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Understanding the Combustion Kinetics of Alternative Fuels: Hydrogen Blends, Bio- and E-Fuels

by

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Comprendre la Cinétique de Combustion des Carburants Alternatifs : Mélanges d'Hydrogène, Biocarburants et E-carburants

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"Yesterday I was clever, so I wanted to change the world. Today I am wise, so I am changing myself."

~Rumi

Abstract

The urgent need to transition from fossil fuel combustion to greener energy solutions requires exploring multiple alternatives. Each potential solution comes with its own set of advantages and limitations, making it impractical to rely on a single option. While combustion generates pollutants, its high energy density is essential for many sectors. However, emissions vary depending on the fuel used. In contrast, electrification is often regarded as the cleanest energy option, though it carries high implementation costs and environmental impacts throughout the battery life cycle. This thesis investigates the combustion kinetics of various fuel alternatives, including hydrogen blends, e-fuels, and biofuels in the low to intermediate-temperature range of combustion. Using a rapid compression machine to measure ignition delay times, the study validates newly developed kinetic models and evaluates existing ones from the literature. Hydrogen, a carbon-free fuel, is studied in a blend with other fuels regarding its hazard as a highly flammable and explosive gas. The blended fuels consist of C₅-chain compounds, each with a different chemical functional group, to assess hydrogen's influence on each group. The study is done by varying the hydrogen content from 0 to 50 mol% in each fuel mixture and examining these blends under a wide range of conditions: pressures of 20, 15 and 10 bar; stoichiometric and fuel-lean mixtures; in the temperature range of 600–950 K. The fuels studied include *n*-pentane, 1-pentene, 3-pentanone, and 3-pentanol. Existing models from the literature are tested for the first three fuels, while a new model is developed and validated for 3-pentanol based on IDT and species mole fraction profiles. The same set of experiments was conducted under pressure conditions of 15, 10, and 5 bar at stoichiometric conditions to develop a new kinetic model for tetrahydropyran, a secondgeneration biofuel. Additionally, IDTs for trimethoxymethane, an e-fuel, were measured under stoichiometric and fuel-lean conditions in the same pressure range. These results were used to test a new model in development and compare it with existing models from the literature. Finally, an *ab initio* study is performed on alkyl carbonates—key combustible components in lithium batteries-to compute the kinetic rates of Habstraction reactions by H and CH₃, and their subsequent reactions at the liquid and the gas phase. This thesis contributes to a deeper understanding of the combustion kinetics of promising candidates for alternative energy sources.

Keywords: Combustion, Low-temperature combustion, Rapid compression machine, Hydrogen, C₅-Chain fuels, Bio-fuels, E-fuels, Alkyl-carbonates, Kinetic modeling, Chemical kinetics, Ignition delay.

Résumé

L'urgence de la transition de la combustion vers des solutions énergétiques plus soutenables que les combustibles fossiles nécessite l'exploration de plusieurs alternatives. Chaque solution potentielle présente ses propres avantages et limitations, rendant impossible le choix d'une seule option. Bien que la combustion génère des polluants, sa haute densité énergétique est essentielle pour de nombreux secteurs. Cependant, les émissions varient selon le carburant utilisé. En revanche, l'électrification est souvent considérée comme l'option énergétique la plus propre, bien qu'elle entraîne des coûts de mise en œuvre élevés et des impacts environnementaux importants tout au long du cycle de vie des batteries. Cette thèse étudie la cinétique de combustion de divers carburants alternatifs, y compris les mélanges contenant de l'hydrogène, les e-carburants et les biocarburants dans la gamme des basses et intermédiaires températures de combustion. Grâce à l'utilisation d'une machine à compression rapide pour mesurer les délais d'auto-inflammation, l'étude valide à la fois des modèles cinétiques nouvellement développés et évalue ceux existants dans la littérature. L'hydrogène, un carburant sans carbone, est étudié en mélange avec d'autres carburants en raison de son haut caractère inflammable et explosif. Les carburants mélangés sont constitués de composés à chaîne C₅, chacun ayant un groupe fonctionnel chimique différent, afin d'évaluer l'influence de l'hydrogène sur chaque groupe. L'étude fait varier la teneur en hydrogène de 0 à 50 mol% dans chaque mélange de carburant et examine ces mélanges dans diverses conditions : des pressions de 10, 15 et 20 bar ; des mélanges stœchiométriques et pauvres en carburant ; et dans une gamme de températures de 600 à 950 K. Les carburants étudiés incluent le *n*-pentane, le 1-pentène, la 3-pentanone et le 3-pentanol. Des modèles existants dans la littérature sont testés pour les trois premiers carburants, tandis qu'un nouveau modèle est développé et validé pour le 3-pentanol sur la base des temps de délai d'autoinflammation et des profils temporels des fractions molaires des espèces. Le même ensemble d'expériences a été mené sous des conditions de pression de 15, 10 et 5 bar en conditions stæchiométriques pour développer un nouveau modèle cinétique pour le tétrahydropyrane, un biocarburant de deuxième génération. De plus, les temps de délai d'auto-inflammation pour le triméthoxyméthane, un e-carburant, ont été mesurés en conditions stœchiométriques et pauvres en carburant en utilisant la même gamme de pression. Ces résultats ont été utilisés pour tester un nouveau modèle en cours de développement et le comparer avec des modèles existants dans la littérature. Par ailleurs, une étude *ab initio* a été réalisée sur les carbonates—des composants combustibles clés dans les batteries au lithium—afin de calculer les vitesses des réactions d'arrachement d'hydrogène par H et CH₃, ainsi que leurs réactions ultérieures en phase liquide et gazeuse. Cette thèse contribue à une compréhension plus approfondie de la cinétique de combustion de candidats prometteurs pour les sources d'énergie alternatives.

Mots clés : Combustion, Cinétique chimique, Machine à compression rapide, Hydrogène, Carburants à chaîne C₅, Biocarburants, E-carburants, Alkylcarbonates, Modélisation cinétique, Delai d'auto-inflammation, Combustion de basses températures.

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Finally, to the little child still living inside me—you are my favorite person. You can stop hiding in the shadow of the door now, because in the end, everything is never going to be okay, and that's the motif of going on.

List Acronyms and Definitions

RCM: Rapid Compression Machine ST: Shock Tube HPST: High-pressure Shock Tube JSR: Jet-Stirred Reactor TOF-MS: Time of Flight – Mass Spectrometry PI - MBMS: PhotoIonization Molecular - Beam Mass Spectrometry SVUV - PIMS: Synchrotron-based Vacuum Ultraviolet PhotoIonization Mass Spectrometry LC: Liquid Chromatography GC: Gas Chromatography **IDT: Ignition Delay Time** FSIDT: First-Stage Ignition Delay Time i² PEPICO: Double Imaging PhotoElectron PhotoIon Coincidence KHP: Keto-Hydro-Peroxide FTIR: Fourier-Transform Infrared HRMS: High Resolution Mass Spectrometry MPIMS: Multiplexed PhotoIonization Mass Spectrometry **NTC: Negative Temperature Coefficient** SI: Spark Ignition LTC: Low Temperature Combustion **EOC: End of Compression BDE: Bond Dissociation Energy ICE:** Internal Combustion Engine **TCD: Thermal Conductivity Detector FID: Flame Ionization Detector** CF: Cool flame, aka, First-stage ignition

Knock: is abnormal combustion in engines where fuel ignites prematurely, causing a knocking sound

E.R.: Equivalence ratio

Global introduction

In the context of escalating climate change and the ongoing deterioration of atmospheric air quality, there is a growing global imperative to explore alternative energy sources that mitigate these environmental challenges. The transportation sector, in particular, remains one of the most significant contributors to greenhouse gas emissions and air pollutants. Decarbonizing this sector presents a formidable challenge due to the high energy demands required for operation. Combustion remains the predominant energy source across many industries, and despite the push for electrification, certain sectors— such as aviation, steel and glass production—require energy densities that current electrical systems cannot efficiently provide. Therefore, the search for viable, cleaner fuel alternatives is critical in reducing emissions while maintaining operational feasibility. It is also essential to recognize that *no single energy strategy will provide a universal solution to the diverse energy demands across sectors*. The complexity of global energy needs necessitates a multifaceted approach, involving various fuel alternatives tailored to specific applications.

This thesis focuses on the exploration of various fuels by examining their ignition properties, with particular attention to *ignition delay times* (IDTs) and, in specific cases, the species produced during ignition, targeting the *low-temperature range of combustion*. The goal is to contribute to the development of reliable chemical kinetic models, either by validating existing models from the literature or by developing new ones. Investigating low-temperature combustion chemistry (LTC) is of significant importance, not only for its potential to reduce emissions of nitrogen oxides (NO_x) and particulate matter [1] but also for its role in complex combustion phenomena. These include issues like engine knock in spark-ignition engines and ignition behavior in compression-ignition engines, both of which are strongly influenced by the intricate processes occurring at low temperatures [2]. This investigation is accomplished by utilizing a *Rapid Compression Machine* (RCM) to measure IDTs, and employing Gas Chromatography to separate, and flame ionization and thermal conductivity detectors (FID-TCD), coupled with a mass spectrometer (MS) to

identify and track the evolution of species produced during ignition. The experimental data gathered are then used to develop and validate chemical kinetic models through simulations conducted using the open-source solver Cantera.

Hydrogen was the first fuel considered in this study due to its carbon-free nature, which eliminates carbon-based emissions during combustion. However, for various practical reasons like the very high flame speed, and the ability to detonate, hydrogen is often preferred as a blend with other fuels rather than used in its pure form [3]. Consequently, this thesis focuses on examining the influence of hydrogen in a blend with different fuels, C5-chain fuels, each representing distinct chemical functional group: *n-pentane, 1-pentene, 3-pentanone, and 3-pentanol.* This approach not only enables the investigation of the impact of hydrogen on each fuel family but also facilitates comparisons between the fuels, providing insight into how different chemical functional groups affect ignition behavior. In addition to hydrogen blends, this thesis also explores other alternative fuels, such as *tetrahydropyran, a second-generation biofuel, and trimethoxymethane, an e-fuel.* Both fuels are considered carbon-neutral due to their closed carbon loop throughout their life cycle. Given their potential to contribute to sustainable energy solutions, this research aims to look deeper into the combustion characteristics and kinetic behavior of these promising fuel alternatives.

In addition to the experimental and modeling work conducted in this thesis, a theoretical chemistry study was performed on alkyl carbonates, key components in lithium batteries, to understand their oxidation mechanisms. This study aimed to contribute to the literature by providing kinetic rate data for hydrogen abstraction reactions and their subsequent reaction pathways to be a part of more trusted kinetic mechanisms. In the light of this, this thesis is structured into seven chapters as follows:

Chapter 1 provides an overview of the different topics related to this work.

Chapter 2 starts by introducing the molecules examined in this thesis, and it provides an overview of previous studies conducted under similar conditions for each molecule. It also highlights the fundamentals of low-temperature combustion chemistry.

Chapter 3 details the experimental facilities utilized in this work, including an explanation of the methodologies and operational concepts behind them. It also provides a brief overview of kinetic modeling, covering simulations and model development. The chapter concludes with an introduction to the *ab initio* methods employed in this thesis. Each section includes a summary of the specific molecules studied, along with the experimental conditions and the kinetic models either taken from the literature or developed for this research.

Then the results and discussions are separated into 3 different chapters:

Chapter 4 presents the findings from the study of C₅-chain molecule blends with hydrogen. For each C₅ molecule—*n*-pentane, 3-pentanone, and 1-pentene—the chapter includes IDTs measured using the U-Lille RCM, both with and without hydrogen, as well as simulations using various models from the literature, that are also used for the kinetic analyses. Additionally, it covers the same experimental results for 3-pentanol, including sampling experiments, and introduces a kinetic model developed as part of this work used for simulations.

Chapter 5 presents the findings from studies on tetrahydropyran, including IDTs and sampling experiments using the RCM, and simulations conducted with a newly developed model by our research group. Additionally, chapter 5 covers IDT data for trimethoxymethane, alongside simulations using two different models: one from the literature and another developed in the Laboratory of Chemical Technology at the University of Ghent as part of collaborative work, to highlight the key differences between these two models.

All of the experiments presented in these chapters have been performed at the PC2A (PhysicoChimie des Processus de Combustion et de l'Atmosphère) Laboratory.

Chapter 6, presents the *ab initio* research conducted on alkyl-carbonate molecules during a three-month stay at the Chair of High Pressure Gas Dynamics, Shock wave Laboratory (HGD) at RWTH University of Aachen. The computations were performed using the "RWTH High Performance Computing" cluster, with supervision provided by Professor Alexander Heufer and Dr. Malte Döntgen.

Chapter 7 provides a summary of the manuscript, and it includes a comparison between all the C₅-chain molecules from this thesis. It also outlines potential directions for future research.

Chapter 1 The Environmental Crisis and the Role of Sustainable Energy Alternatives

1.1 Introduction

1.1.1 July 2024 – A new record

July 2024 set a new record as the hottest month of July globally in NOAA's (National Oceanic and Atmospheric Administration) 175-year history [4]. The global surface temperature of the Earth for the month was 1.21°C higher than the 20th-century average of 15.8°C, edging out the previous year's record by 0.03°C. This marks the 14th month in a row with unprecedented global temperatures, breaking the longest streak of record warmth in the modern era, which previously occurred from May 2015 to May 2016. Additionally, July 2024 was the 48th consecutive month of July with global temperatures exceeding the 20th-century average. Climatologically, July is typically the warmest month of the year. Given that July 2024 was the hottest July ever recorded, it was likely the warmest month globally since records began in 1850. Notably, the last ten Julys have all ranked as the warmest on record.



Fig 1 – Global temperatures of July 2024 compared to average [4].

Record-high July temperatures affected vast regions across northern and southern Africa as presented in Fig 1, southeastern Europe, and large parts of Asia, as well as areas in the western U.S. and western Canada. Most of Greenland experienced much warmer-thanaverage July temperatures, with many areas witnessing temperatures more than 4°C above average. In July 2024, 13.8% of the world's surface recorded its highest-ever July temperature, surpassing the previous record set in 2023 by 5.4%. Additionally, nearly one-fifth (19.2%) of the global land surface saw record-high July temperatures, while only 0.3% of the global land and ocean surface experienced a record-cold July temperature.

In eastern Europe, monthly mean temperatures were widely more than 2°C above average, while much of southern Europe experienced July temperatures exceeding the average by more than 1°C. In Spain and other Mediterranean countries, heatwaves resulted in several days of temperatures surpassing 38°C, creating severe wildfire conditions and leading to reports of hundreds of heat-related deaths. Morocco faced even more extreme heat, with daily highs exceeding 41°C in many areas. Researchers from World Weather Attribution determined that the intensity of this heatwave would not have been possible without the influence of climate change.

1.1.2 The role of carbon dioxide

Carbon dioxide (CO₂) is Earth's most important greenhouse gas (GHG) [5], responsible for absorbing and radiating heat. Unlike oxygen (O₂) and nitrogen (N₂), which constitute the majority of our atmosphere, GHGs like CO₂ absorb infrared radiation emitted from the Earth's surface and re-radiate it in all directions, including back towards the surface as shown in Fig 2.



Fig 2 – Schematic representation of solar radiation absorption and reflection [6].

Without CO₂, Earth's natural greenhouse effect would be too weak to maintain an average global surface temperature above freezing. However, human activities have added more CO₂ to the atmosphere, intensifying the natural greenhouse effect and causing global temperatures to rise. According to observations by the NOAA Global Monitoring Lab [7], in 2021, *CO₂ alone accounted for approximately two-thirds of the total warming impact from all human-produced greenhouse gases*.

Another critical role of CO_2 in the Earth system is its ability to dissolve into the ocean, much like the carbonation in a can of soda. When CO_2 reacts with water, it forms carbonic acid, which lowers the ocean's pH, increasing its acidity. Since the beginning of the Industrial Revolution, the pH of the ocean's surface waters has decreased from 8.21 to 8.10 [8], a process known as ocean acidification, which risks destabilizing global ecosystems, economies, and food security [9].

Since the start of the Industrial Revolution in 1750, atmospheric CO₂ levels (represented by the blue line in Fig 3) have risen alongside human emissions (depicted by the gray line). Emissions increased gradually to around 5 gigatons per year—where one gigaton equals a billion metric tons—by the mid-20th century. However, they increased dramatically to over 35 billion tons per year by the end of the century.



Fig 3 – Global atmospheric carbon dioxide compared to annual emissions (1751-2022) [8]. Today's levels of CO_2 are unprecedented in human history. The last time atmospheric CO_2 concentrations were this high was approximately 3 million years ago, during the Mid-Pliocene Warm Period. During that era, global surface temperatures were 2.5–4 °C warmer than before the industrial era, and sea levels were at least 5 m higher than in 1900, with estimates suggesting they could have been up to 25 m higher [10].

The primary source of CO_2 emissions globally is the energy sector, which accounts for about 75.6% of human-caused greenhouse gas emissions [11]. This sector includes electricity and heat generation, transportation, and industrial processes. Among these, 'electricity and heat production' is the largest contributor, responsible for roughly 31.8% of total global emissions, see Fig 4. Transportation is another major contributor, making up about 17% of total emissions. These emissions arise primarily from the combustion of fossil fuels for vehicles, aircrafts, ships, and other modes of transport. Industrial activities also contribute significantly to CO_2 emissions, particularly through the production of chemicals, cement, and other materials.



Fig 4 - CO₂ emissions by sector in the world. [11].

If global energy demand continues to rise rapidly and is primarily met with **fossil fuels**, human CO₂ emissions could exceed 75 billion tons per year by the end of the century. Atmospheric CO₂ levels could reach 800 ppm or more, conditions not experienced on Earth for nearly 50 million years [8].

1.1.3 Environmental impact beyond CO₂

While CO₂ is a significant driver of climate change, one should recognize that burning fossil fuels results in a variety of harmful emissions beyond CO₂. The combustion process releases pollutants such as unburnt hydrocarbons, carbon monoxide (CO), nitrogen oxides (NOx), particulate matter (PM), and sulfur dioxide (SO₂), all of which contribute to air quality degradation, public health issues, and further environmental impact. By seeking and adopting alternative energy solutions, we can mitigate the emission of different harmful pollutants. This broader approach is essential for creating a cleaner, healthier, and more sustainable future.

1.2 Alternative Sustainable Fuels

1.2.1 Hydrogen

The concept of hydrogen as a means of energy storage and the idea of a hydrogenpowered economy have been around for decades. Before the 1960s, many countries utilized hydrogen in the form of town gas (a mixture of several gases, including hydrogen, methane, carbon monoxide, and other hydrocarbons, of which hydrogen made up around 50% of the gas mixture), for street lighting and household energy needs, including cooking, heating, and lighting. The vision of a hydrogen-based energy system gained further traction following the oil crises of the 1970s, sparking renewed interest in hydrogen as a potential alternative to fossil fuels. The renewed interest in hydrogen was largely driven by advancements in fuel cell technology in the late 1990s.

Although hydrogen has a range of potential uses—spanning mobile, stationary, and portable applications—the transportation sector plays a key role in facilitating its widespread adoption [12]. In the early 2000s, BMW launched the Hydrogen 7, a series production vehicle equipped with a modified 6-liter V12 gasoline engine that utilized hydrogen port fuel injection, [13], [14]. Around the same time, Ford [15], [16] and other companies also conducted significant research and development on hydrogen internal combustion engines (H₂-ICEs) [17].

Hydrogen presents numerous advantages as a clean energy carrier, especially when produced from renewable sources. These benefits are increasingly recognized as critical in the context of evolving policy priorities. Developing a substantial market for hydrogen as an energy vector could provide powerful solutions for reducing emissions and enhancing energy security. Hydrogen, when used as a fuel, produces no carbon-based emissions at the point of use, eliminating CO₂ and unburnt hydrocarbon air pollutant emissions from transportation. However, the environmental benefits of hydrogen depend heavily on its production method.

As of the end of 2021, almost 47% of the global hydrogen production is from natural gas, 27% from coal, 22% from oil (as a by-product) and only around 4% comes from electrolysis [18]. In fact, the production of hydrogen through the electrolysis of water using wind or solar energy is still very costly [19], [20]. A study by the Fuel Cells and Hydrogen (FCH) on "green hydrogen" [21] identified approximately ten methods for generating hydrogen from renewable resources. Among these, biogas emerged as the most cost-effective and promising option. Biogas, primarily composed of methane (CH₄) and CO₂, serves as a valuable raw material for hydrogen production. In 2014, Europe had over 17,000 biogas plants, generating more than 8,000 MW of power [22]. The following year, the European Union produced 15.6 million tons of primary energy from biogas, reflecting an annual growth rate of over 5% compared to the previous decade [23].

Highlighting the advantages of hydrogen doesn't negate the challenges associated with its use. It's crucial to address the difficulties that come with hydrogen. For instance, as the smallest molecule, hydrogen is more prone to leakage through small openings compared to other gases or liquids, and can diffuse through materials. Additionally, prolonged exposure to hydrogen can weaken certain high-strength steels, leading to potential structural failure, making careful material selection essential. Hydrogen is also more diffusive and buoyant than fuels like gasoline, propane, or methane, meaning it disperses faster when released. Its broad flammability range compared to other fuels presents a safety concern, as a hydrogen vapor cloud can occupy a larger flammable volume than, for example, a methane cloud under similar conditions [24]. Accordingly, hydrogen is currently employed as an alternative fuel in combination with other fuels in vehicles. Additionally, it can be used alongside conventional fuels in ICEs without requiring significant modifications to the vehicle [24], [25], [26], [27], [28].

1.2.2 Bio-, and Electro-fuels (E-fuels)

1.2.2.1 Biofuels

Biofuels have been utilized since the early days of the automotive industry. For example, Rudolph Diesel tested his first engine using peanut oil [29] after discovering that pulverized coal was not a suitable fuel. Interest in biofuels has grown significantly in the past decade, driven by the development of climate change mitigation policies and strategies aimed at reducing GHG emissions in the transport sector. Since then, over 60 countries have initiated biofuel programs and established targets for blending biofuels into their fuel supplies [30]. Among the most notable are the Renewable Fuel Standard (RFS) in the USA [31] and the Renewable Energy Directive (RED) in Europe [32].

Biofuels can be categorized based on several key characteristics, such as the type of feedstock, the conversion process, the technical specifications of the fuel, and its intended use, see Fig 5. Due to the wide range of possible distinctions, various definitions exist for different types of biofuels. Among these, the terms "first, second, and third generation" are commonly used. Biofuels derived from food or animal feed crops are known as first-generation biofuels. These fuels can negatively impact food security and have limited yield potential [33]. To address these issues, there is a need to develop advanced biofuels using non-edible feedstocks. Second-generation biofuels, for instance, are produced from lignocellulosic materials, non-food sources, algal biomass, and energy crops cultivated on marginal lands.



Fig 5 - An overview of feedstocks and production processes for different biofuels. Simplified from [34], adapted from [35].

According to the International Energy Agency (IEA) [36], biofuel demand is projected to increase by 38 billion liters between 2023 and 2028, see Fig 6, representing nearly a 30% rise compared to the previous five-year period. By 2028, total biofuel demand is expected to reach 200 billion liters, with renewable diesel and ethanol contributing to two-thirds of this growth, while biodiesel and biojet fuel account for the remaining share.



Fig 6 – Global biofuel demand, historical, main and accelerated case, 2016-2028 [36].

1.2.2.2 Electro-fuels

E-fuels come in various forms, including synthetic hydrocarbons like oxymethylene ethers (OMEs). E-fuels can be produced through various methods [37], as represented in Fig 7:

- H₂ and CO₂: H₂ is combined with CO₂ to create e-methane or e-methanol. These can further be converted into e-DME (dimethyl ether), *OME*, or e-diesel/e-gasoline.
- H₂ and CO: Hydrogen is reacted with CO to produce e-diesel, e-kerosene, e-gasoline, or e-DME/OME.
- H_2 and N_2 : Hydrogen is combined with N_2 to produce e-ammonia.

CO can be generated from carbon dioxide CO_2 through the Reverse Water Gas Shift (RWGS) reaction. CO_2 can be captured via carbon capture utilization and storage (CCUS) techniques or directly from the air using direct air capture (DAC). For the synthesis of e-

ammonia, N_2 is sourced from the atmosphere [38], [39]. To ensure the sustainability of these technologies, it is essential that all these processes utilize renewable electricity, and that H_2 is produced through renewable methods.



Fig 7 – *Different e-fuels production pathways with highlight on the necessary raw materials.* [37]. Currently, e-fuel prices are high, but future models indicate a decrease in costs. Electrolysis, which constitutes a significant portion of e-fuel production costs, is expected to become cheaper and more efficient as technology advances. Additionally, price forecasts for hydrogen, methanol/methane, and ammonia suggest substantial reductions by 2030, with estimated prices falling to 2.16€, 0.65€, and 0.46€ per kilogram [40], compared to approximately 10€, 0.71€, and 0.58€ respectively in 2024 [41]. However, the production of e-fuels requires a lot of energy. Due to the efficiency loss in the transformation process, energy is lost at every stage [42].

Although the combustion of biofuels and e-fuels produces CO_2 , they are considered carbon neutral because the CO_2 released during their use is balanced by the CO_2 absorbed during their production. In the case of biofuels, the carbon emitted when they are burned is offset by the CO_2 absorbed by plants during their growth, making it part of a short-term carbon cycle. Similarly, e-fuels achieve carbon neutrality by using CO_2 captured from industrial processes or the atmosphere in their production, ensuring that the CO_2 released during combustion was previously removed from the atmosphere. This closed carbon loop is fundamental to their sustainability and their potential to mitigate the impacts of climate change.

1.2.3 Electricity

Although interest in and consumption of electric and hybrid vehicles (EVs and HEVs) have increased significantly, they are far from being a new phenomenon in the market. Historically, these vehicles have competed closely with combustion-engine cars.

In 2023, nearly 14 million new electric cars were registered worldwide, as depicted in Fig 8, increasing the total number of electric vehicles on the road to 40 million. Electric car sales in 2023 were 3.5 million higher than in 2022, marking a 35% year-on-year increase—more than six times the sales in 2018, just five years earlier [43].



Fig 8 – Electric cars registrations and sales share in China, United states and Europe, 2018-2023 [43].

In 2023, Europe saw nearly 3.2 million new electric car registrations, marking an increase of almost 20% compared to 2022. Within the European Union, sales reached 2.4 million, with similar growth trends.

1.3 Closing Remarks

While hydrogen combustion, bio- and e-fuels, and electricity represent promising alternatives to traditional fossil fuels, they are by no means the only solutions available. The landscape of sustainable energy is broad and evolving, with numerous other technologies and approaches contributing to the reduction of CO₂ and other emissions and the mitigation of environmental damage. *The focus on these alternatives in this thesis is driven by the specific studies and analyses conducted within this work*. As the global community continues to innovate and seek out new energy solutions, it is essential to keep exploring and expanding our understanding of all viable options, ensuring a comprehensive approach to addressing the challenges posed by climate change.

Chapter 2 Bibliography

2.1 Introduction

As outlined in the introductory chapter, there are various alternatives to fossil fuels. This thesis delves into research studies covering different facets within this domain:

- Experimental and modeling investigations into the combustion chemistry at low temperatures for:

a- Hydrogen: Employed as an additive to C₅-chain molecules with diverse chemical group functionalities: *n*-pentane, 1-pentene, 3-pentanone, 3-pentanol.

b- Next generation fuels:

- I. Bio-fuel: Tetrahydro-pyran.
- II. E-fuel: Trimethoxy-methane (an oxymethylene-ether).

- An *ab initio* study on the oxidation of alkyl carbonates: crucial components in lithium batteries.

In this chapter, a concise background on the rationale behind selecting these topics is provided, along with a brief historical overview of the literature associated with each studied molecule. Before delving into the detailed studies, some fundamental understanding of the combustion chemistry is introduced in the following section.

2.2 Combustion Chemistry

Combustion is a highly intricate process involving numerous intermediate chemical species and thousands of elementary reactions, culminating in the production of final combustion products. While the primary outcomes of fuel combustion typically include carbon dioxide and water, the process also includes the generation of additional byproducts such as carbon monoxide, nitrogen oxides, soot, and unburnt hydrocarbons. Owing to the environmental risks associated with the release of these pollutants, clean combustion emerges as the foremost and prime requirement for a fuel candidate. Consequently, the main focus of the research has been on the kinetics of the elementary reactions in order to understand the combustion behavior of these fuels over wide

temperature and pressure ranges. Fig 9 highlights a kinetic scheme of the primary oxidation reactions in the simplest fuel molecules that are alkanes (RH).

The reactions are grouped into different reaction classes according to the enormous number of elementary reactions. These reaction classes can be relevant in different temperature and pressure regions, and are therefore classified as high- or lowtemperature reaction classes.



Fig 9 - Schematic of typical reaction paths in hydrocarbon combustion [44], [45].

The combustion of the fuel can be initiated by radicals like \dot{H} , HO \dot{O} , \dot{O} H, \dot{C} H₃, which abstract H-atoms from RH, operating effectively at both low and high temperatures. In elevated temperature conditions, the predominant mechanism involves the β -scission of the fuel radical (\dot{R}) into an olefin and smaller alkyl radical. Conversely, at lower temperatures, the major reaction involves the addition of alkyl radicals to molecular O₂, leading to the formation of alkyl-peroxy radicals ($\dot{R}\dot{O}_2$) which can further undergo direct elimination of HO \dot{O} radicals and forming olefins. The HO \dot{O} radicals demonstrate relatively low reactivity, and their reactions involve the formation of H₂O₂. Due to the stability of H₂O₂ up to approximately 1100 K [44], this pathway results in chain-termination at low temperatures.

The reaction of the \dot{R} + O_2 proceed through many reaction channels depending on the temperature and pressure conditions, significantly influencing the overall reactivity of the fuel. It can proceed through a vibrationally excited alkylperoxy complex (\dot{RO}_2^*), leading to the generation of olefin and HOO radical [46], this is what is called the chemically activated channel. Under high-pressure and low-temperature conditions, \dot{RO}_2^* radicals undergo collisional stabilization. With increasing temperature, the equilibrium between \dot{R} + O_2 and the formation of \dot{RO}_2 tends to favor the reactants, leading to the predominant consumption of fuel radicals through β -scission reactions. Investigating the intricate competition among these diverse elementary reaction channels is crucial for a detailed understanding of ignition processes. Another noteworthy reaction involving \dot{RO}_2 species is their isomerization, resulting in the production of hydroperoxy-alkyl (\dot{QOOH}) species. Thus, the kinetics of the \dot{R} + O_2 reaction pathways play a crucial role in the negative temperature coefficient regime, where the reactivity is inhibited (IDT increases) with the increase of temperature, Fig 10.



Fig 10 - Representation of an NTC behavior. Fuel mixture: n-pentane/'air' mixture.

In the intermediate-temperature regime, $\dot{Q}OOH$ can engage in reactions such as cyclic ether formation, β -scission reactions, and the elimination of HOO. The formation of highly reactive $\dot{O}H$ radical via cyclic ether formation makes this reaction channel important for the chain-propagation.

Additionally, QOOH can react with molecular O_2 , leading to the formation of hydroperoxyl-alkyl-peroxyl (\dot{O}_2 QOOH) radicals. Previous studies by Curran et al. [46], [47] provided detailed insights into the elementary reactions involved in the oxidation of *n*-heptane and iso-octane. However, Miyoshi [48] and Bugler et al. [45] introduced low-temperature reaction classes that were not considered in earlier mechanisms. These

reactions involve \dot{O}_2 QOOH radicals, sharing similarities with $R\dot{O}_2$ species, such as direct elimination of HOO and the formation of dihydroperoxyl-alkyl radicals $\dot{P}(OOH)_2$. However, the latter pathway is more energetically favored as illustrated in Fig 11. The dissociation of $\dot{P}(OOH)_2$ results in the generation of a hydroxyl radical and a ketohydroperoxide which ultimately decomposes into a pool of radicals triggering chainbranching at low temperatures.



Fig 11 - Averaged energy diagram for the unimolecular reaction of β -O₂QOOH. The energies are the average over the sets of methyl substitutions, and the error bars indicate the range of variation by methyl substitution. The minimum-size molecules are shown as representatives. [48].

Understanding the mentioned reaction classes is imperative for the development of a comprehensive chemical kinetic model, especially when focusing on a specific fuel. Practical applicability of these models relies on obtaining accurate reaction rates for elementary reactions, coupled with essential transport data and thermodynamic properties of the involved chemical species, including standard enthalpy of formation, entropy, and heat capacities. This information is crucial for constructing reliable and practical chemical kinetic models. In these scenarios, computational chemistry assumes a pivotal role, providing essential parameters crucial for kinetic modeling. Theoretical approaches become particularly valuable in offering information that may be challenging to obtain through experimental means. For instance, while the enthalpy of formation or entropy is relatively well-established experimentally for stable molecules, this is not the
case for reactive intermediates like free radicals. Quantum chemistry methods contribute significantly to comprehending the kinetics of complex reaction systems, such as \dot{R} + O₂. The continuous progress in both quantum chemistry and reaction kinetics has facilitated a synergistic relationship between theoretical and experimental methods [44].

2.3 Experimental and modeling studies

2.3.1 Low temperature combustion of C5-chain molecules

We have opted to focus our study on fuels containing 5 carbon atoms for several compelling reasons. Given the low -intermediate temperature range we study within our facility (650 – 1100 K), it is essential that the selected fuels exhibit convenient reactivity at these temperatures, where an ignition can take place within a pressure range of 5-25 bar while being less diluted as possible. Generally, species with longer alkyl chains tend to be more reactive. However, as this study is in the gas phase, selecting even longer chains may result in higher boiling points, posing the risk of undesirable condensation within our experimental facility and potentially compromising the reliability of our results. Further elaboration on this aspect is provided in the experimental sections later in this manuscript. This selection thus represents an optimal balance, enabling a direct comparison between fuels with different chemical group functions under fixed experimental conditions.

2.3.1.1 Alkanes

While *n*-pentane is the most straightforward C₅-chain fuel and it would help unravel the effect of an added chemical group function on the reactivity, it is also of interest to study because it is a component of gas-turbine [49]. It is proposed as a biofuel additive used to enhance the performance of diesel and gasoline engines, and for its environmental benefits: reduction of NOx, hydrocarbons (HC), and CO emissions [50]. Accordingly, its combustion characteristics have been widely reported.

In the following table (Table 1) is a summary of the studies done only at the low temperature range of combustion of *n*-pentane, followed by a brief description on the most relevant studies to our work.

Author	Year	Conditions	Reactor/Approach
Dahm et al [51]	1968	T _c = 595 – 732 K	ST
		p _c = 591 – 760 mmHg	
		O_2/n -pentane: 1:1 to	
		8:1	
Hughes et al [52]	1969	T = 257° - 280°C	Conventional static
		p ₀ = 150 Torr	system (pyrex reaction
			vessel inside an electric
			furnace)
Knox et al [53]	1971	T = 523.15 – 673.15 K,	Glass high vacuumed
		$p_{total} = 90 torr n$ -	system
		pentane-O ₂	
Van Sickle et al [54]	1973	T = 100 and 125°C	Sealed glass bulb in a
			thermostatic bath
Westbrook et al [55]	1998	T _c = 675 – 980 K, p _c = 8	RCM
		-20 bar, $\Phi = 0.5 - 2$	
Ribaucour et al [56]	2000	T _c = 640 – 900 K, p ₀ =	RCM
		$300 \& 400 \text{ torr}, \Phi = 1$	
Zhukov et al [57]	2005	T _c = 867 – 1534 K, p _c =	ST
		11 to 530 atm, $\Phi = 0.5$	
Healy et al [58]	2010	T _c = 630 – 1550 K, p _c =	ST and RCM
		$8 - 30$ bar, $\Phi = 0.5, 1, 2$	
Astaryan et al [59]	2010	Quantum modeling	
Bugler et al [45], [49]	2015 - 2016	$T_c = 643 - 1718 \text{ K}, p_c =$	ST and RCM
		1, 10, 20 atm, $\Phi = 0.5$, 1,	
		2	
Bugler et al [60]	2017	T = 500 – 1100 K, p = 1	JSR
5 1 2		& 10 atm, $Φ = 0.3 - 2$, τ	-
		= 0.7 s	
Rodriguez et al [61]	2017	T = 500 – 1100 K, quasi	JSR
		atmospheric pressure,	
		$\Phi = 0.5 - 2, \tau = 2 s$	
Bu et al [62]	2017	Quantum modeling	
Tran et al [63]	2020	T = 400 – 1100 K	JSR
		p = 2.5 – 10 bar,	
		Φ = 1, τ = 2 s	
Bourgalais et al [64]	2020	T = 580 – 675 K,	JSR
Battin-Leclerc [65]	2021	quasi-atmospheric	
		pressure, τ = 3 s, Φ =	
		1/3 and 0.5	
Belhadj et al [50]	2022	T = 520 - 800 K,	JSR
		p = 10 atm, Φ = 0.5, τ =	
		1.5 s	
Liu et al [66]	2023	T = 500 – 825 K,	JSR
		Atmospheric pressure,	
		τ = 0.75 s	
Amiri et al [67]	2023		Mechanism generation

Table 1 – Summary of the studies found in literature on n-pentane at the low-temperature range of combustion. T_c: Compressed temperature, P_c: Compressed pressure, Φ : Equivalence ratio.

Knox and Kinnear [53] investigated the oxidation pathways of *n*-pentyl + O_2 at different temperatures. Their trends in product yields with composition at 290 °C indicate three different pathways for $\dot{R}O_2$ radicals: (a) H-abstraction from RH to give ROOH, (b)

decomposition homogeneously to pentenes and O-heterocycles, and (c) diffusion to the walls to give predominantly acetone, specifically at temperatures below 250 °C which was previously concluded also by Hughes et al. [52]. At temperatures above 350°C, the major products arise from homogeneous pyrolysis of RO₂ radicals, which gives a lower olefin and a lower alkane.

After that, Westbrook et al. [55] showed that the reactivity of *n*-pentane increases with the increase of pressure and equivalence ratio using a rapid compression machine (RCM). The $\dot{R}+O_2 <-> R\dot{O}_2$ system is pressure-dependent, with reactivity being influenced by pressure-induced branching. They used a kinetic mechanism to understand the reasons for these variations. Two-stage ignition was reported at most cases. The first stage is caused by low temperature alkyl-peroxy radical isomerization pathways, whose importance decreases when the temperature reaches a level where dissociation reactions are favored over the reverse addition steps. The second stage is controlled by the onset of dissociation of hydrogen peroxide.

Later on, Ribaucour et al. [56] performed a study on the effects on the autoignition variations in fuel molecular structure also by using an RCM for all pentane isomers. Among the three different isomers, *n*-pentane possesses the highest reactivity, followed by neo-pentane, and lastly iso-pentane. The difference in the ignition kinetics of these isomers is explained by the different reaction rates of isomerization of peroxy radicals into hydroperoxide radicals that depend on the molecular structure.

Zhukov et al. [57] studied the auto-ignition of a lean mixture ($\Phi = 0.5$) of *n*-pentane and air over a wide range of pressures (11 to 530 atm) and a wide temperature range from 867 to 1534 K using a shock tube (ST). They used a model that is a combination of two models from literature (RAMEC mechanism of oxidation of methane [68] and the mechanism of oxidation of *n*-heptane [47]) to simulate their results. This model includes mechanisms of ignition at high and low temperatures and a mechanism of ignition in the range of intermediate (1000 – 1200 K) temperatures. Consequently, it well predicted the ignition delay times (IDTs) of *n*-pentane/air mixtures. Then, Healy et al. [58] performed a comprehensive study on alkanes from C₁ to C₅ at high pressures using an RCM and a ST to target temperatures ranging from 630 to 1550 K and pressures from 8 to 30 bar at three different equivalence ratios ($\Phi = 0.5$, 1 and 2). They developed a kinetic mechanism based

on approximate similar fuels but it needed improvement to account for the poor agreement at high pressure and low temperature.

Bugler et al. performed three consecutive studies on the isomers of pentane. The first one [45] provides a systematic evaluation of the rate rules in the literature and their suitability for application to mechanisms for the low-temperature oxidation of straight-chained, branched-chained, and highly branched alkanes and proposes that revisions to both the thermochemistry and the kinetics are required in order to replicate experiments well. In their second paper [49], experimental measurements are done using two STs and an RCM, and the results are used to validate the model developed in their previous study. The conditions targeted are pressures of 1,10, and 20 atm in the shock tube, and 10 and 20 atm in the RCM, temperatures from 643 to 1718 K at stoichiometric conditions. Their results were well predicted for all isomers over all ranges of temperature, pressure, and mixture composition. They then performed a study on *n*-pentane oxidation in two JSRs [60] to dig into the importance of pressure-dependent kinetics and new reaction pathways. Minor modifications were done to the mechanism they developed earlier resulting in exceptional agreement with the major species detected in both reactors.

The model from Bugler et al. [60] was tested by Rodriguez et al. [61] who measured the hydroperoxide chain-branching agents during *n*-pentane low-temperature oxidation in an atmospheric-pressure JSR using three different diagnostics: time-of-flight mass spectrometry (TOF-MS) combined with tunable synchrotron photoionization, time-offlight mass spectrometry combined with laser photoionization, and continuous wavecavity ring-down spectroscopy. The species evolution with temperature has been followed for ketene, diones, and eight hydroperoxides including C1, C2, C5 alkylhydroperoxides, C₅ ketohydroperoxides, C₃, C₄, C₅ alkenylhydroperoxides, and H₂O₂. It predicts the formation of H₂O₂, ketene, methylhydroperoxide, ethylhydroperoxide, and pentylhydroperoxides well, but it shows considerable deviations when simulating unsaturated hydroperoxides. Also, Tran et al. [63] tested the model from Bugler et al. [60] in their study. They performed an experimental JSR speciation data for the oxidation of *n*pentane/'air' mixture, and as a mixture with di-ethyl ether at stoichiometric fuels ratio, at temperatures of 400 – 1100K, and pressures ranging from 2.5 up to 10 bar. 36 species were identified and quantified for *n*-pentane oxidation at 5 and 10 bar. The simulation results showed a very good agreement with the experiments.

Bourgalais et al. [64] coupled a JSR with advanced photoionization MS based upon a double imaging PhotoElectron PhotoIon COincidence (i²PEPICO) scheme for the first time to investigate the low-temperature oxidation of *n*-pentane. This technique supports isomer identification and is an efficient diagnostic tool for complex chemical gas-phase combustion analysis. Interestingly, they found that this technique is more sensitive to ketones than gas chromatography (GC), which implies that a revision is required for the existing models. A continuation of this study by Battin-Leclerc et al. [65] has validated the predictions of the existing models about 4-hydroperoxypentan-2-one being the dominant KHP produced. New information on the first steps of the fragmentation pathways of C₅ ketohydroperoxides (KHP) is also provided by this study, thus improving the quantification of the KHP mole fractions.

Belhadj et al. [50] performed an experimental and kinetic modeling study of *n*-pentane oxidation at 10 atm to detect complex low-temperature products. They used GC, Fourier-transform infrared spectrometry (FTIR), and electron impact ionization-quadrupole mass spectrometry (EI-qMS) to analyze oxidation products in the gas phase, and they also dissolved gaseous products in acetonitrile for characterization using flow injection analysis (FIA), high-pressure and ultra-high-pressure liquid chromatography (HPLC and UHPLC) coupled to atmospheric pressure chemical ionization (APCI) and Q-Exactive®-Orbitrap high resolution mass spectrometry (HRMS). This enabled them to detect lower and higher mass oxygenated molecules, among many, 15 molecules were reported for the first time. They also developed a mechanism but the simulation of their results showed discrepancies with the experiments.

Liu et al. [66] used two JSRs, the first is coupled with synchrotron-based vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS), and the other with FTIR/GC/LC-HRMS to study the low-temperature oxidation of *n*-pentane. Numerous intermediate species were identified including $C_5H_{10}O_3$ (KHPs), $C_5H_{10}O$ (cyclic ether), C_5H_{10} (pentene isomers), CH₃CHO (acetaldehyde), C₂H₅CHO (propanal), CH₃COCH₃ (acetone), C₂H₅COCH₃ (2-butanone), C₁–C₃ acids. These results were used, in addition to the available literature, to develop an accurate kinetic model by updating the rate constants of hydroperoxide decomposition, including pressure-dependent rate constants of key reaction classes, and by adding more detailed sub-mechanisms for important intermediate species such as C₅ cyclic ethers and C₅ KHPs. The updated model is validated

against the measurements from their work and experimental data available from the literature, including JSR species data and IDT data from both RCMs and STs.

Amiri et al. [67] employed automated mechanism generation tools to construct a detailed chemical kinetic model for the combustion of *n*-pentane as a step toward the generation of compact kinetic models for larger alkanes. The model was generated and tested against data from the literature across a range of temperatures 650 – 1350 K and equivalence ratios 0.5,1 and 2 at pressures of 1 and 10 atm. They state that the final version of the model predicts IDTs as accurately as the best manually constructed mechanisms while remaining much more compact. And it also predicts flame speeds to within 10% deviation of published experimental results.

2.3.1.2 Alkenes

Alkenes, produced through the cracking of heavier fractions during the refining of crude oil into gasoline, are found in transportation fuels, constituting as high as 15-20% of the composition in gasoline [69]. Alkenes commonly found in gasoline include isomers ranging from C₅ to C₈. The shorter the chain is, the higher the knock resistance compared to their saturated analogue [70]. 1-pentene is included in gasoline to 1% with a research octane number of 90.9 [71], so it has been adopted as representative alkene component in gasoline surrogate models. Furthermore, 1-pentene holds significance as a crucial intermediate in the oxidation and pyrolysis of *n*-pentane and of larger alkanes and alcohols, playing a pivotal role in fuel consumption under combustion conditions [72].

In the following table (Table 2) we present the low temperature studies performed on 1pentene, followed by a brief description on relevant studies.

Author	Year	Conditions	Reactor/Approach
Hughes et al [73]	1973	T = 280 – 330°C	Pyrex vessel inside an
			electric furnace
Baldwin et al [74]	1980	T = 480 °C	Aged boric-acid-coated
			vessel
Prabhu et al [75]	1996	T = 600 – 800 K, p = 6	Plug flow reactor
		atm, $\Phi = 0.4$	
Ribaucour et al [76]	1998	$T_c = 600 - 900$ K, $p_c = 6$	RCM
Minetti et al [77]	1999	-9 bar, $\Phi = 1$	
Touchard et al [71]	2005		<u>Mechanism</u>
			<u>development</u>
Kikui et al [78]	2016	T = 300 – 1300 K, Φ = 1,	Micro flow reactor
		flow velocity <i>u</i> = 2 cm/s	

Table 2 - Summary of the studies found in literature on 1-pentene at the low-temperature range of combustion.

Cheng et al [79]	2017	T = 353 – 433 K, p = 1 –	Constant volume
		4 atm, Φ = 0.7- 1.6	combustion bomb
Dong et al [80]	2021	$T_c = 600 - 1300$ K, $p_c =$	RCM, ST & JSR
		$15 \& 30 atm, \Phi = 0.5, 1$	
		& 2, τ = 2 s	
Zhou et al [69]	2022		<u>A review on Alkenes</u>
Zhisong et al [81]	2023	T = 500 – 1000 K, p = 1	JSR
		atm, τ = 2 s	

The first systematic study on the low temperature oxidation of pentenes was conducted by Hughes and Prodhan [73] using a pyrex vessel inside an electric furnace. Among the three different isomers of pentene, 1-pentene showed the highest reactivity, which is still less than that of *n*-pentane. A later study by Baldwin et al. [74] aimed at analyzing the products of 1-pentene addition to a reacting mixture of H_2/O_2 at 480°C. The product analysis suggested that H atom adds to 1-pentene in the ratio of 0.65 ± 0.2 for k_{non-} terminal/kterminal. However, a study by Prabhu et al. [75] revealed that hydrogen abstraction reactions leading to allyl radicals are more important than radical addition to the double bond.

Ribaucour and Minetti et al. [76], [77] conducted two consecutive studies on the lowtemperature oxidation characteristics of *n*-pentane and 1-pentene for a direct comparison. Both fuels exhibit a negative temperature coefficient region, although it is less pronounced in the case of 1-pentene, which also demonstrates lower reactivity compared to *n*-pentane. A kinetic model was developed for the low-temperature range for both fuels to scrutinize the differences in the chemistry involved. The distinctive behavior is attributed to the presence of a carbon-carbon double bond in 1-pentene, enabling HOO and OH addition. Additionally, it enables allylic hydrogen abstraction and internal isomerization on allylic sites, thus stabilization by resonance. The lower reactivity of 1pentene, in comparison to *n*-pentane, is suggested to result from competition between somewhat restricted isomerization channels and the addition of radicals to the double bond. These experiments, along with the experiments from Prabhu et al. [75] were used by Touchard et al. [71] to build a mechanism. New kinetic rules have been implemented in the EXGAS system (described in [82], [83]) to generate a kinetic model for 1-pentene. The findings indicate satisfactory agreement between simulated and experimental data concerning autoignition delays and product distribution. The study confirms the notable influence of the addition reaction of hydroxyl radicals to the double bond and the specific reactivity of the allylic radical.

Kikui et al. [78] studied a 1-pentene flame using a micro-flow reactor with a controlled temperature profile to investigate its combustion characteristics. The results show that reactions with H, Ö and OH radicals consume alkenes. The H-atom addition on the double bond is a unique reaction compared to alkanes and consumes a significant amount of the fuel. And the H-atom abstraction reaction with OH, which is important in alkane oxidation, is also important in alkene combustion.

The laminar flame speed of pentene isomers and *n*-pentane were studied by Cheng et al. [79] at initial temperatures ranging from 353 to 433 K using a constant volume combustion bomb. The findings reveal that 1-pentene exhibits the highest flame speed. The kinetic model on pentane isomers by Bugler et al. [45] was optimized and used. The analysis indicates that the lower adiabatic flame temperature of *n*-pentane primarily accounts for its slower laminar flame speed compared to that of 1-pentene.

A comprehensive study was conducted by Dong et al. [80] on 1-pentene and 2-pentene, including IDTs measurements using an RCM and a high-pressure shock tube (HPST), species profiles measurements through a JSR, and CO time-histories via the HPST to validate the model from Bugler [45] with their incorporated pentene sub-mechanism. The newly developed chemical kinetic model captures the autoignition behavior of both 1- and 2-pentene across various temperatures and pressures. Flux and sensitivity analyses indicate that, at low temperatures, hydroxyl radicals add on the double bond, leading to subsequent addition to molecular oxygen, forming hydroxy-alkylperoxy radicals. These radicals can proceed through the Waddington mechanism or alternate internal H-atom isomerization reactions in a chain-branching mechanism akin to alkanes. This chain-branching reaction pathway is pivotal for the high fuel reactivity of 1-pentene compared to 2-pentene at low temperatures.

A review on alkenes, gathered by Zhou et al. [69] highlighted the progress made towards understanding the detailed chemistry for the low-, intermediate- and high-temperature alkene oxidation. In summary, reactions with important radicals like OH, HOO, H, O etc., will occur in different ways over different temperature ranges. For example, at lower temperatures (600 – 850 K) OH adds to or abstract H from alkenes, at intermediate temperatures (850 – 1200 K) recombination reactions take place between the allylic radicals themselves or with other radicals like HOO and CH₃, and at high temperatures (> 1200 K) additions of H and Ö to the double bond are important to open the double bond. Additionally, the presence of easily formed unreactive resonance-stabilized allylic radicals hinders the reactivity of unsaturated hydrocarbons.

2.3.1.3 Ketones

Ketones emerge as promising transportation biofuels, producible through fungal conversion of lignocellulosic biomass [84], [85], [86], or via synthesis using acetone–*n*-butanol–ethanol (ABE) fermentation [87], [88], [89]. Their superior energy density [90], high knock resistance due to low autoignition tendency [91], and reduced soot emissions [92], [93] compared to alkanes make ketones favorable for applications as transportation fuels or fuel additives. Additionally, ketones are abundant intermediate species in the low-temperature oxidation of alkanes [44], [94]. Therefore, studies on the combustion kinetics of ketones contribute to a deeper understanding of the intricate pathways involved in low-temperature oxidation reactions.

In this thesis, 3-pentanone is studied, and a summary of the studies at the low temperature region is presented in the following table (Table 3), and a brief description of each study follows.

Author	Year	Conditions	Reactor/Approach
Scheer et al [95]	2013	T = 550 – 650 K, p = 8	MPMS
		torr	
Fenard et al [96]	2020	T _c = 650 – 950 K, p _c =	RCM
		$20 \& 40 \text{ bar, } \Phi = 1$	
		T = 800 – 1050 K, p =	Laminar flow reactor
		$0.97 \text{ bar}, \Phi = 0.8$	
Kang et al [97]	2021	T_c = 890 – 1050 K, p_c =	RCM
		$10 \& 20 \text{ bar, } \Phi = 0.5 \& 1$	
Kang et al [98]	2023	$T_c = 640 - 820$ K, $p_c =$	RCM
		15 & 25 bar, Φ = 1	
		T = 600 – 1000 K, p =	JSR
		93.3 kPa, Φ = 0.5, τ = 2	
		S	

Table 3 - Summary of the studies found in literature on 3-pentanone at the low-temperature range of combustion.

The first low-temperature study was conducted by Scheer et al. [95], which investigated the Cl-initiated oxidation of 3-pentanone and its deuterated derivatives using multiplexed

photoionization mass spectrometry (MPMS) with tunable synchrotron ionizing radiation. The study highlights that the secondary radical generated through H-abstraction reactions is resonance-stabilized, resulting in a shallow well for O₂ addition (24 kcal.mol⁻ ¹) as shown in Fig 12. This characteristic makes the radical less reactive towards addition to O₂ at the temperatures within the conditions of this study (550–650 K).



Fig 12 - Potential energy surface for the reaction of the secondary diethyl ketone radical $R_s + O_2$. Energies at 0 K are at the CBS-QB3 level. [95].

Calculated potential energy surfaces indicate barriers to the formation of oxidation products of the secondary radical lying above the radical + O₂ entrance channel. Conversely, the most energetically favorable pathway (the black pathway) for the decomposition of the primary radical involves resonance-stabilized QOOH, leading to the observed cyclic ether product (2-methyltetrahydrofuran-3-one).

Fenard et al. [96] investigated the reactivity of 2- and 3-pentanone in an RCM by measuring IDTs. Additionally, they analyzed mole fraction profiles for the oxidation of these pentanones, including identification of intermediate species and products, using a laminar flow reactor coupled to a mass spectrometer. Both fuels exhibited a negative temperature coefficient (NTC). The main stable intermediates observed during the oxidation of 3-pentanone included methane, formaldehyde, methyl ketene, ethylene, and ethyl vinyl ketone. They also formulated a mechanism including low-temperature combustion reactions, and the model's accuracy was confirmed through validation against the reported experimental results. Thermochemical data for 2- and 3-pentanone, fuel radicals, and related alkylperoxyl radicals were computed using the B3LYP – G4 level of theory. The study underscored the significance of considering reactions like pentanonyl

+ $R\dot{O}_2$ = oxypentanone + $R\dot{O}$ to precisely predicted IDTs for pentanone/air mixtures, especially when compared to the equivalent alkane *n*-pentane. Furthermore, the carbonyl group was identified as a factor attenuating low-temperature branching reactions due to the slow addition of resonance-stabilized radicals on O_2 .

Kang et al. conducted two consecutive studies also focusing on the oxidation of 2- and 3pentanone. In their initial investigation [97], IDTs were measured using an RCM under fuel-lean and stoichiometric conditions, with temperature ranging from 890 to 1050 K at pressures $p_c = 10 \& 20$ bar. Mole fraction time histories of major species were obtained through a fast sampling system. A kinetic model was developed, demonstrating satisfactory predictive performance and enabling the interpretation of speciation behaviors related to the structural features of both ketones. While no NTC was observed, a notable amount of acetaldehyde indicated potential low-temperature reactivity. In their subsequent study [98], Kang et al. delved into the low-temperature range and observed NTC behavior at conditions: $T_c = 640 - 820$ K, $p_c = 15$ and 25 bar, and stoichiometric fuel ratio. They added to their previous model a new sub-mechanism for low-temperature chemistry, which exhibited satisfactory predictive performance. Compared to the model proposed by Fenard et al. [96], Kang et al.'s developed model demonstrated better prediction of species concentrations under two-stage ignition conditions. However, discrepancies persisted between experimental and simulated concentration profiles of CO₂, CH₄, CH3CHO, and C2H5CHO.

2.3.1.4 Alcohols

In the introduction to his 1931 book, "The High-Speed Internal Combustion Engine," Ricardo [99] endorsed the utilization of alcohol fuels. Ricardo subsequently presented a series of experimental findings that examined various hydrocarbon fuels, including a detailed exploration of alcohol fuels in both spark-ignition (SI) and compression ignition (CI) engines. His groundbreaking early investigations into pre-ignition, which ultimately contributed to the establishment of fuel octane ratings, revealed that ethanol facilitated operation at higher compression ratios owing to its diminished pre-ignition tendency. Ricardo also observed that alcohol fuels exhibited higher latent heats of vaporization and lower flame temperatures compared to their petroleum-based counterparts. He suggested that these distinctive properties could be leveraged to amplify power output and decrease thermal losses. Nevertheless, alcohols characterized by high molecular weights, containing up to five or even more carbon atoms, are deemed advantageous for practical applications owing to their elevated energy densities and low vapor pressure which are closer to those of conventional diesel fuels [100].

In this thesis, 3-pentanol is investigated, and below is a brief history on the few studies performed on this fuel, preceded by a summary in the table below (Table 4)

Table 4 -Summary of the studies found in literature on 3-pentanol at the low-temperature range of combustion.

Author	Year	Conditions	Reactor/Approach
Wallington et al [101]	1988	T = 298 K, p = 0.0333 – 0.0667 bar	Flash photolysis
			resonance fluorescence
Kohler et al [102]	2015	Flow rate = 4.55 slm (standard liter	EI-MBMS
		per min), Φ = 1.5, v = 131 cm/s	
Carbonnier et al [103]	2019	T = 730 – 1180 K, Φ = 0.35, 0.5, 1, 2	JSR
		& 4, τ = 0.7 s	
		$T_c = 1000 - 1470$ K, $p_c = 20 \& 40$	ST
		bar, Φ = 0.5,1 &2	
Feng et al [104]	2021	T _c = 920 – 1450 K, p _c = 6, 10 & 20	ST
		bar, Φ = 0.5,1 &1.5	Ab initio study
Chatterjee et al [105]	2023	T _c = 650 – 1300 K, p _c = 15 & 30 bar,	RCM & ST
		Φ = 0.5, 1 &2	

Employing the flash photolysis resonance fluorescence technique, Wallington et al. [101] determined the absolute rate constants at 298 K for gas-phase reactions involving hydroxyl radicals and various aliphatic alcohols, including 3-pentanol. The obtained result for the reaction involving 3-pentanol was found to be $12.1\pm0.7 \times 10^{-12}$.cm³.molecule⁻¹.s⁻¹.

Kohler et al. [102] presented the first comparative flame study focusing on 1-, 2-, and 3pentanol, incorporating both experimental speciation data and kinetic modeling. The investigation into alcohol combustion chemistry is conducted within pentanol-doped hydrogen flames. Speciation is accomplished through electron ionization molecular-beam mass spectrometry (EI-MBMS) with subsequent quantification, leading to new quantitative species profiles encompassing up to 27 species, including the pentanonyl radicals. The constructed model is shown to accurately replicate the overall flame structure (i.e. the major species profiles) in the doped hydrogen flames, and provides satisfactory predictions for crucial intermediate species across all three pentanols. The detailed speciation information is utilized to scrutinize significant reaction pathways, revealing that the primary decomposition pathway for all three pentanols involves the abstraction of a hydrogen atom in the α -position. Subsequent decomposition channels are deemed reasonable, with elevated concentrations of pentanal observed for the 1-pentanol fuel, 2-pentanone for the 2-pentanol fuel, and 3-pentanone for the 3-pentanol fuel.

Carbonnier et al. [103] conducted the first exploration into the high-pressure oxidation of 3-pentanol utilizing a JSR and a ST. Mole fraction profiles of reactants, final products, and stable intermediates were identified and measured through GC-MS, and FTIR spectrometry, employing sonic probe sampling at five equivalence ratios. Additionally, IDTs were measured using the ST at elevated temperatures. Notably, 3-pentanol did not exhibit any cool flame behavior under the investigated conditions, and it was observed to generate various aldehydes, ketones, and the olefin 2-pentene as one of its C₅ intermediates. To represent the data effectively, a sub-mechanism for 3-pentanol was developed, demonstrating globally good performance. However, some discrepancies were noted in the species profiles. Accordingly, Feng et al. [104] calculated the highpressure limit rate constants for H-abstraction reaction by H, CH₃, HOO, and OH radicals over a broad range of temperature (400-2000 K) with the phase-space theory and conventional transition state theory. The Carbonnier model [103] was subsequently updated with these calculated results, followed by a modification based on the computed results of 3-pentanol + HOO to obtain the revised model. Validation of the revised model against measurements from ST and JSR experiments, both from the same study by Carbonnier [103] and this study, demonstrated its optimal performance.

Chatterjee et al. [105] conducted the first low-temperature oxidation study of the secondary alcohols, 2- and 3-pentanol, using an RCM. Based on the analogy to 1-pentanol, they introduced detailed kinetic models for the low-temperature oxidation of 2- and 3-pentanol, marking the first development of such models for these compounds. The proposed kinetic models for all three pentanol isomers were validated against data obtained from HPST and RCM experiments conducted in their study, as well as relevant data from Carbonnier's study [103]. The proposed model exhibited a fair agreement with experimental results across a broad spectrum of operating conditions.

It is important to emphasize two comprehensive reviews on the combustion chemistry of alcohols, encompassing diverse studies in the field. The first review, by Sarathy et al.

[106], serves as an initial reference source and guide for combustion experiments on alcohols. It primarily focuses on models of alcohol combustion, particularly for smallchain alcohols, up until the year 2014. The second review, conducted by Cai et al. [100] in 2021, extends the former to longer-chain alcohols. This review aims to enhance the understanding of the fundamental combustion characteristics of longer-chain alcohols and their practical application performance in engines. Together, these reviews offer a valuable compilation of knowledge on alcohol combustion chemistry across different chain lengths.

2.3.2 Hydrogen

2.3.2.1 Properties

As discussed earlier in the introduction of this thesis, the significance of hydrogen as a fuel for decarbonizing the transportation sector has been emphasized. So, few of hydrogen chemical and physical properties are presented below, in comparison to other fuels:

Hydrogen is a colorless, odorless, tasteless, non-toxic, and non-poisonous gas. While it is non-corrosive, it has the potential to cause embrittlement in certain metals. As the lightest and smallest element, hydrogen exists as a gas at atmospheric conditions and is approximately 57 times lighter than gasoline vapor and 14 times lighter than air (see Fig 13). Due to its small molecular size and low viscosity, hydrogen is highly prone to leakage [107]. In confined areas, leaked hydrogen can accumulate to flammable levels. The auto-ignition temperature, the minimum temperature at which a substance can ignite without an external flame or spark, is similar for both hydrogen and natural gas, and significantly higher than that of gasoline vapor as presented in Fig 13.



Fig 13 - Left: Relative vapor density to air, data from [108]. Right: Auto-ignition temperature at ambient pressure, data from [109].

Hydrogen has an exceptionally wide flammability range, between 4.7% and 75% in air, compared to other fuels, Fig 14. At the ideal combustion condition, with a 29% hydrogento-air volume ratio, the energy needed to ignite hydrogen is much lower than that for most other fuels—meaning even a small spark produced from the friction of clothes can trigger combustion (see Fig 14). If a large hydrogen cloud encounters an ignition source, it is likely that the flame will flash back to the hydrogen source [107].



Fig 14 – left: Flammability range in air, data from [109]. Right: Minimum ignition energy at stoichiometric H₂/O₂ conditions, data from [108].

In open spaces without confinement, flames will propagate through a flammable hydrogen-air cloud at speeds of several meters per second, with even faster propagation if the cloud is above ambient temperature. This leads to a rapid release of heat but generates little overpressure, and the combustion product is primarily steam. Hydrogen combustion is notably faster than that of most other fuels as shown in Fig 15. In fact, hydrogen's laminar flame speed at stoichiometric conditions is nearly five times higher than that of gasoline, which can enhance engine efficiency [109]. However, this high flame speed, combined with hydrogen's low ignition energy, increases the likelihood of engine

knock. When hydrogen ignites in a confined space, the resulting combustion can produce extremely high pressures capable of rupturing equipment, demolishing structures, and scattering shrapnel. Therefore, placing hydrogen equipment and piping outdoors provides a significant safety advantage by reducing the risk of overpressure explosions in confined environments.



Fig 15 – Laminar burning velocity of different fuels at stoichiometric fuel conditions. Data from [109].

2.3.2.2 Kinetics

Hydrogen is the simplest fuel capable of undergoing oxidation, and the 'H₂ + O₂' reaction is the most extensively studied combustion system. The key radicals involved— \dot{H} , $\dot{O}H$, \ddot{O} and HO \dot{O} — play a central role in the progression of hydrogen oxidation. Understanding the elementary reactions of these species forms the foundation for interpreting chainpropagation and branching processes, not only in hydrogen combustion but also in the oxidation of all carbon-hydrogen-oxygen (C-H-O) based fuels. But this thesis will not delve into the specific details of the combustion mechanism of hydrogen, but rather focus on the competition between reactions A and B in Fig 16 [110].

In the scheme shown in the figure, the competition between chain-branching and nonbranching reactions is emphasized based on varying temperature and pressure conditions. At temperatures above the indicated line, the formation of OH and O radicals dominates, particularly at lower pressures (below 100 kPa) and temperatures under 1000 K. However, when pressures exceed 1 MPa, a higher temperature—greater than 1400 K—is needed to promote these chain-branching reactions [110]. This balance between branching and non-branching pathways significantly impacts the overall reactivity in hydrogen combustion under different conditions.



Fig 16 – Pressure and temperature at which the rate of the reaction $\dot{H} + O_2 \rightarrow \dot{O}H + \ddot{O}$ is equal to that of $H + O_2 + M$. The third body efficiency of M is taken to be that of air. Scheme to the left adapted from [110].

At temperatures below the line in Fig 16, the HOO radicals formed react as follows:

 $RH + HO\dot{O} \rightarrow \dot{R} + H_2O_2$

The H₂O₂ is stable at this temperature range, but above 1000 K, it decomposes as follows:

 $H_2O_2 + M \rightarrow 2\dot{O}H + M$, which in turn triggers the ignition [110].

2.3.3 Hydrogen blends with fuels

Indeed, studies indicate that the inclusion of hydrogen in fuel blends reduces the carbonto-hydrogen ratio, promoting particle oxidation. This results in higher concentrations of \dot{H} and $\dot{O}H$ radicals, and under specific operating conditions, elevated in-cylinder temperatures [111]. The addition of hydrogen to a spark ignition engine extends the leanoperational limits, and allows an SI engine to operate at leaner conditions with reduced NO_x emissions [112], [113], [114], [115]. In light of these considerations, and to the different hydrogen properties previously mentioned in section 2.3.2.1, our focus is on investigating hydrogen as a blend with the previously introduced C₅ chain molecules, to investigate its effects and comprehend the chemistry unfolding in the low-temperature range of combustion.

Many studies in the existing literature focus on investigating the ignition properties of methane, or methane blends with higher carbon chain fuels, when mixed with hydrogen. However, there is a comparatively limited number of studies that explore the ignition characteristics of hydrogen blends with longer carbon chains.

Authors	Fuel	Year	Conditions	Reactor/Approach
Sher et al [116]	<i>n</i> -Butane	1992	T = 270 - 410 K, atmospheric pressure, $\Phi = 0.52$ - 1.2	Flat flame burner
Sung et al [117]	Butane isomers	2001		Computational study
Cheng et al [118]	C ₁ –C ₄ <i>n</i> -alkanes	2014		Computational study
An et al [119]	<i>n</i> -Heptane, Iso- octane	2015	T _c = 735 – 847 K, p _c = 27.6 bar, Φ = 0.3 – 0.6	RCM
Lee et al [120]	methyl- butanoate/ <i>n-</i> heptane mixture	2016	$T_c = 716 - 858$ K, p _c = 15 bar, Φ = 0.5	RCM
Comandini et al [111]	n-Heptane	2019	$T_{c} = 730 - 1200 \text{ K},$ $p_{c} = 20 \text{ bar}, \Phi =$ 0.832, 1, & 1.248 T = 294 K, p = 1 $bar, \Phi = 0.8 \& 1.35$	ST Spherical bomb
Lee et al [121]	<i>n</i> -Butane, <i>n</i> - Heptane	2020	T _c = 722 – 987 K, p _c = 20 & 25 bar, Φ = 0.5, 1, & 1.5	RCM

Table 5 - Summary of the studies found in literature on 'longer carbon chain fuel'/ H_2 blends at low to intermediate temperatures

An et al. [119] conducted measurements of ignition delay using an RCM for *n*-heptane/air and iso-octane/air mixtures across temperatures ranging from 735 K to 850 K at a fixed compressed pressure of 27.6 bar. The equivalence ratios were varied between 0.3 and 0.6. The study aimed to investigate the effects of hydrogen concentration based on temperature and equivalence ratio. For *n*-heptane, as the H₂ energy ratio increased, the first-stage ignition time exhibited a more pronounced increase than the second-stage ignition delay. On the other hand, with iso-octane, both delays showed an increase, but the addition of H₂ had a more significant effect on the second stage. The study explained that in the case of *n*-heptane, the decrease in the OH mole fraction in the first-stage region as the compressed temperature decreased was attributed to the competition between chain-branching and HOO formation reactions. The depletion of radical pool due to H₂ + OH decreases the rate of RH + OH, and the FSIDT is more sensitive to OH concentration than the total IDT. Conversely, with iso-octane, the first stage did not change significantly with the H₂ concentration. Due to the identical reaction mechanisms during the first-stage reaction with fuels, the second stage exhibited a stronger dependence on the H₂ concentration.

Lee et al. [120] investigated the impact of hydrogen addition in different proportions (0, 25, 50, and 75%) within a methyl-butanoate/*n*-heptane mixture. The mixture exhibited two-stage ignition and NTC behavior. The experimental results consistently showed an increase of the ignition delay with hydrogen addition. The numerical analysis conducted using a developed model from this study matched well the experimental findings. Sensitivity and rate of production analyses were performed to elucidate the change in ignition delay. Most of the added H₂ molecules were found to react with $\dot{O}H$ radicals in the $\dot{O}H + H_2 = \dot{H} + H_2O$ reaction, resulting in the production of H atoms. These H atoms then participate in the H + O₂(+M) = HO $\dot{O}(+M)$ reaction, generating HO \dot{O} radicals. As a result, the overall reactivity was reduced by hydrogen addition, primarily due to the change in the amounts of $\dot{O}H$ and HO \dot{O} radicals.

The impact of hydrogen enrichment on the combustion properties of *n*-heptane/air has been investigated by Comandini et al. [111] through a combination of experimental and numerical approaches using kinetic models available in the literature [122], [123]. Laminar flame speed measurements were conducted for *n*-heptane/air, (75% *n*-heptane + 25% hydrogen)/air, and (50% *n*-heptane + 50% hydrogen)/air mixtures. The results revealed that the flame speed increased by approximately 3% and 10% with 25% and 50% hydrogen enrichment of *n*-heptane, respectively. Experiments on the IDTs of fuel/air mixtures containing varying levels of hydrogen enrichment (from 0% to 75%) were also conducted. It was observed that only for significant hydrogen enrichment did the IDT become longer compared to the reference *n*-heptane/air case.

The influence of hydrogen addition on the laminar flame speed of *n*-alkanes was also studied for the hydrogen/*n*-butane blend by Sher and Ozdor [116] using a flat flame burner. They observed a significant increase in burning velocity, up to about 35%, even with a 5% hydrogen blending. In a computational study by Sung et al. [117], the laminar burning velocities of hydrogen added to butane isomers were investigated, noting that hydrogen blending had more pronounced effects for fuel mixtures deviating from stoichiometric conditions and that the addition of hydrogen to a fuel mixture can enhance the ignitability and flammability. Cheng et al. [118] numerically explored the laminar premixed combustion of hydrogen-enriched C₁–C₄*n*-alkanes based on a one-step reaction assumption, and the influence of hydrogen addition was explained considering kinetics, Lewis number, and adiabatic flame temperature.

Lee et al. [121] conducted a study to investigate the impact of hydrogen on *n*-butane at low temperatures using an RCM and the NUIG Aramco 2.0 mechanism [124], [125], [126], [127], [128] for kinetic modeling. The results obtained from both the experimental and numerical aspects of this study were found to be in good agreement with previous research. The study identified an NTC trend for *n*-butane, and it was observed that the ignition delay increased with the addition of hydrogen. This increase in ignition delay was attributed to both chemical and dilution effects. Sensitivity and reaction path analyses were performed at different temperatures (750 K, 830 K, and 910 K), and the same reasoning of Lee et al. [120] on the addition of H₂ to *n*-heptane was employed in this case as well.

2.3.4 Next-generation biofuel: Tetrahydropyran

Next-generation biofuels primarily originate from lignocellulose, non-food materials, algal biomass, and energy crops cultivated on marginal lands. These biofuels are considered sustainable and offer the potential to address concerns related to climate change and energy security [129]. One such biofuel is tetrahydropyran (THP), derived from lignocellulose and resembling cyclohexane with the substitution of a methylene group ($-CH_2-$) by an ether functional group (-O-) [130].

THP serves as the fundamental structure for various sugars and polysaccharides, including glucose, a common feedstock for biogenic fuels that encompasses multiple furan and THP-based isomers [131]. The pyrolysis of these sugars can generate biofuels and bio-derived industrial chemicals, many of which are substituted furans and pyrans [130], [132]. Apart from its applications in organic synthesis and as a solvent, recent research has highlighted the potential of tetrahydropyran as a promising fuel [133].

The studies on THP are scarce in literature, so in the following table (Table 6) we present a summary of all the work done on THP, followed by a brief elaboration on each study.

Author	Year	Conditions	Reactor/diagnostic
Dagaut et al [134]	1997	T = 800 – 1700 K, p = 2 – 10 atm, Φ =	JSR – ST
		0.5 – 2	
Labbe et al [135]	2013	p = 20 torr, Φ = 1.75	Flat flame + VUV – PI-
		-	MBMS
Tran et al [136]	2015	T = 913 – 1133 K, p = 170 kPa, τ =	Plug flow reactor
		0.5 & 0.2 s	Premixed flame burner
		P = 6.7 kPa, Φ = 1 & 1.3	

Table 6 - Summary of the studies found in literature on THP combustion.

		T _c = 1350 – 1613 K, p _c = 885 – 914	ST
		kPa, $\Phi = 0.5 \& 2$	
Rotavera et al [137]	2017	T = 500 – 700 K, p = 10 & 1520 Torr	MPIMS
Chen et al [138]	2018	T = 500 – 750 K, p = 20 torr	IR laser absorption –
			Herriot multipass gas
			cell
Telfah et al [139]	2018	Room temperature	Cavity ring-down
			spectra
Davis et al [140]	2019	T = 500, 600 & 700 K, p = 10 & 1520	PI-MPMS
		torr	
Zou et al [141]	2024	T = 450 – 900 K, p = atmospheric	JSR – SVUV-PIMS – GC
		pressure, $\Phi = 0.25 - 1$	
Hoblos et al [142]	2024	T = 480 – 1260 K, p = 10 atm, Φ =	JSR – GC – FTIR
		0.5, 1, 2 & 4	

Dagaut et al. [134] measured IDTs using a ST and species profiles in a JSR. Among the species produced, the conjugated alkenes were detected in trace levels, so they were not included in their developed mechanism. This mechanism was the first to be applicable across a pressure range of 2–10 atm and a temperature range of 800–1700 K. The sensitivity analyses and reaction path analyses conducted in their study suggested that the modeling of the oxidation of THP relies on the kinetics of THP reacting with OH, as well as on the kinetics of the oxidation of two major intermediates, formaldehyde, and ethylene.

THP combustion has been studied by Labbe et al. [135] in a low-pressure premixed flat flame at $\Phi = 1.75$ using VUV- PI-MBMS. Flame species with up to six heavy atoms have been detected, and their results show that under the low-pressure conditions, THP decomposition is dominated by H-abstraction, and the three resulting THP-yl radicals decompose primarily by β -scissions to two- and four-heavy-atom species that are generally converted by β -scission, abstraction, or oxidation. Tran et al. [136] studied the pyrolysis and high-temperature ignition and flame properties of tetrahydropyran. They also built a chemical kinetic model covering a broader parameter space in temperature, pressure, and fuel concentration than the one introduced beforehand by Dagaut et al. [134]. Their findings are consistent with the study of Labbe et al. [135], because the dominant pathways appear to be the H-abstraction reactions at the α -carbon at both pyrolysis and oxidation conditions, and the resultant radicals were presumed to decompose via β -scission through several channels.

Rotavera et al. [137] employed multiplexed photoionization mass spectrometry (MPIMS) to determine branching fractions of conjugate alkenes from \dot{R} + O₂ oxidation reactions for

THP. They concluded that chain-termination is more favourable at lower temperature and pressure in THP oxidation than in cyclohexane oxidation, this is due to coupled effects of the lower C-H bond energy on the α -carbon that leads to α -tetrahydropyranyl being the dominant initial radical, and the barrier to direct HOO formation on the α tetrahydropyranyl + O_2 surface being lower by approximately 5 kcal.mol⁻¹. With increasing temperature, however, competition from α -tetrahydropyranyl ring opening reduced the flux through \dot{R} + O₂ and subsequent product formation thereafter, an effect augmented by the fact that abstraction at the weakest C-H bond produces the initial radical most prone to ring opening. The study further extended its scope [138] to include the direct measurement of OH and HOO formation in the R+O2 reactions of tetrahydropyran and cyclohexane using IR laser absorption. The observed significant differences in HOO formation kinetics and OH formation yield for THP oxidation are attributed to contributions related to ring-opening pathways in the tetrahydropyranyl + O_2 system that compete with the typical \dot{R} + O_2 reaction scheme. The Davis et al. [140] study expands on Rotavera et al. [137] by quantifying branching fractions of intermediates formed via QOOH ring-opening reactions that diminish the overall production of KHP in tetrahydropyran oxidation. The results are contextualized by comparison to analogous reactions in cyclohexane oxidation, for which intermediates from such reactions were not detected. Three main pathways were confirmed via photoionization spectral analysis: (i) γ - QOOH \rightarrow pentanedial + OH, (ii) γ - QOOH \rightarrow vinyl formate + ethene + $\dot{O}H$, and (iii) γ - $\dot{Q}OOH \rightarrow 3$ -butenal + formaldehyde + $\dot{O}H$. The flux of QOOH radicals through unimolecular decomposition channels reduces the overall rate of the second-O₂-addition step and, by extension, diminishes KHP formation owing to the presence of the ether group.

Talfah et al. [139] produced THP-yl peroxy radicals in a reaction cell using CI-initiated oxidation THP and they detected these peroxy radicals using cavity ring down spectroscopy (CRDS) of their $\tilde{A} \leftarrow \tilde{X}$ electronic transitions, in addition to conducting quantum chemical calculations to determine Franck-Condon factors for vibronic transitions and indicated that ~80% of the peroxy radicals are conformers of α -tetrahydropyranylperoxy, the majority of which are axial, as illustrated in Fig 17.



Fig 17 – Axial α-tetrahydropyranylperoxy. [139].

The only two studies investigating the low-temperature combustion of THP are both recent and were conducted concurrently with the research presented in this thesis. Both studies utilized a JSR and identified similar species, while also developing a kinetic model that accounts for both high- and low-temperature chemistry. The model from Zou et al. [141] emphasizes the conformational effects of the heterocyclic ring, specifically incorporating distinct cis-00yQ00H and trans-00yQ00H conformers. Their mechanism includes analogies to cyclohexane and tetrahydrofuran, and for high-temperature chemistry, it adopts the Tran et al. mechanism. However, discrepancies between their simulated and experimental data at low temperatures suggest potential gaps in their mechanism. In contrast, the study by Hoblos et al. [142] developed a new sub-mechanism for THP, which demonstrated improved performance compared to the Tran et al. mechanism. For low-temperature chemistry, Hoblos et al. did not rely on cyclohexane analogies but rather used rate constants from calculated alkyl group values in the literature. Discrepancies between experimental and simulated data are observed, highlighting the need for advanced theoretical calculations to better understand the THP kinetic behavior.

2.3.5 E-fuel: Trimethoxy-methane (TMM)

Synthetic fuels from renewable sources are prospective replacements for conventional, crude oil-based fuels whose use is motivated by the need to reduce the global carbon footprint, as well as soot and particle emissions in the transportation sector [143]. Oxymethylene ethers (OMEs) are among the promising synthetic biofuels that have the potential to reduce CO₂ emissions. They are also known as polyoxymethylene dimethyl ethers (OME_n) with a general chemical structure of CH₃O[-CH₂O]_n-CH₃ [144], [145]. One distinctive feature of OMEs is the absence of direct carbon-carbon bonds, resulting in reduced soot formation during combustion [146], [147]. Holzer et al. [148] tested pure OME and various HVO-OME blends (hydrogenated vegetable oil – OME) as alternative fuels for diesel engines. Their primary objective was to characterize each fuel mixture with respect to its emission reduction potential. Their results for pure OME₃₋₅ show that

no soot emission occur, providing that no soot-forming blend components are present. Throughout the entire parameter range investigated, soot emissions are either nonexistent or below the detection limit of the measurement technology, even at the highest EGR (exhaust gas recirculation) rates applied during the investigation as shown in Fig 18.



Fig 18 - Specific soot emissions depending on the EGR rate adapted from [148].

OMEs offer significant advantages, allowing for controlled properties through chain length variations, influencing characteristics such as boiling point, cetane number, and viscosity [149]. Their high cetane number positions OMEs as promising additives for compression-ignition engines (CI-engines) [150]. Furthermore, the inclusion of OMEs in diesel fuels enhances lubricity, contributing to reduced engine wear and increased overall engine efficiency [151].

The catalytic synthesis process for OMEs yields various compounds, with linear forms such as OME₁ to OME₅, even longer that they can transition to solids, and branched structures exemplified by trimethoxymethane (TMM).

A plethora of studies on Oxymethylene Ethers (OMEs) is available in the literature, and a comprehensive review conducted by Fenard and Vanhove [150] synthesizes the key findings up until 2021. In their mini-review, they provide a succinct overview of various OMEs:

 Methylal (OME_n, n = 1) stands out as the most extensively studied after DME among e-fuels. Experimental investigations cover a wide range of parameters, including reactivity, laminar burning velocity, and mole fraction profiles of combustion intermediates. The symmetrical structure of methylal facilitated early kinetic modeling, and recent advancements in *ab initio* calculations have contributed to high-level theoretical work. Detailed kinetic models span conditions from pyrolysis to oxidation across low-to-high-temperature ranges, encompassing roaming reactions and low-temperature chemistry in this fuel class. However, discrepancies persist in reaction pathways, particularly at elevated temperatures, and the branching between the formation of potential fuel radicals remains incompletely understood, introducing variations in reactivity and intermediates mole fraction profiles.

- 2) While higher-order OME_n (n = 2–4) have been examined experimentally, less focus has been given compared to OME_1 . OME_3 , due to its diesel-compatible properties, has garnered specific attention in dedicated studies. Kinetic models for OME_n (n > 1) found in the literature are developed by applying fuel-specific reactions based on analogies with OME_1 . The reactivity of OME_{2-4} is slightly higher than that of OME_1 , and these trends are reasonably captured by models [152], [153], [154]. However, the development of dedicated *ab initio* studies for long-chain OME_n is crucial to confirm the applicability of reaction class methods in kinetic model development.
- 3) Experimental studies have focused on the cyclic OME_n 1,3,5-trioxane, primarily because it acts as a formaldehyde source. Consistent findings from experimental kinetic modeling studies indicate that this compound predominantly undergoes thermal decomposition, resulting in the production of three molecules of formaldehyde, with minimal to no influence from H atom abstraction reactions.
- 4) A modeling study for OME_n [155] focuses on the five-membered cycle 1,3dioxolane. The model, developed with analogies to OME₁ and diethyl ether, incorporates a low-temperature chemistry sub-mechanism. Calculations of betascission kinetic parameters for dioxolanyl radicals, crucial in the oxidation of 1,3dioxolane, were included. While the model provides insights into the kinetics of 1,3-dioxolane, additional kinetic modeling work is warranted for a comprehensive understanding.

Exploring the combustion kinetics of branched or ramified OME_n is of particular interest, as these compounds can be derived from biomass and various enzymatic or catalytic processes. In this thesis, the low-temperature oxidation of TMM is investigated. In Table

7 we provide a summary of the studies performed on TMM, followed by a brief description for each.

Author	Year	Conditions	Reactor/diagnostic
Platz et al [156]	1999	T = 296 K	Pulse radiolysis
Potter et al [157]	2018	T = 298 – 744 K	Laser induced
			fluorescence
Du et al [158]	2019		Ab initio study
Döntgen et al [159]	2022	T _c = 1413 – 1783 K, p _c =	ST – GC/MS – laser-
		52, 98 & 182 mbar	schlieren densitometry
Döntgen et al [127]	2023	T _c = 734 – 1112 K, p _c =	ST
		20& 40 bar, Φ = 0.5, 1 &	
		2	

Table 7 - Summary of the studies found in literature on TMM combustion.

The study of Platz et al. [156] aimed to focus on the atmospheric chemistry of trimethoxymethane. They measured the kinetics of reactions resulting from the atmospheric degradation of (CH₃O)₃CH. This degradation process is initiated by the abstraction of H-atom via OH radicals, which generate alkyl radicals as presented by reaction 1 and 2. These alkyl radicals further react with O₂ to form alkyl peroxy radicals as presented by reactions 3 and 4.

$$(CH_{3}O)_{3}CH + \dot{O}H \rightarrow (CH_{3}O)_{2}CHO\dot{C}H_{2} + H_{2}O \qquad (1)$$

$$(CH_{3}O)_{3}CH + \dot{O}H \rightarrow (CH_{3}O)_{3}\dot{C} + H_{2}O \qquad (2)$$

$$(CH_{3}O)_{2}CHO\dot{C}H_{2} + O_{2} + M \rightarrow (CH_{3}O)_{2}CHOCH_{2}\dot{O}_{2} + M \qquad (3)$$

$$(CH_{3}O)_{3}\dot{C} + O_{2} + M \rightarrow (CH_{3}O)_{3}C\dot{O}_{2} + M \qquad (4)$$

Potter et al. [157] also determined rate coefficients for H-atom abstraction reactions by $\dot{O}H$ but under conditions relevant to low-temperature combustion. This was done by measuring the concentration of \dot{H} radicals using laser-induced fluorescence diagnostics. The authors offered a total rate coefficient for TMM + $\dot{O}H$ for the 298 to 744 K temperature range. Only shortly after, the TMM + $\dot{O}H$ rate coefficient measurements were complemented with theoretically derived rate coefficients by Du and Zhang [158]. They employed the QCISD(T)//M06-2X-GD3 level of theory to determine the rate coefficients of TMM + $\dot{O}H$ and TMM radicals + O₂. They found that the TMM + $\dot{O}H$ rate coefficients agreed well with experimental data obtained by Potter et al. [157].

Döntgen et al. [159] recently investigated the pyrolysis of trimethoxymethane (TMM) using a combination of theoretical calculations and ST experiments. They employed

techniques such as laser-schlieren densitometry, GC-MS, and CO laser absorption. According to the authors, TMM predominantly undergoes unimolecular decomposition through H-atom migration, known as a roaming reaction. This process results in the formation of methanol and a singlet diradical (a carbene) as shown in Fig 19.



Fig 19 - Reaction fluxes of TMM oxidation predicted with the present TMM model for T = 800 K (black) and 1100 K (red) at 20 bar, $\Phi = 1.0$. Reaction flux analyses were performed after 20% initial fuel consumption. Numbers are in normalized flux. [127].

A detailed model is developed by the same group [127], based on a previous model of dimethoxymethane DMM [160] and recent literature data [157], [158], [159], experiments on IDTs were conducted using a ST in the temperature range of 740 to 1110 K. The model demonstrated good agreement with the experiments, showing weak non-Arrhenius behavior originating from low-temperature oxidation chemistry of TMM. However, under fuel-rich and low-temperature conditions, the model underestimated reactivity, and the root cause for this discrepancy is not specified.

2.4 Ab initio study on Alkyl Carbonates

Electrifying the transportation sector presents a formidable challenge, far more complex than one might initially anticipate. While it stands as a promising solution toward achieving zero emissions, it is essential to recognize the intricacies involved. These complexities demand a thorough understanding to mitigate potential hazards and safety concerns. Central to this endeavor is comprehending lithium batteries: their composition, functionality, and operational mechanisms.

2.4.1 Lithium ion batteries

Lithium-ion batteries are characterized by their lightweight, compact design, and operate at voltages around 4 V, offering specific energy levels ranging from approximately 100 Wh kg⁻¹ to 150 Wh kg⁻¹. In their conventional configuration, a lithium-ion battery comprises a graphite anode (such as mesocarbon microbeads, MCMB), a cathode composed of lithium metal oxide (LiMO2, for example, LiCoO2), and an electrolyte consisting of a lithium salt solution (e.g., LiPF6) in a mixed organic solvent (e.g., ethylene carbonate–dimethyl carbonate, EC–DMC), all encased within a separator felt [161].

The first primary lithium batteries entered the market in the 1970s. It wasn't until 1990, when Sony Energytec commercialized the first rechargeable Li-ion battery, equipped with a LiCoO2 cathode and a graphitic carbon anode [162]. However, shortly after, safety concerns emerged when one of these Li-ion batteries exploded in hand-held video cameras, highlighting the risk of thermal runaway and battery fires. This safety issue not only poses risks but also incurs substantial costs. For example, in 2006, Dell had to recall 4.1 million notebook computer Sony batteries due to battery fires, with an estimated cost of 300 million dollars. Another challenge has been to increase the energy and power densities, initially for portable applications and subsequently for hybrid electric vehicles (HEVs) and electric vehicles (EVs) [163].

While all elements of a lithium battery play a role in safety concerns, our focus here is on the electrolyte, particularly in the context of a graphite negative electrode. In such cases, the main components of the electrolyte are **carbonates**, including ethylene carbonate, diethyl carbonate, ethyl-methyl carbonate, and/or dimethyl carbonate, a requirement for forming a stable passivation layer known as the solid-electrolyte interface (SEI) on the carbon's surface. The presence of carbonates in the electrolyte makes it highly flammable. Additionally, the resistive nature of SEI may lead to heat generation during the battery's operation [163].

It is also important to note that these carbonate esters are believed to be potential biofuel additives or replacements to petroleum-derived diesel fuels. Given their oxygenated

nature, it is plausible that their use could lead to a reduction in soot and particulate matter (PM) emissions [164], [165], [166].

Based on the preceding discussions, understanding the pyrolysis and oxidation mechanisms of these carbonates becomes crucial. In this context, we contribute through an *ab initio* study focusing on the hydrogen abstraction reactions of **dimethyl**, **diethyl**, **and ethyl-methyl carbonates** by H and CH₃, along with their subsequent reactions. This is particularly significant given that the existing models for these molecules in the literature heavily rely on the estimation of reaction rates based on different molecules. This is done for the first time although various studies are available in the literature, including different types of investigations on these carbonates. A summary of relevant studies is available in the SM (7.3).

Chapter 3 Experimental Computational Methods

3.1 Introduction

In the previous chapter, the molecules that have been studied were introduced. In this chapter, we outline the experimental and computational methods employed for the study.

and

To delve into the chemistry of ignition processes, chemical kinetic models are developed. These models are constructed by considering the molecular structure of the fuel and proposing relevant reaction pathways. The validation of these models is based on data collected from various sources, including rapid compression machines (RCMs) [167], motored engines [168], jet reactors [169], [170], and shock tubes [171]. Each reactor operates within specific ranges as summarized in Fig 20 and Table 8 provided in [172]. The choice of the apparatus depends on the need to ensure feasibility and control of the combustion environment across a broad spectrum of experimental conditions.



Fig 20 - Temperature - pressure diagram of typical operating conditions for experimental devices and combustion engines reproduced from [172].

Table 8 - Typical features and operating	conditions of devices	used to acquire d	lata for autoignition
/ LTC phenomena adapted from [172].			

Method	Motored engine	Flow / jet reactor	Shock tube	RCM
Temperature (K)	400 - 900	<1500	800 - 2500	400 - 1200
Pressure (bar)	5 - 40	<30	2 - 80	5 - 150
Reaction times	1 - 10	10 - 10000	0.01 – 2	2 - 150
(ms)				

Operation	Multi-shot,	Continuous	Single-shot,	Single-shot,
			unsteady	unsteady
Flow conditions	Turbulent	Laminar/Turbulent	Laminar	Laminar,
			(transition to	Turbulent
			turbulent)	
Advantages	Moderate	Continuous	High	Inexpensive,
	pressures /		pressures,	high pressures,
	temperatures		intermediate	low to
			to high	intermediate
			temperatures,	temperatures,
			instantaneous	pressure
			compression	history similar
				to engines
Disadvantages	Limited range,	Limited range of	Single shot,	Single shot,
	turbulent, high	isothermal	boundary	heat transfer
	residual	residence times /	layers, test	
	concentrations	significant dilution required	times	

Speciation data is frequently obtained through the use of flow and jet-stirred reactors. These continuous reactors allow for physical sampling, and the well-controlled mixing and dilution conditions within the combustion chamber make it possible to neglect gradients of temperature, pressure, and species concentration. Jet-stirred reactors, however, only allow for diluted conditions, while plug-flow reactors permit investigations under both diluted and non-diluted conditions, as well as ignition delay measurements.

Closed single-shot reactors, such as shock tubes and rapid compression machines, are commonly employed for measuring ignition delay times. Shock tubes are particularly useful for investigating very short reaction times, utilizing the compressive heating of a shock wave to create the required compressed, high-temperature conditions. RCMs, on the other hand, operate based on a rapid compression of the reactive mixture, employing a piston blocked at the end of the stroke to maintain a constant volume. In the course of this study, an RCM is utilized. Subsequent sections will delve into more detailed explanations regarding the specifics of this device.

3.2 Rapid Compression machine

3.2.1 History

The rapid compression machine, though increasingly prevalent in experimental setups, is not a recent invention. Its origins can be traced back to 1906 when K. G. Falk [173] designed a compression equipment, based on the suggestion of W. Nernst, to measure the ignition temperature of hydrogen/oxygen mixtures. Falk's design was rooted in the hypothesis (later disproven) that pressure did not influence ignition temperature. Since that time, RCMs have seen substantial improvements in design [7–15] aimed at enhancing control over experimental conditions. Further elaboration on these improvements and their origins can be found in reference [172].

3.2.2 ULille RCM

3.2.2.1 Operation

The ULille – RCM depicted in Fig 21 was developed between 1988 and 1992, inspired by existing machines [174] designed for measuring IDTs. It operates at temperatures ranging from 600 to 1100 K and pressures from 1 to 30 bar, approximating nearly adiabatic conditions [175]. Over the past 30 years, the ULille RCM has been extensively used to investigate the autoignition of pure hydrocarbons, mixtures, and combustion phenomena relevant to engines, including cool flames, NTC, and knock.



Fig 21 - Picture and schematic of the ULille RCM.

Using the RCM, the gaseous mixture undergoes compression to reach predetermined pressure and temperature conditions. In this specific RCM with right-angle configuration shown in Fig 22, when compression is initiated, a locking mechanism releases the driving piston. Compressed air then propels the piston, which, in turn, pulls a cam along a rail. As the cam advances, it pushes the compressing piston inside the combustion chamber. The piston has a diameter of 50 mm, and the compression stroke is 200 mm.



Fig 22 – Schematic of the right-angle RCM, top view for the cam, and front view of the combustion chamber.

The chamber volume at the End-Of-Compression (EOC) condition is adjustable by using different end plates, allowing for variations in the volumetric compression ratio ($\rho = V_0/V_{EOC}$). This flexibility enables the adaptation of experimental conditions to cover a broad range of temperatures and pressures while staying within the commonly accepted limitations of measurable IDTs, typically ranging from 2 to 200 ms in a such setup [172]. The right-angle configuration provides a highly reproducible compression phase, a critical factor for variable-volume kinetic modeling as explained in section 3.5 and maintains a reasonably short compression time, set and monitored at 45 ms in this case. It is worth noting that shorter compression times can be achieved with setups like twinpiston RCMs [176], but these may face challenges related to piston synchronization, affecting the reproducibility of the compression phase. Following compression, the driving piston is brought to a stop by a hydraulic brake within a distance of a few centimeters.

To ensure accurate IDT measurements, maintaining homogeneous temperature and composition fields at the EOC is crucial. However, challenges arise due to issues such as the piston corner roll-up vortex, as depicted in Fig 23. The compressing piston's movement through the combustion chamber can disturb the thermal boundary layer, resulting in a vortex of colder gases mixing with the hotter core. To address this, a piston crevice is incorporated to capture the thermal boundary layer during compression. However, mass transfer to the crevice can lead to longer IDTs, especially in cases of two-stage ignition where the first stage results in strong heat release. The additional dead volume introduced by the crevice must be considered during speciation experiments, and it will be discussed in detail in section 3.3.2.3.



Fig 23 – Illustration from [167] of the piston corner rollup vortex formation and its avoidance with help from a creviced piston.

3.2.2.2 Instrumentation and data acquisition

3.2.2.2.1 Pressure measurement

The ULille RCM is equipped with piezoelectric transducers responsible for measuring dynamic pressure during compression. Two different thermal shock-insulated pressure transducers are installed in the RCM chamber to ensure no degradation occurs. The first, a Kistler 601CA, is flush-mounted on the bottom of the combustion chamber for monitoring purposes. The second, a Kistler 6052, is mounted in a recess for optimal accuracy and frequency response. Both transducers are connected to Kistler charge amplifiers (Kistler 5017 and 5045) for data acquisition. The signal is processed through a National Instruments interface controlled by custom LabVIEW programs, providing a time resolution of 40 μ s, which is also used to control and operate the RCM. Using this acquisition, the total IDT, representing the time between the EOC and the overall maximum of the pressure derivative indicating autoignition, can be measured as illustrated in Fig 24. In some cases, autoignition occurs in two stages, and the first stage ignition delay time (FSIDT), or cool flame delay, is represented by the time between the EOC and the first pressure rise (cool flame). The RCM is also equipped with an optocoupler

associated with an optical comb to measure the piston position during the experiment. This information is used to monitor the compression time.



Fig 24 – Representative pressure profile during a two-stage ignition delay experiment. Mixture 75% n-pentane/25% H_2 , $\Phi = 1$, $T_c = 732$ K & $p_c = 10$ bar.

3.2.2.2.2 Temperature measurement

The initial temperature (T₀) of the RCM is measured and regulated using a PID setup with assistance from type K thermocouples. Regulation is achieved using a thermocouple fixed at the outer chamber wall surface, while the initial temperature is measured using a thermocouple that protrudes 1 mm inside the combustion chamber. The accuracy of the initial temperature measurement is assumed to be ± 1 K, and the temperature profile along the chamber axis is periodically verified with a deviation of ± 1 K from the mean value. However, the core gas temperature cannot be measured using thermocouples because of their longer response time compared to the operation time of the RCM. Therefore, it is standard practice in RCM studies to calculate the temperature from the isentropic law. This core gas temperature T_c represents the temperature of the hot gases inside the chamber, considered not impacted by the thermal losses at the walls. T_c is calculated using the measured pressure at EOC p_c, the initial temperature T₀, and the pressure p₀ that is initially introduced in the combustion chamber:

$$\int_{T_0}^{T_C} \frac{\gamma}{\gamma - 1} \frac{dT}{T} = ln \left(\frac{P_C}{P_0}\right)$$

Eq. 1

This approach has been validated experimentally [177] using in-line tunable diode laser absorption, with an uncertainty of about \pm 5 K. The thermochemical properties of the initial mixture are used to determine the mixture's heat capacity ratio γ , relying on recent thermochemical data in the NASA polynomial format. This temperature can be altered depending on the inert gas used to prepare the fuel mixture. This is further discussed in section 3.2.3.

3.2.2.3 Adaptations to the combustion chamber for hydrogen experiments

As mentioned earlier in section 2.3.2.1, hydrogen possesses a high laminar burning velocity. In a compressed environment like the RCM post-EOC, the autoignition of fresh gases near the walls and ahead of the flame front is occasionally witnessed, resembling a phenomenon akin to engine knock. When the laminar burning velocity is elevated, this can lead to the development of multiple supersonic flame fronts in the combustion chamber and the occurrence of local detonation spots. In such scenarios, severe high-frequency pressure oscillations are observed, as depicted in Fig 25.



Fig 25 - Example of pressure profiles obtained with (black) and without pressure relief (red) at ignition for pure hydrogen cases.

To address this issue, a pressure relief system was devised (Fig 26). Mylar films were employed to create diaphragms with calibrated thickness corresponding to the pressure
at EOC. These diaphragms were placed inside one of the combustion chamber ports and ruptured during ignition. This mechanism effectively curtailed the duration of the pressure peak at ignition, minimizing potential damage to the combustion chamber, gas insertion valve, and pressure sensors. The exhaust from the pressure relief port was then directed to the RCM's exhaust pump.





3.2.3 Fuel mixture preparation

The gas mixtures used to fill the combustion chamber are prepared using two mixture preparation facilities, following the partial pressure method. The first system presented in Fig 27 operates at room temperature and is used for volatile fuels at room temperature. It consists of 13 Pyrex bulbs of 10L and 3 of 15L, all externally coated with aluminum paper to prevent the decomposition of photosensitive compounds. The system is equipped with two MKS Baratron pressure gauges, model 627D12TDC1B (0 - 100 torr) and model 627D13TDC1B (0 - 1000 torr), and a vacuum pump.

To prepare the mixture, the bulbs are initially vacuumed thoroughly. Subsequently, the liquid fuel is connected to the bench to start filling the bulb. It is important to note that these liquid fuels are purified from potential dissolved gases through freezing/pumping cycles using liquid nitrogen. After filling the fuel or fuels in the order of their increasing vapor pressure, oxygen is added, followed by the inert gases. Then the mixture is left to homogenize for one night before usage.

The selection of the inert gas composition is determined by the desired core gas temperature. As previously mentioned, the isentropic law is utilized to calculate this temperature, and it is dependent on the heat capacities of the mixture composition. Consequently, higher heat capacity leads to lower temperatures. The employed inert gases include argon, nitrogen, and carbon dioxide, with respectively increasing heat capacities.



Fig 27 – Unheated mixture preparation system adapted from [178]. 1: 0-100 torr pressure gauge, 2: 0-1000 torr pressure gauge, 3: pressure reader, 4: vacuum pump access valve, 5: 15 L balloon, 6: 10 L balloon, 7: RCM access valve.

On the contrary, the second system presented in Fig 28 is heated and is employed for liquid fuels with high boiling points. It comprises 3 Pyrex bulbs of 15L housed within an oven-like container to prevent undesirable condensation. This system is equipped with two MKS Baratron type 628 F gauges (0-100 Torr and 0-1000 Torr), heated to 100°C, to measure the pressure, along with a pump. The liquid fuel is connected to the system after heating the entire setup to a temperature high enough to achieve double the desired fuel partial pressure. The temperature inside this bench can vary between 40 and 90°C, measured by a K-type thermocouple placed on the bulb wall. A PID regulator controls the temperature, and a thin resistor (1000 W) is positioned under a fan to ensure homogeneous heat distribution inside the bench. The lines connecting the bench to the RCM and to the inlet of the inert gases are also heated to a temperature higher than that inside the bench.

The mixture is left to homogenize for about 1 hour, to avoid any fuel conversion that could take place.



Fig 28 – Thermostatic gas mixture preparation system. 1: inlets to the 15L bulbs, 2: inlet to atmospheric air or different gases, 3: vacuum pump, 4: controller of gases getting in or from the bench, 5: pressure reader, 6: temperature reader, 7: 0 – 100 torr pressure gauge, 8: 0 – 1000 pressure gauge, 9: temperature controller for the line connecting the bench to the RCM.

3.2.4 Equivalence Ratio

The equivalence ratio is the ratio of the actual fuel-to-air ratio to the stoichiometric fuelto-air ratio in a combustion process, indicating whether the mixture is fuel-rich (greater than 1) or fuel-lean (less than 1).

$$\Phi = \frac{(Fuel/Air)_{actual}}{(Fuel/Air)_{stoichiometric}}$$

3.2.5 Summary of the experiments done during this thesis

A summary of the mole fractions and conditions of the different fuels studied during this PhD using the RCM is in Table 9.

Table 9 – Summary of the experimental conditions used on different fuel mixtures: E.R. = Equivalence ratio, T_c = compressed temperature, p_c = compressed pressure, C.R = compression ratio.

Fuel	E.R.	Mole fractions	T _c (K)	P _c (bar)	C.R
	1	$F = 0.0256, O_2 =$			
		0.2046, Inert =			
<i>n</i> -pentane		0.7698			
	0.5	F = 0.0129, O ₂ =	650 - 950	20 - 15 -	9.65
		0.20724, Inert =		10	
		0.7797			

	1	F = 0.02486, H ₂ =			
75%n-		$0.00829, O_2 = 0.203,$			
pentane/25%H ₂		Inert = 0.7638			
	0.5	$F = 0.01264, H_2 =$	680 - 970	20 – 15 –	9.65
		0.00421, O ₂ =		10	
		0.2064, Inert =			
		0.7766			
	1	F = 0.02354, H ₂ =			
50% <i>n</i> -		0.02354, O ₂ =			
pentane/ 50% H ₂		0.2001, Inert =	680 - 970	20 - 15 -	9.65
		0.7528		10	
	0.5	$F = 0.01206, H_2 =$			
		0.01206, O ₂ =			
		0.2049, Inert =			
		0.7709			
	1	$F = 0.02724, O_2 =$			
		0.2043, Inert =			
1-pentene		0.7685	660 - 980	20 – 15 –	9.65
	0.5	$F = 0.0138, O_2 =$		10	
		0.2071, Inert =			
		0.77909			
	1	$F = 0.02643, H_2 =$			
/5%1-		$0.0088, 0_2 = 0.2026,$			0.65
pentene/25%H ₂	0 5	Inert = 0.7622	660 - 980	20 - 15 -	9.65
	0.5	$F = 0.01345, H_2 =$		10	
		$0.00448, 0_2 =$			
		0.2062, Inert =			
	1	U.7750			
500%1-	1	$\Gamma = 0.02494, \Pi_2 = 0.02494, \Omega_2 = $			
50701- nontono/5006Ho		0.02494, 02 = 0.1005 Inort =	660 - 990	20 - 15 -	965
pentene/ 50 %112		0.1995, mert =	000-990	20 - 13 -	9.05
	05	$F = 0.01279 H_2 =$		10	
	0.5	$0.01279 \Omega_2 =$			
		0.2046. Inert =			
		0.7698			
	1	$F = 0.029.0_2 =$			
3-pentanone	_	0.20380. Inert =			
- p		0.767	650 - 950	20 - 15 -	9.65
	0.5	$F = 0.0147, O_2 =$		10	
		0.2068, Inert =			
		0.7783			
	1	F = 0.0282, H ₂ =			
75%3-		$0.0094, O_2 = 0.2021,$			
pentanone/25%H ₂		Inert = 0.76029	650 - 950	20 - 15 -	9.65
	0.5	$F = 0.01437, H_2 =$		10	
		0.00479, O ₂ =			
		0.2059, Inert =			
		0.7748			
50%3-	1	$F = 0.02652, H_2 =$			
pentanone/ 50% H ₂		0.02652, O ₂ =	655 - 930	20 - 15 -	9.65
		0.1988, Inert =		10	
		0.7481			

	0.5	F = 0.01362, H ₂ =			
		0.01362, O ₂ =			
		0.2043, Inert =			
		0.76848			
	1	$F = 0.029, O_2 =$			
3-pentanol		0.20380, Inert =	690 - 950	20 - 15 -	9.65
		0.767		10	
	0.5	$F = 0.0147, O_2 =$			
		0.2069, Inert =			
		0.778			
	1	$F = 0.027, H_2 =$			
75%3-		$0.009, O_2 = 0.2024,$			
pentanol/25%H ₂		Inert = 0.7615	690 - 950	20 - 15 -	9.65
	0.5	$F = 0.0137, H_2 =$		10	
		0.0046, O ₂ =			
		0.20615, Inert =			
		0.7755			
	1	$F = 0.0265, H_2 =$			
50%3-		$0.0265, O_2 = 0.1988,$			
pentanol/ 50% H ₂		Inert = 0.7481	690 - 950	20 – 15 –	9.65
	0.5	F = 0.0136, H ₂ =		10	
		$0.0136, O_2 = 0.2043,$			
		Inert = 0.7685			
Tetrahydro-pyran	1	$F = 0.0291, O_2 =$	650 - 880	15 – 10 –	9.65
		0.2038, Inert =		5	
		0.767			
	1	$F = 0.0206, O_2 =$			
		0.1028, Inert =			
Trimethoxy-		0.8766	660 - 1050	15 – 10 –	9.65
methane	0.5	$F = 0.0104, O_2 =$		5	
		0.1039, Inert =			
		0.8857			

Note that all the experiments mentioned above have also been conducted by replacing O_2 with N_2 for simulation purposes. This will be further elaborated in 3.5.

3.3 Mixture speciation procedure

During the ignition delay, numerous intermediates are produced. However, gaining insight into the ongoing reactivity is not straightforward. Therefore, a special procedure must be implemented to halt the reactivity at a desired time during ignition, collect a sample, and then analyze it. This is a very valuable tool for the detailed validation of combustion kinetic models in engine relevant conditions [175].

3.3.1 Getting the sample

The ULille RCM enables physical sampling through the combustion chamber design. A sampling system is attached to the upper port as illustrated in Fig 29, the same port where mylar films are used during hydrogen experiments, but in this case aluminum diaphragms are used for a faster perforation.



Fig 29 – RCM sampling system scheme.

Before the sampling event takes place, a metallic needle is held in the high position by an electromagnet, while the sampling chamber is under vacuum. An electric signal then allows the needle to be propelled down with help from a spring before the total ignition, thus perforating its way through the diaphragm and into the combustion chamber. At this moment, the reacting gas mixture expands into the sampling chamber, where it is collected and preserved at a desired temperature for analysis.

A comparison of pressure profiles between a typical RCM IDT experiment and a sampling experiment is shown in Fig 30. It illustrates the sudden decrease in pressure during the diaphragm perforation. The pressure drops by 50% in less than 0.5 ms due to the volumetric ratio between the combustion chamber and the sampling chamber, which is approximately 1/40. This ensures the instantaneous quenching of chemical reactivity.



Fig 30 – Pressure profiles for 3-pentanol/ $O_2/N_2/Ar$ stoichiometric mixture, $p_c = 20$ bar, $T_c = 735$ K. Red line: Reactive mixture, green line: Non-reactive mixture, blue line: pressure profile of the mixture during sampling at 36.5 ms.

Each sampling experiment provides the mole fractions of the detected species at a specific time. To construct a species mole fraction time-history profile, multiple sampling experiments are conducted at different sampling times, allowing for the observation of the fuel and product evolution throughout the total IDT. To ensure experiment reproducibility, the combustion chamber is thoroughly cleaned and allowed to return to its original temperature after each sampling experiment.

3.3.2 Analyzing the sample

Following the collection of the desired sample using the sampling system, the sampling chamber is connected to a speciation system for qualitative and quantitative analysis.

3.3.2.1 Speciation system

The speciation system used in our experiments illustrated in Fig 31 comprises two Gas Chromatographs (GCs). The first is the Bruker Scion 456 – GC, coupled to a mass spectrometer, a Thermal Conductivity Detector (TCD), and a Flame Ionization Detector (FID). The second GC is the Agilent 6890 with a TCD/FID line. Both GCs are connected to an external inlet where the sampling chamber is attached, with a pressure sensor (MKS Baratron type 628 F gauges 0-1000 Torr) directly positioned above the inlet. All the lines are heated to a specific temperature depending on the fuel under investigation.



Fig 31 – Speciation system composed of two GCs.

The Scion 456 – GC is used to perform qualitative and quantitative analysis of products ranging from C_2 to C_{10} , and its configuration is presented in Fig 32. The sample is injected into two columns, and then split in two lines leading to the FID/TCD and the MS.



Fig 32 – Bruker Scion 456 – GC configuration.

The two columns in this GC are the RT bond Q and the HP 5 columns. Each column possesses different properties, summarized in Table 10. Usually, the smaller species are well detected using the RT bond Q, and the heavier ones are better separated with the HP 5 column.

The other GC; the Agilent 6890, is used for the detection of light gases such as: CH₄, CO, CO₂, & O₂. It is equipped with a ShinCarbon ST packed column which properties are also given in Table 10.

Column	RT bond Q	HP 5	ShinCarbon ST
Products analyzed	C_2 to C_6 (up to C_{10} for	C ₅ to C ₃₀	$C_{1,}O_{2} \& N_{2}$
	alkanes)		
Length	30 m	30 m	2 m
Internal diameter	0.25 mm	0.25 mm	0.53 mm
Stationary phase 8 µm		0.25 μm	-
Mesh -		-	80/100
Composition 100% divinylbenze		(5%-phenyl)-	ShinCarbon ST
		methylpolysiloxane	
Temperature -60 to 300 °C		up to 325 °C	Up to 300 °C
range			
Polarity	Polarity Non-polar		Non-polar

Table 10 – Properties of RT bond Q [179], HP 5 [180], & ShinCarbon ST [181] columns.

After the separation of the species with the help of the columns, the FID and the TCD deliver a signal that is used for quantification analysis, and the MS provides the mass spectra of the species that help identifying each using the NIST spectral library, or by studying their fragmentation scheme.

The FID employs a flame fueled by a mixture of hydrogen/air. As the analytes pass through this flame, carbo-cations are formed and collected at the detector's electrodes. The accumulated ions generate an electrical current, subsequently converted into a signal. Detection of a component in the sample relies on the creation of temporary intermediate carbon-radical ions, eventually oxidized to CO₂ and H₂O. However, certain species, such as formaldehyde, do not form intermediate carbon-radical ions [182], making their quantification challenging with FID. This limitation is noteworthy as formaldehyde is a species frequently formed during combustion at low temperatures.

The TCD operates by detecting changes in the thermal conductivity of the column effluent. It compares this thermal conductivity to a reference flow of carrier gas, here helium. The TCD consists of an electrically heated filament within a temperature-controlled cell. Under normal conditions, there is a stable heat flow from the filament to the detector body. When an analyte elutes from the GC column, the thermal conductivity of the column effluent is reduced. Consequently, the filament heats up, leading to a change in resistance. A Wheatstone bridge circuit is needed to measure this change in resistance, resulting in a measurable voltage shift.

3.3.2.2 Quantifying the species

As mentioned earlier, the FID and TCD signals are used for quantifying the species mole fractions. In order to do that, a calibration factor should be measured using a mixture with a well-known concentration. This is done according to the following equation:

$$F_i = \frac{A_i}{x_i \cdot p_{inj}}$$

Eq. 2

 $\begin{array}{l} F_i: \mbox{ calibration factor of the species i.} \\ A_i: \mbox{ Area under the curve and above the base line of the species i.} \\ x_i: \mbox{ mole fraction of species i.} \\ P_{inj}: \mbox{ injection pressure of the mixture in the GC.} \end{array}$

Then using the same equation, the mole fractions are calculated for the sampled species, each according to its specific calculated calibration factor.

Nonetheless, some molecules cannot be calibrated using the conventional method because of limitations in availability. Instead, they are calibrated employing the Equivalent Carbon Number rule (ECN). This calibration is feasible due to the linear response of the FID, as a function of the number of carbons atoms for a given chemical family. The ECN is calculated based on the contribution of each functional group in the considered species [183], as presented in Fig 33.

Atom	Derivatized form	Туре	ECN contribution
A. As	determined by Sternbe	erg et al. (1)	
С		Aliphatic	1
С		Aromatic	1
С		Olefinic	0.95
С		Acetylenic	1.30
С		Carbonyl	0
С		Carboxyl	0
С		Nitrile	0.3
0		Ether	-1.0
0		Primary alcohol	-0.5
0		Secondary alcohol	-0.75
0		Tertiary alcohol	-0.25
N		Amine	As 0 in alcohols
CI		2+-Aliphatic	-0.12 per chlorine
CI		On olefinic C	+0.05
B. As	determined in this stud	dy for derivatized compou	nds
	H-C-O-TMS (alcohol)		3.69-3.78
	CO ₂ -TMS (acid)		3.0
	CH=N-O-TMS (silyl o	xime)	3.3
	CH=N-O-CH ₃ (metho:	xime)	0.92-1.04

Fig 33 – Contributions to the effective carbon number from [183].

For a reference species k, for which the calibration factor is determined in advance, and a species i, whose calibration factor is unknown, the calibration factor of i can be calculated as follows:

$$F_i = F_k \cdot \frac{ECN_i}{ECN_k}$$

Eq. 3

3.3.2.3 Crevice dilution correction

It was explained before that a creviced piston is used to suppress the formation of the rollup vortex for the sake of homogenizing the gas mixture temperature. However, this implies a dead volume trapped in the crevice, leading to the dilution of the sample. Subsequently, this dilution must be considered whilst calculating the mole fractions of the species. Considering an ideal mixture, the test volume should be the summation of V_{RCM} (33 cm³) and $V_{crevice}$ (3.3 cm³) as depicted in Fig 34. The gases confined in the crevice are assumed to remain unreacted, in line with the anticipated lower temperature in the crevice [184].



Fig 34 - Transversal section of the endplate, combustion chamber and creviced piston of the ULille RCM.

The mole fraction of each species is:

$$x_i = \frac{n_i}{n_{total}} = \frac{n_i}{\frac{pv}{RT}}$$

Eq. 4

$$x_{i,measured} = \frac{n_{i,RCM} + n_{i,crevice}}{n_{total,RCM} + n_{total,crevice}} = \frac{n_{i,RCM} + n_{i,crevice}}{\frac{pv_{RCM}}{T_c} + \frac{pv_{crevice}}{T_{crevice}}}$$

Eq. 5

In the initial phase, the combustion chamber only contains the initial fuel mixture (fuel/ O_2 /inert). Therefore, the corrected mole fraction of the reactants is determined in a manner distinct from the mole fraction calculation for the species generated during combustion.

For the reactants, the equation is as follows:

$$x_{i,measured (reactants:n_{i,crevice}=n_{i,0})} = \frac{x_{i(reactants),RCM}(\frac{v_{RCM}}{T_c}) + x_{i,o}(\frac{v_{crevice}}{T_{crevice}})}{(\frac{v_{RCM}}{T_c} + \frac{v_{crevice}}{T_{crevice}})}$$

Eq. 6

$$x_{i(reactants),RCM} = \frac{x_{i,measured}(\frac{v_{RCM}}{T_c} + \frac{v_{crevice}}{T_{crevice}}) - x_{i,o}(\frac{v_{crevice}}{T_{crevice}})}{\frac{v_{RCM}}{T_c}}$$

Eq. 7

And that for the products:

$$x_{i,measured (products:n_{i,crevice}=0)} = \frac{\left(\frac{p_{i,RCM}v_{RCM}}{RT_c}\right)}{\frac{p}{R}\left(\frac{v_{RCM}}{T_c} + \frac{v_{crevice}}{T_{crevice}}\right)} = \frac{x_{i,RCM}\left(\frac{v_{RCM}}{T_c}\right)}{\left(\frac{v_{RCM}}{T_c} + \frac{v_{crevice}}{T_{crevice}}\right)}$$

 $x_{i (products),RCM} = x_{i,measured} \left(1 + \frac{\frac{v_{crevice}}{T_{crevice}}}{\frac{v_{RCM}}{T}}\right)$

Eq. 8

Eq. 9

The corrected mole fractions of the reactants and products were calculated while considering the temperature extremes, i.e, $T_{crevice}$ was replaced by the initial temperature T_0 and the compressed temperature T_c , leading to two different results. The average of the two values is the subsequent considered mole fraction.

In this thesis, sampling experiments were performed for two different fuel mixtures. In Table 11 are the conditions of which each mixture was sampled.

Fuel mixture	Mole fractions	E.R.	N ₂ :O ₂	P _c (bar)	T _c (K)
THP/O ₂ /Inert	$F = 0.014, O_2 =$	1	90:10	10	737
	0.0986, N ₂ =				
	0.8873				
3-pentanol/O ₂ /Inert	$F = 0.029, O_2 =$	1	78:21	20	735
	0.2038, N ₂ =				
	0.437133, Ar =				
	0.32976				

Table 11 - Summary of the used conditions during sampling experiments.

3.4 Uncertainty analysis

To employ the experimental results for validating kinetic models, it is crucial to accurately assess the associated uncertainties that accompany all measurements. This ensures the reliability of the measurements and allows them to be utilized in estimating the model accuracy.

The sources of uncertainty vary across different parameters during different stages of the experimental process. In an RCM experiment, uncertainty sources are linked to measurements of p_c , T_0 , and T_c , as well as compression time, cool flame time, and autoignition time definition. Among these, the measurements of the initial conditions of the combustion chamber are reported to be the most significant source of uncertainties, particularly the initial pressure p_0 [167]. This is attributed to the pressure gauges used in the mixture preparation facilities, which read the pressure transferred to the combustion chamber. Their accuracy is 0.25% of the reading, meaning that, for a 1000 torr full-scale manometer, the error could be up to 2.5 torr [185].

Estimating uncertainties in IDT measurements is challenging due to the numerous nonlinear effects influencing ignition. Instead of assigning arbitrary error bars, the experiment's repeatability is demonstrated by reproducing all experimentally observed data points in the figures a minimum of three times. Nevertheless, the uncertainty linked to the calculated core gas temperature (mentioned earlier in 3.2.2.2.2), is believed to contribute to the overall error. In the current work, an uncertainty of T_c ± 5 K is considered. Concerning the uncertainty in compressed pressure p_c measurements, the two Kistler pressure sensors present a 0.05% error as mentioned by the manufacturer. In speciation experiments, the uncertainty is linked to mole fraction measurements, contingent on the quantification method. When the calibration factor is derived from a mixture with a well-known concentration prepared in our lab, the estimated uncertainty is 10%. However, if the ECN rule is applied, the uncertainty is estimated to be 20%. All the chemical products utilized in this work, along with their respective purities and suppliers, are detailed in the appendices (7.4).

In order to verify the quantification done during the speciation experiment, a carbon balance is calculated. This carbon balance compares the number of carbon atoms inserted in the initial mixture, and the collected carbon atoms from the measured species. The quantity of each oxidation product i at time t is expressed as the number of carbon atoms in species i per 100 carbon atoms introduced in the form of a reactant. This percentage of carbon is given by:

$$\%C_i(t) = \frac{n_i}{n_{0,reactant}} * \frac{\gamma_i}{\gamma_{reactant}} * 100$$

Eq. 10

Where n_i is the number of moles of species i, $n_{0,reactant}$ is the number of moles of the initial reactant, γ_i is the number of carbon atoms in species i, and $\gamma_{reactant}$ is the number of carbon atoms in the reactant, or mixture of reactants.

For a mixture of hydrocarbons j, $n_{0,reactant}$. $\gamma_{reactant}$ becomes $\sum_{j} n_{0,j}$. γ_{j} .

3.5 Kinetic modeling

In the previous sections we presented how to measure data experimentally. In this section, we introduce the numerical approach used to simulate the experimental data. To do that, chemical kinetic models are developed to reproduce the whole combustion process of a fuel. These models consist of all the relevant elementary reactions between relevant species. The kinetic parameters of each reaction, as well as the thermodynamic properties of each species are also included. This will be detailed further, but first the procedure of using these models for simulations in our work is introduced.

3.5.1 Simulation procedure

It is mentioned before that for each reactive experiment, a non-reactive duplicate is performed by replacing O_2 with N_2 , as both gases have the same heat capacity.

Compressing the non-reactive mixture under the same conditions as the reactive one enables the generation of the volume profile, which accounts for heat losses during the experiments. Initially, the volume profile is computed from the pressure profiles using a custom Python script including initial conditions (p_0 , T_0 and x_i) based on the isentropic law after applying a Savitzky-Golay filter to remove high-frequency noise from the data.

In this study, the open-source solver Cantera [186] is employed to solve the system of ordinary differential equations (ODEs) governing the mole fractions and energy. Cantera, a suite of object-oriented software, offers a versatile tool for incorporating intricate chemistry into combustion simulations. The simulation involves an isentropic reactor where the gas mixture undergoes volumetric compression initiated by the movement of an adiabatic wall. The steps to generate a volume profile are depicted in Fig 35.



Fig 35 - volume profile generation

After generating the volume profiles, they are then used for computing the IDTs following the steps illustrated in Fig 36.



Fig 36 - Scheme of numerical simulation used by Cantera.

During the modeling, the determination of the IDTs relies on the user's discretion; it can be either the maximum of the pressure derivative or the peak in the mole fraction of a user-specified species. In this work, the FSIDT is calculated according to the maximum of a ketohydroperoxide mole fraction chosen for each fuel, and the total IDT is calculated from the occurrence of the maximum of dp/dt. The movement of the adiabatic wall is constrained by the volume profile, which is utilized to calculate the wall's velocity. Two user-defined parameters, the final temperature (end_temp) and the simulation time (Sim_time), limit the test duration. The simulation terminates if the temperature surpasses (end_temp) or the time exceeds (Sim_time). If autoignition is not achieved after a simulation, (Sim_time) can be extended to allow sufficient time to reach ignition.

3.5.2 Development of a kinetic mechanism

To develop a kinetic mechanism, all the species must be reported in the mechanism, i.e: reactants, intermediates (molecules, atoms and free radicals) and products, along with their thermo-data, and their possible reactions. The development is therefore done following a hierarchical methodology, successively adding the reactions of the species containing an increasing number of carbon atoms. To obtain this mechanism we need several essential components split between different files, an input file (.inp), a thermo file (.dat), and a transport data file, subsequently giving the final mechanism form.

Following a reaction, three coefficients are indicated, A, n and E representing respectively the pre-exponential factor, the corrective coefficient of variation of the pre-exponential factor with temperature, and the activation energy. Each coefficient corresponds to a parameter from the modified Arrhenius equation:

$$k = A * T^n * exp(-\frac{E}{RT})$$

Eq. 11

With T being the temperature in K, and R is the ideal gas constant in cal.K⁻¹.mol⁻¹. The three coefficients can be either retrieved experimentally by measuring the rate constant of the reaction, or by *ab initio* methods introduced in later in 3.6. In many cases, these coefficients are estimated based on similar reactions of a different molecule with structural similarities.

The thermodynamic data for the species are presented in the form of polynomial coefficients used by the NASA "Chemical Equilibrium Program"[187]. The NASA format includes two sets of seven coefficients, enabling the calculation of thermodynamic properties in two temperature ranges: a low-temperature range, typically between 300 K and an intermediate temperature close to 1000 K, and a high-temperature range between

this intermediate temperature and a high temperature (e.g., 3000 or 5000 K). An example is shown below:

```
H2H2200.0006000.0001000.0001+2.93286575E+00+8.26608026E-04-1.46402364E-07+1.54100414E-11-6.88804800E-162-8.13065581E+02-1.02432865E+00+2.34433112E+00+7.98052075E-03-1.94781510E-053+2.01572094E-08-7.37611761E-12-9.17935173E+02+6.83010238E-01+0.00000000E+004
```

For each species, we find the name of the species as declared in the input file, the number of chemical elements composing the species, the limits of the two temperature domains, and the series of coefficients.

The thermodynamic properties: heat capacity, enthalpy, and entropy, are calculated from the equations below:

$$\frac{C_{p,k}}{R} = a_{1,k} + a_{2,k}T + a_{3,k}T^2 + a_{4,k}T^3 + a_{5,k}T^4$$

Eq. 12

$$\frac{H_k^{\circ}}{R} = a_{1,k} + a_{2,k}\frac{T}{2} + a_{3,k}\frac{T^2}{3} + a_{4,k}\frac{T^3}{4} + a_{5,k}\frac{T^4}{5} + a_{6,k}\frac{1}{T}$$

Eq. 13

$$\frac{S_k^{\circ}}{R} = a_{1,k} lnT + a_{2,k}T + a_{3,k}\frac{T^2}{2} + a_{4,k}\frac{T^3}{3} + a_{5,k}\frac{T^4}{4} + a_{7,k}$$

Eq. 14

The equation $G^\circ=H^\circ-TS^\circ$ allows the calculation of Gibbs free energy, and thus, the calculation of the equilibrium constants of different reactions of the mechanism as well as the rate constants of the reverse reactions.

$$\Delta G^{\circ} = G^{\circ}_{products} - G^{\circ}_{reactants} = -RTln(K_p)$$

Eq. 15

$$K_{c} = \frac{k_{dir}}{k_{rev}} = K_{p} \left(\frac{P}{RT}\right)^{\sum v_{products} - \sum v_{reactants}}$$

Eq. 16

Where C_p is the heat capacity at constant pressure, H is the enthalpy, S is the entropy, and v represents the stoichiometric coefficients.

3.5.3 Validating a kinetic mechanism

In our work, several mechanisms are developed or used from literature. All are summarized in the following table.

Table 12 - Summary of the mechanisms used in this thesis.

Fuel	Mechanism
<i>n</i> -pentane	Bugler et al. [45]
1-pentene	Dong et al. [80]
3-pentanone	Fenard et al. [96]
3-pentanol	Sub-mechanism developed in this work
	[SAAB]
ТНР	Sub-mechanism developed in this work
	[Fenard]
ТММ	Developed in a collaborative work with the
	university of Gent

To validate mechanisms from the literature, the simulated data were compared with our RCM experimental results. However, to validate developed mechanisms in this thesis, such as the THP and 3-pentanol mechanisms, sampling experiments and data from literature were also used for validation.

3.6 Computational Chemistry Methods and Tools

Computational chemistry is a branch of chemistry that utilizes computer simulations to address and solve problems related to molecular structures and properties. It involves the use of various computer programs to obtain detailed information about chemical systems. In this thesis, our attention will be directed solely towards the methods and tools utilized for the computations carried out in this work, given that quantum mechanics constitutes a vast field of study on its own.

3.6.1 Methods

3.6.1.1 *Ab initio* methods

Ab initio methods refer to computational chemistry methods based on quantum chemistry. The term "*ab initio*," derived from Latin, means "from the beginning," indicating calculations grounded in fundamental principles. Coined by Robert Parr and colleagues [190], *ab initio* calculations utilize the accurate Hamiltonian (Ĥ) and do not rely on experimentally determined data, instead employing fundamental physical constants. The Hartree-Fock (HF) method is the most basic *ab initio* electronic structure calculation method, however, in this method, instantaneous electron-electron interactions are not considered; instead, their average effects are incorporated. In reality, electron motions are correlated with each other, a factor not accounted for in the HF method.

The primary sources of error in *ab initio* molecular electronic calculations stem from 1) the neglect or incomplete treatment of electron correlation and 2) the incompleteness of the basis set. To address these issues, post-HF methods have been developed to enhance HF calculations. Post-HF methods incorporate instantaneous electron correlation to consider repulsions between electrons and attempt to minimize errors arising from the incomplete basis set. Some of the post-HF methods are: Configuration Interaction (CI), Moller-Plesset perturbation theory (MP2, MP3, MP4, etc), Quantum chemistry composite methods, and the coupled-cluster (CC) method that is employed in our work to calculate the single point energies (SPEs).

3.6.1.1.1 Coupled-Cluster (CC) method

The Coupled Cluster (CC) method for molecular electronic calculations was developed by Cizek, Paldus, Sinanoglu, and Nesbet in the 1960s, followed by contributions from Pople and coworkers as well as Bartlett and co-workers in the 1970s [191]. The fundamental equation in CC theory is expressed as:

$$\psi = e^T \Phi_0$$

Eq. 17

Wherein, ψ is the exact non-relativistic ground-state molecular electronic wave function, Φ_0 is the normalized ground-state HF wave function, and the $e^{\hat{T}}$ is the operator which is defined by the Taylor-series expansion:

$$e^{\hat{T}} = 1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \dots = \sum_{k=0}^{\infty} \frac{\hat{T}^k}{k!}$$

Eq. 18

The \hat{T} is the cluster operator which is given as:

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \dots + \hat{T}_n$$

Eq. 19

Where n is the number of electrons in the molecule. $\hat{T}_1 \& \hat{T}_2$ are the one-particle and twoparticle excitation operators respectively. In the CC method, two approximations are made. Firstly, a finite basis set is used instead of a complete and infinite set of basis functions. Secondly, the operator \hat{T} in Eq. 18 is approximated by including only some of the operators; if $\hat{T} = \hat{T}_1 + \hat{T}_2$, this gives CC singles and doubles (CCSD) method, and if $\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3$, one obtains CC singles, doubles, and triples (CCSDT) method. The CCSDT calculations are computationally demanding and are feasible only for small molecules. All the CC calculations in this work were done using double- and triple- zeta basis functions.

3.6.1.2 Density functional methods

Density Functional Theory (DFT) methods are occasionally regarded as *ab initio* methods for determining molecular structures. In 1964, Pierre Hohenberg and Walter Kohn demonstrated that for molecules with a non-degenerate ground state, the ground-state molecular energy, wave function, and all molecular electronic properties are uniquely determined by the ground-state electron probability density, $\rho_0(x, y, z)$ [192]. The zero subscript in ρ indicates the ground state. Unlike *ab initio* methods, DFT methods do not directly calculate the molecular wave function. Instead, they aim to determine the groundstate electronic energy from the ground-state electron density (ρ_0). However, the Hohenberg-Kohn theorem does not provide a method for calculating E_0 (ground-state molecular energy) from ρ_0 , nor does it offer guidance on finding ρ_0 without first determining the wave function. Therefore, in 1965, Kohn and Sham [193] developed a method for determining ρ_0 and subsequently E_0 from ρ_0 . Comprehensive details of this method can be found in quantum chemistry textbooks [194].

Overall, the energy of the system in DFT (EDFT) is given as follows:

$$E_{DFT} = E_{NN} + E_T + E_v + E_{coul} + E_{exch} + E_{corr}$$

Eq. 20

With E_{NN} : nuclear-nuclear repulsion, E_T : kinetic energy of electrons, E_v : nuclear-electron attraction energy, E_{coul} : classical electron-electron Coulomb repulsion energy, E_{exch} : non-classical electron-electron exchange energy, E_{corr} : energy due to the correlated movement of electrons of different spin. All DFT calculations were done using the B3Lyp functional and the DEF2-TZVP basis set for the geometries and vibrational harmonic frequencies.

3.6.2 Tools

3.6.2.1 Gaussian software package

Gaussian 09 [195] was utilized for conducting electronic structure calculations, and these computations were carried out on the RWTH High Performance Computing Cluster in Aachen, Germany. This section provides a concise overview of Gaussian 09, highlighting some essential keywords. GaussView [196] is employed for visualizing input and output files.

In electronic structure calculations, the first step, as illustrated in Fig 37, is to construct the molecule (1), then optimize its geometry (2) then compute the vibrational frequencies. This is achieved by specifying the 'opt+freq' keyword in the input file, which also includes information about the type of calculations, level of theory, basis set, and more as given in this example: # opt=tight freq b3lyp geom=connectivity def2tzvp empiricaldispersion=gd3bj. The input file additionally contains details such as the charge and spin multiplicity of the molecule. The spin multiplicity is represented by 2S+1, where S is the total electron spin. For instance, paired electrons result in a net zero spin, and for one unpaired electron, the spin multiplicity is 2. The Cartesian coordinates of the molecule, along with the corresponding atomic symbols, are also included in the file.



Fig 37 – Flow plan for the electronic structure (1-5) and the rate constants (6) calculations.

The objective is to identify the optimized geometry with the lowest energy before determining all the vibrational frequencies within a molecule. This is accomplished by executing loops of relaxed 1D rotor scans with a 30° increment (3), selecting the configuration with the least energy at each loop as shown in Fig 38. Once the minimum energy configuration is reached, it is employed for calculating the vibrational frequencies (4).

After the frequencies for the optimized structure are computed, the energy is computed (5) by choosing the keyword 'Energy' this time, and assigning the method desired. In our case, we apply the CCSD and the CCST, and the final energy is computed using the following equation:

$$E = \frac{(3^3.E_{TZ}) - (2^3.E_{DZ})}{3^3 - 2^3} + E_{Zp}$$

Eq. 21

Of which E_{TZ} is the energy computed using the CCST method and the E_{DZ} is the energy computed using the CCSD method, and E_{zp} is the zero-point energy taken from the output of the frequency calculation.



Fig 38 - Assigning the configuration with the least energy during a dihedral scan performed on one of EMC C-C bonds.

After computing the energies of all the molecules, it is then possible to construct the potential energy surface.

3.6.2.2 Rate constant calculation

The rate constants of hydrogen abstraction reactions, unimolecular β -scission, internal radical migration, and isomerization are calculated via the Master Equation using the MESS software package [197]. This is done by preparing a comprehensive input file including different inputs.

The temperature and the pressure lists are specified as desired. In the study of alkylcarbonates, we aimed at two different temperature lists: 500 – 2000 K, to provide rates for future kinetic models, and 300 – 700 K for a direct comparison between rates computed in gas phase, and rates that are computed after considering the solvation effects (this will be in 3.6.2.2.1).

Collisional relaxation has been modeled using the Lennard-Jones (LJ) collision frequency model [198] in combination with the single-exponential down model. For the collision frequency model, the LJ parameters σ = 4.93, 5.23, and 5.48 Å and ε = 693.2, 786.7, and 877.7 K have been used for DMC, EMC, and DEC, respectively. These parameters have been obtained using the adopted 1D-min approach as detailed in [159]. For the bath gas nitrogen the parameters σ = 3.7 Å and ε = 85.2 K have been obtained from $\langle E_{down} \rangle$ = 200 cm⁻¹ · (*T*/300K)^{0.85}. . The single-exponential down model uses an average energy deactivation of $\langle E_{\rm down} \rangle = 200 \text{ cm}^{-1} \cdot (T/300 \text{K})^{0.85}$.

The conventional transition state theory (cTST) and the zero-curvature Eckart approach for tunneling are used to calculate the reaction rate constants for hydrogen abstraction. Because of the high energy barriers and imaginary frequencies, variational effects are expected to be of minor importance.

The same was done in the study of 3-pentanol but only at 500 – 2000 K, and without computing the hydrogen abstraction reactions. The LJ parameters used were: σ = 5.921 Å, and ϵ = 430.83 K.

3.6.2.2.1 Solvation

We study the solvation effects regarding the fact that the carbonates in a lithium battery are solvents, and it is important to investigate the differences in reaction rates between the gas and the liquid phase. To determine solvation rate parameters, we re-optimized the gas-phase structures at the same theoretical level but with the polarizable continuum model (PCM) in the Gaussian software package. While rotor scans haven't been recalculated, as they're expected to change minimally, the single-point energies (SPEs) have been recalculated using the same theoretical approach but with the PCM.

The permittivity used for the three solvents is $\varepsilon = 18.7 \pm 0.4$ for EMC, and $\varepsilon = 19$ for DMC and DEC. This value has been verified and taken from Self et al. [200]. Rate coefficients have been calculated using the MESS software package, yet only the high-pressure limit was taken into account in the discussion for the sake of clarity. Note that the reference state has not been changed and that a change of reference will retain in the transition state for all bimolecular reactions. This affects all H-atom abstractions and reverse reactions of the decompositions. When aiming at using the present liquid phase kinetics, the reference state fitting the indented use must be selected and the barrier heights must be corrected by the corresponding change in free enthalpy.

Chapter 4 Hydrogen Blended with C₅-Chain Fuels

4.1 Introduction

In order to investigate the influence of hydrogen on the reactivity of different fuels, RCM experiments were performed to measure the ignition delay times of each pure fuel and with different percentages of hydrogen. The experimental conditions of each study are summarized in Table 9. Part of these results have been published in the *Proceedings of the Combustion Institute 2022* [201].

4.2 *n*-Pentane

4.2.1 Pure *n*-pentane

4.2.1.1 RCM experiments and Kinetic modeling

The IDTs of *n*-pentane were measured at $p_c = 20$, 15 and 10 bar, at stoichiometric and fuellean conditions, in the temperature range 650 – 950 K. The results for both experiments and simulations are presented in Fig 39. The model used for simulations is the Bugler et al. model [45].



Fig 39 – IDT measurements of n-pentane/'air' mixture at different pressures and equivalence ratios. Solid circles: measured IDT, Empty circles: measured FSIDT, Solid line: simulated IDTs, Dashed line: simulated FSIDTs.

A first stage ignition is observed for $T_c < 770$ K and a strong NTC can be observed. The ignition delay times increase with the decrease of pressure, and are relatively low so that at certain conditions (higher pressures and temperatures) the IDTs are below 2ms making them unreportable.

The model predictions are in a good agreement with the experimental results, with a slight over-estimation at the highest temperatures at $p_c = 10$ bar, and a lower NTC starting temperature at E.R. = 0.5 and $p_c = 20$ bar.

Comparing the two graphs, the IDTs at stoichiometric conditions are lower than those at fuel-lean conditions at all pressure conditions. This result has been previously reported by Westbrook et al. [55] when increasing the E.R. from 0.5 to 1. Plotting the two pressure profiles of the same experiment at $p_c = 10$ bar, $T_c \sim 730$ K and at different E.R. (Fig 40) shows that the time delay before the first stage ignition is not increased significantly, but the extent of the pressure rise during the first stage at E.R. = 0.5 is considerably lower than that at E.R. = 1, which indicates a reduced extent of heat release and smaller temperature increase during the first stage. This behavior is also predicted by the model, although it does not capture the slight increase in the FSIDT.



Fig 40 - Pressure profiles of n-pentane/'air mixture' at $p_c = 10$ bar and $T_c = 730$ K.

4.2.2 *n*-Pentane/Hydrogen blends

4.2.2.1 RCM experiments and Kinetic modeling

Fig 41 and Fig 42 present the effect of hydrogen addition on the ignition of *n*-pentane at stoichiometric and lean conditions respectively. The results are shown for the three different pressures investigated in this study ($p_c = 20$, 15, and 10 bar), and three different *n*-pentane/H₂ blends with 0%, 25% and 50% H₂. The IDTs increase with the increase of the hydrogen proportion mostly at the lowest temperatures. As the temperature increases, the effect of H₂ appears to be less significant. The model is able to predict this effect with a slight underestimation of the IDTs in the case of blends with hydrogen.



Fig 41 - IDT measurements of n-pentane/ H_2 at different pressures and at E.R. = 1. Solid circles: measured IDT, Empty circles: measured FSIDT, Solid line: simulated IDTs, Dashed line: simulated FSIDTs.

At fuel-lean conditions, the influence of hydrogen is not as pronounced as it is at stoichiometric conditions, and the model's performance is best at $p_c = 10$ bar.



Fig 42 - IDT measurements of n-pentane/ H_2 at different pressures and at E.R. = 0.5. Solid circles: measured IDT, Empty circles: measured FSIDT, Solid line: simulated IDTs, Dashed line: simulated FSIDTs.

In the study of Lee et al. [121] on the blends of *n*-butane/H₂, they explained that the influence of hydrogen on the IDTs is caused by two principle reasons: first, the direct chemical effect of hydrogen on the combustion processes, and second, the dilution of the fuel by replacing part of it with hydrogen. To test this theory, they used an imaginary hydrogen (IH₂), which possesses the same thermodynamic properties of hydrogen without being reactive. So, when IH2 is added, it doesn't participate in the reaction, but reduces the mole fraction of the fuel. Their final results showed that the chemical effect on the change in the IDTs is approximately twice that of the dilution effect at 750 K and 830 K. At 910 K, the hydrogen effect is mostly caused by the dilution effect. The results are shown in Table 13.

Table 13 – The dilution and chemical effects of hydrogen addition on the ignition delay at $\Phi = 1$ and $p_c = 25$ bar. Reproduced from Lee et al. [121].

Temperature	0%H ₂	50%IH ₂	50%H ₂	Dilution/chemical
750 K	7.40	8.00	9.23	32.8/62.7%
830 K	7.52	8.88	11.13	37.7/62.3%
910 K	7.14	8.05	8.07	97.8/2.2%

4.2.3 Kinetic analyses

4.2.3.1 Rate of production and sensitivity analyses

A pathway analysis for *n*-pentane without hydrogen was carried out at $\phi = 1$, $p_c = 10$ bar and $T_c = 765$ K, i.e. the temperature at which the NTC domain begins, at 10% fuel conversion, to first understand the reactivity of *n*-pentane at these conditions. The results are shown in Fig 43. The fuel is mainly converted through hydrogen abstraction reactions by radicals, the $\dot{O}H$ radical being the major one. Then the main reaction pathway for the resulting fuel radicals is addition to O₂. At this point, alkyl-peroxy radicals (R \dot{O}_2) are formed, and they either undergo isomerization to form hydroperoxyalkyl radicals ($\dot{Q}OOH$), or concerted elimination reactions forming an alkene and a hydroperoxyl radical (HO \dot{O}).

This competition plays an important role in low-temperature oxidation. The produced QOOH will lead to the low temperature chain-branching reaction sequence, which increases the reactivity by forming hydroxyl radicals (OH). However, concerted elimination reaction will lead to the production of less reactive hydroperoxyalkyl radicals

(HOO). Fig 43 shows that H-atom abstraction from two of three sites on *n*-pentane results mainly in the formation of a QOOH radical (1-pentyl radical and 2-pentyl radical), with the abstraction from the third site (3-pentyl radical) leading mostly to the formation of an alkene and a hydro-peroxyl radical.



Fig 43 - Pathway analysis carried out for n-pentane oxidation at $\phi = 1$, $p_c = 10$ bar, $T_c = 765$ K and 10% fuel consumption.

Fig 44 shows that when hydrogen is added, it reacts mostly through an H-atom abstraction reaction by $\dot{O}H$ radical to give hydrogen atoms. These mostly react with oxygen to yield H \dot{O}_2 radicals that are far less reactive than hydroxyl radicals. This explains the increase of the ignition delay times observed when hydrogen is added to the blend.



Fig 44 - Pathway analysis carried out for n-pentane 50%/hydrogen 50% oxidation at $\phi = 1$, $p_c = 10$ bar, $T_c = 765$ K and 10% fuel consumption.

A brute-force sensitivity analysis has been performed in the same conditions as the pathway analysis and is displayed in Fig 45. One can first note that the reactions between n-pentane and $\dot{O}H$ forming the pentyl radicals do not all contribute to an increase of the reactivity. The formation of the pentan-3-yl radical only marginally leads to radical chainbranching, as the elimination of H \dot{O}_2 from the R \dot{O}_2 radical is preferential to internal

isomerization into the QOOH radical in that case. 63.7% of the 3-peroxypentyl radical forms pent-2-ene and a hydroperoxyl radical, a reaction with a strongly positive sensitivity coefficient. The formation of 1- and 2-pentyl radicals on the opposite, increases reactivity, as well as the relevant addition to O_2 or decomposition of 4-hydroperoxypentan-2-one. The influence of hydrogen in this reaction scheme can be understood with help from Fig 44. Sensitivity analysis in the presence of hydrogen shows an inhibiting effect of reactivity via $H_2 + \dot{O}H = \dot{H} + H_2O$, a reaction whose sensitivity coefficient is negligible without hydrogen. This reaction converts $\dot{O}H$ radicals into water and H-atoms in large quantities, as demonstrated in Fig 44. At high pressures, and as previously highlighted by Fig 16, H-atoms will proceed mainly to form HOO through $\dot{H}+O_2+M=HO\dot{O}+M$. However, $\dot{O}H$ is essential to the initial conversion of the fuel in the low temperature combustion temperature range, and its conversion will therefore result in a reduction of the reactivity.



Fig 45 – Brute-force Sensitivity analysis on the ignition delay time of stoichiometric npentane/ O_2/N_2 mixtures at $\phi = 1 p_c = 10$ bar and $T_c = 765$ K.

4.3 3-pentanone

4.3.1 Pure 3-pentanone

4.3.1.1 RCM experiments and kinetic modeling

The IDTs of 3-pentanone were measured at $p_c = 20$, 15 and 10 bar, at stoichiometric and fuel-lean conditions and for the temperature range 650 – 950 K. The results for both

experiments and simulations are presented in Fig 46. The model used for simulations is from Fenard et al. [96].

The results show a negative temperature coefficient behavior and a first stage ignition. It should be noted that the IDTs measured are longer than what is normally reported from an RCM (2 – 200 ms), however, all the data points show a very good reproducibility.

As in the case of *n*-pentane/'air' mixture, the IDTs of 3-pentanone/'air' mixture decrease with the increase of pressure at both equivalence ratios. Similarly, at fuel-lean conditions higher IDTs are reported at 20 bar, and no ignition was observed at pressures 10 and 15 bar except at the highest temperature (\sim 950 K).

The simulated IDTs are in a good agreement with the experimental data at stoichiometric ratios with a slight underestimation at 10 bar. At fuel-lean conditions the discrepancy between the experimental and the modeling values increases, which could be a result of the very long IDTs that are far beyond the limit of the adiabatic core assumption. The model also shows good prediction ability for the FSIDTs at stoichiometric conditions at 20 and 15 bar, however it underestimates the results at 10 bar and at fuel-lean conditions about 30%.



Fig 46 - IDT measurements of 3-pentanone/'air' mixture at different pressures and equivalence ratios. Full circles: measured IDT, Empty circles: measured FSIDT, Solid lines: simulated IDTs, Dashed lines: simulated FSIDTs.

4.3.2 3-pentanone/Hydrogen blends

4.3.2.1 RCM experiments and kinetic modeling

The influence of hydrogen on the ignition of 3-pentanone has been investigated at two equivalence ratios in Fig 47 and Fig 48 respectively, at different pressures: 20, 15, and 10 bar. The hydrogen proportions were 0%, 25% and 50%.



Fig 47- IDT measurements of 3-pentanone/ H_2 at different pressures and at E.R. = 1. Solid circles: measured IDT, full circles: measured FSIDT, Solid lines: simulated IDTs, Dashed lines: simulated FSIDTs.

As the case of *n*-pentane/hydrogen, the addition of hydrogen increases the IDTs throughout all the studied temperature range for stoichiometric mixtures. However; at fuel-lean conditions, adding hydrogen decreases the IDTs at temperatures above 860 K. One might also notice that the addition of hydrogen has almost no effect below 50%.

The model captures this behavior, but predicts the same IDTs for the three blends at high temperatures in the fuel-lean case, and needs improvement regarding the first stage ignition.



Fig 48 - IDT measurements of 3-pentanone/ H_2 at different pressures and at E.R. = 0.5. Solid circles: measured IDT, Empty circles: measured FSIDT, Solid line: simulated IDTs, Dashed line: simulated FSIDTs.

In order to better understand this increase in the IDTs, the model is used to perform different analyses in the next section.

4.3.3 Kinetic analysis

4.3.3.1 Rate of production and sensitivity analyses

Fig 49 shows the most important reactions of the oxidation of 3-pentanone during ignition at $p_c = 20$ bar, $T_c = 700$ K, and 10% fuel consumption.



Fig 49 - Pathway analysis carried out for 3-pentanone oxidation at $\phi = 1$, $p_c = 20$ bar, $T_c = 700$ K and 10% fuel consumption.

The fuel undergoes H-abstraction by \dot{O} H radicals, to give two possible radicals (pentan-3on-1- yl and pentan-3-on-2-yl). Then these radicals add to O₂ to give alkyl-peroxy radicals (R \dot{O}_2). The former radical, for which abstraction took place at the terminal position, undergoes intramolecular migration of H-atom, and then forms a cyclic ether along with a hydroxyl radical. In the case of the latter of these radicals, 57% of the R \dot{O}_2 gives a $\dot{Q}OOH$ radical, the formation of 1-penten-3-one also being significant. Further addition of the $\dot{Q}OOH$ to O₂ followed by an intramolecular H-atom migration yields a ketohydroperoxide + $\dot{O}H$. The decomposition of this ketohydroperoxide produces a second $\dot{O}H$ radical, along with another radical, which lead to the overall increase in reactivity in the low temperature region. This type of analysis was also performed by Fenard et al. [96] and very similar results were reported at 750 K, and a fuel conversion of 20%.

A brute-force sensitivity analysis of 3-pentanone/'air' mixtures on the IDTs without and with hydrogen is presented in Fig 50. Globally, the reactions forming the pentan-3-on-2-yl radical and the reactions leading to the formation of the ketohydroperoxide CC(OOH)C(=O)C(=O)C promote the reactivity. The reactions of elimination of HOO forming pentenone inhibit the reactivity. The blending of pentanone with H₂ has a very similar effect as for *n*-pentane. H₂ depletes the radical pool by undergoing H-atom abstraction, mainly by OH, slowing the fuel conversion and therefore reducing the overall reactivity. This also increases the sensitivity coefficient of the reaction of 3-pentanone and OH to give C5KET3-R2, which is crucial for chain-branching.



Fig 50 -Brute-force sensitivity analysis on the ignition delay time of stoichiometric 3pentanone/ O_2/N_2 mixtures at $p_c = 20$ bar and $T_c = 700$ K.

4.4 1-pentene

4.4.1 Pure 1-pentene

4.4.1.1 RCM experiments and kinetic modeling

1-pentene was studied in the same experimental conditions as *n*-pentane and 3pentanone. A negative temperature coefficient behavior is also reported with two stageignition at the lowest temperatures. The model used for the simulations is taken from Dong et al. [80].



Fig 51 - IDT measurements of 1-pentene/'air mixture' at different pressures and equivalence ratios. Solid circles: measured IDT, Empty circles: measured FSIDT, Solid line: simulated IDTs, Dashed line: simulated FSIDTs.

As the pressure increases, the IDTs decrease. The model's predictions of the IDTs align well with the experimental data, with only a slight overestimation at intermediate temperatures. However, the model significantly overestimates the FSIDTs under fuel-lean conditions.

4.4.2 1-pentene/hydrogen blends

4.4.2.1 RCM experiments and kinetic modeling

Looking at the influence of hydrogen addition on *n*-pentane and 3-pentanone, one might expect the same behavior with 1-pentene. However, at both equivalence ratios and all pressures illustrated in Fig 52 and Fig 53, no significant effect of hydrogen on 1-pentene has been observed using the studied proportions (25 % and 50% of H₂), except for the case of E.R. = 0.5, $p_c = 20$ bar, and $T_c = 800$ K, where the IDT is slightly longer in the case of 50% hydrogen blend, and at E.R. = 0.5, $p_c = 10$ bar and $T_c \sim 1000$ K, where the IDT is much lower with 50%H₂, as expected for hydrogen to act at the high temperature range of combustion.



Fig 52 - IDT measurements of 1-pentene/ H_2 at different pressures and at E.R. = 1. Solid circles: measured IDT, Empty circles: measured FSIDT, Solid line: simulated IDTs, Dashed line: simulated FSIDTs.

The model generally reproduces this behavior, but under certain conditions, it predicts a slight increase in the IDTs, particularly in fuel-lean cases. As for the FSIDTs, the model fails to accurately predict the values, overestimating them by up to five times in the worst scenarios. These results suggest that the model is unable to provide a fully accurate analysis, but it is however still valuable for gaining some insight.



Fig 53 - IDT measurements of 1-pentene/H₂ at different pressures and at E.R. = 0.5. Solid circles: measured IDT, Empty circles: measured FSIDT, Solid line: simulated IDTs, Dashed line: simulated FSIDTs.

4.4.3 Kinetic analyses

4.4.3.1 Rate of production and sensitivity analyses

The ROP analysis for the oxidation of 1-pentene is illustrated in Fig 54 at $T_c = 770$ K and p = 10 bar. The reactions involving the $\dot{O}H$ radical are of two types: either abstraction of an H-atom or an addition on the double bond, followed by addition to oxygen, known as the Waddington mechanism [202].


Fig 54 - Pathway analysis carried out for 1-pentene oxidation at $\phi = 1$, $p_c = 10$ bar, $T_c = 770$ K and 10% fuel consumption.

H-atom abstraction leads to the formation of three different pentenyl radicals, with 1penten-3-yl (C5H91–3) being the predominant radical formed (22%) due to its resonance-stabilization. Part of these radicals react with HOO, ultimately producing C5H9O1–3 and OH radicals. The subsequent decomposition of C5H9O1–3 radicals primarily yields ethyl radicals and acrolein. The other two pentenyl radicals, 1-penten-4yl (C5H91–4) and 1-penten-5-yl (C5H91–5), mainly react with O₂ to form alkenyl-peroxy radicals.

Approximately half of 1-pentene is converted through the Waddington mechanism, where hydroxyl radicals add across the double bond, resulting in the formation of C5H10OH1–2 and C5H10OH2–1 radicals. These radicals then react with molecular oxygen to produce C5H10OH1–2O2 and C5H10OH2–1O2 radicals, which can further react by abstracting an alkoxy H-atom. The subsequent decomposition of the hydroperoxy-alkoxy radical produces aldehydes and OH radicals. In addition to this Waddington reaction pathway, C5H10OH1–2O2 and C5H10OH2–1O2 radicals can also undergo internal H-atom rearrangements involving available H-atoms on other carbon sites, leading to the formation of alcoholic hydroperoxyl-alkyl radicals, which can add to O2 and promote chain-branching.

The NTC behavior observed in *n*-alkanes primarily stems from the competition between chain-branching and chain-propagating reaction pathways, as illustrated in Fig 30. The chain-propagating pathway predominantly produces HOO radicals, which reduce the

system's reactivity and, as a result, lead to a more pronounced NTC behavior. However, in the case of 1-pentene, the H-atom abstraction pathways that produce alkenyl radicals, along with the Waddington mechanism, compete with the chain-branching reaction pathways. Both the Waddington mechanism and the reaction pathway involving 1penten-3-yl radicals with HOO lead to the production of reactive OH radicals, unlike the less reactive HOO radicals generated from alkyl-peroxy radical elimination or from the β scission of alkyl radicals in alkanes. Since the chain-propagation process primarily generates reactive OH radicals instead of HOO radicals, the competition between chainpropagation and chain-branching pathways has a relatively smaller impact on autoignition for alkenes compared to alkanes. Consequently, 1-pentene exhibits a less pronounced NTC behavior (Fig 26).

To understand why hydrogen does not have a significant effect on 1-pentene, sensitivity analyses were performed with and without hydrogen in Fig 55. In contrast with the *n*-pentane and 3-pentanone cases shown in Fig 45 and Fig 36, the sensitivity analysis does not show any specific reaction to the hydrogen sub-mechanism, and the sensitivity coefficients for the other reactions are very similar with and without hydrogen.



Fig 55 – Brute-force sensitivity analysis on the ignition delay time of stoichiometric 1pentene/ O_2/N_2 mixtures at $p_c = 15$ bar and $T_c = 770$ K.

The reaction with the lowest sensitivity coefficient is the formation of pent-1-en-5-yl radical by H-atom abstraction by a hydroxyl radical. As shown in Fig 40, this radical can add onto O₂, leading to the low-temperature chain-branching reaction sequence. To the contrary, the most abundant radicals formed by H-atom abstractions are pent-1-en-3-yl

and pent-1-en-4-yl, their formation showing an inhibiting effect on reactivity. Both of them mainly add to O₂ and yield pentadiene and an hydroperoxyl radical. The reaction of the resonance-stabilized radical pent-1-en-3-yl with HOÓ exhibits a large negative sensitivity coefficient, promoting reactivity by converting HOÔ into the more reactive ÔH. As previously observed for unsaturated hydrocarbons, the reactivity in the low temperature range is controlled by the reactions with HOÔ [125]. HOÔ radicals are formed when H₂ reacts with ÔH radicals. Unlike previous fuels, these radicals actively contribute to the conversion process, which explains why 1-pentene is not significantly affected by the depletion of ÔH radicals. Additionally, ÔH radicals are compensated through an alternate reaction pathway. In this process, hydrogen atoms produced from the recombination reaction add to the double bond of 1-pentene, forming a pentyl radical. This radical then enters the chain-branching pathway, ultimately leading to the regeneration of ÔH radicals.

4.5 3-pentanol

4.5.1 Introduction

As provided by the literature review in section 2.3.1.4, there is only one existing kinetic model for 3-pentanol including the low-temperature reactivity [105]. This model however doesn't show a good agreement with our experimental results, and accordingly a new model is developed in this work, and validated against a wide range of experimental results.

4.5.2 Model development

Base model

The base model used to describe the C_0 - C_4 chemistry is adapted from the NUIGmech1.1. This is a very extensive mechanism and has been validated in a wide range of studies [58], [128], [203], [204], [205]. The sub-mechanism of 2-pentene and 3-pentanone; products of 3-pentanol oxidation, were introduced based on the studies by Dong et al. [80] and Kang et al. [98], respectively.

Few modifications were done to the Kang et al. mechanism for 3-pentanone, which is an updated version of the Fenard et al. mechanism used previously in this study. These modifications include changing the rates of the H atom abstraction by a hydroxyl radical, originally based on analogies to ethyl methyl ketone, with rates calculated for 3pentanone by Serinyel et al. [206]. Recombination reactions were also included after detecting the relevant species during the experiments, which will be further discussed later. It is important to highlight the significance of the 3-pentanone sub-mechanism, which highly influences the performance of the model.

The 3-pentanol sub-mechanism was developed following the reaction classes provided by Pelucchi et al. [207] in their study on nC_3 - C_6 linear alcohols, presented in Fig 56. And the final form of the mechanism consists of 1346 species, and 6142 reactions.



Fig 56 - Simplified kinetic scheme for the pyrolysis, as well as high- and low-temperature oxidation, of linear alcohols. [207].

Unimolecular decompositions

The reaction rate parameters for water elimination from 3-pentanol are taken as an analogy with 2-butanol (to give 2-butene and water as in Fig 57) which was studied by Rosado-Reyes et al. in a shock tube [208].



Fig 57 - Water elimination from 2-butanol.

The kinetic parameters concerning the C-C and C-H bond dissociations in 3-pentanol were considered similar as 2-butanol and taken from the modeling work of Sarathy et al [209].

Bimolecular initiations and H-atom abstractions

For the reactions of 3-pentanol with O_2 and 0-atoms, the reactions rates are chosen similar to 2-butanol [209].

The reaction rate constants for the reaction of 3-pentanol + $X \rightarrow$ pentanolyl radicals + XH were selected based on analogies with recent literature values for 2-butanol, 1- & 2-propanol, given the similarities in their BDEs compared to 3-pentanol as illustrated in Fig 58.



Fig 58 - BDEs in kcal/mol of C-H bonds in different molecules. [210].

These rates were recently evaluated using high-level theoretical calculations. For: - X=OH, analogy with 2-butanol [211]. - X=H, analogy with 1- and 2- propanol [212].

- X=HOO, analogy with 1- and 2- propanol. The published reaction rates are multiplied by a factor of 3 in our model. The reaction rates are still within the typical uncertainties of theoretical calculations [213].

- X=ĊH₃, analogy with 1- and 2- propanol [214].

Fuel's radical isomerization and beta-scission

The rates of the isomerization and β -scission reactions are computed in this work as described in section 3.6 and are incorporated into the mechanism. In the following potential energy surface (PES) in Fig 59, it is evident that PENT3OH-3 (R3) is the most stable radical. Conversely, PENT3O (R4) is the least stable radical and has the lowest energy barriers for isomerizing into the other radicals. The β -scission of C-H bonds shows higher energy barriers than C-C or C-O bonds. The rates are found in the SM (7.5).



Fig 59 - Potential energy surface of 3-pentanol radical isomerization and β-scission. The energy of R1 is set to zero. The energies are zero point corrected at 0 K.

Low temperature chain-branching

The rate constants of the first and second additions to O₂ were taken from the study by A. Miyoshi [215], who computed the rate constants for the addition reactions of alkyl

radicals with O_2 for C_2H_5 , i- C_3H_7 , n- C_4H_9 , s- C_4H_9 , and t- C_4H_9 . The rates of the reactions between alkyl radicals and R O_2 were taken from Sarathy et al. [209], using an analogy to 2-butanol.

The internal H-migration from RO₂ to QOOH reaction rates were taken from Sharma et al. [216], who calculated the rate coefficients for a series of reactions and molecules involved in the intramolecular hydrogen transfer in alkylperoxy radicals and hydroperoxyalkylperoxy radicals.

The HOO elimination from RO₂ and QOOH, as well as the cyclic ether formation, were taken from Villano et al. [217], who calculated the high-pressure rate coefficients for several reactions of β -, γ -, and δ -QOOH isomers: isomerization to RO₂, cyclic ether formation, and selected β -scission reactions for a series of small to intermediate-sized hydroperoxy alkyl radicals for alkanes.

The rate constants for the Waddington mechanism for alcohols were taken from Li et al. [218] for butanol isomers.

Thermochemical and transport data

The thermodynamic data for the high temperature species in the 3-pentanol sub-model were taken from Carbonnier et al. [103]. The missing thermochemical data and the transport data were estimated via group additivity method on RMG website [219].

4.5.3 RCM experiments and modeling

4.5.3.1 Pure 3-pentanol

The IDTs of 3-pentanol were measured using the RCM under the same experimental conditions as the other fuels discussed in this chapter: $p_c = 20$, 15 and 10 bar, E.R. = 1 and 0.5, in the range of 650 – 950 K. No FSIDTs were detected during the experiments, and the IDTs did not exhibit a strong NTC behavior, although they did not perfectly follow the Arrhenius behavior. The IDTs decreased with increasing pressure, and no ignition occurred at a pressure of 10 bar, or at the lowest temperatures at 15 bar under fuel-lean conditions.

The model developed in this study accurately predicts the experimental results across all conditions presented. The simulated IDTs fall within a 20% uncertainty range compared to the experiments, except at 15 bar under stoichiometric conditions, where the model

underpredicts the IDTs at the lowest temperatures by nearly 30%. To the contrary, the Chatterjee et al. mechanism shows a discrepancy of more than 50% at most cases, in addition to predicting an NTC behavior which was not observed experimentally.



Fig 60 – 3-pentanol IDT measurements at different pressures and equivalence ratios. Solid circles: measured IDT, solid lines: simulated IDTs using the model from this study, dashed lines: simulated IDTs using the model from Chatterjee et al. [105].

4.5.3.2 **3-Pentanol/Hydrogen blends**

3-pentanol was also studied in blends with hydrogen at different pressures: $p_c = 20$ and 15 bar, and at equivalence ratios of 1 and 0.5, and are presented in Fig 61 and Fig 62 respectively. At stoichiometric conditions, as the hydrogen proportion in the blend increases from 0 to 50%, the IDTs increase, similar to what was observed with *n*-pentane and 3-pentanone. The model shows qualitative agreement; however, with 50% hydrogen, it underestimates the IDTs by up to 50% at the lowest temperatures, and IDTs above 200 ms. This implies that there is some space for improvement in the LTC pathways.



Fig 61 - The influence of hydrogen addition on the IDTs of 3-pentanol at different pressures and E.R. = 1. Solid circles: measured IDT, lines: simulated IDTs.



Fig 62 - The influence of hydrogen addition on the IDTs of 3-pentanol at different pressures and E.R. = 0.5. Solid circles: measured IDT, lines: simulated IDTs.

Under fuel-lean conditions, below 800 K, the addition of hydrogen leads to the increase of the IDTs at 20 bar, while no ignition was observed at 15 bar. Above 800 K, the IDTs are minimally affected by hydrogen addition, as captured by the model. However, as the hydrogen content increases, the discrepancy between simulated and experimental IDTs reaches 50% at lower temperatures, where the measured IDTs are very long (~415 ms).

4.5.4 Sampling experiments

A separate set of sampling experiments was conducted under EOC conditions of 735 K and 20 bar, where the IDT was 71 ms. During oxidation, 11 different intermediate species were identified as presented in Fig 63.



Fig 63 – Chromatogram of 3-pentanol/'air mixture' sample at 64 ms of the total ignition delay using PBQ column and FID detector. Each peak is assigned to its respective molecule and retention time (RT).

The experimental and simulated evolution of 3-pentanol mole fractions, along with the identified species, are illustrated in Fig 64.



Fig 64 - The evolution of the mole fraction of the fuel and the intermediates formed during the ignition delay time of 3-pentanol/'air mixture' at $\Phi = 1$, $p_c = 20$ bar and $T_c = 735$ K. The red tick presents the total ignition delay time. Solid lines present simulation done using the model from this study, and dashed lines present simulations with Chatterjee's mechanism [105].

The fuel shows minimal conversion before 40 ms of its total IDT, with most species beginning to form around this time. 3-pentanone and 2-pentene however, were observed as soon as the EOC. A mixture of 3-pentanol/'air' was injected in the GC to confirm that no traces of these species were formed as a result of any reactivity prior to ignition. Three species derived from 3-pentanone identified: 1-pentene-3-one, 2were methyltetrahydrofuran-3-one, a cyclic ether produced during the low-temperature oxidation of 3-pentanone (presented in Fig 12 and Fig 49), and 2-methyl-3-pentanone, a recombination product of the 3-pentanone radical at the secondary carbon with a methyl radical. The last two were not considered in the Chatterjee mechanism. 2-Methyl-3pentanone and MVK were not quantified according to their very low quantities, however potential routes to their formation were still incorporated into the mechanism.

The graphs in Fig 64 are not normalized with respect to the IDT. The model developed in this study accurately predicts both the IDT and the evolution of the fuel's mole fraction, unlike the Chatterjee mechanism, which overestimates the IDT by 43% and qualitatively misrepresents the evolution of the mole fractions. The Chatterjee model predicts that fuel conversion primarily occurs at the point of ignition, which consequently results in the delayed formation of species.

The present mechanism also captures the overall trend for 3-pentanone, propanal, and 2butanone, with overestimation of their production peak by a factor of 2 for the former two species, and a factor of 1.6 for the latter. It also predicts very well the evolution of acetaldehyde, 1-pentene-3-ol, 1-pentene-3-one and 2-methyl-tetrahydrofuran-3-one.

Acetaldehyde and propanal are produced through the reactivity of $R\dot{O}_2$ as illustrated below:



Acetaldehyde was observed in more quantities than propanal, as it is also a dissociation product of KHP.

The mole fraction of 2-pentene remains nearly constant throughout the ignition delay, which the model fails to capture, suggesting missing reaction pathways. Additionally, the model predicts a peak in ethylene production just before ignition, which was not observed experimentally due to the very short time resolution of this peak.

4.5.5 Kinetic Analyses

4.5.5.1 Rate of production and sensitivity analyses

The rate of production analysis in Fig 65 and the sensitivity analysis with and without hydrogen in Fig 66, were performed using conditions relevant to sampling experiments, of which $T_c = 735$ K, and $p_c = 20$ bar, at stoichiometric fuel conditions. The species detected during sampling are highlighted in green in the ROP analysis of 3-pentanol in Fig 65 and 3-pentanone in Fig 49.

The hydrogen abstraction from 3-pentanol produces four different radicals: primary, secondary, tertiary, and an alkoxy radical. The decomposition of 3-pentanol primarily leads to the formation of secondary radicals, as there are four hydrogen atoms at the secondary carbon site, compared to only one at the tertiary carbon site. Although the primary carbon sites have the highest number of attached hydrogens (six), hydrogen abstraction reactions do not primarily form primary radicals due to the higher BDE of primary C-H bonds. The BDE of O-H bonds is the highest, making the formation of the alkoxy radical the least favorable (see Fig 58). Two out of the 4 produced radicals, i.e., the secondary and the primary radicals, proceed into chain-branching, to finally give a pool of radicals responsible for driving the reactivity. They also take part in chain-propagation and give PENT3OH-D1 and PENT3OH-D2 along with hydroperoxyl radicals. The QOOH formed during branching can also decompose to give alkoxy and hydroxyl radicals. The tertiary radical of 3-pentanol gives 3-pentanone and a hydroperoxyl radical, and 3-pentanone then follows the pathway shown in Fig 49. The 3-pentanoxyl radical decomposes into propanal and an ethyl radical.



Fig 65 - Pathway analysis performed for 3-pentanol oxidation at $\phi = 1$, $p_c = 20$ bar, $T_c = 735$ K and 10% fuel consumption.

The sensitivity analysis in Fig 66 suggests that the formation of the 3-pentanol tertiary radicals inhibits reactivity. This is due to the chain-propagation leading to the formation

of 3-pentanone and HOO radicals, rather than chain-branching species. The reactivity is primarily driven by the primary and secondary 3-pentanolyl radicals (PENT3OH-1 and PENT3OH-2, respectively), whose initial production shows a negative sensitivity coefficient, indicating their crucial role in driving reactivity. In particular, the reactions with the greatest impact on increasing reactivity are those involved in the low-temperature chain-branching of the secondary 3-pentanolyl radicals. Conversely, the reaction that most inhibits reactivity is the decomposition of 2-peroxy-3-pentanolyl (TC5H100H-202) into HOO radicals and 2-pentene-3-ol (PENT3OH-D2). This pathway competes with the chain-branching pathway that primarily drives reactivity, ultimately reducing the overall reactivity.



Fig 66 – Brute-force sensitivity analysis carried out for 3-pentanol oxidation at $\phi = 1$, $p_c = 20$ bar, $T_c = 735$ K.

To understand the impact of hydrogen on IDTs, the sensitivity analysis was also conducted for a 3-pentanol/H₂ blend mixture at the same conditions. Similar to the behavior observed with *n*-pentane and 3-pentanone, the reaction between $\dot{O}H$ and H₂ is the primary reason for reduced reactivity when hydrogen is added. This reaction shows a positive sensitivity coefficient in the hydrogen case, whereas its influence is negligible without hydrogen. Additionally, the H radicals produced react with O₂ to form HOO radicals, a reaction that exhibits nearly double the positive sensitivity coefficient in the presence of hydrogen.

4.6 Conclusion of the chapter

The effects of hydrogen addition on *n*-pentane, 3-pentanone, 1-pentene, and 3-pentanol were investigated both experimentally and numerically, leveraging their similar chemical structures but different functional groups. Experiments were conducted at varying pressures (20, 15, and 10 bar), equivalence ratios (1 and 0.5), and hydrogen proportions (0%, 25%, and 50%) using the U-Lille rapid compression machine. Three existing models from the literature were tested for the first three fuels, while a new model was developed for 3-pentanol and validated under a wide range of conditions. Rate of production and sensitivity analyses were performed to gain deeper insight into the effect of hydrogen across the temperature range of 650 K to 970 K.

In the case of *n*-pentane, 3-pentanone, and 3-pentanol, a decrease of the global reactivity towards ignition is observed when hydrogen is added in all conditions. This effect is moderate however reproducible, demonstrating a clear trend for these fuels. Kinetic analysis shows that the conversion of hydroxyl radicals through reaction with H₂ to form water and H-atoms is responsible for this effect. H-atoms are indeed quickly converted into hydroperoxyl radicals, whose contribution to low-temperature chain-branching is limited.

Hydrogen has no detectable effect on the ignition delay times of 1-pentene. This is because the H radicals produced add to the double bond of 1-pentene, creating a new reaction pathway that leads to chain-branching. This new pathway effectively compensates for the hydroxyl radicals initially consumed, thereby nullifying any impact on ignition delay times.

Chapter 5 Next Generation Fuels: Tetrahydro-pyran and Trimethoxymethane

5.1 Introduction

In this chapter, two distinct sustainable fuels are studied: tetrahydropyran, a secondgeneration bio-fuel, and trimethoxy methane, an e-fuel. These studies were conducted in collaboration with different groups across various laboratories. The research on THP has is published in the Proceedings of the Combustion Institute.

5.2 Tetrahydro-pyran (THP)

The reactivity and LTC behavior of THP were studied using the RCM to measure IDTs at pressures of 5, 10, and 15 bar under stoichiometric fuel conditions. To further explore the reactivity and validate the underlying chemical mechanisms, sampling experiments were performed. This study represents the first investigation of THP within the LTC regime using this experimental approach. Based on the experimental results, our team developed and tested a corresponding model to simulate the observed behavior.

Note that the mechanisms recently developed by Zou et al. [141] and Hoblos et al. [142] were also tested using our results and did not demonstrate better accuracy than the model developed in this work.

5.2.1 IDT results

The evolution of the IDTs of THP vs temperature is illustrated in Fig 67. FSI is observed with an NTC that becomes less steep as the pressure increases. The model captures this trend, showing a very good agreement with the experiments at 15 and 10 bar, but exhibits quantitative discrepancies below 700 K at 5 bar, where total IDTs are overpredicted by

almost 50% in the worst cases. This could be a result of the possibly non-homogeneous core at very low pressures, which is not taken into account in the modeling.



Fig 67 – THP IDT measurements of non-diluted THP/'air' mixture at $p_c = 15$, 10 & 5 bar and at stoichiometric conditions.

5.2.2 Sampling results

A separate set of gas sampling experiments was conducted under EOC conditions of 730 K and 10 bar. Unlike the non-diluted mixtures used for IDT measurements, this mixture was diluted with a 90:10 $N_2:O_2$ ratio to extend the IDT to 54 ms at the specified temperature and pressure, enabling finer resolution for sample collection.

Fig 68 presents a sampling profile of the mixture after ignition at 70 ms, alongside the evolution of fuel concentration during and after the ignition delay. The sampling times were strategically chosen to cover all phases of the ignition delay, allowing for the identification of different species formed before the first stage of ignition, during the cool flame, between the cool flame and total ignition delay, and during ignition.

Two significant mole-fraction drops are observed: the first during the cool flame phase and the second during ignition. Each point represents a different compression/sampling experiment, and while the fuel is getting converted, other intermediates are produced.



Fig 68 – Evolution of THP mole-fraction during the ignition delay and after.

Thirteen intermediates, in addition to CO, were identified and are depicted in Fig 69. Our collaborators at the University of Georgia also detected these intermediates, along with others, during their JSR experiments using EI-MS and VUV detectors [220].



Fig 69 – *Chromatogram of THP sampling at* 45 *ms using PBQ column.*

Some species are produced in too low quantities to yield reliable quantification, such as pentanedial and tetrahydropyran-3-one. The other species' mole-fraction profiles are illustrated in Fig 70.



Fig 70 - Experimental and simulated (lines) mole fraction profiles of the fuel and intermediates formed during two-stage ignition of THP mixture at $p_c = 10$ bar, $T_c = 730$ K, E.R. = 1 and at 90:10 $N_2:O_2$ diluted condition.

It is important to note that a relatively small uncertainty ($\sim 11\%$) is observed between the experimental IDT (54 ms) and the simulated IDT (47.9 ms). However, this uncertainty can complicate the comparison between the experimental and modeled mole fractions. To address this, the profiles are presented in normalized time with regards to ignition.

The influence of the FSI on the conversion of THP is evident. As discussed earlier in Fig 68, during the cool flame phase, the mole-fraction drops by about 3000 ppm (21% of the original fuel mole-fraction). This drop is well predicted by the model. However, after the cool flame, the model predicts higher rates of conversion than what is experimentally observed. Carbon monoxide is produced during the cool flame and its mole fraction increases monotonically until the total ignition. The simulated mole fractions of CO are well predicted at all times, however, close to ignition the CO mole fraction peak takes place for a very short time, which makes it not possible to capture experimentally.

The oxidation of tetrahydropyran forms two conjugate alkenes: 3,4-dihydro-2H-pyran and 3,6-dihydro-2H-pyran, via the scheme shown in Fig 71.



Fig 71 - THP radicals, pathways, and corresponding conjugate alkenes formed in tetrahydropyran oxidation from \dot{R} + O_2 reactions.

The findings by Rotavera et al. [137] explain the prevalence of 3,4-dihydro-2H-pyran (3,4-DHP) over the other isomer, 3,6-dihydro-2H-pyran (3,6-DHP). In their MPIMS experiments on Cl-initiated oxidation, 76% of the α -radical was produced, while only 8% of the γ -radicals formed. This α -radical subsequently leads to the formation of the 3,4-DHP isomer. This observation is consistent with the fact that the BDE of the C-H bond at the α position is the lowest, followed by the γ position, and then the β position.



Fig 72 – C-H BDEs in kcal/mol of different bonds using RMG website [219].

The predicted shape of the mole fraction profiles of the alkene intermediates is similar to that measured experimentally, but there exist quantitative discrepancies, especially for the 3,6-DHP. The mole-fraction of 3,4-DHP decreases at a normalized time of 0.50 in the experiment versus 0.25 in the model, which is influenced in the first place by the predicted conversion time of the fuel. However, the amounts of 3,4-DHP formed at these inflection points are comparable between the experiment and the model, with mole-fractions of 540 ppm and 480 ppm, respectively. In contrast, the mole-fractions of 3,6-DHP are overestimated by as much as a factor of 5.

Furthermore, some of the species presented, other than the conjugated alkenes, were also part of the decomposition products detected by Rotavera et al. [137], like ethylene, acrolein, and oxirane (which further transforms to acetaldehyde) as products of the following reactions.



Fig 73 - Decomposition of THP-R \dot{O}_2 into different products by Rotavera et al. [137].

The production of these species is well described by the model, with an overprediction of the amount of ethylene produced before ignition.

Propene and 1-butenal, are well-captured by the mechanism qualitatively and quantitatively, and their mechanism of production is elaborated later in this chapter.

In spite of the success of the mechanism regarding these species, it shows significant discrepancies with others like butene, butadiene, and tetrahydrofuran, indicating that the model still requires further improvement. More data on this topic, including another RCM IDT dataset acquired by another group, and JSR data are provided in the collaborative work, entitled "Low-temperature ignition and oxidation mechanisms of tetrahydropyran", published in the Proceedings of the Combustion Institute [220].

5.2.3 Rate of production and sensitivity analyses

As previously mentioned, the model shows discrepancies with part of the species detected during sampling experiments. To gain a deeper understanding of these discrepancies, a reaction pathway analysis and a sensitivity analysis are shown in Fig 74 and Fig 75 respectively. They were conducted at $T_c = 730$ K and $p_c = 10$ bar, after 20% of the fuel had been converted.



Fig 74 - Pathway analysis carried out for THP oxidation at $\phi = 1$, $p_c = 10$ bar, $T_c = 730$ K and 20% fuel consumption. Labels according to the species names in the model.

The formation of THP1R through hydrogen abstraction at the α -position relative to the ether group significantly enhances reactivity, as indicated by reactions R1 and R2 in the sensitivity analysis. This pathway promotes chain-branching, which further increases reactivity, as highlighted by R6. Additionally, the formation of pentanal-5-yl (R5) also contributes to increased reactivity, as pentanal-5-yl decomposes into 1-butyl and carbon

monoxide. Another branching pathway may emerge from the addition of O_2 to 1-butyl, further driving reactivity, as suggested by R7, R9, and R10.

In contrast, hydrogen abstraction at the β -position (R20) reduces reactivity. Pathway analysis shows that THP2R can undergo ring-opening via C–O bond scission, forming an alkoxy radical. This pathway, represented by R18, also leads to decreased reactivity. Similarly, pathways producing conjugated alkenes (R14, R15, and R19) exhibit positive sensitivity coefficients, as they generate less reactive HOO radicals. The pathway leading to THPO15 (R11) also reduces reactivity, largely due to the formation of the highly stable pentanedial.



Fig 75 – Brute-force sensitivity analysis conducted at T_c = 730 K and p_c = 10 bar at stoichiometric condition.

As mentioned earlier, the α - \dot{R} undergoes ring-opening and form pentanal-5-yl. In this case, a favorable intramolecular H-transfer results in the formation of pentanal-1-yl, which likely decomposes into 1-butyl and CO through decarbonylation (R1') [221]. The absence of intermediates that arise solely from the reaction of O₂ with pentanal-5-yl, such as 4-pentenal, further highlights that the primary consumption pathway for pentanal-5-yl leads to the formation of 1-butyl and CO.



Accordingly, the connection between tetrahydropyran and *n*-butane oxidation becomes clear and shows that fundamental understanding of peroxy-radical reactions in alkanes is also important for modeling cyclic ether combustion. Branching fractions for H-abstraction from linear aldehydes almost exclusively favor the aldehydic carbon site [207].

If O₂ addition to pentanal-5-yl occurs instead, a similar reaction mechanism involving intramolecular H-transfer of the aldehydic H-atom to the peroxy group and subsequent decarbonylation may take place, resulting in hydroperoxy-but-4-yl (R2'). This directly links to the peroxy-radical reactions explaining the oxidation of 1-butyl.



One way that results in the formation of propene is the direct decomposition of the resulting hydroperoxy-but-4-yl. If the latter isomerizes into hydroperoxy-but-2-yl, the decomposition leads to the production of 1-butenal.

Pentanedial, a stable product formed from the ring opening of α - α '-QOOH, was not quantified in our experiments as mentioned earlier. Fig 76 highlights the pathways leading to this species, and its consumption. The current mechanism dictates that pentanedial consumption occurs exclusively through the abstraction of one of the two aldehydic H atoms, followed by decarbonylation to form butanal-4-yl. Given the experimental conclusion that the primary pathway for pentanyl-5-yl consumption is the formation of 1-butyl, it is reasonable to expect that butanal-4-yl follows a similar pathway to yield 1-propyl and CO. So, one way to improve the model is by including the latter in the mechanism.

These pathways also suggest ways for the production of propene, butene, and tetrahydrofuran.



Fig 76 - Reaction mechanism describing fate of tetrahydropyran-1-yl ring-opening pathways leading via decarbonylation to 1-butyl and 1-propyl radicals. Subsequent reaction of the alkyl radicals with O₂ may contribute to chain-branching during tetrahydropyran oxidation. Similar decarbonylation reactions of tetrahydrofuran-1-yl provide another pathway to 1-propyl, which may subsequently contribute to chain-branching via second-O₂-addition. [220].

The ability of α -radicals to undergo ring-opening highlights two deficiencies in the current model, partially explaining the discrepancies in predicted IDTs. First, the ring-opening of α -R introduces additional chain-branching pathways through O₂ addition to QOOH radicals formed from the oxidation of 1-butyl [222] and 1-propyl [223], [224]. Accurate modeling of the balance between QOOH-mediated pathways is crucial, particularly the rates for unimolecular pathways (QOOH \rightarrow products) relative to bimolecular pathways (QOOH + O₂ \rightarrow products).

5.3 Trimethoxy-methane (TMM)

The low temperature oxidation of TMM was investigated using the RCM at pressures of 15, 10 and 5 bar, at stoichiometric and fuel-lean conditions, the inert-to-oxygen ratio was fixed at 8.52:1. Two models were tested upon our results; the model from Döntgen et al. [159], and a model that is still under development at Laboratory of Chemical Technology of the University of Ghent by De Ras and his co-authors as part of collaborative work [225]. This model is developed using the AramcoMech1.3 [124] as a base model, in addition to the OME₂ sub-mechanism previously developed by the same team [226], and finally by including the tertiary carbon chemistry of TMM using the automatic kinetic model generation code Genesys [227].

5.3.1 IDT measurements

Fig 77 shows experimental TMM IDTs at the mentioned conditions. The range of temperature at which the results were obtained is 680 – 935 K, and was limited by the

reactivity of TMM. TMM IDTs display a modest non-Arrhenius behavior in the current investigated temperature, pressure, and equivalence ratio ranges. The reactivity of TMM monotonously increases with all three parameters. No NTC behavior is observed; this could be explained by the absence of the chain-propagating pathways leading to further production of HOO radicals. However, a first stage ignition takes place at lower temperatures.



Fig 77 – Evolution of the IDTs of TMM at different equivalence ratios and pressures.

Both mechanisms are tested against all experimental conditions studied, and are presented in Fig 78.

The model by Döntgen et al. predicts the total IDTs more accurately under almost all conditions except at the lowest temperatures for stoichiometric mixtures at 15 and 10 bar, and for fuel-lean mixtures at 15 bar. In these specific scenarios, the model developed by De Ras et al. demonstrates superior performance, providing a highly accurate prediction of the FSIDTs, where the Döntgen model falls short. This suggests that the latter may benefit from further refinement in this area to enhance its predictive capabilities. Additionally, the Döntgen model fails to predict ignition at the lowest temperature for E.R. = 0.5 and $p_c = 15$ bar, while it predicts ignition during compression at the highest temperatures for E.R. = 0.5 at 10 bar and 5 bar.



Fig 78 – Comparison between Döntgen et al. and De Ras et al. models on TMM IDTs. Solid circles: measured IDT, Empty circles: measured FSIDT, Solid line: simulated IDTs, Dashed line: simulated FSIDTs.

5.3.2 Rate of production and sensitivity analyses

Reaction pathway and sensitivity analyses are provided at $T_c = 770$ K, $p_c = 10$ bar, and E.R. = 1 using both models to better monitor the differences between them.



Fig 79 – TMM reaction pathway analysis performed at 20% fuel conversion, Tc = 770 K, pc = 10 bar, and E.R. = 1. The numbers in black represent Döntgen model and the numbers in green represent De Ras model.

The model from Döntgen suggests that the majority of TMM is converted by H-atom abstraction via $\dot{O}H$ radicals, resulting primarily in the formation of the primary TMM radical. In contrast, the model from De Ras also indicates a significant role for HO \dot{O} in the H-atom abstraction reactions. Both models concur that only a small fraction of TMM leads to the formation of the non-terminal (tertiary) TMM radical. This is primarily due to hydrogen abstraction occurring at just one site, compared to three sites available for forming the terminal radical. Additionally, the steric hindrance caused by the two neighboring oxygen atoms further complicates hydrogen abstraction from this site, making the formation of the non-terminal radical less favorable. In the De Ras model, this tertiary radical almost exclusively undergoes β -scission to form dimethyl carbonate and the methyl radical. However, the Döntgen model proposes that the tertiary radical could

also proceed into the chain-branching pathway, which also results in dimethyl carbonate as well as a hydroxyl radical and formaldehyde.

The produced primary radical mostly undergoes addition to O₂, forming a peroxy radical (RO₂). The De Ras model suggests that internal isomerization mostly occurs from the tertiary carbon, whereas the Döntgen model suggests it can take place on both the tertiary and terminal carbons. This difference is important because the final products of these pathways contribute significantly to the overall reactivity towards FSI. Looking at the sensitivity analysis done using both models, the pathway proceeding from the tertiary radical QOOH (C4H905r_3_m41) to give the DMC-ROOH shows a strong negative sensitivity coefficient. This reaction produces methyl radicals and the ROOH compound of dimethyl carbonate (DMC), thus would usually be considered to be a reactivity-inhibiting reaction. But the DMC-ROOH, decomposes towards CH3OC(=O)OH and produces two highly reactive radicals in the process (OH and HC=O), (R3').



As a consequence, the DMC-ROOH yielding pathway acts as chain-branching reaction in the TMM mechanism.

Another significant distinction between the two models lies in the second O₂ addition to the QOOH radicals C4H9O5r_3_m41 and C4H9O5r_3_m42. While both models agree on the O₂ addition to the latter, only the Döntgen model proposes that the former radical also undergoes this O₂ addition. The Döntgen model suggests that these additions exhibit a negative sensitivity coefficient, indicating their crucial role in enhancing reactivity. In contrast, the De Ras model does not consider the second O₂ addition relevant in the oxidation of TMM, instead attributing the reactivity to QOOH radicals that exclusively drive low-temperature chain-propagation, which explains the weak non-Arrhenius behavior observed in the IDT measurements.

On the other hand, the two most important reactions with an inhibiting effect as presented by Döntgen model are the β -scission of the primary radical (\dot{R}) and the H-atom abstraction via $\dot{O}H$ at the tertiary site of TMM. Both reactions lead to the production of $\dot{C}H_3$ radicals, which are considered less reactive than $\dot{O}H$ radicals. Consequently, these reactions compete with the primary TMM radical low-temperature oxidation pathway, which is responsible for producing $\dot{O}H$ radicals. Additionally, most of the remaining reactivity-inhibiting reactions involve the β -scission of $\dot{Q}OOH$ radicals. Although these reactions directly or indirectly yield $\dot{O}H$ radicals, they also produce relatively stable cyclic ethers, or carbonate compounds. The model of De Ras also suggests that the β -scission of the primary TMM radical has an inhibiting effect on the reactivity, however the pathway with the most inhibiting effect is the dissociation of the $\dot{Q}OOH$ with a tertiary radical to give DMC, formaldehyde and $\dot{O}H$ radical.



Fig 80 – Brute-force sensitivity analysis using De Ras and Döntgen models at Tc = 770 K, Pc = 10 bar, and E.R. = 1.

5.4 Conclusion to this chapter

IDTs were measured for THP/'air' mixtures using the RCM from 5 to 15 bar bar, at stoichiometric fuel conditions in the low temperature region of combustion (600 K – 950 K). FSIDTs were observed, followed by an NTC behavior. Sampling experiments were conducted using diluted mixtures to track the evolution of the mole fractions of the fuel and the produced species. A kinetic model developed by our group was tested against these experimental results, showing good agreement. The species profiles and sensitivity analysis suggest that direct rate calculations for hydrogen abstraction reactions from THP by OH and HOO radicals, which are currently based on analogy, are necessary.

Additionally, more accurate rates for competing reactions of tetrahydropyranyl radicals—specifically ring-opening versus O₂ addition—are also required.

This study also presents IDTs for trimethoxy-methane under the same temperature and pressure conditions, at equivalence ratios of 0.5 and 1. The results show a deviation from Arrhenius behavior and the absence of an NTC behavior. A model in development by De Ras et al. from the Laboratory of Chemical Technology at the University of Ghent was tested and compared with the Döntgen et al. model from the literature. The De Ras model showed good agreement with our experimental data and provided more accurate predictions for the FSIDTs than the Döntgen model. The key differences between the two models are primarily attributed to the pathway leading to the formation of DMC-ROOH, which acts as a chain-branching mechanism producing reactive hydroxyl radicals, and the second O₂ addition. According to Döntgen et al., the second O₂ addition plays a significant role in enhancing reactivity, whereas De Ras et al. suggest it does not have the same impact.

Chapter 6 From Solvation to Gas phase: An *ab initio* Study on Dimethyl-, Diethyl-, and Ethylmethyl Carbonates

6.1 Introduction

In this study, rate constant calculations were done for H-abstraction reactions by \dot{H} and $\dot{C}H_3$, β -scission, isomerization, and internal H-transfer reactions for three different carbonate esters: dimethyl-, diethyl, and ethyl-methyl carbonate. The B3LYP-D3BJ/Def2-TZVP level of theory was employed for the geometries and vibrational harmonic frequencies, and CCSD(T) level of theory with augmented double- and triple-zeta basis functions (aug-cc-pV(T+D)Z) to calculate the single-point energies. In addition, to investigate the solvation effects, this study is performed in both gas and liquid phases for the first time. This study was performed during a three months stay at the HGD Laboratory – RWTH University in Aachen. All the reaction rates are included in the SM.

6.2 Potential Energy Surfaces

The potential energy surfaces (PESs) for each of the studied molecules are illustrated in Fig 81 for DMC, Fig 82 for DEC, and Fig 83 for EMC. These PESs present a unified view of the chemical processes, including both hydrogen abstraction reactions and unimolecular fuel radical reactions. The hydrogen abstraction reaction energies have been adjusted by considering the products of the abstracting radicals, such as H₂ and CH₄, to ensure accurate representation on the same PES.



Fig 81 - Potential energy surface of DMC H-abstraction by \dot{H} and $\dot{C}H_3$, radical isomerization, internal radical migration, and β -scission. The energy of DMC \dot{R} is set to zero and energetic differences due to different stoichiometric formulas are accounted for by subtracting the energies of H_2 and CH_4 . The energies are zero point corrected at 0 K.

The three PESs each feature three distinct pathways for every radical. Among these, the PES for DMC is the simplest, yielding only one radical, followed by DEC, which produces two radicals, and EMC, which generates three different radicals. For clarity, the most likely pathways for each radical are highlighted in black. In all three cases, the β -scission pathways consistently have the lowest energy barriers, with certain isomerization pathways also being favored in the cases of DEC and EMC. The pathways involving radical migration to the ether-oxygen exhibit the highest energy barriers across all cases, followed by migrations to the solvent's central carbon. However, when the latter pathway converges to produce the same products as β -scission, its energy barrier becomes comparable to that of the β -scission pathway.



Fig 82 - Potential energy surface of DEC H-abstraction by \dot{H} and $\dot{C}H_3$, radical isomerization, internal radical migration, and β -scission for two radicals. The energy of DEC $\dot{R}1$ is set to zero and energetic differences due to different stoichiometric formulas are accounted for by subtracting the energies of H_2 and CH_4 . The energies are zero point corrected at 0 K.



Fig 83 - Potential energy surface of EMC H-abstraction by H and CH₃, radical isomerization, internal radical migration, and β-scission for three radicals. The energy of EMC R1 is set to zero and energetic differences due to different stoichiometric formulas are accounted for by subtracting the energies of H₂ and CH₄. The energies are zero point corrected at 0 K.

6.3 H atom abstraction by hydrogen and methyl radicals in gas phase

For all three carbonates, hydrogen radical abstraction reactions by hydrogen radicals are faster than abstractions by methyl radicals. This trend aligns with similar abstraction reactions reported in the literature [228] and is supported by the PESs, which consistently show a lower energy barrier for hydrogen radical abstraction.



Fig 84 - Site specific rate constants for hydrogen abstraction reactions by H and CH₃ for DMC, DEC, and EMC.

Three-parameter Arrhenius expressions have been fitted to the reaction rate constants and are shown for all abstractions in Fig 84. A comparison of the rate constants for the three solvents' radicals during hydrogen radical abstraction reveals that the fastest abstraction occurs in EMC, leading to the formation of a secondary carbon radical. This is followed by DEC, which also favors the formation of a secondary carbon radical. In both cases, hydrogen abstraction from a secondary carbon is kinetically more favorable than from a primary carbon. However, this trend does not hold for methyl radical abstraction. According to the presented rates, the fastest hydrogen abstraction occurs at the secondary carbon of DEC (except at the lowest temperature), followed by abstraction from EMC's methyl group. This behavior is attributed to stereochemical hindrance from the carbonate moiety, which prevents the bulkier methyl radical from easily approaching the secondary carbon site, as illustrated in Fig 85.



Fig 85 - A scheme of the hydrogen abstraction from the secondary carbon by a methyl group.

To validate our results, we directly compared our calculated H atom abstraction reaction rates for DMC with those for methyl formate from [229]. Given that the H atom is abstracted from the same methyl group in both molecules, and the bond dissociation energies (BDEs) of the C-H bonds highlighted in Fig 86 are nearly identical—98.8 kcal/mol for DMC and 98.6 kcal/mol for methyl formate [210]—we anticipated similar rates. Fig 87 illustrates this comparison for both types of abstraction (by H and CH₃). On the same graph, we also included estimated rates from Glaude et al. [230] for these abstractions, which show a significant deviation from our results. This underscores the importance of providing more accurate input data for existing models in the literature, as well as for those that will be developed in the future.



Fig 86 – Detailed formula of DMC (left) and methyl-formate (right).



Fig 87 - DMC rates from this study and from Glaude et al. [230], and methyl-formate rates from Tan et al. [229]. Abstraction by H in violet and by CH₃ in black.

6.4 β-scission and isomerization

As depicted in the PESs of the solvents, the β -scission and isomerization pathways are the most prominent. In certain instances, the β -scission pathway exhibits the highest reaction rates. Fig 88 provides a comparison of the rates across all β -scission pathways.



Fig 88 - Site specific Rate constants for thermal β -scission.

These rates are influenced by the position of the radical within the molecule. The highest rates are observed for the β -scission of primary radicals on the ethyl group of DEC and EMC, while the lowest rate corresponds to the DMC radical. Conversely, some radicals preferentially undergo isomerization rather than β -scission. The results are consistent between the PESs and the reaction rates presented in Fig 89. For instance, in the case of the R2 radical in DEC, the isomerization pathway has higher rates at lower temperatures, but as the temperature increases, the β -scission reaction becomes dominant. However, for EMC radicals 2 and 3, isomerization between these radicals exhibits higher rates across the entire temperature range.


Fig 89 - Difference between β -scission and Isomerization pathways for DEC and EMC in gas and liquid phases.

As documented in the PES of EMC in Fig 83, the energy barriers for the β -scission pathways are higher than the barrier of isomerization between the two radicals. Comparing the rates of this isomerization between R2 and R3, it appears that the direction towards R2 is faster. This means that the amplified production of R3 leads to more production of R2 via isomerization, and thus indirectly to more R2 dissociation products.

6.5 Solvation

6.5.1 H-atom abstraction reactions

While the rates of H atom abstraction reactions for DMC and DEC are minimally impacted by solvation effects, the hydrogen abstractions in EMC exhibit significant differences. Fig 90 presents the rates for abstraction reactions by both hydrogen and methyl radicals. Compared to Fig 84, the relative importance of the H atom abstraction rates from EMC by H shifts between R2 and R3. Specifically, the rate of R3 production increases, while the rate for R2 remains mostly unchanged. Conversely, in the case of abstraction by $\dot{C}H_3$, the rate of R3 production decreases, leading to a higher production of R2. These shifts would influence the distribution of species in the subsequent β -scission and isomerization reactions. It is important to note that the shape of the profile for the hydrogen abstraction by H rate vs temperature in the case of EMC-R3 is influenced by uncertainties arising during the calculation process. Solvation refers to the electrostatic interaction between molecules and the surrounding solvent, where the solute's dipole moment largely determines the solvent's impact. DMC and DEC are symmetric, meaning their dipole moments are perfectly aligned with the carbonyl group of the carbonate functional group. In contrast, EMC is asymmetric, causing its center of charge to shift towards the ethyl side chain. As a result, the dipole moment of EMC is not aligned with the carbonyl group and is more pronounced. This misalignment appears to be the primary reason why EMC is more significantly affected by solvation effects.



Fig 90 - Rate parameters for hydrogen abstraction by \dot{H} *and* $\dot{C}H_3$ *for EMC in solvation.*

6.5.2 β-scission vs isomerization

The dominant reactions remain the same in both the gas and liquid phases, but their rates differ. As shown in Fig 89, the interception point between isomerization and β -scission for DEC-R2 occurs at higher temperatures in the liquid phase, indicating that more isomerization reactions take place at lower temperatures under solvation compared to the gas phase. For EMC radicals 2 and 3, the extrapolated interception point lies at lower temperatures because the isomerization rates are reduced under solvation compared to the gas phase, although they still surpass the β -scission rates. This indicates that isomerization reactions are the most influenced by solvation effects. Fig 91 presents the rates of the dominant isomerization reactions in both phases, clearly illustrating this difference.

For DEC radicals, the isomerization reaction rates under solvation conditions are nearly two orders of magnitude higher than those in the gas phase at the lowest temperatures. In contrast, for EMC radicals, the reaction rates in the gas phase exceed those in the liquid phase by more than five orders of magnitude. This discrepancy is attributed to the more pronounced dipole moment of EMC, which results in a stronger interaction with the solvent. Consequently, the solvation effects are more significant for EMC, leading to a greater difference in reaction rates between the gas and liquid phases. It is important to note that the limitations of the polarization field method, such as its simplified treatment of induced dipoles, could impact the accuracy of the simulations.



Fig 91 - Effect of solvation on isomerization reactions of DEC and EMC.

All calculated kinetic parameters for the aforementioned reactions are provided in the SM (7.6), which also includes a glossary for easy reference and identification of each parameter.

6.6 Conclusion to this chapter

In this work, the rate parameters of H-abstraction reactions by \dot{H} and $\dot{C}H_3$ of dimethyl-, diethyl-, and ethyl-methyl carbonates, and the subsequent reactions were computed using B3LYP-D3BJ/Def2-TZVP level of theory for the geometries and vibrational harmonic frequencies, and the CCSD(T) level of theory with augmented double- and

triple-zeta basis functions (aug-cc-pV(T+D)Z) to calculate single-point energies (SPEs). This has been done at both gas and liquid phases.

The results show that the rate of hydrogen abstraction reactions by \dot{H} are always faster than the abstractions by $\dot{C}H_3$ which is consistent with the results from literature. For the unimolecular radical chemistry, the β -scission and the isomerization reactions dominate. In contrast, the energy barriers of the internal radical migration reactions are very high, except for the radical migration to the central carbon leading to the same products as for the corresponding β -scission. The rates for β -scission reactions are higher than isomerization rates in all cases, except for the case of EMC radicals 2 and 3, and DEC radical 2 at low temperatures. The direct comparison between the rates with and without solvation effects did not show an important change for most of the reactions using this level of theory. However, certain reactions of EMC, such as isomerization, were substantially affected, potentially due to the polarity of this asymmetric reactant.

Chapter 7 Conclusions Perspectives

7.1 Summary of this thesis

The prolonged burning of fossil fuels has significantly increased greenhouse gas levels in the atmosphere, driving global temperature changes. These temperature shifts can disrupt ecosystems, threatening plant and animal habitats and potentially lead to widespread species extinction. The broader impacts of climate change are extensive and severe, making it clear that these consequences are unacceptable and demand urgent action. One of the most significant greenhouse gases is carbon dioxide (CO₂), which remains in the atmosphere for hundreds to thousands of years. This means that the CO₂ we emit today will continue to impact the climate for generations to come. Unfortunately, our current primary energy sources contribute substantial amounts of CO₂ to the atmosphere, highlighting the urgent need to explore and transition to alternative energy sources. This thesis explores a range of studies focused on alternatives to traditional fossil fuels for energy generation.

Indeed, there are numerous alternatives to fossil fuels, and research efforts are actively exploring various solutions to address this challenge. In this thesis, we focus on three key alternatives: hydrogen, bio- and synthetic fuels, and batteries in the context of electrifying the transportation sector. These options represent pathways toward reducing carbon emissions and transitioning to a more sustainable energy future.

The work on hydrogen in this thesis focuses on blending it with various C₅-chain fuels, each containing a different functional group. This is the first time it has been blended with *n*-pentane and non-alkane groups. Specifically, this study investigates the influence of hydrogen when blended with 3-pentanone (ketone), 1-pentene (alkene), and 3-pentanol (alcohol). The effects are assessed by measuring the ignition delay times (IDTs) of these hydrogen/fuel blends under varying hydrogen proportions (0, 25, & 50%), pressures (10, 15, and 20 bar), and equivalence ratios (E.R. = 0.5 and 1), in the low-temperature combustion range of 600–950 K. Several combustion models from the literature were

evaluated, including the Bugler et al. [45] model for *n*-pentane, the Dong et al. [80] model for 1-pentene, and the Fenard et al. [96] model for 3-pentanone. The simulation results showed good agreement with our experimental data, except for the first-stage ignition delay times (FSIDTs) of 1-pentene, which were overestimated by the Dong et al. model. The model used for 3-pentanol was developed in this work, and was validated on IDT experiments and speciation experiments also performed within the study.

IDTs for tetrahydropyran (THP) were also measured under various pressure conditions (5, 10, and 15 bar) at stoichiometric fuel conditions. Additionally, the evolution of mole fractions of the species produced over time was measured. These experiments were employed to test a newly developed kinetic model for THP, which was based on the low-temperature combustion chemistry of alkanes. The results provided insight into new reactions that could enhance the accuracy and performance of the model.

<u>A comparison between C₅ molecules</u>

Studying several C₅ chain molecules in this thesis allows to investigate the influence of the different chemical group functions on the total ignition, which is illustrated in Fig 94. Among the molecules studied, *n*-pentane and THP exhibit the highest reactivity, followed by 1-pentene, with 3-pentanone and 3-pentanol showing the lowest reactivity.

For carbonyl-containing compounds, like 3-pentanone, the alkyl groups adjacent to the carbonyl have a low C–H bond dissociation energy (BDE) as shown in Fig 92 due to resonance-stabilization of the resulting radical which leads to the delocalization of the radical over the CO group.



Fig 92 - Diagram showing the effect of radical stabilization on the C-H BDE. Adapted from [62].

This also lowers the energy barrier for peroxy radical ($R\dot{O}_2$) dissociation, see Fig 93, which competes with the formation of $\dot{Q}OOH$ —a critical step in chain-branching. This competition explains the high IDTs observed for 3-pentanone.



Fig 93 - Diagram showing the effect of carbonyl group on the R–OO BDE. Adapted from [62].

For alcohols, the reaction of the peroxy radical to give aldehydes or ketones is fast and reduces the formation of QOOH. In the case of 3-pentanol, this mechanism results in the production of HOO and 3-pentanone as follows, further increasing the IDTs.



For ethers, like THP, the situation is different. Ethers have low energy barriers for the formation of QOOH from RO₂, even lower than pentane [62], resulting in short IDTs.

For 1-pentene, the reduced reactivity compared to *n*-pentane is due to the competition between two processes: radical addition to the double bond and hydrogen atom abstraction. This competition limits the overall reactivity, as the presence of the double bond introduces alternative reaction routes that slow down the chain-branching mechanisms essential for ignition.



Fig 94 - *The effect of different chemical group functions on the reactivity, pc* = 15 bar, *E.R.* = 1.

Influence of H₂ on the IDTs

To understand hydrogen's impact on the underlying chemistry, the models mentioned previously were used for analysis leading to several key conclusions:

- For alkanes, ketones, and alcohols, adding hydrogen increases the IDTs at low temperatures. This effect is attributed to the interaction between the added hydrogen and the $\dot{O}H$ radicals in the system, producing \dot{H} and H_2O . On one hand, the reactive $\dot{O}H$ radicals—key drivers of reactivity—are being consumed. On the other hand, the newly formed \dot{H} radicals participate in the reaction $\dot{H} + O_2(+M) = HO\dot{O}(+M)$, generating HOO radicals, which are relatively unreactive. This process ultimately reduces overall reactivity and prolongs IDTs.
- For alkenes, the addition of hydrogen had minimal impact on IDTs. This is primarily because the production of HOO radicals drives the reactivity in the case of unsaturated molecules, in addition to a new chain-branching pathway similar to that of alkanes, created by the addition of the produced H radicals to the double bond of the alkene. This pathway eventually compensates for the OH radicals

consumed earlier, maintaining overall reactivity and preventing a significant change in IDTs.

Hydrogen was not only studied as a blend with C₅-fuels, but also it was studied as a lone fuel, or as a blend with a mixture of natural gas, Fig 95. This project is a collaboration between our team and General Electric and it aims to assess the impact of hydrogen addition on fundamental combustion properties, particularly under high-pressure and moderate-temperature conditions typical of gas turbine auxiliaries.



Fig 95 – Part of the results obtained for NG/H₂.

Due to the confidential nature of this project, the results are not yet to be shared.

In addition to studying hydrogen blends and THP, trimethoxy-methane was also studied using the RCM to measure the IDTs at stoichiometric and fuel-lean conditions, at pressures of 5, 10 and 15 bar. These experiments are used as a validation set of a new kinetic mechanism being under development by the Laboratory of Chemical Technology in the University of Ghent. Although still under development, it shows good agreement with our results. A comparison was also provided between this mechanism and a mechanism from literature to show the key differences between both.

Finally, this thesis also presents an *ab initio* study of various reactions involving alkyl carbonates—specifically dimethyl carbonate, diethyl carbonate, and ethylmethyl carbonate—in both gas and liquid phases. These compounds are used as solvents in lithium batteries. The study focuses on hydrogen abstraction reactions by \dot{H} and $\dot{C}H_3$ radicals, along with subsequent reactions such as beta-scission, isomerization, and internal radical migration. Developing reliable kinetic models for these molecules is essential to better understand their combustion properties and mitigate the risks of

thermal runaway. This research was conducted at the High Pressure Gas Dynamics and Shock Waves Laboratory at RWTH Aachen University.

7.2 Perspectives

1 – During hydrogen's production and storage, its low collision cross-section allows it to easily diffuse through materials, leading to an expected increase in atmospheric hydrogen. Two significant consequences must be considered: first, the potential destruction of stratospheric ozone due to the formation of stratospheric water vapor, and second, indirect climate forcing caused by disruptions to greenhouse gas concentrations. Accordingly, a kinetic study of hydrogen/oxidant mixtures using several kinetic reactors would clarify the reaction mechanism of hydrogen in conditions that have been little explored but are relevant to many energy production sectors.

2 – The continued reliance on practical fuels is essential in the present energy landscape, making it critical to deepen our understanding of their combustion kinetics. However, the complexity of this task lies in the vast number of intermediates generated during the oxidation of long-chain hydrocarbons. These intermediates span various chemical families, each contributing to the intricate combustion process. To develop a reliable and comprehensive kinetic model for practical fuels, it is crucial to validate the submechanisms associated with these intermediates. The surrogate fuels examined in this thesis, each representing distinct chemical functional groups, provide valuable insight into this process. Further studies, including investigations of longer-chain hydrocarbons, will be necessary to build robust models that can support a range of applications.

3 – While studying the combustion kinetics of fuels is crucial, it is equally important to consider other factors, such as fuel ageing, that can significantly impact performance. Biofuels, in particular, are more susceptible to ageing than fossil fuels due to their chemical composition and lower oxidative stability. This makes them more prone to degradation during storage, which can result in poor combustion, engine knock, and incomplete combustion. Therefore, developing comprehensive kinetic models that account for the oxidative stability of biofuels is essential to ensure their efficient and reliable use.

Scientific Valorization

Publications

I. <u>Published articles</u>:

1 – "On the influence of hydrogen on the low-temperature reactivity of *n*-pentane,
1-pentene and 3-pentanone: an experimental and modeling study". Marwa Saab,
Guillaume Vanhove, Yann Fenard.

DOI: <u>10.1016/j.proci.2022.07.145</u>

2- **"Low-temperature ignition and oxidation mechanisms of tetrahydropyran".** Samuel W. Hartness, Marwa Saab, Matthias Preußker, Rosalba Mazzotta, Nicholas S. Dewey, Annabelle W. Hill, Guillaume Vanhove, Yann Fenard, K. Alexander Heufer, Brandon Rotavera.

DOI: <u>10.1016/j.proci.2024.105528</u>

II. <u>Submitted articles</u>:

1 – "*Ab initio* study of the gas- and liquid- phase hydrogen abstraction from dimethyl-, diethyl-, and ethyl-methyl carbonates by H and CH₃ and subsequent reactions". Marwa Saab, Yann Fenard, Guillaume Vanhove, Malte Döntgen, K. Alexander Heufer.

Journal: International Journal of Chemical Kinetics

2 – "Low-temperature ignition of 3-pentanol-hydrogen blends: experimental and model development study". Marwa Saab, Yann Fenard, Guillaume Vanhove.

Journal: Combustion and Flame

III. <u>To be submitted</u> :

"An experimental and kinetic modeling study on the high- and low-temperature oxidation of trimethoxymethane". Kevin De Ras, Marwa Saab, Yann Fenard, Guillaume Vanhove, Kevin M. Van Geem.

Communications

I. <u>Oral</u>:

1 – **Journée Francois Lacas**, Nancy, 17-18 March – 2022: *On the influence of hydrogen on the low-temperature reactivity of n-pentane, 1-pentene and 3-pentanone: an experimental and modeling study.*

2 – **26th "Journées d'Etudes"** of the Belgian section of the Combustion Institute, Ghent – Belgium, 29-30 March – 2022: *On the influence of hydrogen on the low-temperature reactivity of n-pentane, 1-pentene and 3-pentanone: an experimental and modeling study.*

3 – **Graduate program**, Lille, 28 September 2023: *The application of quantum mechanics in the field of kinetic modeling.*

4 – **IREPSE journée scientifique**, Lille, 5 October 2023: *The influence of hydrogen on the low-temperature reactivity of C₅-chain fuels.*

5 – **Journée Combustion H**₂, Orleans, 19 October 2023: Impact of Hydrogen on Low-Temperature Fuel Oxidation: A Comparative Study of 5-Carbon Fuels with Diverse Chemical Groups.

6 – **27th "Journées d'Etudes"** of the Belgian section of the Combustion Institute, Brussels - Belgium, 3 – 5 April 2024: *From Solvation to Gas phase, ab initio study on Alkyl Carbonates for an improved battery safety better understanding of Lithium Batteries.*

II. <u>Poster</u>:

1 - **39**th **International Symposium on Combustion,** Vancouver – Canada, July 2022: *A kinetic modeling and experimental study of the ignition delay times of 3-pentanol/hydrogen blends at low temperatures of combustion.*

2 - **11th European Combustion Meeting**, Rouen, 26 – 28 April 2023: *On the reactivity of Trimethoxy Methane in the low-temperature range of combustion.*

3 - **40**th **International Symposium on Combustion,** Milan – Italy, July 2024: *On the Oxidation of Trimethoxy-methane: An Experimental and Modeling Study.*

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Appendices

7.3 Bibliography on the relevant studies on Alkyl carbonates:

7.3.1 DMC

Table 14 - Summary of the studies found in literature on DMC.

Authors	Year	Conditions	Reactor/Approach
Sinha et al [231]	2004	T = 200 – 2000 K,	Opposed-flow diffusion
		Atmospheric pressure	flames
Glaude et al [230]	2005		Mechanism
			development
Bardin et al [232]	2013	T = 298, 318 K,	Heat flux
		Atmospheric pressure	
Hu et al [233]	2015	T_c = 1100 – 1600 K, p_c =	ST
		0.12 – 1 MPa, Φ = 0.5 –	
		2	
Sun et al [234]	2016	p = 40, 200 & 1040	Flow reactor
		mbar, Φ = 1 & 1.5	
Alzueta el al [235]	2017	T = 700 – 1400 K,	Flow reactor
		atmospheric pressure,	
		λ= 0, 0.3, 1 & 35	
Alexandrino et al	2018	T_c = 795 – 1585 K, p_c =	RCM & ST
[236]		2, 20, & 40 atm, Φ = 0.5,	
		1 & 2	
Henriksen et al [237]	2020	T = 300 K, p = 100 kPa	20-liter explosion
			sphere
Atherley et al [238]	2021	T = 318, 363, & 463 K,	Spherical vessel
		$\Phi = 0.7 - 1.5$	
		T _c = 1260 – 2500 K, p =	ST
		$1.3 \pm 0.2, \Phi = 0.5, 1 \& 2$	

The combustion of DMC was studied by Sinha et al. [231] using a counterflow diffusion flame in which the species concentrations were measured. The absence of C-C bonds was identified as the reason for the reduced formation of ethylene, acetylene, and propylene, with formaldehyde being the primary intermediate. Glaude et al. [230] used the same experiments to build a kinetic mechanism for DMC of which a new molecular elimination path was proposed, and its rate was calculated using CBS-Q methods, in addition to using different literature mechanisms to estimate the rates of other reactions. Then all of these reaction rates were added to previous mechanism for dimethoxy methane and dimethyl ether [239]. The predicted composition profiles were in reasonable agreement with the measured profiles. Then, Bardin et al. [232] used this mechanism in their study to model the measured laminar burning velocity of DMC, and it accurately reproduced the temperature power exponent α . Alzueta et al. [235] used the model from Glaude et al. [230] to evaluated the impact of the thermodynamic data on the modeling results, and found that the enthalpy of formation of the DMC radical significantly influences the DMC conversion results.

Hu et al. [233] were the first to measure the ignition delay times of DMC using a shock tube at different conditions. They tested the mechanism of Glaude et el. [230], and although it showed a good agreement with the experiments done using the opposed flow and the heat flux, yet it did not show a good agreement with the measured IDTs. Therefore, in an attempt to enhance the mechanism, the sub-mechanisms of DMC by Glaude [230] and methyl butanoate by Dooley [240] were added to the AramcoMech1.3 [124]. The proposed model yielded fairly good agreement with the measured IDTs and it was as well validated against the diffusion flame data [231]. This model was tested also by Sun et al. [234] in their study, where both pyrolysis of DMC in a flow reactor, and its oxidation in laminar premixed low-pressure flames, and the model was validated against their results. And it was also tested by Alexandrino et al. [236] who measured the IDTs of DMC at low temperatures using an RCM for the first time, and the model also showed a good agreement.

Henriksen et al. [237] used 20-liter explosion sphere to determine the laminar burning velocity of DMC and tested both mechanisms: Glaude [230] and Sun [234], and the latter showed better predictions than the former.

Atherley et al. [238] used a shock tube for spectroscopic measurements to measure time histories of CO and H₂O, and measured the laminar flame speed of DMC. Both mechanisms were tested over the wide range of conditions targeted, and neither was able to adequately predict the data over the entire range of conditions.

7.3.2 DEC

Table 15 - Summary of the studies found in literature on DEC. The symbol * refers to the studies that also include EMC.

Authors	Year	Conditions	Reactor/Approach
Gordon et al* [241]	1965	T = 350 °C	Quartz reaction vessel
Cross et al* [242]	1976	$T = 300 - 400^{\circ}C$	Reaction vessel
Herzler et al [243]	1997	T _c = 550 – 1300 K, p _c =	ST
		2 – 4 bar	
Notario et al* [244]	2004		Ab initio calculations

Nakamura et al [245]	2015	T _c = 660 – 1300 K, p _c =	RCM & ST
		30 bar, Φ = 0.5, 1 & 2	
		T = 500 – 1200 K, p =	
		10 atm, Φ = 0.5, 1 & 2	
			JSR
Sun et al [246]	2017	T = 30, 150, & 780 torr	Flow reactor - GC
Shahla et al [247]	2017	T = 680 – 1220 K, p = 1	JSR
		atm, Φ = 0.5, 1 & 2	
		T = 393 K, p = 1 – 3 atm,	Pressure-release dual
		$\Phi = 0.7 - 1.4$	chamber
AlAbbad et al [248]	2017	$T_c = 900 - 1200$ K, $p_c =$	ST
		1.2 – 2.8 bar,	
Sela et al [249]	2021	T _c = 830 – 1224 K, p _c =	ST
		1.7 – 2 atm	
		T = 663 – 770 K, p = 1 -	Flow reactor
		bar	

The ignition delay times of DEC were measured using a rapid compression machine and a shock tube, as well as species profiles using a JSR by Nakamura et al. [245]. The rate constants for the isomerization reactions of 5-, 8-, and 9-membered ring $\dot{R}O_2 \rightleftharpoons \dot{Q}OOH$ in DEC were calculated through *ab-initio* computations (CCSD(T)/cc-pVTZ), and these calculations aligned well with rate rules derived from *ab* initio data for alkane $\dot{R}O_2 \rightleftharpoons \dot{Q}OOH$ isomerization reactions. A chemical kinetic model for DEC including both high-temperature and low-temperature oxidation mechanisms was developed, and the model predictions were compared with the experimental data. The model captures the overall trends of intermediate species concentrations and ignition delay times as a function of temperature.

Theoretical calculations were performed to acquire pressure-dependent rate coefficients for unimolecular decompositions of DEC and its dominant products in the study of Sun et al. [246], where the geometries and rovibrational properties of all stationary points were determined at the B3LYP/cc-pVTZ level, and then single point energies for these structures were obtained with the CCSD(T)-F12/cc-pVTZ-F12 method. The resulting theoretical data, in addition to few updates of relevant rate coefficients, were incorporated into the mechanism developed by Nakamura et al. [245]. As a result, the updated model demonstrated satisfactory predictions for all high-temperature measurements.

Shahla et al. [247] measured stable species using a jet stirred reactor, in addition to measuring the burning velocities of DEC/air mixtures. They tested the model from Nakamura et al. [245] and a good agreement was found.

The initial pyrolytic steps of DEC were experimentally and theoretically investigated by AlAbbad et al. [248] using a shock tube. They compared their experimental data with rates calculated by Notario et al. [244], who employed the MP2/6-311++G(2d, p)//MP2/6-31G(d) level of theory and classical transition-state theory. The resulting mechanism was in a good agreement with most of the low-temperature data from this study. However, when extrapolating the values from Notario et al. [244], an overprediction by at least a factor of 2 was observed in the shock tube data from Herzler et al. [243], who measured the rate constants at T > 950 K. Their measured rates were in very good agreement with the experimental data from this study. Additionally, AlAbbad et al. [248] computed temperature and pressure-dependent rate coefficients using the G3//MP2/aug-cc-pVDZ ab initio method combined with master equation calculations, and the computed rate coefficients agreed very well with their experimental results.

Sela et al. [249] aimed to extend the temperature range of directly measured rate constant data for the unimolecular decomposition of DEC. They employed multiple analytical techniques, including shock-tube measurements with GC/MS and high-repetition-rate time-of-flight mass spectrometry (HRR-TOF-MS), and flow-reactor measurements with GC/MS. Similar to Sun et al. [246], they calculated temperature- and pressure-dependent rate constants to describe the measured data. However, instead of using the coupled cluster method, they used the G4 composite method. While there are some differences between the two predictions, both studies refer to the same transition state as the preferred one, as noted by Notario et al. [244]. The results obtained from different experimental techniques are consistent, showing good agreement with the data reported by Cross et al. [242]. In contrast, a significant deviation is observed when comparing to the rate-constant data reported by Gordon and Norris [241]. In comparison to Herzler et al. [243], Sela et al. [249] demonstrate an excellent agreement.

7.3.3 EMC

Table 16 - Summary of the studies found in literature on EMC.

Authors	Year	Conditions	Reactor/Approach
Al-Awadi et al [250]	1979	T = 570 K	Packed tube

Taylor et al [251]	1983	T = 725 – 775 K	Reaction vessel
Chuchani et al [252]	2003	T = 323 – 435 °C, p =	Static reaction system
		28.5 – 242 torr	
Añez et al [253]	2006		Ab initio calculations

Few pyrolysis studies have been performed on EMC. Using a reaction vessel, Taylor et al. [251], Cross et al. [242], Gordon et al. [241], and Al-Awadi et al. [250] measured decomposition rates of EMC around 600 K. There exist huge differences between the rate coefficient reported by Gordon et al that quote a value of 6.9 and that measured by Al-Awadi et al. quoting a value of 52. Therefore, Taylor et al. re-performed the measurements to validate the latter's measurements. After that, Chuchani et al. [252] studied the kinetics of the homogeneous, unimolecular elimination of 2-substituted ethyl methyl-carbonate, as they believe that the previous studies did not take into consideration other mechanisms of decomposition.

Theoretical decomposition rates have been computed by Notario et al. [244], Añez et al. [253], each using a different level of theory, MP2/6–31G(d) and MP2/6–311++G(2d,p) and B3LYP/6-31G* - B3LYP/6-31+ G^{**} respectively.

Table 17 - Summary of the studies found in literature including the three carbonates: DMC, DEC & EMC.

Authors	Year	Conditions	Reactor/Diagnostic
Kanayama et al [254],	2022	T = 700 – 1300K,	MFR (micro flow
[255]		atmospheric pressure,	reactor) - GC
		$\Phi = 1$	
Grégoire et al	2023 - 2024	T _c = 1230 – 2375 K,	ST, MFR – GC
-		atmospheric pressure	

Kanayama et al. [254] is the first study that encompassed the three linear carbonates considered herein. They obtained major species profiles (H₂, CO, CO₂, CH₄, C₂H₄, and C₂H₆) in a micro-flow reactor with a controlled temperature profile, spanning temperatures from 700 to 1300 K, under atmospheric pressure, for both stoichiometric ($\phi = 1$) and pyrolysis conditions. In a complementary study [255], they developed a chemical kinetic mechanism for EMC based on the mechanism of Nakamura et al. [245] for DEC. This mechanism accurately reproduced the measured species data and weak flame position. Recently, Grégoire et al. [256] utilized shock tube spectroscopic CO measurements to investigate the pyrolysis of the three carbonates. They developed a new detailed chemical kinetics pyrolysis mechanism that accurately reproduced the results for DMC and DEC but

faced challenges with EMC. Additional measurements, including IDTs and CO spectroscopic laser measurements, were added in a complementary study [257]. Both their previously developed mechanism and the mechanism of Takahashi [255] were tested, suggesting that improvements are needed for the formed intermediates.

7.4 Purity of used compounds

Species	Purity	Supplier
	Fuel components	
Oxygen, Nitrogen, Argon, Carbon-dioxide	Gas - ≥99.99%	Air Liquid
Hydrogen	Gas - 99.95%	Air Liquid
<i>n</i> -pentane	Liquid - ≥99%	Sigma-Aldrich
3-pentanone	Liquid - ≥99%	Sigma-Aldrich
3-Pentanol	Liquid - 98%	Thermo Scientific
1-Pentene	Liquid - 98%	Sigma-Aldrich
ТНР	Liquid - 98+%	Thermo Scientific
ТММ	Liquid - 99%	Thermo Scientific
	Calibrated species	
Mixture of gases (Alkanes-Alkenes-N ₂)	Gas - ≥99.99% (Standard gas mixture 15 ppm)	Air Products
Mixture of gasesGas - ≥99.99%		Air Products
$(CO-CO_2-H_2-O_2-N_2)$	(Standard gas mixture 15 ppm)	
Acetaldehyde	Liquid - 99%	Sigma-Aldrich
3,4-Dihydropyran	Liquid - 99%	Acros Organics
Tetrahydrofuran	Liquid - ≥99%	Sigma-Aldrich
2-Butanone	Liquid - ≥99%	Sigma-Aldrich
7.5 3-pentanol computed rate constants

	P (atm) A	(cm ³ /mol/s)	n (-)	Ea (cal/mo	1)		
PENT3OH-1<=>PENT3OH-D1 + 1	Н	2.357e+11	0.356	37202.5 !	500.0-2000.0K;	fit err.:	5.12e-03
PLOG/	0.0010	8.627e+50	-13.956	42674.5/ !	500.0-1000.0K;	fit err.:	2.68e-02
PLOG/	0.0050	1.393e+48	-12.629	42855.6/ !	500.0-1200.0K;	fit err.:	4.60e-02
PLOG/	0.0100	3.852e+51	-13.478	45000.0/ !	500.0-1200.0K;	fit err.:	4.36e-02
PLOG/	0.0500	1.369e+50	-12.593	46371.0/ !	500.0-1400.0K;	fit err.:	5.84e-02
PLOG/	0.1000	8.043e+51	-12.948	48048.6/ !	500.0-1400.0K;	fit err.:	5.19e-02
PLOG/	0.2000	7.074e+52	-13.062	49390.1/ !	500.0-1400.0K;	fit err.:	4.38e-02
PLOG/	0.5000	5.121e+48	-11.606	48804.0/ !	500.0-1600.0K;	fit err.:	5.39e-02
PLOG/	1.0000	9.923e+47	-11.251	49345.2/ !	500.0-1600.0K;	fit err.:	3.99e-02
PLOG/	10.0000	8.409e+37	-7.871	47189.9/ !	500.0-2000.0K;	fit err.:	2.22e-02
PLOG/	20.0000	1.175e+35	-6.940	46435.6/ !	500.0-2000.0K;	fit err.:	9.43e-03
PLOG/	50.0000	4.516e+30	-5.541	44992.1/ !	500.0-2000.0K;	fit err.:	2.68e-02
PLOG/	100.0000	9.449e+26	-4.399	43630.7/ !	500.0-2000.0K;	fit err.:	4.03e-02
PENT3OH-1<=>propanol-1-yl	+ CH2CH2	3.883e+11	0.470	26497.0 !	500.0-2000.0K;	fit err.:	1.54e-04
PLOG/	0.0010	2.345e+56	-14.443	37469.8/ !	500.0-1000.0K;	fit err.:	2.52e-02
PLOG/	0.0050	1.711e+50	-12.272	36465.9/ !	500.0-1200.0K;	fit err.:	3.89e-02
PLOG/	0.0100	3.503e+51	-12.550	37668.5/ !	500.0-1200.0K;	fit err.:	3.52e-02
PLOG/	0.0500	7.114e+46	-10.862	37216.9/ !	500.0-1400.0K;	fit err.:	4.34e-02
PLOG/	0.1000	5.243e+46	-10.718	37793.6/ !	500.0-1400.0K;	fit err.:	3.60e-02
PLOG/	0.2000	6.555e+45	-10.349	38005.0/ !	500.0-1400.0K;	fit err.:	2.60e-02
PLOG/	0.5000	3.759e+41	-8.954	36906.3/ !	500.0-1600.0K;	fit err.:	3.28e-02
PLOG/	1.0000	9.922e+39	-8.400	36728.7/ !	500.0-1600.0K;	fit err.:	2.07e-02
PLOG/	10.0000	2.414e+31	-5.614	34269.4/ !	500.0-2000.0K;	fit err.:	1.04e-02
PLOG/	20.0000	1.119e+29	-4.872	33527.9/ !	500.0-2000.0K;	fit err.:	1.45e-02
PLOG/	50.0000	4.087e+25	-3.798	32299.0/ !	500.0-2000.0K;	fit err.:	2.87e-02
PLOG/	100.0000	8.732e+22	-2.975	31272.1/ !	500.0-2000.0K;	fit err.:	3.64e-02
PENT3OH-1<=>PENT3OH-2		6.624e+08	0.876	34925.3 !	500.0-2000.0K;	fit err.:	1.45e-02
PLOG/	0.0010	1.415e+62	-18.015	41859.9/ !	500.0-1000.0K;	fit err.:	2.63e-02
PLOG/	0.0050	7.236e+59	-16.780	43505.6/ !	500.0-1200.0K;	fit err.:	4.07e-02
PLOG/	0.0100	3.051e+62	-17.349	45732.6/ !	500.0-1200.0K;	fit err.:	3.85e-02
PLOG/	0.0500	4.148e+61	-16.573	48073.0/ !	500.0-1400.0K;	fit err.:	4.69e-02
PLOG/	0.1000	2.838e+62	-16.618	49592.6/ !	500.0-1400.0K;	fit err.:	4.33e-02
PLOG/	0.2000	3.365e+62	-16.444	50767.6/ !	500.0-1400.0K;	fit err.:	3.43e-02
PLOG/	0.5000	3.779e+58	-15.012	50507.9/ !	500.0-1600.0K;	fit err.:	4.13e-02
PLOG/	1.0000	1.170e+57	-14.393	50879.3/ !	500.0-1600.0K;	fit err.:	2.82e-02
PLOG/	10.0000	4.970e+45	-10.548	48676.9/ !	500.0-2000.0K;	fit err.:	1.80e-02
PLOG/	20.0000	1.015e+42	-9.348	47672.0/ !	500.0-2000.0K;	fit err.:	2.75e-02
PLOG/	50.0000	2.787e+36	-7.583	45877.2/ !	500.0-2000.0K;	fit err.:	5.68e-02
PLOG/	100.0000	1.317e+32	-6.227	44403.9/ !	500.0-2000.0K;	fit err.:	7.67e-02
PENT3OH-1<=>PENT3OH-3		8.685e+00	3.045	29742.1 !	500.0-2000.0K;	fit err.:	2.20e-02

PLOG/	0.0010	7.902e+51	-15.739	32652.3/ !	500.0-1000.0K;	fit err.:	4.49e-02
PLOG/	0.0050	1.639e+41	-12.072	30163.2/ !	500.0-1200.0K;	fit err.:	7.84e-02
PLOG/	0.0100	6.280e+42	-12.377	31624.0/ !	500.0-1200.0K;	fit err.:	7.72e-02
PLOG/	0.0500	1.453e+46	-12.983	34918.0/ !	500.0-1200.0K;	fit err.:	6.91e-02
PLOG/	0.1000	1.533e+48	-13.413	36669.5/ !	500.0-1200.0K;	fit err.:	6.56e-02
PLOG/	0.2000	1.111e+50	-13.792	38380.3/ !	500.0-1200.0K;	fit err.:	6.11e-02
PLOG/	0.5000	3.491e+52	-14.307	40704.2/ !	500.0-1200.0K;	fit err.:	5.23e-02
PLOG/	1.0000	2.597e+44	-11.660	38272.6/ !	500.0-1400.0K;	fit err.:	8.13e-02
PLOG/	10.0000	3.800e+48	-12.369	43227.8/ !	500.0-1400.0K;	fit err.:	5.44e-02
PLOG/	20.0000	2.327e+48	-12.158	44026.2/ !	500.0-1400.0K;	fit err.:	4.15e-02
PLOG/	50.0000	5.510e+46	-11.491	44407.5/ !	500.0-1400.0K;	fit err.:	2.01e-02
PLOG/	100.0000	9.877e+45	-11.128	45070.3/ !	500.0-1400.0K;	fit err.:	1.09e-02
PENT3OH-1<=>PENT30		6.239e+02	2.240	17974.9 !	500.0-2000.0K;	fit err.:	6.31e-03
PENT3OH-2<=>PENT3OH-D1 +	Н	1.041e+08	1.734	37059.5 !	500.0-2000.0K;	fit err.:	7.54e-03
PLOG/	0.0010	3.045e+55	-14.559	46514.1/ !	500.0-1200.0K;	fit err.:	4.58e-02
PLOG/	0.0050	7.222e+60	-15.769	50543.2/ !	500.0-1200.0K;	fit err.:	3.54e-02
PLOG/	0.0100	1.458e+55	-13.862	49036.3/ !	500.0-1400.0K;	fit err.:	5.93e-02
PLOG/	0.0500	3.350e+57	-14.189	52128.3/ !	500.0-1400.0K;	fit err.:	4.07e-02
PLOG/	0.1000	1.778e+57	-13.952	52907.9/ !	500.0-1400.0K;	fit err.:	2.89e-02
PLOG/	0.2000	7.010e+52	-12.482	51862.3/ !	500.0-1600.0K;	fit err.:	4.58e-02
PLOG/	0.5000	1.114e+51	-11.770	52147.5/ !	500.0-1600.0K;	fit err.:	2.58e-02
PLOG/	1.0000	1.504e+47	-10.495	51169.1/ !	500.0-1800.0K;	fit err.:	3.32e-02
PLOG/	10.0000	3.022e+37	-7.302	48777.5/ !	500.0-2000.0K;	fit err.:	2.22e-02
PLOG/	20.0000	1.091e+34	-6.212	47649.6/ !	500.0-2000.0K;	fit err.:	4.24e-02
PLOG/	50.0000	9.722e+28	-4.642	45796.0/ !	500.0-2000.0K;	fit err.:	6.52e-02
PLOG/	100.0000	1.268e+25	-3.448	44273.5/ !	500.0-2000.0K;	fit err.:	7.60e-02
PENT3OH-2<=>PENT3OH-D2 +	Н	4.888e+07	1.482	33964.4 !	500.0-2000.0K;	fit err.:	5.74e-03
PLOG/	0.0010	8.860e+55	-14.742	45028.5/ !	500.0-1200.0K;	fit err.:	4.41e-02
PLOG/	0.0050	3.860e+59	-15.481	48306.6/ !	500.0-1200.0K;	fit err.:	3.31e-02
PLOG/	0.0100	6.765e+53	-13.582	46710.6/ !	500.0-1400.0K;	fit err.:	5.51e-02
PLOG/	0.0500	4.965e+54	-13.514	48963.8/ !	500.0-1400.0K;	fit err.:	3.45e-02
PLOG/	0.1000	5.586e+53	-13.099	49338.1/ !	500.0-1400.0K;	fit err.:	2.33e-02
PLOG/	0.2000	3.159e+49	-11.699	48243.3/ !	500.0-1600.0K;	fit err.:	3.80e-02
PLOG/	0.5000	1.535e+47	-10.861	48143.6/ !	500.0-1600.0K;	fit err.:	1.91e-02
PLOG/	1.0000	3.215e+43	-9.662	47133.8/ !	500.0-1800.0K;	fit err.:	2.69e-02
PLOG/	10.0000	1.743e+34	-6.644	44639.6/ !	500.0-2000.0K;	fit err.:	2.46e-02
PLOG/	20.0000	8.788e+30	-5.608	43504.9/ !	500.0-2000.0K;	fit err.:	4.28e-02
PLOG/	50.0000	2.362e+26	-4.191	41801.1/ !	500.0-2000.0K;	fit err.:	6.21e-02
PLOG/	100.0000	7.252e+22	-3.113	40410.3/ !	500.0-2000.0K;	fit err.:	6.93e-02
PENT3OH-2<=>C5H10-2 + OH		2.320e+10	0.556	30946.2 !	500.0-2000.0K;	fit err.:	1.54e-03
PLOG/	0.0010	2.050e+56	-14.603	42841.3/ !	500.0-1200.0K;	fit err.:	4.08e-02
PLOG/	0.0050	1.686e+58	-14.890	45214.9/ !	500.0-1200.0K;	fit err.:	2.88e-02
PLOG/	0.0100	2.860e+52	-13.017	43494.3/ !	500.0-1400.0K;	fit err.:	4.95e-02

PLOG/	0.0500	6.513e+51	-12.563	44780.9/ !	500.0-1400.0K;	fit err.:	2.90e-02
PLOG/	0.1000	2.510e+50	-12.036	44800.3/ !	500.0-1400.0K;	fit err.:	1.73e-02
PLOG/	0.2000	3.041e+46	-10.762	43699.5/ !	500.0-1600.0K;	fit err.:	3.21e-02
PLOG/	0.5000	8.675e+43	-9.888	43298.4/ !	500.0-1600.0K;	fit err.:	1.55e-02
PLOG/	1.0000	4.148e+40	-8.819	42309.4/ !	500.0-1800.0K;	fit err.:	2.12e-02
PLOG/	10.0000	1.577e+32	-6.112	39816.0/ !	500.0-2000.0K;	fit err.:	2.27e-02
PLOG/	20.0000	2.452e+29	-5.234	38822.1/ !	500.0-2000.0K;	fit err.:	3.70e-02
PLOG/	50.0000	3.360e+25	-4.041	37349.7/ !	500.0-2000.0K;	fit err.:	5.13e-02
PLOG/	100.0000	4.673e+22	-3.165	36211.0/ !	500.0-2000.0K;	fit err.:	5.78e-02
PENT3OH-2<=>SC3H5OH + CH	НЗСН2	2.927e+11	0.524	29606.5 !	500.0-2000.0K;	fit err.:	1.82e-03
PLOG/	0.0010	5.448e+56	-14.331	41724.1/ !	500.0-1200.0K;	fit err.:	4.01e-02
PLOG/	0.0050	1.432e+58	-14.488	43829.3/ !	500.0-1200.0K;	fit err.:	2.71e-02
PLOG/	0.0100	3.807e+52	-12.683	42153.0/ !	500.0-1400.0K;	fit err.:	4.70e-02
PLOG/	0.0500	2.734e+51	-12.098	43124.6/ !	500.0-1400.0K;	fit err.:	2.60e-02
PLOG/	0.1000	8.689e+49	-11.554	43062.9/ !	500.0-1400.0K;	fit err.:	1.58e-02
PLOG/	0.2000	1.045e+46	-10.288	41908.9/ !	500.0-1600.0K;	fit err.:	2.84e-02
PLOG/	0.5000	2.891e+43	-9.417	41452.4/ !	500.0-1600.0K;	fit err.:	1.24e-02
PLOG/	1.0000	1.950e+40	-8.398	40496.3/ !	500.0-1800.0K;	fit err.:	1.83e-02
PLOG/	10.0000	1.377e+32	-5.787	38027.1/ !	500.0-2000.0K;	fit err.:	2.40e-02
PLOG/	20.0000	2.844e+29	-4.948	37069.4/ !	500.0-2000.0K;	fit err.:	3.66e-02
PLOG/	50.0000	6.290e+25	-3.819	35674.4/ !	500.0-2000.0K;	fit err.:	5.06e-02
PLOG/	100.0000	1.233e+23	-2.991	34590.3/ !	500.0-2000.0K;	fit err.:	5.59e-02
PENT3OH-2<=>PENT3OH-3		3.467e+03	2.481	35314.5 !	500.0-2000.0K;	fit err.:	1.97e-02
PLOG/	0.0010	8.552e+35	-10.977	30110.4/ !	500.0-1000.0K;	fit err.:	4.82e-02
PLOG/	0.0050	4.928e+25	-7.318	28725.8/ !	500.0-1200.0K;	fit err.:	7.35e-02
PLOG/	0.0100	1.716e+27	-7.587	30202.6/ !	500.0-1200.0K;	fit err.:	7.17e-02
PLOG/	0.0500	7.856e+30	-8.262	33364.4/ !	500.0-1200.0K;	fit err.:	6.59e-02
PLOG/	0.1000	1.860e+25	-6.450	30761.2/ !	500.0-1200.0K;	fit err.:	4.82e-02
PLOG/	0.2000	7.579e+34	-9.113	36352.0/ !	500.0-1200.0K;	fit err.:	5.87e-02
PLOG/	0.5000	2.954e+52	-14.075	46358.3/ !	500.0-1200.0K;	fit err.:	7.80e-02
PLOG/	1.0000	2.310e+30	-7.364	35785.2/ !	500.0-1400.0K;	fit err.:	5.63e-02
PLOG/	10.0000	6.034e+21	-4.414	32444.5/ !	500.0-1400.0K;	fit err.:	1.25e-02
PLOG/	20.0000	9.881e+20	-4.046	32682.1/ !	500.0-1400.0K;	fit err.:	2.83e-02
PLOG/	50.0000	3.027e+03	1.218	23593.9/ !	500.0-1400.0K;	fit err.:	1.13e-01
PLOG/	100.0000	1.280e+68	-17.380	62032.5/ !	500.0-1400.0K;	fit err.:	7.04e-02
PENT3OH-2<=>PENT3O		3.220e+02	2.556	25685.8 !	500.0-2000.0K;	fit err.:	1.35e-02
PENT3OH-3<=>PENT3OH-D2 +	+ Н	2.249e+03	2.499	33744.9 !	500.0-2000.0K;	fit err.:	9.03e-04
PLOG/	0.0010	3.107e+53	-15.425	41950.9/ !	500.0-1000.0K;	fit err.:	3.06e-02
PLOG/	0.0050	8.957e+46	-13.065	40077.0/ !	500.0-1200.0K;	fit err.:	5.20e-02
PLOG/	0.0100	4.501e+49	-13.734	41615.1/ !	500.0-1200.0K;	fit err.:	5.10e-02
PLOG/	0.0500	2.227e+55	-15.110	45207.4/ !	500.0-1200.0K;	fit err.:	4.66e-02
PLOG/	0.1000	3.253e+57	-15.615	46735.1/ !	500.0-1200.0K;	fit err.:	4.41e-02
PLOG/	0.2000	2.029e+59	-16.009	48152.9/ !	500.0-1200.0K;	fit err.:	4.08e-02

PLOG/	0.5000	1.770e+61	-16.400	49930.4/ !	500.0-1200.0K;	fit err.:	3.42e-02
PLOG/	1.0000	2.308e+55	-14.466	48236.9/ !	500.0-1400.0K;	fit err.:	5.92e-02
PLOG/	10.0000	4.129e+56	-14.394	51345.0/ !	500.0-1400.0K;	fit err.:	3.19e-02
PLOG/	20.0000	3.171e+55	-13.936	51606.9/ !	500.0-1400.0K;	fit err.:	2.08e-02
PLOG/	50.0000	6.057e+52	-12.968	51359.2/ !	500.0-1400.0K;	fit err.:	6.63e-03
PLOG/	100.0000	5.690e+49	-11.955	50701.1/ !	500.0-1400.0K;	fit err.:	1.45e-02
PENT3OH-3<=>SC4H7OH-1 +	CH3	1.220e+09	2.091	29634.3 !	500.0-2000.0K;	fit err.:	1.03e-02
PLOG/	0.0010	1.611e+62	-16.168	40160.6/ !	500.0-1000.0K;	fit err.:	3.08e-02
PLOG/	0.0050	1.279e+54	-13.405	38027.7/ !	500.0-1200.0K;	fit err.:	5.07e-02
PLOG/	0.0100	9.819e+55	-13.856	39333.8/ !	500.0-1200.0K;	fit err.:	4.88e-02
PLOG/	0.0500	4.340e+59	-14.679	42185.0/ !	500.0-1200.0K;	fit err.:	4.36e-02
PLOG/	0.1000	9.578e+60	-14.964	43376.0/ !	500.0-1200.0K;	fit err.:	3.95e-02
PLOG/	0.2000	7.783e+61	-15.118	44402.5/ !	500.0-1200.0K;	fit err.:	3.47e-02
PLOG/	0.5000	4.313e+62	-15.185	45593.9/ !	500.0-1200.0K;	fit err.:	2.78e-02
PLOG/	1.0000	9.709e+56	-13.353	43910.6/ !	500.0-1400.0K;	fit err.:	4.97e-02
PLOG/	10.0000	4.606e+55	-12.597	45507.8/ !	500.0-1400.0K;	fit err.:	2.08e-02
PLOG/	20.0000	9.967e+53	-11.999	45394.9/ !	500.0-1400.0K;	fit err.:	1.05e-02
PLOG/	50.0000	5.680e+50	-10.906	44735.1/ !	500.0-1400.0K;	fit err.:	1.25e-02
PLOG/	100.0000	3.877e+47	-9.874	43876.5/ !	500.0-1400.0K;	fit err.:	2.43e-02
PENT3OH-3<=>C5KET3 + H		3.637e+08	1.141	31292.4 !	500.0-2000.0K;	fit err.:	2.64e-03
PLOG/	0.0010	1.879e+58	-16.112	40609.1/ !	500.0-1000.0K;	fit err.:	3.10e-02
PLOG/	0.0050	6.150e+50	-13.522	38685.7/ !	500.0-1200.0K;	fit err.:	5.11e-02
PLOG/	0.0100	5.927e+52	-13.999	40011.8/ !	500.0-1200.0K;	fit err.:	4.95e-02
PLOG/	0.0500	8.075e+56	-14.961	43036.8/ !	500.0-1200.0K;	fit err.:	4.46e-02
PLOG/	0.1000	2.328e+58	-15.278	44263.5/ !	500.0-1200.0K;	fit err.:	4.13e-02
PLOG/	0.2000	4.141e+59	-15.533	45425.2/ !	500.0-1200.0K;	fit err.:	3.72e-02
PLOG/	0.5000	3.721e+60	-15.661	46704.0/ !	500.0-1200.0K;	fit err.:	2.93e-02
PLOG/	1.0000	6.603e+54	-13.796	44970.6/ !	500.0-1400.0K;	fit err.:	5.35e-02
PLOG/	10.0000	9.239e+53	-13.180	46762.7/ !	500.0-1400.0K;	fit err.:	2.43e-02
PLOG/	20.0000	2.636e+52	-12.619	46695.6/ !	500.0-1400.0K;	fit err.:	1.22e-02
PLOG/	50.0000	2.389e+49	-11.587	46117.7/ !	500.0-1400.0K;	fit err.:	9.67e-03
PLOG/	100.0000	2.140e+46	-10.591	45302.5/ !	500.0-1400.0K;	fit err.:	2.00e-02
PENT3OH-3<=>PENT30		2.944e+04	2.007	31155.5 !	500.0-2000.0K;	fit err.:	1.41e-02
PENT3O<=>C5KET3 + H		3.667e+11	0.723	19501.1 !	500.0-2000.0K;	fit err.:	4.57e-03
PENT3O<=>C2H5CHO + CH3CH	12	4.066e+14	-0.100	13293.1 !	500.0-2000.0K;	fit err.:	2.94e-04

7.6 Alkyl-Carbonates Computed rates

7.6.1 DMC

7.6.1.1 Gas phase

P (atm) A (cm³/mol/s) n (-) Ea (cal/mol)

DMC + H<=>DMC-R		3.873e+06	2.339	9691.4 !	500.0-2000.0K;	fit err.:	3.37e-03
DMC + CH3<=>DMC-R		7.324e+01	3.273	12253.0 !	500.0-2000.0K;	fit err.:	2.41e-03
DMC-R<=>OringO + CH3		3.266e+12	-0.143	53788.8 !	500.0-2000.0K;	fit err.:	3.82e-03
PLOG/	0.0010	1.156e+41	-10.981	57143.5/ !	500.0-1600.0K;	fit err.:	7.01e-02
PLOG/	0.0050	1.253e+45	-11.723	59266.3/ !	500.0-1800.0K;	fit err.:	8.60e-02
PLOG/	0.0100	1.290e+48	-12.420	61122.6/ !	500.0-1800.0K;	fit err.:	8.11e-02
PLOG/	0.0500	2.451e+49	-12.351	63362.3/ !	500.0-2000.0K;	fit err.:	8.63e-02
PLOG/	0.1000	3.674e+50	-12.519	64779.2/ !	500.0-2000.0K;	fit err.:	7.66e-02
PLOG/	0.2000	9.364e+50	-12.469	65871.1/ !	500.0-2000.0K;	fit err.:	6.40e-02
PLOG/	0.5000	1.670e+50	-12.042	66710.1/ !	500.0-2000.0K;	fit err.:	4.38e-02
PLOG/	1.0000	4.289e+48	-11.432	66818.7/ !	500.0-2000.0K;	fit err.:	2.59e-02
PLOG/	10.0000	6.600e+37	-7.885	63994.7/ !	500.0-2000.0K;	fit err.:	4.27e-02
PLOG/	20.0000	4.410e+33	-6.580	62503.9/ !	500.0-2000.0K;	fit err.:	5.64e-02
PLOG/	50.0000	1.015e+28	-4.842	60324.1/ !	500.0-2000.0K;	fit err.:	6.39e-02
PLOG/	100.0000	1.171e+24	-3.638	58732.2/ !	500.0-2000.0K;	fit err.:	6.07e-02
DMC-R<=>CH3OC=O + CH2=O		8.300e+13	-0.202	38111.6 !	500.0-2000.0K;	fit err.:	2.03e-03
PLOG/	0.0010	3.906e+54	-13.388	49704.3/ !	500.0-1600.0K;	fit err.:	5.61e-02
PLOG/	0.0050	1.977e+51	-12.160	49602.8/ !	500.0-1800.0K;	fit err.:	6.33e-02
PLOG/	0.0100	7.720e+50	-11.941	50011.3/ !	500.0-1800.0K;	fit err.:	5.54e-02
PLOG/	0.0500	6.920e+46	-10.526	49471.9/ !	500.0-2000.0K;	fit err.:	5.18e-02
PLOG/	0.1000	3.767e+45	-10.069	49425.1/ !	500.0-2000.0K;	fit err.:	3.89e-02
PLOG/	0.2000	8.787e+43	-9.509	49169.5/ !	500.0-2000.0K;	fit err.:	2.61e-02
PLOG/	0.5000	1.394e+41	-8.588	48477.5/ !	500.0-2000.0K;	fit err.:	1.26e-02
PLOG/	1.0000	4.304e+38	-7.784	47717.2/ !	500.0-2000.0K;	fit err.:	1.73e-02
PLOG/	10.0000	1.266e+29	-4.808	44337.9/ !	500.0-2000.0K;	fit err.:	5.06e-02
PLOG/	20.0000	1.904e+26	-3.939	43261.0/ !	500.0-2000.0K;	fit err.:	5.29e-02
PLOG/	50.0000	6.721e+22	-2.883	41905.2/ !	500.0-2000.0K;	fit err.:	4.92e-02
PLOG/	100.0000	4.044e+20	-2.206	41023.2/ !	500.0-2000.0K;	fit err.:	4.24e-02
DMC-R<=>CH3OC (=0) CH2O		9.089e+12	-0.373	36235.5 !	500.0-2000.0K;	fit err.:	3.68e-03
PLOG/	10.0000	3.246e+12	-1.226	31455.2/ !	500.0-1000.0K;	fit err.:	1.88e-02
PLOG/	20.0000	4.649e+20	-3.600	34992.5/ !	500.0-1000.0K;	fit err.:	2.16e-02
PLOG/	50.0000	6.402e+28	-5.918	38852.3/ !	500.0-1000.0K;	fit err.:	1.96e-02
PLOG/	100.0000	2.319e+32	-6.875	40856.8/ !	500.0-1000.0K;	fit err.:	1.58e-02
CH3OC (=0) CH2O<=>CH3OC=0 +	CH2=0	2.590e+14	-0.136	17150.7 !	500.0-2000.0K;	fit err.:	2.54e-03
PLOG/	10.0000	9.390e+33	-6.793	21215.5/ !	500.0-1000.0K;	fit err.:	9.67e-03

PLOG/	20.0000	3.899e+34	-6.876	21973.0/ !	500.0-1000.0K;	fit err.:	8.72e-03
PLOG/	50.0000	4.987e+34	-6.775	22712.0/ !	500.0-1000.0K;	fit err.:	7.13e-03
PLOG/	100.0000	6.363e+33	-6.408	22870.7/ !	500.0-1000.0K;	fit err.:	4.82e-03

7.6.1.2 Liquid phase

	P (atm) A	A (cm ³ /mol/s)	n (-)	Ea (cal/mol)	
DMC + H<=>DMC-R		3.748e+06	2.342	9970.6 ! 500.0-2000.0K;	; fit err.: 3.76e-03
DMC + CH3<=>DMC-R		2.007e-03	5.273	11887.9 ! 500.0-2000.0K;	; fit err.: 3.29e-03
DMC-R<=>OringO + CH3		3.236e+12	-0.119	53737.5 ! 500.0-2000.0K;	; fit err.: 3.64e-03
PLOG/	0.0010	4.746e+39	-10.580	56426.7/ ! 500.0-1600.0K;	; fit err.: 7.06e-02
PLOG/	0.0050	1.987e+44	-11.491	58782.9/ ! 500.0-1800.0K;	; fit err.: 8.68e-02
PLOG/	0.0100	3.032e+47	-12.236	60705.5/ ! 500.0-1800.0K;	; fit err.: 8.17e-02
PLOG/	0.0500	1.156e+49	-12.251	63076.4/ ! 500.0-2000.0K;	; fit err.: 8.72e-02
PLOG/	0.1000	2.208e+50	-12.449	64539.5/ ! 500.0-2000.0K;	; fit err.: 7.71e-02
PLOG/	0.2000	6.615e+50	-12.418	65666.4/ ! 500.0-2000.0K;	; fit err.: 6.53e-02
PLOG/	0.5000	1.631e+50	-12.029	66582.3/ ! 500.0-2000.0K;	; fit err.: 4.56e-02
PLOG/	1.0000	4.838e+48	-11.435	66729.6/ ! 500.0-2000.0K;	; fit err.: 2.76e-02
PLOG/	10.0000	1.066e+38	-7.930	64012.1/ ! 500.0-2000.0K;	; fit err.: 4.16e-02
PLOG/	20.0000	5.711e+33	-6.595	62479.7/ ! 500.0-2000.0K;	; fit err.: 5.47e-02
PLOG/	50.0000	1.485e+28	-4.871	60334.7/ ! 500.0-2000.0K;	; fit err.: 6.34e-02
PLOG/	100.0000	1.684e+24	-3.664	58743.6/ ! 500.0-2000.0K;	; fit err.: 6.12e-02
DMC-R<=>CH3OC=0 + CH2=0		7.487e+13	-0.188	38046.9 ! 500.0-2000.0K;	; fit err.: 1.77e-03
PLOG/	0.0010	8.063e+52	-12.916	48291.0/ ! 500.0-1600.0K;	; fit err.: 5.40e-02
PLOG/	0.0050	6.461e+49	-11.747	48301.7/ ! 500.0-1800.0K;	; fit err.: 6.10e-02
PLOG/	0.0100	2.990e+49	-11.549	48751.8/ ! 500.0-1800.0K;	; fit err.: 5.28e-02
PLOG/	0.0500	3.210e+45	-10.158	48253.8/ ! 500.0-2000.0K;	; fit err.: 4.89e-02
PLOG/	0.1000	1.779e+44	-9.703	48212.0/ ! 500.0-2000.0K;	; fit err.: 3.61e-02
PLOG/	0.2000	4.197e+42	-9.144	47964.1/ ! 500.0-2000.0K;	; fit err.: 2.32e-02
PLOG/	0.5000	6.944e+39	-8.229	47281.7/ ! 500.0-2000.0K;	; fit err.: 1.29e-02
PLOG/	1.0000	2.351e+37	-7.436	46545.4/ ! 500.0-2000.0K;	; fit err.: 2.04e-02
PLOG/	10.0000	1.526e+28	-4.556	43417.0/ ! 500.0-2000.0K;	; fit err.: 5.36e-02
PLOG/	20.0000	4.378e+25	-3.766	42534.2/ ! 500.0-2000.0K;	; fit err.: 5.38e-02
PLOG/	50.0000	4.259e+22	-2.833	41497.1/ ! 500.0-2000.0K;	; fit err.: 4.89e-02
PLOG/	100.0000	4.571e+20	-2.226	40815.2/ ! 500.0-2000.0K;	; fit err.: 4.09e-02
DMC-R<=>CH3OC (=O) CH2O		1.168e+13	-0.403	35017.8 ! 500.0-2000.0K;	; fit err.: 3.60e-03
PLOG/	10.0000	1.154e+14	-1.702	30742.0/ ! 500.0-1000.0K;	; fit err.: 2.29e-02

PLOG/	20.0000	1.158e+22	-4.027	34226.4/ !	500.0-1000.0K;	fit err.:	2.40e-02
PLOG/	50.0000	2.385e+30	-6.394	38199.0/ !	500.0-1000.0K;	fit err.:	2.00e-02
PLOG/	100.0000	7.591e+33	-7.333	40194.5/ !	500.0-1000.0K;	fit err.:	1.54e-02
CH3OC (=0) CH2O<=>CH3OC=0 +	CH2=0	3.745e+14	-0.172	17595.1 !	500.0-2000.0K;	fit err.:	2.45e-03
PLOG/	10.0000	5.944e+34	-7.017	21941.5/ !	500.0-1000.0K;	fit err.:	1.18e-02
PLOG/	20.0000	3.688e+35	-7.154	22774.0/ !	500.0-1000.0K;	fit err.:	1.02e-02
PLOG/	50.0000	3.119e+35	-6.998	23445.7/ !	500.0-1000.0K;	fit err.:	7.14e-03
PLOG/	100.0000	2.751e+34	-6.583	23535.6/ !	500.0-1000.0K;	fit err.:	4.58e-03

7.6.2 DEC

7.6.2.1 Gas phase

:	P (atm) A	(cm ³ /mol/s)	n (-)	Ea (cal/mol)	
DEC + H<=>DEC-R1		1.725e+07	2.196	9481.6 ! 500.0-2000.0K; fit err.: 3.	.30e-03
DEC + H<=>DEC-R2		4.680e+04	3.048	7673.3 ! 500.0-2000.0K; fit err.: 6.	.97e-03
DEC + CH3<=>DEC-R1		1.241e+03	3.039	13448.9 ! 500.0-2000.0K; fit err.: 6.	.71e-04
DEC + CH3<=>DEC-R2		2.439e+01	3.352	9504.8 ! 500.0-2000.0K; fit err.: 4.	.98e-03
DEC-R1<=>oxirane + CH3CH2C	OC (=0)	1.492e+11	0.453	63596.8 ! 500.0-2000.0K; fit err.: 4.	.01e-04
PLOG/	0.0010	7.462e-38	9.373	30544.7/ ! 500.0-1000.0K; fit err.: 1.	.41e-01
PLOG/	0.0050	6.022e+50	-15.226	80910.4/ ! 500.0-1200.0K; fit err.: 1.	.12e-01
PLOG/	0.0100	3.422e+19	-5.920	60785.3/ ! 500.0-1200.0K; fit err.: 4.	.93e-02
PLOG/	0.0500	5.906e+38	-11.171	64776.9/ ! 500.0-1200.0K; fit err.: 4.	.97e-02
PLOG/	0.1000	5.877e+47	-13.587	67869.9/ ! 500.0-1200.0K; fit err.: 4.	.80e-02
PLOG/	0.2000	4.667e+45	-12.609	66965.5/ ! 500.0-1400.0K; fit err.: 7.	.70e-02
PLOG/	0.5000	2.106e+55	-15.071	71785.7/ ! 500.0-1400.0K; fit err.: 6.	.89e-02
PLOG/	1.0000	5.025e+60	-16.353	75086.1/ ! 500.0-1400.0K; fit err.: 5.	.88e-02
PLOG/	10.0000	9.331e+56	-14.239	77934.5/ ! 500.0-1800.0K; fit err.: 7.	.06e-02
PLOG/	20.0000	5.461e+55	-13.635	78739.9/ ! 500.0-1800.0K; fit err.: 4.	.62e-02
PLOG/	50.0000	6.154e+49	-11.603	77612.6/ ! 500.0-2000.0K; fit err.: 3.	.54e-02
PLOG/	100.0000	3.958e+45	-10.199	76708.2/ ! 500.0-2000.0K; fit err.: 7.	.77e-03
DEC-R1<=>CH3CH2OCO(=0) + C	H2=CH2	5.969e+12	0.208	27311.8 ! 500.0-2000.0K; fit err.: 4.	.33e-03
PLOG/	0.0010	1.253e+60	-15.558	38841.6/ ! 500.0-1000.0K; fit err.: 2.	.97e-02
PLOG/	0.0050	7.332e+52	-13.051	37418.0/ ! 500.0-1200.0K; fit err.: 4.	.61e-02
PLOG/	0.0100	1.530e+54	-13.331	38614.0/ ! 500.0-1200.0K; fit err.: 4.	.29e-02
PLOG/	0.0500	2.550e+55	-13.432	40675.8/ ! 500.0-1200.0K; fit err.: 2.	.79e-02
PLOG/	0.1000	5.355e+54	-13.118	41043.3/ ! 500.0-1200.0K; fit err.: 1.	.95e-02
PLOG/	0.2000	1.597e+49	-11.340	39354.4/ ! 500.0-1400.0K; fit err.: 3.	.56e-02
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PLOG/	0.5000	3.455e+47	-10.715	39414.9/ !	500.0-1400.0K;	fit err.:	2.20e-02
PLOG/	1.0000	2.947e+45	-10.007	39060.5/ !	500.0-1400.0K;	fit err.:	1.10e-02
PLOG/	10.0000	1.537e+35	-6.696	36007.1/ !	500.0-1800.0K;	fit err.:	1.04e-02
PLOG/	20.0000	3.029e+32	-5.837	35135.1/ !	500.0-1800.0K;	fit err.:	1.22e-02
PLOG/	50.0000	9.816e+28	-4.740	33935.9/ !	500.0-2000.0K;	fit err.:	1.51e-02
PLOG/	100.0000	2.132e+26	-3.913	32954.6/ !	500.0-2000.0K;	fit err.:	2.43e-02
DEC-R1<=>DEC-R2		1.114e-24	10.144	10875.3 !	500.0-2000.0K;	fit err.:	3.67e-02
PLOG/	0.0010	3.577e+60	-16.885	37591.9/ !	500.0-1000.0K;	fit err.:	2.45e-02
PLOG/	0.0050	2.367e+53	-14.432	36160.8/ !	500.0-1200.0K;	fit err.:	3.65e-02
PLOG/	0.0100	2.896e+53	-14.351	36829.4/ !	500.0-1200.0K;	fit err.:	3.13e-02
PLOG/	0.0500	3.725e+51	-13.536	37505.8/ !	500.0-1200.0K;	fit err.:	1.18e-02
PLOG/	0.1000	4.010e+49	-12.841	37293.4/ !	500.0-1200.0K;	fit err.:	4.00e-03
PLOG/	0.2000	7.655e+45	-11.620	36323.3/ !	500.0-1400.0K;	fit err.:	1.44e-02
PLOG/	0.5000	3.582e+42	-10.496	35655.9/ !	500.0-1400.0K;	fit err.:	1.03e-02
PLOG/	1.0000	1.153e+39	-9.359	34701.9/ !	500.0-1400.0K;	fit err.:	2.07e-02
PLOG/	10.0000	1.582e+28	-5.829	31733.9/ !	500.0-1800.0K;	fit err.:	1.13e-01
PLOG/	20.0000	1.815e+21	-3.677	29142.9/ !	500.0-1800.0K;	fit err.:	1.07e-01
PLOG/	50.0000	3.309e+16	-2.162	27710.7/ !	500.0-2000.0K;	fit err.:	1.82e-01
PLOG/	100.0000	9.736e+08	0.146	24712.5/ !	500.0-2000.0K;	fit err.:	1.60e-01
DEC-R1<=>CH3CH2OC (=O) CH2CH	120	7.834e+07	0.600	38115.8 !	500.0-2000.0K;	fit err.:	4.91e-03
PLOG/	50.0000	4.419e+24	-5.276	40669.3/ !	500.0-1000.0K;	fit err.:	2.59e-02
PLOG/	100.0000	4.162e+31	-7.263	44143.1/ !	500.0-1000.0K;	fit err.:	2.41e-02
DEC-R2<=>CH3CH2OC=O + CH3C	CH=O	1.865e+14	-0.178	34579.9 !	500.0-2000.0K;	fit err.:	5.16e-03
PLOG/	0.0010	3.617e+69	-17.976	51308.8/ !	500.0-1200.0K;	fit err.:	3.65e-02
PLOG/	0.0050	4.688e+62	-15.615	50017.0/ !	500.0-1400.0K;	fit err.:	5.31e-02
PLOG/	0.0100	2.225e+62	-15.409	50539.2/ !	500.0-1400.0K;	fit err.:	4.31e-02
PLOG/	0.0500	8.293e+58	-14.146	50506.7/ !	500.0-1400.0K;	fit err.:	1.65e-02
PLOG/	0.1000	1.871e+54	-12.658	49054.4/ !	500.0-1600.0K;	fit err.:	3.55e-02
PLOG/	0.2000	1.354e+52	-11.935	48642.3/ !	500.0-1600.0K;	fit err.:	2.16e-02
PLOG/	0.5000	2.906e+48	-10.739	47654.2/ !	500.0-1600.0K;	fit err.:	1.10e-02
PLOG/	1.0000	8.117e+44	-9.610	46503.3/ !	500.0-1800.0K;	fit err.:	1.51e-02
PLOG/	10.0000	1.088e+35	-6.498	43174.7/ !	500.0-2000.0K;	fit err.:	2.82e-02
PLOG/	20.0000	9.615e+31	-5.552	42027.3/ !	500.0-2000.0K;	fit err.:	4.01e-02
PLOG/	50.0000	7.668e+27	-4.295	40406.7/ !	500.0-2000.0K;	fit err.:	4.93e-02
PLOG/	100.0000	9.634e+24	-3.411	39217.6/ !	500.0-2000.0K;	fit err.:	5.04e-02

PLOG/	50.0000	2.176e-145	46.302	-14941.7/ !	500.0-1000.0K;	fit	err.: 2.34e-01	
PLOG/	100.0000	5.392e-80	26.218	11397.3/ !	500.0-1000.0K;	fit	err.: 1.12e-01	
CH3CH2OC(=0)CH2CH2O<=>CH2 err.: 4.56e-03	=O + CH3CH	20C (=0) CH2	1.664e+12	0.509	16137.9	!	500.0-2000.0K;	fit
PLOG/	50.0000	2.330e+35	-6.930	23200.3/ !	500.0-1000.0K;	fit	err.: 7.78e-03	
PLOG/	100.0000	2.950e+33	-6.264	22951.5/ !	500.0-1000.0K;	fit	err.: 3.11e-03	

7.6.2.2 Liquid phase

P (atm) A (cm³/mol/s) n (-) Ea (cal/mol)

DEC + H<=>DEC-R1		1.528e+08	1.932	10559.1 !	500.0-2000.0K;	fit err.:	1.37e-03
DEC + H<=>DEC-R2		1.564e+06	2.296	7461.8 !	500.0-2000.0K;	fit err.:	3.05e-03
DEC + CH3<=>DEC-R1		7.819e+02	3.125	13996.8 !	500.0-2000.0K;	fit err.:	1.37e-03
DEC + CH3<=>DEC-R2		2.853e+03	3.020	11557.4 !	500.0-2000.0K;	fit err.:	6.10e-04
DEC-R1<=>oxirane + CH3CH2OC	(=0)	5.298e+10	0.454	62872.7 !	500.0-2000.0K;	fit err.:	3.69e-04
PLOG/	0.0010	6.675e-31	7.593	36335.4/ !	500.0-1000.0K;	fit err.:	1.95e-01
PLOG/	0.0050	4.850e+03	-1.440	54748.2/ !	500.0-1200.0K;	fit err.:	3.50e-02
PLOG/	0.0100	9.416e+15	-4.903	58037.2/ !	500.0-1200.0K;	fit err.:	4.64e-02
PLOG/	0.0500	1.965e+38	-11.025	63896.9/ !	500.0-1200.0K;	fit err.:	5.01e-02
PLOG/	0.1000	3.678e+47	-13.502	67360.1/ !	500.0-1200.0K;	fit err.:	4.75e-02
PLOG/	0.2000	5.464e+45	-12.589	66816.1/ !	500.0-1400.0K;	fit err.:	7.49e-02
PLOG/	0.5000	6.444e+54	-14.863	71665.4/ !	500.0-1400.0K;	fit err.:	6.51e-02
PLOG/	1.0000	8.716e+52	-13.956	71984.7/ !	500.0-1600.0K;	fit err.:	8.71e-02
PLOG/	10.0000	3.933e+53	-13.197	76879.5/ !	500.0-1800.0K;	fit err.:	5.69e-02
PLOG/ 2	20.0000	1.128e+49	-11.625	76096.1/ !	500.0-2000.0K;	fit err.:	5.50e-02
PLOG/	50.0000	3.287e+44	-10.041	75495.3/ !	500.0-2000.0K;	fit err.:	1.52e-02
PLOG/ 10	0.0000	2.912e+39	-8.404	74051.8/ !	500.0-2000.0K;	fit err.:	1.77e-02
DEC-R1<=>CH3CH2OCO(=O) + CH2	2=CH2	3.328e+12	0.155	25808.0 !	500.0-2000.0K;	fit err.:	3.94e-03
PLOG/	0.0010	5.462e+55	-14.288	36073.3/ !	500.0-1000.0K;	fit err.:	2.84e-02
PLOG/	0.0050	2.359e+49	-12.050	34990.4/ !	500.0-1200.0K;	fit err.:	4.43e-02
PLOG/	0.0100	5.418e+50	-12.343	36207.2/ !	500.0-1200.0K;	fit err.:	4.11e-02
PLOG/	0.0500	5.757e+51	-12.391	38161.8/ !	500.0-1200.0K;	fit err.:	2.61e-02
PLOG/	0.1000	6.826e+50	-12.006	38404.1/ !	500.0-1200.0K;	fit err.:	1.80e-02
PLOG/	0.2000	4.793e+45	-10.344	36853.2/ !	500.0-1400.0K;	fit err.:	3.26e-02
PLOG/	0.5000	5.721e+43	-9.647	36766.5/ !	500.0-1400.0K;	fit err.:	1.78e-02
PLOG/	1.0000	7.073e+39	-8.390	35585.5/ !	500.0-1600.0K;	fit err.:	2.78e-02
PLOG/	10.0000	2.962e+31	-5.673	33229.5/ !	500.0-1800.0K;	fit err.:	8.19e-03

PLOG/	20.0000	6.336e+28	-4.831	32328.8/ !	500.0-2000.0K;	fit err.:	9.11e-03
PLOG/	50.0000	3.321e+25	-3.805	31168.9/ !	500.0-2000.0K;	fit err.:	1.84e-02
PLOG/	100.0000	9.343e+22	-3.018	30194.1/ !	500.0-2000.0K;	fit err.:	2.46e-02
DEC-R1<=>DEC-R2		2.792e-20	8.626	9577.0 !	500.0-2000.0K;	fit err.:	3.01e-02
PLOG/	0.0010	1.147e+54	-14.837	33406.4/ !	500.0-1000.0K;	fit err.:	2.36e-02
PLOG/	0.0050	4.557e+47	-12.644	32179.7/ !	500.0-1200.0K;	fit err.:	3.42e-02
PLOG/	0.0100	5.990e+47	-12.582	32812.4/ !	500.0-1200.0K;	fit err.:	2.82e-02
PLOG/	0.0500	7.589e+45	-11.788	33350.8/ !	500.0-1200.0K;	fit err.:	9.24e-03
PLOG/	0.1000	9.757e+43	-11.128	33099.4/ !	500.0-1200.0K;	fit err.:	4.26e-03
PLOG/	0.2000	3.148e+40	-9.988	32154.7/ !	500.0-1400.0K;	fit err.:	1.40e-02
PLOG/	0.5000	3.030e+37	-8.976	31513.6/ !	500.0-1400.0K;	fit err.:	1.08e-02
PLOG/	1.0000	6.204e+34	-8.096	30812.0/ !	500.0-1600.0K;	fit err.:	1.04e-02
PLOG/	10.0000	2.289e+24	-4.762	27582.3/ !	500.0-1800.0K;	fit err.:	4.65e-02
PLOG/	20.0000	2.843e+21	-3.836	26677.6/ !	500.0-2000.0K;	fit err.:	7.04e-02
PLOG/	50.0000	9.418e+13	-1.537	23747.5/ !	500.0-2000.0K;	fit err.:	7.28e-02
PLOG/	100.0000	1.127e+08	0.274	21361.9/ !	500.0-2000.0K;	fit err.:	7.40e-02
DEC-R1<=>CH3CH2OC (=O) CH2CH2O		4.743e+07	0.565	37669.6 !	500.0-2000.0K;	fit err.:	4.97e-03
PLOG/	50.0000	3.334e+16	-2.883	37234.9/ !	500.0-1000.0K;	fit err.:	2.63e-02
PLOG/	100.0000	7.019e+25	-5.594	41567.4/ !	500.0-1000.0K;	fit err.:	2.70e-02
DEC-R2<=>ring4 + CH3-CH2		8.068e+12	-0.442	50255.4 !	500.0-2000.0K;	fit err.:	5.98e-03
PLOG/	0.0010	2.264e+65	-18.607	60574.3/ !	500.0-1200.0K;	fit err.:	5.04e-02
PLOG/	0.0050	3.963e+63	-17.551	61696.4/ !	500.0-1400.0K;	fit err.:	7.57e-02
PLOG/	0.0100	2.896e+66	-18.201	63863.5/ !	500.0-1400.0K;	fit err.:	6.89e-02
PLOG/	0.0500	8.696e+69	-18.780	67749.4/ !	500.0-1400.0K;	fit err.:	4.64e-02
PLOG/	0.1000	3.794e+64	-16.980	66472.7/ !	500.0-1600.0K;	fit err.:	7.05e-02
PLOG/	0.2000	1.806e+64	-16.712	67345.4/ !	500.0-1600.0K;	fit err.:	5.58e-02
PLOG/	0.5000	1.213e+62	-15.857	67641.4/ !	500.0-1600.0K;	fit err.:	3.20e-02
PLOG/	1.0000	1.069e+57	-14.207	66247.8/ !	500.0-1800.0K;	fit err.:	4.53e-02
PLOG/	10.0000	7.751e+44	-10.241	63034.8/ !	500.0-2000.0K;	fit err.:	1.47e-02
PLOG/	20.0000	5.030e+40	-8.922	61614.6/ !	500.0-2000.0K;	fit err.:	3.28e-02
PLOG/	50.0000	6.930e+34	-7.103	59441.1/ !	500.0-2000.0K;	fit err.:	5.50e-02
PLOG/	100.0000	2.729e+30	-5.750	57708.1/ !	500.0-2000.0K;	fit err.:	6.48e-02
DEC-R2<=>CH3CH2OC=O + CH3	CH=O	7.174e+13	-0.061	34157.3 !	500.0-2000.0K;	fit err.:	3.67e-03
PLOG/	0.0010	4.623e+68	-17.724	50625.3/ !	500.0-1200.0K;	fit err.:	3.68e-02
PLOG/	0.0050	8.684e+61	-15.411	49404.9/ !	500.0-1400.0K;	fit err.:	5.32e-02

PLOG/	0.0100	4.156e+61	-15.205	49935.0/ !	500.0-1400.0K;	fit err.: 4.40e-02	
PLOG/	0.0500	2.519e+58	-14.005	49995.1/ !	500.0-1400.0K;	fit err.: 1.69e-02	
PLOG/	0.1000	6.709e+53	-12.538	48579.8/ !	500.0-1600.0K;	fit err.: 3.53e-02	
PLOG/	0.2000	4.734e+51	-11.811	48168.4/ !	500.0-1600.0K;	fit err.: 2.22e-02	
PLOG/	0.5000	1.525e+48	-10.667	47266.0/ !	500.0-1600.0K;	fit err.: 1.10e-02	
PLOG/	1.0000	3.527e+44	-9.513	46078.7/ !	500.0-1800.0K;	fit err.: 1.52e-02	
PLOG/	10.0000	5.428e+34	-6.417	42787.8/ !	500.0-2000.0K;	fit err.: 2.87e-02	
PLOG/	20.0000	5.059e+31	-5.478	41653.4/ !	500.0-2000.0K;	fit err.: 3.95e-02	
PLOG/	50.0000	4.057e+27	-4.221	40034.9/ !	500.0-2000.0K;	fit err.: 4.95e-02	
PLOG/	100.0000	5.067e+24	-3.335	38850.9/ !	500.0-2000.0K;	fit err.: 5.12e-02	
CH3CH2OC(=0)CH2CH2O<=>CH2 err.: 4.62e-03	=0 + CH3CH	20C (=0) CH2	1.356e+12	0.467	15180.6	! 500.0-2000.0K;	fit
PLOG/	50.0000	6.002e+32	-6.187	21382.2/ !	500.0-1000.0K;	fit err.: 7.32e-03	
PLOG/	100.0000	1.229e+31	-5.588	21196.4/ !	500.0-1000.0K;	fit err.: 3.43e-03	

7.6.3 EMC

7.6.3.1 Gas phase

	P (atm) A	(cm ³ /mol/s)	n (-)	Ea (cal/mol)	
EMC + H<=>EMC-R1		6.147e+06	2.238	9396.0 ! 500.0-2000.0K;	fit err.: 3.52e-03
PLOG/	0.5000	4.308e+46	-10.668	21145.7/ ! 500.0-1000.0K;	fit err.: 1.94e-02
PLOG/	1.0000	1.253e+41	-8.817	19801.3/ ! 500.0-1000.0K;	fit err.: 1.54e-02
PLOG/	10.0000	3.052e+29	-4.875	17454.2/ ! 500.0-1400.0K;	fit err.: 3.58e-02
PLOG/	20.0000	7.546e+27	-4.295	17388.0/ ! 500.0-1800.0K;	fit err.: 6.34e-02
PLOG/	50.0000	1.435e+21	-2.181	15061.5/ ! 500.0-2000.0K;	fit err.: 5.68e-02
PLOG/	100.0000	4.901e+15	-0.500	12906.6/ ! 500.0-2000.0K;	fit err.: 3.59e-02
EMC + H<=>EMC-R2		1.734e+06	2.509	6765.2 ! 500.0-2000.0K;	fit err.: 6.89e-03
PLOG/	0.1000	7.629e+56	-14.037	20956.3/ ! 500.0-1000.0K;	fit err.: 1.97e-02
PLOG/	0.2000	7.393e+52	-12.638	20252.4/ ! 500.0-1000.0K;	fit err.: 1.89e-02
PLOG/	0.5000	2.365e+47	-10.747	19201.4/ ! 500.0-1000.0K;	fit err.: 1.79e-02
PLOG/	1.0000	5.277e+47	-10.709	20173.2/ ! 500.0-1200.0K;	fit err.: 3.96e-02
PLOG/	10.0000	1.226e+32	-5.567	16084.1/ ! 500.0-1400.0K;	fit err.: 4.78e-02
PLOG/	20.0000	8.074e+28	-4.520	15288.0/ ! 500.0-1600.0K;	fit err.: 6.19e-02
PLOG/	50.0000	2.272e+25	-3.353	14412.7/ ! 500.0-2000.0K;	fit err.: 8.73e-02
PLOG/	100.0000	1.953e+19	-1.487	12032.1/ ! 500.0-2000.0K;	fit err.: 6.91e-02
EMC + H<=>EMC-R3		1.219e+05	2.669	8051.8 ! 500.0-2000.0K;	fit err.: 6.62e-03
PLOG/	0.0100	4.159e+57	-14.483	22790.1/ ! 500.0-1000.0K;	fit err.: 1.90e-02

PLOG/ (0.0500	1.737e+49	-11.549	21437.7/ !	500.0-1000.0K;	fit err.:	1.72e-02
PLOG/	0.1000	1.543e+50	-11.695	22649.8/ !	500.0-1200.0K;	fit err.:	3.80e-02
PLOG/	0.2000	1.354e+45	-10.020	21384.1/ !	500.0-1200.0K;	fit err.:	3.69e-02
PLOG/	0.5000	8.727e+41	-8.890	21052.8/ !	500.0-1400.0K;	fit err.:	5.19e-02
PLOG/	1.0000	6.384e+35	-6.926	19131.2/ !	500.0-1400.0K;	fit err.:	5.12e-02
PLOG/ 10	0.0000	7.728e+23	-3.079	15679.8/ !	500.0-2000.0K;	fit err.:	9.19e-02
PLOG/ 20	0.0000	1.155e+18	-1.293	13353.8/ !	500.0-2000.0K;	fit err.:	7.19e-02
PLOG/ 50	0.0000	2.040e+12	0.459	10976.3/ !	500.0-2000.0K;	fit err.:	3.66e-02
PLOG/ 100	0.0000	1.318e+10	1.125	10060.5/ !	500.0-2000.0K;	fit err.:	2.18e-02
EMC + CH3<=>EMC-R1		2.007e+03	2.975	12659.8 !	500.0-2000.0K;	fit err.:	2.00e-04
EMC + CH3<=>EMC-R2		1.194e+01	3.589	7685.0 !	500.0-2000.0K;	fit err.:	7.81e-03
PLOG/	1.0000	2.666e+62	-16.320	25450.4/ !	500.0-1000.0K;	fit err.:	2.14e-02
PLOG/ 10	0.0000	6.415e+48	-11.630	22980.1/ !	500.0-1000.0K;	fit err.:	2.18e-02
PLOG/ 20	0.0000	6.023e+50	-12.101	24574.8/ !	500.0-1200.0K;	fit err.:	5.05e-02
PLOG/ 50	0.0000	4.132e+42	-9.455	22217.6/ !	500.0-1200.0K;	fit err.:	5.46e-02
PLOG/ 100	0.0000	8.834e+41	-9.144	22624.7/ !	500.0-1400.0K;	fit err.:	7.09e-02
EMC + CH3<=>EMC-R3		2.531e-01	3.959	9350.3 !	500.0-2000.0K;	fit err.:	9.39e-03
PLOG/ (0.2000	6.139e+62	-16.639	27537.1/ !	500.0-1000.0K;	fit err.:	2.08e-02
PLOG/	0.5000	8.082e+58	-15.231	27196.6/ !	500.0-1000.0K;	fit err.:	2.12e-02
PLOG/	1.0000	1.354e+55	-13.917	26585.0/ !	500.0-1000.0K;	fit err.:	2.21e-02
PLOG/ 10	0.0000	1.144e+45	-10.394	25212.0/ !	500.0-1200.0K;	fit err.:	5.25e-02
PLOG/ 20	0.0000	8.434e+44	-10.240	25875.8/ !	500.0-1400.0K;	fit err.:	7.13e-02
PLOG/ 50	0.0000	7.739e+35	-7.374	22896.8/ !	500.0-1400.0K;	fit err.:	7.83e-02
PLOG/ 100	0.0000	2.165e+34	-6.818	22817.1/ !	500.0-1600.0K;	fit err.:	1.02e-01
EMC-R1<=>oxirane + CH3OC(=O)		3.121e+10	0.579	64049.8 !	500.0-2000.0K;	fit err.:	2.09e-04
PLOG/	0.0010	2.253e-46	11.598	24720.5/ !	500.0-1200.0K;	fit err.:	1.43e-02
PLOG/ (0.0050	9.003e+02	-1.718	52758.7/ !	500.0-1200.0K;	fit err.:	3.18e-02
PLOG/	0.0100	4.468e+23	-7.501	63492.2/ !	500.0-1200.0K;	fit err.:	6.04e-02
PLOG/	0.0500	2.201e+22	-6.285	63466.8/ !	500.0-1400.0K;	fit err.:	7.18e-02
PLOG/ (0.1000	4.374e+25	-7.043	63234.5/ !	500.0-1400.0K;	fit err.:	6.00e-02
PLOG/	0.2000	9.885e+33	-9.284	65546.2/ !	500.0-1400.0K;	fit err.:	6.06e-02
PLOG/	0.5000	3.029e+37	-9.927	66333.7/ !	500.0-1600.0K;	fit err.:	8.43e-02
PLOG/	1.0000	2.179e+44	-11.665	69509.1/ !	500.0-1600.0K;	fit err.:	7.89e-02
PLOG/ 10	0.0000	2.089e+48	-11.852	74444.6/ !	500.0-2000.0K;	fit err.:	8.87e-02
PLOG/ 20	0.0000	1.239e+49	-11.827	76100.0/ !	500.0-2000.0K;	fit err.:	6.95e-02

PLOG/	50.0000	1.666e+47	-10.983	76877.1/ !	500.0-2000.0K;	fit err.:	3.57e-02
PLOG/	100.0000	7.864e+43	-9.818	76425.8/ !	500.0-2000.0K;	fit err.:	8.78e-03
EMC-R1<=>CH3OCO(=O)	+ CH2=CH2	5.131e+11	0.492	27155.3 !	500.0-2000.0K;	fit err.:	1.01e-03
PLOG/	0.0010	3.567e+47	-11.738	34380.2/ !	500.0-1200.0K;	fit err.:	4.38e-02
PLOG/	0.0050	9.790e+50	-12.506	37121.0/ !	500.0-1200.0K;	fit err.:	3.83e-02
PLOG/	0.0100	8.065e+51	-12.667	38101.9/ !	500.0-1200.0K;	fit err.:	3.43e-02
PLOG/	0.0500	4.037e+47	-11.097	37779.5/ !	500.0-1400.0K;	fit err.:	4.45e-02
PLOG/	0.1000	3.960e+47	-10.989	38405.0/ !	500.0-1400.0K;	fit err.:	3.80e-02
PLOG/	0.2000	1.238e+47	-10.737	38788.4/ !	500.0-1400.0K;	fit err.:	2.90e-02
PLOG/	0.5000	9.049e+42	-9.367	37768.3/ !	500.0-1600.0K;	fit err.:	3.82e-02
PLOG/	1.0000	4.267e+41	-8.884	37726.8/ !	500.0-1600.0K;	fit err.:	2.74e-02
PLOG/	10.0000	1.324e+33	-6.112	35411.5/ !	500.0-2000.0K;	fit err.:	1.89e-02
PLOG/	20.0000	8.724e+30	-5.409	34778.8/ !	500.0-2000.0K;	fit err.:	1.04e-02
PLOG/	50.0000	4.015e+27	-4.358	33647.6/ !	500.0-2000.0K;	fit err.:	1.86e-02
PLOG/	100.0000	8.627e+24	-3.529	32661.3/ !	500.0-2000.0K;	fit err.:	2.78e-02
EMC-R1<=>EMC-R2		9.133e-12	6.345	15129.4 !	500.0-2000.0K;	fit err.:	3.19e-02
PLOG/	0.0010	3.531e+53	-14.342	35828.2/ !	500.0-1200.0K;	fit err.:	5.06e-02
PLOG/	0.0050	4.360e+42	-10.827	32462.4/ !	500.0-1200.0K;	fit err.:	3.48e-02
PLOG/	0.0100	8.245e+42	-10.810	33155.3/ !	500.0-1200.0K;	fit err.:	3.64e-02
PLOG/	0.0500	3.913e+42	-10.492	34303.6/ !	500.0-1400.0K;	fit err.:	1.91e-02
PLOG/	0.1000	4.741e+37	-8.946	32535.6/ !	500.0-1400.0K;	fit err.:	2.84e-02
PLOG/	0.2000	5.427e+34	-7.987	31658.5/ !	500.0-1400.0K;	fit err.:	3.84e-02
PLOG/	0.5000	3.021e+31	-6.931	30641.2/ !	500.0-1600.0K;	fit err.:	3.52e-02
PLOG/	1.0000	3.053e+29	-6.272	30082.3/ !	500.0-1600.0K;	fit err.:	2.51e-02
PLOG/	10.0000	1.393e+28	-5.634	30997.2/ !	500.0-2000.0K;	fit err.:	7.93e-02
PLOG/	20.0000	1.557e+24	-4.392	29622.8/ !	500.0-2000.0K;	fit err.:	7.34e-02
PLOG/	50.0000	1.922e+18	-2.560	27410.0/ !	500.0-2000.0K;	fit err.:	7.01e-02
PLOG/	100.0000	2.295e+13	-1.048	25467.2/ !	500.0-2000.0K;	fit err.:	6.49e-02
EMC-R2<=>CH3CH2OC=O	+ CH3CH=O	1.536e+12	-0.174	50599.7 !	500.0-2000.0K;	fit err.:	4.36e-03
PLOG/	0.0010	1.472e+59	-16.360	60851.8/ !	500.0-1400.0K;	fit err.:	7.12e-02
PLOG/	0.0050	3.923e+71	-19.580	67572.0/ !	500.0-1600.0K;	fit err.:	1.76e-01
PLOG/	0.0100	2.808e+55	-14.588	61649.3/ !	500.0-1600.0K;	fit err.:	3.91e-02
PLOG/	0.0500	8.075e+56	-14.598	64416.5/ !	500.0-1800.0K;	fit err.:	7.01e-02
PLOG/	0.1000	2.859e+53	-13.433	63628.0/ !	500.0-1800.0K;	fit err.:	3.93e-02
PLOG/	0.2000	1.256e+47	-11.428	61432.5/ !	500.0-1800.0K;	fit err.:	2.28e-02

PLOG/	0.5000	1.053e+46	-10.928	62014.2/ !	500.0-2000.0K;	fit err.:	1.90e-02
PLOG/	1.0000	2.764e+45	-10.632	62479.9/ !	500.0-2000.0K;	fit err.:	1.74e-02
PLOG/	10.0000	3.671e+34	-7.069	59398.8/ !	500.0-2000.0K;	fit err.:	2.44e-02
PLOG/	20.0000	3.741e+30	-5.808	58021.2/ !	500.0-2000.0K;	fit err.:	4.21e-02
PLOG/	50.0000	3.589e+25	-4.244	56161.9/ !	500.0-2000.0K;	fit err.:	5.13e-02
PLOG/	100.0000	1.128e+22	-3.167	54781.1/ !	500.0-2000.0K;	fit err.:	5.00e-02
EMC-R2<=>ring4 + CH3		2.071e+13	-0.116	34410.8 !	500.0-2000.0K;	fit err.:	4.61e-03
PLOG/	0.0010	2.240e+61	-15.485	49908.1/ !	500.0-1400.0K;	fit err.:	5.31e-02
PLOG/	0.0050	8.385e+65	-16.597	53047.7/ !	500.0-1600.0K;	fit err.:	1.39e-01
PLOG/	0.0100	1.062e+36	-7.612	40971.4/ !	500.0-1600.0K;	fit err.:	1.71e-01
PLOG/	0.0500	9.624e+47	-10.967	47142.4/ !	500.0-1800.0K;	fit err.:	3.51e-02
PLOG/	0.1000	4.016e+34	-6.989	41056.1/ !	500.0-1800.0K;	fit err.:	6.98e-02
PLOG/	0.2000	8.786e+38	-8.174	43668.2/ !	500.0-1800.0K;	fit err.:	3.60e-02
PLOG/	0.5000	1.699e+36	-7.299	42765.9/ !	500.0-2000.0K;	fit err.:	2.35e-02
PLOG/	1.0000	5.186e+28	-5.095	38936.9/ !	500.0-2000.0K;	fit err.:	3.31e-02
PLOG/	10.0000	1.071e+27	-4.320	39925.2/ !	500.0-2000.0K;	fit err.:	2.58e-02
PLOG/	20.0000	2.643e+24	-3.503	38989.1/ !	500.0-2000.0K;	fit err.:	3.37e-02
PLOG/	50.0000	1.307e+21	-2.483	37711.1/ !	500.0-2000.0K;	fit err.:	3.67e-02
PLOG/	100.0000	9.123e+18	-1.823	36836.7/ !	500.0-2000.0K;	fit err.:	3.28e-02
EMC-R2<=>EMC-R3		2.730e+08	0.496	11764.6 !	500.0-2000.0K;	fit err.:	5.41e-03
PLOG/	0.5000	2.670e+17	-2.441	14229.8/ !	500.0-1000.0K;	fit err.:	8.07e-05
PLOG/	1.0000	6.905e+15	-1.898	13938.0/ !	500.0-1200.0K;	fit err.:	1.21e-03
PLOG/	10.0000	5.714e+14	-1.446	14268.1/ !	500.0-2000.0K;	fit err.:	2.34e-02
PLOG/	20.0000	1.019e+14	-1.203	14061.2/ !	500.0-2000.0K;	fit err.:	2.99e-02
PLOG/	50.0000	5.365e+12	-0.805	13594.2/ !	500.0-2000.0K;	fit err.:	3.42e-02
PLOG/	100.0000	5.597e+11	-0.504	13198.9/ !	500.0-2000.0K;	fit err.:	3.17e-02
PLOG/	0.5000	3.583e+30	-7.063	72295.9/ !	500.0-1000.0K;	fit err.:	2.61e-02
PLOG/	1.0000	3.018e+24	-5.045	70588.6/ !	500.0-1200.0K;	fit err.:	4.99e-02
PLOG/	10.0000	8.409e+49	-12.188	86032.5/ !	500.0-2000.0K;	fit err.:	6.89e-02
PLOG/	20.0000	5.118e+47	-11.379	86966.1/ !	500.0-2000.0K;	fit err.:	1.17e-01
PLOG/	50.0000	8.908e+40	-9.226	86370.4/ !	500.0-2000.0K;	fit err.:	1.87e-01
PLOG/	100.0000	1.244e+33	-6.836	84449.3/ !	500.0-2000.0K;	fit err.:	2.35e-01
EMC-R3<=>OringO + CH3-CH2		2.162e+14	-0.645	54458.5 !	500.0-2000.0K;	fit err.:	2.43e-03
PLOG/	0.5000	1.062e+25	-4.269	57647.5/ !	500.0-1000.0K;	fit err.:	1.95e-02
PLOG/	1.0000	1.707e+20	-2.778	55691.6/ !	500.0-1200.0K;	fit err.:	3.58e-02

PLOG/	10.0000	5.964e+40	-8.838	64660.3/ ! 500.0-2000.0K; fit err.: 3.74e-02	
PLOG/	20.0000	1.034e+38	-7.931	63861.6/ ! 500.0-2000.0K; fit err.: 4.91e-02	
PLOG/	50.0000	3.844e+33	-6.521	62374.7/! 500.0-2000.0K; fit err.: 6.44e-02	
PLOG/	100.0000	7.106e+29	-5.360	60971.9/ ! 500.0-2000.0K; fit err.: 6.97e-02	
EMC-R3<=>CH3CH2OC(=O) + C	H2=0	9.072e+13	-0.042	38373.7 ! 500.0-2000.0K; fit err.: 2.20e-03	
PLOG/	0.5000	4.192e+06	2.018	34989.2/ ! 500.0-1000.0K; fit err.: 1.59e-02	
PLOG/	1.0000	1.402e+06	2.131	34326.6/ ! 500.0-1200.0K; fit err.: 3.22e-02	
PLOG/	10.0000	4.174e+31	-5.485	45286.4/ ! 500.0-2000.0K; fit err.: 4.29e-02	
PLOG/	20.0000	5.055e+29	-4.860	44740.4/ ! 500.0-2000.0K; fit err.: 4.83e-02	
PLOG/	50.0000	3.141e+26	-3.852	43615.3/ ! 500.0-2000.0K; fit err.: 5.41e-02	
PLOG/	100.0000	8.226e+23	-3.055	42618.4/ ! 500.0-2000.0K; fit err.: 5.45e-02	
EMC-R3<=>CH3CH2OC (=0) CH2O		7.097e+11	-0.041	36041.8 ! 500.0-2000.0K; fit err.: 4.08e-04	
PLOG/	50.0000	4.139e+26	-5.272	37973.4/ ! 500.0-1000.0K; fit err.: 2.22e-02	
PLOG/	100.0000	1.274e+31	-6.511	40407.8/ ! 500.0-1000.0K; fit err.: 2.01e-02	
CH3OC(=0)CH2CH2O<=>CH2=0 4.36e-03	+ CH3OC (=0)CH2 9.302e+1	1 0.5	35 16134.6 ! 500.0-2000.0K; fit er:	r.:
PLOG/	20.0000	7.553e+34	-6.931	22564.9/ ! 500.0-1000.0K; fit err.: 8.77e-03	
PLOG/	50.0000	5.753e+33	-6.465	22824.2/! 500.0-1000.0K; fit err.: 5.28e-03	
PLOG/	100.0000	3.214e+31	-5.694	22408.5/ ! 500.0-1000.0K; fit err.: 1.49e-03	
CH3CH2OC(=0)CH2O<=>CH3CH2 1.75e-03	OC (=0) + C	H2=0 2.314e+1	4 -0.0	01 16712.0 ! 500.0-2000.0K; fit er:	r.:
PLOG/	50.0000	4.825e+35	-7.057	22595.0/! 500.0-1000.0K; fit err.: 1.02e-02	
PLOG/	100.0000	1.009e+35	-6.754	22856.7/ ! 500.0-1000.0K; fit err.: 6.54e-03	

7.6.3.2 Liquid phase

P	(atm) A	(cm ³ /mol/s)	n (-)	Ea (cal/mol)
EMC + H<=>EMC-R1		7.615e+07	1.934	10580.0 ! 500.0-2000.0K; fit err.: 1.38e-03
EMC + H<=>EMC-R2		8.934e+06	2.222	7740.7 ! 500.0-2000.0K; fit err.: 3.77e-03
EMC + H<=>EMC-R3		4.432e+04	3.089	9839.6 ! 500.0-2000.0K; fit err.: 6.82e-03
EMC + CH3<=>EMC-R1		3.871e+03	2.903	13808.0 ! 500.0-2000.0K; fit err.: 2.64e-04
EMC + CH3<=>EMC-R2		2.061e+02	2.985	11001.7 ! 500.0-2000.0K; fit err.: 1.43e-03
EMC + CH3<=>EMC-R3		7.641e+01	3.270	12761.1 ! 500.0-2000.0K; fit err.: 2.73e-03
EMC-R1<=>oxirane + CH3OC(=0))	2.431e+10	0.548	63691.6 ! 500.0-2000.0K; fit err.: 3.86e-04
PLOG/	0.0010	1.114e-46	11.371	21390.8/ ! 500.0-1200.0K; fit err.: 1.70e-01
PLOG/	0.0050	4.544e-33	8.355	32580.6/ ! 500.0-1200.0K; fit err.: 6.55e-02
PLOG/	0.0100	7.191e+27	-9.025	64805.1/ ! 500.0-1200.0K; fit err.: 5.05e-02
PLOG/	0.0500	4.088e+30	-8.880	69642.3/ ! 500.0-1400.0K; fit err.: 1.12e-01
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PLOG/	0.1000	2.794e+19	-5.410	61740.9/ !	500.0-1400.0K;	fit err.:	6.22e-02
PLOG/	0.2000	3.732e+25	-7.009	62683.8/ !	500.0-1400.0K;	fit err.:	6.11e-02
PLOG/	0.5000	1.862e+36	-9.850	65873.2/ !	500.0-1400.0K;	fit err.:	6.04e-02
PLOG/	1.0000	2.799e+37	-9.879	66120.0/ !	500.0-1600.0K;	fit err.:	8.40e-02
PLOG/	10.0000	1.106e+49	-12.297	73799.0/ !	500.0-1800.0K;	fit err.:	7.69e-02
PLOG/	20.0000	8.611e+46	-11.392	74090.6/ !	500.0-2000.0K;	fit err.:	8.74e-02
PLOG/	50.0000	7.634e+46	-11.058	75774.9/ !	500.0-2000.0K;	fit err.:	5.31e-02
PLOG/	100.0000	3.117e+44	-10.147	75855.9/ !	500.0-2000.0K;	fit err.:	2.60e-02
EMC-R1<=>CH3OCO(=O) + CH2=	=CH2	9.742e+11	0.418	26147.4 !	500.0-2000.0K;	fit err.:	7.45e-04
PLOG/	0.0010	5.099e+43	-10.636	31393.5/ !	500.0-1200.0K;	fit err.:	4.42e-02
PLOG/	0.0050	3.587e+47	-11.531	34211.6/ !	500.0-1200.0K;	fit err.:	4.04e-02
PLOG/	0.0100	1.003e+49	-11.852	35396.4/ !	500.0-1200.0K;	fit err.:	3.76e-02
PLOG/	0.0500	2.085e+45	-10.465	35299.3/ !	500.0-1400.0K;	fit err.:	4.89e-02
PLOG/	0.1000	6.445e+45	-10.505	36133.8/ !	500.0-1400.0K;	fit err.:	4.32e-02
PLOG/	0.2000	6.971e+45	-10.411	36765.7/ !	500.0-1400.0K;	fit err.:	3.63e-02
PLOG/	0.5000	8.153e+44	-10.001	37153.9/ !	500.0-1400.0K;	fit err.:	2.48e-02
PLOG/	1.0000	1.302e+41	-8.768	36067.2/ !	500.0-1600.0K;	fit err.:	3.59e-02
PLOG/	10.0000	1.087e+34	-6.405	34498.1/ !	500.0-1800.0K;	fit err.:	1.39e-02
PLOG/	20.0000	2.011e+31	-5.534	33634.1/ !	500.0-2000.0K;	fit err.:	1.46e-02
PLOG/	50.0000	1.846e+28	-4.566	32678.8/ !	500.0-2000.0K;	fit err.:	1.05e-02
PLOG/	100.0000	5.495e+25	-3.776	31787.0/ !	500.0-2000.0K;	fit err.:	1.99e-02
EMC-R1<=>EMC-R2		6.052e-12	6.400	15708.1 !	500.0-2000.0K;	fit err.:	2.92e-02
PLOG/	0.0010	4.056e+46	-12.533	31672.0/ !	500.0-1200.0K;	fit err.:	3.29e-02
PLOG/	0.0050	2.399e+48	-12.803	33802.7/ !	500.0-1200.0K;	fit err.:	2.77e-02
PLOG/	0.0100	4.156e+48	-12.759	34541.6/ !	500.0-1200.0K;	fit err.:	2.50e-02
PLOG/	0.0500	6.992e+46	-11.960	35312.8/ !	500.0-1400.0K;	fit err.:	1.03e-02
PLOG/	0.1000	3.824e+45	-11.471	35419.7/ !	500.0-1400.0K;	fit err.:	9.44e-03
PLOG/	0.2000	8.148e+43	-10.863	35341.0/ !	500.0-1400.0K;	fit err.:	6.24e-03
PLOG/	0.5000	1.181e+41	-9.882	34908.0/ !	500.0-1400.0K;	fit err.:	5.20e-03
PLOG/	1.0000	9.679e+40	-9.768	35433.6/ !	500.0-1600.0K;	fit err.:	5.04e-02
PLOG/	10.0000	7.464e+33	-7.380	33995.9/ !	500.0-1800.0K;	fit err.:	1.49e-01
PLOG/	20.0000	5.645e+12	-1.022	24699.6/ !	500.0-2000.0K;	fit err.:	2.46e-01
PLOG/	50.0000	1.180e+36	-7.879	36142.5/ !	500.0-2000.0K;	fit err.:	2.69e-01
PLOG/	100.0000	3.622e+17	-2.320	27910.3/ !	500.0-2000.0K;	fit err.:	1.36e-01
EMC-R1<=>CH3OC (=O) CH2CH2O		1.348e+08	0.558	38373.0 !	500.0-2000.0K;	fit err.:	5.27e-03

PLOG/	50.0000	4.163e+14	-2.268	36793.3/ !	500.0-1000.0K;	fit err.:	2.18e-02
PLOG/	100.0000	2.406e+24	-5.107	41190.7/ !	500.0-1000.0K;	fit err.:	2.39e-02
EMC-R2<=>CH3CH2OC=O +	CH3CH=O	1.396e+12	-0.147	49064.9 !	500.0-2000.0K;	fit err.:	4.51e-03
PLOG/	0.0010	3.668e+54	-14.889	57385.3/ !	500.0-1400.0K;	fit err.:	8.28e-02
PLOG/	0.0050	5.947e+54	-14.492	59133.0/ !	500.0-1600.0K;	fit err.:	9.83e-02
PLOG/	0.0100	3.552e+56	-14.839	60710.5/ !	500.0-1600.0K;	fit err.:	8.49e-02
PLOG/	0.0500	3.452e+55	-14.126	62271.8/ !	500.0-1800.0K;	fit err.:	5.51e-02
PLOG/	0.1000	1.679e+54	-13.567	62604.3/ !	500.0-1800.0K;	fit err.:	6.43e-02
PLOG/	0.2000	2.247e+53	-13.153	63122.2/ !	500.0-2000.0K;	fit err.:	3.55e-02
PLOG/	0.5000	1.244e+49	-11.703	62303.5/ !	500.0-2000.0K;	fit err.:	5.02e-02
PLOG/	1.0000	7.817e+46	-10.928	62068.9/ !	500.0-2000.0K;	fit err.:	2.98e-02
PLOG/	10.0000	9.124e+34	-7.099	58463.4/ !	500.0-2000.0K;	fit err.:	4.47e-02
PLOG/	20.0000	4.592e+30	-5.770	56828.0/ !	500.0-2000.0K;	fit err.:	5.67e-02
PLOG/	50.0000	1.939e+25	-4.123	54685.9/ !	500.0-2000.0K;	fit err.:	6.11e-02
PLOG/	100.0000	5.152e+21	-3.035	53206.2/ !	500.0-2000.0K;	fit err.:	5.55e-02
EMC-R2<=>ring4 + CH3		1.895e+12	0.173	33421.2 !	500.0-2000.0K;	fit err.:	9.45e-04
PLOG/	0.0010	1.610e+55	-13.704	46181.8/ !	500.0-1400.0K;	fit err.:	5.36e-02
PLOG/	0.0050	5.167e+51	-12.412	46009.2/ !	500.0-1600.0K;	fit err.:	4.81e-02
PLOG/	0.0100	6.744e+51	-12.347	46655.3/ !	500.0-1600.0K;	fit err.:	2.93e-02
PLOG/	0.0500	1.913e+48	-11.067	46431.9/ !	500.0-1800.0K;	fit err.:	2.54e-02
PLOG/	0.1000	1.755e+44	-9.777	45152.3/ !	500.0-1800.0K;	fit err.:	2.98e-02
PLOG/	0.2000	4.245e+44	-9.813	45862.1/ !	500.0-2000.0K;	fit err.:	8.67e-02
PLOG/	0.5000	3.240e+38	-7.903	43634.6/ !	500.0-2000.0K;	fit err.:	1.75e-02
PLOG/	1.0000	1.160e+36	-7.117	42910.7/ !	500.0-2000.0K;	fit err.:	1.30e-02
PLOG/	10.0000	3.257e+26	-4.141	39451.3/ !	500.0-2000.0K;	fit err.:	4.68e-02
PLOG/	20.0000	3.776e+23	-3.243	38270.9/ !	500.0-2000.0K;	fit err.:	5.12e-02
PLOG/	50.0000	1.275e+20	-2.187	36831.4/ !	500.0-2000.0K;	fit err.:	4.82e-02
PLOG/	100.0000	7.624e+17	-1.513	35886.1/ !	500.0-2000.0K;	fit err.:	4.08e-02
EMC-R2<=>EMC-R3		1.694e+08	0.558	21805.8 !	500.0-2000.0K;	fit err.:	6.21e-03
PLOG/	0.0010	4.002e+42	-10.546	31932.6/ !	500.0-1200.0K;	fit err.:	2.39e-02
PLOG/	0.0050	8.402e+38	-9.205	31738.7/ !	500.0-1400.0K;	fit err.:	2.86e-02
PLOG/	0.0100	3.313e+38	-8.998	32098.1/ !	500.0-1400.0K;	fit err.:	1.97e-02
PLOG/	0.0500	2.854e+34	-7.612	31371.0/ !	500.0-1600.0K;	fit err.:	1.63e-02
PLOG/	0.1000	1.749e+32	-6.891	30766.3/ !	500.0-1800.0K;	fit err.:	2.24e-02
PLOG/	0.2000	8.100e+30	-6.441	30511.8/ !	500.0-1800.0K;	fit err.:	1.45e-02

PLOG/	0.5000	3.606e+28	-5.681	29843.9/ !	500.0-2000.0K;	fit err.:	1.56e-02
PLOG/	1.0000	8.189e+26	-5.153	29357.2/ !	500.0-2000.0K;	fit err.:	1.87e-02
PLOG/	10.0000	1.355e+20	-3.044	26876.2/ !	500.0-2000.0K;	fit err.:	5.09e-02
PLOG/	20.0000	8.602e+17	-2.373	25988.8/ !	500.0-2000.0K;	fit err.:	5.49e-02
PLOG/	50.0000	1.747e+15	-1.555	24868.8/ !	500.0-2000.0K;	fit err.:	5.46e-02
PLOG/	100.0000	2.453e+13	-0.994	24076.5/ !	500.0-2000.0K;	fit err.:	4.87e-02
EMC-R3<=>OringO + CH3-CH2		1.256e+14	-0.621	53097.7 !	500.0-2000.0K;	fit err.:	1.92e-03
PLOG/	0.0010	2.311e+52	-14.462	59647.7/ !	500.0-1200.0K;	fit err.:	3.21e-02
PLOG/	0.0050	3.969e+54	-14.543	61906.0/ !	500.0-1400.0K;	fit err.:	5.03e-02
PLOG/	0.0100	5.040e+57	-15.240	64023.3/ !	500.0-1400.0K;	fit err.:	4.17e-02
PLOG/	0.0500	8.966e+57	-14.808	66284.5/ !	500.0-1600.0K;	fit err.:	4.70e-02
PLOG/	0.1000	3.399e+55	-13.895	66168.5/ !	500.0-1800.0K;	fit err.:	6.02e-02
PLOG/	0.2000	3.371e+55	-13.726	67109.6/ !	500.0-1800.0K;	fit err.:	4.40e-02
PLOG/	0.5000	1.351e+52	-12.521	66715.4/ !	500.0-2000.0K;	fit err.:	4.54e-02
PLOG/	1.0000	1.792e+50	-11.838	66645.9/ !	500.0-2000.0K;	fit err.:	2.55e-02
PLOG/	10.0000	4.015e+38	-8.087	63193.3/ !	500.0-2000.0K;	fit err.:	5.18e-02
PLOG/	20.0000	2.032e+34	-6.757	61579.3/ !	500.0-2000.0K;	fit err.:	6.53e-02
PLOG/	50.0000	6.210e+28	-5.066	59377.5/ !	500.0-2000.0K;	fit err.:	7.20e-02
PLOG/	100.0000	1.131e+25	-3.927	57835.1/ !	500.0-2000.0K;	fit err.:	6.75e-02
EMC-R3<=>CH3CH2OC(=O) + CH	12=0	3.080e+13	-0.024	37985.2 !	500.0-2000.0K;	fit err.:	2.63e-03
PLOG/	0.0010	2.920e+54	-13.670	48006.9/ !	500.0-1200.0K;	fit err.:	1.77e-02
PLOG/	0.0050	5.496e+50	-12.189	48050.9/ !	500.0-1400.0K;	fit err.:	2.83e-02
PLOG/	0.0100	1.101e+51	-12.135	48933.6/ !	500.0-1400.0K;	fit err.:	1.97e-02
PLOG/	0.0500	1.086e+48	-10.937	49311.9/ !	500.0-1600.0K;	fit err.:	1.66e-02
PLOG/	0.1000	3.595e+45	-10.090	48849.8/ !	500.0-1800.0K;	fit err.:	2.51e-02
PLOG/	0.2000	1.240e+44	-9.562	48778.3/ !	500.0-1800.0K;	fit err.:	1.25e-02
PLOG/	0.5000	8.265e+40	-8.513	48013.3/ !	500.0-2000.0K;	fit err.:	1.40e-02
PLOG/	1.0000	4.427e+38	-7.771	47426.6/ !	500.0-2000.0K;	fit err.:	1.83e-02
PLOG/	10.0000	1.917e+29	-4.828	44280.1/ !	500.0-2000.0K;	fit err.:	5.65e-02
PLOG/	20.0000	3.017e+26	-3.962	43255.0/ !	500.0-2000.0K;	fit err.:	5.94e-02
PLOG/	50.0000	1.095e+23	-2.905	41963.7/ !	500.0-2000.0K;	fit err.:	5.64e-02
PLOG/	100.0000	6.342e+20	-2.221	41107.1/ !	500.0-2000.0K;	fit err.:	4.81e-02
EMC-R3<=>CH3CH2OC (=O) CH2O		6.145e+11	-0.066	34515.4 !	500.0-2000.0K;	fit err.:	7.61e-04
PLOG/	50.0000	6.500e+28	-6.018	37157.0/ !	500.0-1000.0K;	fit err.:	2.45e-02
PLOG/	100.0000	2.771e+33	-7.303	39641.2/ !	500.0-1000.0K;	fit err.:	2.15e-02

CH3OC(=0)CH2CH2O<=>CH2=0 - 3.60e-03	+ CH3OC (=0)	CH2 1.025e+12	2 0.50	15246	.1 !	500.0-2	000.0K;	fit	err.:
PLOG/	50.0000	2.803e+32	-6.105	21252.1/ !	500.0-100	0.0K; fi	t err.:	6.29e-03	3
PLOG/	100.0000	8.699e+30	-5.559	21138.9/ !	500.0-1000	0.0K; fi	t err.:	3.56e-03	3
CH3CH2OC(=0)CH2O<=>CH3CH2C 1.77e-03	DC (=0) + CH	12=0 4.211e+14	-0.09	90 17655	.5 !	500.0-2	000.0K;	fit	err.:
PLOG/	50.0000	1.364e+38	-7.765	24173.9/ !	500.0-1000	0.0K; fi	t err.:	1.07e-02	2
PLOG/	100.0000	3.826e+37	-7.498	24510.7/ !	500.0-1000	0.0K; fi	t err.:	7.80e-03	3

7.6.4 Glossary

Name	formula
DMC	
DMC-R	-o , O CH ₂
OringO	< <mark>0</mark> >=0
CH3OC=O	~ ⁰ ,_0
CH3OC(=O)CH2O	~°o.
DEC	
DEC-R1	H ₂ ċ
DEC-R2	, °, °, °, °, °, °, °, °, °, °, °, °, °,
oxirane	○
CH3CH2OC(=O)	<u> </u>
CH3CH2OCO(=O)	
ring4	

Name	formula
CH3CH=O	∕ ∼ ₀
CH3CH2OC(=O)CH2	H ₂ Ċ
CH3CH2OC(=O)CH2CH2O	0. 0.
EMC	
EMC-R1	H ₂ Ċ O O
EMC-R2	
EMC-R3	ĊH ₂
CH3OCO(=O)	~ ⁰ _ 0.
CH3OC(=O)CH2	H ₂ Ċ 0
CH3OC(=O)OCH2CH2	H ₂ Ċ O O
CH3CH2OC(=O)CH2O	0