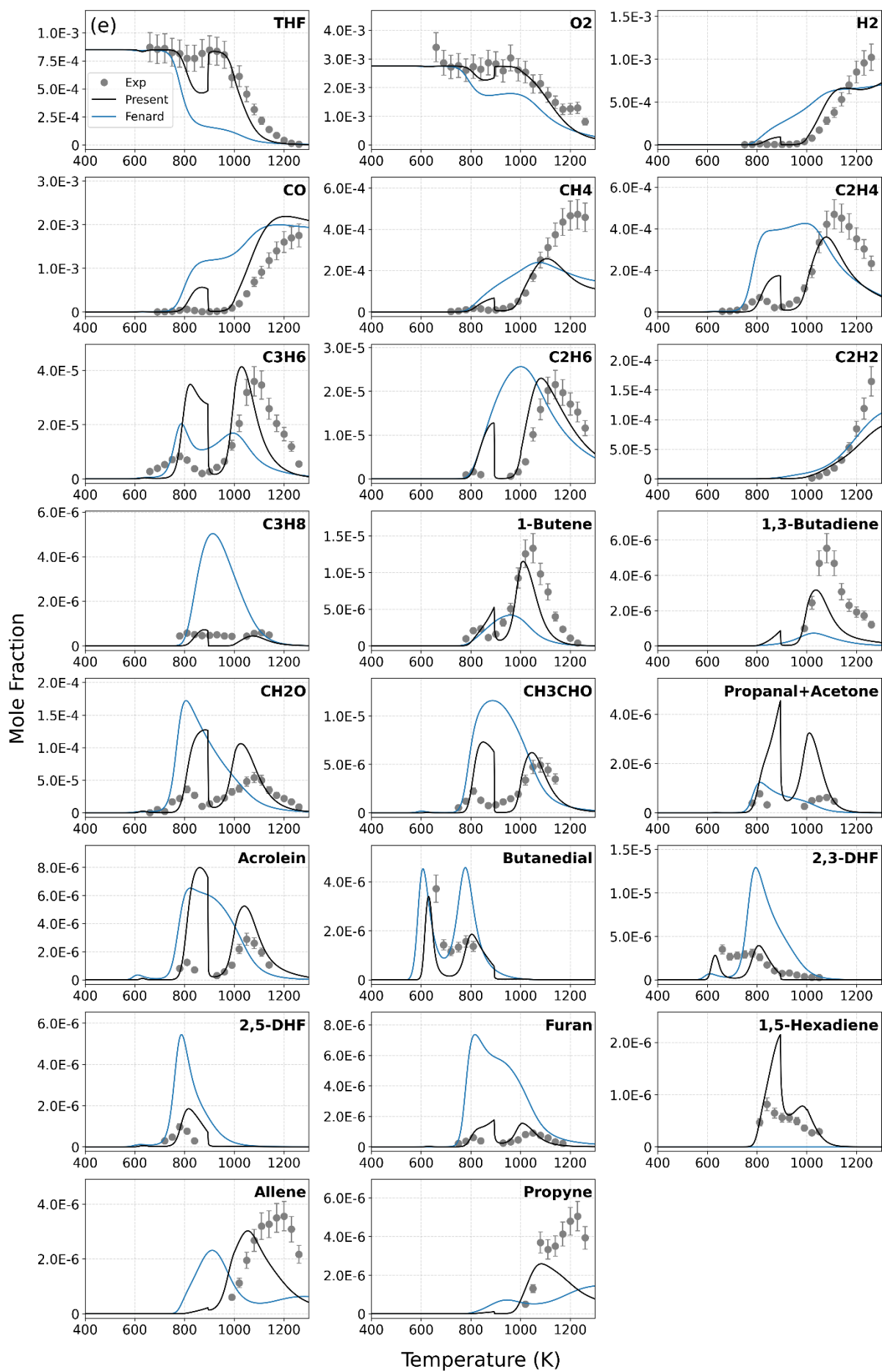


Figure 5.28: Experimental (symbols with error bars of $\pm 15\%$) and simulated (lines) mole fraction profiles of reactant, product, and intermediate species during THF oxidation in a JSR at $p = 10$ bar, $\tau = 0.7$ s, $X_0(\text{fuel}) = 850$ ppm, and: (a) $\phi = 0.425$; (b) $\phi = 0.85$; (c) $\phi = 1.275$; (d) $\phi = 1.53$; (e) $\phi = 1.7$. Black: present work; Blue: Fenard et al. [127].

Overall, the mechanism demonstrates generally good performance in representing the mole fraction profiles of the distinct species observed, including the impact of the sharp reactivity suppression at $\phi = 1.53$ on their evolution. Nevertheless, some discrepancies remain, primarily in the absolute values (which tend to be more often overpredicted), whereas the general trends are well captured. Therefore, further investigation is still required to achieve a more robust mechanism for THF oxidation.

5.3.4 Mechanism Evaluation

Following the assessment of the present mechanism against the experimental data obtained in this work, it is also valuable to evaluate its performance against other existing THF oxidation mechanisms. Accordingly, simulations from the mechanism of Fenard et al. [127], providing the only published sub-mechanism covering low- and high-temperature chemistry of THF, are included for comparison in Figures 5.28a–e. Overall, our mechanism provides the most accurate representation of the experimental species profiles across the various tested conditions, although Fenard mechanism performs better for some species within certain temperature ranges.

For the leanest mixture, while the present mechanism reproduces well the mole fraction of the fuel within the LTR and NTC regions, Fenard mechanism captures its experimental trend in these regions more closely but underestimates the reactivity. In the intermediate-temperature range (specifically 750–800 K), Fenard mechanism accurately predicts the fuel mole fraction, whereas the present mechanism slightly overestimates it. Above 800 K, Fenard mechanism overpredicts the reactivity of THF until its complete consumption, while the present mechanism remains in good agreement with the experimental data.

For the fuel-specific species, the present mechanism globally reproduces their experimental profiles better than the literature mechanism. Although, it overpredicts formaldehyde at low temperatures, our mechanism matches the high-temperature data of this species more closely than Fenard mechanism. Acetaldehyde and oxirane are reasonably captured with the present mechanism, while Fenard mechanism performs better only for acetaldehyde at high temperatures. Acrolein is generally overpredicted by both mechanisms, and neither predicts sufficient formation of propanal/acetone at low temperatures. At high temperatures, ethylene is underestimated and methyloxirane is overpredicted by our mechanism, whereas Fenard mechanism shows the opposite trend. Finally, propene is accurately represented by our mechanism but underpredicted by that of Fenard.

Unlike the present mechanism, Fenard mechanism increasingly overpredicts the HTR of THF, as the equivalence ratio increases. Consequently, it fails to capture the reactivity drop seen at the two richest conditions and thus loses the ability to accurately represent both the trends and levels of mole fraction profiles for most species across nearly the entire studied temperature range.

5.3.5 Reaction Pathways

In order to examine the most important reactions consuming THF at low temperatures, a reaction pathway analysis was performed with the present mechanism at $\phi = 0.425$ and $T = 600$ K (Figure 5.29). The two possible radicals derived from the fuel are formed via H-abstraction by OH radicals, with the α -radical being the most abundant, as expected. Then, the most common reaction pathway followed by these radicals is the typical LTR pathway: a first addition to O_2 , followed by an internal isomerization, a second O_2 addition, and finally the formation of an OH radical and a ketohydroperoxide (KHP). The latter rapidly decomposes into chain-branching fragments and another OH radical, thereby promoting overall reactivity. However, small fluxes follow other low-temperature routes competing with the dominant chain-branching channel. These pathways lead to the formation of unsaturated and bicyclic ethers derived from THF, as well as β -scission products such as butanedial. Additionally, a portion of the αRO_2 radical flux undergoes disproportionation reactions yielding αRO radicals, which subsequently decompose into smaller radicals and molecules.

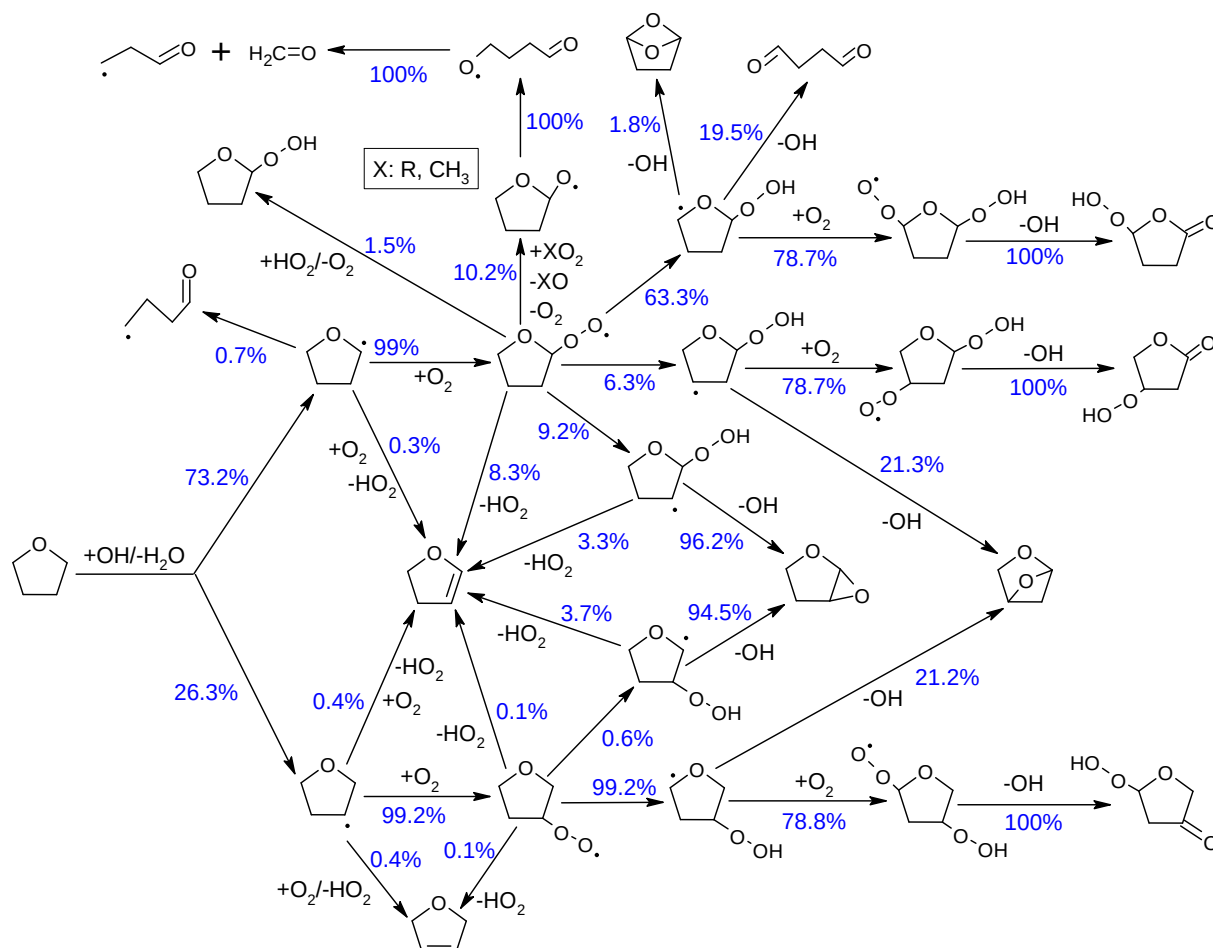


Figure 5.29: Reaction pathways during THF oxidation in a JSR at $T = 600$ K, $p = 10$ bar, and $\tau = 0.7$ s, for the leanest mixture studied ($\phi = 0.425$), as predicted by the present mechanism.

Figure 5.30a presents high-temperature reaction pathway analyses conducted directly before and after the sharp reactivity suppression at $\varphi = 1.53$. The α -radical remains the most abundant fuel radical, but the importance of β -radical becomes comparable and the underlying reactions are different. Again, the fuel is consumed through H-abstraction reactions mainly by OH radicals but also by HO₂, CH₃, H, and O. Under these conditions, the resulting fuel radicals

predominantly undergo β -scission accompanied by ring opening. The newly formed radicals can then undergo a second β -scission or isomerization. However, as previously mentioned, an isomerization must be sufficiently favorable to compete with β -scission. This is the case for the primary n-butanal radical (c3h6cho-4) formed from the ring-opening of the fuel α -radical. Indeed, this radical can undergo a favorable isomerization via internal H-transfer, involving a five-membered transition state and the transfer of an aldehydic H, leading to the formation of the acyl radical (nc3h7co) of n-butanal. The nc3h7co radical totally decomposes through α -scission (decarbonylation) to form a 1-propyl radical, which dominantly decomposes through β -scission into ethylene and a methyl radical. Therefore, the most important reaction pathway of the favored fuel α -radicals produces methyl radicals, highlighting the crucial role of their reactions in determining the global reactivity under the present conditions and explaining why such reactions previously appeared among the most sensitive under same conditions. Moreover, the 1-propyl radical can still add to O₂ before either eliminating an HO₂ radical to form propene or isomerizing and then losing OH to form a cyclic ether: mostly methyloxirane, with only a small flux producing oxetane, in line with the experimental identification of the former and the absence of the latter. Furthermore, the high overprediction of methyloxirane, alongside the underestimation of ethylene by the present mechanism, might be explained – at least partially – by an overestimation in the ratio of the rate constant for O₂ addition to that for β -scission of the 1-propyl radical. This again supports, as previously observed for THP, the involvement of alkyl radicals in the oxidation of cyclic ethers and highlights the potential need to revisit their sub-mechanisms.

The second most favored pathway of THF leads to the formation of formaldehyde and allyl radicals from the fuel β -radical via two consecutive β -scission reactions, the first of which involves ring opening. The impact of this pathway on the overall reactivity is not less important than that of the most favored route previously discussed. In fact, the chemistry of the resonance-stabilized allyl radicals plays the most crucial role in sharply suppressing reactivity between 910 and 912 K. At 910 K, these radicals mainly react with HO₂ radicals to produce allyloxy and OH radicals, either directly or via an allyl-hydroperoxide intermediate. At 912 K, however, the recombination of allyl radicals into the relatively stable 1,5-hexadiene (a terminating step) becomes the predominant consumption pathway and explains the experimental identification of this compound. Although the two allyl+HO₂ reactions that promote reactivity still together account for a higher flux than that of allyl self-recombination, other inhibiting reactions must not be overlooked, particularly the reaction of allyl radicals with the highly abundant CH₃ radicals and their reaction with HO₂ radicals forming propene and O₂. Along with allyl self-recombination, these reactions dominate at 912 K and collectively lead to the sharp drop in reactivity observed between 910 and 912 K.

Figure 5.30b illustrates the main reactions consuming the CH₃ radicals formed via the most favored reaction pathway of THF under $\phi = 1.53$ at 910 and 912 K. At 910 K, just before the sharp reactivity drop, radical–radical reactions dominate, particularly those of CH₃ with HO₂, with allyl, and its self-recombination. At 912 K, radical–radical reactions are no longer dominant due to the depletion of the radical pool; instead, CH₃ primarily reacts with the fuel and with O₂, both of which strongly accumulate following the pronounced decline in reactivity.

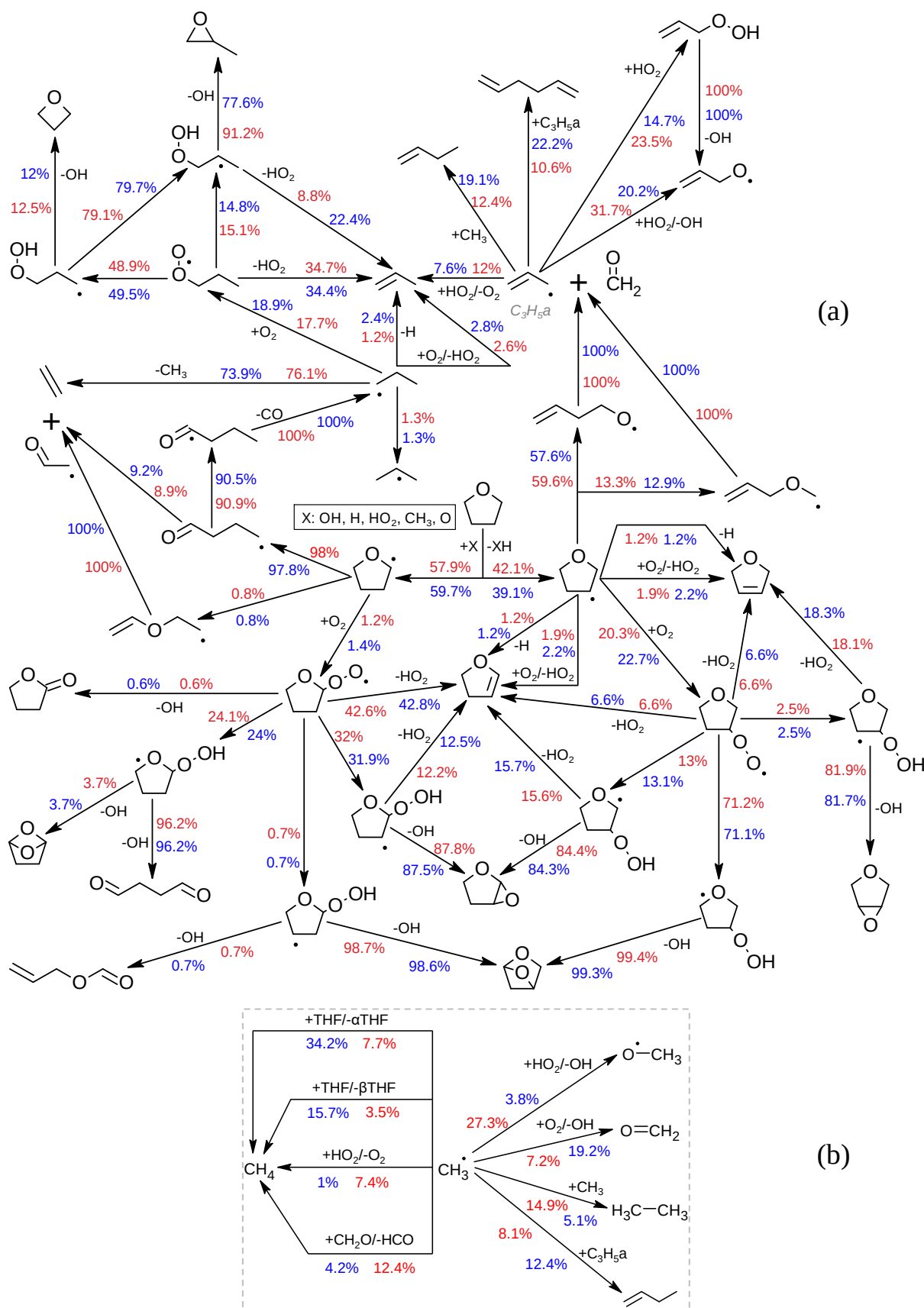


Figure 5.30: Reaction pathways (a), and main reactions of methyl radicals formed (b), during THF oxidation in a JSR at $p = 10$ bar and $\tau = 0.7$ s, with fluxes indicated at 910 K (red) and 912 K (blue) for the rich mixture ($\phi = 1.53$), as predicted by the present mechanism.

It is well known that the transition from the NTC to the HTR regime, and thus the intermediate-to-high temperature reactivity of a fuel, is mainly driven by the chain-branching decomposition of H_2O_2 , formed via HO_2 self-disproportionation, into two highly reactive OH radicals. At higher temperatures, this role is progressively taken over by H atoms reacting with O_2 molecules to produce O atoms and OH radicals. The dependence of fuel reactivity on HO_2 evolution as well as the effect of allyl and methyl radicals in the intermediate-to-high temperature range is illustrated in Figure 5.31a for THF and CPT (both of which exhibit a drop in reactivity at high temperatures), as well as for THP (which does not, and thus considered as a reference case).

Figure 5.31a shows that the HTR of THF and THP starts in parallel with the increase in HO_2 mole fraction around 720 K, exhibiting identical behavior for both fuels up to 770 K. Above this temperature, however, the HO_2 profile of THF begins to deviate from that of THP: the rate of HO_2 production becomes slower for THF, leading to a less pronounced reactivity. As a result, the HO_2 mole fraction for THF peaks earlier (≈ 850 K instead of 870 K), reaching a maximum nearly half that of THP, and then decreases more rapidly. This decrease results in a progressive slowdown of reactivity, which levels off into a plateau (and even decreases slightly) before undergoing a sharp drop. Thereafter, the reactivity continues to decrease slightly before increasing again as HO_2 mole fraction begins to increase again.

As with THP and other fuels that do not exhibit reactivity decline at high temperatures, the eventual decrease in the mole fraction of HO_2 radicals above a certain temperature in the case of both CPT and THF is due to their excessive consumption through self-disproportionation (Figure 5.31b). This occurs because such consumption is no longer sufficiently compensated by their production pathways: notably, the reactions of fuel radicals with O_2 yielding unsaturated compounds and HO_2 , which become increasingly dominated by β -scission channels.

The specificity of CPT lies in the enhanced consumption of HO_2 by the increasingly abundant allyl radicals formed via the ring-opening pathway of fuel radicals. At a certain stage, the mole fraction of allyl radicals becomes comparable to, or even exceeds, that of HO_2 (Figure 5.31a). Consequently, reactions between HO_2 and allyl radicals (primarily R3 and R4) compete and even dominate over HO_2 self-disproportionation (R1), supported by their higher rate constants (Figure 5.31c). However, while R1 leads to the production of two OH radicals via H_2O_2 , R3 and R4 each yields only one, thereby slowing down the overall reactivity. With the considerable accumulation of allyl radicals, their recombination (a terminating step) is promoted, resulting in the observed reactivity decline, as previously reported in [167]. This excessive self-recombination subsequently leads to a decrease in allyl mole fraction, allowing HO_2 to accumulate again and reinitiate the reactivity, as shown in Figure 5.31a.

Like CPT, THF leads to the formation of allyl radicals, but to a lesser extent, through the ring-opening pathway of its β -radicals. However, THF additionally exhibits a particular feature that makes its reactivity suppression stronger, sharper, and shifted toward lower temperatures. In fact, the presence of the oxygen atom in THF weakens the neighboring bonds, thereby facilitating the β -scission reactions of its radicals over their reactions with O_2 that yield HO_2 and explaining the lower HO_2 formation compared with CPT (as shown in Figure 5.31a). This also leads to another particularity for THF: the abundant formation of methyl radicals from the

favored α -radical pathway (absent in CPT, which has only one possible primary radical). Like allyl radicals, methyl radicals react with HO_2 (mainly via R2) and compete with R1.

Together, abundant allyl and methyl radicals react extensively with HO_2 and further accelerate its consumption (Figure 5.31b), explaining the deviation observed near 770 K in the HO_2 profile of THF compared to fuels that do not exhibit a high-temperature reactivity drop, such as THP, under same conditions (Figure 5.31a). Although allyl and methyl radicals are also produced during THP oxidation, their formation is less pronounced than in THF prior to its reactivity drop. Moreover, in the case of THP, the presence of an additional γ -radical (located far enough from the ether group to be considered similar to the CPT radical) promotes higher HO_2 formation, thereby reducing the relative impact of both allyl and methyl radicals and sustaining the increasing reactivity.

In parallel to the decrease of HO_2 mole fraction above 850 K, Figure 5.31a shows that, in the case of THF, methyl and allyl radicals continue to accumulate, with allyl radicals becoming more abundant than methyl. As a result, their inhibiting self- and cross-recombination reactions eventually reach a point where they dominate their reactions with HO_2 (particularly those promoting reactivity by producing OH radicals), leading to the abrupt reactivity decline. This dominance arises from the higher rate constants of these recombination reactions (Figure 5.31c), even though allyl and methyl radicals are still less abundant than HO_2 radicals. Conversely, the earlier dominance of R1 was due to the high abundance of HO_2 radicals, despite this reaction having the lowest rate constant among the compared reactions. As is well known, the rate of a chemical reaction depends on both its rate constant and the concentrations of its reactants.

It is also worth noting that the self-recombination of methyl radicals (R9), as well as their mutual recombination with allyl radicals (R8), involves a third body. Therefore, the accumulation of stable molecules accompanying the reactivity drop further promotes these reactions, thus contributing to the amplification of the decline.

After its brutal drop, THF reactivity increases again. In fact, the accumulation of the fuel resulting from this decline promotes its H-abstraction reactions by CH_3 radicals, which become the main pathway for CH_3 consumption after the drop, as previously shown in Figure 5.30b. This allows HO_2 to accumulate again and eventually react with allyl and methyl radicals to produce OH and reinitiate reactivity. Once HO_2 becomes sufficiently abundant, it can also undergo self-disproportionation again to form H_2O_2 and subsequently two OH radicals, thereby fully restoring the previous reactivity growth rate.

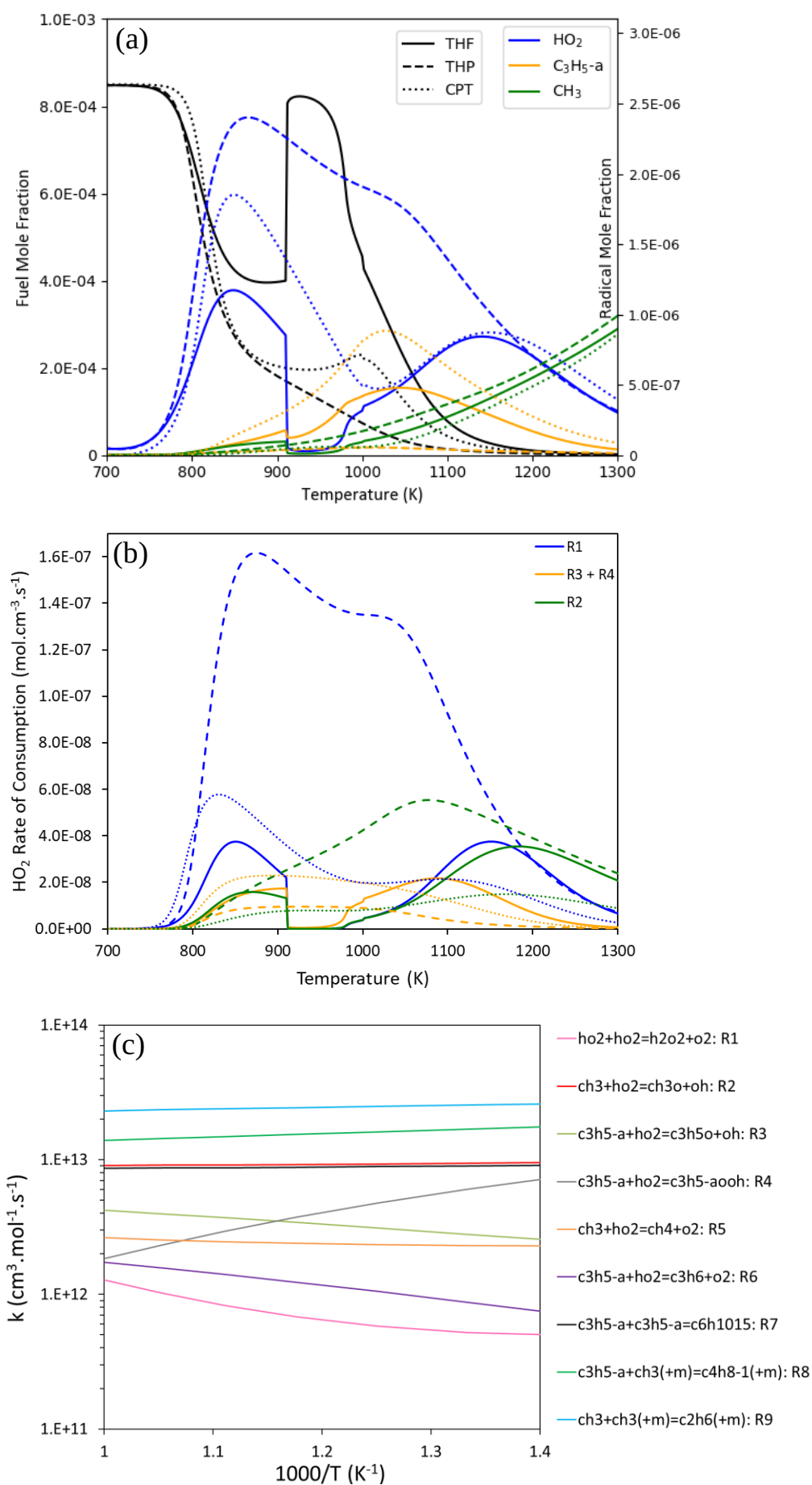


Figure 5.31: (a) Predicted mole fraction profiles of THF, THP, and CPT, as well as of three radicals (HO_2 , allyl, and methyl), during the oxidation of each fuel in a JSR at $X_0(\text{fuel}) = 850$ ppm, $p = 10$ bar, $\tau = 0.7$ s, and $\phi = 1.53$; (b) Rate of consumption of HO_2 by the main reactions during THF (solid lines), THP (dashed lines), and CPT (dotted lines) oxidation under same conditions; (c) Rate constants of the self and mutual reactions (R1–9) of the three key radicals.

5.3.6 Further Validation

The present mechanism is further evaluated against the additional JSR speciation data we obtained at 10 bar under the two following conditions: the stoichiometric case studied with 1000 ppm of THF, and the lean case ($\phi = 0.5$) with 5000 ppm of THF and an extended residence time of 2 s. Moreover, the mechanism is evaluated against atmospheric JSR speciation data from the literature [124] [133] at $\phi = 0.5$, $\tau = 2$ s, and $X_0(\text{fuel}) \approx 1\%$. Furthermore, our mechanism is tested against IDTs measured in shock tubes [120] [131]. Overall, the mechanism captures the general trends of these datasets reasonably well, although discrepancies remain in the absolute values. In order to provide a more comprehensive assessment, we compare the performance of the present mechanism in predicting our additional JSR data of THF against Fenard mechanism, the atmospheric JSR data against the mechanism of Sharma et al. [133], and the IDT data against the mechanism of Do et al. [131]. In fact, the mechanisms of Sharma and Do were specifically developed to simulate atmospheric speciation data and IDTs, respectively, and are both based on that of Fenard (same THF sub-mechanism). Finally, the validation of our mechanism is extended to CPT in **Appendix E**, using similar data as for THF.

5.3.6.1 High-pressure stoichiometric oxidation of 1000 ppm THF in a JSR

The stoichiometric oxidation of THF was investigated at 10 bar using a slightly higher initial fuel mole fraction (1000 ppm) than previously studied (850 ppm), with the same residence time (0.7 s). The experimental results are presented in Figure 5.32, together with the corresponding simulations obtained using our mechanism and that of Fenard. Both mechanisms reproduce well the fuel data in the weak LTR and NTC regimes, but the present mechanism predicts more accurately the broad non-reactive transition (670–780 K) from the NTC to the HTR. In contrast, Fenard mechanism anticipates the HTR onset (700 K instead of 780 K), resulting in a significant overprediction of reactivity up to 930 K. Our mechanism also overestimates reactivity at intermediate temperatures (up to 870 K) but then underpredicts reactivity up to 1050 K. Similar to its behavior under the near-stoichiometric condition ($\phi = 0.85$) studied with an initial fuel mole fraction of 850 ppm, each mechanism shows comparable trends for the different observed species, although discrepancies increase for some species and decrease for others. The most notable differences in the current condition, compared to the previous one, are the following:

- For Fenard mechanism: it shifts the profiles of most species toward lower temperatures, as with the fuel, leading to reduced predictive performance compared to previous data and less accurate predictions relative to our mechanism.
- For the present mechanism: it tends to underpredict the fuel-specific products, acetaldehyde, oxirane, and propane at high temperatures. Meanwhile, it shows better agreement for the remaining species, except for ethylene and methyloxirane, which continue to be highly under- and over-predicted, respectively.

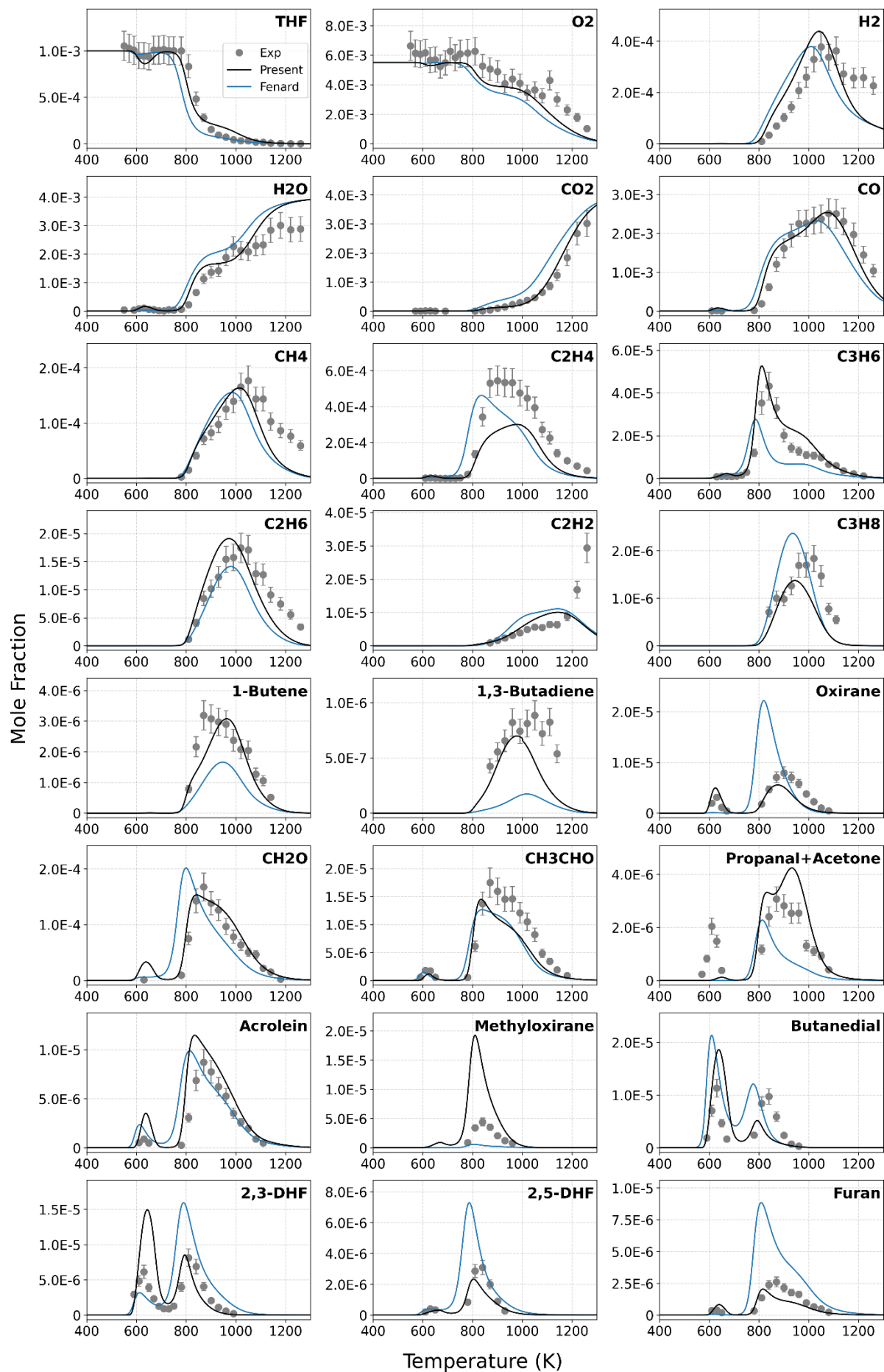


Figure 5.32: Experimental (symbols with error bars of $\pm 15\%$) and simulated (lines) mole fraction profiles of reactant, product, and intermediate species during THF oxidation in a JSR at $p = 10$ bar, $\tau = 0.7$ s, $X_0(\text{fuel}) = 1000$ ppm, and $\phi = 1$. Black: present work; Blue: Fenard et al. [127].

5.3.6.2 High-pressure JSR oxidation of 5000 ppm THF at lean conditions

The oxidation of THF was investigated at 10 bar using a higher initial fuel mole fraction (5000 ppm) than previously studied, with the residence time extended to 2 s, in order to enhance the weak cool flame of THF and enable a more detailed examination. This reactivity enhancement leads to the formation of formic acid and a new fuel-specific product not observed under the previously studied conditions): γ -butyrolactone (maximum ≈ 15 ppm in the LTR regime). More species were also detected in this case, but most could not be identified, either because several compounds were possible candidates or because their GC peaks were too small for reliable identification (see Fig. D2 in **Appendix D**). Figure 5.34 evaluates the ability of our mechanism to predict the main speciation results obtained, against that of Fenard mechanism.

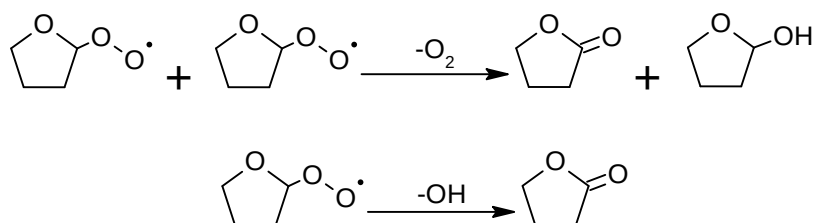


Figure 5.33: Formation reactions of γ -butyrolactone during THF oxidation as considered in the present mechanism.

The potential formation pathways of γ -butyrolactone considered in the present mechanism are shown in Figure 5.33. The mechanism predicts that γ -butyrolactone is formed during both the LTR and HTR regimes of THF, mainly through α -RO₂ self-disproportionation and OH elimination, respectively. Negligible under previously studied conditions, these reactions begin to contribute to the α -RO₂ flux due to the enhanced reactivity at the present condition.

Although it underpredicts intermediate-temperature reactivity between 700 and 800 K, the present mechanism reproduces the fuel profile more closely than that of Fenard, which significantly overestimates the fuel mole fraction in the LTR and NTC regimes. Formic acid is also better represented by the present mechanism. While γ -butyrolactone formation is entirely absent in Fenard mechanism predictions, our mechanism reproduces its trend despite underestimating mole fraction values. In addition to these two species not detected at previous conditions, the present mechanism captures the general trends of the main species more accurately and predicts their mole fractions more closely than Fenard mechanism. However, under the present condition, both mechanisms again fail to predict propanal/acetone formation at low temperatures and show more shortcomings compared to previous conditions:

- Fenard mechanism markedly overpredicts butanedial and ethylene.
- The present mechanism considerably overestimates formaldehyde at intermediate-to-high temperatures, and underpredicts oxirane and propene.

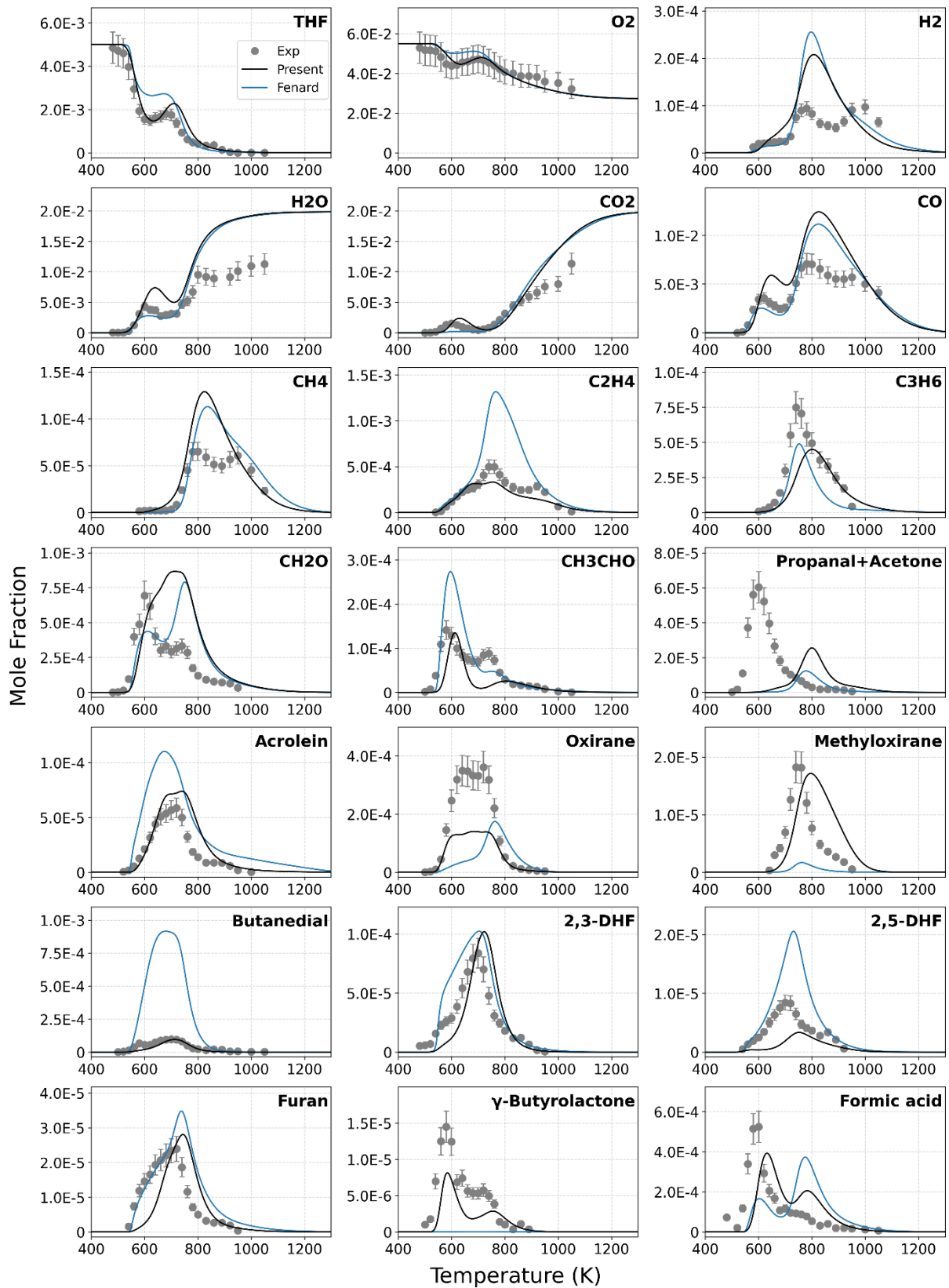


Figure 5.34: Experimental (symbols with error bars of $\pm 15\%$) and simulated (lines) mole fraction profiles of reactant, product, and intermediate species during THF oxidation in a JSR at $p = 10$ bar, $\tau = 2$ s, $X_{O(\text{fuel})} = 5000$ ppm, and $\phi = 0.5$. Black: present work; Blue: Fenard et al. [127].

Finally, it is worth noting that under the present condition, our mechanism provides a better overall representation of methyloxirane, though the profile is shifted toward higher temperatures, whereas it was highly overpredicted under previously studied conditions.

5.3.6.3 Atmospheric-pressure JSR oxidation of 1% THF at lean conditions

Atmospheric oxidation of THF was studied by Vanhove et al. [124] in a 95 cm³ JSR and by Sharma et al. [133] in a 32.5 cm³ JSR with the same residence time ($\tau = 2$ s) and equivalence ratio ($\phi = 0.5$) as in our preceding condition, but with approximately twice the initial fuel mole fraction (1% and 1.083%, respectively) and using He and Ar as diluents, respectively.

Using the THF sub-mechanism of Fenard et al. [127] combined with a different base mechanism, Sharma et al. [133] developed their own mechanism to reproduce their experimental data. Figure 5.35 presents a comparison between that mechanism and the present one in terms of their ability to capture the speciation data reported in the two mentioned studies.

Although the conditions in both studies are similar, notable discrepancies between their speciation data are observed, highlighting the need for further experimental investigations to clarify the underlying causes and provide more reliable data for kinetic modeling. While the experimental profiles for the fuel obtained in both cases generally agree within the respective uncertainty bands, most formed species display larger discrepancies. In particular, at high temperatures, the data of Sharma reveal a slowdown in reactivity, shown in the fuel profile and reflected in the profiles of most species with earlier consumption compared to the data of Vanhove.

Overall, the two tested mechanisms show similar or better agreement with Vanhove data than with those of Sharma, either in terms of absolute values, overall trends, or both. Both mechanisms perform similarly for CO, CO₂, CH₂O, and C₂H₆. The profile of the latter reported by Vanhove is well reproduced by both mechanisms, but Sharma reported unexpectedly considerable formation for this species at both low and high temperatures. As in the previously discussed conditions, the present mechanism underpredicts C₂H₄ formation at high temperatures, while Sharma mechanism captures it more closely. C₂H₂ and C₃H₆ profiles reported by Vanhove et al. are reasonably well predicted by the present mechanism, whereas that of Sharma shows closer agreement with their own experimental data for these two species. The low-temperature formation of propanal remains unclear for both the present mechanism and that of Sharma. Oxirane formation is also underestimated by both mechanisms at low temperatures.

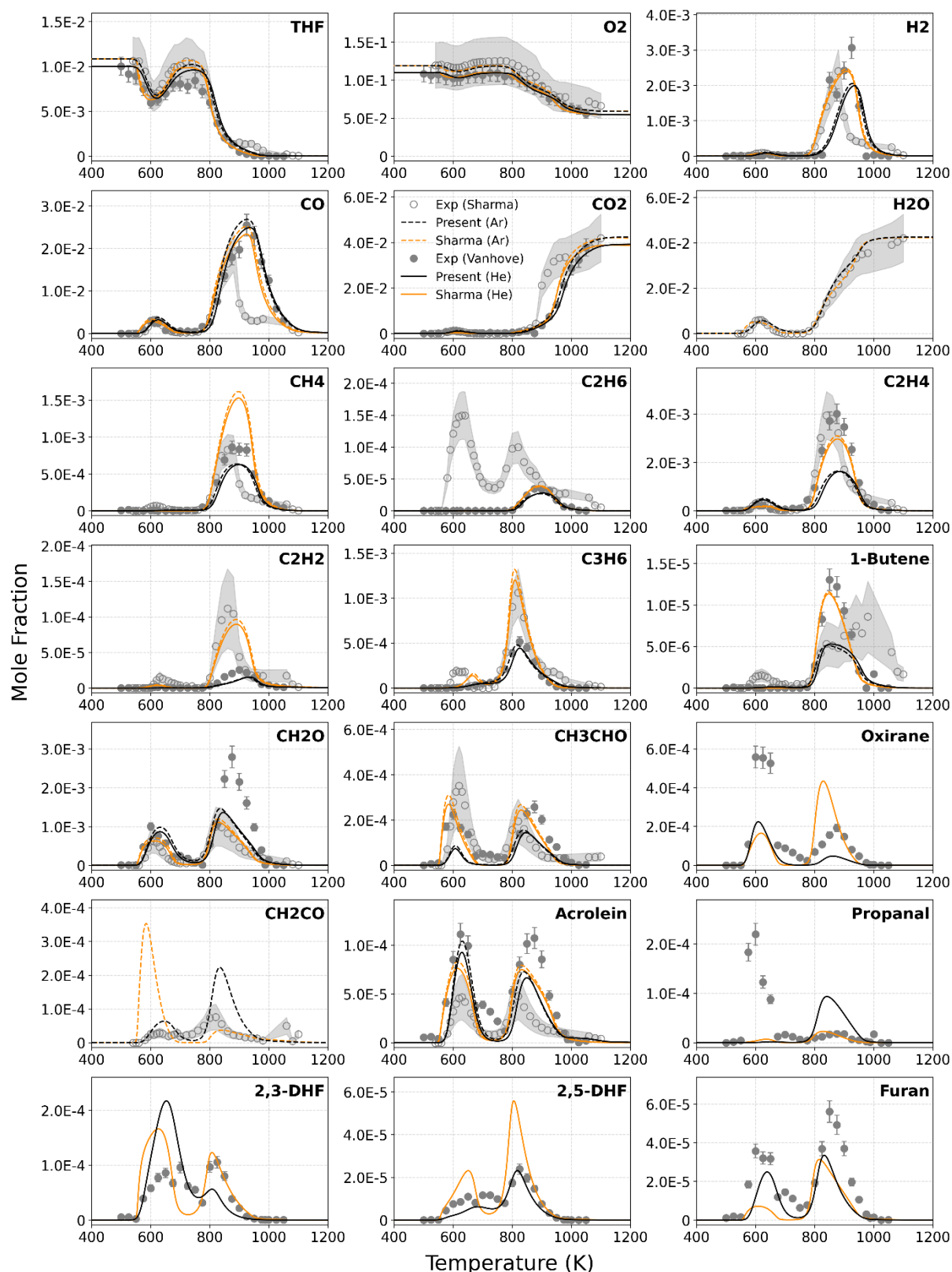


Figure 5.35: Experimental (symbols: Vanhove et al. [124] and Sharma et al. [133]) and simulated (lines) mole fraction profiles of reactant, product, and intermediate species during atmospheric JSR oxidation of $\approx 1\%$ THF at $\phi = 0.5$, $\tau = 2$ s, and using He and Ar as diluents, respectively. Vanhove data: filled symbols with error bars and solid lines; Sharma data: open symbols with shaded uncertainty bands and dashed lines.

5.3.6.4 Ignition of THF in shock tubes

For the ignition of THF in shock tubes [120,131], both the present mechanism and that of Do et al. [131] capture well the observed increase in reactivity, whether due to rising pressure, decreasing equivalence ratio, or increasing initial fuel mole fraction (Figure 5.36). However, the two mechanisms performed differently in representing the IDT values under the various simulated conditions.

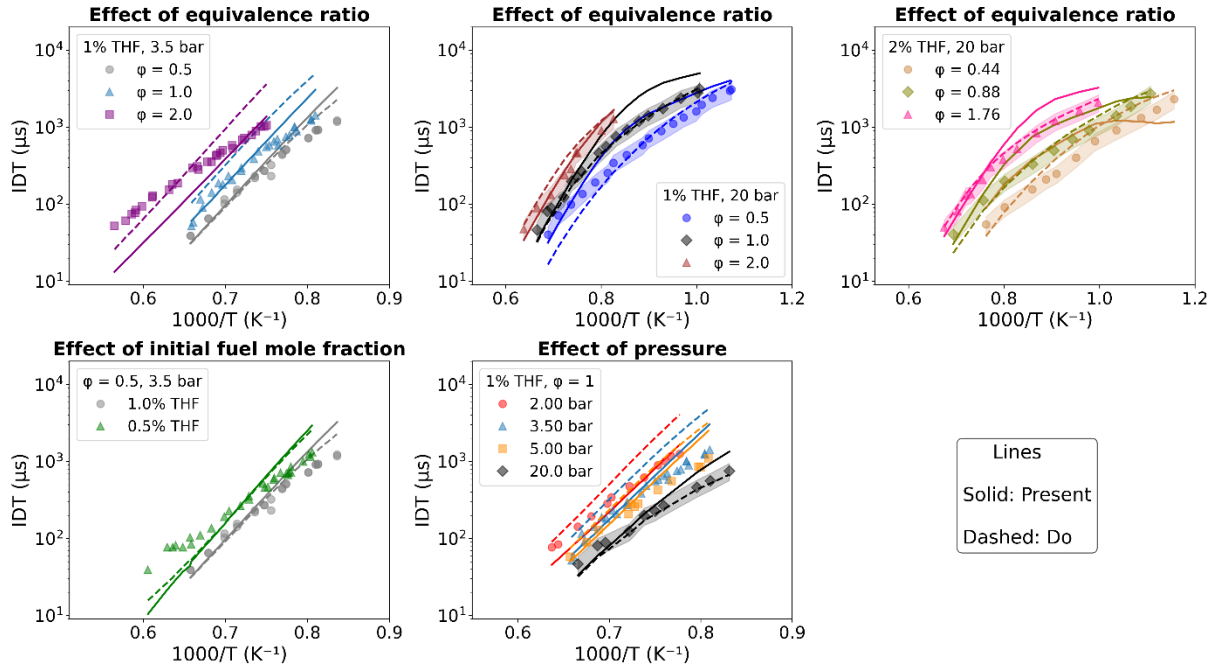


Figure 5.36: Ignition delay times (symbols: experimental; lines: simulated) of THF/O₂/Ar mixtures measured in shock tubes at 2, 3.5 and 5 bar (Dagaut et al. [120]) or 20 bar (Do et al. [131]). Solid lines: Present work; Dashed lines: Do et al. [131].

Overall, the mechanism of Do provides a better representation of the experimental data they reported compared to the present mechanism. However, it tends to underestimate IDTs under lean conditions above ≈ 1250 K, and to slightly overpredict them for the rich mixture at $\phi = 2$ above the same temperature. It also tends to overpredict IDTs below 1150 K under lean conditions. Our mechanism exhibits an even stronger overprediction in this region, which persists across stoichiometric and rich conditions, but shifts toward lower temperatures as the equivalence ratio increases. At the lowest tested temperatures under lean conditions, our mechanism additionally shows a plateau (or even a slight decrease in reactivity) that is not observed experimentally nor predicted by Do mechanism. This behavior is likely due to our mechanism shifting the NTC regime toward higher temperatures than experimentally expected. Nevertheless, the performance of the present mechanism improves with increasing equivalence ratio and/or temperature, eventually falling within the experimental uncertainty band and providing an even better match to the data than Do mechanism.

Despite its good performance in reproducing IDTs at 20 bar under stoichiometric conditions, Do mechanism highly overpredicts the full set of IDT data when the pressure decreases, although this overprediction becomes less pronounced with increasing temperature. Our mechanism also continues to overestimate IDTs at lower temperatures as the pressure decreases, but it shows a closer match to the data compared to Do mechanism in this range.

Furthermore, our mechanism well reproduces the data with increasing temperature, except at the lowest studied pressure (2 bar), where it underestimates them above ≈ 1400 K.

Both mechanisms provide similar simulations for the lean mixtures studied at 3.5 bar, even when the initial fuel mole fraction is decreased from 1% to 0.5%. They both show good agreement with the data in the intermediate temperature range, whereas they tend to deviate slightly from each other and to a greater extent from the data, showing overprediction at lower temperatures and underprediction at higher temperatures.

While we observed that our mechanism reproduces the IDTs reasonably well at 3.5 bar under lean and stoichiometric conditions (similarly to or better than Do mechanism, respectively), it significantly underpredicts them above ≈ 1400 K for the rich mixture. In contrast, Do mechanism agrees with the IDT data of this mixture only in the range 1500–1600 K, while it increasingly overpredicts them at lower temperatures and tends to underpredict them at higher temperatures.

5.3.7 Conclusion

In summary, the JSR oxidation of THF was studied at a high pressure of 10 bar and a residence time of 0.7 s over a wide range of conditions using both experimental and modeling approaches. The study covered the low- and high-temperature chemistry of THF, which exhibited the three typical reactivity zones, although with weak LTR and NTC behavior. In order to explore its cool flame in more detail, reactivity was enhanced by using a higher mole fraction of 5000 ppm and extending residence time to 2 s at $\phi = 0.5$. In addition to the combustion end-products and the common hydrocarbons and oxygenated species, five fuel-specific compounds were identified: 2,3-DHF, 2,5-DHF, furan, butanedial (the most important among them), and γ -butyrolactone (formed only after enhancing reactivity).

The present mechanism demonstrated strong performance in predicting the experimental data obtained in this work and, overall, outperformed the mechanism of Fenard et al. [127], which provide the only existing literature sub-mechanism of THF covering both LTR and HTR. However, some discrepancies remain leaving room for further refinement. Like for THP, these discrepancies can be attributed to uncertainties in the estimated rate constants of reactions and thermochemical data of species in the newly developed sub-mechanism of THF, for which advanced theoretical calculations are required to achieve better accuracy. Another source of discrepancies may be missing reactions specific to THF that have not yet been explored. The main discrepancies shown by the present mechanism are the overprediction of methyloxirane and the underestimation of ethylene at high temperatures. Also, as was the case for THP, the formation of propanal/acetone at low temperatures remains unclear by either mechanism.

Under the richest conditions studied, a novel behavior in THF oxidation was observed for the first time in this work, with no prior reports except for its analogous hydrocarbon, CPT. This behavior manifests as a progressive inhibition of HTR with increasing equivalence ratio. It begins with a progressive slowdown in reactivity growth, reaching a critical point ($\phi = 1.53$ under our conditions) where reactivity sharply decreases. With further increases in equivalence ratio, the reactivity decline becomes more gradual and less pronounced, resembling the NTC regime that separates the LTR and HTR. However, unlike NTC, it occurs at higher temperatures, effectively splitting the HTR regime into two distinct parts, and arises from

different reaction classes and their associated kinetics. Unlike Fenard mechanism, the present mechanism was able to capture the novel behavior of THF.

As expected, the α -radical of THF was identified as the most favored fuel radical regardless of the condition. Its reaction pathways reveal the involvement of 1-propyl radicals and elucidate the formation of species characteristic of their oxidation, such as methyloxirane. As previously observed for THP, this again illustrates the reciprocal contribution of cyclic ethers and alkanes to their respective oxidation, and indicates a potential need to revisit propane sub-mechanism, in addition to that of THF, when aiming to improve the present mechanism.

Although less favored than the α -radical, the significance of THF β -radical, and consequently its reaction pathways, increases with temperature to be comparable to that of the α -radical. These pathways lead to the formation of resonance-stabilized allyl radicals. As previously observed for CPT, the chemistry of these radicals plays the key role in the inhibition of HTR with increasing equivalence ratio, particularly through their self-recombination to produce 1,5-hexadiene. In the case of THF, this inhibition is even more pronounced than for CPT due to the additional formation of methyl radicals from α -radical pathways. Their self-recombination, as well as cross-recombination with allyl radicals, further contributes to the inhibition. Before allyl and methyl radicals accumulate sufficiently to undergo recombination, their primary sink is reactions with HO_2 . These reactions compete with HO_2 self-disproportionation, which produces H_2O_2 that subsequently decomposes into two OH radicals, the main driver of reactivity in the intermediate-to-high temperature range. Allyl and methyl reactions with HO_2 fall into two classes: (i) inhibiting reactivity by forming O_2 and a relatively stable product (propene and methane, respectively), and (ii) promoting reactivity by producing an alkoxy radical (allyloxy and methoxy, respectively) and one OH radical. Although the latter reactions enhance reactivity, their impact is weaker than that of HO_2 self-disproportionation, since only one OH is formed instead of two, leading to a slowdown in reactivity growth. Ultimately, as HO_2 is excessively consumed and allyl and methyl radicals continue to accumulate, their recombination reactions (favored by their higher rate constants) begin to dominate over HO_2 reactions, causing the observed drop in reactivity.

Finally, more data of THF were used to further validate the present mechanism, which demonstrated good performance in representing additional experimental results from this work compared to Fenard mechanism, or reported in the literature (atmospheric speciation data and IDTs) compared to the mechanisms originally established to reproduce them. Nevertheless, more accurate atmospheric speciation measurements and additional data (including laminar flame speeds), along with further improvement of the present mechanism, are still required in order to complete this validation and to fully understand the oxidation kinetics of THF.

5.4 Fuel Comparison

In this section, THP and THF are compared with linear ethers and/or analogous alkanes previously studied by our team under identical conditions.

We compare THP to the two symmetric linear ethers with one more and one fewer carbon atom, DPE [31] and DEE [29]. The comparison is performed under the same lean conditions and is shown in Figure 5.37a. The two linear ethers exhibit a strong LTR starting at temperatures as low as 450 K, with DEE being the most reactive (up to 75% conversion). In contrast, THP shows a weaker LTR (about 55% conversion), slightly less pronounced than that of DPE (around 60% conversion), starting around 570 K (at which the two linear ethers already reached their maximum reactivity) and thus totally shifted by ≈ 100 K toward higher temperatures. Similar to the LTR, DEE shows the strongest NTC behavior, bringing the fuel mole fraction almost back to its initial value. Meanwhile, THP and DPE exhibit similar NTC behavior, at the end of which each recovers about 400 ppm of the fuel converted during the LTR. The HTR onset is slightly shifted by 30 K toward higher temperatures for THP compared to DEE and DPE. The latter shows the strongest HTR, followed by DEE, and then THP.

In turn, THF is compared with both the linear ether having the same number of carbon atoms (DEE [29]) and its alkane analog (CPT [167]) at nearly identical stoichiometric conditions in Figure 5.37b. The alkane analog of DEE (n-pentane [58]) is also included in the comparison to further examine the effects of the ether group and the cyclic structure on the overall reactivity. Compared to DEE which shows a strong LTR (more than 60% conversion) between 450 and 540 K, THF exhibits a very weak LTR (less than 10% conversion) shifted significantly toward higher temperatures (extending from 590 to 650 K). Similar to THF, the LTR of n-pentane extends in the same temperature range but is stronger ($\approx 30\%$ conversion). Meanwhile, no LTR and consequently no NTC were detected for CPT. DEE, THF, and n-pentane display each an NTC behavior consistent with their respective LTR regimes, bringing the fuel mole fraction back to its initial value. While the transition from the NTC to the HTR regime is direct for n-pentane, it passes through a broad non-reactive range of about 90 K for DEE and 110 K for THF. However, the onset of HTR is shifted toward higher temperatures by 60 K for THF and by 80 K for n-pentane, compared to DEE. The HTR of CPT begins at the same temperature as that of THF (≈ 780 K), but it is as strong as that of DEE (and even slightly more pronounced), while THF shows the weakest reactivity (even weaker than that of n-pentane above 900 K). As a result, complete fuel consumption is achieved around 950 K for CPT and DEE, whereas for n-pentane and THF, it requires temperatures as high as 1020 and 1150 K, respectively.

THF is also compared to DEE [29], CPT [167], and n-pentane [58] under nearly identical rich conditions in Figure 5.37c. As the cool flame of THF is no longer observed at the current equivalence ratio ($\phi = 2$), the comparison focuses only on the HTR regime although DEE and n-pentane remain reactive at low temperatures. While DEE and CPT show similar HTR below 900 K, that of n-pentane is shifted toward high-temperatures. THF exhibits only very weak reactivity between 780 and 840 K, which then decreases directly (bringing THF mole fraction back to its initial value) before completely ceasing over a 60 K interval. Above 900 K, DEE and n-pentane continues to react without interruption until their total consumption around 1050 and 1100 K, respectively. In contrast, CPT becomes less reactive and then displays a sharp reactivity drop over a narrow 30 K window (950–980 K), during which its mole fraction increases from 200 to 600 ppm. Thereafter, CPT regains its reactivity and proceeds to complete

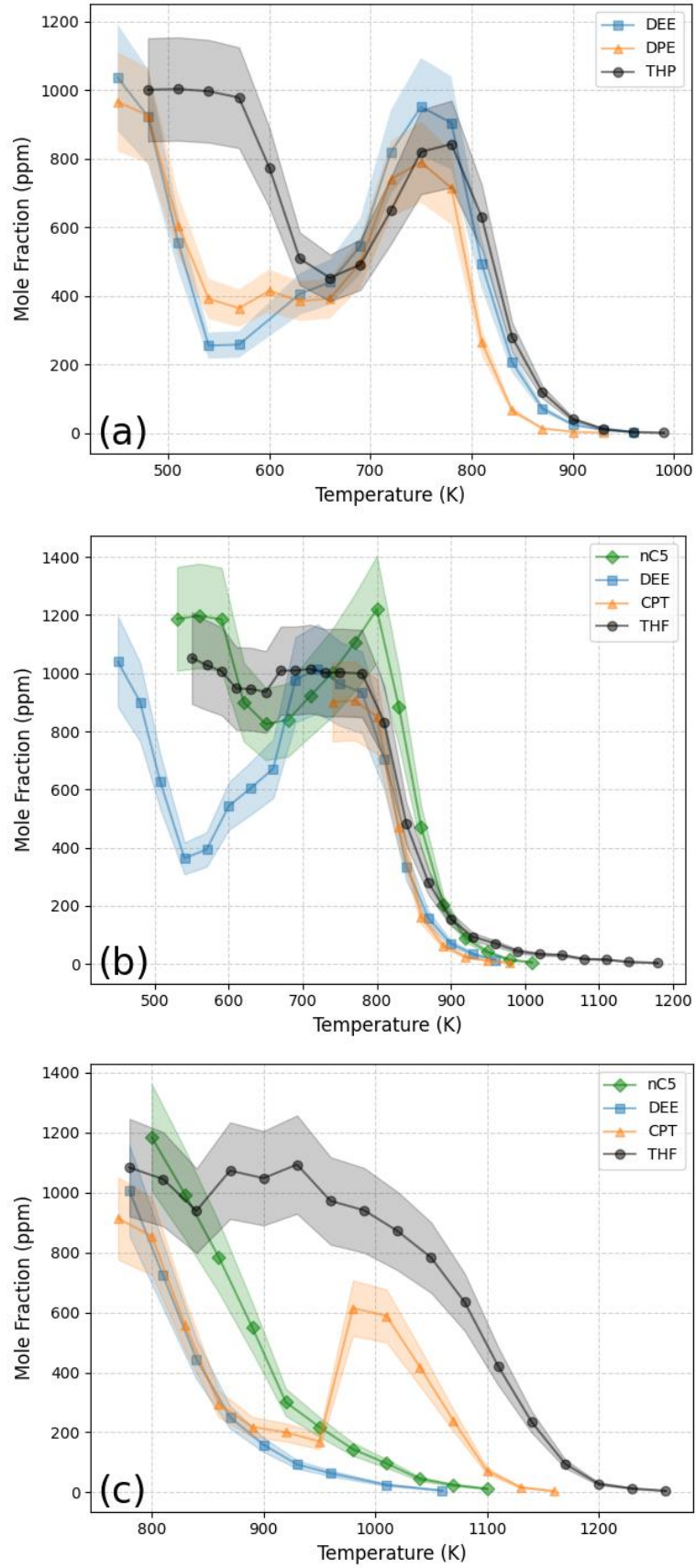


Figure 5.37: Comparison of fuel mole fraction profiles (with $\pm 15\%$ uncertainty) at $p = 10$ bar, $\tau = 0.7$ s, $X_0(\text{fuel}) \approx 1000$ ppm for: THF (present work), DEE [29], and DPE [31] at $\phi = 0.5$ (a); THF (present work), DEE [29], CPT [167], and n-pentane [58] (nC5) at $\phi = 1$ (b) and $\phi = 2$ (c).

consumption around 1150 K. Meanwhile, after regaining its reactivity near 950 K, THF continues to be consumed gradually until its complete depletion around 1250 K. While the observed reactivity suppression was previously discussed in the work of Al Rashidi et al. [167] for CPT, more detailed discussion is provided in the previous section of the present work for both THF and CPT. It has been attributed mainly to the complex chemistry of allyl radicals, which are formed through ring-opening pathways of fuel radicals, with additional characteristics specific to THF arising from its ether group.

After comparing their oxidation behavior and before discussing their blends in the next section, it is important to highlight the distinctions between THF and DEE, which explain their reactivity differences relative to each other and to their alkane analogs. Figure 5.38 compares the BDEs of the various bonds in these fuels.

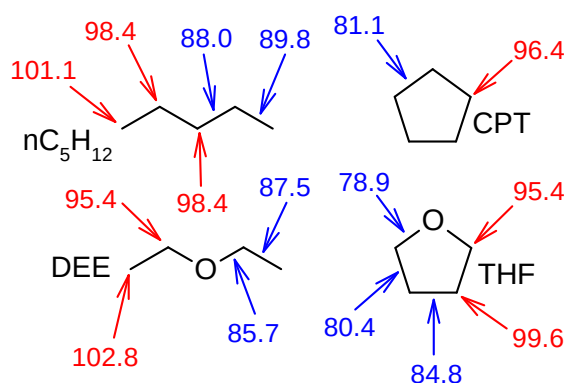


Figure 5.38: BDEs (in kcal/mol) calculated for C–H bonds (shown in red) and for C–C and C–O bonds (shown in blue) in n-pentane, CPT, DEE, and THF, based on thermochemical data obtained using the RMG group additivity method [139].

DEE versus n-Pentane

The presence of an oxygen atom in DEE weakens the adjacent (α) C–H bonds by 3 kcal/mol but strengthens the β C–H bonds by 1.7 kcal/mol. This not only makes the α site more favorable compared to its counterpart in n-pentane, but also much more so than the β site, thereby markedly enhancing the LTR; both by initiating it at lower temperatures and by increasing its intensity. This additionally explains the observed enhancement of the LTR of n-pentane by DEE in their blend studied by Tran et al. [168]. Although the C–O and C–C bonds in DEE are also weaker than their counterparts in n-pentane by 2.3 kcal/mol, β -scissions of DEE radicals (especially α -radicals) remain largely uncompetitive with the low-temperature pathways in the LTR temperature range. In contrast, the weakness of these bonds makes β -scissions more important at lower temperatures compared to n-pentane, leading to the observed shift of DEE HTR toward lower temperatures.

THF versus CPT

Unlike CPT, THF is reactive at low temperatures. This suggests that, similar to the stronger LTR observed for DEE compared to n-pentane, the presence of oxygen in THF enhances LTR relative to its alkane analog. This enhancement can be attributed to the weaker α C–H bonds (by 1 kcal/mol) compared to CPT, making the α site more favorable. In addition, β C–H bonds

in THF are stronger by 3.2 kcal/mol relative to CPT, further favoring H-abstraction at the α site and thus reinforcing the LTR. However, the very weak C–O and adjacent C–C bonds in THF facilitate ring opening, which accounts for its relatively weak LTR and NTC compared to typical n-alkanes such as n-pentane under same conditions. Although these bonds are even weaker than the corresponding C–C bonds in CPT, they do not shift the HTR of THF toward lower temperatures; rather, they shift it toward higher temperatures since they promote inhibiting reactions (an effect that becomes more pronounced with increasing equivalence ratio), as discussed previously.

THF versus DEE

Compared to THF, DEE exhibits not only stronger LTR but also beginning at lower temperatures under same conditions. This suggests that the strong tendency for ring opening in THF (as indicated by the weaker BDEs of C–O and C–C bonds in Figure 5.38) reduces the LTR-enhancing effect of oxygen atom relative to DEE, even though in both ethers the oxygen atom weakens the neighboring bonds. Moreover, although the α C–H bonds have the same BDE in both ethers, the β C–H bond in DEE (primary) is about 3 kcal/mol stronger than that in THF (secondary). Consequently, the α -radical is relatively more favored in DEE than in THF, further enhancing the LTR of the former compared to the latter.

While the BDE comparison provides valuable insights into the reactivity differences between fuels, more targeted investigations are needed to confirm and expand upon these findings, similar to the studies of Rotavera et al. [107] and Davis et al. [110], which compared specific features between THP and CHX. For instance, such investigations could extend to THF the observations made for THP in those studies: its relatively low propensity to form KHPs and high tendency to promote pathways that compete with the chain-branching channels at low temperatures.

5.5 Ether Blends

We previously observed and explained the weak LTR of THF compared to other fuels under similar conditions, and we further investigated its JSR oxidation using a high initial fuel mole fraction (5000 ppm) and an extended residence time (2 s) in order to enhance this reactivity and explore it in more detail. The same objective can be achieved through another approach that can be inferred from the preceding section: adding a linear ether with a strong LTR, such as DEE, to the weakly reactive THF. This not only enhances and triggers the reactivity of THF at lower temperatures but also allows, for the first time, the study of the interaction between the chemistry of a linear and a cyclic ether, along with the reaction pathways of the radicals produced during such oxidation, which are rarely studied in detail at low temperatures.

Figure 5.39 illustrates the effect of DEE addition on THF oxidation. Adding DEE to THF shifts the LTR onset of THF by 50 K, from 590 to 540 K, for the blend with 230 ppm DEE (B1), and by even more (80 K) for the two other blends, B2 and B3, with 530 and 830 ppm DEE, respectively. Additionally, the LTR of THF – originally showing less than 10% conversion – becomes more pronounced as the proportion of DEE in the blend increases. Consequently, THF conversion during its LTR increases progressively, from 25% in B1 to 35% in B2 and 45% in B3. Thereafter, as observed for neat THF (B0), the blends exhibit an NTC behavior that restores THF mole fraction to nearly its initial value of 1000 ppm, followed by an HTR regime slightly shifted toward lower temperatures.

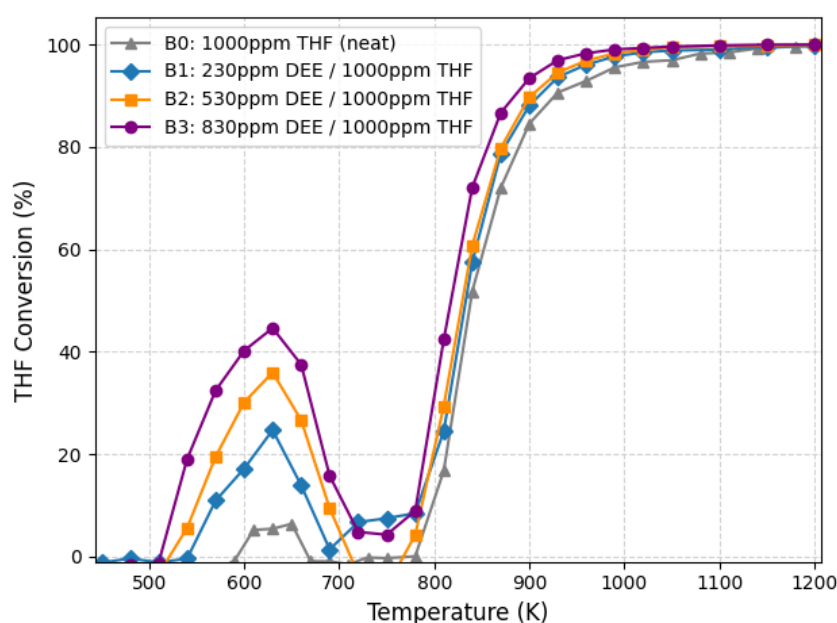


Figure 5.39: Conversion of THF as a function of temperature during its JSR oxidation, as neat fuel (B0) or blended with DEE (B1, B2, and B3), studied at $p = 10$ bar, $\tau = 0.7$ s, and $\phi = 1$ (lines are added to represent the trend).

The enhancement in overall reactivity, observed when increasing the proportion of DEE in the blend, is reflected in the mole fraction profiles of the various species formed with a corresponding increase in their production, as shown in Figure 5.40. These species can be classified into three distinct groups: those specific to THF (2,3-DHF, 2,5-DHF, butanedial, and γ -butyrolactone), those specific to DEE (2-methyl-1,3-dioxolane, ethanol, acetic acid, and traces of ethyl vinyl ether), and those in common to both (all remaining). While 2-methyl-1,3-

dioxolane is observed even in the blend with the lowest DEE proportion, the other DEE-specific products start to appear as the DEE proportion increases further. On the other hand, the THF specific-product, γ -butyrolactone, is only detected in the most reactive blend and in very small amounts (1–2 ppm maximum), in line with its previous absence in all neat THF experiments except when reactivity was enhanced by increasing the initial fuel mole fraction to 5000 ppm and extending the residence time to 2 s. Hence, this species can be regarded as a characteristic marker of THF reactivity enhancement.

As noted in **Chapter 4**, our previously developed DEE sub-mechanism [29] was integrated into the present mechanism in order to enable simulations of DEE/THF blends. Cross-reactions between the primary (R) and peroxy (RO₂) radicals of both DEE and THF were taken into account, with rate constants estimated using RMG [139] or by analogy with similar reactions in the mechanism (see Table B3 in **Appendix B**). The simulations performed with the resulting mechanism are compared with the corresponding experimental data in Figure 5.40.

The present mechanism predicts reasonably well the reactivity of THF across the blends and the general trends of the various species observed, as shown in Figure 5.40. However, it presents discrepancies in the absolute values that need further investigation. Notably, it slightly anticipates the reactivity onset, leading to an overestimation of LTR – particularly for DEE – which is clearly reflected in the profiles of certain major DEE-derived species, such as acetaldehyde. Thereafter, the mechanism accurately reproduces the NTC regime of both fuels. Although our mechanism overpredicts then the first phase of HTR (at intermediate temperatures below ≈ 850 K), this overestimation becomes less pronounced as the DEE proportion in the blend increases. Above this temperature, the mechanism continues to slightly underpredict reactivity in all blends, as it does for neat THF.

Also, the following patterns can be noticed for the intermediate-to-high temperature range:

- C₂H₄ formation continues to be underpredicted, and that of methyloxirane continues to be overpredicted.
- Although the mechanism continues to overpredict acrolein formation, it shows comparable simulations within this range across all blends. This is consistent with the experimental observation that, unlike at low temperatures, DEE addition has almost no effect on acrolein production at higher temperatures.
- Our mechanism predicts nearly identical profiles of propene across all blends, whereas experiments indicate a slight increase in its formation with rising DEE amount (its peak is increased by less than 20 ppm between B0 and B3). Consequently, the profile is best captured for the blend with the highest DEE fraction (B3), while overprediction persists between 870 and 1050 K across blends (as in neat THF) in line with the slight overestimation of fuel mole fraction in this interval. This behavior likely arises from the reactivity-inhibiting reaction of allyl with HO₂ radicals yielding O₂ and propene, whose impact under stoichiometric conditions appears to be slightly overpredicted by the present mechanism.

For the highest tested temperatures, the following patterns can be observed:

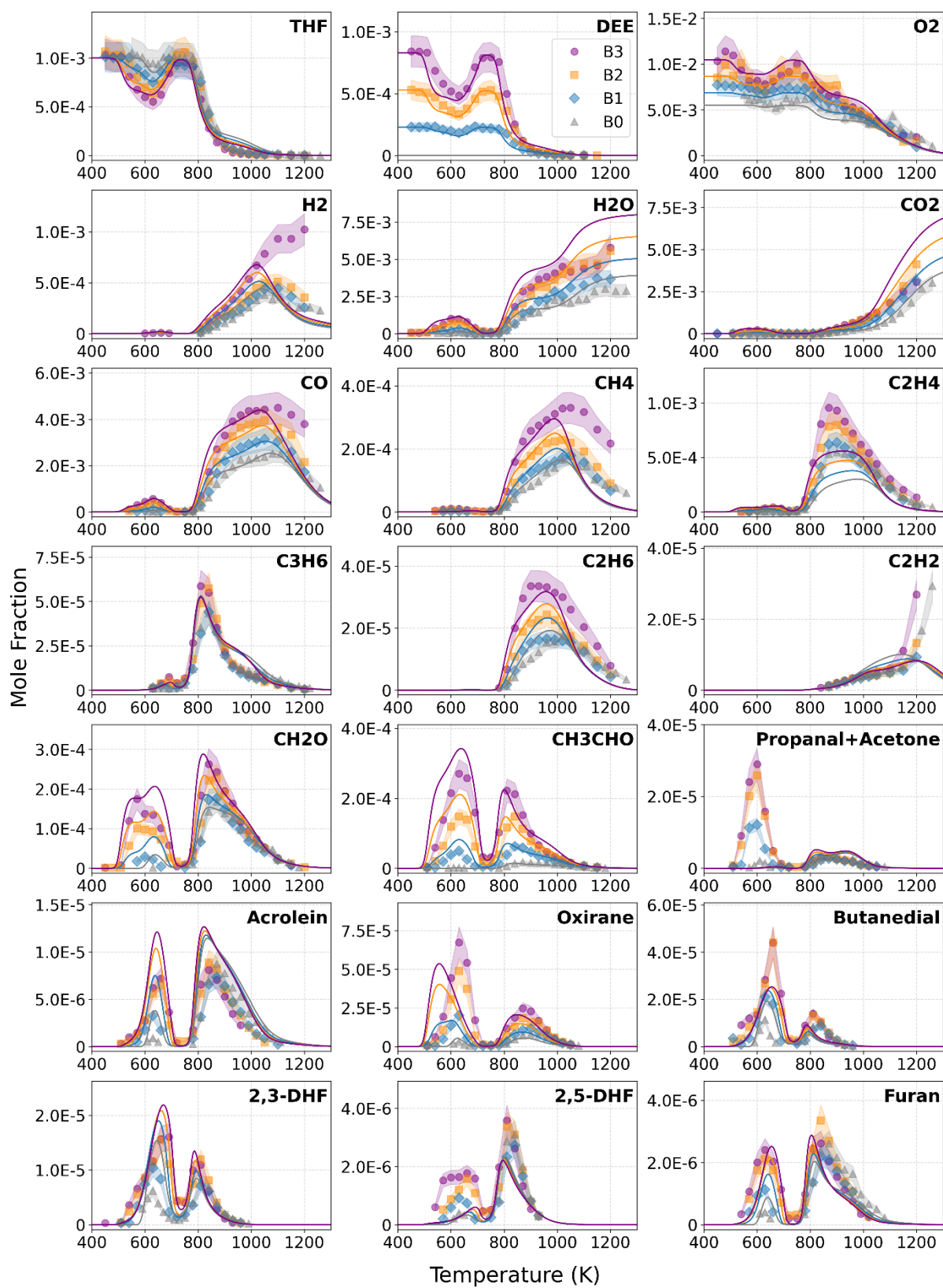
- The present mechanism tends to underpredict H_2 , CO , and light hydrocarbons, while it tends to overestimate H_2O and CO_2 .
- H_2 formation reaches much higher levels in B3 compared to the other blends with lower DEE proportions and, unlike them, continues to rise even above 1100 K (a behavior not captured by the mechanism).
- For acetylene, the mechanism predicts earlier consumption than experimentally observed across all blends, as is also the case for neat THF.

In order to identify the reactions driving the low temperature reactivity of THF, particularly those enhanced by DEE addition, a reaction pathway analysis (Figure 5.41) was carried out using the present mechanism. It was performed for the neat THF reference case (B0) at 605 K, corresponding to about half of the maximum THF conversion in the low temperature reactivity regime, and for the blend with the highest DEE content (B3) both at the same temperature and at the temperature giving the same relative THF conversion level (520 K).

Figure 5.41 shows that both ethers are mainly consumed via H-abstraction by OH radicals, and their resulting primary radicals proceed through the typical LTR chain-branching sequence: first addition to O_2 , isomerization to QOOH, second addition to O_2 , then formation and decomposition of ketohydroperoxides. Competing chain-propagating pathways, such as QOOH decomposition, gain importance with increasing temperature.

By triggering THF reactivity at lower temperatures, adding DEE strongly promotes an otherwise quasi-latent pathway: the self-disproportionation reaction of $\alpha\text{-RO}_2$ radicals derived from THF, leading to the formation of $\alpha\text{-RO}$ radicals. These radicals then undergo two consecutive β -scissions (the first accompanied by ring opening) to yield formaldehyde and propanal-3-yl radicals. Thus, the low-temperature chemistry of the latter becomes the main reactivity driver. The reactivity initiation at lower temperatures by DEE addition also suppresses the less reactive chain-propagating pathways followed by THF (e.g., QOOH decomposition into butanedial) in favor of chain-branching channels, thereby further enhancing its LTR.

Figure 5.41 also indicates that the main low-temperature pathway of DEE forms acetaldehyde and CH_3CO_2 radicals. These radicals then decompose into CO_2 and CH_3 radicals, which primarily react with O_2 to form CH_3O_2 radicals. By abundantly generating these radicals, DEE promotes their cross-disproportionation with $\alpha\text{-RO}_2$ radicals of THF. Finally, a minor contribution to the overall disproportionation flux of $\alpha\text{-RO}_2$ radicals of THF arises from their cross-reaction with the $\alpha\text{-RO}_2$ radicals of DEE. The high importance of disproportionation pathways for THF compared to DEE can be attributed to the much weaker C–O bond in THF, which facilitates the ring opening of its $\alpha\text{-RO}$ radicals formed via these pathways.



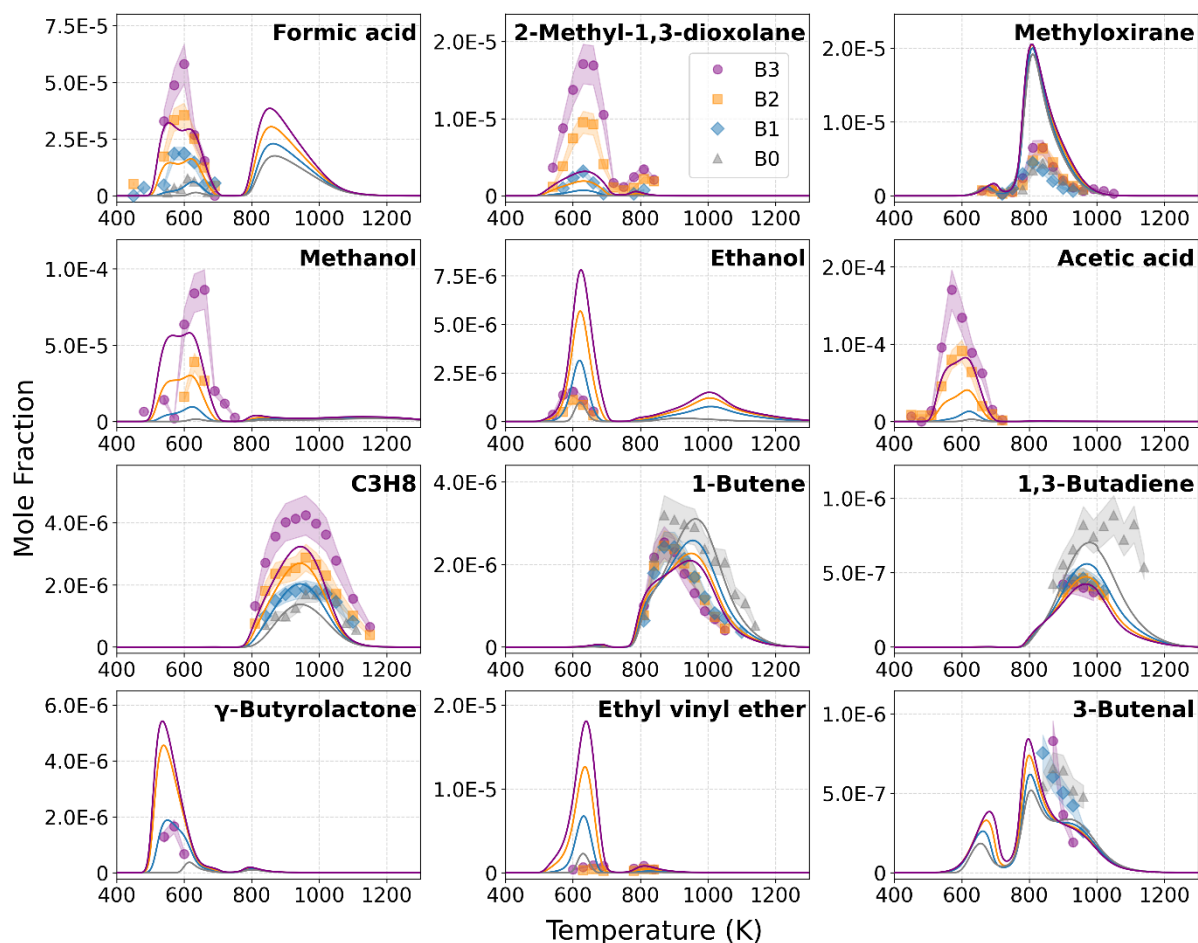


Figure 5.40: Experimental (symbols with shaded uncertainty bands of $\pm 15\%$) and simulated (lines) mole fraction profiles of reactant, product, and intermediate species during the oxidation of 1000 ppm THF – neat (B0) or blended with 230, 530, and 830 ppm DEE (B1, B2, and B3, respectively) – at $p = 10$ bar, $\tau = 0.7$ s, and $\phi = 1$.

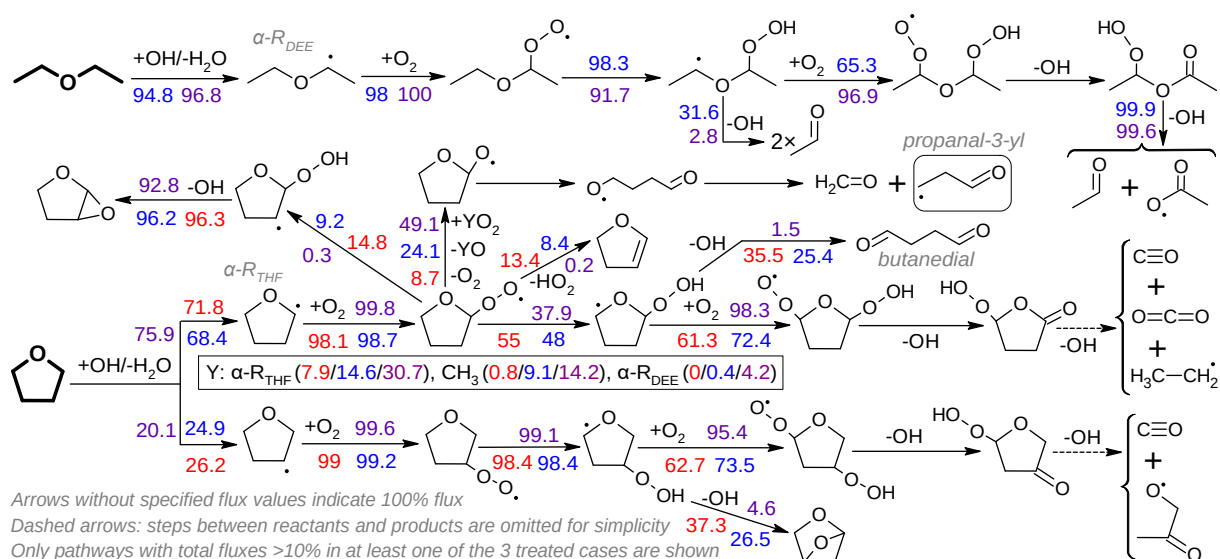


Figure 5.41 Main reaction pathways with fluxes (in %) for THF during its neat oxidation at 605 K (red), and for THF and DEE during the oxidation of their blend B3 at 605 K (blue) and 520 K (purple).

6 Conclusions and Perspectives

This work is an extension of the ongoing efforts of our team at ICARE laboratory to elucidate the oxidation pathways of ethers, the most recent of which was the thesis of Giorgia Cenedese [169], who focused on the study of linear ethers from different perspectives. As a possible continuation of her work, Cenedese pointed to cyclic ethers, which are the main subject of the present study.

This thesis is the result of three years of research on the gas-phase oxidation kinetics of cyclic ethers and their blends with linear ethers. Both classes of ethers can be produced from biomass and are considered promising biofuel candidates, as they have the potential to reduce emissions, improve combustion efficiency, and remain compatible with current engine technologies. Therefore, the understanding of their combustion behavior is of paramount importance. While linear ethers have been extensively studied in recent years by our team and others, research on cyclic ethers has remained relatively limited, and no studies have yet addressed blends of the two ether classes. Thus, this work focuses on the experimental investigation and kinetic modeling of the high-pressure oxidation of two cyclic ethers, THP and THF, the latter studied either in its pure form and blended with DEE. The aim is to thoroughly exploring the oxidation of cyclic ethers and the effect of adding a linear ether on this oxidation.

The experimental setup selected for this study is the JSR, which enables the measurement of mole fractions of reactants, products, and intermediate species involved in the gas-phase oxidation of the studied fuels. In parallel, a kinetic model was developed and used to simulate the experimental results obtained in this work. In addition, the core mechanism was revisited and updated to improve and validate its performance against novel and previous datasets of methanol and ethanol, in comparison with other efficient mechanisms.

For both cyclic ethers, THP and THF, the three classical zones of reactivity were identified, with the low-temperature oxidation resembling that of n-alkanes more closely than that of linear ethers, which begins at much lower temperatures under the same conditions, in line with their strong potential as cetane-improver additives. This difference supports the idea that blending linear and cyclic ethers constitutes a promising solution compatible with existing CI engines, although their characterization is still in progress.

With increasing equivalence ratio, the reactivity regimes of both THP and THF become less pronounced. Additionally, THF displays weaker reactivity regimes than THP under similar conditions. At high temperatures, while THP shows noticeably weaker reactivity under highly rich conditions compared to lower equivalence ratios, THF exhibits a novel and more pronounced reactivity-inhibition behavior that intensifies progressively with equivalence ratio: even moderately rich conditions are sufficient to almost completely suppress its intermediate-to high-temperature reactivity. Whereas, for THF, reactivity drops over a certain temperature range, first sharply and then more gradually with increasing equivalence ratio, it only slows down without ceasing or declining for the richest THP mixture. Different recombination reactions are responsible for such reactivity inhibitions. In the case of THP, the slowdown in reactivity is mainly due to the recombination of ethyl radicals. In contrast, for THF, the chemistry of allyl radicals plays the key role in the newly observed behavior, particularly through their self-recombination. The abundantly formed methyl radicals also contribute in the case of THF: their self-recombination, as well as recombination with allyl radicals, further amplifies this behavior.

The species formed during the oxidation of THP and THF can be classified into three groups. The first group includes products specific to THP: 3,4- and 3,6-dihydro-2H-pyran, pentanedial, and tetrahydropyran-2-one. The second group consists of products specific to THF: 2,3- and 2,5-dihydrofuran, butanedial, and γ -butyrolactone. The third group comprises products common to both cyclic ethers: combustion end-products, syngas components, and typical hydrocarbons and oxygenates.

The developed mechanism shows reasonable agreement with the present speciation data for both cyclic ethers. Also, it accurately captures both the slowdown in the high-temperature reactivity of THP and the sharp suppression in that of THF under rich conditions. In contrast, none of the mechanisms from the literature were able to reproduce these behaviors.

In addition to the common methyl and ethyl radicals, other alkyl radicals play a crucial role in the oxidation of cyclic ethers: 1-propyl radicals in the case of THF, and both 1-propyl and 1-butyl radicals in the case of THP. These radicals are reflected in cyclic ether oxidation through the formation of their characteristic products, including cyclic ethers that are themselves key intermediates in alkane oxidation; e.g.: methyloxirane and THF, derived from the primary radicals of propane and n-butane, respectively. Therefore, this thesis demonstrates the reciprocal importance of cyclic ethers and alkanes in each other's oxidation.

The present mechanism was further validated for both THP and THF against additional speciation data and ignition delay times measured in shock tubes. It is worth noting that these speciation data include atmospheric-pressure JSR measurements reported by different sources, which show notable and unexplained discrepancies despite having been obtained under the same conditions.

The effect of DEE addition on THF oxidation was investigated using three DEE/THF blends, differing only in their DEE content. Adding DEE to THF amplifies its reactivity and triggers it at lower temperatures. The enhancement in overall reactivity was reflected in the mole fraction profiles of the various species formed with a corresponding increase in their production. These species involve the oxidation products of THF, with additional compounds specific to DEE: 2-methyl-1,3-dioxolane, ethanol, acetic acid, and ethyl vinyl ether. The present mechanism, which combines our previously published DEE sub-mechanism [29] with the newly developed THF sub-mechanism, represents an important step toward establishing a robust DEE/THF mechanism. This mechanism reveals that DEE-induced initiation of THF reactivity at lower temperatures promotes self-disproportionation of THF α -peroxy radicals, a pathway that would otherwise remain quasi-inactive. Although less significant, chemical interactions between the two ethers also occur, manifesting mainly indirectly via cross-disproportionation of THF α peroxy radicals with CH_3O_2 , and only slightly via direct cross-disproportionation with DEE α -peroxy radicals.

In summary, this thesis provides an extensive JSR speciation dataset on the oxidation of two important cyclic ethers, THP and THF, covering a wide range of conditions that have not been investigated before. It also explores, for the first time, the effect of adding a linear ether (DEE) on the oxidation of a cyclic one (THF). Additionally, the current work presents a kinetic model, with an updated core mechanism, that performs satisfactorily in representing present and previous data for THP and THF (neat or blended with DEE), as well as for basic species such as methanol and ethanol. Nevertheless, several discrepancies remain, leaving room for improvement.

In order to achieve a better understanding of the kinetic behavior of cyclic and blended ethers, it is essential to further enhance the performance of the mechanism developed in the present work. While the rate constants estimated by analogy appear reasonable, they remain less accurate than those obtained from direct calculations. Moreover, thermochemical properties can be as important as kinetic parameters. Indeed, the group additivity method used in this work to determine them may have limitations, particularly for complex species involved in low-temperature chemistry.

For the future continuation of this study, from modeling and simulation perspectives, the possible steps include:

- Performing advanced theoretical calculations on both the rate constants of the main reactions and the thermodynamic data of the primary species in the sub-mechanisms developed as part of this work.
- Validating the present mechanism against additional data types that were not tested for THP and THF in this thesis, such as laminar flame speeds and ignition delay times measured in rapid compression machines.
- Reviewing the C₃–C₄ sub-mechanism of our mechanism, particularly by validating it against various experimental data for propane and n-butane, whose primary radicals play a significant role in the oxidation of the two studied cyclic ethers.
- Considering the implementation of additional DEE/THF cross-reactions as an attempt to enhance the predictive performance of the current mechanism for DEE/THF blends.

On the other hand, from an experimental perspective, the following steps can be envisaged:

- For the two cyclic ethers studied in this work (THP and THF): conducting atmospheric-pressure JSR experiments under the same conditions as those of existing literature datasets, given the discrepancies observed, in order to provide reliable data for kinetic model validation.
- For other cyclic ethers and analogous compounds: studying smaller cyclic ethers (such as oxetane), substituted cyclic ethers (such as 2-methyltetrahydrofuran), unsaturated cyclic ethers (such as furan), and other heterocyclic counterparts (such as pyrrolidine) to assess the effect of ring size, branching, unsaturation, and heteroatom type, respectively.
- For ether blends: explore rich conditions for DEE/THF blends to study the effect of adding DEE on the reactivity suppression exhibited by THF at high temperatures, and further extend the study of blends of cyclic and linear ethers to include mixtures of THP with DEE or DPE.

In light of the results presented in this thesis, cyclic and blended ethers show promising characteristics and interesting behaviors. The kinetic mechanism developed, together with the experimental data collected, represents a significant step toward a comprehensive understanding of the combustion of these potential biofuel candidates.

Résumé

Introduction

Contexte

L'énergie occupe une place essentielle dans notre vie quotidienne et dans le développement des sociétés modernes. La croissance démographique mondiale s'accompagne d'une augmentation de la demande énergétique. Aujourd'hui encore, le charbon, le pétrole et le gaz naturel constituent les principales sources d'énergie à l'échelle planétaire. Cependant, leur épuisement rapide et leurs conséquences environnementales majeures, notamment en matière de réchauffement climatique et de pollution atmosphérique, posent des défis considérables. Pour répondre à ces enjeux, le recours à des sources d'énergie renouvelables et plus propres s'impose progressivement comme une nécessité.

Le secteur des transports figure parmi les plus grands consommateurs d'énergie au monde, représentant près de 30% de la consommation totale. Cette forte demande s'explique par la croissance continue des déplacements de personnes et de marchandises. En Europe, et particulièrement en France, le transport constitue désormais le premier secteur consommateur d'énergie, devant l'industrie et le résidentiel, avec près d'un tiers de la consommation finale.

La majorité des véhicules en circulation repose encore sur des moteurs à combustion interne, alimentés par des carburants fossiles. Il convient de souligner qu'un grand nombre de ces véhicules continueront à circuler bien au-delà de 2050, ce qui complique la transition énergétique du secteur. C'est pourquoi de nombreuses politiques et réglementations ont été mises en place afin de réduire l'impact climatique du transport et d'atteindre l'objectif de neutralité carbone à l'horizon 2050.

Dans cette perspective, la substitution progressive des véhicules par des solutions à zéro émission apparaît indispensable. L'électrification des véhicules légers constitue une voie prometteuse, mais il est également crucial de développer des carburants alternatifs compatibles avec les moteurs existants. L'avenir énergétique du transport semble ainsi reposer sur une combinaison entre véhicules électriques et moteurs alimentés par des carburants à faible empreinte carbone.

Parmi ces alternatives, les biocarburants présentent plusieurs atouts. Lorsqu'ils sont produits à partir d'une biomasse renouvelable sur un cycle court, ils peuvent être considérés comme quasiment neutres en carbone. De plus, leur teneur en oxygène favorise une combustion plus complète, contribuant ainsi à réduire les émissions polluantes. Afin d'exploiter pleinement leur potentiel, il est essentiel de mieux comprendre leurs mécanismes de combustion, de manière à prévoir leur comportement dans les moteurs et à identifier les produits formés susceptibles d'avoir un impact sur l'environnement.

Objectifs

Les éthers constituent une famille de composés organiques susceptibles d'être utilisés comme biocarburants, et leur oxydation a fait l'objet de nombreuses études au cours des dernières

décennies. La majorité de ces travaux s'est concentrée sur les éthers à chaînes linéaires, tandis que la combustion des éthers cycliques demeure encore peu explorée. De plus, à notre connaissance, aucune étude n'a jusqu'à présent examiné les interactions entre ces deux familles d'éthers, notamment entre un éther linéaire fortement réactif à basse température et un éther cyclique présentant une faible réactivité dans les mêmes conditions.

Cette thèse vise à étudier la cinétique d'oxydation des éthers cycliques, en particulier le tétrahydropyrane (THP) et le tétrahydrofurane (THF), considérés seuls ou en mélange avec un éther linéaire, le diéthyl éther (DEE). L'ajout de ce dernier permet d'amplifier la réactivité des éthers cycliques à plus basse température, offrant ainsi la possibilité d'analyser en détail les interactions chimiques entre les deux types d'éthers. Ce travail cherche également à étudier les voies réactionnelles empruntées par les radicaux formés lors de l'oxydation, en particulier celles actives à basse température, encore rarement décrites dans la littérature. Les voies réactionnelles sont analysées grâce à l'identification expérimentale des espèces formées au cours de l'oxydation, complétée par une modélisation cinétique détaillée.

Ce projet repose sur une approche combinée, expérimentale et de modélisation. Ainsi, sur le plan expérimental, les études sont menées dans des réacteurs auto-agités par jets gazeux, permettant d'explorer un large domaine de conditions : des températures comprises entre 400 et 1300 K, des pressions de 1 à 10 bar, ainsi que des richesses et des temps de passage variés. Les réactifs, les produits et les espèces intermédiaires sont analysés par chromatographie en phase gazeuse et spectroscopie infrarouge à transformée de Fourier. Sur le volet modélisation, ce travail s'appuie sur les études antérieures menées par notre équipe. Dans ce travail, le mécanisme cinétique de base a d'abord été actualisé, puis de sous-mécanismes spécifiques relatifs aux éthers cycliques ont été développés et y ont été intégrés.

Revue de littérature

Mécanisme d'oxydation

L'oxydation des biocarburants oxygénés suit, dans ses grandes lignes, les mêmes mécanismes que celle des hydrocarbures, bien qu'elle puisse comporter également certaines réactions spécifiques liées à la présence d'atomes d'oxygène dans leurs molécules. De manière générale, cette oxydation présente trois régimes de réactivité distincts, en fonction de la température : la réactivité à basse température (LTR), la zone à coefficient de température négatif (NTC) et la réactivité à haute température (HTR).

À basse température ($T < \approx 650$ K), les réactions dominantes sont les additions de radicaux primaires du carburant sur les molécules d'oxygène, conduisant à la formation de radicaux peroxyliques (RO_2). Ces derniers subissent ensuite des isomérisations intramoléculaires (formation des QOOH) et des réactions de propagation donnant naissance à des espèces peroxydées, des hydroperoxydes ($ROOH$) et des carbonyl-hydroperoxydes (CHPs). Ces composés jouent un rôle clé dans l'apparition de la réactivité à basse température et dans le déclenchement de l'auto-inflammation. En raison de la faible énergie de liaison O–OH, ils se décomposent aisément, générant deux radicaux, dont l'un est le radical hydroxyle (OH), particulièrement réactif. Ces radicaux réagissent ensuite avec d'autres molécules de carburant, produisant de nouveaux radicaux dérivés. Dans le cas des CHPs, la décomposition libère un

radical OH supplémentaire. Ce processus de ramification dégénérée entraîne une augmentation exponentielle de la réactivité du système, due à la multiplication rapide du nombre de radicaux libres, en particulier des radicaux OH.

À température intermédiaire ($650\text{ K} < T < 770\text{ K}$), l'équilibre des réactions d'addition sur O_2 tend à s'inverser, tandis que d'autres voies réactionnelles deviennent prépondérantes. Les voies de propagation des radicaux QOOH (formation d'éther cyclique et formation d'une espèce insaturée et HO_2 ainsi que les décompositions par β -scission) deviennent des voies plus importantes que le branchement de basse température. Cette évolution des chemins réactionnels conduit à la région à coefficient de température négatif (NTC), caractérisée par une diminution de la réactivité lorsque la température augmente sur un certain intervalle.

Enfin, à haute température ($T > \approx 770\text{ K}$), la réactivité croît de nouveau, dominée cette fois par les réactions de β -scission et d'isomérisation des radicaux du carburant.

Éthers cycliques

Les éthers cycliques jouent un rôle important dans l'oxydation à basse température des hydrocarbures, en tant qu'intermédiaires réactionnels clés. Leurs voies de formation entrent en compétition avec les voies de ramification des chaînes caractéristiques de la chimie de basse température, contribuant ainsi à la zone NTC, qui marque la transition vers la chimie de haute température.

Par ailleurs, les éthers cycliques sont considérés comme des biocarburants de deuxième génération, produits à partir de la biomasse lignocellulosique, notamment via l'hydrolyse de la cellulose et de l'hémicellulose. Étant à la fois parmi les principaux candidats biocarburants dans ce domaine et dotés de structures cycliques particulièrement stables, seuls les éthers cycliques à cinq et six chaînons, en particulier le THP et le THF, sont étudiés dans le cadre de cette thèse.

La première étude consacrée à la combustion du THP remonte à 1991, menée par Leppard [\[102\]](#), qui a examiné son auto-inflammation à l'aide d'un moteur d'essai. Quelques années plus tard, Dagaut et al. [\[104\]](#) ont étudié son inflammation dans un tube à choc et son oxydation dans un réacteur auto-agité, sous hautes pressions et températures. Les flammes de THP ont ensuite été étudiées dans des brûleurs à flamme plate par Labbe et al. [\[105\]](#) et Tran et al. [\[106\]](#). Ce dernier a également étudié la pyrolyse de ce composé dans un réacteur tubulaire à écoulement piston, ainsi que son inflammation dans un tube à choc. Alors que ces premières études portaient principalement sur la réactivité du THP à haute température, les chemins réactionnels à basse température ont été ensuite précisés par Rotavera et al. [\[107\]](#), Chen et al. [\[108\]](#), Telfah et al. [\[109\]](#) et Davis et al. [\[110\]](#). Ces travaux ont ouvert la voie à des études plus récentes couvrant la cinétique détaillée du THP sur une large gamme de températures. Ces recherches ont été poursuivies dans des réacteurs auto-agités à pression élevée par notre équipe [\[113\]](#), ainsi qu'à pression atmosphérique par Wang et al. [\[114\]](#), Zou et al. [\[111\]](#) et Hartness et al. [\[112\]](#). Ces derniers ont également mesuré les délais d'auto-inflammation du THP à l'aide de machines à compression rapide.

L'oxydation en phase gazeuse du THF a été étudiée pour la première fois par Molera et al. [\[119\]](#) dans un réacteur statique. Par la suite, son auto-inflammation a été étudiée dans un moteur d'essai par Leppard [\[102\]](#), puis dans un tube à choc par Dagaut et al. [\[120\]](#), qui ont également

étudié son oxydation à haute pression et haute température dans un réacteur auto-agité. Les flammes de THF ont ensuite été étudiées dans des brûleurs à flamme plate par Kasper et al. [121] et Tran et al. [123], ces derniers ayant également conduit des études d'inflammation dans un tube à choc, similaires à celles réalisées pour le THP. Des recherches complémentaires, menées dans des tubes à choc sous diverses conditions, ont été rapportées par Uygun et al. [122] et Giri et al. [126]. Vanhove et al. [124] ont ensuite étendu ces travaux à des températures plus basses, en utilisant une machine à compression rapide et un réacteur auto-agité à pression atmosphérique. Les réactions initiales de l'oxydation du THF à basse température ont été examinées par Antonov et al. [125] et Telfah et al. [109]. Hansen et al. [128] ont identifié et quantifié les céto-hydroperoxydes formés lors de la flamme froide d'un mélange pauvre en THF, dans un réacteur auto-agité fonctionnant à pression quasi atmosphérique. Ces travaux ont été approfondis par Belhadj et al. [130], qui ont caractérisé, en plus des céto-hydroperoxydes, plusieurs produits spécifiques hautement oxygénés, formés dans des conditions de flamme froide à 10 atm. Par la suite, Do et al. [131] ont élargi l'étude de l'auto-inflammation d'un mélange stœchiométrique de THF, initié par Wu et al. [129] (à une pression d'environ 20 bar dans une machine à compression rapide), en menant des expériences à plus haute température dans un tube à choc, incluant également des mélanges pauvres et riches. Enfin, plus récemment, Sharma et al. [133] ont étudié l'oxydation du THF dans un réacteur auto-agité, dans des conditions comparables à celles des mélanges pauvres de Vanhove et al. [124], mais en utilisant l'argon comme gaz diluant à la place de l'hélium.

Étude expérimentale

Le dispositif expérimental employé dans le cadre de cette thèse repose sur le réacteur auto-agité par jets gazeux (JSR) du laboratoire ICARE. Deux réacteurs similaires ont été utilisés, ne différant que par leur volume : l'un de 42 cm³, l'autre de 34 cm³.

Chaque réacteur est constitué d'une sphère en silice fondue équipée de quatre injecteurs disposés selon une géométrie pyramidale, assurant une agitation homogène du mélange gazeux. Le carburant et l'oxygène sont introduits séparément afin d'éviter toute réaction prématurée avant leur entrée dans la chambre de réaction. Le mélange réactif est fortement dilué dans l'azote, de manière à limiter le dégagement de chaleur et prévenir toute élévation excessive de température susceptible d'endommager le dispositif.

Le réacteur est chauffé au moyen d'un système électrique, et une enceinte en acier permet d'atteindre des pressions pouvant aller jusqu'à 10 bar. Une sonde de prélèvement et un thermocouple sont insérés dans le réacteur pour, respectivement, recueillir des échantillons gazeux et contrôler la température. Les gaz prélevés sont ensuite transférés par une ligne en Téflon chauffée vers un spectromètre infrarouge à transformée de Fourier (FTIR). Une dérivation de cette ligne permet également de collecter les échantillons dans des ballons en Pyrex d'un litre destinés à des analyses complémentaires par chromatographie en phase gazeuse (GC). Différents détecteurs et colonnes chromatographiques ont été employés afin d'identifier et de quantifier un large éventail d'espèces chimiques.

Les carburants étudiés sont deux éthers cycliques, comportant respectivement cinq et quatre atomes de carbone : le THP et le THF. L'oxydation de mélanges associant le THF au DEE a

également été examinée. Les expériences ont été conduites à une pression (p) de 10 bar et sur un large domaine de conditions opératoires : un temps de passage (τ) de 0,7 à 2 s, une fraction molaire initiale (X_0) du carburant comprise entre 800 et 5000 ppm, une température (T) variant de 450 à 1260 K, et une richesse (ϕ) comprise entre 0,4 et 3,2.

Modélisation cinétique

Construction du modèle

L'un des objectifs majeurs de cette thèse était de développer un mécanisme cinétique détaillé capable de reproduire fidèlement les données expérimentales de spéciation obtenues à l'aide de réacteurs auto-agités. Pour ce faire, des sous-mécanismes spécifiques ont été élaborés pour l'oxydation du THF et du THP, couvrant leur réactivité à basse et haute température, sur la base de travaux antérieurs et par analogie avec des molécules chimiquement proches. Les propriétés thermochimiques des nouvelles espèces introduites ont été déterminées à l'aide de la méthode d'additivité des groupes, en utilisant l'outil RMG [139].

Le mécanisme de base retenu repose sur un schéma C_0 – C_6 , développé et publié précédemment par notre équipe [65], intégrant la chimie de diverses familles de composés (alcools, aldéhydes, hydrocarbures, etc.). Le mécanisme noyau (C_0 – C_2) de cette base a été mis à jour dans le cadre de ce travail. Afin de représenter les mélanges DEE/THF, le sous-mécanisme développé précédemment par notre équipe pour le DEE [29] a également été intégré, avec l'ajout de réactions croisées pour tenir en compte les interactions chimiques entre les deux éthers.

Les constantes de vitesse associées aux réactions d'amorçage bimoléculaires avec O_2 et aux réactions d'arrachement d'hydrogène ont été considérées identiques pour le THP et le THF : les radicaux α et β du THF ont été assimilés à ceux du THP ; ce dernier possède cependant un radical supplémentaire en position γ . De même, la chimie à basse température a été considérée similaire pour les deux composés, conformément aux travaux antérieurs de notre équipe sur les éthers linéaires [29] [31] [33] [138]. Cette chimie démontre une fois de plus sa bonne capacité prédictive, cette fois pour les éthers cycliques dans des conditions de flamme froide.

Les constantes de vitesse des réactions d'amorçage et d'arrachement d'hydrogène ont été estimées par analogie avec des travaux antérieurs, réalisés sur :

- Le di-n-propyl éther (DPE) ou le THF pour les liaisons C–H en position α ;
- Le cyclohexane (CHX) pour celles en position β (et γ dans le cas du THP).

Plus précisément :

- Pour les sites α : les constantes de vitesse des réactions d'amorçage bimoléculaire et d'arrachement de H par les radicaux OH, HO_2 , O, CH_3 , CH_3O_2 et C_2H_5 proviennent de Serinyel et al. [31]. Celles impliquant H, HCO, CH_2OH et CH_3O sont issues de Fenard et al. [127].
- Pour les sites β et γ : les constantes ont été reprises des travaux de Zou et al. [59] et Serinyel et al. [143], puis réduites d'un facteur trois et six, respectivement, afin de tenir

compte du nombre de liaisons C–H équivalentes (quatre en position β , deux en position γ pour le THP, contre douze pour le CHX).

Une correction supplémentaire a été appliquée aux réactions d'arrachement d'hydrogène par OH et H, dont les facteurs pré-exponentiels ont été diminués de 50%, afin d'obtenir un meilleur accord entre le modèle et les données expérimentales, tout en conservant des valeurs cinétiquement plausibles.

Les réactions d'addition des radicaux R sur O₂, menant à la formation de radicaux peroxyliques (RO₂), ont été paramétrées à partir de Goldsmith et al. [144]. Les mêmes constantes de vitesse ont été attribuées aux réactions d'addition des radicaux QOOH sur O₂, mais divisées par deux pour tenir compte de l'effet stérique lié à la présence du groupe –OOH, qui diminue la probabilité de collision efficace. Les réactions entre R et O₂ produisant des espèces insaturées et HO₂ ont été reprises de DeSain et al. [145] puis diminuées de 50%, sauf pour le radical γ du THP, afin de prendre en compte les quatre liaisons C–H équivalentes en position β de ce radical. Les constantes de vitesse des réactions d'isomérisation des radicaux RO₂ en QOOH, ainsi que celles de leur décomposition en composés insaturés et HO₂ et celles de formation des CHPs et éthers bicycliques, ont été reprises de Villano et al. [146,147] selon la méthodologie appliquée précédemment au di-n-butyl éther (DBE) [33] :

- L'énergie d'activation des isomérisations de RO₂ en QOOH a été diminuée de 3 kcal/mol lorsque l'hydrogène transféré se trouve en position α du groupe éther.
- Les constantes de vitesse de décomposition des radicaux RO₂ et QOOH, ainsi que celles de formation des éthers bicycliques, ont été conservées.
- L'énergie d'activation des réactions conduisant à la formation des CHPs a été abaissée de 3 kcal/mol lorsque le groupe carbonyle est formé en position α , afin de représenter l'influence des deux groupes oxygénés (hydroperoxyde et éther).

De plus, afin de prendre en compte les quatre liaisons C–H équivalentes aux positions α et β du groupe éther, le facteur pré-exponentiel des réactions d'isomérisation et de décomposition des radicaux RO₂ a été doublé lorsque le groupe peroxyde se trouve en position γ (cas du THP).

Les éthers bicycliques formés sont ensuite consommés par arrachement d'hydrogène (OH, H, HO₂), avec des constantes de vitesse issues de Serinyel et al. [31].

Enfin, les réactions de décomposition des CHPs ont été paramétrées à partir des données de Vasudevan et al. [148].

Simulations

Les simulations présentées dans cette thèse ont été réalisées à l'aide du logiciel Chemkin, de la suite ANSYS [149]. Dans ce cadre, le dispositif expérimental a été représenté à l'aide du modèle de réacteur parfaitement agité (PSR) [150]. Ce modèle permet de décrire un réacteur isotherme et ouvert, alimenté par un écoulement stationnaire de réactifs qui réagissent durant un temps de passage défini. Pour chaque simulation, plusieurs paramètres d'entrée doivent être spécifiés : la température, la pression, le volume du réacteur, le temps de passage, ainsi que les fractions molaires initiales du carburant, de l'oxydant et du diluant. En résolvant les équations de conservation de la masse et de l'énergie, Chemkin calcule les fractions molaires d'équilibre et

transitoires de l'ensemble des espèces présentes dans le mécanisme réactionnel, permettant ainsi de suivre leurs profils d'évolution en fonction de la température.

Le modèle PSR a également été utilisé, conjointement à d'autres modules du logiciel Chemkin, pour simuler des jeux de données expérimentales issues de la littérature, renforçant ainsi la validation du modèle cinétique développé dans ce travail et contribuant à l'affinement du mécanisme central. Plus précisément, les modules PLUG [151], PREMIX [152] et SENKIN [153] ont été employés pour simuler respectivement : des données de spéciation obtenues dans des réacteurs tubulaires à écoulement piston, des vitesses de flamme laminaire mesurées dans des chambres de combustion, et des temps d'auto-inflammation déterminés dans des tubes à choc.

Résultats et discussion

Méthanol et éthanol

De nouvelles mesures de vitesses de flamme laminaire pour le méthanol et l'éthanol ont été récemment obtenues à l'aide du dispositif OPTIPRIME [157], développé au laboratoire ICARE.

Ces données ont mis en évidence la nécessité de réviser le mécanisme noyau C_0 – C_2 , qui a donc été actualisé dans le cadre de cette thèse. Les Figures 5.1–5.3 présentent la validation du mécanisme mis à jour sur ces nouvelles données expérimentales, couvrant une large gamme de conditions, incluant des pressions et températures élevées rarement explorées. La comparaison avec d'autres mécanismes issus de la littérature [158–163] montre que notre mécanisme présente une capacité prédictive supérieure sur l'ensemble du domaine étudié.

Des analyses de sensibilité (Figure 5.4) ont également été réalisées pour les deux carburants, en conditions pauvres et riches. Ces analyses soulignent le rôle déterminant de la chimie du gaz de synthèse et du méthane dans le contrôle de la vitesse de flamme laminaire du méthanol et de l'éthanol. Certaines réactions spécifiques au méthanol exercent une influence notable sur la vitesse de flamme, alors que celles propres à l'éthanol ont un effet plus limité.

Enfin, des validations complémentaires (Figures 5.5–5.9) confirment notre mécanisme, qui reproduit de manière satisfaisante les données expérimentales antérieures [158] [164–166], incluant des vitesses de flamme laminaire supplémentaires, des délais d'auto-inflammation et des profils de spéciation. Ce mécanisme constitue ainsi une base solide pour le développement de futurs modèles cinétiques, dont celui proposé dans cette thèse.

Tétrahydropyrane

La conversion du THP est présentée dans la Figure 5.10 pour les quatre rapports de richesse étudiés, avec une fraction molaire initiale du carburant fixée à 800 ppm.

La Figure 5.11 illustre plus en détail le profil de fraction molaire du THP pour le mélange le plus pauvre ($\varphi = 0,4$), en mettant en évidence les différentes zones de réactivité en fonction de la température.

Les trois régimes classiques sont clairement identifiés :

- La réactivité à basse température (LTR), débutant vers 540 K et s'étendant jusqu'à 660 K, durant laquelle environ la moitié du carburant est consommée.
- La zone à coefficient de température négatif (NTC), sur une fenêtre d'environ 90 K, caractérisée par une diminution nette de la réactivité, la fraction molaire du THP ramenée à environ 90% de sa valeur initiale.
- Enfin, la réactivité à haute température (HTR) apparaît, conduisant à la consommation complète du THP vers 1100 K.

En complément, la Figure 5.10 montre qu'avec l'augmentation de la richesse, le régime LTR devient progressivement moins fort. Par ailleurs, ce régime ainsi que la zone NTC se décalent légèrement en température : l'apparition du LTR est retardée, tandis que celle du NTC se produit plus tôt. Un HTR nettement plus faible est observé à $\phi = 3,2$ par rapport aux mélanges plus pauvres.

La Figure 5.12 compare les fractions molaires du THP mesurées et simulées avec le mécanisme cinétique développé dans cette thèse pour l'ensemble des richesses étudiées. Pour le mélange le plus pauvre, les simulations reproduisent correctement l'évolution de la fraction molaire du carburant en fonction de la température ($\pm 25\%$ d'incertitude), mais anticipent la transition NTC (à 630 K au lieu de 660 K), entraînant une fin prématurée du LTR et une sur-prédiction mineure de la fraction molaire du carburant dans le régime NTC. Bien que ces écarts persistent à $\phi = 0,8$, ils disparaissent dans les conditions riches, restant entièrement compris dans la plage d'incertitude.

La Figure 5.13 met en évidence les réactions et espèces clés responsables de la formation des radicaux OH. Dans le régime LTR, la formation et la décomposition des CHPs dérivés du carburant – en particulier du CHP principal issu du radical α du carburant – sont les principales réactions produisant des radicaux OH. Lorsque la température augmente, ces réactions deviennent progressivement moins actives, entraînant une diminution globale de la réactivité (la zone NTC). Enfin, la transition vers la dernière zone, le régime HTR, s'effectue grâce à la décomposition des molécules H_2O_2 , qui devient alors la principale source de radicaux OH.

Une analyse de sensibilité (Figure 5.14) effectuée à $\phi = 3,2$ et $T = 900$ K révèle le rôle inhibiteur de la recombinaison des radicaux éthyles en n-butane. Cette réaction, la plus positivement sensible vis-à-vis du carburant, ralentit la réactivité globale par rapport aux mélanges moins riches. Cependant, cette seule analyse ne suffit pas à expliquer la formation et l'accumulation importantes de radicaux éthyles permettant leur recombinaison. Une analyse des voies réactionnelles effectuée ultérieurement dans les mêmes conditions apporte des précisions supplémentaires.

Les Figures 5.16a–d montrent les profils des fractions molaires des réactifs, produits et intermédiaires principaux pour l'ensemble des richesses étudiées. À part CO , CO_2 et H_2O , l'espèce oxygénée la plus formée lors de l'oxydation du THP est le formaldéhyde, un marqueur typique de la réactivité, surtout à basse température, pour de nombreux carburants. En outre, d'autres aldéhydes et composés oxygénés ont été quantifiés : l'acétaldéhyde, le propanal (et/ou l'acétone), l'acroléine, l'oxirane, l'acide formique, le tétrahydropyran-2-one (THP-2-one) et les deux dérivés mono-insaturés du THP (3,4- et 3,6-dihydro-2H-pyrane : 3,4-DHP et 3,6-DHP).

Toutes ces espèces se forment à la fois à basse et à haute température. Des traces de méthyloxirane, d'éthyloxirane, de THF, de n-butanal et de pentanedial ont également été détectées. L'éthylène est l'hydrocarbure le plus abondant parmi ceux identifiés dans toutes les conditions testées, comprenant aussi : le méthane, l'éthane, l'acétylène, le propène, le 1-butène et le 1,3-butadiène. De plus, à haute température, la formation de propane est observée à partir de $\phi = 0,8$, tandis que le benzène, l'allène et le propyne apparaissent sous les conditions riches.

Les simulations obtenues avec le mécanisme actuel, ainsi qu'avec trois mécanismes récents [111,112] [114], sont également représentées dans les Figures 5.16a–d. Globalement, notre mécanisme reproduit le mieux les résultats expérimentaux, malgré quelques désaccords persistants sur les valeurs absolues, tandis que les tendances sont correctement reproduites. Comme le propanal et l'acétone co-éluent lors de l'analyse par chromatographie en phase gazeuse, leurs fractions molaires individuelles ne peuvent être distinguées lorsque les deux espèces sont présentes. La fraction molaire totale des deux espèces combinées a donc été considérée dans les simulations afin d'assurer la cohérence avec les données expérimentales correspondant à leur pic commun. Il convient de souligner que la formation de ces deux composés, en particulier à basse température, reste encore imparfaitement décrite par les modèles actuels.

L'analyse des voies réactionnelles à basse température (Figure 5.17) montre que les trois radicaux du carburant sont formés, le radical α étant le plus abondant. Sa prépondérance s'explique par la faiblesse des liaisons C–H adjacentes au groupe éther. Comme on peut le constater, le carburant est consommé via les réactions d'arrachement d'hydrogène par les radicaux OH, conduisant à la formation de ses trois radicaux. La voie réactionnelle la plus fréquente suivie par ces radicaux correspond au chemin typique du régime LTR : une première addition sur O_2 , suivie d'une isomérisation interne, d'une seconde addition sur O_2 , et enfin de la formation d'un radical OH et d'un CHP. Ce dernier se décompose rapidement en libérant un autre radical OH (processus auto-accélééré), favorisant ainsi la réactivité globale.

D'autre part, l'analyse des voies réactionnelles à haute température, présentée dans la Figure 5.18, montre que le radical α reste le radical du carburant le plus abondant, bien que les réactions impliquées soient différentes. D'abord, le carburant est consommé via les réactions d'arrachement d'hydrogène principalement par les radicaux OH, mais également par H, HO_2 , O et CH_3 . Ensuite, chaque radical du carburant subit majoritairement une réaction de β -scission accompagnée de l'ouverture du cycle. Les radicaux ainsi formés peuvent, à leur tour, subir une nouvelle β -scission ou une isomérisation. Toutefois, pour qu'une réaction d'isomérisation ait lieu, elle doit être suffisamment compétitive avec la β -scission, comme c'est le cas pour le radical primaire (c4h8cho-5) du n-pentanal formé par l'ouverture du cycle du radical α du carburant. En effet, c4h8cho-5 peut subir une isomérisation favorisée par transfert interne d'un atome d'hydrogène, impliquant à la fois un état de transition à six membres et le transfert d'un hydrogène aldéhydique, conduisant à la formation du radical acyle (nc4h9co) de n-pentanal. Une autre isomérisation est également possible via un transfert interne d'hydrogène avec un état de transition à cinq membres, formant le radical secondaire (c4h8cho-2) de n-pentanal. Cette dernière voie est cependant beaucoup moins favorisée. Une fois formé, le radical nc4h9co se décompose entièrement par α -scission (décarbonylation) pour donner un radical 1-butyle, qui se décompose principalement par β -scission en éthylène et radical éthyle. Par conséquent, la voie réactionnelle la plus importante des radicaux α les plus favorisés conduit à la production

des radicaux éthyloxy, confirmant l'effet inhibiteur significatif de leur recombinaison sur la réactivité globale à haute température dans le cas du mélange le plus riche.

Les voies réactionnelles à haute température conduisant à la formation de 1,3-butadiène sont également identifiées dans la Figure 5.18. Cette espèce est le produit dominant issu des réactions suivies par les radicaux β et γ du THP. En effet, après deux β -scissions consécutives, ces radicaux donnent du formaldéhyde et le radical primaire (c4h714) du 1-butène. Le 1,3-butadiène se forme ensuite à partir de ce radical par β -scission impliquant la rupture de liaisons C–H, et dans une moindre mesure par transfert de H vers O₂. Étant donné que la formation de formaldéhyde à haute température est correctement reproduite par notre mécanisme dans toutes les conditions testées, la sur-prédiction de 1,3-butadiène semble être le résultat d'une surestimation du rapport de ramification de la β -scission des liaisons C–H sur celle de la liaison C–C du radical c4h714. Cela pourrait également expliquer, au moins partiellement, la sous-prédiction de l'éthylène à haute température, comme c'est un produit de la β -scission de la liaison C–C de c4h714.

La Figure 5.19 illustre le rôle crucial des radicaux alkyles (autres que les typiques radicaux méthyle et éthyle) dans l'oxydation du THP, en particulier les radicaux 1-butyle et 1-propyle formés par α -scission des radicaux acyles. Les voies réactionnelles représentées montrent comment ces radicaux alkyles participent au processus d'oxydation et expliquent la formation de plusieurs espèces caractéristiques, associées à leurs chemins réactionnels et observées expérimentalement. Ainsi, si l'étude de l'oxydation des éthers cycliques est essentielle pour la compréhension complète de celle des alcanes, on voit ici que l'inverse est aussi vrai.

Contrairement aux éthers linéaires tels que le DBE, pour lequel l'implication des radicaux 1-propyle et 1-butyle conduit à un double phénomène de flamme froide et de zone NTC [33], ces radicaux n'induisent pas un tel comportement lors de l'oxydation du THP. En effet, les régimes de réactivité de ces radicaux apparaissent dans les mêmes plages de températures que celles du THP lui-même, tandis que la réactivité du DBE débute environ 100 K plus tôt. Cette différence explique pourquoi deux comportements de réactivité distincts sont observés : le premier provenant de l'éther et le second des radicaux alkyles, dans le cas du DBE mais pas pour le THP.

Le mécanisme actuel est en outre évalué à l'aide de données expérimentales issues de la littérature, comprenant des données de spéciation obtenues lors de l'oxydation du THP à pression atmosphérique dans des réacteurs auto-agités [111,112] (Figure 5.20 et Figure 5.21) et lors de sa pyrolyse dans un réacteur tubulaire à écoulement piston [106] (Figure 5.22), ainsi que des délais d'auto-inflammation mesurés dans un tube à choc [104] (Figure 5.23). Le mécanisme reproduit de manière satisfaisante les tendances générales de ces données, bien que certains écarts persistent sur les valeurs absolues. Afin de fournir une évaluation plus complète, nous comparons également notre mécanisme à celui initialement développé pour chaque série de données. Enfin, il convient de noter que la comparaison des données de spéciation rapportées par différentes études révèle encore des écarts notables et inexpliqués, malgré des conditions expérimentales identiques.

Tétrahydrofurane

L'oxydation du THF a été étudiée dans un réacteur auto-agité sous des conditions comparables à celles du THP. La Figure 5.24 montre la conversion du THF pour les cinq conditions de richesse étudiées avec une fraction molaire initiale du carburant fixée à 850 ppm. Comme pour le THP, les trois régimes classiques de réactivité sont également observés pour le THF. Cependant, le THF présente des régimes LTR et NTC moins forts que ceux du THP en conditions pauvres similaires, devenant négligeables – voire disparaissant – en conditions riches. La Figure 5.25 se concentre sur le profil de fraction molaire du THF pour le mélange le plus pauvre, en mettant en évidence les différentes zones de la réactivité en fonction de la température. Le THF présente un faible régime LTR à $\phi = 0,425$, débutant vers 570 K et s'étendant jusqu'à 630 K, au cours duquel seulement 20% du THF initial est consommé. Celui-ci est suivi par une région NTC faible, couvrant une plage de températures similaire de 60 K, caractérisée par une légère diminution de la réactivité et la régénération de moins de 4% du carburant initial. Enfin, le régime HTR apparaît, entraînant la consommation complète du THF vers 1100 K.

La Figure 5.24 montre également qu'avec l'augmentation de la richesse, le régime HTR se décale vers des températures plus élevées. De plus, contrairement au THP, la réactivité du THF ralentit nettement au-delà de 900 K, sans toutefois s'interrompre complètement. À $\phi = 1,53$, une baisse marquée de la réactivité est observée entre 900 et 930 K, après quoi celle-ci retrouve un rythme similaire à celui qui précédait cette transition. Lorsque la richesse est encore augmentée jusqu'à $\phi = 1,7$, la réduction de réactivité devient plus progressive, se produisant à des températures plus basses sur un intervalle plus large (60 K au lieu de 30 K) ; de 840 à 900 K. Alors qu'une diminution de réactivité séparant les régimes LTR et HTR est un phénomène bien connu pour de nombreux carburants, désigné sous le nom de NTC, une baisse de réactivité survenant au sein même du régime HTR est rapportée ici pour la première fois dans le cas du THF. Un tel comportement n'a, à notre connaissance, aucun précédent documenté, à l'exception de celui observé pour son analogue hydrocarbure, le cyclopentane (CPT), dans des conditions expérimentales comparables [167]. En revanche, aucune diminution similaire de la réactivité n'a été observée à pression atmosphérique en conditions riches, ni pour le THF ni pour le CPT, comme l'ont respectivement montré les travaux de Vanhove et al. [124] et Dayma et al. [137].

La Figure 5.26 illustre la comparaison entre les profils de fractions molaires du THF obtenus expérimentalement et ceux prédits par le modèle cinétique élaboré au cours de cette thèse, pour l'ensemble des rapports de richesse étudiés. En considérant d'abord le mélange le plus pauvre et en tenant compte de l'incertitude expérimentale de $\pm 15\%$, on constate que notre mécanisme reproduit de manière satisfaisante l'évolution de la fraction molaire du carburant en fonction de la température. Cependant, il décale le début du régime HTR d'environ 50 K vers des températures plus élevées, sous-estimant alors la réactivité entre 720 et 820 K. Cet écart diminue lorsque la richesse augmente, disparaissant complètement au-delà de $\phi = 0,85$. Néanmoins, une surestimation de la réactivité apparaît à la fin du régime HTR, à des températures qui varient entre ≈ 1000 et 1050 K selon la richesse. De plus, le mécanisme sous-estime la réactivité entre 880 et 1020 K à $\phi = 1,275$. En revanche, le mécanisme reproduit bien la forte suppression de réactivité à $\phi = 1,53$ entre 900 et 930 K, bien qu'il montre une légère surestimation de la réactivité en dessous de cette plage, se terminant par un plateau étroit juste avant la chute brutale. À $\phi = 1,7$, le mécanisme parvient également à déplacer cette chute vers des températures plus basses et à montrer une réactivité moins prononcée avant la chute, mais

de manière insuffisante, entraînant une sous-estimation significative de la fraction molaire du carburant entre 800 et 900 K.

Le mécanisme actuel prédit que la forte suppression de réactivité observée à $\varphi = 1,53$ entre 900 et 930 K se produit précisément entre 910 et 912 K. Afin de comprendre ce comportement, une analyse de sensibilité a été réalisée sur le carburant à ces deux températures. Cette analyse, illustrée dans la Figure 5.27, met en évidence l'importance de trois radicaux clés (HO_2 , CH_3 et $\text{C}_3\text{H}_5\text{-a}$), en particulier à travers leurs réactions mutuelles. Ces réactions comprennent la dismutation des radicaux HO_2 (R1), les réactions des radicaux allyles ($\text{C}_3\text{H}_5\text{-a}$) avec les radicaux HO_2 (R2) et CH_3 (R5), ainsi que les réactions des radicaux CH_3 avec HO_2 (R3 et R13). À 910 K, toutes ces réactions inhibent fortement la réactivité globale. La seule exception est la réaction R13, au cours de laquelle CH_3 et HO_2 forment CH_3O et OH , favorisant ainsi la réactivité. Bien que R1 freine la réactivité, elle produit H_2O_2 qui se décompose ensuite en deux radicaux OH ; la réaction principale qui conduit la réactivité aux températures intermédiaires et marque la transition de la zone NTC au régime HTR. En revanche, R2, R3 et R5 conduisent à la formation de molécules relativement stables (propène, méthane et 1-butène, respectivement). Ces réactions semblent être les responsables primaires de la chute de réactivité observée. Comme R13, les réactions d'arrachement d'hydrogène du THF (R10 et R11) et du CH_2O (R14) par les radicaux HO_2 figurent également parmi les plus sensibles réactions promotrices de réactivité. Les radicaux HCO ainsi formés à partir du CH_2O subissent principalement une décomposition unimoléculaire (R4) ou réagissent avec O_2 pour former CO et HO_2 (R12) : la première inhibe la réactivité, tandis que la seconde la favorise. Lorsque la température augmente à 912 K, toutes les réactions mentionnées précédemment continuent d'influencer la réactivité dans le même sens, mais avec une sensibilité beaucoup plus faible, en accord avec la forte suppression de la réactivité et l'épuisement associé du réservoir de radicaux (en particulier HO_2). Seule la réaction R13 passe d'une sensibilité négative à une sensibilité légèrement positive. Pourtant, les réactions d'arrachement d'hydrogène du carburant par les radicaux OH (R6 et R9) et CH_3 (R8), ainsi que l'ouverture du cycle de son radical β (R7), deviennent plus sensibles. Leurs effets sur la réactivité globale sont les suivants : R8 favorise la réactivité, R7 la freine, R6 a un effet promoteur à 910 K mais agit comme inhibiteur à 912 K, tandis que R9 montre une tendance opposée à R6. Cette analyse de sensibilité fournit une première clarification mécanistique du nouveau comportement du THF. Toutefois, cette analyse ne permet pas d'expliquer l'ensemble du phénomène observé. Une étude plus détaillée des voies réactionnelles a donc été menée ultérieurement.

Les Figures 5.28a–e présentent les profils des fractions molaires des réactifs, produits et intermédiaires principaux pour l'ensemble des richesses étudiées. En dehors des produits finaux de combustion, le formaldéhyde constitue l'espèce oxygénée la plus abondante dans le régime HTR lors de l'oxydation du THF, atteignant environ 100 ppm, comme cela avait déjà été observé pour le THP. Cependant, dans le régime LTR, la formation est dominée par un produit caractéristique du THF, le butanedial, dont la concentration maximale atteint environ 20 ppm. D'autres produits spécifiques au carburant ont également été quantifiés : le furane, le 2,3-dihydrofurane (2,3-DHF) et le 2,5-dihydrofurane (2,5-DHF), ainsi que plusieurs composés oxygénés déjà observés lors de l'oxydation du THP : l'oxirane, l'acétaldéhyde, l'acroléine et le propanal/acétone. Tous ces composés ont été formés aussi bien lors de l'oxydation à basse température que lors de l'oxydation à haute température du THF. Le méthyloxirane a également été détecté, mais uniquement à haute température. Comme pour le THP, l'éthylène est l'hydrocarbure le plus abondant parmi ceux identifiés dans toutes les conditions testées dans le

cas du THF, incluant : le méthane (formé en quantités comparables à l'éthylène dans les conditions les plus riches), l'éthane, l'acétylène, le propane, le propène, le 1-butène et le 1,3-butadiène. Des traces d'allène, de propyne et de 1,5-hexadiène ont également été détectées à haute température en conditions riches.

Les simulations obtenues avec le mécanisme actuel, ainsi qu'avec le mécanisme de Fenard et al. [127], sont également présentées dans les Figures 5.28a–e. Globalement, notre mécanisme reproduit mieux les résultats expérimentaux, malgré quelques désaccords persistants sur les valeurs absolues, tandis que les tendances sont correctement captées. Alors que notre mécanisme parvient à représenter le nouveau comportement du THF observé dans ce travail, en particulier la chute brutale de réactivité à $\phi = 1,53$, le mécanisme de Fenard échoue à le reproduire. Par ailleurs, il convient de souligner que, comme dans le cas du THP, la formation de propanal et d'acétone lors de l'oxydation du THF à basse température n'est encore correctement expliquée par aucun mécanisme.

Afin d'examiner les réactions les plus importantes consommant le THF pendant son régime LTR, une analyse des voies réactionnelles a été effectuée avec le mécanisme actuel à $\phi = 0,425$ et $T = 600$ K (Figure 5.29). Les deux radicaux issus du carburant sont effectivement générés, le radical α se révélant, conformément aux prévisions, le plus abondant. Il apparaît clairement que le carburant est quasi intégralement consommé par des réactions d'arrachement d'hydrogène dues aux radicaux OH, aboutissant à la formation de ses deux radicaux principaux. Ceux-ci suivent ensuite le schéma réactionnel caractéristique du régime LTR : une première addition sur O_2 , suivie d'une isomérisation interne, d'une deuxième addition sur O_2 , et enfin de la formation d'un radical OH et d'un CHP. Ce dernier se décompose rapidement en libérant un autre radical OH, ce qui favorise ainsi la réactivité globale.

La Figure 5.30a illustre les voies réactionnelles dominantes à haute température, analysées de part et d'autre de la chute marquée de réactivité à $\phi = 1,53$. Le radical α demeure le radical du carburant le plus abondant, mais l'importance du radical β devient comparable et les réactions impliquées diffèrent. D'abord, le carburant est consommé par les réactions d'arrachement d'hydrogène majoritairement par les radicaux OH, mais aussi par HO_2 , CH_3 , H et O. Ensuite, chaque radical du carburant subit principalement une β -scission accompagnée de l'ouverture du cycle. Les radicaux ainsi formés peuvent, à leur tour, subir une deuxième β -scission ou une isomérisation. Toutefois, une isomérisation doit être suffisamment favorable pour concurrencer la β -scission. C'est le cas pour le radical primaire (c3h6cho-4) du n-butanal formé via l'ouverture du cycle du radical α du carburant. En effet, c3h6cho-4 peut subir une isomérisation favorable via un transfert interne d'hydrogène, impliquant à la fois un état de transition à cinq membres et le transfert d'un hydrogène aldéhydique, menant à la formation du radical acyle (nc3h7co) du n-butanal. Le radical nc3h7co se décompose totalement par α -scission pour former un radical 1-propyle, qui se dissocie majoritairement par β -scission en éthylène et en un radical méthyle. La voie réactionnelle principale suivie par les radicaux α du carburant mène à la formation de radicaux méthyles, soulignant ainsi l'influence majeure de ces derniers sur la réactivité globale dans les conditions étudiées. Cette observation justifie le fait que leurs réactions aient précédemment été identifiées comme parmi les plus sensibles dans les mêmes conditions. De plus, le radical 1-propyle peut encore s'ajouter sur O_2 avant soit d'éliminer un radical HO_2 pour former du propène, soit de s'isomériser, puis de perdre un radical OH pour former un éther cyclique : principalement le méthyloxirane, avec seulement un faible flux produisant de l'oxétane, ce qui est cohérent avec l'identification expérimentale de la première

et l'absence de la seconde. Par ailleurs, la sur-prédiction considérable du méthyloxirane, combinée à la sous-estimation de l'éthylène par le mécanisme actuel, pourrait s'expliquer, au moins partiellement, par une possible surestimation de la constante de vitesse de l'addition sur O_2 par rapport à celle de la β -scission du radical 1-propyle. Une nouvelle fois, l'implication majeure des radicaux alkyles dans l'oxydation des éthers cycliques est ainsi confirmée.

La Figure 5.30a montre également que la deuxième voie la plus fréquente du THF conduit à la formation du formaldéhyde et des radicaux allyliques à partir des radicaux β du carburant, via deux réactions successives de β -scission, dont la première implique l'ouverture du cycle. L'impact de cette voie sur la réactivité globale n'est pas moins important que celui de la voie la plus favorisée précédemment décrite. En réalité, la chimie des radicaux allyliques stabilisés par résonance joue un rôle déterminant dans la forte suppression de la réactivité entre 910 et 912 K. À 910 K, ces radicaux réagissent principalement avec les radicaux HO_2 pour produire des radicaux « allyloxy » et OH, soit directement, soit via l'intermédiaire hydroperoxyde allylique. En revanche, à 912 K, la recombinaison des radicaux allyles en 1,5-hexadiène, qui est un composé relativement stable, devient la réaction principale et explique l'identification expérimentale de ce composé. Bien que les deux réactions « allyle + HO_2 », qui favorisent la réactivité, représentent encore ensemble un flux supérieur à celui de l'auto-recombinaison des radicaux allyles, d'autres réactions inhibitrices ne doivent pas être négligées, en particulier la recombinaison des radicaux allyles avec les radicaux méthyles conduisant au 1-butène, ainsi que leur réaction avec les radicaux HO_2 menant à la formation de propène et d' O_2 . Avec l'auto-recombinaison des radicaux allyles, ces réactions dominent à 912 K et conduisent collectivement à la forte chute de réactivité observée entre 910 et 912 K.

La Figure 5.30b illustre les principales réactions consommant les radicaux CH_3 formés via la voie réactionnelle la plus favorisée du THF sous $\phi = 1,53$ à 910 et 912 K. À 910 K, juste avant la forte chute de réactivité, les réactions radical-radical dominant, en particulier celles des radicaux CH_3 avec les radicaux HO_2 et allyles, ainsi que leur auto-recombinaison. À 912 K, les réactions entre radicaux ne sont plus dominantes en raison de l'appauvrissement de leur réservoir ; les radicaux méthyles réagissent alors principalement avec le carburant et avec l' O_2 , tous deux fortement accumulés à la suite du déclin brutal de réactivité.

Le mécanisme actuel est par ailleurs évalué à l'aide de données supplémentaires de spéciation obtenues au cours du présent travail dans des réacteurs auto-agités à 10 bar, sous les deux conditions suivantes : la condition stœchiométrique étudiée avec 1000 ppm de THF (Figure 5.32), et la condition pauvre ($\phi = 0,5$) avec 5000 ppm de THF et un temps de passage prolongé de 2 s (Figure 5.34).

De plus, le mécanisme est validé sur des données de spéciation, issues de la littérature [124] [133], obtenues dans des réacteurs auto-agités à pression atmosphérique, sous la même richesse et le même temps de passage que dans la dernière condition mais avec une fraction molaire initiale du carburant doublée (Figure 5.35).

Notre mécanisme est également testé sur des délais d'auto-inflammation mesurés dans deux tubes à choc [120] [131] (Figure 5.36). Globalement, le mécanisme reproduit de manière satisfaisante les tendances générales de ces données, bien que des écarts persistent sur les valeurs absolues.

Afin de fournir une évaluation plus complète, la performance du mécanisme actuel dans la prédiction des différentes données a été aussi comparée à des mécanismes disponibles dans la littérature :

- Pour nos données supplémentaires de spéciation : comparaison avec le mécanisme de Fenard et al. [127].
- Pour les données de spéciation à pression atmosphérique : comparaison avec le mécanisme de Sharma et al. [133].
- Pour les délais d'auto-inflammation : comparaison avec le mécanisme de Do et al. [131].

Enfin, il convient de noter que, comme dans le cas du THP, la comparaison des données de spéciation à pression atmosphérique rapportées par deux études distinctes sur le THF révèle des écarts demeurant inexplicables, malgré des conditions expérimentales quasi identiques.

Comparaison des carburants

Le THP est comparé aux éthers linéaires possédant respectivement un atome de carbone de plus et un de moins, le DPE [31] et le DEE [29]. La comparaison est effectuée sous une même condition pauvre ($\phi = 0,5$) et est présentée à la Figure 5.37a. Les deux éthers linéaires présentent chacun un fort régime LTR débutant à une température aussi basse que 450 K, le DEE étant le plus réactif (conversion de 75%). En revanche, le THP montre le plus faible LTR (conversion d'environ 55%), légèrement moins prononcé que celui du DPE (conversion d'environ 60%), et décalé d'environ 100 K vers des températures plus élevées. Comme pour le régime LTR, le DEE présente le comportement NTC le plus prononcé, ramenant sa fraction molaire presque à sa valeur initiale. D'autre part, le THP et le DPE présentent des zones NTC similaires, à l'issue desquelles chacun récupère environ 400 ppm de sa fraction molaire convertie lors de la phase LTR. L'apparition du régime HTR est légèrement décalée de 30 K vers des températures plus élevées pour le THP par rapport au DEE et au DPE, avec le DPE montrant le HTR le plus fort, suivi du DEE, puis du THP.

De manière identique, le THF est comparé à l'éther linéaire possédant le même nombre d'atomes de carbone (le DEE [29]) ainsi qu'à son alcane analogue (le CPT [137]) sous une même condition stœchiométrique, comme illustré dans la Figure 5.37b. L'alcane analogue du DEE (le n-pentane [58]) est également inclus dans la comparaison afin d'examiner plus en détail les effets du groupe éther et de la structure cyclique sur la réactivité globale. Ainsi, comparé au DEE, qui présente un LTR marqué (conversion supérieure à 60%) entre 450 et 540 K, le THF montre un LTR très faible (conversion inférieure à 10%), décalé considérablement vers des températures plus élevées, s'étendant de 590 à 650 K. De manière similaire au THF, le LTR du n-pentane s'étend sur la même plage de températures, mais il est plus prononcé (conversion d'environ 30%). En revanche, aucun régime LTR, et par conséquent aucune zone NTC, n'a été détecté pour le CPT. Le DEE, le THF et le n-pentane présentent tous un comportement NTC cohérent avec leurs régimes LTR respectifs, ramenant leur fraction molaire à sa valeur initiale d'environ 1000 ppm. Alors que la transition de la zone NTC au régime HTR est directe pour le n-pentane, elle passe par une large plage non réactive d'environ 90 K pour le DEE et 110 K dans le cas du THF. Cependant, l'apparition du régime HTR est décalée vers des températures plus élevées de 60 K pour le THF et de 80 K pour le n-pentane, par rapport au DEE. Bien que

le régime HTR du CPT commence à la même température que celui du THF (≈ 780 K), il est aussi fort que celui du DEE (voire légèrement plus marqué), tandis que le THF montre la réactivité la plus faible (inférieure même à celle du n-pentane au-delà de 900 K). Ainsi, la consommation complète est atteinte vers 950 K pour le CPT et le DEE, alors que pour le n-pentane et le THF, des températures aussi élevées que 1020 et 1150 K, respectivement, sont nécessaires pour assurer leur conversion totale.

Le THF est également comparé au DEE, au CPT et au n-pentane sous une même condition riche ($\phi = 2$), comme illustré dans la Figure 5.37c. Puisque la flamme froide du THF n'est plus observée à la richesse actuelle, la comparaison se concentre uniquement sur le régime HTR, bien que le DEE et le n-pentane restent encore réactifs à basse température. Alors que le DEE et le CPT présentent tous deux une forte HTR en dessous de 900 K, celui du n-pentane est décalé vers des températures plus élevées. Le THF ne montre qu'une très faible réactivité entre 780 et 840 K, qui diminue tout de suite pour ramener la fraction molaire du carburant à sa valeur initiale avant de cesser complètement sur un intervalle de 60 K. Au-delà de 900 K, le DEE et le n-pentane poursuivent leur réactivité sans interruption jusqu'à leur consommation totale autour de 1050 et 1100 K, respectivement. En revanche, le CPT devient progressivement moins réactif puis subit une chute brutale de réactivité dans une fenêtre étroite de 30 K (950–980 K), durant laquelle sa fraction molaire augmente d'environ 200 jusqu'à 600 ppm. Par la suite, le CPT retrouve sa réactivité et est entièrement consommé vers 1150 K. De son côté, après avoir retrouvé sa réactivité vers 950 K, le THF continue à être consommé progressivement jusqu'à son épuisement complet autour de 1250 K. La suppression de réactivité observée dans une certaine plage de températures élevées a déjà été discutée dans ce chapitre pour le THF, et rapportée précédemment par Al Rashidi et al. [167] pour le CPT. Elle a été principalement attribuée à la chimie complexe des radicaux allyles, formés via les voies d'ouverture du cycle des radicaux dérivés du carburant (radicaux β dans le cas du THF). En outre, les radicaux caractéristiques α favorisent ce nouveau phénomène chez le THF en conduisant à la formation de radicaux méthyle.

Mélanges d'éthers

Trois mélanges de THF et de DEE ont été étudiés sous des conditions identiques, en maintenant constante la fraction molaire initiale de THF tout en faisant varier uniquement celle de DEE. La Figure 5.39 illustre l'effet de l'addition du DEE sur la conversion du THF. L'ajout du DEE décale le début du régime LTR du THF d'environ 50 K, passant de 590 à 540 K pour le mélange contenant 230 ppm de DEE (B1), et d'environ 80 K pour les deux autres mélanges, B2 et B3, contenant respectivement 530 et 830 ppm de DEE. De plus, le régime LTR du THF, initialement très faible (conversion inférieure à 10%), devient de plus en plus important à mesure que la proportion du DEE dans le mélange augmente. Ainsi, la conversion du THF lors de la phase LTR passe progressivement de 25% pour B1 à 35% pour B2, puis à 45% pour B3. De manière identique, pour le THF pur (B0), les mélanges présentent un comportement NTC cohérent avec leur régime LTR respectif, ramenant la fraction molaire du THF à sa valeur initiale de 1000 ppm. Enfin, le régime HTR du THF est légèrement décalé vers des températures plus basses.

L'amélioration de la réactivité globale observée lorsque la proportion du DEE dans le mélange augmente, se reflète dans les profils de fraction molaire des différentes espèces formées, avec une production accrue de celles-ci, comme illustré dans la Figure 5.40. Ces espèces peuvent

être classées en trois groupes distincts : celles spécifiques au THF (2,3-DHF, 2,5-DHF, butanedial et γ -butyrolactone), celles spécifiques au DEE (2-méthyl-1,3-dioxolane, éthanol, acide acétique, ainsi que quelques traces d'éthyl vinyl éther), et celles communes aux deux carburants (toutes les autres). Il convient de noter que la γ -butyrolactone n'est détectée que dans le mélange le plus réactif, ce qui est cohérent avec son absence dans toutes les conditions étudiées pour le THF dans ce travail, sauf lorsque sa réactivité avait été renforcée en augmentant sa fraction molaire initiale à 5000 ppm et en prolongeant le temps de passage à 2 s. Cette espèce peut donc être considérée comme un marqueur caractéristique de l'amélioration de la réactivité du THF.

Notre sous-mécanisme du DEE précédemment développé [29] a été intégré au mécanisme actuel afin de permettre la simulation des résultats obtenus pour les mélanges DEE/THF. Les réactions croisées entre les radicaux primaires (R) et les radicaux peroxydes (RO_2) du DEE et du THF ont été prises en compte, avec des constantes de vitesse estimées à l'aide de RMG [139] ou par analogie avec des réactions similaires du mécanisme. Les simulations réalisées avec le mécanisme résultant sont comparées aux données expérimentales correspondantes dans la Figure 5.40.

Le mécanisme actuel prédit de manière raisonnable la réactivité du THF dans les différents mélanges ainsi que les tendances générales des principales espèces observées, comme le montre la Figure 5.40. Cependant, des écarts apparaissent dans les valeurs absolues, nécessitant des investigations supplémentaires. Notamment, le mécanisme anticipe légèrement le déclenchement de la réactivité, conduisant à une surestimation de la réactivité à basse température – en particulier pour le DEE – ce qui se reflète clairement dans les profils de certaines espèces majoritairement dérivées du DEE, telles que l'acétaldéhyde. Par la suite, le mécanisme reproduit avec précision le régime NTC des deux carburants. Bien que notre mécanisme surestime ensuite la première phase du HTR (aux températures intermédiaires inférieures à ≈ 850 K), cette surestimation devient moins marquée à mesure que la proportion de DEE dans le mélange augmente. Au-delà de cette température, le mécanisme continue de sous-estimer légèrement la réactivité dans tous les mélanges, comme c'était également le cas pour le THF pur.

À l'aide d'une analyse des voies réactionnelles (Figure 5.41), le mécanisme actuel montre que l'initiation de la réactivité du THF à basse température, induite par l'addition du DEE, favorise l'auto-dismutation des radicaux α -peroxy du THF, une voie qui resterait autrement largement inactive. Bien que moins significatives, des interactions chimiques entre les deux éthers se produisent également, principalement de manière indirecte par dismutation croisée des radicaux α -peroxy du THF avec les radicaux CH_3O_2 (largement formés à partir du DEE), et seulement dans une faible mesure par dismutation directe avec les radicaux α -peroxy du DEE.

Conclusions et perspectives

Ce travail s'inscrit dans la continuité des efforts de notre équipe visant à élucider les voies d'oxydation des éthers, le plus récent étant la thèse de Giorgia Cenedese [169], consacrée à l'étude des éthers linéaires sous différents angles. Dans la continuité de ses travaux, Cenedese avait suggéré d'étendre l'étude aux éthers cycliques, qui constituent l'objet principal de l'étude présentée.

Cette thèse est le fruit de trois années de recherche sur la cinétique d'oxydation en phase gazeuse des éthers cycliques et de leurs mélanges avec des éthers linéaires. Les deux classes d'éthers peuvent être dérivées de la biomasse et sont considérées comme des candidats prometteurs pour les biocarburants, car elles présentent une tendance de réduction des émissions, d'amélioration de l'efficacité de combustion et de compatibilité avec les moteurs actuellement utilisés. Dès lors, l'étude de leur comportement en combustion apparaît comme un levier scientifique et technologique majeur pour contribuer à la réduction de l'empreinte climatique. Si les éthers linéaires ont été largement étudiés ces dernières années par notre équipe ainsi que par d'autres chercheurs, les recherches sur les éthers cycliques restent relativement limitées, et aucune étude n'a encore porté sur les mélanges des deux classes d'éthers. Ainsi, ce travail se concentre sur l'investigation expérimentale et la modélisation cinétique de l'oxydation à haute pression de deux éthers cycliques, le THP et le THF, ce dernier étant étudié soit sous sa forme pure, soit en mélange avec le DEE. L'objectif est d'étudier l'oxydation des éthers cycliques et l'effet de l'addition d'un éther linéaire sur cette oxydation.

Le dispositif expérimental choisi pour cette étude est le réacteur auto-agité par jets gazeux, qui permet de mesurer les fractions molaires des réactifs, produits et espèces intermédiaires impliqués dans l'oxydation en phase gazeuse des carburants étudiés. Parallèlement, un modèle cinétique a été développé et utilisé pour simuler les résultats expérimentaux obtenus dans ce travail. De plus, le mécanisme noyau de ce modèle a été revisité et mis à jour afin d'améliorer et de valider ses performances à l'égard de nouvelles séries de données et de données antérieures sur le méthanol et l'éthanol, en comparaison avec des mécanismes performants disponibles dans la littérature.

Pour le THP comme pour le THF, les trois zones classiques de réactivité ont été identifiées, avec la phase d'oxydation à basse température étant plus similaire à celle des alcanes qu'à celle des éthers linéaires ; i.e., se produisant environ 100 K plus tard que pour ces derniers dans les mêmes conditions. Avec l'augmentation de la richesse, le régime LTR du THP et du THF devient moins prononcé. De plus, le THF présente un régime LTR plus faible que celui du THP dans des conditions similaires. À haute température, tandis que le THP présente une réactivité moins importante en conditions très riches par rapport aux richesses plus faibles, le THF manifeste un nouveau comportement d'inhibition de la réactivité, plus marqué, qui s'intensifie progressivement avec la richesse : des conditions modérément riches suffisent déjà à presque supprimer complètement sa réactivité dans la plage de températures intermédiaires à élevées. Ainsi, pour le THF, la réactivité décroît sur une certaine plage de températures, d'abord de manière brutale, puis plus progressivement avec l'augmentation de la richesse, alors que pour le mélange le plus riche du THP, la réactivité ne fait que ralentir sans s'arrêter ni décroître. Différentes réactions de recombinaison sont responsables de ces inhibitions de réactivité. Dans le cas du THP, le ralentissement de la réactivité est principalement dû à la recombinaison des radicaux éthyliques. En revanche, pour le THF, la chimie des radicaux allyliques joue le rôle clé dans le comportement nouvellement observé, notamment par leur auto-recombinaison. Les radicaux méthyliques, formés en abondance dans le cas du THF, contribuent aussi : leur auto-recombinaison, ainsi que leur recombinaison avec les radicaux allyliques, amplifie encore ce comportement.

Le mécanisme développé montre un accord satisfaisant avec les données de spéciation actuelles pour les deux éthers cycliques. Il reproduit également avec précision le ralentissement de la réactivité à haute température du THP ainsi que la forte suppression de celle du THF dans des

conditions riches. En revanche, aucun des mécanismes issus de la littérature n'a été capable de reproduire ces comportements.

Outre les typiques radicaux méthyle et éthyle, d'autres radicaux alkyles jouent un rôle crucial dans l'oxydation des éthers cycliques : les radicaux 1-propyle dans le cas du THF, et les radicaux 1-propyle et 1-butyle dans le cas du THP. Ces radicaux se traduisent dans l'oxydation des éthers cycliques par la formation de leurs produits caractéristiques, y compris des éthers cycliques qui constituent eux-mêmes des intermédiaires clés dans l'oxydation des alcanes ; e.g. : le méthyloxirane et le THF, issus respectivement des radicaux primaires du propane et du n-butane. Ainsi, cette thèse met en évidence l'importance réciproque des éthers cycliques et des alcanes dans l'oxydation respective de chacun.

Le mécanisme présent a été en outre validé pour le THP et le THF à l'aide de données de spéciation supplémentaires et de délais d'auto-inflammation mesurés dans des tubes à choc. Cependant, ces données comprennent des mesures effectuées à pression atmosphérique dans des réacteurs auto-agités, qui présentent des écarts notables et inexpliqués malgré des conditions expérimentales similaires. Des études complémentaires demeurent donc nécessaires.

L'effet de l'addition du DEE sur l'oxydation du THF a été étudié à l'aide de trois mélanges stœchiométriques de ces deux éthers, ne différant que par leur teneur en DEE. L'ajout de DEE au THF permet de déclencher sa réactivité à des températures plus basses et de l'amplifier. L'augmentation de la réactivité globale se reflète dans les profils de fractions molaires des diverses espèces formées, avec une production correspondante plus élevée. Le mécanisme actuel, qui combine notre sous-mécanisme du DEE précédemment publié [29] et celui du THF nouvellement développé, constitue une étape cruciale vers l'élaboration d'un mécanisme robuste d'oxydation des mélanges DEE/THF. Il met en évidence l'importance des voies de dismutation des radicaux α -peroxy du THF, favorisées par l'initiation de la réactivité à basse température induite par l'addition du DEE.

En résumé, cette thèse fournit une large base de données de spéciation sur l'oxydation dans des réacteurs auto-agités de deux éthers cycliques importants, le THP et le THF, couvrant une vaste gamme de conditions jamais étudiées auparavant. Elle examine également, pour la première fois, l'effet de l'addition d'un éther linéaire (le DEE) sur l'oxydation d'un éther cyclique (le THF). De plus, le présent travail propose un modèle cinétique, dont le mécanisme noyau a été mis à jour et qui reproduit de manière satisfaisante les données actuelles et antérieures pour le THP, le THF (pur ou en mélange avec le DEE), ainsi que pour des espèces de base telles que le méthanol et l'éthanol. Néanmoins, certains désaccords persistent, laissant place à des améliorations futures.

Afin de mieux comprendre le comportement cinétique des éthers cycliques et de leurs mélanges, il est essentiel d'améliorer les performances du mécanisme développé dans le présent travail. Bien que les constantes de vitesse estimées par analogie semblent raisonnables, elles restent moins précises que celles obtenues par des calculs directs. De plus, les propriétés thermochimiques peuvent être autant importantes que les paramètres cinétiques. En effet, la méthode d'additivité des groupes utilisée dans ce travail pour les déterminer peut présenter des limites, notamment pour les espèces complexes impliquées dans la chimie à basse température.

Comme prolongement de cette étude, du point de vue de la modélisation et de la simulation, les étapes possibles incluent :

- Réaliser des calculs théoriques avancés à la fois sur les constantes de vitesse des réactions principales et sur les données thermodynamiques des espèces primaires des sous-mécanismes développés dans le cadre de ce travail.
- Valider le présent mécanisme à l'aide de types de données supplémentaires qui n'ont pas été testés pour le THP et le THF dans cette thèse, tels que les vitesses de flamme laminaire et les délais d'auto-inflammation mesurés dans des machines à compression rapide.
- Réviser le sous-mécanisme C₃-C₄ de notre modèle, notamment en le validant sur diverses données expérimentales pour le propane et le n-butane, dont les radicaux primaires jouent un rôle crucial dans l'oxydation des deux éthers cycliques étudiés.
- Envisager l'implémentation de réactions croisées supplémentaires, traduisant des interactions potentielles encore non prises en compte entre les chimies du DEE et du THF, afin d'améliorer la performance prédictive du mécanisme actuel pour l'oxydation de leurs mélanges.

D'un autre côté, du point de vue expérimental, les étapes suivantes peuvent être envisagées :

- Pour les deux éthers cycliques étudiés dans ce travail (le THP et le THF) : réaliser des manipulations dans un réacteur auto-agité à pression atmosphérique sous des conditions identiques à celles des données disponibles dans la littérature, compte tenu des écarts observés entre ces dernières, afin de fournir des résultats fiables pour la validation des modèles cinétiques.
- Pour d'autres éthers cycliques et composés analogues : étudier des éthers cycliques plus petits (tels que l'oxétane), des éthers cycliques substitués (comme le 2-méthyltétrahydrofurane) et insaturés (comme le furane), ainsi que d'autres analogues hétérocycliques (comme la pyrrolidine) afin d'évaluer respectivement l'effet de la taille du cycle, de la ramification, de l'insaturation et de la nature de l'hétéroatome.
- Pour les mélanges d'éthers : étudier des conditions riches pour les mélanges DEE/THF afin d'évaluer l'effet de l'ajout de DEE sur la suppression de réactivité observée pour le THF à haute température, et étendre l'étude des mélanges d'éthers cycliques et linéaires pour inclure des mélanges de THP avec le DEE ou le DPE.

À la lumière des résultats présentés dans cette thèse, les éthers cycliques et leurs mélanges avec des éthers linéaires montrent des caractéristiques prometteuses et des comportements à la fois nouveaux et intéressants. Le mécanisme cinétique développé, ainsi que les données expérimentales collectées, constituent un avancement significatif vers une compréhension complète de la combustion de ces potentiels biocarburants.

Appendices

Appendix A

Key modifications applied to the core mechanism in this work

Table A1: Key reactions modified in the core mechanism during this thesis, with their original and updated rate constants.

Reactions	Original					Modified				
	k	A	n	E _a	Ref.	k	A	n	E _a	Ref.
HCO+M⇌H+CO+M	k _∞	4.90E16	-0.93	19724	[170]	k ₀	1.85E17	-1.00	17090	[171]
	k ₀	7.40E21	-2.36	19383						
	Tr	0.103, 139, 10900, 4550								
	M/x/	N ₂ /1.5/ He/1.3/ O ₂ /1.5/ CO/1.5/ H ₂ /2/ CH ₄ /5/ CO ₂ /3/ H ₂ O/15/								
		H ₂ O/16.25/ H ₂ /1.9/ CO/1.875/ CO ₂ /3.75/ CH ₄ /16.25/ C ₂ H ₆ /16.25/ He/1.25/								
HCO+OH⇌CO+H ₂ O	k _f	1.00E14	0.00	0	[172]	k _f	3.01E13	0.00	0	[173]
HCO+O ₂ ⇌CO+HO ₂	k _f	6.90E06	1.90	-1371	[174]	k _f	7.58E12	0.00	410	[175]
CH ₃ OH+HO ₂ ⇌CH ₂ OH+H ₂ O ₂	k _f	1.13E13	0.00	19360	[176]	k _f	3.27E13	0.00	18282	[177]
CH ₃ OH+HO ₂ ⇌CH ₃ O+H ₂ O ₂	k _r	3.42E04	2.00	-2593.8	[65]	k _f	1.22E12	0.00	20071	
CH ₃ OH+OH⇌CH ₂ OH+H ₂ O	k _f	7.10E06	1.80	-596	[178]	k _f	3.08E04	2.65	-806.7	[179]
CH ₃ OH+OH⇌CH ₃ O+H ₂ O	k _f	1.00E06	2.10	496.7		k _f	1.50E02	3.03	-763	
C ₂ H ₅ OH+H⇌pC ₂ H ₄ OH+H ₂	k _f	1.98E07	2.08	8980	[180]	k _f	5.31E04	2.81	7495	[181]
C ₂ H ₅ OH+H⇌CH ₃ CHOH+H ₂	k _f	5.40E06	2.16	4140		k _f	8.79E04	2.68	2915	
C ₂ H ₅ OH+H⇌CH ₃ CH ₂ O+H ₂	k _f	3.60E06	2.11	9830		k _f	9.46E02	3.14	8701	
CH ₃ +O ₂ ⇌CH ₂ O+OH	k _f	2.64E00	3.283	8105	[182]	k _f	2.53E08	1.75	1200	[183]

Reactions	Original					Modified				
	k	A	n	E_a	Ref.	k	A	n	E_a	Ref.
$\text{CH}_3 + \text{H}(+\text{M}) \rightleftharpoons \text{CH}_4(+\text{M})$	k_∞	1.27E16	-0.60	383	[182]	k_∞	6.47E13	0.185	-54	[184]
	k_0	1.98E33	-4.76	2444		k_0	8.54E32	-4.69	2200	
	Tr	0.783, 74, 2940, 6960				Tr	0.516, 3637.8, 1, 1E30			
	M/x/	$\text{H}_2/2/ \text{H}_2\text{O}/6/ \text{Ar}/0.7/$ $\text{CO}/1.5/ \text{CO}_2/2/ \text{CH}_4/2/$ $\text{C}_2\text{H}_6/3/ \text{He}/0.7/$				M/x/	$\text{H}_2/4/ \text{H}_2\text{O}/12/ \text{CO}/2.3/$ $\text{CO}_2/4/ \text{Ar}/1/ \text{CH}_4/5/$ $\text{C}_2\text{H}_6/4/ \text{N}_2/1.5/ \text{He}/0.7/$ $\text{CH}_3\text{OH}/6/ \text{O}_2/1.5/$			
$\text{C}_2\text{H}_4 + \text{H}(+\text{M}) \rightleftharpoons \text{C}_2\text{H}_5(+\text{M})$	k_∞	5.27E09	1.183	1272.7	[185]	k_∞	2.79E18	0.00	755	[186]
	k_0	2.03E40	-6.64	5769.0		k_0	8.54E32	-4.69	2200	
	Tr	0.976, 9.99E9, 384, 3.29E9				Tr	0.76, 40, 1025, --			
	M/x/	$\text{H}_2/2/ \text{H}_2\text{O}/6/ \text{CH}_4/2/$ $\text{CO}/1.5/ \text{CO}_2/2/ \text{C}_2\text{H}_6/3/$ $\text{Ar}/0.7/$				M/x/	$\text{H}_2\text{O}/16.25/ \text{CO}/1.875/$ $\text{CO}_2/3.75/ \text{CH}_4/16.25/$ $\text{C}_2\text{H}_6/16.25/$			
$\text{C}_2\text{H}_4 + \text{OH} \rightleftharpoons \text{pC}_2\text{H}_4\text{OH}$	k_{f1}	6.02E37	-8.14	8043	[187]	$p_{0.010}$	1.74E43	-10.5	7698.7	[188]
						$p_{0.025}$	3.25E37	-8.63	5214.7	
						$p_{0.100}$	1.84E35	-7.75	4908.9	
						$p_{1.000}$	2.56E36	-7.75	6946.1	
	k_{f2}	7.29E31	-6.91	2855		$p_{10.00}$	3.70E33	-6.57	7605.9	
						$p_{100.0}$	1.12E26	-4.10	5757.0	

Reactions	Original					Modified				
	k	A	n	E_a	Ref.	k	A	n	E_a	Ref.
$\text{CH}_3\text{CHOH}\rightleftharpoons\text{CH}_3\text{CHO}+\text{H}$	k_r	1.74E06	2.20	7511	[181]	$p0.001$	5.69E52	-13.4	45049	[188]
						$p0.010$	3.29E56	-14.1	48129	
						$p0.100$	8.58E57	-14.2	50743	
						$p1.000$	5.36E55	-13.2	51886	
						$p10.00$	1.66E48	-10.6	50297	
						$p20.00$	8.26E44	-9.59	49218	
						$p50.00$	1.01E40	-8.06	47439	
	$p100.0$	1.10E36	-6.84	45899						
$\text{CH}_3\text{CHOH}\rightleftharpoons\text{C}_2\text{H}_3\text{OH}+\text{H}$	k_∞	6.36E09	1.33	35971	[189]	$p0.001$	5.40E46	-11.6	44323	[188]
						$p0.010$	1.21E51	-12.6	47240	
						$p0.100$	2.87E54	-13.2	50702	
	k_0	8.18E14	0.00	21515		$p1.000$	3.79E53	-12.5	52560	
						$p10.00$	6.33E46	-10.2	51441	
	Tr	0.473, 10, 2218, 2615	$p20.00$	3.87E43		-9.17	50440			
			$p50.00$	5.08E38		-7.65	48713			
					$p100.0$	5.12E34	-6.41	47182		

Rate constants are expressed in the modified Arrhenius form: $k_i = A \times T^{\eta} \times \exp(-E_a/RT)$; units are cal, cm³, mol, and s⁻¹; i = {f: forward, r: reverse, ∞ : high-pressure limit, 0: low-pressure limit}; Tr: Troe parameters (α , T^{***} , T^* , T^{**}); M/x/: third-body/efficiency/; py: pressure of y atm (PLOG).

Appendix B

Sub-mechanisms developed in this work

Table B1: Rate constants of reactions in the THP sub-mechanism developed in this work. The Arrhenius parameters are given in units of s^{-1} , cm^3 , mol^{-1} , cal.

Reaction	A	n	E _a
Fuel pericyclic reactions [140]			
cy(occcccc)<=>pent4en1ol	2.42E+07	1.897	73547
cy(occcccc)=cy(ocjccccc)+h2	2.08E+13	0.172	79353
Fuel diradical and carbenic reactions [118]			
cy(ocjccccc)=cy(ocjcccjc)	1.58E+12	0.412	54729.4
cy(ocjccccc)=DHP1	6.27E+11	0.3	18953.2
cy(ocjccccc)=carbene5	1.32E+12	0.277	40448.6
cy(ocjccccc)=co+c4h8-1	8.88E+12	0.415	78892.8
cy(ocjcccjc)=DHP1	4.23E+12	-0.078	14164.3
cy(ocjcccjc)=c*ccccho	4.30E+12	-0.078	4464.3
cy(ocjcccjc)=c3h5oc2h3	2.16E+13	-0.024	25895
carbene5=c3h6+ch2co	7.04E+12	0.223	16105.5
carbene5=co+c4h8-1	7.10E+13	0.506	35627.9
Fuel ring-opening (with isomerization via H-transfer [142] or decomposition via β -scission [118])			
cy(occcccc)=>nc4h9cho	6.50E+19	-0.639	87520
cy(occcccc)=>c4h7och3	6.50E+19	-0.639	91020
cy(occcccc)=>c3h7oc2h3	6.50E+19	-0.639	94520
cy(occcccc)=2c2h4+ch2o	1.08E+26	-2.96	95111
Fuel unimolecular initiation reactions [33]			
cy(ocjccccc)+h<=>cy(occcccc)	1.00E+14	0	0
cy(occcccc)+h<=>cy(occcccc)	1.00E+14	0	0
cy(occcccc)+h<=>cy(occcccc)	1.00E+14	0	0
Fuel bimolecular initiation by O ₂ : α -site [31] ; β -site [59] (A/3); γ -site [59] (A/6)			
cy(occcccc)+o2=cy(ocjccccc)+ho2	4.00E+13	0	46800
cy(occcccc)+o2=cy(occcccc)+ho2	8.00E+13	0	47590
cy(occcccc)+o2=cy(occcccc)+ho2	4.00E+13	0	47590
Fuel H-abstraction (metathesis): α -site [31] [127] ; β -site [59] [143] (A/3); γ -site [59] [143] (A/6)			
cy(occcccc)+oh=cy(ocjccccc)+h2o	1.13E+03	2.93	-4039
cy(occcccc)+oh=cy(occcccc)+h2o	9.75E+04	2.45	-1164
cy(occcccc)+oh=cy(occcccc)+h2o	4.88E+04	2.45	-1164
cy(occcccc)+h=cy(ocjccccc)+h2	5.80E+06	2.015	3203.8
cy(occcccc)+h=cy(occcccc)+h2	4.50E+09	1.385	8229
cy(occcccc)+h=cy(occcccc)+h2	2.25E+09	1.385	8229
cy(occcccc)+o=cy(ocjccccc)+oh	2.90E+05	2.41	876
cy(occcccc)+o=cy(occcccc)+oh	8.60E+05	2.6	2565
cy(occcccc)+o=cy(occcccc)+oh	4.30E+05	2.6	2565
cy(occcccc)+ch3=cy(ocjccccc)+ch4	3.98E+01	3.37	7635
cy(occcccc)+ch3=cy(occcccc)+ch4	3.02E+00	3.46	5480
cy(occcccc)+ch3=cy(occcccc)+ch4	1.51E+00	3.46	5480

cy(occcccc)+ho2=cy(ocjccccc)+h2o2	6.86E-02	4.08	9106
cy(occcccc)+ho2=cy(occjccc)+h2o2	3.73E+04	2.5	14163
cy(occcccc)+ho2=cy(occcjcc)+h2o2	1.87E+04	2.5	14163
cy(occcccc)+hco=cy(ocjccccc)+ch2o	2.20E+07	1.9	17000
cy(occcccc)+hco=cy(occjccc)+ch2o	2.17E+07	1.9	17000
cy(occcccc)+hco=cy(occcjcc)+ch2o	1.08E+07	1.9	17000
cy(occcccc)+ch2oh=cy(ocjccccc)+ch3oh	1.20E+02	2.95	12000
cy(occcccc)+ch2oh=cy(occjccc)+ch3oh	1.20E+02	2.95	12000
cy(occcccc)+ch2oh=cy(occcjcc)+ch3oh	6.00E+01	2.95	12000
cy(occcccc)+ch3o=cy(ocjccccc)+ch3oh	2.90E+11	0	4500
cy(occcccc)+ch3o=cy(occjccc)+ch3oh	2.90E+11	0	4500
cy(occcccc)+ch3o=cy(occcjcc)+ch3oh	1.45E+11	0	4500
cy(occcccc)+ch3o2=cy(ocjccccc)+ch3o2h	3.82E-02	4.23	9023
cy(occcccc)+ch3o2=cy(occjccc)+ch3o2h	6.00E+12	0	17500
cy(occcccc)+ch3o2=cy(occcjcc)+ch3o2h	3.00E+12	0	17500
cy(occcccc)+c2h5=cy(ocjccccc)+c2h6	1.00E+11	0	10400
cy(occcccc)+c2h5=cy(occjccc)+c2h6	4.00E+11	0	11000
cy(occcccc)+c2h5=cy(occcjcc)+c2h6	2.00E+11	0	11000
Isomerization of fuel radicals (R) [112]			
cy(ocjccccc)<=>cy(occjccc)	6.58E-25	11.18	17550
cy(ocjccccc)<=>cy(occcjcc)	1.83E-53	19.42	16450
C–C β-scission (ring opening) of R [59] [127]			
cy(ocjccccc)=c3h6oc2h3	1.04E+41	-8.51	40814
cy(ocjccccc)=c4h8cho-5	4.50E+11	0.56	22200
cy(occjccc)=c5h9o	4.50E+11	0.56	22200
cy(occjccc)=c3h5oc2h4	1.04E+41	-8.51	40814
cy(occcjcc)=c4h7och2	2.07E+41	-8.51	40814
C–H β-scission of R (R=DHP+H) [33]			
cy(ocjccccc)=DHP1+h	2.85E+11	0.34	32520
cy(occjccc)=DHP1+h	2.85E+11	0.34	35520
cy(occjccc)=DHP2+h	2.85E+11	0.34	35520
cy(occcjcc)=DHP2+h	5.70E+11	0.34	35520
Low-temperature reactivity			
R+O ₂ =RO ₂ (1 st addition to O ₂) [144]			
cy(ocjccccc)+o2=jo2cy(cocccc) cy(occjccc)+o2=jo2cy(ccoccc) cy(occcjcc)+o2=jo2cy(cccocc)	1.00E+11	0	0
PLOG/ 0.01	7.33E+05	1.330	-6345.640/
PLOG/ 0.1	2.24E+11	-0.105	-3697.870/
PLOG/ 1	1.54E+18	-2.020	-498.567/
PLOG/ 10	6.74E+27	-4.850	3779.820/
PLOG/ 100	1.67E+29	-5.150	5036.450/
Isomerization RO ₂ =QOOH: H-atom shift from β-position [33]			
jo2cy(cocccc)=ho2cy(coccccj)	4.32E+08	1.26	28600
jo2cy(ccoccc)=ho2cy(ccjoccc)	6.15E+08	1.05	25600

jo2cy(ccoccc)=ho2cy(ccocccj)	6.15E+08	1.05	28600
jo2cy(cccocc)=ho2cy(ccjcocc)	8.64E+08	1.26	28600
Isomerization RO ₂ =QOOH: H-atom shift from γ -position [33]			
jo2cy(cocccc)=ho2cy(cocjccc)	6.18E+08	0.93	15400
jo2cy(cocccc)=ho2cy(cocccjc)	6.18E+08	0.93	18400
jo2cy(ccoccc)=ho2cy(ccocccj)	5.34E+05	1.12	15700
jo2cy(cccocc)=ho2cy(cccjocc)	1.24E+09	0.93	15400
Isomerization RO ₂ =QOOH: H-atom shift from δ -position [33]			
jo2cy(cocccc)=ho2cy(cocccjc)	2.86E+06	1.27	17000
jo2cy(ccoccc)=ho2cy(ccocjcc)	2.86E+06	1.27	14000
Bicyclic ether formation [33]			
ho2cy(cocjccc)=cy(o)26THP+oh	2.68E+09	0.62	15900
ho2cy(coccccj)=bicy(o)(cocccc)+oh	4.78E+09	0.79	9600
ho2cy(cocccjc)=cy(o)24THP+oh	2.68E+09	0.62	15900
ho2cy(cocccjc)=cy(o)25THP+oh	2.42E+07	1.01	10300
ho2cy(ccjoccc)=bicy(o)(cocccc)+oh	4.78E+09	0.79	9600
ho2cy(ccocccj)=bicy(o)(ccoccc)+oh	4.78E+09	0.79	9600
ho2cy(ccocccjc)=cy(o)35THP+oh	2.68E+09	0.62	15900
ho2cy(ccocjcc)=cy(o)25THP+oh	2.42E+07	1.01	10300
ho2cy(ccjcocc)=bicy(o)(ccoccc)+oh	4.78E+09	0.79	9600
ho2cy(cccjocc)=cy(o)24THP+oh	2.68E+09	0.62	15900
QOOH β -scission (radical in γ -position from -OOH) [127] [143]			
ho2cy(cocjccc)=ohcccccho+oh	2.30E+14	-0.23	20100
ho2cy(cocccjc)=c*cccocho+oh	3.50E+13	0.06	33300
ho2cy(ccocccjc)=c*ccoccho+oh	3.30E+12	0.248	20440
ho2cy(cccjocc)=c*ccccho+oh	3.50E+11	0.06	33300
QOOH=DHP+HO ₂ (concerted elimination) [33]			
ho2cy(coccccj)=DHP1+ho2	3.01E+11	0.35	15200
ho2cy(ccjoccc)=DHP1+ho2	7.82E+09	0.9	14900
ho2cy(ccocccj)=DHP2+ho2	3.50E+11	0.37	14900
ho2cy(ccjcocc)=DHP2+ho2	3.50E+11	0.37	14900
RO ₂ =DHP+HO ₂ (concerted elimination) [33]			
jo2cy(cocccc)=ho2+DHP1	4.48E+09	0.95	29200
jo2cy(ccoccc)=ho2+DHP1	4.48E+09	0.95	29200
jo2cy(ccoccc)=ho2+DHP2	4.48E+09	0.95	29200
jo2cy(cccocc)=ho2+DHP2	8.96E+09	0.95	29200
R+O ₂ =DHP+HO ₂ [145] (A/2; except for γ -site)			
cy(ocjcccc)+o2=DHP1+ho2	1.85E+16	-1.63	3418
cy(occjccc)+o2=DHP1+ho2	1.85E+16	-1.63	3418
cy(occjccc)+o2=ho2+DHP2	1.85E+16	-1.63	3418
cy(occcjcc)+o2=ho2+DHP2	3.70E+16	-1.63	3418
QOOH+O ₂ =O ₂ QOOH (2 nd addition to O ₂) [144] (A/2)			

<chem>ho2cy(cocjccc)+o2=qcy(coc(o2j)ccc)</chem> <chem>ho2cy(coccccj)+o2=qcy(cocccc(o2j))</chem> <chem>ho2cy(coccccjc)+o2=qcy(cocccc(o2j)c)</chem> <chem>ho2cy(cocccjcc)+o2=qcy(coccc(o2j)cc)</chem> <chem>ho2cy(ccjoccc)+o2=qcy(cc(o2j)occc)</chem> <chem>ho2cy(ccocccjc)+o2=qcy(ccoccc(o2j)c)</chem> <chem>ho2cy(ccocjcc)+o2=qcy(ccoc(o2j)cc)</chem> <chem>ho2cy(ccocccj)+o2=qcy(ccoccc(o2j))</chem> <chem>ho2cy(ccjcocc)+o2=qcy(cc(o2j)cocc)</chem> <chem>ho2cy(cccjocc)+o2=qcy(ccc(o2j)occ)</chem>	5.00E+10	0	0
PLOG/ 0.01	3.67E+05	1.330	-6345.640/
PLOG/ 0.1	1.12E+11	-0.105	-3697.870/
PLOG/ 1	7.70E+17	-2.020	-498.567/
PLOG/ 10	3.37E+27	-4.850	3779.820/
PLOG/ 100	8.35E+28	-5.150	5036.450/
O ₂ QOOH=KHP+OH [33]			
<chem>qcy(coc(o2j)ccc)=o*cy(cocqccc)+oh</chem>	2.79E+07	1.13	12400
<chem>qcy(cocccc(o2j))=o*cy(coccccq)+oh</chem>	2.86E+07	1.38	22600
<chem>qcy(cocccc(o2j)c)=o*cy(coccccqc)+oh</chem>	2.79E+07	1.13	12400
<chem>qcy(coccc(o2j)cc)=o*cy(cocccqcc)+oh</chem>	1.49E+08	0.71	12000
<chem>qcy(cc(o2j)occc)=o*cy(ccqoccc)+oh</chem>	2.86E+07	1.38	25600
<chem>qcy(ccoccc(o2j)c)=o*cy(ccocccqc)+oh</chem>	1.13E+06	0.82	13800
<chem>qcy(ccoc(o2j)cc)=o*cy(ccocqcc)+oh</chem>	1.49E+08	0.71	15000
<chem>qcy(ccoccc(o2j))=o*cy(ccocccq)+oh</chem>	2.86E+07	1.38	25600
<chem>qcy(cc(o2j)cocc)=o*cy(ccqcocc)+oh</chem>	2.86E+07	1.38	25600
<chem>qcy(ccc(o2j)occ)=o*cy(cccqocc)+oh</chem>	2.79E+07	1.13	15400
KHP decomposition [148]			
<chem>o*cy(coccccq)=>oh+co+c3h6cho-4o</chem>	2.50E+15	0	43000
<chem>o*cy(coccccq)=>oh+c2h4+ch2o+choco</chem>	2.50E+15	0	43000
<chem>o*cy(coccccqc)=>oh+ch2co+ch2o+ch2cho</chem>	2.50E+15	0	43000
<chem>o*cy(coccccqc)=>oh+c2h4+co2+ch2cho</chem>	2.50E+15	0	43000
<chem>o*cy(cocccqcc)=>oh+ch2o+c2h4+hco+co</chem>	2.50E+15	0	43000
<chem>o*cy(cocqccc)=>c3h6cho-4+co2+oh</chem>	2.50E+15	0	43000
<chem>o*cy(cocqccc)=>c2h4+ch2co+ocho+oh</chem>	2.50E+15	0	43000
<chem>o*cy(ccqoccc)=>hco+ch2o+c2h4+co+oh</chem>	2.50E+15	0	43000
<chem>o*cy(ccocqcc)=>c2h4+hco+co+ch2o+oh</chem>	2.50E+15	0	43000
<chem>o*cy(ccocccqc)=>ch2cho+ch2co+ch2o+oh</chem>	2.50E+15	0	43000
<chem>o*cy(ccocccq)=>c2h4+ch2o+co+hco+oh</chem>	2.50E+15	0	43000
<chem>o*cy(ccqcocc)=>hco+ch2o+c2h4+co+oh</chem>	2.50E+15	0	43000
<chem>o*cy(cccqocc)=>c2h4+ocho+ch2co+oh</chem>	2.50E+15	0	43000
<chem>o*cy(cccqocc)=>ch2o+ch2co+ch2cho+oh</chem>	2.50E+15	0	43000
Bicyclic ether reactions with OH, H, and HO ₂ [31]			
<chem>bicy(o)(cocccc)+oh=>hcco+c2h4+ch2o+h2o</chem>	2.93E+04	2.53	-1659
<chem>bicy(o)(cocccc)+oh=>hco+ch2co+c2h4+h2o</chem>	2.93E+04	2.53	-1659
<chem>bicy(o)(cocccc)+h=>hcco+c2h4+ch2o+h2</chem>	6.02E+05	2.4	2583
<chem>bicy(o)(cocccc)+h=>hco+ch2co+c2h4+h2</chem>	6.02E+05	2.4	2583

bicy(o)(cocc) + ho2 => hcco + c2h4 + ch2o + h2o2	4.34E+02	3.01	12094
bicy(o)(cocc) + ho2 => hco + ch2co + c2h4 + h2o2	4.34E+02	3.01	12094
bicy(o)(ccoc) + oh => c2h3 + ch2co + ch2o + h2o	2.93E+04	2.53	-1659
bicy(o)(ccoc) + oh => hcco + c2h4 + ch2o + h2o	2.93E+04	2.53	-1659
bicy(o)(ccoc) + h => c2h3 + ch2co + ch2o + h2	6.02E+05	2.4	2583
bicy(o)(ccoc) + h => hcco + c2h4 + ch2o + h2	6.02E+05	2.4	2583
bicy(o)(ccoc) + ho2 => c2h3 + ch2co + ch2o + h2o2	4.34E+02	3.01	12094
bicy(o)(ccoc) + ho2 => hcco + c2h4 + ch2o + h2o2	4.34E+02	3.01	12094
cy(o)24THP + oh => ac3h5co + ch2o + h2o	2.93E+04	2.53	-1659
cy(o)24THP + oh => c2h3oc2h4p + co + h2o	2.93E+04	2.53	-1659
cy(o)24THP + ho2 => ac3h5co + ch2o + h2o2	4.34E+02	3.01	12094
cy(o)24THP + ho2 => c2h3oc2h4p + co + h2o2	4.34E+02	3.01	12094
cy(o)24THP + h => ac3h5co + ch2o + h2	6.02E+05	2.4	2583
cy(o)24THP + h => c2h3oc2h4p + co + h2	6.02E+05	2.4	2583
cy(o)25THP + oh => c4h714 + co2 + h2o	2.93E+04	2.53	-1659
cy(o)25THP + oh => pc2h4cho + ch2co + h2o	2.93E+04	2.53	-1659
cy(o)25THP + ho2 => c4h714 + co2 + h2o2	4.34E+02	3.01	12094
cy(o)25THP + ho2 => pc2h4cho + ch2co + h2o2	4.34E+02	3.01	12094
cy(o)25THP + h => c4h714 + co2 + h2	6.02E+05	2.4	2583
cy(o)25THP + h => pc2h4cho + ch2co + h2	6.02E+05	2.4	2583
cy(o)26THP + oh => ohcccccj*o + h2o	2.93E+04	2.53	-1659
cy(o)26THP + ho2 => ohcccccj*o + h2o2	4.34E+02	3.01	12094
cy(o)26THP + h => ohcccccj*o + h2	6.02E+05	2.4	2583
cy(o)35THP + oh => ac3h5co + ch2o + h2o	2.93E+04	2.53	-1659
cy(o)35THP + ho2 => ac3h5co + ch2o + h2o2	4.34E+02	3.01	12094
cy(o)35THP + h => ac3h5co + ch2o + h2	6.02E+05	2.4	2583
R+HO ₂ =RO+OH [33]			
cy(ocjccc) + ho2 = jocy(cocc) + oh	7.00E+12	0	-1.00E+03
cy(occjcc) + ho2 = jocy(ccoc) + oh	7.00E+12	0	-1.00E+03
cy(occcjc) + ho2 = jocy(cccocc) + oh	7.00E+12	0	-1.00E+03
R+CH ₃ O ₂ =RO+CH ₃ O [33]			
cy(ocjccc) + ch3o2 = jocy(cocc) + ch3o	4.50E+12	0	0
cy(occjcc) + ch3o2 = jocy(ccoc) + ch3o	4.50E+12	0	0
cy(occcjc) + ch3o2 = jocy(cccocc) + ch3o	4.50E+12	0	0
R+R'O ₂ =RO+R'O [33]			
jo2cy(cocc) + cy(ocjccc) = jocy(cocc) + jocy(cocc)	4.50E+12	0	-500
jo2cy(ccoc) + cy(ocjccc) = jocy(ccoc) + jocy(ccoc)	4.50E+12	0	0
jo2cy(cccocc) + cy(ocjccc) = jocy(cccocc) + jocy(cccocc)	4.50E+12	0	0
jo2cy(cocc) + cy(occjcc) = jocy(cocc) + jocy(ccoc)	4.50E+12	0	-500
jo2cy(ccoc) + cy(occjcc) = jocy(ccoc) + jocy(ccoc)	4.50E+12	0	0
jo2cy(cccocc) + cy(occjcc) = jocy(cccocc) + jocy(cccocc)	4.50E+12	0	0
jo2cy(cocc) + cy(occcjc) = jocy(cocc) + jocy(cccocc)	4.50E+12	0	-500
jo2cy(ccoc) + cy(occcjc) = jocy(ccoc) + jocy(cccocc)	4.50E+12	0	0
jo2cy(cccocc) + cy(occcjc) = jocy(cccocc) + jocy(cccocc)	4.50E+12	0	0

RO ₂ +HO ₂ =ROOH+O ₂ [33]			
jo2cy(cocccc)+ho2=ho2cy(cocccc)+o2	2.00E+11	0	650
jo2cy(ccoccc)+ho2=ho2cy(ccoccc)+o2	2.00E+11	0	650
jo2cy(cccocc)+ho2=ho2cy(cccocc)+o2	2.00E+11	0	650
RO ₂ +H ₂ O ₂ =ROOH+HO ₂ [33]			
jo2cy(cocccc)+h2o2=ho2cy(cocccc)+ho2	2.40E+12	0	5000
jo2cy(ccoccc)+h2o2=ho2cy(ccoccc)+ho2	2.40E+12	0	5000
jo2cy(cccocc)+h2o2=ho2cy(cccocc)+ho2	2.40E+12	0	5000
RO ₂ +CH ₃ O ₂ =RO+CH ₃ O+O ₂ [33]			
jo2cy(cocccc)+ch3o2=jocy(cocccc)+ch3o+o2	3.40E+16	-1.61	1500
jo2cy(ccoccc)+ch3o2=jocy(ccoccc)+ch3o+o2	3.40E+16	-1.61	2000
jo2cy(cccocc)+ch3o2=jocy(cccocc)+ch3o+o2	3.40E+16	-1.61	2000
RO ₂ +R'O ₂ =RO+R'O+O ₂ [33]			
jo2cy(cocccc)+jo2cy(cocccc)=jocy(cocccc)+jocy(cocccc)+o2	6.80E+16	-1.61	2000
jo2cy(cocccc)+jo2cy(ccoccc)=jocy(cocccc)+jocy(ccoccc)+o2	6.80E+16	-1.61	2500
jo2cy(cocccc)+jo2cy(cccocc)=jocy(cocccc)+jocy(cccocc)+o2	6.80E+16	-1.61	2500
jo2cy(ccoccc)+jo2cy(ccoccc)=jocy(ccoccc)+jocy(ccoccc)+o2	6.80E+16	-1.61	3000
jo2cy(ccoccc)+jo2cy(cccocc)=jocy(ccoccc)+jocy(cccocc)+o2	6.80E+16	-1.61	3000
jo2cy(cccocc)+jo2cy(cccocc)=jocy(cccocc)+jocy(cccocc)+o2	6.80E+16	-1.61	3000
RO ₂ +R'O ₂ =R'O+R'OH+O ₂ [59]			
jo2cy(cocccc)+jo2cy(cocccc)=o*cy(cocccc)+hocy(cocccc)+o2	4.51E+13	-0.263	2589.8
jo2cy(cocccc)+jo2cy(ccoccc)=o*cy(cocccc)+hocy(ccoccc)+o2	4.51E+13	-0.263	3089.8
jo2cy(cocccc)+jo2cy(cccocc)=o*cy(cccocc)+hocy(cccocc)+o2	4.51E+13	-0.263	3089.8
jo2cy(ccoccc)+jo2cy(ccoccc)=o*cy(ccoccc)+hocy(ccoccc)+o2	4.51E+13	-0.263	3589.8
jo2cy(ccoccc)+jo2cy(cccocc)=o*cy(cccocc)+hocy(cccocc)+o2	4.51E+13	-0.263	3589.8
jo2cy(cccocc)+jo2cy(cccocc)=o*cy(cccocc)+hocy(cccocc)+o2	4.51E+13	-0.263	3589.8
jo2cy(cccocc)+jo2cy(cccocc)=o*cy(cccocc)+hocy(cccocc)+o2	4.51E+13	-0.263	3589.8
jo2cy(cccocc)+jo2cy(cccocc)=o*cy(cccocc)+hocy(cccocc)+o2	4.51E+13	-0.263	3589.8
RO ₂ =R'O+OH [59]			
jo2cy(cocccc)=o*cy(cocccc)+oh jo2cy(ccoccc)=o*cy(ccoccc)+oh jo2cy(cccocc)=o*cy(cccocc)+oh	486070	2.2717	35199
PLOG/ 0.01	5.34E+47	-11.78	45113/
PLOG/ 0.1	4.61E+39	-8.9363	43767/
PLOG/ 1	2.25E+30	-5.7798	41750/
PLOG/ 10	1.21E+23	-3.3381	40104/
PLOG/ 100	2.21E+17	-1.4369	38711/
PLOG/ 1000	6.47E+12	0.0367	37492/
ROOH=RO+OH [148]			
ho2cy(cocccc)=jocy(cocccc)+oh	2.50E+15	0	43000
ho2cy(ccoccc)=jocy(ccoccc)+oh	2.50E+15	0	43000
ho2cy(cccocc)=jocy(cccocc)+oh	2.50E+15	0	43000
RO β-scission (ring opening) [33]			

jocy(cocccc)=>ohcccccoj	3.15E+43	-9.45	30900
jocy(ccoccc)=>ohccccocj	3.53E+36	-7.24	35800
jocy(cccocc)=>ohccccoccj	4.38E+40	-8.36	39900

Table B2: Rate constants of reactions in the THF sub-mechanism developed in this work. The Arrhenius parameters are given in units of s^{-1} , cm^3 , mol^{-1} , cal.

Reaction	A	n	E _a
Fuel pericyclic reactions [140]			
cy(occcc)<=>but3en1ol	3.78E+05	2.301	75741
cy(occcc)=cy(ocjcccj)+h2	1.41E+09	1.159	79047
Fuel diradical and carbenic reactions [118]			
cy(ocjcccj)=c2h3oc2h3	2.16E+13	-0.024	25895
cy(ocjcccj)=cy(ocjccjc)	1.58E+12	0.412	54729.4
cy(ocjcccj)=DHF1	6.27E+11	0.3	18953.2
cy(ocjcccj)=carbene4	1.32E+12	0.277	40448.6
cy(ocjcccj)=co+c3h6	8.88E+12	0.415	78892.8
cy(ocjccjc)=DHF1	4.23E+12	-0.078	14164.3
cy(ocjccjc)=ac3h5cho	4.30E+12	-0.078	4464.3
carbene4=c2h4+ch2co	7.04E+12	0.223	16105.5
carbene4=co+c3h6	7.10E+13	0.506	35627.9
Fuel ring-opening (with isomerization via H-transfer [137] or decomposition via β -scission [127])			
cy(occcc)=>nc3h7cho	5.04E+15	-0.639	79840
cy(occcc)=>c3h5och3	5.04E+15	-0.639	81840
cy(occcc)=>c2h5oc2h3	2.52E+15	-0.639	84840
cy(occcc)=c3h6+ch2o	1.08E+26	-2.96	95111
cy(occcc)=ch3cho+c2h4	1.10E+10	1.57	85300
Fuel unimolecular initiation reactions [33]			
cy(ocjccc)+h<=>cy(occcc)	1.00E+14	0	0
cy(occjcc)+h<=>cy(occcc)	1.00E+14	0	0
cy(occcjc)+h<=>cy(occcc)	1.00E+14	0	0
Fuel bimolecular initiation by O ₂ : α -site [31] ; β -site [59] (A/3)			
cy(occcc)+o2=cy(ocjccc)+ho2	4.00E+13	0	46800
cy(occcc)+o2=cy(occjcc)+ho2	8.00E+13	0	47590
Fuel H-abstraction (metathesis): α -site [31] [127] ; β -site [59] [143] (A/3)			
cy(occcc)+oh=cy(ocjccc)+h2o	1.13E+03	2.93	-4039
cy(occcc)+oh=cy(occjcc)+h2o	9.75E+04	2.45	-1164
cy(occcc)+h=cy(ocjccc)+h2	5.80E+06	2.015	3203.8
cy(occcc)+h=cy(occjcc)+h2	4.50E+09	1.385	8229
cy(occcc)+o=cy(ocjccc)+oh	2.90E+05	2.41	876
cy(occcc)+o=cy(occjcc)+oh	8.60E+05	2.6	2565

cy(occcc)+ch3=cy(ocjccc)+ch4	3.98E+01	3.37	7635
cy(occcc)+ch3=cy(occjcc)+ch4	3.02E+00	3.46	5480
cy(occcc)+ho2=cy(ocjccc)+h2o2	6.86E-02	4.08	9106
cy(occcc)+ho2=cy(occjcc)+h2o2	3.73E+04	2.5	14163
cy(occcc)+hco=cy(ocjccc)+ch2o	2.20E+07	1.9	17000
cy(occcc)+hco=cy(occjcc)+ch2o	2.17E+07	1.9	17000
cy(occcc)+ch2oh=cy(ocjccc)+ch3oh	1.20E+02	2.95	12000
cy(occcc)+ch2oh=cy(occjcc)+ch3oh	1.20E+02	2.95	12000
cy(occcc)+ch3o=cy(ocjccc)+ch3oh	2.90E+11	0	4500
cy(occcc)+ch3o=cy(occjcc)+ch3oh	2.90E+11	0	4500
cy(occcc)+ch3o2=cy(ocjccc)+ch3o2h	3.82E-02	4.23	9023
cy(occcc)+ch3o2=cy(occjcc)+ch3o2h	6.00E+12	0	17500
cy(occcc)+c2h5=cy(ocjccc)+c2h6	1.00E+11	0	10400
cy(occcc)+c2h5=cy(occjcc)+c2h6	4.00E+11	0	11000
Isomerization of fuel radicals (R) [127]			
cy(ocjccc)<=>cy(occjcc) DUP	2.20E+08	1.56	43800
cy(ocjccc)<=>cy(occjcc) DUP	1.30E+07	1.72	46500
C–C β -scission (ring opening) of R [127]			
cy(ocjccc)=c2h3oc2h4p	6.80E+11	0.66	33000.0
cy(ocjccc)=c3h6cho-4	4.50E+11	0.56	22200.0
cy(occjcc)=c4h714o	2.00E+12	0.27	31100.0
cy(occjcc)=c3h5och2	4.50E+10	0.71	32365.5
C–H β -scission of R (R=DHF+H) [33]			
cy(ocjccc)=DHF1+h	2.85E+11	0.34	32520
cy(occjcc)=DHF1+h	2.85E+11	0.34	35520
cy(occjcc)=DHF2+h	2.85E+11	0.34	35520
Low-temperature reactivity			
R+O ₂ =RO ₂ (1 st addition to O ₂) [144]			
cy(ocjccc)+o2=jo2cy(coccc) cy(occjcc)+o2=jo2cy(ccocc)	1.00E+11	0	0
PLOG/ 0.01	7.33E+05	1.330	-6345.640/
PLOG/ 0.1	2.24E+11	-0.105	-3697.870/
PLOG/ 1	1.54E+18	-2.020	-498.567/
PLOG/ 10	6.74E+27	-4.850	3779.820/
PLOG/ 100	1.67E+29	-5.150	5036.450/
Isomerization RO ₂ =QOOH: H-atom shift from β -position [33]			
jo2cy(coccc)=ho2cy(cocccj)	4.32E+08	1.26	28600
jo2cy(ccocc)=ho2cy(ccjocc)	6.15E+08	1.05	25600
jo2cy(ccocc)=ho2cy(ccoccj)	6.15E+08	1.05	28600
Isomerization RO ₂ =QOOH: H-atom shift from γ -position [33]			
jo2cy(coccc)=ho2cy(cocjcc)	6.18E+08	0.93	15400
jo2cy(coccc)=ho2cy(coccjc)	6.18E+08	0.93	18400
jo2cy(ccocc)=ho2cy(ccocjc)	6.18E+08	0.93	15400

Bicyclic ether formation [33]			
ho2cy(cocjcc)=cy(o)25THF+oh	2.68E+09	0.62	15900
ho2cy(cocccj)=bicy(o)(coccc)+oh	4.78E+09	0.79	9600
ho2cy(cocccj)=cy(o)24THF+oh	2.42E+07	1.01	10300
ho2cy(ccjocc)=bicy(o)(coccc)+oh	4.78E+09	0.79	9600
ho2cy(ccocccj)=bicy(o)(ccoccc)+oh	4.78E+09	0.79	9600
ho2cy(ccocjcc)=cy(o)24THF+oh	2.42E+07	1.01	10300
QOOH β -scission (radical in γ -position from -OOH) [127]			
ho2cy(cocjcc)=choc2h4cho+oh	2.30E+14	-0.23	20100
ho2cy(cocccj)=c*ccocho+oh	3.50E+13	0.06	33300
ho2cy(ccocjcc)=c*coccho+oh	3.50E+11	0.06	33300
QOOH=DHF+HO ₂ (concerted elimination) [33]			
ho2cy(cocccj)=DHF1+ho2	3.01E+11	0.35	15200
ho2cy(ccjocc)=DHF1+ho2	7.82E+09	0.9	14900
ho2cy(ccocccj)=DHF2+ho2	3.50E+11	0.37	14900
RO ₂ =DHF+HO ₂ (concerted elimination) [33]			
jo2cy(coccc)=ho2+DHF1	4.48E+09	0.95	29200
jo2cy(ccoccc)=ho2+DHF1	4.48E+09	0.95	29200
jo2cy(ccoccc)=ho2+DHF2	4.48E+09	0.95	29200
R+O ₂ =DHF+HO ₂ [145] (A/2; except for γ -site)			
cy(ocjcc)+o2=DHF1+ho2	1.85E+16	-1.63	3418
cy(occcjcc)+o2=DHF1+ho2	1.85E+16	-1.63	3418
cy(occcjcc)+o2=ho2+DHF2	1.85E+16	-1.63	3418
QOOH+O ₂ =O ₂ QOOH (2 nd addition to O ₂) [144] (A/2)			
ho2cy(cocjcc)+o2=qcy(coc(o2j)cc) ho2cy(cocccj)+o2=qcy(coccc(o2j)) ho2cy(cocccj)+o2=qcy(coccc(o2j)c) ho2cy(ccjocc)+o2=qcy(cc(o2j)occ) ho2cy(ccocjcc)+o2=qcy(ccoc(o2j)c) ho2cy(ccocccj)+o2=qcy(ccoccc(o2j))	5.00E+10	0	0
PLOG/ 0.01	3.67E+05	1.330	-6345.640/
PLOG/ 0.1	1.12E+11	-0.105	-3697.870/
PLOG/ 1	7.70E+17	-2.020	-498.567/
PLOG/ 10	3.37E+27	-4.850	3779.820/
PLOG/ 100	8.35E+28	-5.150	5036.450/
O ₂ QOOH=KHP+OH [33]			
qcy(coc(o2j)cc)=o*cy(cocqcc)+oh	2.79E+07	1.13	12400
qcy(coccc(o2j))=o*cy(cocccq)+oh	2.86E+07	1.38	22600
qcy(coccc(o2j)c)=o*cy(cocccq)+oh	2.79E+07	1.13	12400
qcy(cc(o2j)occ)=o*cy(ccqocc)+oh	2.86E+07	1.38	25600
qcy(ccoc(o2j)c)=o*cy(ccocq)+oh	1.49E+08	0.71	15000
qcy(ccoccc(o2j))=o*cy(ccocccq)+oh	2.86E+07	1.38	25600
KHP decomposition: KHP=ZO+OH [148]			
o*cy(cocccq)=o*cy(coccc(oj))+oh	2.50E+15	0	43000
o*cy(cocccq)=o*cy(coccc(oj)c)+oh	2.50E+15	0	43000

$\text{o*cy}(\text{cocqcc})=\text{o*cy}(\text{coc}(\text{oj})\text{cc})+\text{oh}$	2.50E+15	0	43000
$\text{o*cy}(\text{ccqocc})=\text{o*cy}(\text{cc}(\text{oj})\text{occ})+\text{oh}$	2.50E+15	0	43000
$\text{o*cy}(\text{ccocqc})=\text{o*cy}(\text{ccoc}(\text{oj})\text{c})+\text{oh}$	2.50E+15	0	43000
$\text{o*cy}(\text{ccoccq})=\text{o*cy}(\text{ccocc}(\text{oj}))+\text{oh}$	2.50E+15	0	43000
ZO reactions [29] [65] [190,191]			
$\text{o*cy}(\text{coc}(\text{oj})\text{cc})=\text{co}_2+\text{pc}_2\text{h}_4\text{cho}$	1.27E+20	-2.426	25468.7
$\text{o*cy}(\text{coc}(\text{oj})\text{cc})=\text{ohcoc}(\text{*o})\text{ccj}$	5.25E+13	0.00	11690.0
$\text{o*cy}(\text{ccoc}(\text{oj})\text{c})=\text{ch}_2\text{o}+\text{ohccc}\text{o}$	1.27E+20	-2.426	25468.7
$\text{o*cy}(\text{ccoc}(\text{oj})\text{c})=\text{ohcocc}(\text{*o})\text{cj}$	5.25E+13	0.00	11690.0
$\text{o*cy}(\text{cocc}(\text{oj})\text{c})=\text{ohccc}(\text{*o})\text{ocj}$	5.25E+13	0.00	11690.0
$\text{o*cy}(\text{cocc}(\text{oj})\text{c})=\text{ohccoc}(\text{*o})\text{cj}$	5.25E+13	0.00	11690.0
$\text{o*cy}(\text{ccocc}(\text{oj}))=\text{ohcc}(\text{*o})\text{cocj}$	2.00E+13	0.0	20000
$\text{o*cy}(\text{ccocc}(\text{oj}))=\text{ohccoccj*o}$	3.73E+20	-2.18	17260
$\text{o*cy}(\text{cocco}(\text{oj}))=\text{ohccoccj*o}$	3.73E+20	-2.18	17260
$\text{o*cy}(\text{cocco}(\text{oj}))=\text{ohcc}(\text{*o})\text{occj}$	2.00E+13	0.0	20000
$\text{o*cy}(\text{cc}(\text{oj})\text{occ})=\text{ch}_2\text{o}+\text{ch}_2\text{co}+\text{hco}$	1.27E+20	-2.426	25468.7
$\text{o*cy}(\text{cc}(\text{oj})\text{occ})=\text{ohcoccj*o}$	3.73E+20	-2.18	17260
Bicyclic ether reactions with OH, H, and HO ₂ [31]			
$\text{bicy}(\text{o})(\text{cocco})+\text{oh}=>\text{ch}_2\text{o}+\text{c}_2\text{h}_3\text{co}+\text{h}_2\text{o}$	2.93E+04	2.53	-1659
$\text{bicy}(\text{o})(\text{cocco})+\text{oh}=>\text{c}_2\text{h}_4+\text{choco}+\text{h}_2\text{o}$	2.93E+04	2.53	-1659
$\text{bicy}(\text{o})(\text{cocco})+\text{h}=>\text{ch}_2\text{o}+\text{c}_2\text{h}_3\text{co}+\text{h}_2$	6.02E+05	2.4	2583
$\text{bicy}(\text{o})(\text{cocco})+\text{h}=>\text{c}_2\text{h}_4+\text{choco}+\text{h}_2$	6.02E+05	2.4	2583
$\text{bicy}(\text{o})(\text{cocco})+\text{ho}_2=>\text{ch}_2\text{o}+\text{c}_2\text{h}_3\text{co}+\text{h}_2\text{o}_2$	4.34E+02	3.01	12094
$\text{bicy}(\text{o})(\text{cocco})+\text{ho}_2=>\text{c}_2\text{h}_4+\text{choco}+\text{h}_2\text{o}_2$	4.34E+02	3.01	12094
$\text{bicy}(\text{o})(\text{ccocc})+\text{oh}=>\text{ch}_2\text{o}+\text{c}_2\text{h}_3\text{co}+\text{h}_2\text{o}$	5.86E+04	2.53	-1659
$\text{bicy}(\text{o})(\text{ccocc})+\text{h}=>\text{ch}_2\text{o}+\text{c}_2\text{h}_3\text{co}+\text{h}_2$	1.20E+06	2.4	2583
$\text{bicy}(\text{o})(\text{ccocc})+\text{ho}_2=>\text{ch}_2\text{o}+\text{c}_2\text{h}_3\text{co}+\text{h}_2\text{o}_2$	8.68E+02	3.01	12094
$\text{cy}(\text{o})24\text{THF}+\text{oh}=>\text{co}_2+\text{c}_3\text{h}_5\text{-a}+\text{h}_2\text{o}$	1.47E+04	2.53	-1659
$\text{cy}(\text{o})24\text{THF}+\text{oh}=>\text{ch}_2\text{co}+\text{ch}_2\text{cho}+\text{h}_2\text{o}$	1.47E+04	2.53	-1659
$\text{cy}(\text{o})24\text{THF}+\text{oh}=>\text{co}+\text{c}_3\text{h}_5\text{o}+\text{h}_2\text{o}$	1.47E+04	2.53	-1659
$\text{cy}(\text{o})24\text{THF}+\text{oh}=>\text{co}+\text{c}_2\text{h}_3\text{och}_2+\text{h}_2\text{o}$	1.47E+04	2.53	-1659
$\text{cy}(\text{o})24\text{THF}+\text{ho}_2=>\text{co}_2+\text{c}_3\text{h}_5\text{-a}+\text{h}_2\text{o}_2$	2.17E+02	3.01	12094
$\text{cy}(\text{o})24\text{THF}+\text{ho}_2=>\text{ch}_2\text{co}+\text{ch}_2\text{cho}+\text{h}_2\text{o}_2$	2.17E+02	3.01	12094
$\text{cy}(\text{o})24\text{THF}+\text{ho}_2=>\text{co}+\text{c}_3\text{h}_5\text{o}+\text{h}_2\text{o}_2$	2.17E+02	3.01	12094
$\text{cy}(\text{o})24\text{THF}+\text{ho}_2=>\text{co}+\text{c}_2\text{h}_3\text{och}_2+\text{h}_2\text{o}_2$	2.17E+02	3.01	12094
$\text{cy}(\text{o})24\text{THF}+\text{h}=>\text{co}_2+\text{c}_3\text{h}_5\text{-a}+\text{h}_2$	3.01E+05	2.4	2583
$\text{cy}(\text{o})24\text{THF}+\text{h}=>\text{ch}_2\text{co}+\text{ch}_2\text{cho}+\text{h}_2$	3.01E+05	2.4	2583
$\text{cy}(\text{o})24\text{THF}+\text{h}=>\text{co}+\text{c}_3\text{h}_5\text{o}+\text{h}_2$	3.01E+05	2.4	2583
$\text{cy}(\text{o})24\text{THF}+\text{h}=>\text{co}+\text{c}_2\text{h}_3\text{och}_2+\text{h}_2$	3.01E+05	2.4	2583
$\text{cy}(\text{o})25\text{THF}+\text{oh}=>\text{ch}_2\text{co}+\text{ch}_2\text{cho}+\text{h}_2\text{o}$	2.93E+04	2.53	-1659
$\text{cy}(\text{o})25\text{THF}+\text{ho}_2=>\text{ch}_2\text{co}+\text{ch}_2\text{cho}+\text{h}_2\text{o}_2$	8.68E+02	3.01	12094
$\text{cy}(\text{o})25\text{THF}+\text{h}=>\text{ch}_2\text{co}+\text{ch}_2\text{cho}+\text{h}_2$	1.20E+06	2.4	2583
R+HO ₂ =RO+OH [33]			
$\text{cy}(\text{ocjccc})+\text{ho}_2=\text{jocy}(\text{cocco})+\text{oh}$	7.00E+12	0	-1.00E+03

cy(occjcc)+ho2=jocy(ccocc)+oh	7.00E+12	0	-1.00E+03
R+CH ₃ O ₂ =RO+CH ₃ O [33]			
cy(ocjccc)+ch3o2=jocy(coccc)+ch3o	4.50E+12	0	0
cy(occjcc)+ch3o2=jocy(ccocc)+ch3o	4.50E+12	0	0
R+R'O ₂ =RO+R'O [33]			
jo2cy(coccc)+cy(ocjccc)=jocy(coccc)+jocy(coccc)	4.50E+12	0	-500
jo2cy(ccocc)+cy(ocjccc)=jocy(ccocc)+jocy(coccc)	4.50E+12	0	0
jo2cy(coccc)+cy(occjcc)=jocy(coccc)+jocy(ccocc)	4.50E+12	0	-500
jo2cy(ccocc)+cy(occjcc)=jocy(ccocc)+jocy(ccocc)	4.50E+12	0	0
RO ₂ +HO ₂ =ROOH+O ₂ [33]			
jo2cy(coccc)+ho2=ho2cy(coccc)+o2	2.00E+11	0	650
jo2cy(ccocc)+ho2=ho2cy(ccocc)+o2	2.00E+11	0	650
RO ₂ +H ₂ O ₂ =ROOH+HO ₂ [33]			
jo2cy(coccc)+h2o2=ho2cy(coccc)+ho2	2.40E+12	0	5000
jo2cy(ccocc)+h2o2=ho2cy(ccocc)+ho2	2.40E+12	0	5000
RO ₂ +CH ₃ O ₂ =RO+CH ₃ O+O ₂ [33]			
jo2cy(coccc)+ch3o2=jocy(coccc)+ch3o+o2	3.40E+16	-1.61	1500
jo2cy(ccocc)+ch3o2=jocy(ccocc)+ch3o+o2	3.40E+16	-1.61	2000
RO ₂ +R'O ₂ =RO+R'O+O ₂ [33]			
jo2cy(coccc)+jo2cy(coccc)=jocy(coccc)+jocy(coccc)+o2	6.80E+16	-1.61	2000
jo2cy(coccc)+jo2cy(ccocc)=jocy(coccc)+jocy(ccocc)+o2	6.80E+16	-1.61	2500
jo2cy(ccocc)+jo2cy(ccocc)=jocy(ccocc)+jocy(ccocc)+o2	6.80E+16	-1.61	3000
RO ₂ +R'O ₂ =R'O+R'OH+O ₂ [192]			
jo2cy(coccc)+jo2cy(coccc)=o*cy(coccc)+hocy(coccc)+o2	3.11E+14	-1.61	-2051
jo2cy(coccc)+jo2cy(ccocc)=o*cy(coccc)+hocy(ccocc)+o2	3.11E+14	-1.61	-1551
jo2cy(ccocc)+jo2cy(ccocc)=o*cy(ccocc)+hocy(ccocc)+o2	3.11E+14	-1.61	-1551
jo2cy(ccocc)+jo2cy(ccocc)=o*cy(ccocc)+hocy(ccocc)+o2	3.11E+14	-1.61	-1051
RO ₂ =R'O+OH [59]			
jo2cy(coccc)=o*cy(coccc)+oh	486070	2.2717	35199
jo2cy(ccocc)=o*cy(ccocc)+oh			
PLOG/ 0.01	5.34E+47	-11.78	45113/
PLOG/ 0.1	4.61E+39	-8.9363	43767/
PLOG/ 1	2.25E+30	-5.7798	41750/
PLOG/ 10	1.21E+23	-3.3381	40104/
PLOG/ 100	2.21E+17	-1.4369	38711/
PLOG/ 1000	6.47E+12	0.0367	37492/
ROOH=RO+OH [148]			
ho2cy(coccc)=jocy(coccc)+oh	2.50E+15	0	43000
ho2cy(ccocc)=jocy(ccocc)+oh	2.50E+15	0	43000
RO β-scission (ring opening) [33]			
jocy(coccc)=>ohccccoj	3.15E+43	-9.45	30900
jocy(ccocc)=>ohccccoj	3.53E+36	-7.24	35800

Table B3: Rate constants of DEE/THF cross-reactions considered in this work. The Arrhenius parameters are given in units of s^{-1} , cm^3 , mol^{-1} , cal.

Reaction	A	n	E _a
$\text{R}+\text{R}'\text{O}_2=\text{RO}+\text{R}'\text{O}$ [33]			
$\text{jo2cy}(\text{cocco})+\text{c2h5oc2h4s}=\text{jocy}(\text{cocco})+\text{c2oc2-so}$	4.50E+12	0	-500
$\text{jo2cy}(\text{cocco})+\text{c2h5oc2h4p}=\text{jocy}(\text{cocco})+\text{c2oc2-po}$	4.50E+12	0	-500
$\text{cy}(\text{ocjccc})+\text{c2oc2-so2}=\text{jocy}(\text{cocco})+\text{c2oc2-so}$	4.50E+12	0	-500
$\text{cy}(\text{occjcc})+\text{c2oc2-so2}=\text{jocy}(\text{ccocc})+\text{c2oc2-so}$	4.50E+12	0	-500
$\text{jo2cy}(\text{ccocc})+\text{c2h5oc2h4s}=\text{jocy}(\text{ccocc})+\text{c2oc2-so}$	4.50E+12	0	0
$\text{jo2cy}(\text{ccocc})+\text{c2h5oc2h4p}=\text{jocy}(\text{ccocc})+\text{c2oc2-po}$	4.50E+12	0	0
$\text{cy}(\text{ocjccc})+\text{c2oc2-po2}=\text{jocy}(\text{cocco})+\text{c2oc2-po}$	4.50E+12	0	0
$\text{cy}(\text{occjcc})+\text{c2oc2-po2}=\text{jocy}(\text{ccocc})+\text{c2oc2-po}$	4.50E+12	0	0
$\text{RO}_2+\text{R}'\text{O}_2=\text{RO}+\text{R}'\text{O}+\text{O}_2$ [33]			
$\text{jo2cy}(\text{cocco})+\text{c2oc2-so2}=\text{jocy}(\text{cocco})+\text{c2oc2-so}+\text{o2}$	6.80E+16	-1.61	2000
$\text{jo2cy}(\text{cocco})+\text{c2oc2-po2}=\text{jocy}(\text{cocco})+\text{c2oc2-po}+\text{o2}$	6.80E+16	-1.61	2500
$\text{jo2cy}(\text{ccocc})+\text{c2oc2-so2}=\text{jocy}(\text{ccocc})+\text{c2oc2-so}+\text{o2}$	6.80E+16	-1.61	2500
$\text{jo2cy}(\text{ccocc})+\text{c2oc2-po2}=\text{jocy}(\text{ccocc})+\text{c2oc2-po}+\text{o2}$	6.80E+16	-1.61	3000
$\text{RH}+\text{R}'=\text{R}+\text{R}'\text{H}$ [139]			
$\text{c2h5oc2h5}+\text{cy}(\text{ocjccc})=\text{c2h5oc2h4s}+\text{cy}(\text{occcc})$	1.77E-04	4.54	6405.0
$\text{c2h5oc2h5}+\text{cy}(\text{ocjccc})=\text{c2h5oc2h4p}+\text{cy}(\text{occcc})$	2.34E-05	5.02	7362.5
$\text{c2h5oc2h5}+\text{cy}(\text{occjcc})=\text{c2h5oc2h4s}+\text{cy}(\text{occcc})$	4.24E-06	5.06	4890.0
$\text{c2h5oc2h5}+\text{cy}(\text{occjcc})=\text{c2h5oc2h4p}+\text{cy}(\text{occcc})$	1.59E-01	3.96	8808.5
$\text{R}+\text{R}'$ reactions [139]			
$\text{cy}(\text{ocjccc})+\text{c2h5oc2h4s}=\text{cy}(\text{occcc})+\text{c2h5oc2h3}$	6.59E+08	1.42	0.0
$\text{cy}(\text{ocjccc})+\text{c2h5oc2h4s}=\text{DHF1}+\text{c2h5oc2h5}$	1.35E+03	2.70	0.0
$\text{cy}(\text{ocjccc})+\text{c2h5oc2h4p}=\text{cy}(\text{occcc})+\text{c2h5oc2h3}$	2.71E+10	0.47	0.0
$\text{cy}(\text{ocjccc})+\text{c2h5oc2h4p}=\text{DHF1}+\text{c2h5oc2h5}$	1.35E+03	2.70	0.0
$\text{cy}(\text{occjcc})+\text{c2h5oc2h4p}=\text{cy}(\text{occcc})+\text{c2h5oc2h3}$	2.71E+10	0.47	0.0
$\text{cy}(\text{occjcc})+\text{c2h5oc2h4p}=\text{DHF2}+\text{c2h5oc2h5}$	1.35E+03	2.70	0.0
$\text{cy}(\text{occjcc})+\text{c2h5oc2h4p}=\text{DHF1}+\text{c2h5oc2h5}$	2.71E+10	0.47	0.0
$\text{cy}(\text{occjcc})+\text{c2h5oc2h4s}=\text{cy}(\text{occcc})+\text{c2h5oc2h3}$	6.59E+08	1.42	0.0
$\text{cy}(\text{occjcc})+\text{c2h5oc2h4s}=\text{DHF2}+\text{c2h5oc2h5}$	1.35E+03	2.70	0.0
$\text{cy}(\text{occjcc})+\text{c2h5oc2h4s}=\text{DHF1}+\text{c2h5oc2h5}$	2.71E+10	0.47	0.0

Appendix C

Additional validation of the core mechanism for methanol and ethanol

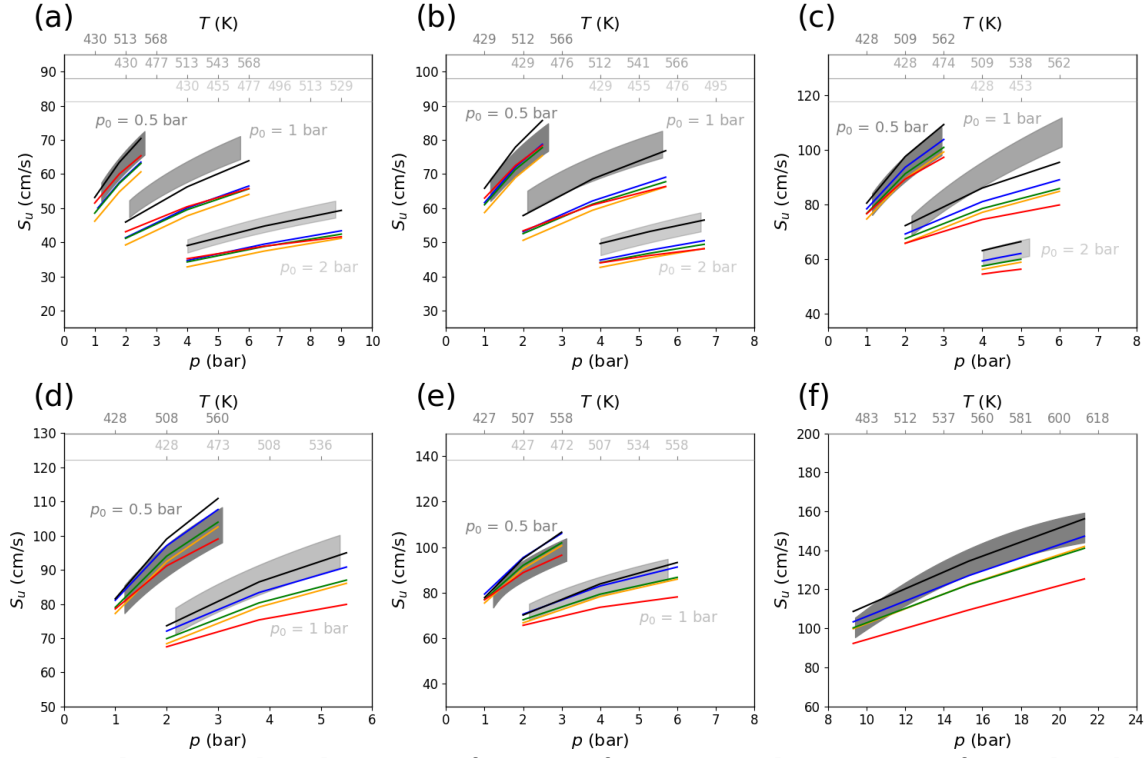


Fig. C1: Flame speed evolution as a function of pressure and temperature for methanol/air mixtures: $\varphi = 0.8$ (a), 0.9 (b), 1.1 (c), 1.2 (d), 1.3 (e); and for a methanol/ O_2 /He/Ar mixture: $\varphi = 1.2$, $p_0 = 4$ bar (f). All these mixtures were tested under the same initial temperature $T_0 = 358$ K. Thickened gray traces correspond to experimental results with their associated uncertainty ($\pm 5\%$). Lines correspond to simulations: Black: present work; Green: Mech15.34 [158]; Red: HPMech [159]; Blue: POLIMI C₁-C₃ [162]; Orange: AramcoMech3.0 [163].

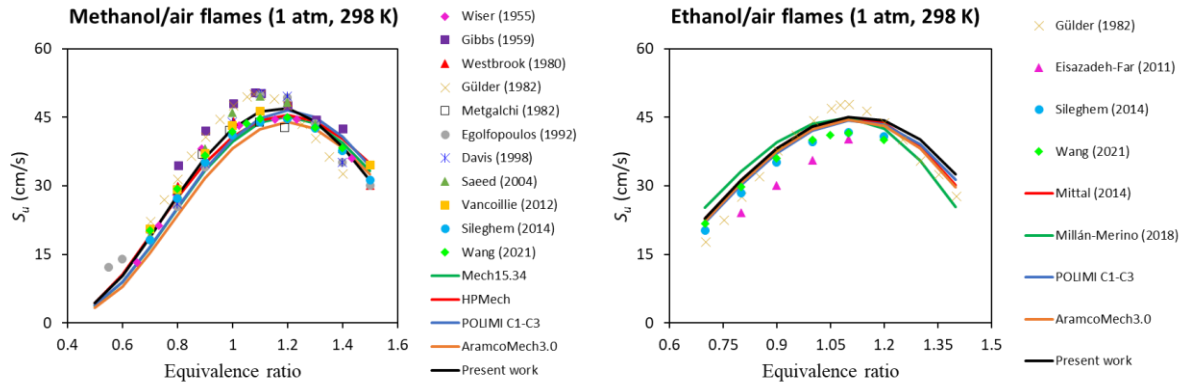


Fig. C2: Laminar flame speeds of methanol/air (left) and ethanol/air mixtures (right) as functions of equivalence ratio at 1 atm and 298 K. Symbols: experiments [193–204], lines: simulations (present work and [158–163]).

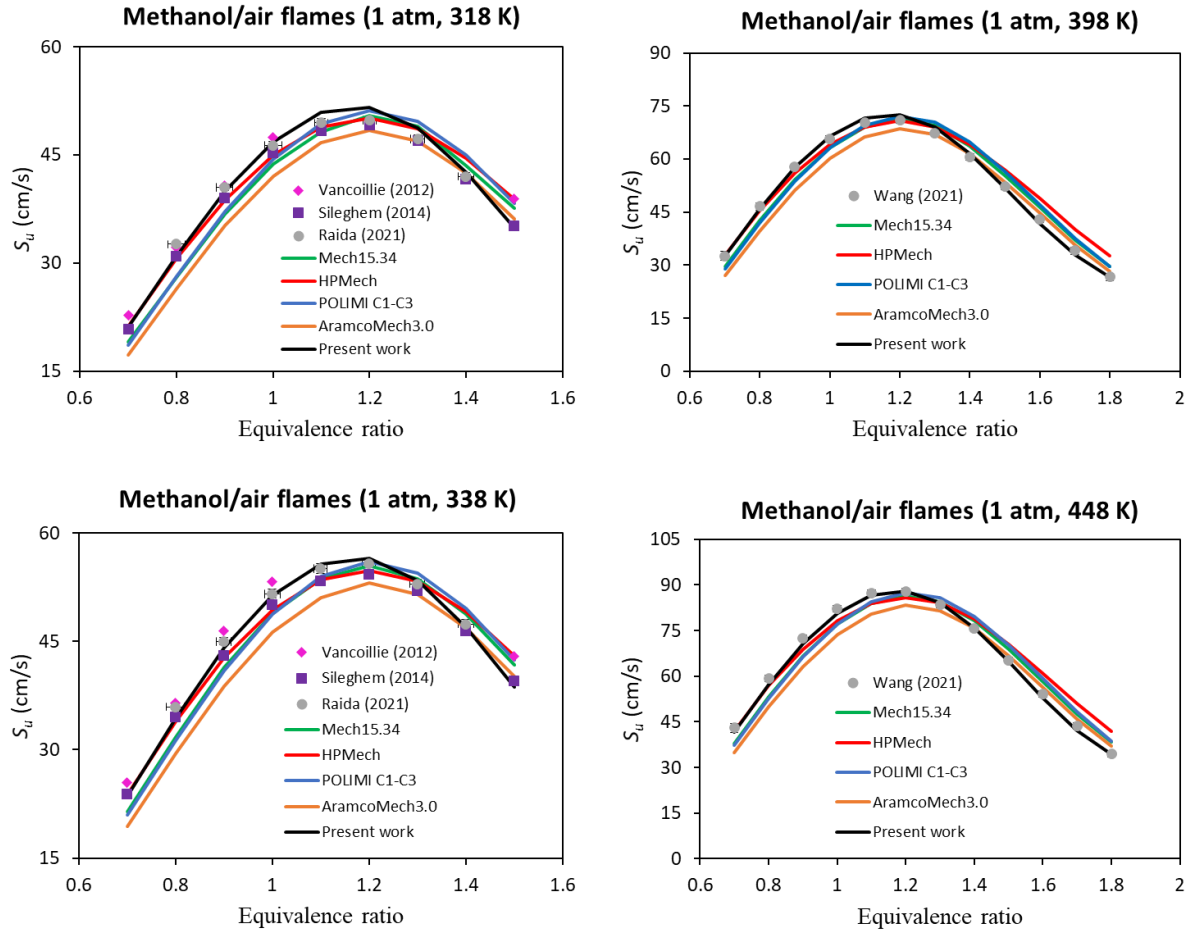


Fig. C3: Laminar flame speeds of methanol/air mixtures as functions of equivalence ratio at 1 atm and 318, 338, 398, 448 K. Symbols: experiments [164] [197–199], lines: simulations (present work and [158,159] [162,163]).

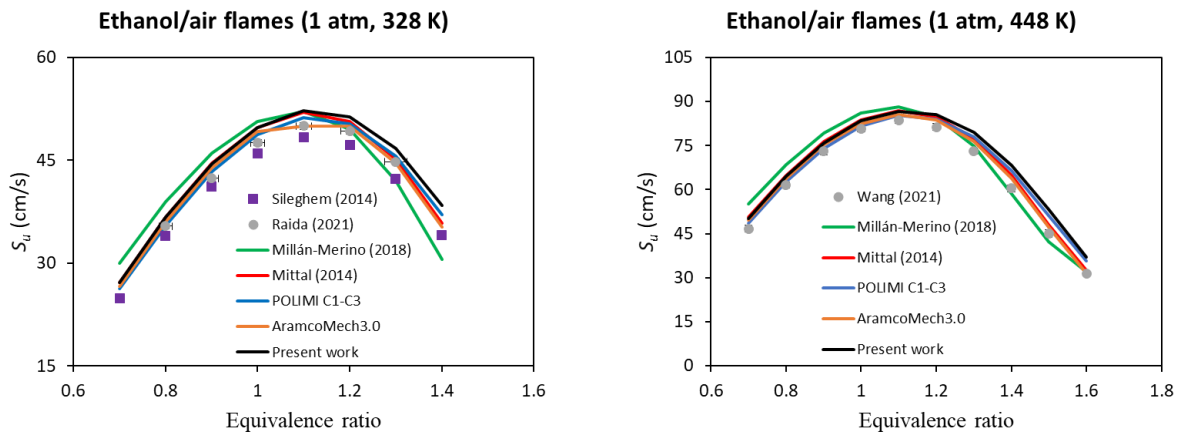


Fig. C4: Laminar flame speeds of ethanol/air mixtures as functions of equivalence ratio at 1 atm and 328 or 448 K. Symbols: experiments [164] [198,199]; lines: simulations (present work and [160–163]).

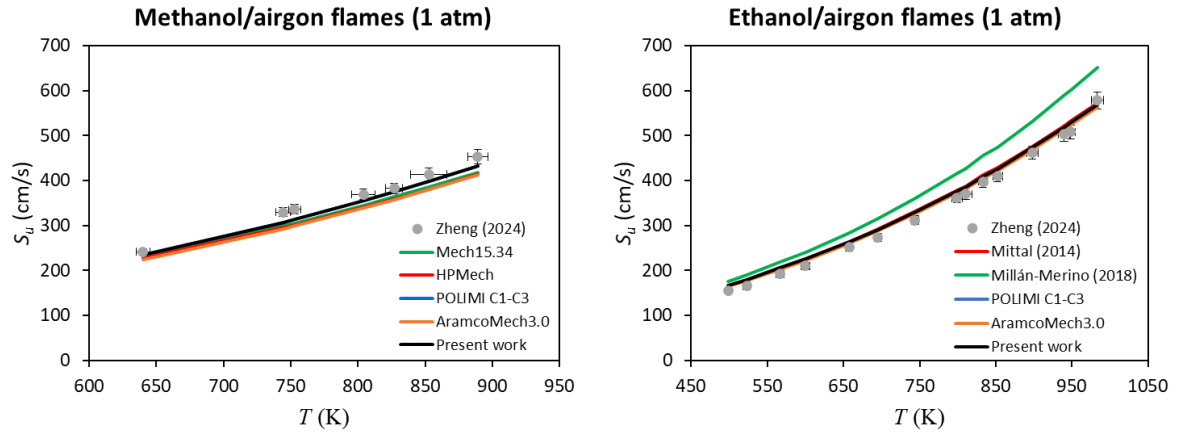


Fig. C5: Laminar flame speeds of stoichiometric methanol/airgon (left) and ethanol/airgon (right) mixtures as functions of temperature at 1 atm. Symbols: experiments [205,206], lines: simulations (present work and [158–163]).

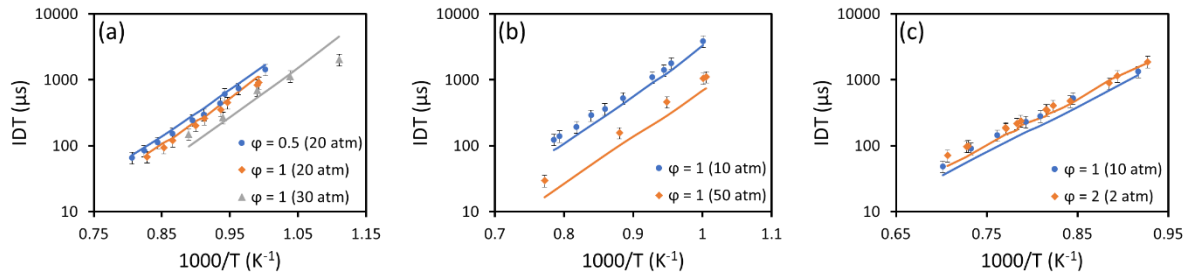


Fig. C6: Experimental (symbols) ignition delay times measured by Burke et al. [158] in a shock tube at different pressures for methanol/O₂/N₂ mixtures (a) and methanol/O₂/Ar mixtures (b and c). Simulations (lines) were performed using the present core mechanism.

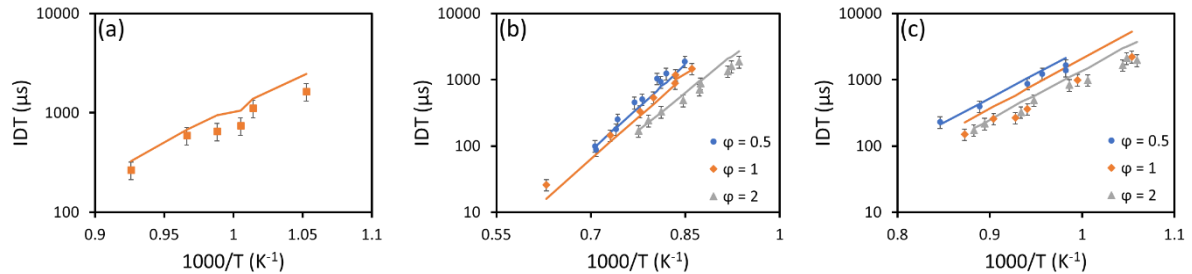


Fig. C7: Experimental (symbols) ignition delay times measured by Mathieu et al. [166] in a shock tube for a stoichiometric ethanol/O₂/N₂ mixture at 27 atm (a), and for different ethanol/O₂/Ar mixtures at about 1.5 atm (b) and 13 atm (c). Simulations (lines) were performed using the present core mechanism.

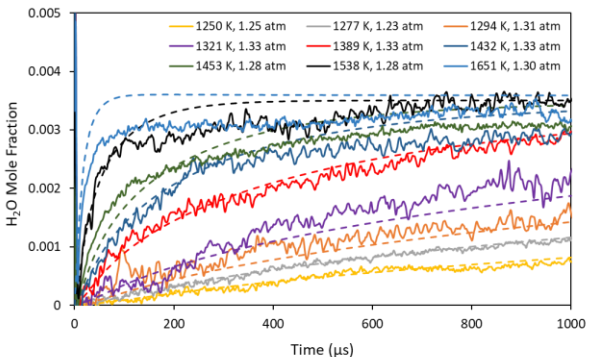
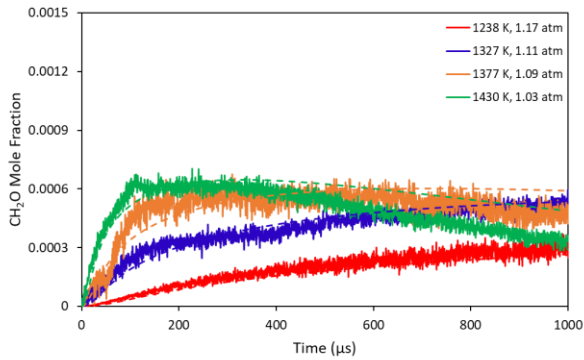
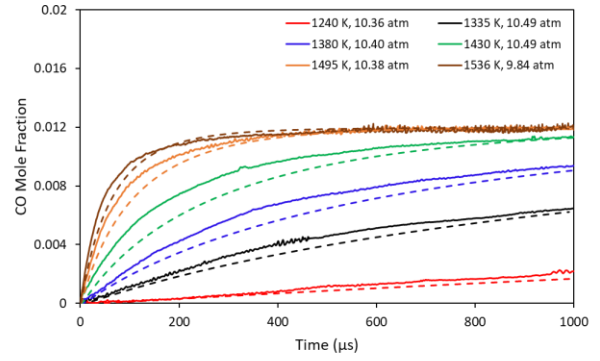
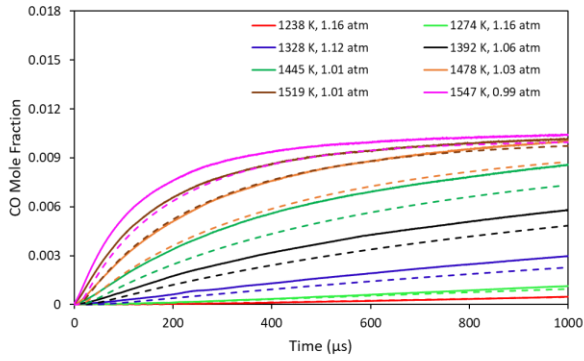
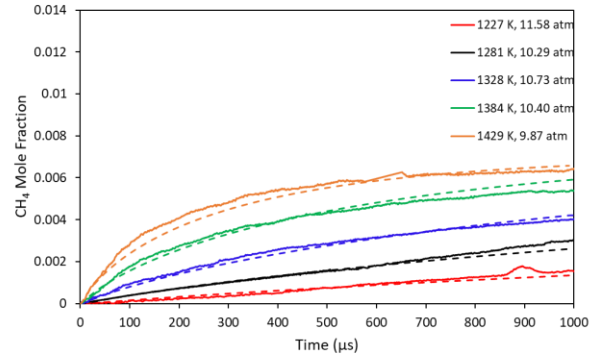
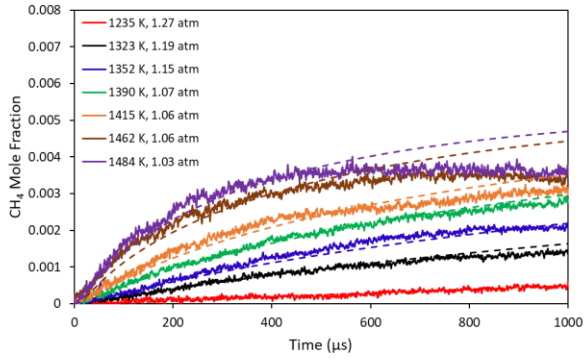
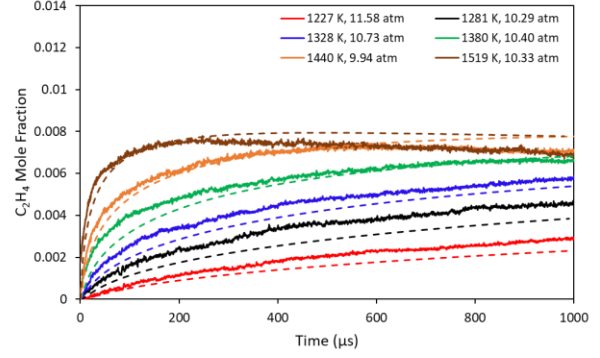
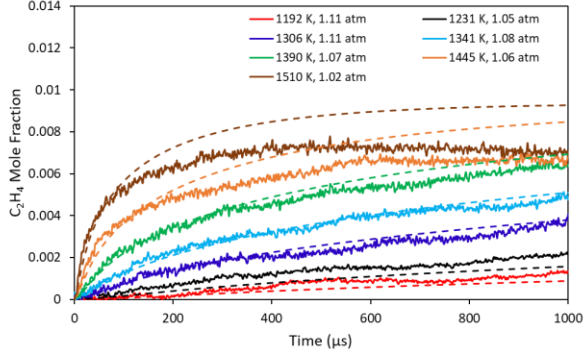
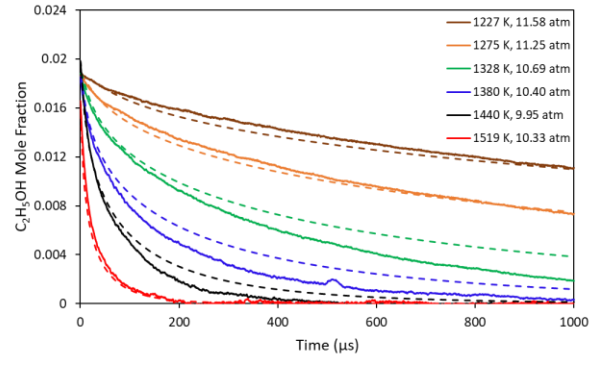
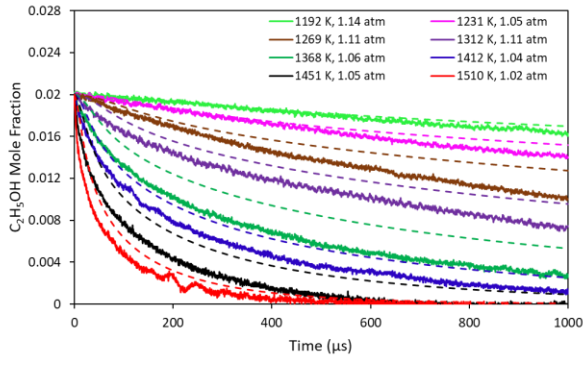


Fig. C8: Experimental (solid lines [207,208]) and computed (dashed lines: this work) time-histories obtained from the pyrolysis of ethanol in a shock tube.

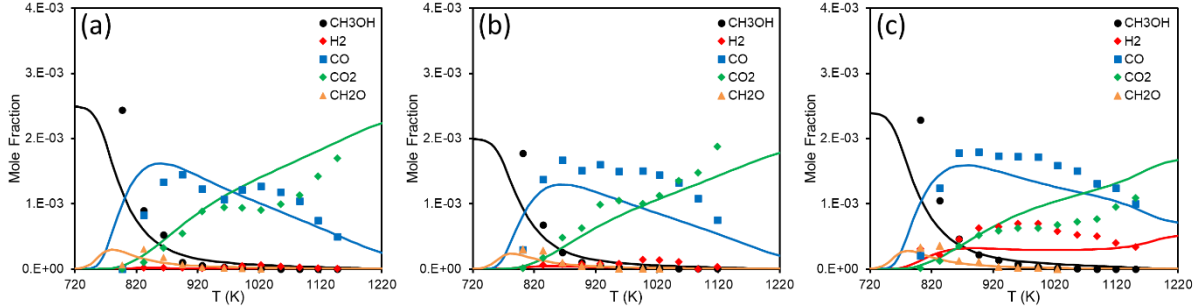


Fig. C9: Experimental (symbols: Burke et al. [158]) and computed (lines: this work) mole fraction profiles of species obtained during the oxidation of methanol in a JSR at $p = 20$ atm, $\tau = 1$ s, and $\phi = 0.2$ (a) / 0.5 (b) / 1 (c).

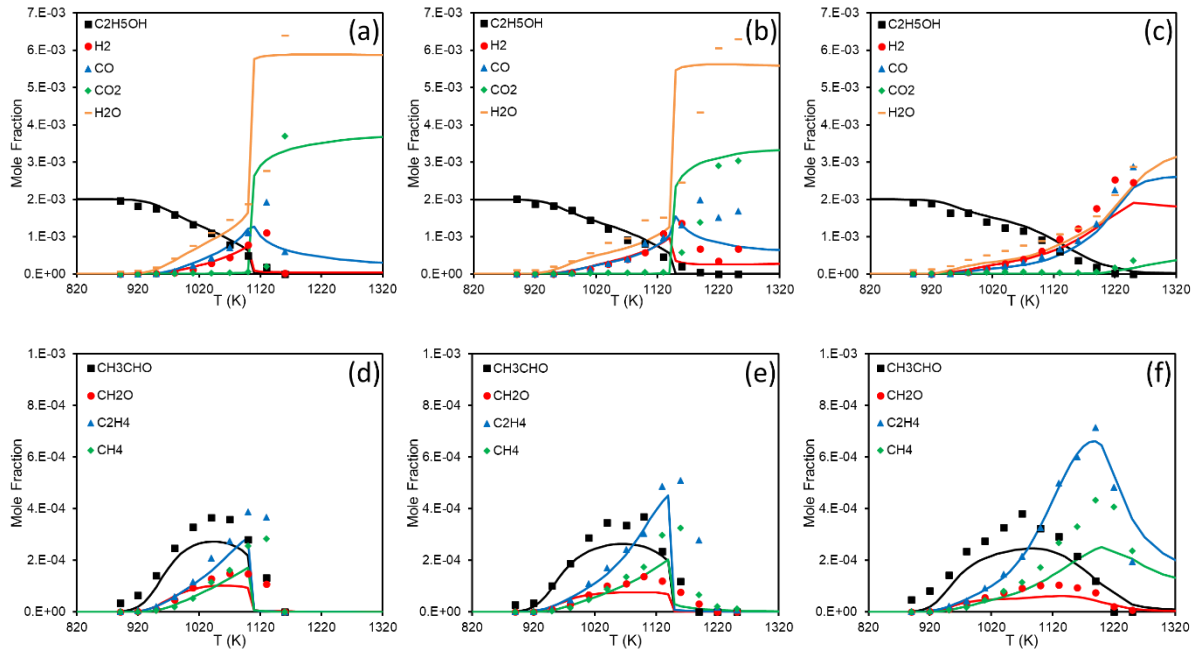


Fig. C10: Experimental (symbols: Leplat et al. [165]) and computed (lines: this work) mole fraction profiles of species obtained during the oxidation of ethanol in a JSR at $p = 1$ atm, $\tau = 0.07$ s, and $\phi = 0.5$ (a,d) / 1 (b,e) / 2 (c,f).

Appendix D

Additional speciation data for cyclic ethers

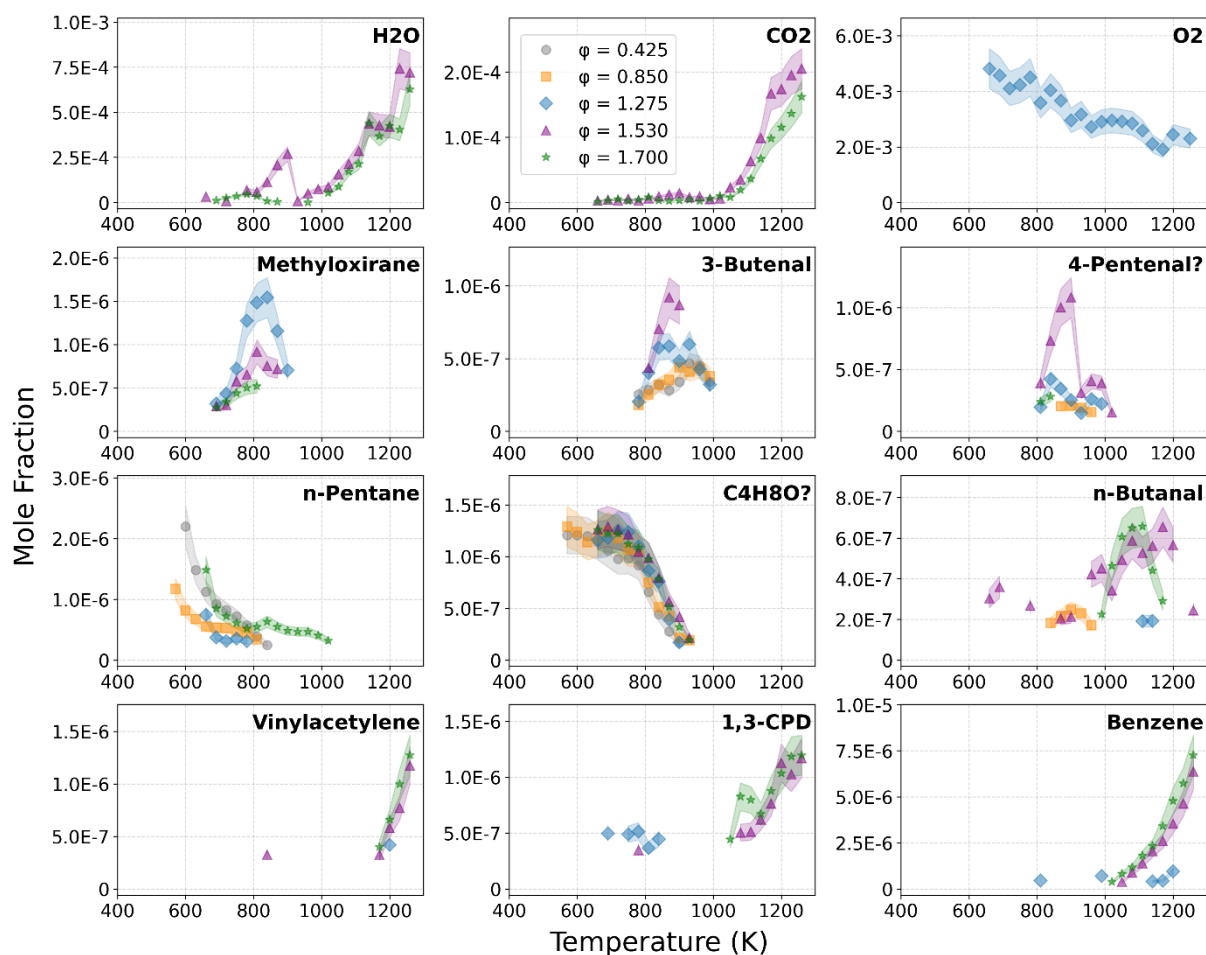


Fig. D1: Mole fraction profiles (with $\pm 15\%$ shaded uncertainty bands) of minor and uncertainly identified/quantified species during the oxidation of THF at $p = 10$ bar, $\tau = 0.7$ s, $X_{o}(\text{fuel}) = 850$ ppm, and $\phi = 0.425$ (gray); 0.85 (orange); 1.275 (blue); 1.53 (purple); 1.7 (green). Species with uncertain identification are indicated by “?” (CPD denotes cyclopentadiene).

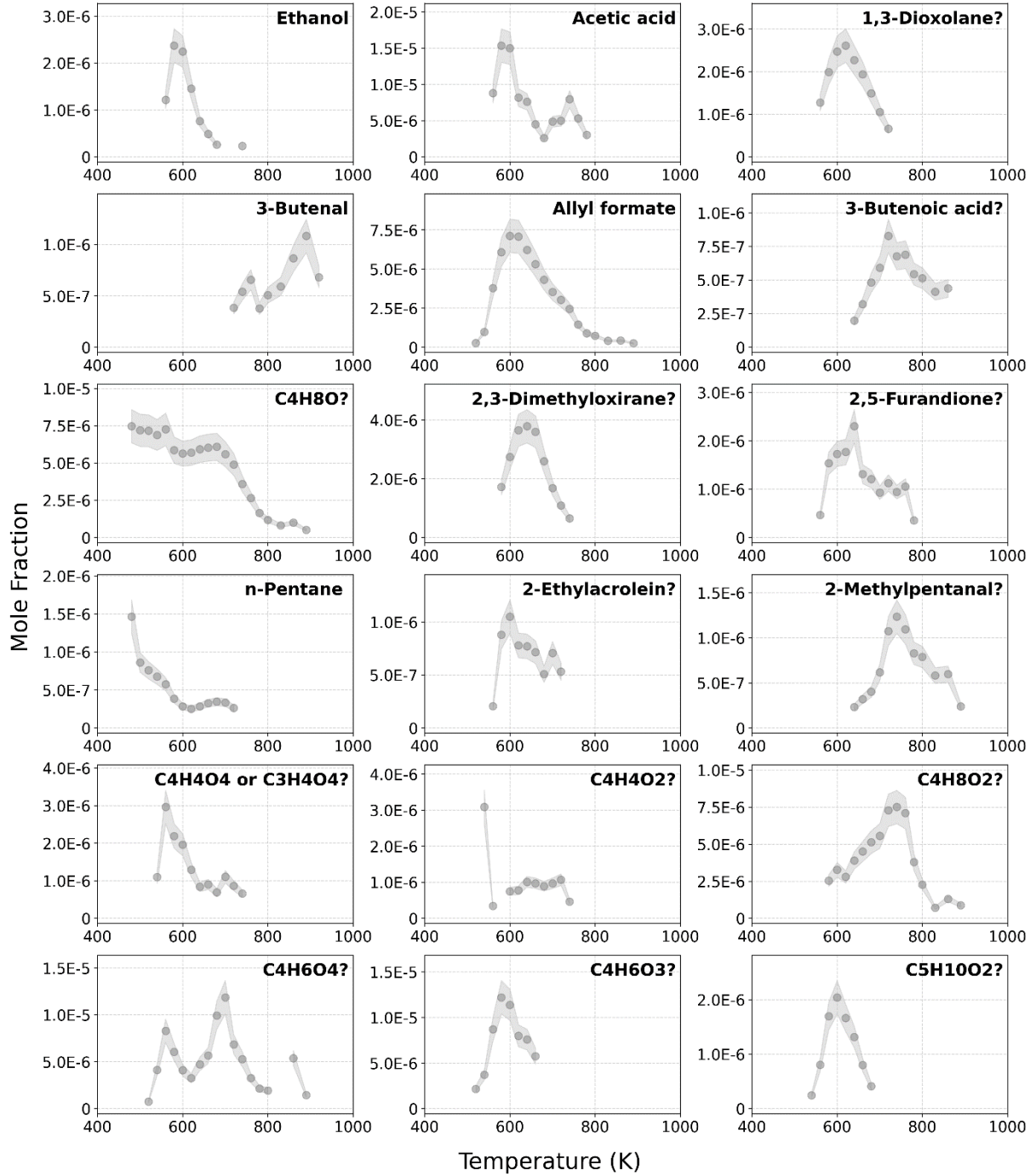
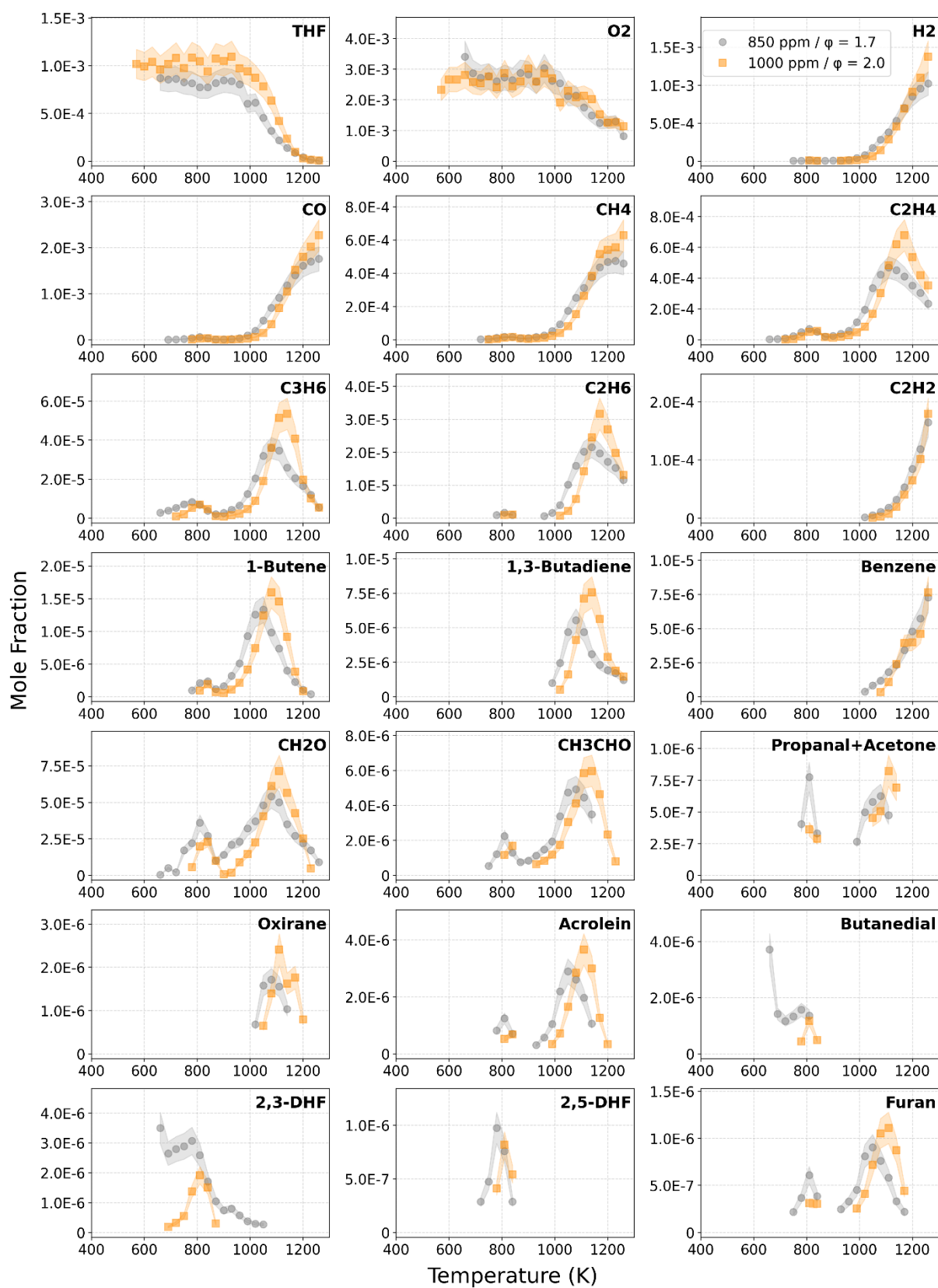


Fig. D2: Mole fraction profiles (with $\pm 15\%$ shaded uncertainty bands) of minor and uncertainly identified species during the oxidation of THF at $p = 10$ bar, $\tau = 2$ s, $X_{O(\text{fuel})} = 5000$ ppm, and $\phi = 0.5$. Species with uncertain identification are indicated by “?”.



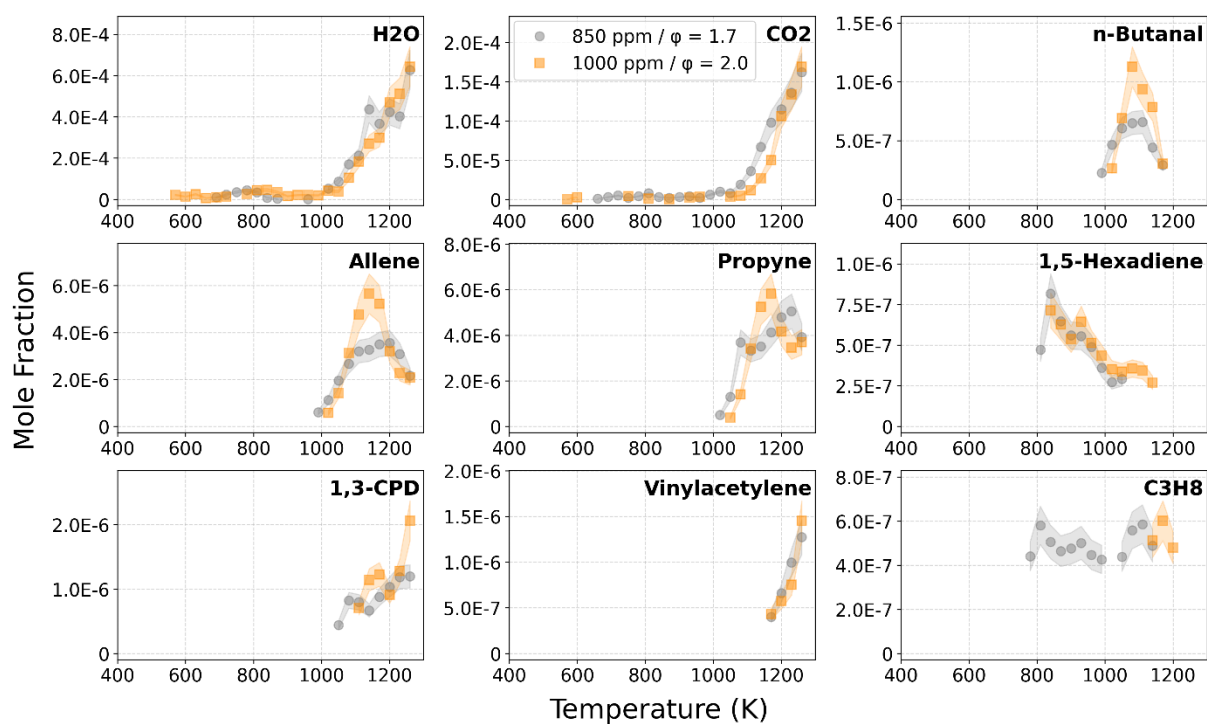


Fig. D3: Mole fraction profiles (with shaded uncertainty bands of $\pm 15\%$) of reactant, product, and intermediate species during THF oxidation in a JSR at $p = 10$ bar, $\tau = 0.7$ s, and: $X_0(\text{fuel}) = 850$ ppm / $\phi = 1.7$ (gray circles); $X_0(\text{fuel}) = 1000$ ppm / $\phi = 2.0$ (orange squares).

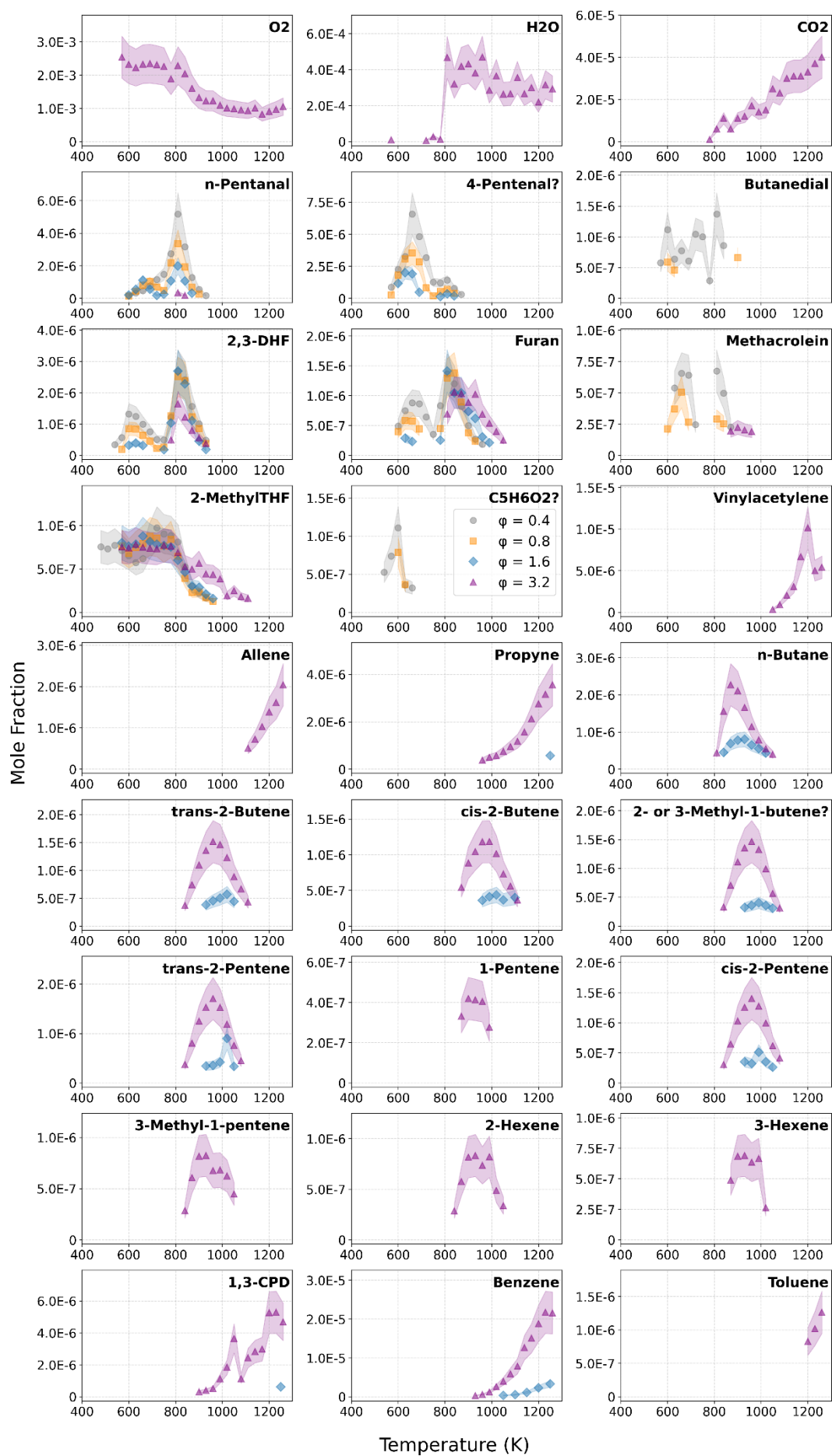


Fig. D4: Mole fraction profiles (with $\pm 25\%$ shaded uncertainty bands) of minor and uncertainly identified/quantified species during the oxidation of THP at $p = 10$ bar, $\tau = 0.7$ s, $X_{O}(\text{fuel}) = 800$ ppm, and $\phi = 0.4$ (gray); 0.8 (orange); 1.6 (blue); 3.2 (purple). Species with uncertain identification are indicated by “?” (CPD denotes cyclopentadiene).

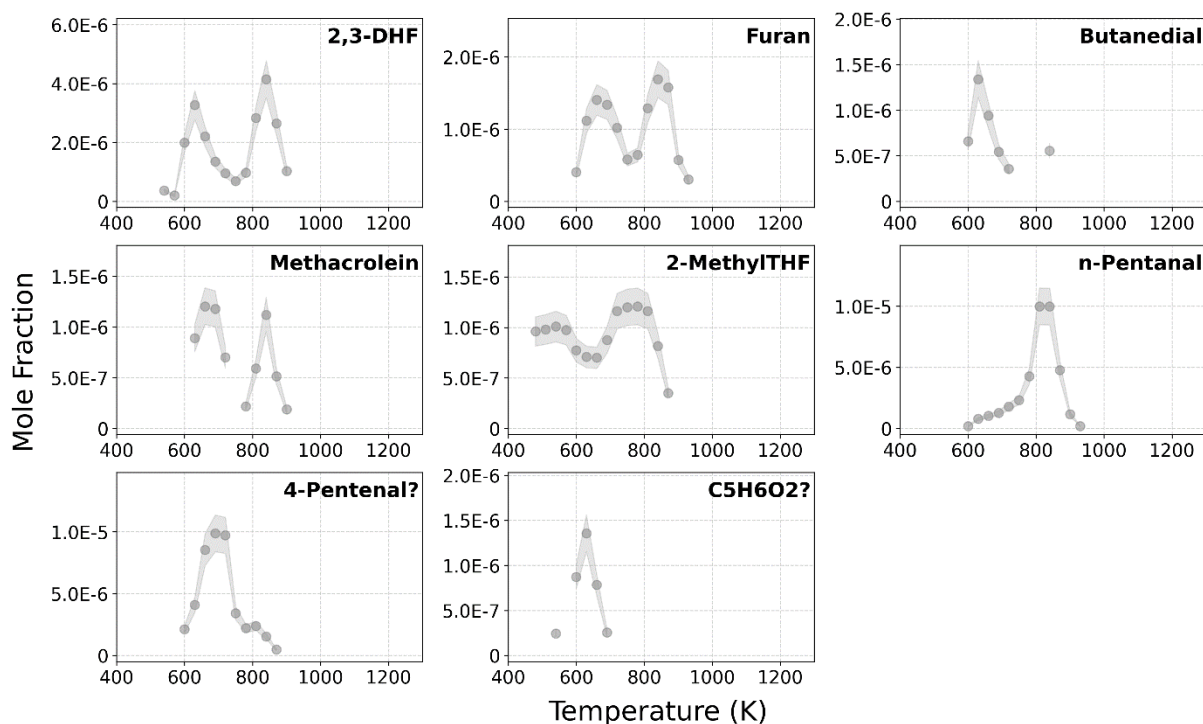
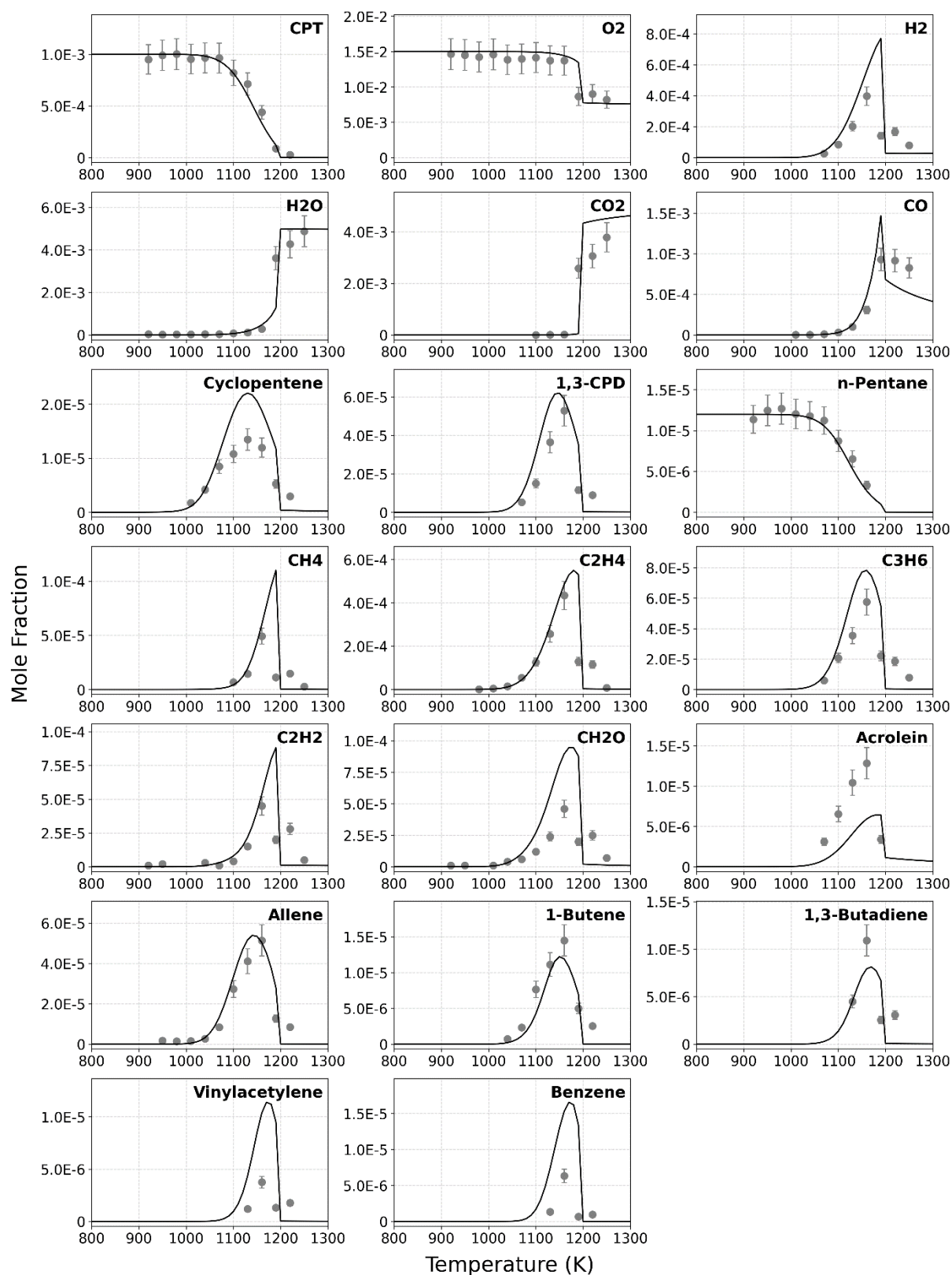
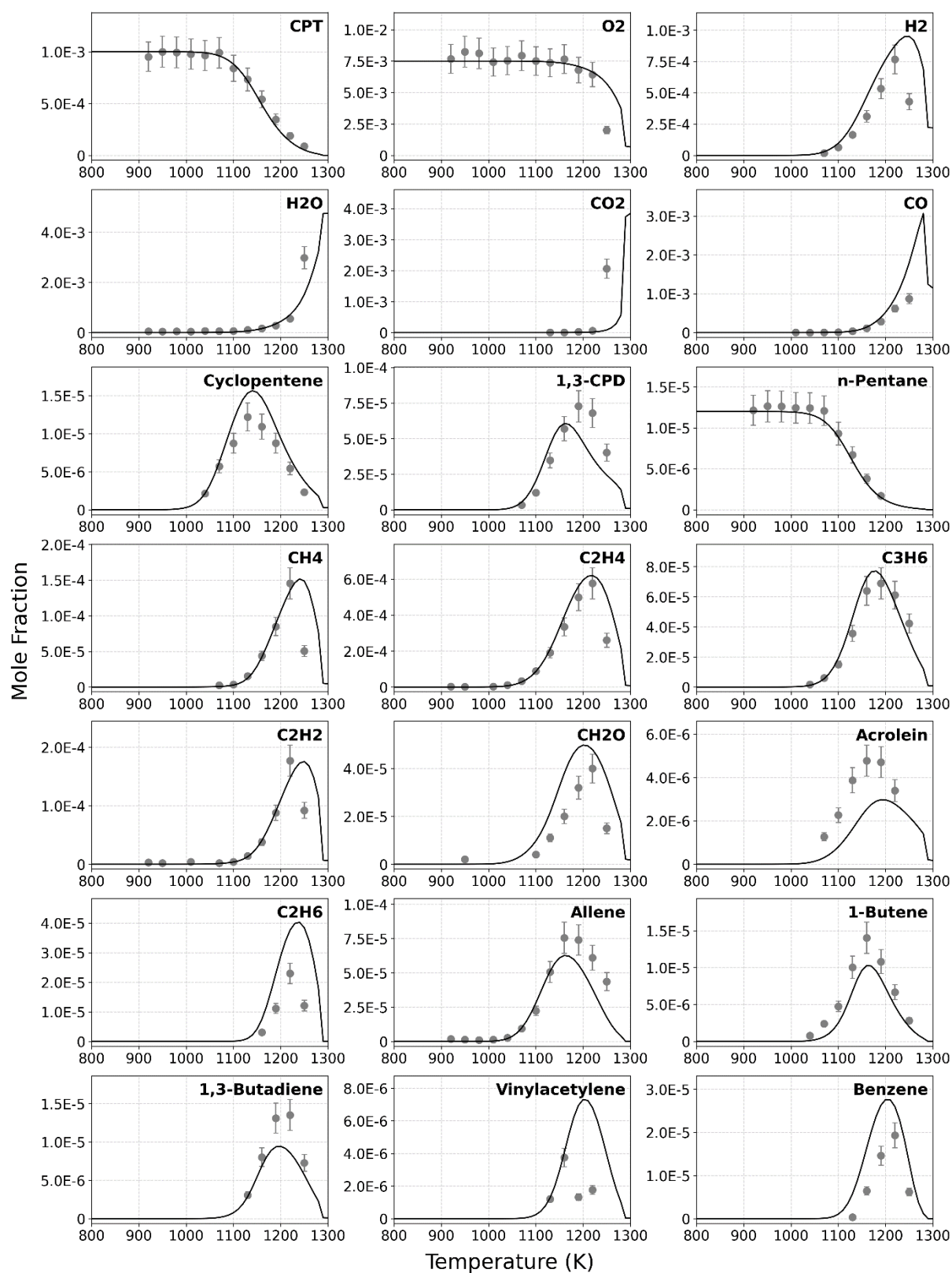


Fig. D5: Mole fraction profiles (with $\pm 15\%$ shaded uncertainty bands) of minor species formed during the oxidation of THP at $p = 10$ bar, $\tau = 0.7$ s, $X_{O}(\text{fuel}) = 1000$ ppm, and $\phi = 0.5$. Species with uncertain identification are indicated by “?”.

Appendix E

Validation of the present model on cyclopentane





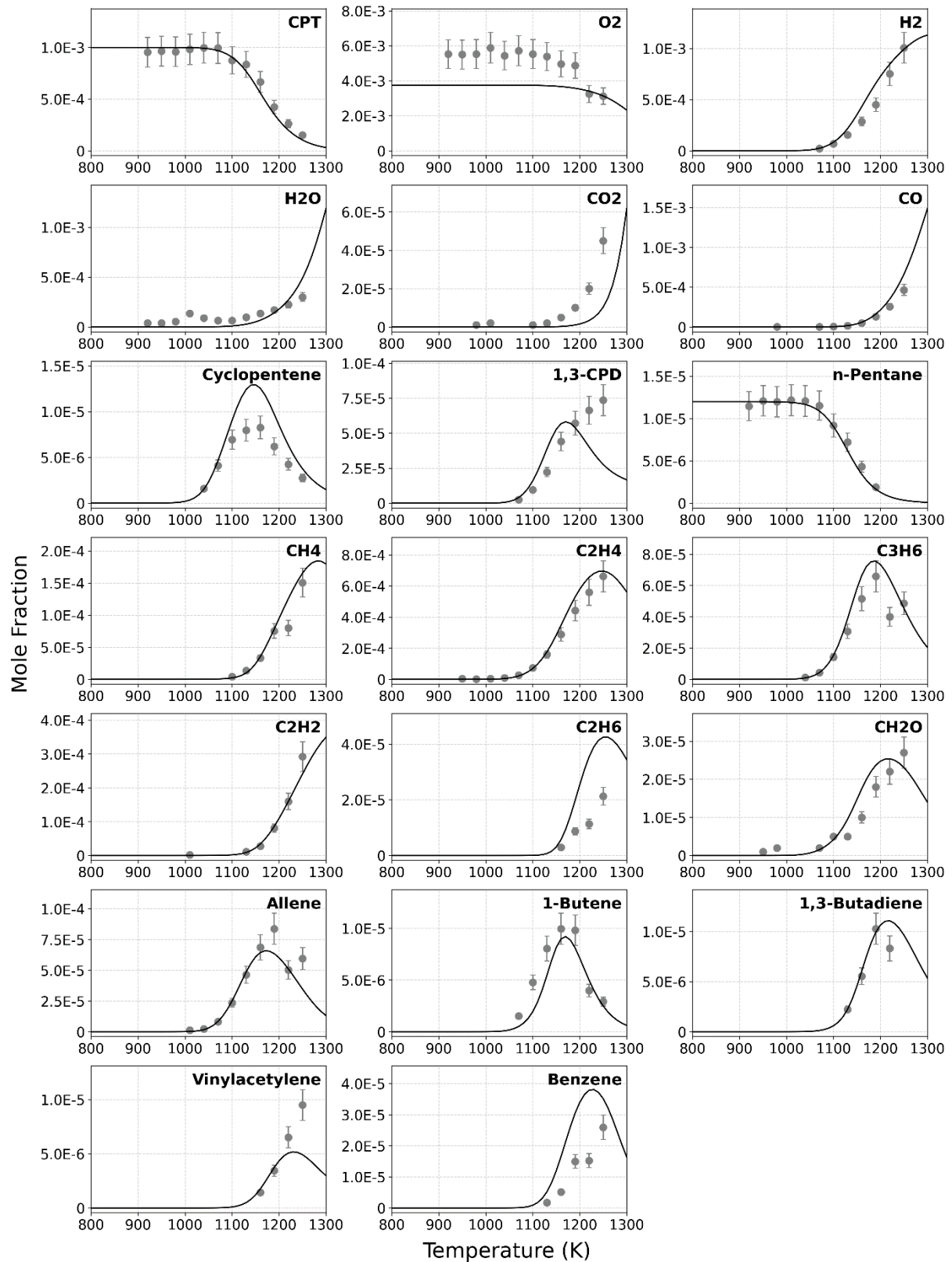
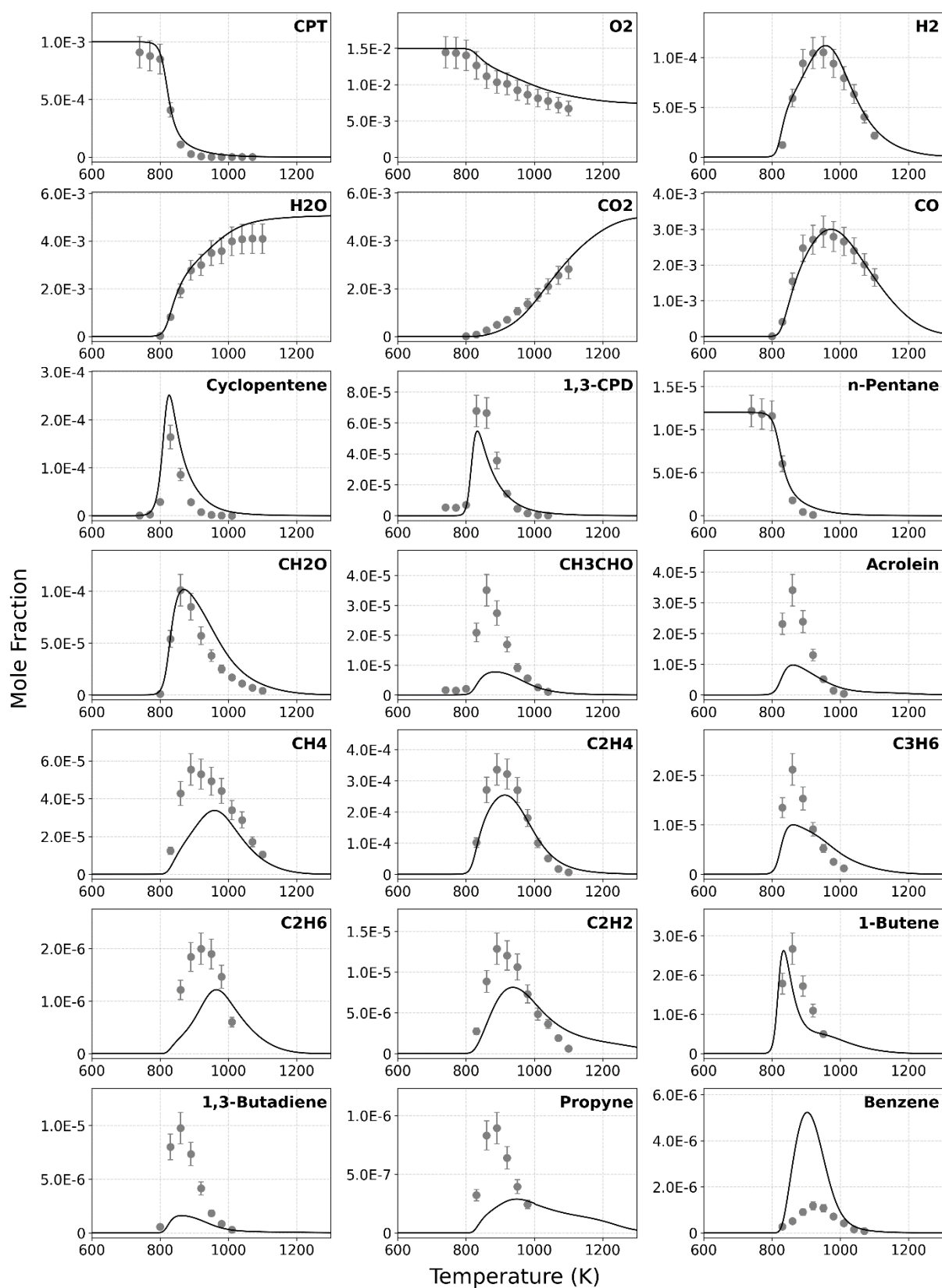
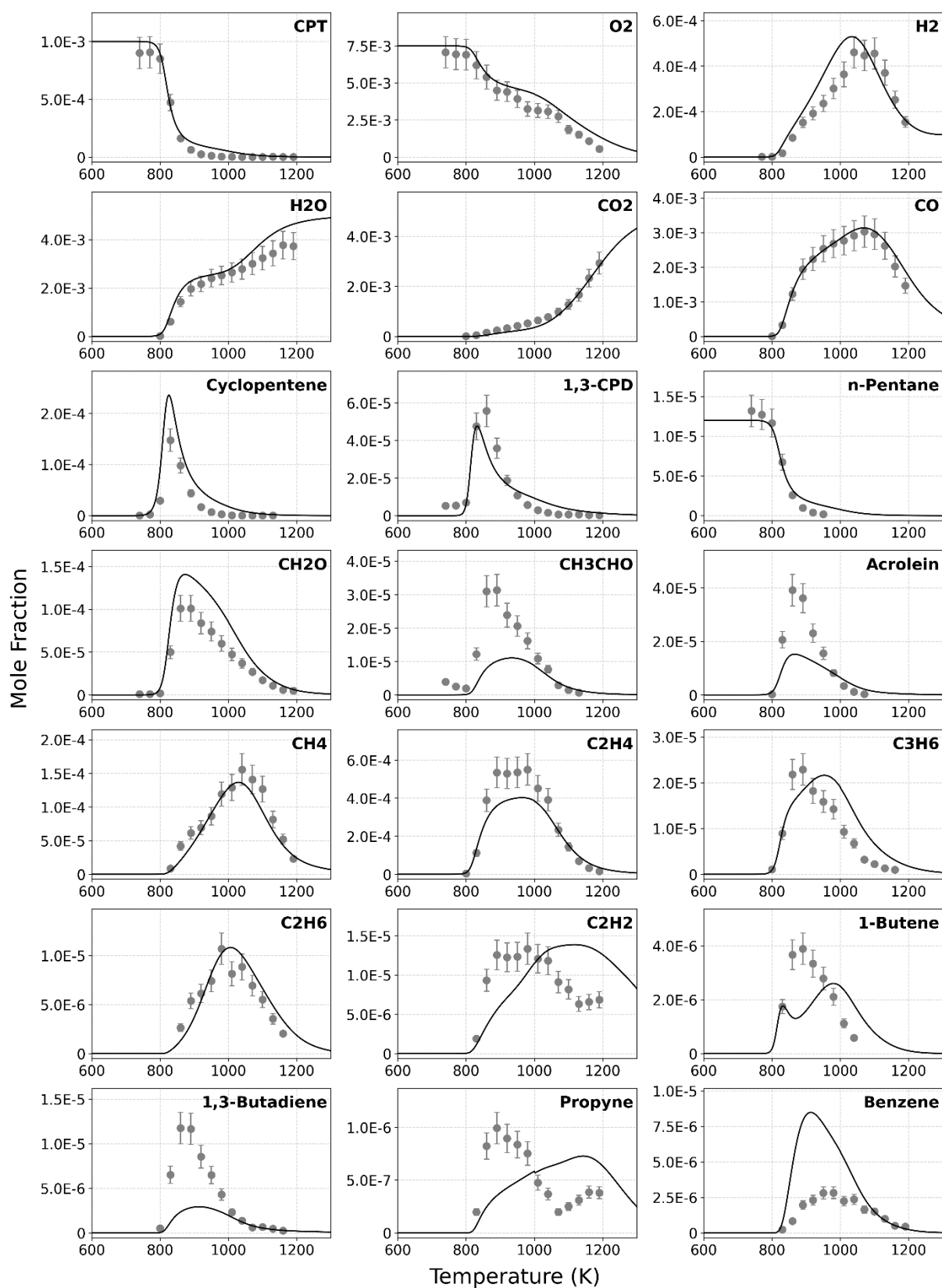
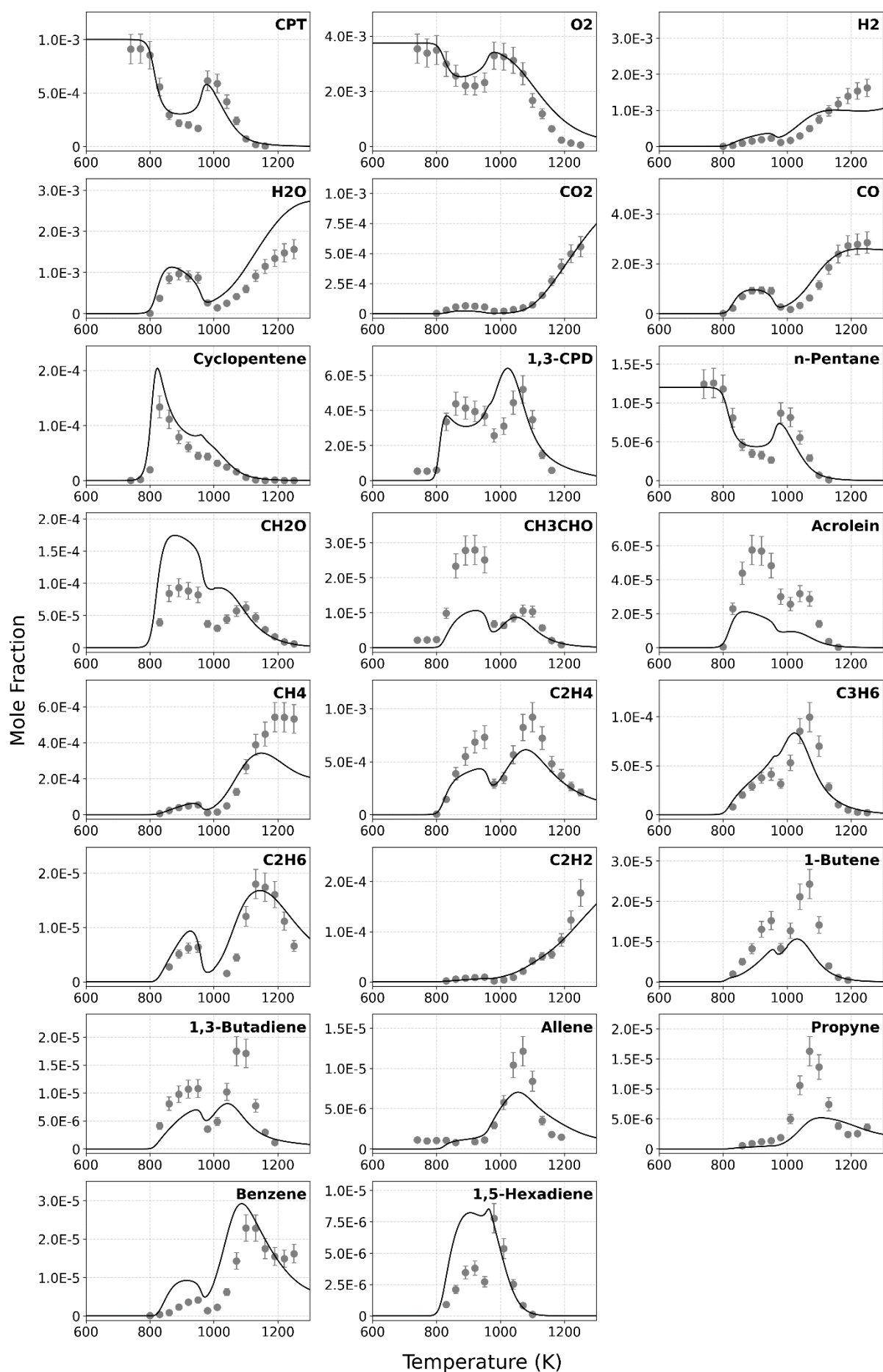


Fig. E1: Experimental (symbols with error bars of $\pm 15\%$: Dayma et al. [137]) and simulated (lines: present work) mole fraction profiles of reactant, product, and intermediate species during CPT oxidation in a JSR at $p = 1$ atm, $\tau = 0.7$ s, $X_0(\text{fuel}) = 1000$ ppm, and: (a) $\phi = 0.5$; (b) $\phi = 1.0$; (c) $\phi = 2.0$.







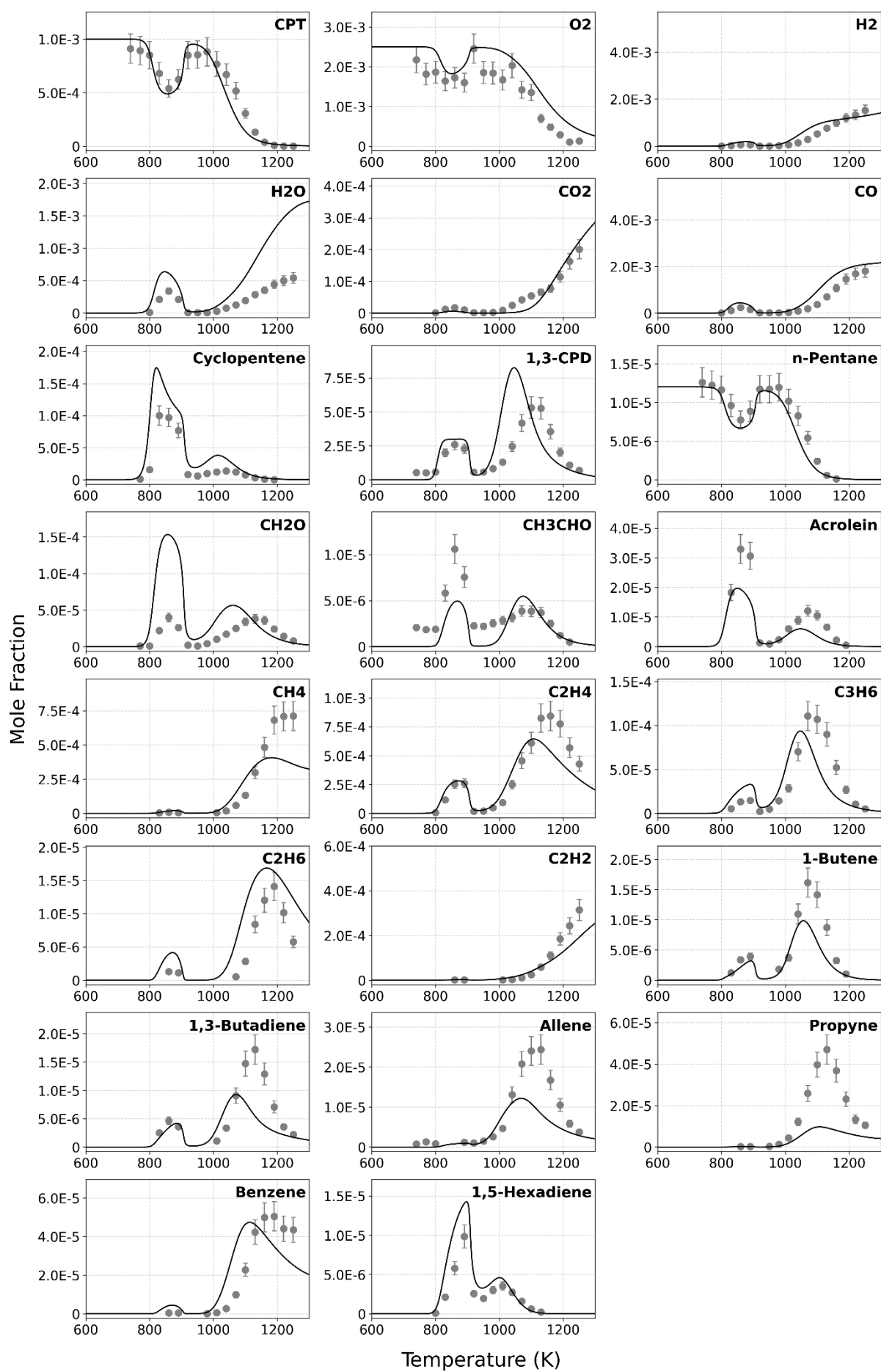


Fig. E2: Experimental (symbols with error bars of $\pm 15\%$: Al Rashidi et al. [167]) and simulated (lines: present work) mole fraction profiles of reactant, product, and intermediate species during CPT oxidation in a JSR at $p = 10$ atm, $\tau = 0.7$ s, $X_0(\text{fuel}) = 1000$ ppm, and: (a) $\phi = 0.5$; (b) $\phi = 1.0$; (c) $\phi = 2.0$; (d) $\phi = 3.0$.

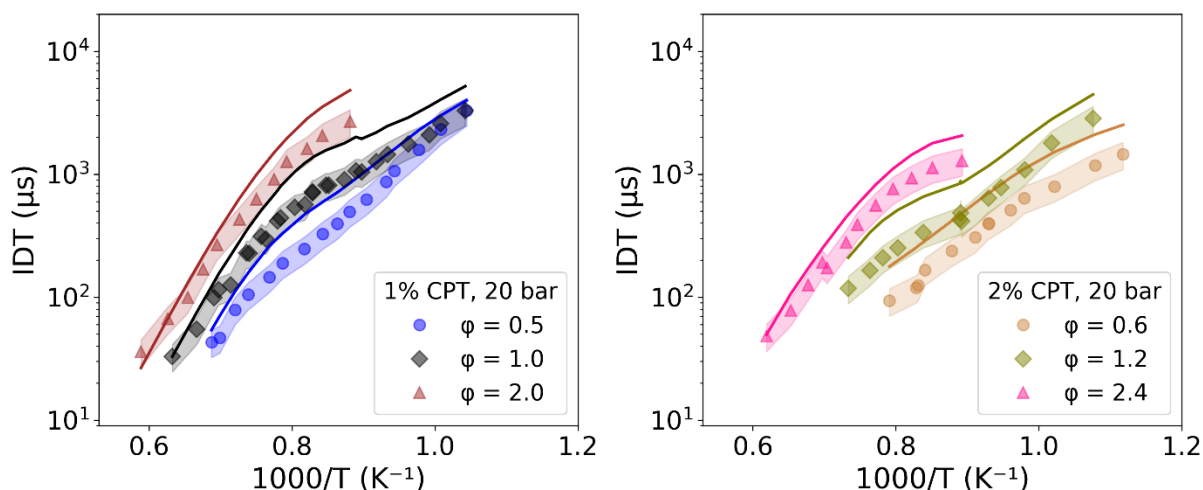


Fig. E3: Ignition delay times of CPT/O₂/Ar mixtures measured in shock tubes at 20 bar. Symbols (with shaded uncertainty bands): Do et al. [131]; Lines: simulations (present work).

While cyclopentane was not a direct target of this work, we showed that understanding its oxidation behavior is essential for elucidating that of THF. The structural similarity between the two fuels leads to analogous oxidation behavior, further intensified by the presence of the oxygen atom in THF. This functional group promotes the underlying reaction pathways in THF relative to CPT, leading to:

- The emergence of an LTR regime (though weak) for THF, which is completely absent for CPT.
- The amplification of the novel reactivity suppression observed at high pressures and intermediate-to-high temperatures under rich conditions, attributed mainly to a common mechanistic rationale; i.e., the allyl radical chemistry.

The latter point, in particular, highlights the need to extend the validation of the present mechanism to CPT, in order to further ensure its robustness and reliability in reproducing this novel behavior; which, prior to the present study, had not yet been explored for THF nor fully characterized for CPT.

Appendix F

Novel speciation data for neopentanal

Work description

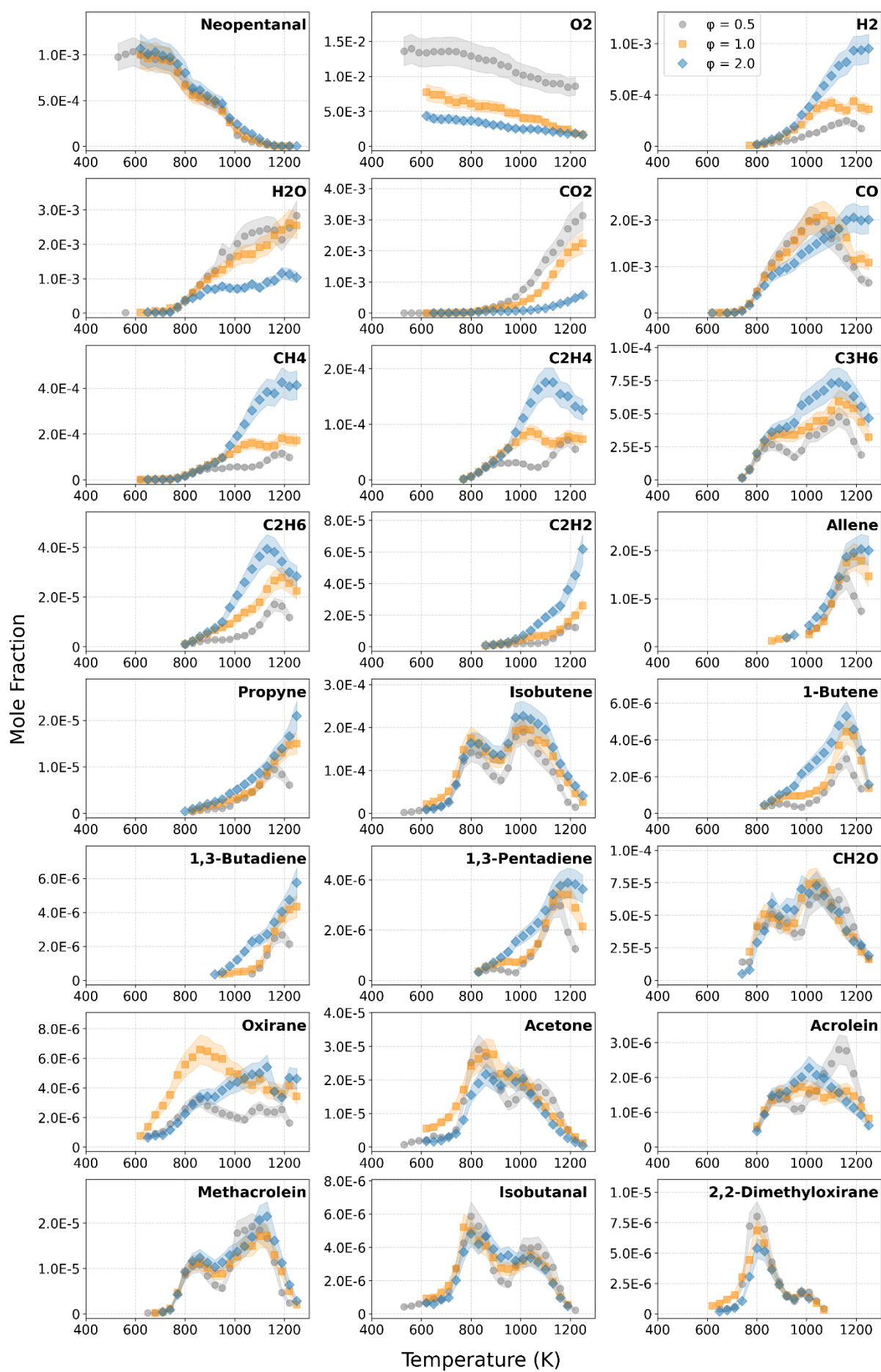
The oxidation kinetics of neopentanal (also known as pivaldehyde), a highly branched C₅ aldehyde, have not been previously characterized.

Experiments were carried out during this thesis on neopentanal as a continuation of our team's previous work on the oxidation of pentanal isomers [65,66]. All these experiments were performed at 10 bar, with two different residence times and initial fuel mole fractions: (0.7 s; 1000 ppm) and (1.5 s; 3500 ppm), respectively. The speciation results are presented and compared in the figures below.

Unlike the previously studied isomers (n-pentanal, 2-methylbutanal, and 3-methylbutanal), neopentanal does not exhibit low-temperature reactivity under same conditions. Its oxidation begins around 750 K, with complete consumption occurring near 1150 K.

While the overall fuel conversion appears to be insensitive to the equivalence ratio, the distinct differences observed in the species profiles indicate that the underlying reaction mechanisms vary with equivalence ratio, suggesting the involvement of different reaction pathways.

While the mixtures at $X_O(\text{fuel}) = 1000$ ppm and $\tau = 0.7$ s were investigated to enable comparison with the previously studied isomers under identical conditions, the lean mixture at $X_O(\text{fuel}) = 3500$ ppm and $\tau = 1.5$ s was tested in an attempt to initiate low-temperature reactivity in neopentanal.



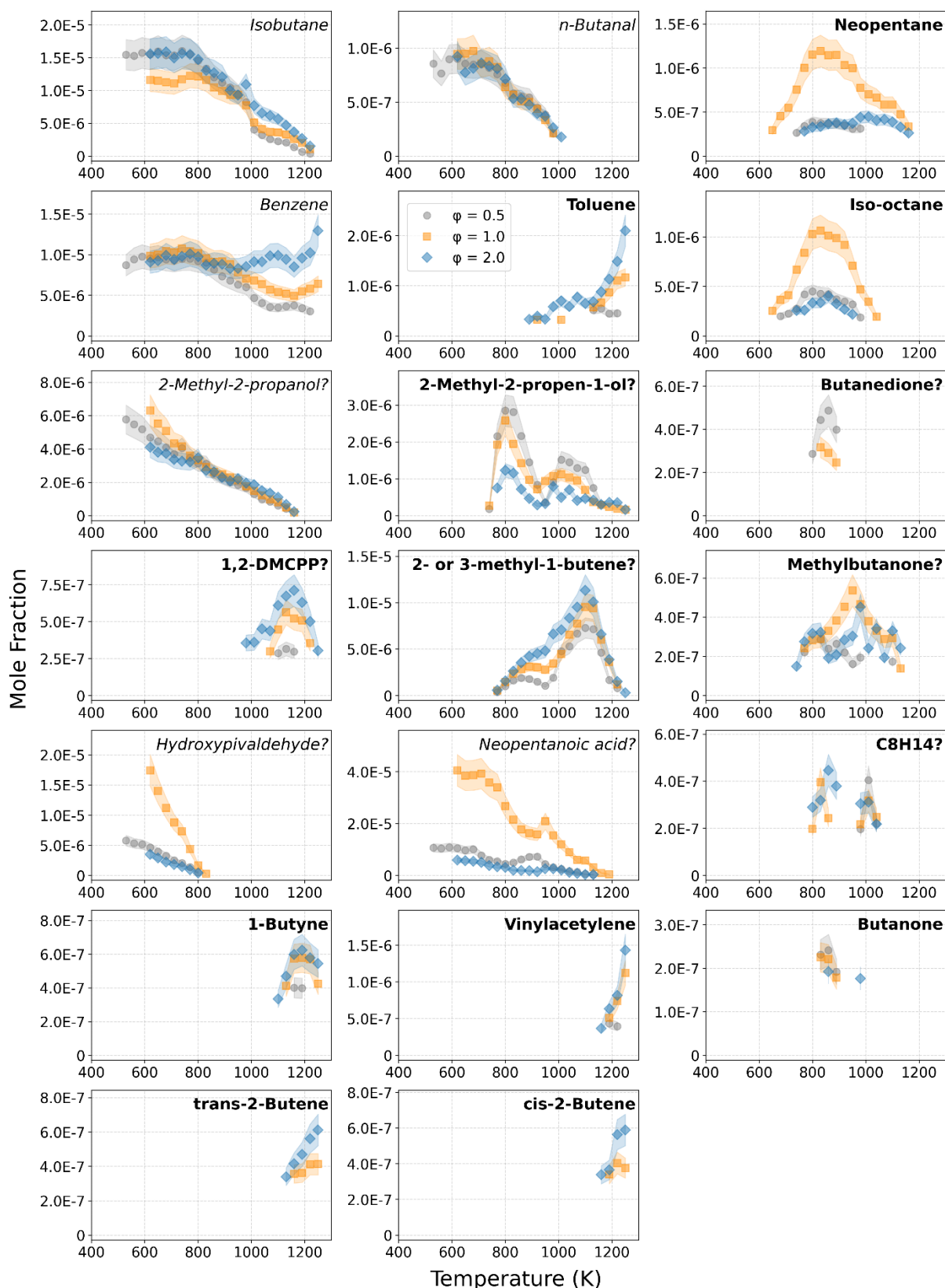
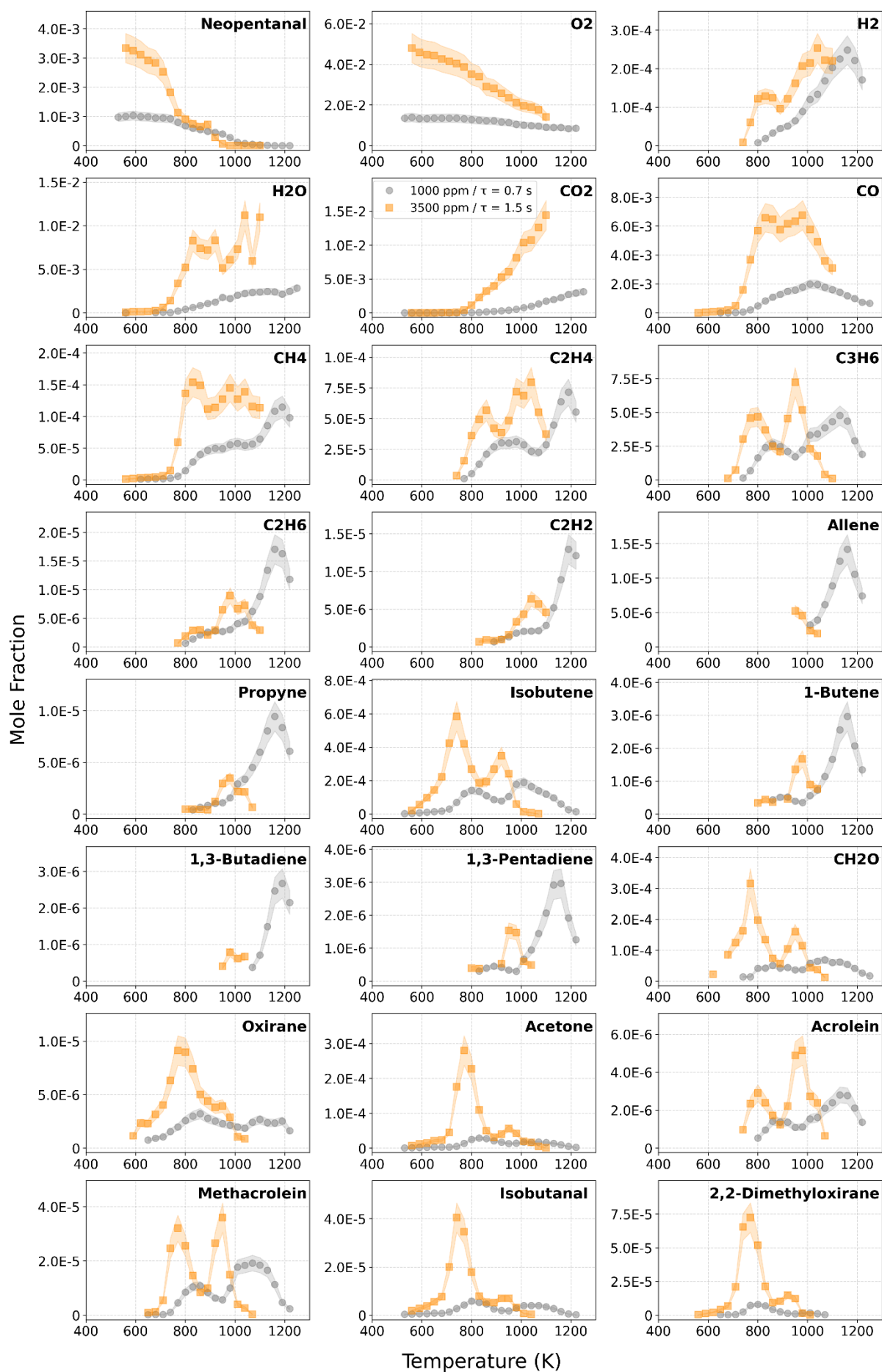


Fig. F1: Mole fraction profiles (with $\pm 15\%$ shaded uncertainty bands) of reactant, product, and intermediate species during the oxidation of neopentanal at $p = 10$ bar, $\tau = 0.7$ s, $X_0(\text{fuel}) = 1000$ ppm, and $\phi = 0.5$ (gray); 1 (orange); 2 (blue). Impurities (originally present in the fuel or rapidly formed upon exposure to air) are shown in italic, and species with uncertain identification are indicated by a question mark “?” (DMCPP denotes dimethylcyclopropane).



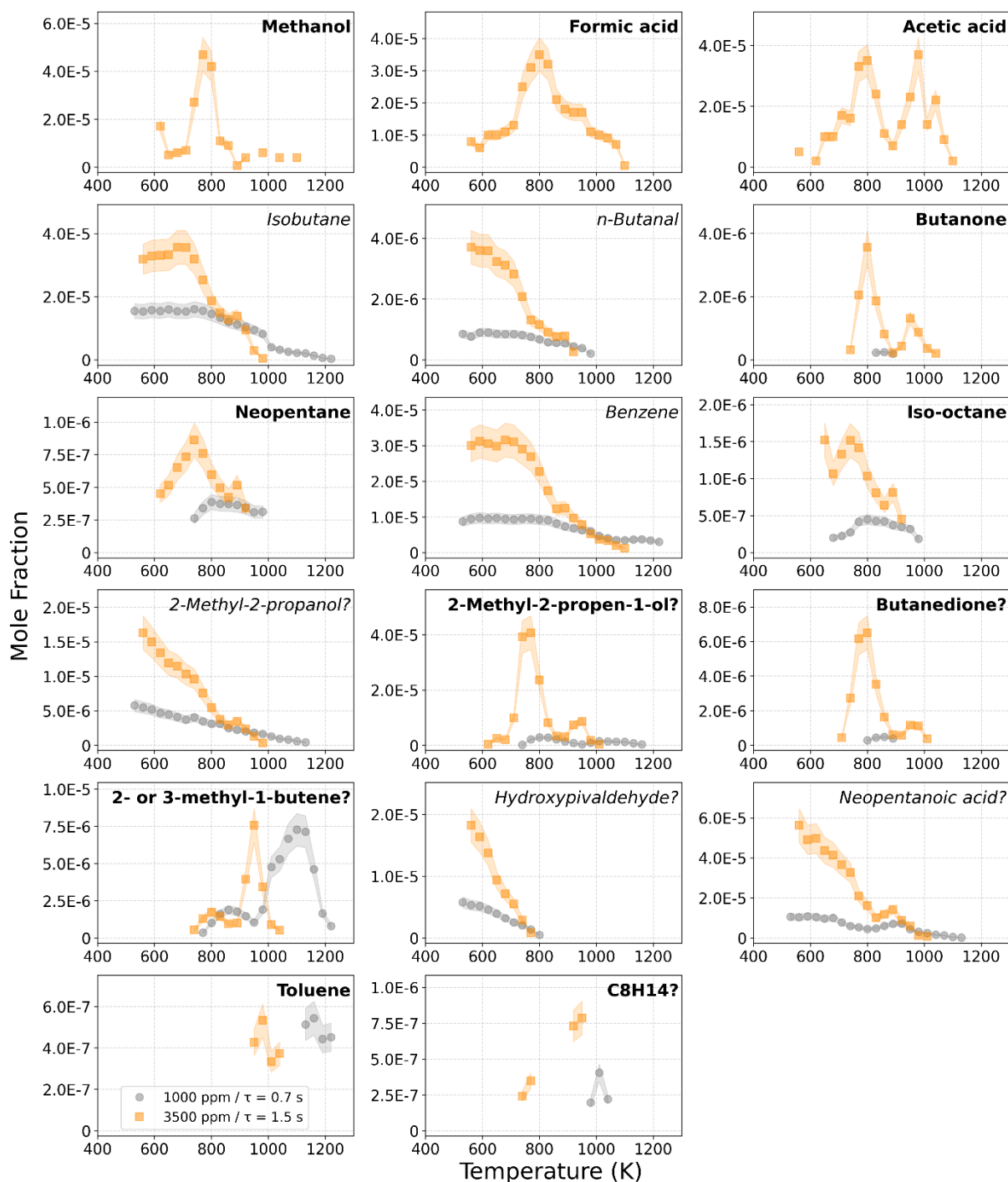


Fig. F2: Mole fraction profiles (with $\pm 15\%$ shaded uncertainty bands) of reactant, product, and intermediate species during the oxidation of neopentanal at $p = 10$ bar, $\phi = 0.5$, and: $X_{O(\text{fuel})} = 1000$ ppm / $\tau = 0.7$ s (gray); $X_{O(\text{fuel})} = 3500$ ppm / $\tau = 1.5$ s (orange). Impurities (originally present in the fuel or rapidly formed upon exposure to air) are shown in italic, and species with uncertain identification are indicated by a question mark “?”.

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Étude expérimentale et modélisation de l'oxydation des éthers et de leurs mélanges

Résumé :

La majorité des carburants liquides actuellement utilisés sont principalement dérivés de sources pétrolières. La transition vers des alternatives renouvelables et moins impactantes sur l'environnement, telles que les biocarburants, s'avère impérative à court terme. Une mise en œuvre efficace de ces biocarburants nécessite une compréhension approfondie de leur cinétique de combustion, de la quantification des espèces intermédiaires / polluants formés lors de leur oxydation, ainsi que des interactions physico-chimiques complexes intervenant tout au long de ces processus. Les éthers se distinguent comme des candidats prometteurs pour une utilisation en tant que biocarburants, et leur comportement en oxydation suscite un intérêt croissant dans la communauté scientifique. Jusqu'à présent, la majorité des travaux se sont focalisés sur les éthers à chaîne linéaire, tandis que les caractéristiques de combustion des éthers cycliques demeurent relativement peu explorées. Par ailleurs, à notre connaissance, aucune étude n'a encore abordé les interactions entre éthers linéaires et cycliques, notamment entre un éther linéaire fortement réactif à basse température et un éther cyclique présentant une réactivité limitée dans des conditions similaires. Cette thèse vise à combler cette lacune en étudiant la cinétique d'oxydation de deux éthers cycliques représentatifs — le tétrahydropyrane et le tétrahydrofurane — tant à l'état pur qu'en mélange avec un éther linéaire, le diéthyléther. La méthodologie adoptée dans ce travail repose sur deux approches complémentaires : des études expérimentales et une modélisation cinétique détaillée. Les expériences sont réalisées dans un réacteur parfaitement agité, capable de fonctionner sur une large plage de conditions de température (400–1300 K), pression (1–10 bar), richesse et temps de passage. Les réactifs, produits et intermédiaires d'oxydation sont mesurés par analyses chromatographiques et par spectroscopie d'absorption infrarouge. Le mécanisme cinétique s'appuie sur un mécanisme détaillé développé par notre équipe de recherche, celui-ci a été affiné et étendu dans ce travail. Le mécanisme initial a été mis à jour par l'intégration de nouvelles données expérimentales de vitesses de flamme laminaire, ainsi que par un large ensemble de données issues de la littérature. Des sous-mécanismes spécifiques à l'oxydation des éthers ont été élaborés puis intégrés au mécanisme complet, permettant ainsi une description fine et prédictive de la cinétique de combustion des éthers.

Mots clés : Combustion, Biocarburants, Éthers, Cinétique chimique, Oxydation, Modélisation cinétique

Experimental and modeling studies of the oxidation of ethers and their blends

Summary:

Most current liquid fuels are predominantly derived from petroleum sources. The transition toward renewable and less environmentally detrimental alternatives, such as biofuels, is imperative in the near future. The effective implementation of biofuels necessitates a comprehensive understanding of their combustion kinetics, the speciation and quantification of pollutants generated during oxidation, and the complex physicochemical interactions that occur throughout these processes. Ethers have emerged as promising candidates for use as biofuels, and their oxidation behavior has recently garnered significant research interest. To date, most investigations have focused on linear-chain ethers, while the combustion characteristics of cyclic ethers remain comparatively underexplored. Moreover, to the best of our knowledge, no prior studies have examined the interactions between linear and cyclic ethers—particularly between a highly reactive linear ether at low temperatures and a cyclic ether exhibiting limited reactivity under similar conditions. This thesis addresses this gap by investigating the oxidation kinetics of two representative cyclic ethers—tetrahydropyran and tetrahydrofuran—both individually and in blends with a linear ether, diethyl ether. The methodology adopted in this work presents two complementary approaches: experimental studies and detailed kinetic modeling. The experiments are carried out in a jet-stirred reactor designed to operate over a wide range of temperatures (400–1300 K), pressures (1–10 bar), equivalence ratios, and residence times. Reactants, products, and oxidation intermediates are measured by chromatographic analyses and by infrared absorption spectroscopy. The kinetic mechanism is based on an existing mechanism developed by our research group, which is refined and extended in this work. The base mechanism is updated through incorporation of novel laminar flame speed data as well as a comprehensive set of experimental data sourced from the literature. The sub-mechanisms of ether oxidation are developed and subsequently integrated into the overall ether mechanism enabling a detailed and predictive description of ether combustion kinetics.

Keywords: Combustion, Biofuels, Ethers, Chemical kinetics, Oxidation, Kinetic modeling