

UNIVERSITÉ CATHOLIQUE DE LOUVAIN

INSTITUTE OF CONDENSED MATTER AND NANOSCIENCES

MOLECULES, SOLIDS AND REACTIVITY



Experimental and kinetic modeling
investigation of benzene and toluene
combustion in premixed, laminar and
one-dimensional flames

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Acknowledgments

The story of this PhD thesis begins in secondary school, when my science professor, Madame Delvigne, taught me the magic of chemistry. Willing to go deeper into this topic, I decided to study chemistry at the university. The following eight years were really enriching and I am very grateful to each person that contributed to my growing knowledge in chemistry.

The last year of my master degree, in 2005, I had to choose a laboratory to perform my final dissertation. Whereas I already knew Pr. Jacques Vandooren, I did not really know the research topic he was interested in. By curiosity, I visited his laboratory with two of my friends, Catherine Duynslaegher and Nicolas Leplat. I knew this was the laboratory I wanted to study in. I discovered a new challenge, combining experiment and modeling of a familiar phenomenon: combustion. As the vast majority of people, I thought almost everything about combustion was known. I quickly discovered I was wrong and that many uncertainties still surrounded several topics. Among the research topics proposed by Pr. Vandooren, I decided to study aromatic flame chemistry.

After my final dissertation Jacques Vandooren proposed me to pursue my research as a PhD student. I would like to show him my deepest gratitude for giving me this great opportunity and to have made me discover the passionating science of combustion. In addition to supervising my work, Pr. Vandooren helped me to share my scientific results in several national and international congresses. I thank him for these highly enriching experiences.

I am equally grateful to my co-supervisor Pr. Daniel Peeters for welcoming me in the CSTR unit and for his continuous availability. To those who share my everyday life in the laboratory: Véronique Dias, Catherine Duynslaegher, Xavier Lories, Christiane Smets and Pierre Van Tiggelen, thank you. To my great friend Nicolas Leplat, thank you for your scientific help and for all the unforgettable stories that we have lived together.

I am thankful to my family who helped me satisfying my curiosity and who still today supports me in each project I undertake. Without these studies, I would perhaps have never met Kim who now walks with me on the magic path of life.

Finally, I would like to thank all members of the jury who have read this PhD Thesis and have given constructive remarks to improve its scientific content, as well as its presentation.

Even though my PhD story comes to an end, I hope it is only a new start for exciting challenges ...

This work would not have been possible without the financial support of the F.R.I.A. (Fonds pour la formation à la Recherche dans l'Industrie et dans l'Agriculture) and of the laboratory.

Abstract

Flames that have an excess of fuel, compared to the stoichiometry, or where the mixing between fuel and oxidizer is imperfect, result in an incomplete combustion. The excess of fuel is principally converted into Polycyclic Aromatic Hydrocarbons (PAH), which are molecular precursors of soot. In addition to the carcinogenic hazard of PAH, soot promotes the atmospheric solar heating or causes the coating of combustion chambers in the industry. It is therefore very important to understand mechanisms involved in the chemistry of soot formation. Such a comprehension is the guiding thread of this work investigating chemical pathways involved in benzene and toluene flames.

One-dimensional, premixed and laminar benzene-oxygen-argon and toluene-oxygen-argon flames have been stabilized at different equivalence ratios and at low pressure on a flat flame burner. Experimental structures have been determined by Gas Chromatography, enabling the detection of major products of combustion, small hydrocarbon intermediates and chemical species from C_6H_x to first PAH. Molecular Beam Mass Spectrometry has been used to detect chemical species of interest that could not be followed by Gas Chromatography. These species include phenoxy radical, benzoquinone, benzyl radical and fulvenallene, which are all thought to be important intermediates of benzene and toluene combustion. Finally, a device has been developed for the measurement of soot concentration in rich hydrocarbon flames.

A detailed kinetic model for aromatic consumption and soot formation has been developed on the basis of a comprehensive literature survey. The good predictive capability of the proposed model has been verified by comparing its predictions to the experimental flame structures. Comparative reaction rate analyses have been carried out to determine the main reaction pathways occurring in aromatic flames.

The comprehensive experimental and kinetic modeling studies presented in this work improve the current understanding of aromatic flame chemistry, and will help the future works devoted to aromatic oxidation, as well as those on PAH and soot formation.

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Publications associated with this work:

- V. Detilleux and J. Vandooren. Experimental and kinetic modeling investigation of toluene combustion in premixed, one-dimensional and laminar toluene-oxygen-argon flames. *Proceedings of the Combustion Institute* 33(1):217–224, 2011.
- V. Detilleux and J. Vandooren. Experimental and kinetic modeling evidences of a C_7H_6 pathway in a rich toluene flame. *The Journal of Physical Chemistry A* 113(41):10913–10922, 2009.
- V. Detilleux and J. Vandooren. Experimental study and kinetic modeling of benzene oxidation in one-dimensional laminar premixed low-pressure flames. *Combustion, Explosion, and Shock Waves*, 45(4):392–403, 2009.
- V. Detilleux and J. Vandooren. Molecular beam mass spectrometry analysis of PAH production pathways in $C_6H_6/O_2/Ar$ and $C_6H_6/C_2H_2/O_2/Ar$ flames. *Combustion Science and Technology*, 180(7):1347–1369, 2008.

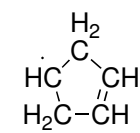
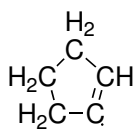
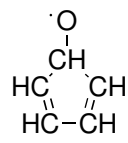
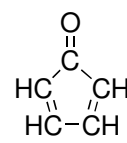
List of main structures, notations and trivial names:

• C₁ to C₄ Hydrocarbons

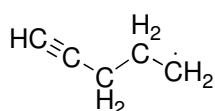
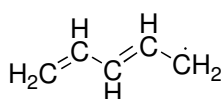
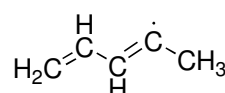
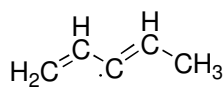
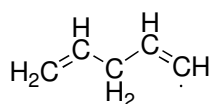
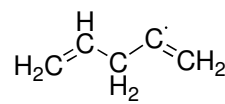
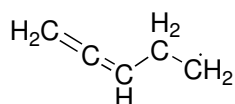
$\text{HC}\equiv\text{CH}$ C₂H₂ acetylene	$\text{H}_2\text{C}=\text{CH}_2$ C₂H₄ ethylene	$\text{HC}\dot{\text{C}}\text{H}_2$ C₂H₃ vinyl radical	$\text{H}_3\text{C}-\text{CH}_3$ C₂H₆ ethane
$\text{H}_3\text{C}-\dot{\text{C}}\text{H}_2$ C₂H₅ ethyl radical	$\text{HC}\dot{\text{C}}=\text{CH}_2$ $\text{HC}\equiv\text{C}-\dot{\text{C}}\text{H}_2$ C₃H₃ propargyl radicals	$\text{H}_2\text{C}=\text{C}=\text{CH}_2$ a-C₃H₄ allene	$\text{H}_3\text{C}-\text{C}\equiv\text{CH}$ p-C₃H₄ propyne
$\text{H}_2\text{C}=\underset{\text{H}}{\overset{\cdot}{\text{C}}}\text{CH}_3$ a-C₃H₅	$\text{HC}=\underset{\text{H}}{\overset{\cdot}{\text{C}}}\text{CH}_3$ s-C₃H₅	$\text{H}_2\text{C}=\underset{\cdot}{\text{C}}\text{CH}_3$ p-C₃H₅	$\text{H}_2\text{C}=\underset{\text{H}}{\overset{\cdot}{\text{C}}}\text{CH}_3$ C₃H₆ propylene
$\text{H}_3\text{C}-\underset{\text{H}_2}{\overset{\cdot}{\text{C}}}-\text{CH}_3$ C₃H₈ propane	$\text{HC}\equiv\text{C}-\text{C}\equiv\text{CH}$ C₄H₂ diacetylene	$\text{H}_2\text{C}=\underset{\text{H}}{\overset{\cdot}{\text{C}}}-\text{C}\equiv\text{CH}$ C₄H₄ vinylacetylene	$\text{H}_2\text{C}=\underset{\text{H}}{\overset{\cdot}{\text{C}}}-\text{CH}=\text{CH}_2$ n-C₄H₅
$\text{H}_2\text{C}=\underset{\text{H}_2\text{C}}{\overset{\cdot}{\text{C}}}-\text{CH}_2$ i-C₄H₅	$\text{H}_3\text{C}-\underset{\text{H}}{\overset{\cdot}{\text{C}}}=\text{C}=\text{CH}_2$ 1,2-C₄H₆ 1,2-butadiene	$\text{H}_2\text{C}=\text{CH}-\underset{\text{H}_2\text{C}}{\overset{\cdot}{\text{C}}}=\text{CH}_2$ 1,3-C₄H₆ 1,3-butadiene	

• C₅ Hydrocarbons

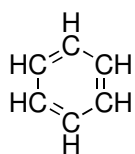
$\text{H}_2\text{C}-\underset{\text{H}_2\text{C}}{\overset{\text{H}_2}{\text{C}}}-\text{CH}=\text{CH}-\text{CH}_2$ C₅H₈ cyclopentene	$\text{HC}-\underset{\text{HC}}{\overset{\text{H}_2}{\text{C}}}-\text{CH}=\text{CH}-\text{CH}_2$ C₅H₆ cyclopentadiene	$\text{HC}-\underset{\text{HC}}{\overset{\cdot\text{H}}{\text{C}}}-\text{CH}=\text{CH}-\text{CH}_2$ C₅H₅ cyclopentadienyl radical	$\text{H}_2\text{C}-\underset{\text{HC}}{\overset{\text{H}_2}{\text{C}}}-\text{CH}=\text{CH}-\text{CH}_2$ C₅H₇(A)
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**C₅H₇(B)****C₅H₇(C)****C₅H₅O**cyclopentadienoxyl
radical**C₅H₄O**

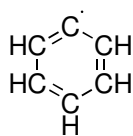
cyclopentadienone

**1-C₅H₇-5-yl****1,3-C₅H₇-5-yl****1,3-C₅H₇-4-yl****1,3-C₅H₇-3-yl****1,4-C₅H₇-5-yl****1,4-C₅H₇-4-yl****1,2-C₅H₇-5-yl**

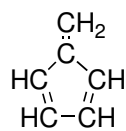
• C₆ Hydrocarbons

**C₆H₆**

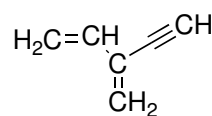
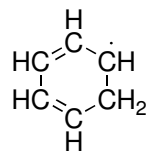
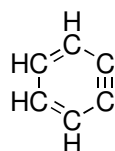
benzene

**C₆H₅**

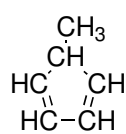
phenyl radical

**f-C₆H₆**

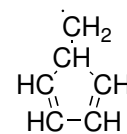
fulvene

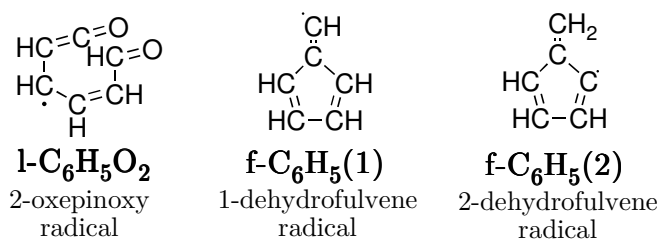
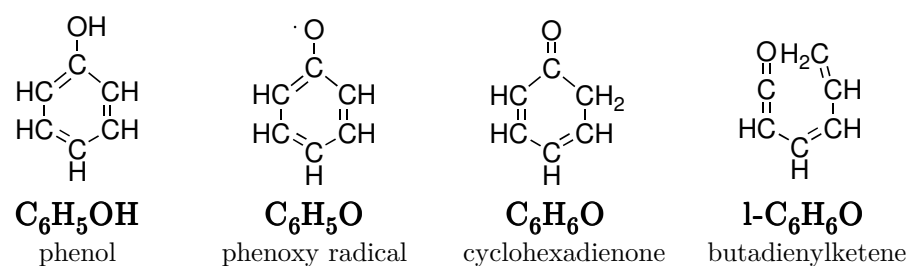
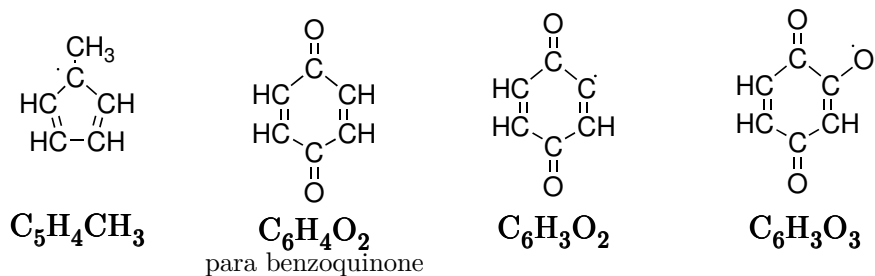
**l-C₆H₆****C₆H₇**cyclohexadienyl
radical**o-C₆H₄**

ortho benzyne

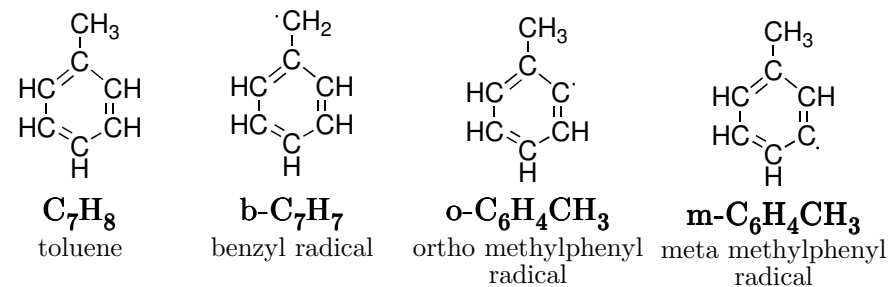
**C₅H₅CH₃**

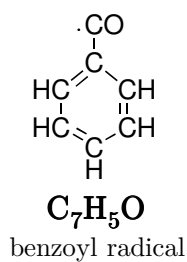
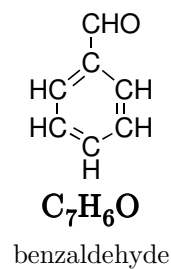
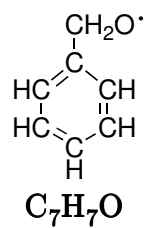
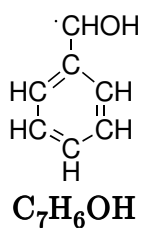
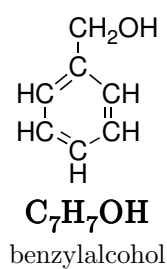
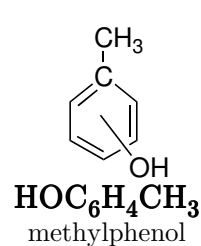
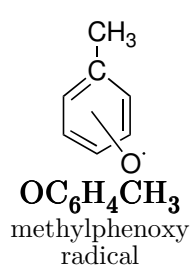
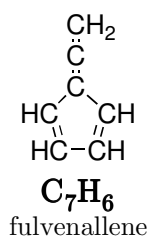
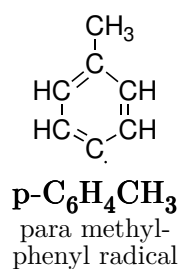
methylcyclopentadiene

**C₅H₅CH₂**

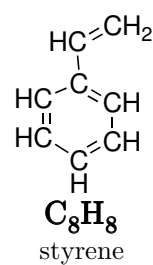
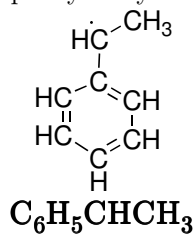
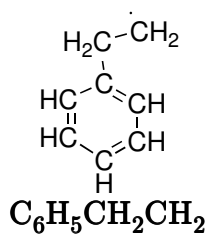
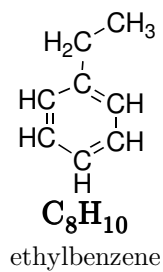
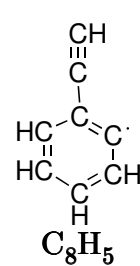
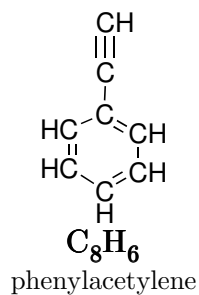
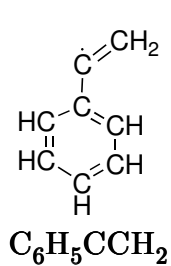
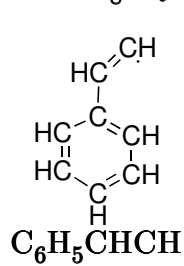


• C₇ Hydrocarbons

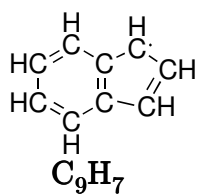




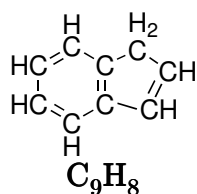
• C₈ Hydrocarbons



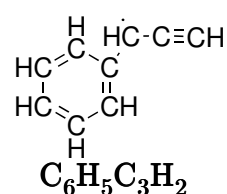
• **C₉ Hydrocarbons**



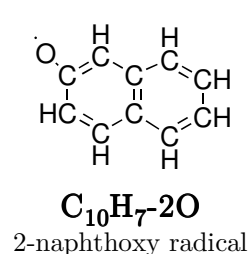
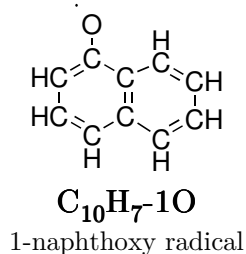
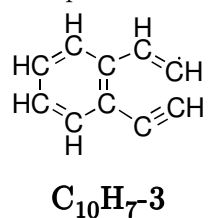
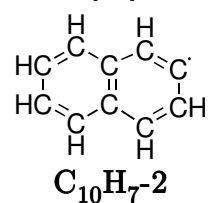
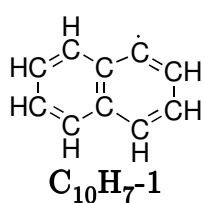
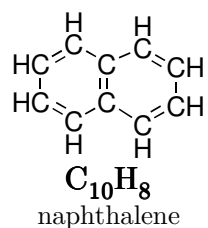
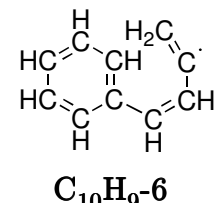
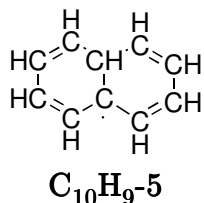
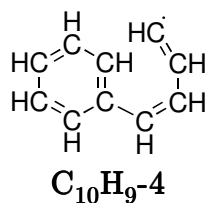
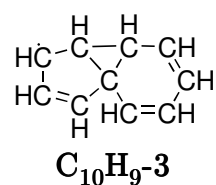
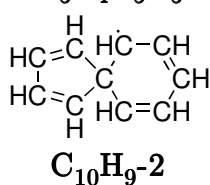
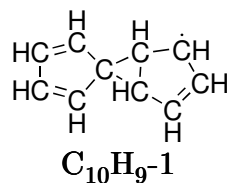
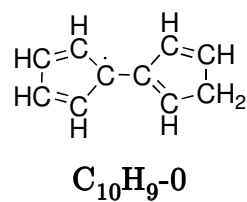
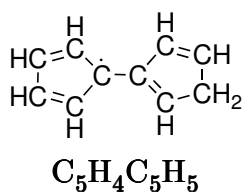
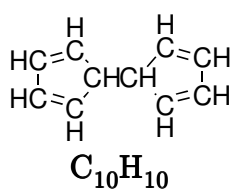
indelyl radical



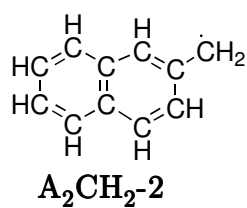
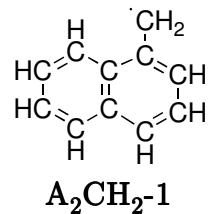
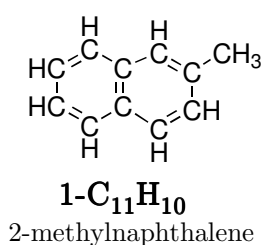
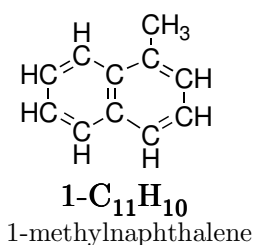
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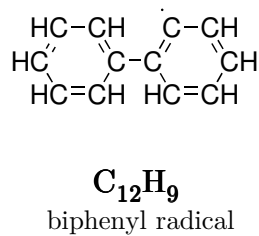
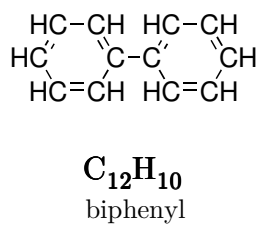
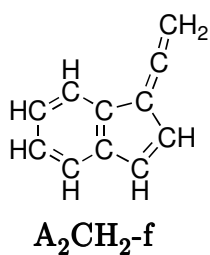
• **C₁₀ Hydrocarbons**



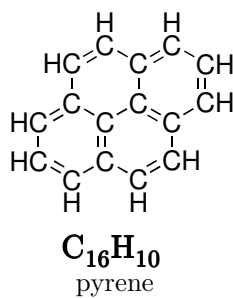
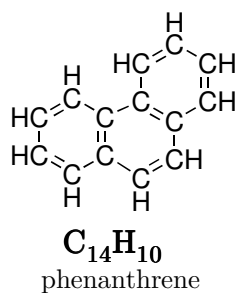
• **C₁₁ Hydrocarbons**



• **C₁₂ Hydrocarbons**



• **Larger Hydrocarbons**



Contents

1	Introduction	1
1.1	A brief history of combustion	1
1.2	The study of aromatic flames	4
1.3	Conceptual framework of combustion	5
1.3.1	Basic flame types	5
1.3.2	The one-dimensional, premixed and laminar flame	6
1.3.3	Combustion chemistry	7
1.3.4	Reaction kinetics	11
1.4	Objectives and strategy	13
1.5	Presentation of the results	15
I	Experimental and kinetic modeling methods	17
2	Experimental setups and methods	19
2.1	Introduction	19
2.2	Flame stabilization	20
2.2.1	Preparation of fresh gas mixtures	20
2.2.2	The combustion chamber	24
2.3	Flame sample analysis	26
2.3.1	Gas Chromatography	26
2.3.2	Molecular Beam Mass Spectrometry	36

2.3.3	GC and MBMS complementarity	42
2.4	Flame temperature measurements	43
2.5	Soot concentration measurements	46
2.6	Conclusions	51
3	Kinetic modeling method	53
3.1	Introduction	53
3.2	Mathematical description of flames	54
3.2.1	The general form of 3 dimensional conservation equations	54
3.2.2	Conservation equations of premixed, laminar and one-dimensional flames	56
3.3	The Cosilab software	61
3.3.1	Boundary conditions	62
3.3.2	The kinetic model	63
3.3.3	The thermodynamic database	67
3.3.4	The transport database	68
3.3.5	System of equations	69
3.3.6	The output file	70
3.4	Postprocessing analysis: contribution calculation	70
3.5	Adiabatic flame temperature	74
3.6	Conclusions	75
II	Benzene and toluene flame chemistry: the fuel ox- idation	77
4	Benzene combustion	79
4.1	Introduction	79
4.2	Experimental results	91
4.2.1	Flame temperatures	92
4.2.2	Influence of equivalence ratio on flame structures	93
4.2.3	Influence of pressure on flame structures	104
4.3	Discussion on benzene flame chemistry	107
4.3.1	The benzene sub-model	107
4.3.2	The phenyl radical sub-model	115

4.3.3	The phenoxy radical sub-model	123
4.3.4	The phenol sub-model	131
4.3.5	The fulvene sub-model	136
4.3.6	The cyclohexadienyl radical sub-model	141
4.3.7	The cyclopentadienyl radical sub-model	143
4.3.8	The cyclopentadiene sub-model	149
4.3.9	The C_5H_7 radicals sub-model	154
4.3.10	The cyclopentadienoxy radical sub-model	156
4.3.11	Further reactions of C_4H_x and smaller hydrocarbons	157
4.3.12	The main chemical species	178
4.3.13	Kinetic modeling of the pressure dependence of BF20	180
4.4	Conclusions	182
5	Toluene combustion	187
5.1	Introduction	187
5.2	Experimental results	192
5.2.1	Investigated flame temperatures	193
5.2.2	Influence of equivalence ratio on flame structures .	194
5.3	Discussion on toluene combustion chemistry	202
5.3.1	The toluene sub-model	202
5.3.2	Path 1: the benzene channel	209
5.3.3	Path 2: the methylphenyl radicals channel	211
5.3.4	Path 3: the benzyl channel	217
5.3.5	Benzene and cyclopentadienyl radical formation . .	229
5.3.6	Further reactions of C_4H_x and smaller hydrocarbons	233
5.3.7	The main chemical species	250
5.4	Conclusions	250
III	Benzene and toluene flame chemistry: the molec- ular growth	255
6	Molecular growth: PAH formation	257
6.1	Introduction	257
6.1.1	The acetylene pathway	258

6.1.2	The benzyl pathway	260
6.1.3	The cyclopentadienyl pathway	262
6.1.4	The ring ring condensation pathway	263
6.1.5	Other pathways of PAH formation and growth . .	264
6.2	Discussion on the mechanism of molecular growth	267
6.2.1	The toluene sub-model	267
6.2.2	The naphthalene sub-model	269
6.2.3	The indene sub-model	276
6.2.4	Styrene and phenylacetylene sub-models	278
6.2.5	The biphenyl sub-model	283
6.2.6	Summary on PAH formation and further growth into phenanthrene and pyrene	284
6.3	Propyne and cyclopentene flames	287
6.3.1	Introduction	287
6.3.2	Experimental results and discussion	290
6.4	Conclusions	302
7	Molecular growth: soot formation	305
7.1	Introduction	305
7.2	The current understanding of soot formation	306
7.3	Available models of soot formation	309
7.3.1	Empirical models	309
7.3.2	Detailed models: the sectional approach	311
7.4	Development of a detailed model including soot formation	317
7.4.1	Thermodynamic and transport databases	318
7.4.2	Modifications required to the Cosilab software . .	318
7.5	Discussion on soot formation	319
7.5.1	General comments on soot formation	319
7.5.2	Model predictions	321
7.5.3	Soot nucleation	322
7.5.4	Chemical growth of BIN material	325
7.5.5	Physical growth of bin material	329
7.5.6	Oxidation of Bins	329
7.5.7	Structural analysis of soot	329
7.6	Conclusions	332

8 Conclusions and perspectives	337
Appendix A	347
Appendix B	351
Appendix C	353
Appendix D	357
Appendix E	361
Bibliography	401

"I remember, as a teenager, watching the yellow flame of the Sabbath candles dancing randomly above the white paraffin cylinders that fueled them. I was too young to think candlelight romantic, but still I found it magical - because of the flickering images created by the fire. They shifted and morphed, grew and waned, all without apparent cause or plan. Surely, I believed, it must be rhyme and reason underlying the flame, some pattern that scientists could predict and explain with their mathematical equations."

Leonard Mlodinow, *The Drunkard's Walk: How Randomness Rules Our Lives* [1]

1.1 A brief history of combustion

Whereas the fire is nowadays domesticated by humans, it is primarily a natural phenomenon that does not require a human action to start. Indeed, the fall of a meteorite, lightnings of a violent storm or the eruption of a volcano are all able to produce enough heat to start a fire, as showed the destruction of Pompei in the first century. Humans were quickly attracted by virtues of fire and palaeontologists estimate that the conquest of fire occurred between 600 000 and 1 million of years ago [2]. The possession of fire enabled humans to see in the dark and provided a constant source of heat for warming themselves and cooking their food. Consequently, the conquest of fire completely changed the way human lived and has conditioned our current standards of living. Thousands of years ago, humans became aware of the technological potential of fire, as they began to harden wood within fires and cook pottery objects made from clay.

The technological potential of fire was equally in the center of the industrial revolution, characterized by the development of steam engines. These machines convert the heat produced by fire into mechanical work, through the formation of water vapor and are consequently referred to as external combustion engines. They contrast with internal combustion

engines that directly convert the heat produced by fire into mechanical work. Although internal combustion engines appeared before the 19th century, their development has been stimulated by the production and the refining of petroleum in the 1850s. Nowadays, these internal and external combustion engines are widely used for transportation and electric power generation, as more than 80% of the world primary energy comes from the combustion process. The understanding of this phenomenon is therefore of particular concern and is the guiding thread of this work.

In the 5th century BC, the Greek philosopher Empedocle postulated that fire is one of the four elements constituting nature, besides water, earth and air. Later, alchemists considered the same four classical elements for a long time. In the 17th century, Johann Joachim Becher replaced fire by three forms of earth and considered that one is responsible of combustible properties. In the early 18th century, Georg Ernst Stahl named this element *phlogiston* and proposed that it is released when combustible substances are burned.

The appearance of a significant interest in the elucidation of the nature of fire came in 1738 with a competition proposed by the French academy of science on the nature and the propagation of fire. One of the successful candidates was Leonhard Euler [3], who suggested to model the combustion phenomenon by a set of small spheres that each contains air at high pressure. According to Euler, the breaking of one sphere allows to break neighboring spheres and therefore propagates the combustion phenomenon. As stated by Louis Boyer [4], this very simple model could be one of the first theory of combustion, which was able to represent the energetic threshold of the lightning of a combustion reaction, as well as its energetic release and its propagation. Moreover, the model proposed by Euler contains the idea of chain branching reactions, which were later identified as key reactions of the combustion phenomenon.

Later in the 18th century, Lavoisier discovered that combustion requires air, and particularly oxygen. This crucial finding refuted the *phlogiston* theory proposed earlier by Stahl and opened the way to a better under-

standing of the combustion phenomenon. In the 19th century, accidents in coal mines due to firedamp explosions drove numerous scientists to study flame propagation. The French researchers François-Ernest Mallard and Henry Le Chatelier began therefore applied and basic investigations on combustion (among others, see [5]). Their comprehensive contribution includes experimental determination of burning velocities of different flames, at various temperatures, dilution ratios and reactant concentrations, as well as significant insights in the theoretical understanding of such phenomenons. Indeed, in 1883 Mallard and Le Chatelier proposed the very first model to predict the normal propagation velocity of laminar flames [6].

The combustion phenomenon has been shown to be a complex process, located at the interplay of thermodynamics, gas kinetics, transport processes and fluid dynamics. Since these subjects reached their peaks in the late 19th century, the understanding of the combustion phenomenon is quite recent. After Lavoisier, Mallard and Le Chatelier, the most recognized scientists that contributed to the current model of combustion are, among others, David Leonhard Chapman, Emile Jouguet, Yakov Borisovich Zel'dovitch, David Albertovich Frank-Kamenetskii and Adolphe Van Tiggelen.

The comprehension of the combustion phenomenon is still a central theme of research, as it is responsible of most of the anthropogenic release of carbon dioxide (CO_2) into the atmosphere. The rise of the atmospheric CO_2 concentration is thought to be responsible of the global warming [7], which consists in one of the biggest challenge of our century. Beside carbon dioxide, combustion is responsible of the emission of several pollutants, like nitrogen oxides and soot particles. As explained in the following section, the understanding of chemical reactions leading to the formation of soot is the main topic of this work.

1.2 The study of aromatic flames

Flames that have an excess of fuel, compared to the stoichiometry, or where the mixing between fuel and oxidizer is imperfect, result in an incomplete combustion and are therefore less efficient than flames where the fuel is perfectly balanced by the oxidizer. When incomplete combustion occurs, the excess of fuel is principally converted into Polycyclic Aromatic Hydrocarbons (PAH), which are molecular precursors of fine particles characterized by a high C/H ratio: the soot [8]. PAH produced in these flames are carcinogenic, as they are metabolized by the human body into high electrophilic compounds (epoxies), which tempt to disturb cellular division through their addition on DNA [9]. Moreover, soot can be compared to a black body and may therefore promotes the atmospheric solar heating, as suggested by Ramanathan and co-workers [10] who showed that brown clouds containing soot may contribute as much as the recent increase in anthropogenic greenhouse gases to lower atmospheric warming trends in Asia. In addition, Xu and co-workers have recently suggested that soot can deposit on glaciers and significantly contributes to their rapid retreat [11]. Beside these climatic and health hazards, soot causes the coating of combustion chambers in the industry and can damage gas turbines of power plants.

However, soot is equally necessary to obtain hydrocarbon flames with high radiative properties, allowing to reach sufficient temperatures in industrial furnaces such as those of the glass industry. Soot is also used for the synthesis of nanomaterial components, such as fullerenes. It is therefore very important to understand mechanisms involved in combustion chemistry of aromatic hydrocarbons and soot formation. Such a comprehension is the guiding thread of this work, investigating chemical pathways involved in benzene and toluene flames. Compared to other hydrocarbon flames, aromatic flames present higher PAH levels, as the first aromatic ring does not have to be formed. They are consequently more convenient for the investigation of PAH and soot formation. The study of toluene combustion is equally important as it is widely used

as a fuel additive or in surrogate mixtures for gasoline, due to its high anti-knocking capacity.

All considered, this work will focus on the oxidation of benzene and toluene, as well as on their growth towards PAH and soot. In the following section, the conceptual framework of the combustion phenomenon is briefly presented in order to understand the specific objectives and the developed strategy, which are exposed at the end of this chapter.

1.3 Conceptual framework of combustion

1.3.1 Basic flame types

Basically, the combustion phenomenon is a self-sustained and exothermic chemical reaction that propagates into a flammable mixture of fuel and oxidizer. The flame is the reactive zone of the mixture that produces light through chemiluminescence reactions. According to the way fuel and oxidizer are mixed and the regime of the fluid motion, four different types of flames can be observed (see figure 1.1).

If fuel and oxidizer are properly mixed, the composition of the fresh reactive mixture is fixed and the flame is referred to as *premixed*. The fluid motion of premixed flames can either be *turbulent* or *laminar*, as in spark ignition engines and Bunsen flames, respectively. If fuel and oxidizer are not premixed, the flame is said *non premixed*. These flames include a more complex chemistry than premixed ones, because the composition of the reactive mixture vary from pure oxidizer to pure fuel, depending

<i>fuel / oxidizer mixing</i>	<i>fluid motion</i>	<i>examples</i>
premixed	turbulent	spark ignition engine
	laminar	Bunsen flame
non premixed	turbulent	Diesel engine
	laminar	candle

Figure 1.1: the four basic flame types [12]

on the position in the flame. Similarly to premixed flames, the fluid motion can be turbulent or laminar, as in the Diesel engine and the candle flame, respectively. Turbulent flames are generally used to maximize the heat production rate, as they allow to increase the combustion rate by enlarging the surface of the flame. In this work, composition of reactive mixtures are fixed and spatial fluctuations of flame properties due to turbulence are avoided in order to focus on combustion chemistry. Each flame presented in following chapters is therefore premixed and laminar.

1.3.2 The one-dimensional, premixed and laminar flame

In addition to be premixed and laminar, flames presented in this work are all *one-dimensional*. This behavior is obtained by stabilizing flames on a flat flame burner, perforated by a huge number of small holes. Properties of premixed, laminar and one-dimensional flames only depend on one coordinate: z , the height above the burner surface. The evolution along the z axis of the temperature and mole fractions of chemical species in the flame is referred to as the *flame structure*. Figure 1.2 presents the typical structure of a one-dimensional, premixed and laminar flame and shows that it can be divided into three main zones.

The first is the preheating zone, where the temperature slightly increases and chemical reactions initiate due to heat conduction and molecular diffusion of radical species from the flame front, which corresponds to the second zone. In its strict sense, the combustion reaction takes place in the flame front, where heat transfer and consumption rates of reactants reach their peaks. The conversion of reactants into final products of combustion goes through the formation of intermediate species, whose mole fraction profiles exhibit Gaussian-like forms, reaching their maximums in the flame front.

The spatial evolution of mole fractions profiles of these intermediate species gives important clues on chemical mechanisms responsible of reactant conversion into combustion products. From a chemical point of view, the flame front is therefore the most interesting region to analyze.

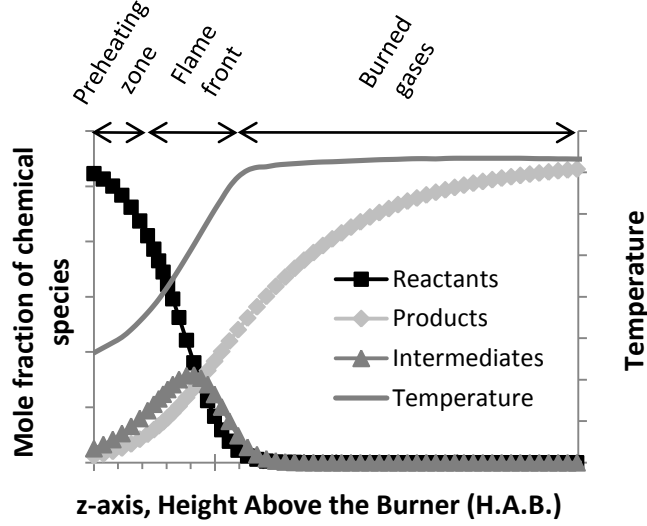


Figure 1.2: structure of a one-dimensional, premixed and laminar flame

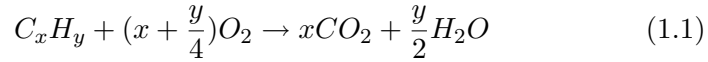
However, at atmospheric pressure, the flame front is excessively narrow (about 10^{-4} m) and consequently difficult to investigate with a sufficient spatial resolution. Fortunately, the thickness of the flame front is a function of the inverse of the working pressure and it can therefore be enlarged by stabilizing flames at lower pressures. At the end of the flame front, the rate of chemical reactions decreases and the region of burnt gases finally appears. In this last zone, the combustion reaction is completed and products subsist together with excess of fuel or oxidizer. In this work, the measurements of premixed, laminar and one-dimensional benzene and toluene-oxygen-argon flame structures, burning at low pressure, will be carried out.

1.3.3 Combustion chemistry

The equivalence ratio

Basically, a premixed flame of a hydrocarbon species (C_xH_y) with molecular oxygen (O_2) is said to be *stoichiometric* if fuel and oxidizer com-

pletely consume each other, forming carbon dioxide (CO_2) and water (H_2O), as represented by the overall reaction 1.1. If the fuel is introduced in excess, the flame is referred to as *rich* and other products such as carbon monoxide (CO), molecular hydrogen (H_2) and even soot subsist in the burnt gases. If the oxidizer is introduced in excess, the system is called *lean* and molecular oxygen subsist at the end of the reaction zone.



The lean, stoichiometric or rich character of a premixed mixture can be determined by calculating its equivalence ratio (ϕ) through equation 1.2, where $\chi_{C_xH_y}$ and χ_{O_2} respectively represent mole fractions of fuel and oxidizer.

$$\phi = \frac{(\chi_{C_xH_y}/\chi_{O_2})_{premixed\ mixture}}{(\chi_{C_xH_y}/\chi_{O_2})_{at\ stoichiometry}} \quad (1.2)$$

According to this equation, the lean, stoichiometric and rich cases respectively correspond to $\phi < 1$, $\phi = 1$ and $\phi > 1$.

The chain branching mechanism

Equation 1.1 corresponds to the overall combustion reaction of a hydrocarbon with O_2 and therefore represents a whole set of individual reactions. These reactions form a chain branching mechanism, which involves the formation of radical species that sustain the combustion reaction through propagation and ramification steps. The four typical steps of a chain branching mechanism are initiation, chain branching, propagation and termination, which respectively consist in reactions R1, R2, R3 and R4 of table 1.1.

The initiation reaction R1 begins the chain branching process through the formation of two radical species R from the dissociation of a reactant A . Then, these radicals R can react with another reactant A , forming more than one radical species R ($\alpha > 1$, see reaction R2). These chain branching reactions allow to considerably speed up the combustion reaction and are necessary to sustain the combustion phenomenon. The propagation step (see reaction R3) involves the reaction between a reac-

Table 1.1: the chain branching mechanism

	general forms	example of the H_2/O_2 system
R1	$\mathbf{A} \rightarrow 2 \mathbf{R}$	$H_2 \rightarrow H + H$ $O_2 \rightarrow O + O$
R2	$\mathbf{A} + \mathbf{R} \rightarrow \alpha \mathbf{R}$	$H + O_2 \rightarrow OH + O$ $O + H_2 \rightarrow OH + H$
R3	$\mathbf{A} + \mathbf{R} \rightarrow \mathbf{P} + \mathbf{R}$	$H_2 + OH \rightarrow H_2O + H$
R4	$\mathbf{R} + \mathbf{R} \rightarrow \mathbf{P}$	$H + H \rightarrow H_2$

tant A and a radical species R , forming another radical R and a stable product P . This step does not change the number of radicals R and therefore only propagates the combustion reaction. Finally, termination reactions neutralize two radicals R , by recombining them into a stable product P . This step decreases the number of radicals R and consequently inhibits the combustion reaction.

On the right side of table 1.1, reactions R1 to R4 are exemplified for a H_2/O_2 flame. The chain branching step consists of reactions $H + O_2 \rightleftharpoons OH + O$ and $O + H_2 \rightleftharpoons OH + H$, which equally play a considerable role in C_xH_y/O_2 flames. Indeed, as presented in the following section, hydrocarbon flames produce H atoms that are able to react with O_2 , in the same way as in the H_2/O_2 system. Since flames have a large concentration of radical species, initiation reactions are generally of lower importance than chain branching, propagation and termination steps.

Typical reactions of a hydrocarbon/ O_2 system

Each step of the chain branching mechanism corresponds to typical reactions of hydrocarbon consumption in C_xH_y/O_2 flames that are briefly presented hereafter.

The initiation step is represented by the *homolytic fission* of a chemical bond of a molecular species, generating two radical fragments. For example, CH bonds of toluene (C_7H_8) and benzene (C_6H_6) can break

forming $C_6H_5 + H$ and $C_7H_7 + H$, respectively. The rate of such reactions depends on the strength of the considered bond. Consequently, the homolytic fission of CC bonds ($\sim 348 \text{ kJ mol}^{-1}$) are generally faster than that of CH bonds ($\sim 412 \text{ kJ mol}^{-1}$).

The chain branching step is represented by *H atom abstraction* reactions involving biradical species such as *O* atom, as they produce two radical species. For example, the *H* abstraction reaction on benzene by *O* atom gives phenyl and hydroxyl (*OH*) radicals. The *dissociation* of a radical through another pathway than a β -scission is equally a chain branching reaction, as it gives a radical and a biradical species. An example is the overall $H + O_2 \rightleftharpoons OH + O$ reaction, which consists in an addition reaction of an *H* atom on O_2 , forming HO_2 , followed by the dissociation of this radical into *OH* and *O* atom.

The propagation step is represented by *H atom abstraction* reactions, where a radical *R* removes a hydrogen atom on a molecule. For example, an *H* atom of benzene can be abstracted by *H* or *OH* radicals, giving $C_6H_5 + H_2$ or $C_6H_5 + H_2O$, respectively. The *dissociation* of a radical is equally a propagation step if it takes the form of a β -scission: a bond breaks two atoms away from the radical position, forming a radical *R* and a stable product having an additional CC bond. These reactions explain the formation of unsaturated molecules in hydrocarbon flames. The *addition* of a radical onto an unsaturated bond equally produces a new radical and therefore corresponds to a propagation step. Finally, the *isomerization* of a radical into another radical is also a propagation reaction.

The termination step is represented by the *recombination* between two radicals, forming a stable product. For example, the recombination between *H* atom and C_6H_5 radical gives benzene, which is unable to continue the propagation of the combustion reaction without a new initiation step.

1.3.4 Reaction kinetics

Reactions discussed in the previous section are either unimolecular or bimolecular, as they respectively involve one or two chemical species. In a flame, these reactions will occur at definite rates that depend on the reaction and the conditions of the system (concentration of chemical species, temperature and pressure).

The reaction rate RR of elementary unimolecular ($B \rightarrow products$) and bimolecular ($B + C \rightarrow products$) reactions can be represented by the Arrhenius theory, as illustrated hereafter.

$$RR_{uni} = [B] \times A \times \exp\left(-\frac{E_a}{RT}\right) \quad (1.3)$$

$$RR_{bi} = [B][C] \times A \times \exp\left(-\frac{E_a}{RT}\right) \quad (1.4)$$

In these expressions, $[B]$ and $[C]$ stand for concentrations of chemical species B and C , R is the ideal gas constant, T is the temperature, E_a is the activation energy of the reaction and A is its pre-exponential factor. The latter accounts for the steric factor of the reaction and the collision frequency between reactants. The exponential term of equations 1.3 and 1.4 gives the fraction of collisions that have an energy higher than E_a , which is required to achieve the considered reaction. Practically, the product of the pre-exponential factor with the exponential term is called the *rate constant* and is noted k .

Over large temperature ranges, such as those observed in flames, rate constants deviate from the normal Arrhenius behavior and it is preferable to use equation 1.5, where n is a temperature exponent taking this deviation into account.

$$k = A \times T^n \times \exp\left(-\frac{E_a}{RT}\right) \quad (1.5)$$

In addition to temperature, the rate of unimolecular reactions is equally found to depend on pressure. Therefore, expression 1.3 could only be used at a definite pressure and has to be modified in order to extrapolate

reaction rates at different pressures. This question has been addressed by Lindemann [13] and Hinshelwood [14], who showed that a unimolecular reaction is rather a two step process than an elementary reaction. As depicted in the following equations, Lindemann and Hinshelwood proposed that the reaction begins with the activation of the reactant B by collision with a non reacting partner M . The rate constant of this reaction is noted k_f . Then, the activated reactant B^* can either be deactivated by another collision with a rate constant k_b , or decomposes into final products with a rate constant k_p .



The reaction rate of a unimolecular reaction should therefore accounts for the concentration of nonreactive partners, which directly depends on the surrounding pressure. Lindemann showed that at low and infinite pressures the rate constant respectively corresponds to equations 1.8 and 1.9.

$$k_0 = k_f \times [M] \quad (1.8)$$

$$k_\infty = \frac{k_f k_p}{k_b} \quad (1.9)$$

In between these two regions, the rate constant is said in the fall-off regime and different formalisms have been proposed to model its behavior. The most popular is that of Troe, which consists in an equation involving k_0 , k_∞ , $[M]$ and 4 additional parameters noted as a , T^* , T^{**} and T^{***} that represent the reaction fall-off [15–17].

The kinetics of all reactions involved in the combustion phenomenon can therefore be parametrized. The gathering of kinetic parameters of reactions describing a definite system is called a *kinetic model*. Recent progresses in computer science have allowed to develop softwares able to compute mole fraction profiles of chemical species involved in premixed, laminar and one-dimensional flames, based on such kinetic

models. These models can therefore be validated against experimental flame structures and indications on major reaction channels can be obtained by comparing the predicted rate of each included reaction. As presented in the following section, the development of such a kinetic model for benzene and toluene combustion and its comparison to relevant experimental data is the key strategy of the present work.

1.4 Objectives and strategy

The main goal

The main goal of the present work is the understanding of benzene and toluene combustion chemistry, including fuel oxidation, as well as PAH and soot formation.

The formulated strategy

To achieve this comprehension, a strategy that consists in two main steps has been formulated. Firstly, relevant structures of benzene-oxygen-argon and toluene-oxygen-argon flames will be measured over a large range of equivalence ratios. As mentioned in previous sections, these flames will be premixed, laminar, one-dimensional and stabilized at low pressure in order to focus on combustion chemistry. Secondly, a kinetic model able to predict experimental measurements will be developed and main reaction channels of benzene and toluene combustion will be determined by comparative reaction rate analyses.

If reaction channels are taken as hypothesis during the development of the kinetic model, they may potentially be verified by performing new measurements in flames. Moreover, the predictive capability of the developed model may be validated by measuring additional flame structures. The formulated strategy is therefore cyclic and should not be seen as two unconnected steps.

As it will be shown in chapters four and five, they are only a few experimental structures of benzene and toluene flames described in the literature. The present strategy will therefore bring new and valuable experimental data to the scientific community, which should allow to validate new kinetic models and improve the current understanding of aromatic combustion. Moreover, it will be shown that many uncertainties remain in previous kinetic models of benzene and toluene combustion, and that recent insights have been performed in this field. Consequently, the development of a new model, based on a comprehensive literature survey that includes recent findings on aromatic combustion should allow to improve the comprehension of chemical pathways involved in such flames.

The operational objectives

The first and second steps of the strategy are implemented by formulating the following operational objectives.

The first step of the strategy

1. To stabilize one-dimensional, premixed and laminar benzene-oxygen-argon and toluene-oxygen-argon flames at 45 mbar and equivalence ratios of 0.7, 1, 1.8 and 2.
2. To develop an experimental setup for sampling at different heights above the burner surface, allowing the measurement of mole fraction profiles of reactants, intermediate species and products in each stabilized flames. The developed setup should be able to detect first PAH in order to describe the molecular growth of benzene and toluene towards soot particles.
3. To develop an experimental setup for measuring soot concentration profiles in rich benzene and toluene flames.
4. To develop an experimental setup for measuring temperature profiles of each investigated flame.

The second step of the strategy

1. To perform a comprehensive literature survey on benzene and toluene reactions at high temperature.
2. To develop a detailed kinetic model with a good predictive capability for experimental benzene and toluene flame structures.
3. To extend this kinetic model to PAH and soot formation and to validate these predictions on measurements performed in flames.
4. To perform comparative reaction rate analyses in order to determine main pathways of oxidation, as well as PAH and soot formation in benzene and toluene flames.
5. To determine how these pathways compete with equivalence ratio and temperature.

1.5 Presentation of the results

As described hereafter, the presentation of the results is divided in three main parts:

- the first presents the experimental setup developed to investigate benzene and toluene flame structures and exposes how such flame structures can be predicted based on kinetic models;
- the second part shows experimental structures of benzene- and toluene-oxygen-argon flames and discusses the development of a kinetic model able to reproduce these measurements. The main reaction channels of benzene and toluene consumption in flames are highlighted and the dependence of these pathways on the equivalence ratio and the temperature is equally discussed;
- the third part presents the molecular growth of benzene and toluene towards PAH and soot and discusses the extension of the developed kinetic model.

Finally, at the end of these three parts, chapter eighth concludes this work by summarizing the main findings and gives some interesting perspectives.

Part I

Experimental and kinetic modeling methods

Experimental setups and methods

2.1 Introduction

This chapter presents experimental setups developed to measure structures of flames presented in this work. Since each flame is laminar, premixed and one-dimensional, flame structures consist in the evolution along an axis perpendicular to the burner surface of mole fractions of chemical species, of the concentration of carbonaceous particles and of the temperature. These axial evolutions are called *profiles*. Flames have been stabilized on flat and circular burners that are located in low pressure combustion chambers. The low pressure analysis increases the mean free path between reactive species and, consequently, the thickness of the flame front and the spatial resolution of measurements. Four different experimental setups have been used to carry out flame structure measurements. The first corresponds to a Gas Chromatography analyzer (GC) that allows to measure mole fraction profiles of stable chemical species inside the flame. The second is a Molecular Beam Mass Spectrometry device (MBMS) that enables to measure mole fraction profiles of radical and stable species that cannot be detected by GC. The third is a thin thermocouple that is inserted into the flame for temperature profiles determination and the last consists of a filter that is introduced into rich flames in order to collect carbonaceous particles and measure soot concentration profiles. Apparatuses used for flame stabilization and

these four experimental setups along with their calibration procedures are described in this chapter.

2.2 Flame stabilization

As GC and MBMS devices require highly different sampling methods, which will be described further, two different apparatuses have been used for flame stabilization. The first is devoted to GC, soot concentration and temperature measurements, while the second is connected to the MBMS device. Except for their sampling methods, these apparatuses are analogous and it has been carefully verified, in this work and in the past [18], that mole fraction measurements performed with each of them are very similar, by analyzing a flame with an identical composition. Therefore, the following discussion does not differentiate between these two apparatuses and collectively presents gas mixture preparations, their admission into the combustion chamber and flame stabilization above the two flat flame burners.

2.2.1 Preparation of fresh gas mixtures

In order to stabilize a premixed flame, dilutant, fuel and molecular oxygen (O_2) have to be blended in their gaseous state before entering into the burner. The use of nitrogen (N_2) as a dilutant was avoided as it may be involved in chemical reactions into the flame that are beyond the scope of this study. Consequently, argon (Ar) has been chosen since it is an inert gas that has a low specific heat capacity ($c_p = 0.52 kJ kg^{-1} K^{-1}$), allowing to efficiently control the flame temperature. High purity molecular oxygen and argon (99.5 % and 99.996 %, respectively) from *Air Liquide* and stored in pressurized gas cylinders have been used. Concerning the fuel, for flames of hydrocarbons that are liquid at room temperature and atmospheric pressure, they are evaporated before to be mixed with Ar and O_2 . The evaporation is conducted in a balloon glass that is immersed in a thermostatic bath of water, as illustrated in figure 2.1. The accessible temperature range of the water bath is approximately 20

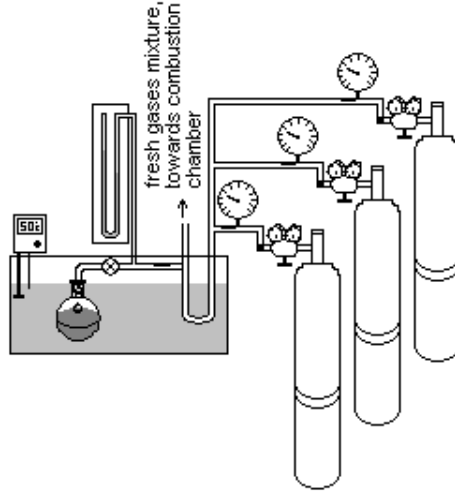


Figure 2.1: the blending of fresh gases

to 70°C. The evaporation setup is connected to the pipe bringing the mixture of argon and molecular oxygen to the combustion chamber in order to fully premix all gases before entering into the burner. Since the developed strategy consists in comparing experimental to predicted flame structures, initial flame compositions have to be measured with precision. The initial composition is defined by partial volumetric flow rates Dv_i of the fuel, the oxidant and the dilutant in the fresh gas mixture and their sum gives the total volumetric flow rate Dv_T , as shown in equation 2.1.

$$\sum_i (Dv_i) = Dv_T \quad (2.1)$$

Considering the ideal gas law, the ratio Dv_i/Dv_T represents the mole fraction χ_i of the compound i at the inlet of the burner, as demonstrated by equation 2.2. In this equation, V_i and V_T are respectively the volume of i and the total volume of gas that exit the burner during the time t , n_i and n_T are the corresponding mole numbers, R is the ideal gas constant, and T and P are the temperature and the pressure at the output of the burner, respectively.

$$\frac{Dv_i}{Dv_T} = \frac{V_i/t}{V_T/t} = \frac{n_i RT/P}{n_T RT/P} = \frac{n_i}{n_T} = \chi_i \quad (2.2)$$

The measurement of partial volumetric flow rates of fuel, oxidant and dilutant is performed with the setup illustrated in figure 2.2. It is based on the sonic nozzle theory [19], which allows to determine the mass flow rate of a gas flowing at a supersonic speed through a capillary orifice, by measuring the upstream pressure. In such a setup, gases flow at a su-

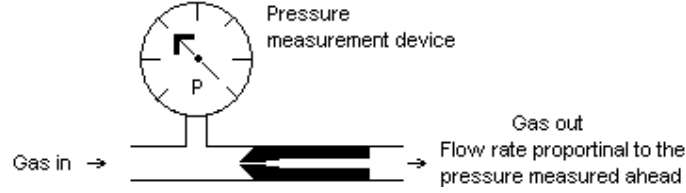


Figure 2.2: setup for flow rate measurement

personic speed if the ratio between upstream and downstream pressures verifies the equation 2.3, where P and γ are the pressure and the ratio between the specific heats of the considered gas, respectively.

$$\frac{P_{upstream}}{P_{downstream}} \geq \left(\frac{2}{1 + \gamma} \right)^{\frac{\gamma}{1-\gamma}} \quad (2.3)$$

Table 2.1 summarizes γ values and critical pressure ratios of each compound present in fresh gases of flames investigated in this work. Since this critical pressure ratio is generally close to 2 and the downstream pressure is close to the working pressure of 45 mbar, equation (2.3) is easily verified for gaseous reactants stored in gas cylinders with pressures above 1 atmosphere, such as O_2 and Ar . However, for chemical species

Table 2.1: values of $\gamma^\dagger$ and critical pressure ratios of reactants

Reactants	$\gamma^\dagger$	critical values of pressure ratios
Ar	1.66	2.05
O_2	1.39	1.88
$C_6H_6 (g)$	1.11	1.72
$C_7H_8 (g)$	1.09	1.70
$C_5H_8 (g)$	1.11	1.72
$p-C_3H_4$	1.16	1.75

[†] $\gamma = C_p / (C_p - R)$ and C_p values are those recommended by the NIST at 300 K [20].

that have to be evaporated, verification of equation (2.3) depends on their partial pressures over the range of temperature that is technically accessible with the thermostatic bath (about 20 to 70°C).

The flow rate calibration of a compound i that verifies equation (2.3) is based on equation (2.4), where Dm_i , γ_i and M_i are respectively the mass flow rate of i , the ratio between its specific heats, and its molar mass. P , A , R and T are the upstream pressure read on the manometer of figure 2.2, the orifice area of the capillary used, the ideal gas constant and the temperature, respectively. For a given capillary diameter and at a constant temperature, the mass flow rate of a compound i becomes proportional to the measured upstream pressure P . Since temperature and pressure are constant at the output of the capillary, the mass flow rate of a compound i is proportional to its volumetric flow rate (see equation 2.5) and calibration curves of the volumetric flow rate versus the upstream pressure can therefore be measured in order to determine the linear equation connecting these two variables.

$$Dm_i = P_{upstream} \cdot A \sqrt{\frac{\gamma_i M_i}{RT} \left(\frac{2}{\gamma_i + 1} \right)^{\frac{\gamma_i + 1}{\gamma_i - 1}}} \quad (2.4)$$

$$Dv_i = Dm_i \times \frac{RT}{PM_i} \quad (2.5)$$

In this work, O_2 , Ar , C_6H_6 , C_5H_8 and $p-C_3H_4$ verify equation (2.3). According to ranges of volumetric flow rates required for the preparation of fresh gas mixtures, capillaries with convenient diameters have been chosen for these chemical species and calibration curves have been measured. Upstream pressures have been measured with *Bourdon* gauges and mercury manometer for capillaries connected to gas cylinders and evaporation setups, respectively. Volumetric flow rates of gases have been directly measured with a flow meter. For liquids, the evaporated mass have been measured and the volumetric flow rate has been deduced from the ideal gas law and the evaporation time.

Under conditions that do not verify equation 2.3, no linear expression can be found between the volumetric flow rate and the upstream pres-

sure. In this work all reactants verify this equation, except toluene that has a low vapor pressure, compared to benzene. For this reactant, the temperature of the thermostatic bath has been fixed to 70°C and an appropriate capillary, giving the desired volumetric flow rate, has been manufactured. Because equation (2.3) is not respected, the volumetric flow rate of toluene is highly sensitive to variations in pressure at the output of the capillary, and therefore to volumetric flow rates of other gases in the mixture. Consequently, the calibration of the toluene flow rate has to be performed for each investigated flame.

The adjustment of fuel, oxidant and dilutant flow rates allows to prepare definite fresh gas mixtures that are directed towards the burner of the combustion chamber. Composition of fresh gas mixtures of each investigated flame will be presented in further chapters.

2.2.2 The combustion chamber

Fresh gas mixtures enter into the stainless and cylindrical combustion chamber depicted in figure 2.3, which is maintained at low pressure thanks to a vacuum pump. The pressure is measured by a diaphragm vacuum gauge and can be easily regulated by manually adjusting a valve situated between the vacuum pump and the chamber. The burner is located inside the combustion chamber and is mounted on a millimetric

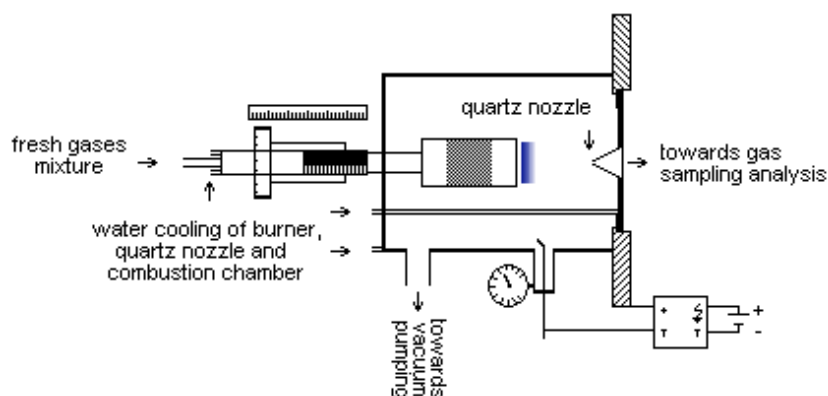


Figure 2.3: the combustion chamber

screw, allowing to move it along an axis that is perpendicular to its surface. In front of the center of the burner surface, a conical quartz nozzle is located for gas sampling. It has an aperture of 0.2 mm and an angle of 45° . The system *millimetric screw-burner-quartz nozzle* is lined up in order to allow sampling in its axis, at different heights above the burner surface and with a spatial resolution close to 10^{-1} millimeters. The body of the burner is thermostatically cooled by water at 30°C and consists of a cylinder that is filled by small glass balls allowing a homogeneous distribution of fresh gases at the burner surface. The brass head of the burner is perforated by about 4500 holes of 1 mm in diameter, uniformly spread into a circle of 8 cm in diameter. This huge number of holes, together with small glass balls filling the body of the burner, allows the stabilization of a flat, homogeneous and one-dimensional flame. At room temperature, the gas mixture whose preparation has been discussed above exits the burner surface with a velocity (v_c), which is determined by equation 2.6, where Dv_T is the total volumetric flow rate of the mixture at the atmospheric pressure P_{atm} , $P_{working}$ is the pressure in the combustion chamber and r is the radius of the burner surface.

$$v_c = Dv_T \times \frac{P_{atm}}{P_{working}} \times \frac{1}{\pi r^2} \quad (2.6)$$

A retractable electrode connected to a high voltage source (2-3 kV) can be placed in front of the burner surface to create sparks, lighting the flame that may be observed through 4 windows. The pressure in the chamber beyond the nozzle is kept lower than that of the combustion chamber in order to sample throughout the apex of the quartz cone. Depending on the analysis that has to be carried out, samples are directed either towards a gas chromatography analyzer (GC) or to a molecular beam mass spectrometry device (MBMS). These both analytical techniques are described hereafter.

2.3 Flame sample analysis

The two methods used in the present work to analyze chemical samples are very different. Although the first (GC) is based on the chemical structure of sample constituents, the second (MBMS) is connected to their mass. Both methods are complementary and are described separately in the following sections.

2.3.1 Gas Chromatography

Conceptual framework

The chromatography is a technique widely used in analytical chemistry to separate mixtures of chemical species and sometimes to identify and to quantify their constituents. It consists in passing the mixture diluted in a mobile phase through a stationary phase which separates the constituents based on their differential partitioning coefficients between the mobile and the stationary phases. Gas Chromatography is a common type of chromatography used to separate mixtures of gaseous or vaporized compounds, as those involved in combustion reactions. Gas Chromatography is therefore frequently used to study flame chemistry [18,21–25]. The mobile phase consists of an inert gas such as helium or argon and the stationary phase is a microscopic layer coated inside a glass or a metal tube called column. Columns mainly differ by physical and chemical properties of their inner coating which is chosen according to the kind of mixture to be analyzed. Based on their partitioning coefficients between the stationary and the mobile phase, each compound flows through the columns with different speeds, leading to characteristic eluting times. These eluting times can be modified by changing the kind of column, the nature of the carrier gas, the flow rate of the mobile phase or the temperature of the oven that contains the column. These four parameters have to be optimized in order to get the best constituent separation.

Connection to the combustion chamber

According to their vapor pressures, chemical species detected inside samples may be divided into 2 classes. The first consists of permanent gases of combustion (O_2 , CO_2 , H_2O , CO , H_2) and hydrocarbons that have high vapor pressures (generally those between C_1 and C_6), while the second class includes lower vapor pressure hydrocarbons (from C_7 to PAH). For each class, the mixture is injected into the Gas Chromatograph by a particular method. The high vapor pressure of compounds belonging to the first class allows to increase their concentrations in samples, without condensing them, by compressing each sample before its injection into the GC (see figure 2.4). The highest chromatographic signals are obtained from the highest sample concentrations, and show the lowest detection limit. The setup developed for analysis of this first class of hydrocarbons is based on one previously developed in the laboratory [18]. At the output of the quartz nozzle, a stainless tube directs samples towards a vessel connected to a vacuum pump and a multiway valve located inside the GC. The multiway valve is connected to the carrier gas, the chromatographic column, the vacuum pump and a 2 ml sample loop. As describe in figure 2.5, the multiway valve has 2 different positions corresponding to 2 sets of connections. In the A position,

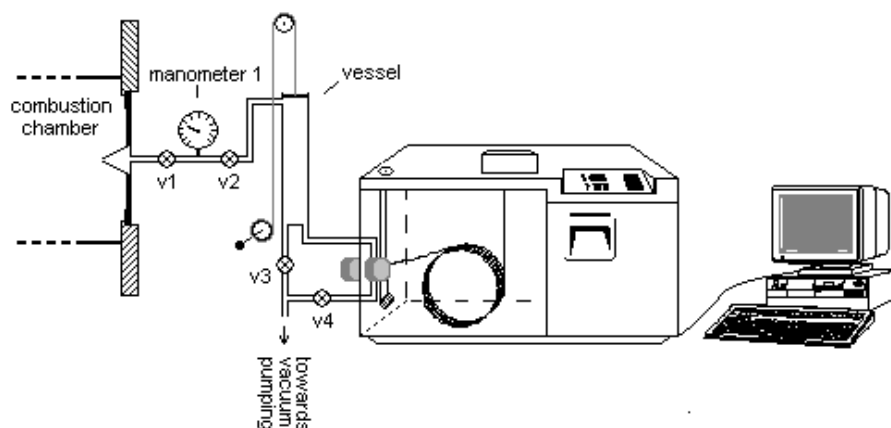


Figure 2.4: injection of samples for analysis of permanent gases of combustion and C_1 to C_7 hydrocarbons

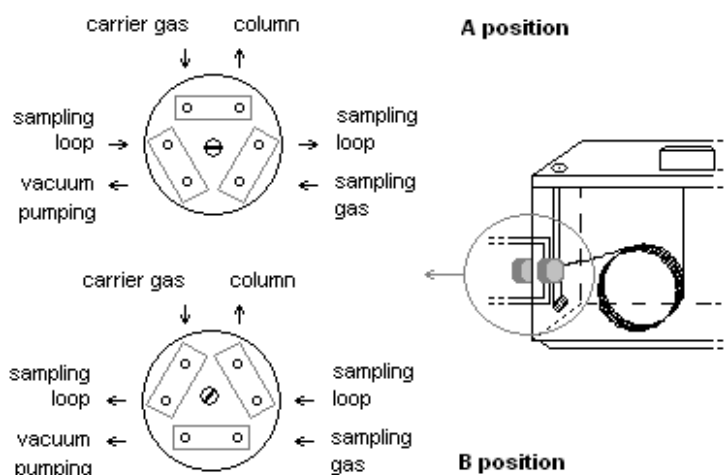


Figure 2.5: the multiway valve of the chromatographic setup

the carrier gas enters directly into the column and the sample loop is connected to the vessel and the vacuum pump. In the B position, the carrier gas directs the content of the sample loop inside the column and the vessel is connected to the vacuum pump. Before injecting a sample into the GC, the burner is moved to the desired position, the multiway valve is moved in its A position and the injection setup of figure 2.4 is cleaned up by closing valve 1 and opening valves 2, 3 and 4 until a pressure lower than 10^{-1} mbar is measured on manometer 1. Then, valve 1 is opened to fill the injection setup with the sampling gas. Afterwards, valve 3 and 4 are closed to fill the vessel containing the piston with the sample until a pressure of about 3.5 mbar is reached on manometer 1. Then, valve 1 is closed and the pressure is adjusted to 3 mbar thanks to valve 3. Subsequently, valve 2 is closed and the sample is compressed into the vessel as well as in the 2 ml sampling loop. Finally, the 2 ml of compressed sample that are located inside the sampling loop are injected into the GC column by changing the multiway valve position from A to B (see figure 2.5).

As defined above, chemical species that belongs to the second class of compounds generally have lower vapor pressures than those of the first class. As depicted in equation 2.7, to ensure its gaseous state before

injection inside the column of the Gas Chromatograph, a compound i must have a vapor pressure Pv_i higher than its partial pressure P_i , which is defined by the product of its mole fraction χ_i with the pressure P inside the injection setup.

$$Pv_i \geq P \times \chi_i \quad (2.7)$$

$$Pv_i = e^{A_i - \frac{B_i}{C_i + T}} \quad (2.8)$$

The vapor pressure of a chemical species i closely depends on the temperature, as described by the Antoine's law depicted in equation 2.8, where A_i , B_i and C_i are coefficients that are specific to i . Consequently, vapor pressures of large hydrocarbons that have to enter into the GC column can be increased by heating the injection setup. Moreover, to ensure the gaseous state of most of constituents having low vapor pressures, the pressure P in the injection setup can be maintained low by bypassing the compression step described in figure 2.4.

Therefore, another injection setup, resistant to high temperatures and bypassing the compression system, has been developed (see figure 2.6). This injection setup is heated at 300°C by a heating wire that is wound up around the main pipe, from the exit of the quartz nozzle to the sampling loop of the GC. The pressure in the setup is adjusted to 30 mbar in order to keep a negative pressure gradient between the combustion

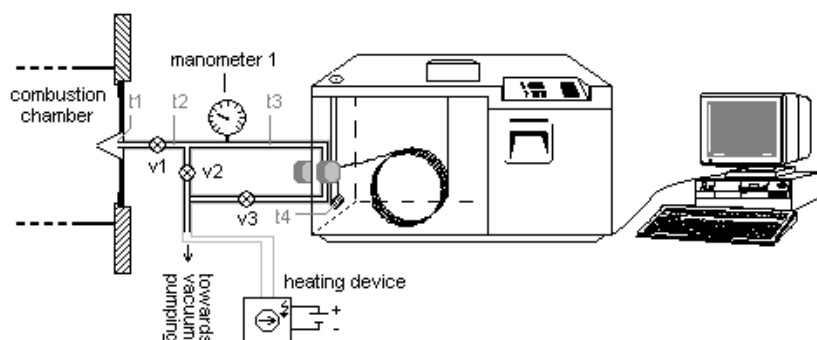


Figure 2.6: injection of samples for analysis of hydrocarbons with more than 7 carbon atoms

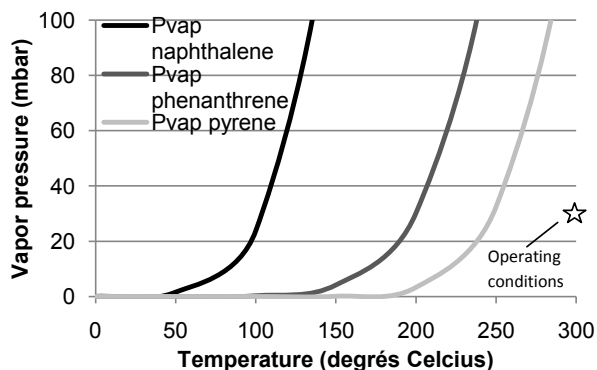


Figure 2.7: vapor pressures of some small PAH in function of temperature. Antoine’s law parameters are those recommended by the NIST [20].

chamber and the injection setup. The combination of low pressure and high temperature in the injection setup ensures that most of PAH are in their gaseous state, as demonstrated by figure 2.7, showing that under these conditions, even a pure pyrene ($C_{16}H_{10}$) flux should be gaseous. Before injecting a sample into the GC, the burner is moved to the desired location, the multiway valve is set to its A position and the injection setup is cleaned up by closing valve 1 and opening valves 2 and 3 of figure 2.6, until a pressure of 10^{-1} mbar is measured on the manometer 1. Then, valve 1 is opened and temperature and pressure are respectively adjusted to 300°C and 30 mbar by changing the voltage applied to the heating wire and by adjusting valve 2. Three thermocouples have been inserted into pipes of the injection setup and one onto the multiway valve in order to measure the sample flux temperature. Once the system has a pressure of 30 mbar and a temperature close to 300°C, valve 3 is closed in order to stop pumping inside the sampling loop. Finally, once the temperature has reached 300°C on thermocouple t4, the multiway valve is moved to its B position for injection of the sample into the GC column. The following section describes how sample constituents are separated and detected, and presents the appropriate calibration procedure of the chromatographic response using both injection setups.

Chromatographic separation and detection

In order to achieve the chromatographic separation of sample constituents, three different columns have been used, in combination with specific oven temperature programs and detector temperatures. The choice of GC columns depends on chemical properties of hydrocarbons that have to be detected and is consequently linked to the setup used for the injection.

Hydrocarbons of the first class defined in the previous section mainly consist of permanent gases of combustion and high vapor pressure hydrocarbons, which have 1 to 6 carbon atoms. For these compounds, an efficient column is the *PORAPLOT Q* from *Varian inc* that allows to separate light hydrocarbons, some permanent gases of combustion and polar compounds such as ketones, aldehydes, acids and alcohols. Nevertheless, among the permanent gases of combustion, only CO_2 and H_2O can be separated with the *PORAPLOT Q* and a second column is consequently required for their complete separation: the *MOLSIEVE 5A*, which is also provided by *Varian inc*. This column consists of a coated molecular sieve that allows a good separation of H_2 , O_2 , Ar and CO at temperatures around $150^\circ C$.

The last column is devoted to compounds of the second class defined above: large hydrocarbons having low vapor pressures. The *CPSIL-PAHCB* column from *Varian inc* is well suited to that kind of applications as it is designed for PAH separation and resists to temperatures up to $400^\circ C$, allowing to speed up the elution of very large compounds. At the output of columns, detection of sample constituents can be achieved by two different detectors. The first is a Flame Ionization Detector (FID) that burns compounds arriving at the output of the column into a H_2/O_2 diffusion flame. Hydrocarbon species burning in this flame form CHO^+ ions that are repelled by the nozzle of the FID burner which is positively charged. They are collected onto a negatively charged plate, inducing a current that can be measured. Even if FID detectors are commercial analyzers for now more than 50 years, the mechanism responsible of CHO^+ ions formation is surrounded by some uncertainties [26]. How-

ever, the main channel is thought to be reaction of oxygen atoms with CH radicals, forming CHO^+ and one electron ($CH + O \rightarrow CHO^+ + e^-$). When a compound i exits the column, the signal S_i of the FID detector first increases, then reaches a maximum, and finally decreases. The time interval between the sample injection and the maximum of the signal intensity of a compound i is called the eluting time of i , noted t_i . It can be measured by introducing each known compound separately and used as a reference for identification of chemical species at the output of the column.

The plot of the detector signal versus time is called a *chromatogram* and if sample constituents are well separated, it presents one peak per chemical species introduced into the column, centered on corresponding eluting times t_i . For each peak, the integration of detector signal over time gives an area A_i that is proportional to the number of positive ions that hit the negative collector plate of the detector. Considering that the combustion of a definite compound i in the FID detector always leads to the formation of the same amount of positive ions per mole, the surface A_i is proportional to the number of moles n_i of the compound i that is detected, as depicted in equation 2.9. Since the sample injection is always performed in the same conditions of pressure, temperature and volume, the total number of moles entering into the column, noted n_t , is identical at each injection. Consequently, in the present work the surface A_i is also proportional to the mole fraction of the compound i , as summarized by equation 2.10.

$$n_i = \alpha_i \times A_i \quad (2.9)$$

$$\chi_i = \frac{n_i}{n_t} = \frac{\alpha_i}{n_t} \times A_i = \beta_i \times A_i \quad (2.10)$$

The FID detector can be used for all organic compounds whose combustion generates CHO^+ ions. This excludes CO , CO_2 , H_2O , H_2 and other compounds that do not contain carbon atoms or are already too oxidized to form CHO^+ ions. Since these compounds have to be measured in the investigated flames, a second chromatographic detector called Thermal Conductivity Detector (TCD) has been used. This detector

compares the thermal conductivity of the eluent at the output of the column to that of the pure carrier gas and any differences caused by the presence of another compound having a different thermal conductivity results in a measurable signal. Therefore, contrarily to the FID detector, the TCD is independent of the chemical nature of compounds and its response only depends on the difference in thermal conductivity between the analyzed compound i and the carrier gas. In the same way as FID detector, the TCD response depends on number of moles of compounds i that passes through the detector and equations 2.9 and 2.10 are equally valid.

Contrarily to the FID detector, the TCD detector does not alter the sample composition and these two detectors can therefore be placed in series with the order TCD - FID to fully benefit of their complementarity. As depicted in table 2.2, this configuration is used with the PORAPLOT Q column that allows to separate light hydrocarbons and some permanent gases of combustion, which cannot be detected with the FID detector. The MOLSIEVE 5A column, devoted to H_2 , O_2 , Ar and CO measurement, is only connected to the TCD detector, as none of these compounds provides an FID signal. Since the difference in thermal conductivity of H_2 and helium is quite low, measurements with the MOLSIEVE 5A column have to be performed twice: firstly with helium as carrier gas and secondly using argon (see table 2.2). The difference in thermal conductivities between argon and H_2 is indeed sufficient to obtain significant TCD signals. Concerning the CPSILPAH CB column,

Table 2.2: chromatographic configurations used in the present work

Chemical species targeted	Injection setup [†]	Column	Carrier Gas	Detectors
O_2 , Ar , CO	A	MOLSIEVE 5A	He	TCD
H_2	A	MOLSIEVE 5A	Ar	TCD
Hydrocarbons from C_1 to C_6 , CO_2 and H_2O	A	PORAPLOT Q	He	FID + TCD
Hydrocarbons from C_7 to PAH	B	CPSILPAH CB	He	FID

[†] Setups A and B are those described in figures 2.4 and 2.6, respectively.

the transit into the TCD detector before the FID detection is avoided as it cools the eluent, causing PAH condensation and decreasing the quality of the chromatographic separation.

Table 2.2 summarizes the different chromatographic configurations that have to be used for measurement of flame structures and shows that four different flame sample analyses have to be carried out to fully determine rich hydrocarbon flame structures of this work. In the future, this number of chromatographic analysis may be reduced to three by adding a multiway valve at the output of the PORAPLOT Q column, in order to direct the H_2 , O_2 , Ar and CO mixture that rapidly flows through the column into the MOLSIEVE 5A for a parallel separation. All parameters used for chromatographic analyses with setups detailed in table 2.2 are describe in appendix A, together with eluting times of each measured compound.

The calibration procedure

The FID and the TCD detectors presented above are calibrated for permanent gases of combustion and a large range of stable hydrocarbons, including those observed in flames. The calibration procedure is divided into two phases. The first consists in measuring molar response factors α_i of equation 2.9 for each detector and each compound i , by measuring response surfaces A_i corresponding to samples with variable quantities of mole n_i . These samples are directly injected into the gas chromatograph with a syringe. According to its physical state at room temperature and atmospheric pressure, each compound i is injected either in the gaseous state (CH_4 , C_2H_2 , etc), in the liquid state (H_2O), or diluted into an appropriate solvent ($C_{10}H_8$, $C_{12}H_8$, $C_{12}H_{10}$, etc).

However, it is more adequate to perform a mole fraction calibration than a molar one, as mole fraction profiles of chemical species detected in flames have to be measured. Equation 2.10 has shown that the mole fraction response factor β_i of a compound i equals its molar response factor divided by the total number of moles that are injected. Since injections are always performed in similar conditions, n_t is a constant

that only depends on the injection setup used for the analysis. Therefore, by measuring n_t corresponding to both injection setups described previously, mole fraction response factors β_i of each compound i could be easily calculated from α_i factors, using equation 2.11.

$$\beta_i = \frac{\alpha_i}{n_t} \quad (2.11)$$

The second phase of the calibration procedure consists in measuring these total quantities of mole n_t injected into the GC using setups of figures 2.4 and 2.6. A_i surfaces corresponding to cold gas mixtures of methane-oxygen-argon with variable methane mole fractions have been measured using both injection setups, in order to determine the mole fraction response factor of methane (β_{CH_4}) with each of them. Then, knowing β_{CH_4} and α_{CH_4} , total molar quantities n_t injected using each setup has been calculated from equation 2.11. For many years it has been shown that the FID detector response A_i of a compound i is proportional to the number of its carbon atoms that are not double bounded to an oxygen atom (see reference [26] and references therein). The reason of this particular behavior is that the FID response is proportional to CHO^+ ions that are formed, which is in turn proportional to the number of carbon atoms that are not double bounded to an oxygen atom. Indeed, CO groups cannot react with O atoms forming CHO^+ ions. This well known relation has been verified in this work by plotting values of $1/\alpha_i$ measured for several hydrocarbons from C_1 to C_{14} in function of their effective carbon atom content (see figure 2.8). The plot consists in a well linear trend that can be approximated by linear regression to equation 2.12 ($1/\alpha_i$ is in $mV \times s \times mol^{-1}$), with a linear correlation coefficient (R^2) of 0.997.

$$\frac{1}{\alpha_i} = 293194 \times N_C \quad (2.12)$$

This equation is used to estimate α_i coefficients of unstable compounds, such as cyclopentadiene (C_5H_6), vinylacetylene (C_4H_4) or diacetylene (C_4H_2), which are not commercially available or difficult to handle. The uncertainty of chromatographic measurements performed in the present

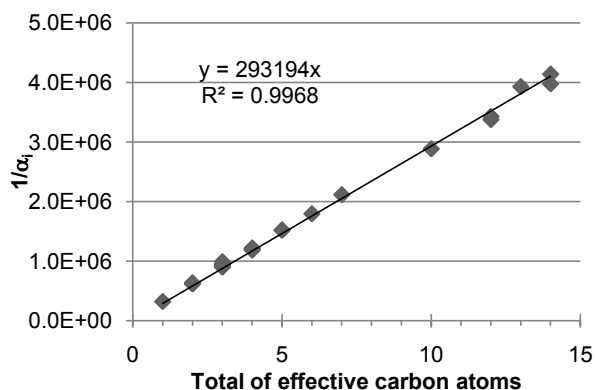


Figure 2.8: evolution of $1/\alpha_i$ (in $mV \times s \times mol^{-1}$) in function of the number of effective carbon atoms in i

work is difficult to determine, as it depends on several factors, including flame composition, the injection setup used, the calibration and the detector signal. For compounds that have been calibrated experimentally and via equation 2.12, it is reasonable to consider relative errors of 10% and 20%, respectively.

2.3.2 Molecular Beam Mass Spectrometry

Conceptual framework

Mass spectrometry is an analytical technique that allows the measurement of mass to charge ratios (m/z) of charged particles. It is widely used for determining elemental composition of samples and elucidating structures of molecules. Basically, a mass spectrometer consists in three main parts. The first is an ionizing source that generates charged molecules or molecule fragments, the second is the mass analyzer that filters ions on the basis of their m/z ratios, and the last is a detector which provides a signal proportional to the number of ions that passes through the mass filter. Beside the qualitative determination of sample constituents, mass spectrometry can be used for a quantitative analysis. Its application to the determination of mole fraction of compounds involved in flames is discussed hereafter.

Connection to the combustion chamber

The great advantage of Mass Spectrometry, compared to Gas Chromatography, is that it operates at a very low pressure (about 10^{-7} mbar), allowing to be coupled with a Molecular Beam sampling method (MBMS). The reason why mass spectrometry needs such a low pressure will be discussed further. A molecular beam is characterized by a high mean free path between molecules that prevents reactions between its constituents. Consequently, highly reactive species such as radicals may be extracted from the flame and safely transported until the ionization source of the mass spectrometer device. Consequently, MBMS is well suited for the quantitative investigation of flame chemistry, as originally demonstrated by Peeters and Mahnen [27], and has been used by several groups [28]. The MBMS device used in this work has been well described in previous studies [18, 29] and will consequently not be presented in much details below.

Practically, the molecular beam is created by sampling into the flame throughout the small apex of the quartz nozzle depicted in figure 2.9. The geometry of the nozzle (orifice diameter of 0.2 mm, a conical angle

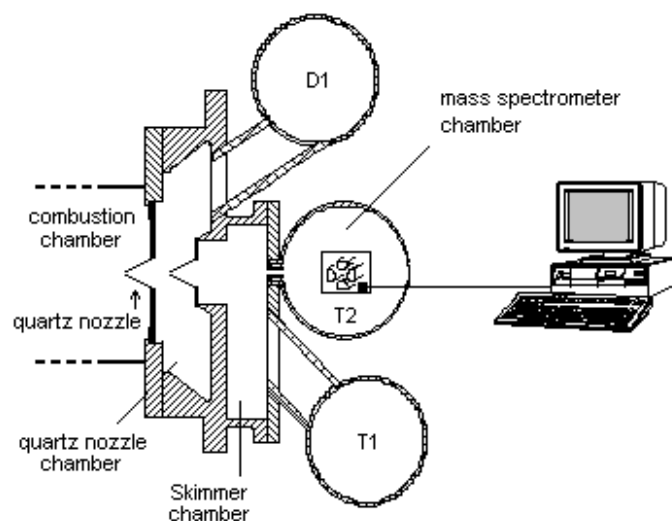


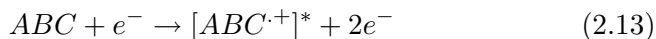
Figure 2.9: Molecular Beam Mass Spectrometry analysis

of 45° and a height of 2 cm) and the low pressure of the downstream chamber (about 10^{-3} mbar), compared to that of the flame (45 mbar), allows the expansion of samples into a molecular beam characterized by a high mean free path. This beam is consequently "frozen" and reactions between reactive species may no longer occur. The vacuum pumping inside the quartz nozzle chamber is achieved by the oil diffusion pump D1 (see figure 2.9). After a certain distance, the expanded sample may undergo a compression into a Mach disc that must be avoided in order to keep the high mean free path characterizing the beam. Therefore, the opened apex (1.5 mm in diameter) of a brass skimmer is introduced into the molecular beam before the Mach disc formation and the beam is directed inside the skimmer chamber, where the pressure is maintained at 10^{-5} mbar thanks to the turbomolecular vacuum pump T1 (see figure 2.9). In this chamber, the molecular beam is chopped at 30 Hz for phase detection and monitoring, allowing enhancement of the signal to noise ratio. Finally, it passes through a 0.8×8 mm collimating slit and enters into the ionization chamber of the mass spectrum device, which will be presented hereafter.

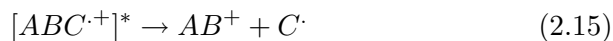
The mass spectrum device

As previously explained, a mass spectrum device consists of 3 main parts that are presented hereafter. The first part is the ionization chamber where molecules of the molecular beam are converted into ions that will be further separated by the mass filter of the spectrometer. Various ionization techniques exist, including the electronic impact ionization (EI), the chemical ionization (CI), the photoionization (PI) and the electrospray ionization (ESI). For this work, the ionization source is the EI, as it operates at low pressure and is therefore compatible with the molecular beam formation. Moreover, an EI source does not require any additional reactant for the ionization of chemical species, contrarily to the CI. The EI source consists of an electron beam of a determined energy that is produced by a tungsten filament and steered across the chamber towards an electron trap. The energy of the beam can be modified by

varying the current crossing the tungsten wire and by changing the potential of the electrode extracting the electrons. According to reaction 2.13, electrons having enough energy may extract an electron of an ABC molecule, forming a radical molecular ion $ABC^{\cdot+}$ that may have an excess of energy, depending on the difference between the electron beam energy and the ionization energy of ABC. EI sources need to operate at very low pressure in order to avoid the burning of the hot tungsten filament. At the same time, a high mean free path is maintained, avoiding chemical reactions of ions before their detection.



If the energy of the electron beam is superior but close to the ionization energy of ABC, the $ABC^{\cdot+}$ radical molecular ion will not subsequently fragment and could be preserved. On the contrary, if the electron beam has an energy that is highly superior to the ionization energy, the $ABC^{\cdot+}$ radical molecular ion will undergo fragmentation reactions like:



In this work mass spectrometry is used to quantify sample constituents. Therefore, fragmentation has to be avoided in order to ensure that the mass signal detected for $ABC^{\cdot+}$ fully corresponds to the quantity of ABC present into the sample. Ionization potentials are therefore always carefully adjusted just above ionization energies of targeted compounds. The second part of the mass spectrum device consists in a quadrupole mass analyzer that is able to filter ions formed in the ionization source according to their mass to charge ratios (m/z). The quadrupole is composed by 4 hyperbolic rods and each opposite rod pair is connected together electrically. A radio frequency voltage V is applied between one pair of rods and the other and a direct current U is superimposed. Inside the quadrupole analyzer, forces that apply on an ion having an m/z ratio depend on m , z , U , V and the distance between rods. Val-

ues of U and V can therefore be adjusted in order to impose to an ion with a determined m/z ratio a trajectory crossing the quadrupole filter. Other ions will collide with the rods and will not reach the output of the quadrupole mass analyzer. Practically, the m/z ratio of the ion to analyze has to be chosen on the control panel of the mass spectrum device and values of U and V are automatically adjusted.

The last part of the mass spectrum device is the detector setup that is composed by an electron multiplier, a preamplifier and an electrometer that allows to measure a mass signal in mV, corresponding to the number of radical molecular ions reaching the detector. Practically, the signal corresponding to the m/z ratio of a targeted chemical species is measured at various distances along the flame. At each distance, the signal is measured at fixed time intervals, during an appropriate time. A software running on the *Windows*[®] operating system and able to acquire mass signals from the electrometer has been developed in the present work. This software allows to choose the number of measurements to perform and the time interval between them. Then, it calculates a mean signal whose evolution as a function of the position in the flame can be plotted on the screen for an easier interpretation of measurements. This software replaces a former version developed in the laboratory, which only supports the *MS DOS*[®] operating system and does not allow an easy transfer of data into *Excel*[®].

The calibration procedure

At a distance z of the burner surface, the mass signal I_i of a compound i that is read on the electrometer can be linked to its mole fraction χ_i by equation 2.16, where S_i represents the sensitivity factor of i . Sensitivity factors highly depend on the temperature (and therefore on the sampling position z in the flame), on the pressure, on the analyzed compound i , and on the working potential of the EI source.

$$[I_i]_z = [S_i]_z \times [\chi_i]_z \quad (2.16)$$

Peeters and Mahnen [27, 29] have shown that for all chemical species, their sensitivity factors vary in the same manner with the temperature. Therefore, for two chemical species i and j , the ratio S_j/S_i is constant all along the flame and mole fraction of i can be obtained by solving equation 2.17 at different heights z of the flame.

$$[\chi_i]_z = \left[\frac{I_i}{I_j} \right]_z \times \frac{S_j}{S_i} \times [\chi_j]_z \quad (2.17)$$

The reference compound j is chosen among those measured by gas chromatography, in order to know its mole fraction profile $[\chi_j]_z$ in the flame. Then, the ratio S_j/S_i is approximated by the additivity of atomic contributions to the ionization cross section through equation 2.18, where n_C , n_H and n_O respectively represent the number of carbon, hydrogen and oxygen atoms of the molecule [29]. The best estimation of S_j/S_i is achieved by considering a compound j that has an ionization cross sections close to i .

$$S_j/S_i = \frac{(1.8n_C + 0.65n_H + 1.3n_O)_j}{(1.8n_C + 0.65n_H + 1.3n_O)_i} \quad (2.18)$$

Knowing the GC mole fraction profile of j and the S_j/S_i ratio, the mole fraction profile of i can be deduced from the measurement of mass signal profiles $[I_i]_z$ and $[I_j]_z$, using equation 2.17. In the same way as gas chromatography measurements, the error on MBMS mole fraction profiles are difficult to address. Indeed, it depends on the S_j/S_i approximation, the error on the χ_j mole fraction determined by GC and the error on the mean mass signal that is calculated. The latter can be significantly reduced by calculating the mean mass signal on a high number of measurements, as this error decreases with the number of measurements performed. Figure 2.10 depicts the mean mass signal profile measured at a m/z ratio corresponding to the phenoxy radical (C_6H_5O) into the lean benzene flame BF07 (see appendix B). Each mean signal is calculated on 20 measurements, with a time interval of 1 second. The bars of errors performed on the mean signals are equally represented with a confidence interval of 95%. Since the C_6H_5O is a radical species and is present in very low concentration in this flame (about $1.0 \cdot 10^{-5}$), this

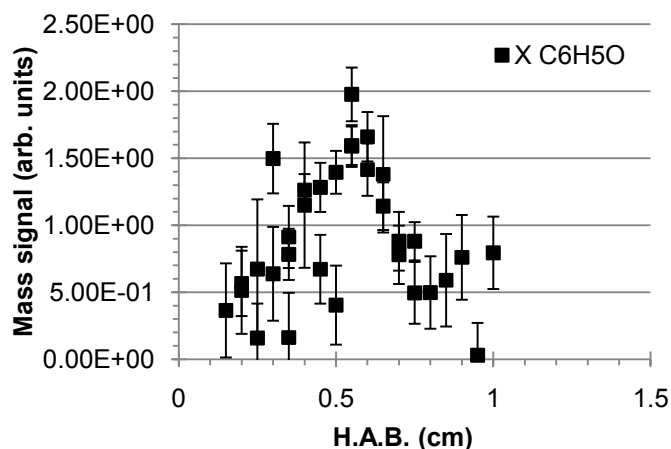


Figure 2.10: mean mass signal profile (arbitrary units) measured at an m/z ratio corresponding to the phenoxy radical (C_6H_5O) in BF07 (see appendix B). Error bars are presented for a confidence interval of 95%.

figure is well representative of the maximum error that should surround mean signals measured by MBMS. A general relative error of 20% should be considered for mole fraction measurements performed by MBMS and presented in this work.

2.3.3 GC and MBMS complementarity

Gas Chromatography and Molecular Beam Mass Spectrometry described above are complementary techniques [18]. The first allows to separate mass isomers but is unable to detect radical species since it operates at atmospheric pressure, which avoids the use of a molecular beam. On the contrary, the second allows to detect radical species but is unable to easily differentiate mass isomers. MBMS has the advantage to define the mass, which is unavailable in GC analyses. However, at a definite position z inside the flame, the GC has the great advantage to allow the analysis of the whole sample composition in one go, although the MBMS requires independent measurements for each chemical species. Consequently, the GC analysis has been chosen as the primary technique and the MBMS has only been used to acquire mole fraction profiles of some

important radicals and species unidentified by GC. In chapters presenting and discussing flame structure measurements, the analysis method will be specified for each considered compound.

2.4 Flame temperature measurements

Conceptual framework

Temperature measurements have been performed by inserting a thin thermocouple composed of platinum and platinum-rhodium 10% into the flames. This technique is based on the Seebeck effect stipulating that when two different metals or alloys are joined together, a voltage depending on the temperature of the junction is created between the two wires. This voltage may be measured and correlated to the temperature at the junction of the Pt and PtRh 10% wires inserted into the flame. The relationship between temperature and voltage is junction specific and different alloys are therefore used for different temperature ranges. The junction between platinum and platinum-rhodium 10% provides a wide temperature range (approximately 300 to 2000 K) that is convenient to typical flame temperatures.

Connection to the combustion chamber

As depicted in figure 2.11, the thermocouple consists of a kind of fork whose the two branches are wires of Pt and Pt/Rh10% (0.5 mm in diameter). These branches are connected together by a wire of 0.1 mm in diameter, constituted of Pt and Pt/Rh 10% whose junction is located at an equal distance of each branch. For temperature measurement, the thinnest wire is inserted well perpendicularly to the burner axis into the flame, in order to avoid any temperature gradient along it. Its junction is placed at about 1 mm in front of the apex of the quartz nozzle for measuring temperatures that are representative of the sampling location. Since the thermocouple is made of platinum which is a powerful catalyst of hydrogen atom recombination into H_2 , the wire of 0.1 mm in diameter

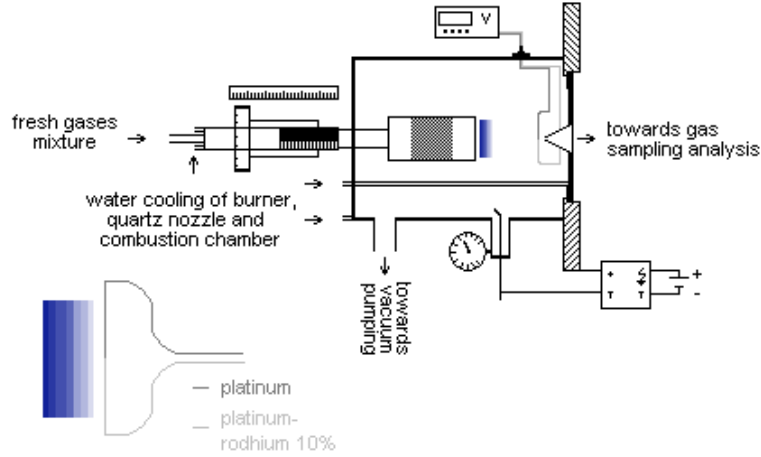


Figure 2.11: measurement of the flame temperature profile using a thermocouple

is coated with a thin ceramic layer (BeO 7% and Y_2O_3 93%) to prevent any chemical interaction of platinum with the flame [30]. Indeed, the recombination reaction of H atoms into H_2 is an exothermic reaction ($\Delta H = -104 \text{ kcal mol}^{-1}$) that may artificially increase the measured temperature. The wires of 0.5 mm in diameters are bended in order to pass through the wall of the combustion chamber, and to be connected to a voltmeter. The crossing of the stainless wall is achieved through a window that is converted into a ceramic sheathing, enabling to easily pass the wires outside the combustion chamber without any leaks. To determine the temperature profile, the voltage between the two branches of the thermocouple has to be measured all along the flame, by moving the position of the burner. Then, these voltages are converted to temperatures by the calibration method presented below.

The calibration procedure

The relationship between the temperature and the voltage of a specific thermocouple, as that used in this work, has been well investigated in the past [29]. Consequently, calibration curves for Pt/PtRh 10% thermocouples exist and may be used to convert the voltage profile into a

temperature profile. However, at temperatures such as those measured in a flame, the thermocouple loses some heat that it receives into radiation and the measured temperature consequently underestimates that of the gas-phase. Therefore, the temperature profile has to be corrected for radiation losses using the electrical compensation method, briefly presented hereafter.

The energy balance describing a thermocouple inserted inside a flame is that of equation 2.19, where α , β , T_g , T_t and T_w are respectively a conduction factor, a radiation factor, temperature of the gas-phase, of the thermocouple and of the walls absorbing radiation. The left side of equation 2.19 represents the heat received by convection from the hot gas-phase and the right side that lost by radiation.

$$\alpha \times (T_g - T_t) = \beta \times (T_t^4 - T_w^4) \quad (2.19)$$

In order to determine the error in temperature that is caused by thermocouple radiation, the term $(T_g - T_t)$ of equation 2.19 has to be known for each T_t measured in the flame. The method consists in first applying an alternative current to the thermocouple placed in a vacuum chamber and measuring the temperature for various current intensities. The energy balance of such a system corresponds to equation 2.20 that does not involve the energy lost by conduction since it is negligible under vacuum conditions. The term RI^2 represents the energy brought by applying a current on the thermocouple.

$$(RI^2)_{vacuum} = \beta \times (T_t^4 - T_w^4) \quad (2.20)$$

Then, the same experiment is performed at different distances inside a flame. The new energy balance is equation 2.21 that depicts a conduction term which is no longer negligible.

$$(RI^2)_{flame} + \alpha \times (T_g - T_t) = \beta \times (T_t^4 - T_w^4) \quad (2.21)$$

If one plots on the same graph RI^2 as a function of the measured temperature T_t at the output of the thermocouple for both experiments (under

vacuum and inside a flame), one can determine intersection points that verify equation 2.22. At these points, equation 2.22 may be inserted into 2.20 giving equation 2.23.

$$RI_{flame}^2 = RI_{vacuum}^2 \quad (2.22)$$

$$(RI^2)_{flame} = \beta \times (T_t^4 - T_w^4) \quad (2.23)$$

Finally, if equation 2.23 is inserted into equation 2.21, considering that α is not null, one obtains that temperature of the gas-phase T_g equals that of the thermocouple T_t . It means that the energy brought by applying a current at the output of the thermocouple corresponds to that loosed by radiation. By applying this method at diverse distances inside the flame, one can deduces the function $f(T_t)$ giving the gas-phase temperature T_g as a function of the thermocouple temperature. Parameters of this latter equation have been determined in the laboratory for many years, with a thermocouple having a composition identical to that used in the present work.

2.5 Soot concentration measurements

Conceptual framework

In addition to the measurement of mole fractions profiles of the gas-phase constituents and of the flame temperature profile, a setup able to measure soot concentration was necessary to fully determine experimental structures of rich hydrocarbon flames investigated in this work. Such setups have already been described in the literature and principally consist either in intrusive gravimetric methods or in non-intrusive laser techniques [31,32].

The simple laser method to measure the soot volume fraction is that of extinction, which is based on the Beer-Lambert law. This law links the ratio of transmitted to incident light intensity with the concentration of the analyzed substance, by a relationship involving its extinction

coefficient and the length of the cell containing the sample. Unfortunately, a large uncertainty is still surrounding the extinction coefficient of soot [31,33]. Indeed, values proposed in the literature for the extinction coefficient of soot vary by a factor close to 4 [33]. Moreover, the low pressure at which flame investigations are conducted in this work considerably decreases the soot concentration. Consequently, the ratio of transmitted to incident light intensity is quite high and difficult to measure. Another light based technique for the measurement of soot volume fraction is the emerging Laser Induced Incandescence method, which consists in rapidly heating soot particles that are on the path of the laser beam by using a pulsed laser source [34–36]. The soot is heated up to incandescence (between 4000 to 4500 K) and the produced light is analyzed by photodetectors that give information on the soot volume fraction and the primary particle diameter. Unfortunately, this method is highly expensive as it necessitates a specific laser and particular detectors. Laser diagnostic setups for the measurement of soot concentrations are thus subject to a high uncertainty or are highly expensive and are therefore not considered in this work.

Beside these laser based techniques, gravimetric methods could be used, but they imply the intrusion of a probe inside the flame to collect soot. This soot can subsequently be weighted and by knowing the volumetric flow rate through the probe and the elapsed time, soot concentration inside the flame can be calculated. Since this technique is cheap and does not require highly specific material, it has been used for soot concentration measurements inside flames investigated in this work.

Connection to the combustion chamber

Based on previous considerations, a quartz probe for soot sampling has been designed. It consists in a quartz tube with a conical extremity that presents a small orifice of 1 mm in diameter, which is introduced inside the flame, perpendicularly to the burner surface. The tube has a 90° bend that allows to exit the combustion chamber throughout a modified window. Outside the combustion chamber, the probe extremity is linked to

a filter connected to a vacuum pump to collect soot. A manometer and a regulating valve have been inserted between the filter and the vacuum pump in order to control the pressure of soot extraction, which has been fixed to 20 mbar. Whereas this setup allows to collect soot material on the filter, a significant amount of soot deposits on the wall inside the probe. The problem is certainly due to the bended geometry of the probe and could not be avoided in the present work.

In 2009, Abid and co-workers developed a soot sampling probe that prevent soot deposition [37]. It consists in a tube that is placed perpendicularly to the burner axis and which presents a small orifice for soot sampling. A nitrogen flow penetrates in one tube extremity, steering particles to the other side for measurement. Unfortunately, such a technique involves too much apparatus modifications and could not be developed in the present work.

The use of a probe has thus been substituted by a filter that is directly introduced into the flame, as depicted in figure 2.12. This filter allows to easily determine the mass of soot that is produced per unit of time at definite positions in the flame, whereas its introduction and dismantling necessitates the opening of the combustion chamber, which is a restrictive operation. The filter is made of ceramic wool that resists to high temperatures such as those encountered in flames. In addition, most of the gas flow is able to cross the ceramic wool filter and the flame is consequently not much perturbed. Nevertheless, the filter cannot be placed

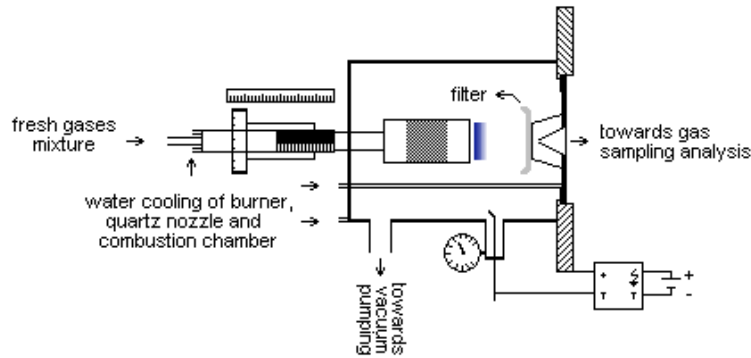


Figure 2.12: setup for soot sampling developed in this work.

too close to the burner (about 8 mm), as it quenches the flame. At too large distances from the burner surface (about 15 mm), the flame begins to curve up as its axis is horizontal and hot gases tend to go upside, bypassing the filter. Therefore, measurements can only be performed in a region spreading from 8 to 15 mm, which fortunately coincides with the soot formation area. Even in this region, some soot seems to bypass the filter since soot deposition is observed on its back side. This indicates that soot recirculation occurs in the combustion chamber and that particles accumulated in the filter might not all correspond to the sampling position.

Quantitative as well as qualitative studies of these soot samples are thus subject to an error that cannot be estimated. Moreover, the soot caught inside the filter is not cooled and subsists in the flame environment, allowing subsequent reactions to occur. However, chapter 7 will show that measurements performed with the present are consistent with other studies of the literature, indicating that the error surrounding the soot concentration might be limited. Anyway, the developed setup consists in a first attempt to measure soot concentrations in the laboratory and it should be further improved or substituted by a more powerful technique.

The calibration procedure

In order to measure soot concentrations at certain distances of the burner surface, a ceramic wool filter consisting in a $12 \times 12 \text{ cm}^2$ square with a thickness of 0.5 cm has first to be prepared and weighted. Then, the combustion chamber is opened to install the filter perpendicularly to the axis of the burner, in front of the quartz nozzle. Afterwards, the combustion chamber is closed and the burner is moved backward in order to ignite a lean fuel-oxygen-argon flame. This non sooting flame allows to carefully adjust the burner position, without the risk of premature soot deposition. Once the burner is in the right position, volumetric flow rates of fuel, oxygen and argon are rapidly adjusted to those of the rich flame that has to be analyzed and the soot sampling is achieved for 30

minutes. Then, the flame is quenched and the combustion chamber is opened to weight the filter containing soot. The mass flow rate of soot Dm_s at the analyzed distance z above the burner can be determined by equation 2.24, where m represents the mass of soot that has been accumulated during the time t .

$$[Dm_s]_z = \frac{[m_s]_z}{t} \quad (2.24)$$

In order to calculate the soot concentration C_s at the distance z , the mass flow rate of soot has to be divided by the total volumetric flow rate of gas Dv_T that has crossed the filter, as depicted in equation 2.25, where V_T represents the total volume of gas that crossed the filter during the time t .

$$[C_s]_z = \left[\frac{Dm_s}{Dv_T} \right]_z = \frac{[m]_z/t}{[V_T]_z/t} = \left[\frac{m}{V_T} \right]_z \quad (2.25)$$

Knowing the total volumetric flow rate Dv_T of the cold gas mixture, that at the distance z can be calculated using the ideal gas law, as demonstrated in equation 2.26, where T_z and P_z respectively represent the temperature and the pressure of the flame at the distance z of the burner surface.

$$[Dv_T]_z = Dv_T \times \frac{P_{atm}}{298K} \times \frac{T_z}{P_z} \quad (2.26)$$

The pressure P_z corresponds to the working pressure and the temperature T_z has been measured by a thermocouple, as described in the previous section. Therefore, all variables are known and the soot concentration can finally be calculated using equation 2.27.

$$[C_s]_z = \frac{[Dm_s]_z}{Dv_T \times \frac{P_{atm}}{298K} \times \frac{T_z}{P_z}} \quad (2.27)$$

The presence of the filter may slightly decreases the flame temperature at the z position and the use of that measured with the thermocouple method presented above may therefore introduce an error on the calculated soot concentration. If the development of this method is to be pursued, more reliable temperature measurements should be performed at the filter position. The method can equally be improved by consider-

ing the variation of the total number of mole of gas accompanying the combustion reaction in equation 2.26.

2.6 Conclusions

This chapter has presented several apparatuses developed to analyze structures of premixed, laminar and one-dimensional benzene and toluene flames that will be presented in following chapters. These flame structures include mole fractions profiles of compounds involved in the combustion reaction, as well as concentration profiles of carbonaceous particles formed in rich conditions and temperature profiles. Sampling is achieved by a quartz nozzle at different heights inside flames and two different techniques are used for the measurement of chemical species mole fractions. The first is Gas Chromatography (GC) that allows to measure mole fractions of non radical species. In order to cover a large range of chemical species, different columns, detectors and injection setups have been used. The GC technique developed in this work is able to detect all permanent gases of combustion and major hydrocarbons from CH_4 to $C_{14}H_{10}$, including small PAH. The second method used for the measurement of mole fractions is the Molecular Beam Mass Spectrometry (MBMS). This technique is complementary to GC, as it allows to detect radical species. However, it is difficult to separate mass isomers with MBMS and this technique necessitates to measure each chemical species individually, whereas GC allows to measure them in one go. Consequently, GC is used as the primary technique and MBMS is only used for selected chemical species that cannot be detected by GC and whose mole fraction measurement is useful for the understanding of aromatic combustion.

Beside mole fraction measurements, a setup has been developed for temperature profile determination. It consists in a thermocouple that is inserted in front of the quartz nozzle and coated to prevent chemical interactions with the flame. The temperature profile can be measured by moving the burner and therefore placing the thermocouple at different

heights in the flame. Finally, a setup to measure soot concentrations in rich hydrocarbon flames has been developed. It consists of a filter made of ceramic wool that is located in front of the quartz nozzle. The soot can be collected at different heights in the flame by moving the burner to different positions. The soot concentration can be deduced from the collected mass of soot, the residence time in the flame, the working pressure and the flame temperature. It is the first attempt to measure soot concentration inside hydrocarbon flames in the laboratory. The setup is still at the first stage of its development and should be further improved in order to avoid soot recirculation inside the combustion chamber and flame perturbation.

Experimental measurements performed with these setups provide valuable data on benzene and toluene oxidation in flames as well as on PAH and soot formation. Detailed kinetic models will be developed to compare with these data and information on flame chemistry will be obtained by a comparative rate analysis of included reactions. Before to present such comparisons, the next chapter exposes the mathematical description of premixed, laminar and one-dimensional flames and explains how predicted flame structures can be computed from kinetic models.

Kinetic modeling method

3.1 Introduction

As stated by Warnatz [12], a chemically reacting flow such as a flame can be completely described at each point in space and time by specifying its pressure, its temperature, its velocity and the density of each chemical species that it contains. These properties can be changing in time and space due to chemical reactions, the fluid flow causing molecular and energy convection, molecular diffusion, energy conduction and radiations. Warnatz therefore stressed that a comprehensive mathematical description of flames has to account for each of these processes. Since some properties such as energy, mass and momentum are conserved across flames, conservation equations can be determined. For non reacting flows, they consist of *Navier-Stokes equations*, which are widely used by scientists to model fluid dynamic phenomena. In order to describe reacting flows such as flames, these equations require some additional terms, accounting for the presence of multiple chemical species and the existence of chemical reactions between them [38]. A comprehensive modeling of flame structures therefore necessitates appropriate conservation equations and a detailed kinetic model containing information on rates of chemical reactions that occur, together with thermodynamic and transport properties of each involved compound. The kinetic modeling of flames has consequently become a multi disci-

plinary task, involving engineers for developing softwares able to solve complex conservation equations and chemists for creating and handling kinetic models that may involve a large number of chemical species. This chapter presents conservation equations for laminar, premixed and one-dimensional flames investigated in this work and briefly describes the way they are solved by the Cosilab software [39]. The development of the associated kinetic model will be comprehensively discussed in the following chapters.

3.2 Mathematical description of flames

The first part of this section briefly presents the general form of three dimensional conservation equations following the approach proposed by Warnatz [12]. Then, these equations are applied to the conservation of the mass, momentums and the energy, for the special case of one-dimensional flames investigated in this work.

3.2.1 The general form of 3 dimensional conservation equations

An arbitrarily three dimensional element Ω with a volume V and a surface S is considered. The value of an extensive variable F of Ω as a function of time t , can be calculated by integration of its density $\rho_F(\vec{r}, t) = dF/dV$ over the volume V , as described by equation 3.1 where $\vec{r}$ is a vector representing the spatial location.

$$F(t) = \int_V \rho_F(\vec{r}, t) dV \quad (3.1)$$

Considering that (i) the element Ω is located inside a flux that may bring or take the variable F away, (ii) F may be consumed or produced within Ω and (iii) interactions with the surrounding of Ω may bring or take F away of the volume V , a change of the extensive variable $F(t)$ can basically be represented by :

- i a change in the flux $\vec{\phi}_F \vec{n} dS$ that crosses the surface S of Ω ($\vec{n}$ is a vector perpendicular to the surface). This flux may be molecular diffusion, heat conduction, convection, etc. The flux density $\vec{\phi}_F$ describes the amount of F that flows per units of time and surface through S .
- ii a change in the term q_F describing the production of F within the volume V of Ω . This change may be due to chemical reactions. The term q_F is the amount of F that is formed per units of time and volume.
- iii a change in the term p_F describing interaction processes with the surrounding of Ω . This change may be due to radiation, gravity, etc and p_F is the amount of F generated per unit of volume.

Considering these three terms, an overall balance equation can be written for F , as depicted in the following equation 3.2.

$$\int_V \frac{\partial \rho_F}{\partial t} dV + \int_S \vec{\phi}_F \vec{n} dS = \int_V q_F dV + \int_V p_F dV \quad (3.2)$$

In this equation, the temporal variation of F contained in Ω has been written according to equation 3.3.

$$\frac{\partial F}{\partial t} = \int_V \frac{\partial \rho_F}{\partial t} dV \quad (3.3)$$

According to the theorem of Gauss, the integral representing the change in the flux $\vec{\phi}_F$ through the surface S of Ω in equation 3.2 can be converted to a volume integral, as depicted in equation 3.4 where $\vec{\nabla} \cdot \vec{\phi}_F$ represents the divergence of the flux.

$$\int_S \vec{\phi}_F \vec{n} dS = \int_V \vec{\nabla} \cdot \vec{\phi}_F dV \quad (3.4)$$

Equation 3.2 can therefore be re-written in the form of equation 3.5

$$\int_V \frac{\partial \rho_F}{\partial t} dV + \int_V \vec{\nabla} \cdot \vec{\phi}_F dV = \int_V q_F dV + \int_V p_F dV \quad (3.5)$$

Finally, considering an infinitesimally small volume element dV instead of the volume V of Ω , $V \rightarrow 0$ and equation 3.5 can be converted to the general equation 3.6 that represents the conservation of an extensive variable F .

$$\frac{\partial \rho_F(\vec{r}, t)}{\partial t} + \vec{\nabla} \cdot \vec{\phi}_F = q_F + p_F \quad (3.6)$$

3.2.2 Conservation equations of premixed, laminar and one-dimensional flames

Laminar and premixed flames that are stabilized in this work are flat and one-dimensional. This means that each flame parameter only changes in one direction z that is perpendicular to the burner surface, as depicted in figure 3.1. In equation 3.6, the term $\vec{\nabla} \cdot \vec{\phi}_F$ can therefore be replaced by the variation of $\vec{\phi}_F$ versus the coordinate z . Laminar flames of this work are equally stationary and their parameters consequently do not exhibit any temporal dependence. Therefore, the function $\rho_F(\vec{r}, t)$ of equation 3.6 is constant over time and its derivative versus time becomes zero. In the present work, p_F represents the effects of gravitation, flame radiation and heat transfer to the burner surface. Whereas the impact of gravitation can be considered as negligible, those of the flame radiation and the heat transfer to the burner may be significant in flames presented in following chapters. However, we will show that p_F is only involved in the conservation equation of energy, which is not resolved for the calculation of flame structures presented in this work, as experimental temperature profiles are provided.

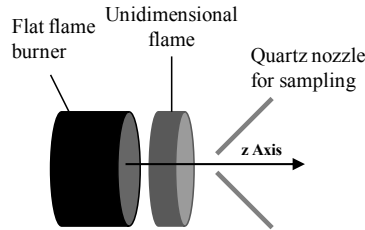


Figure 3.1: a schematic illustration of a laminar, one-dimensional and premixed flame

All considered, the general conservation equation 3.6 can be simplified in equation 3.7, which is specific to premixed, laminar and one-dimensional flames of this work.

$$\frac{\partial \vec{\phi}_F}{\partial z} = q_F + p_F \quad (3.7)$$

The left side of this equation represents the variation of the density flux of an extensive variable F versus the z -axis, and the right side summarizes sources and sinks that respectively produce and consume F within a flame element Ω . In following sections, this equation will be applied to conservation of mass, chemical species and enthalpy in flames of the present study, following the approach proposed by Warnatz [12].

Conservation of the overall mass

The left side of equation 3.7 with F being the total mass corresponds to the variation of the total mass flux density ($\vec{\phi}_m$) with the coordinate z . This total mass flux density is the product of the total mass density ρ with the velocity v of the flow. Since chemical reactions, flame radiation and heat transfer to the burner neither create nor destroy mass, terms q_m and p_m are zero and the conservation equation 3.8 demonstrates that the product $\rho \times v$ is constant all along the flame.

$\frac{\partial(\rho v)}{\partial z} = 0 \quad (3.8)$

Conservation of the mass m_i of chemical species i

In the same way as $\vec{\phi}_m = \rho v$, the mass flux density of a compound i is given by $\vec{\phi}_{m_i} = \rho_i v_i$. Considering that the mass density ρ_i of a species i is given by ρw_i , where w_i is its mass fraction m_i/m , the mass flux density of i can be written as $\vec{\phi}_{m_i} = \rho w_i v_i$. In contrast with the total mass of the mixture, the mass of a compound i can be created or consumed through chemical reactions involving it. The term q_{m_i} is therefore different of zero and corresponds to r_i that describes the

mass rate of production of i through chemical reactions, as depicted in equation 3.9, where $[i]$ is the molar concentration of i and M_i is its molecular mass.

$$r_i = M_i \times (\partial[i]/\partial t) \quad (3.9)$$

In contrast to q_{m_i} , p_{m_i} is zero as the flame radiation and the heat transfer to the burner neither produce nor destroy mass of a compound i . All considered, the conservation equation of m_i is given by equation 3.7.

$$\frac{\partial(\rho w_i v_i)}{\partial z} = r_i \quad (3.10)$$

The flow velocity v_i of a compound i is the resultant of (i) the total flow velocity v that represents the convection of i in the reacting flow and (ii) a diffusion velocity V_i that describes molecular transport through diffusion processes, due to concentration gradients of species i inside the flame. The flow velocity can therefore be written as $v_i = v + V_i$ and once inserted in equation 3.10, after a simple product law differentiation, it gives equation 3.11.

$$w_i \frac{\partial(\rho v)}{\partial z} + \rho v \frac{\partial(w_i)}{\partial z} + \frac{\partial(\rho w_i V_i)}{\partial z} = r_i \quad (3.11)$$

Considering the conservation equation 3.8 of the total mass of the mixture, the first term of the left side of equation 3.11 is zero and the conservation equation for the mass m_i of species i can be written as hereafter, where $j_i = \rho w_i V_i$ and denotes the diffusion flux of a species i .

$$\rho v \frac{\partial(w_i)}{\partial z} + \frac{\partial(j_i)}{\partial z} = r_i \quad (3.12)$$

Conservation of the mixture energy

The energy flux density of the reacting mixture is given by $\sum_i \rho w_i v_i h_i + j_q$, where h_i is the specific enthalpy of the compound i and j_q is a heat flux density that is caused by transport of energy due to temperature gradients in the flame. In the same way as the total mass, since chemical

reactions neither create nor destroy energy but transform it, the conservation equation of the total enthalpy can be written as follows.

$$\sum_i \frac{\partial(\rho w_i v_i h_i)}{\partial z} + \frac{\partial j_q}{\partial z} = p_{h_i} \quad (3.13)$$

In this equation, the term p_{h_i} represents the energy lost by flame radiation and by heat transfer to the burner surface and to the wall of the combustion chamber. Concerning the flame radiation, it is expected to be significant in rich hydrocarbon flames producing soot particles, whereas it is considered negligible in non sooting flames. The heat transfer to the burner surface depends on the position of the flame, but is expected to be significant in all flames of this work. Experimental flame temperature profiles have been introduced as input parameters to account for these energy transfers. Therefore, the conservation equation of energy discussed in this section is not resolved when modeling flame structures depicted in following chapters. However, the following equations are of interest for the calculation of adiabatic and non sooting flame temperatures (see section 3.5).

Considering that $v_i = v + V_i$ and $j_i = \rho w_i V_i$, as previously mentioned, equation 3.13 can be converted into equation 3.14.

$$\sum_i \frac{\partial(\rho v w_i h_i)}{\partial z} + \sum_i \frac{\partial(j_i h_i)}{\partial z} + \frac{\partial j_q}{\partial z} = p_{h_i} \quad (3.14)$$

The first two terms on the left side of equation 3.14 can be developed by the law of product derivation, as depicted below.

$$\begin{aligned} \sum_i \frac{\partial(\rho v w_i h_i)}{\partial z} + \sum_i \frac{\partial(j_i h_i)}{\partial z} = & \\ \left(\sum_i w_i h_i \frac{\partial(\rho v)}{\partial z} + \rho v \sum_i w_i \frac{\partial(h_i)}{\partial z} + \rho v \sum_i h_i \frac{\partial(w_i)}{\partial z} \right) + & \\ \left(\sum_i h_i \frac{\partial(j_i)}{\partial z} + \sum_i j_i \frac{\partial(h_i)}{\partial z} \right) & \end{aligned} \quad (3.15)$$

If one introduces equations 3.15 and 3.8 into equation 3.14, one obtains:

$$\begin{aligned} \rho v \sum_i w_i \frac{\partial(h_i)}{\partial z} + \rho v \sum_i h_i \frac{\partial(w_i)}{\partial z} + \\ \sum_i h_i \frac{\partial(j_i)}{\partial z} + \sum_i j_i \frac{\partial(h_i)}{\partial z} + \frac{\partial j_q}{\partial z} = p_{h_i} \end{aligned} \quad (3.16)$$

Finally, considering the mass conservation equation 3.12 of a species i , equation 3.16 can be simplified into the enthalpy conservation equation 3.17, where $\sum_i h_i r_i$ represents the change in enthalpy due to the production of i through chemical reactions. Terms involving j_i and j_q respectively represent the enthalpy brought by species diffusion and the heat flux caused by temperature conduction.

$$\rho v \sum_i w_i \frac{\partial(h_i)}{\partial z} + \sum_i h_i r_i + \sum_i j_i \frac{\partial(h_i)}{\partial z} + \frac{\partial j_q}{\partial z} = p_{h_i} \quad (3.17)$$

Using $dh_i = c_{p,i}dT$, the temperature T can be introduced into the former equation, giving:

$$\rho v \sum_i w_i c_{p,i} \frac{\partial T}{\partial z} + \sum_i h_i r_i + \sum_i j_i c_{p,i} \frac{\partial T}{\partial z} + \frac{\partial j_q}{\partial z} = p_{h_i} \quad (3.18)$$

Heat and mass transport phenomenons

In equations of chemical species conservation 3.12 and energy conservation 3.18, terms j_i and j_q that respectively represent the transport of mass (molecular diffusion) and heat (heat conduction) have been introduced. The molecular diffusion j_i can be obtained by an extended form of the law of Fick, as depicted in equation 3.19 where c is the molar concentration of the mixture, M_i and M_j are molecular masses of compounds i and j , D_{ij} is the multicomponent diffusion coefficient, χ_j is the mole fraction of j and D_i^T is the thermal diffusion coefficient of i .

$$j_i = \frac{c^2}{\rho} M_i \sum_j M_j D_{ij} \frac{\partial \chi_j}{\partial z} - \frac{D_i^T}{T} \frac{\partial T}{\partial z} \quad (3.19)$$

Concerning the heat conduction, the term j_q can be obtained by the law of Fourier, as shown in equation 3.20, where λ is the heat conductivity of the mixture.

$$j_q = -\lambda \frac{\partial T}{\partial z} \quad (3.20)$$

Information on the calculation of coefficients D_{ij} , D_i^T and λ will be given in next sections.

3.3 The Cosilab software

As highlighted in the introduction of this chapter, a chemically reacting flow can be fully described in time and space by its pressure P , its temperature T , its velocity v and the density ρ_i of each chemical species that it contains. In flames of this work, the pressure P is constant and is measured on the manometer of the combustion chamber. Considering that the density ρ_i of each of the N chemical species constituting the flame is given by the product of its mass fraction w_i with the total density ρ , $N+2$ variables remain unknown: w_i , w_{i+1} , ..., w_{N-1} , T , v and ρ (the mass fraction w_N can be found using $\sum_i^N w_i = 1$).

At each distance z of the burner surface, the *Cosilab* software [39] uses the conservation equations presented in the previous section to find these $N+2$ unknowns, based on a kinetic model, the thermodynamic and transport data of involved compounds and the boundary conditions of a flame. In addition, an experimental temperature profile can be provided in order to account for non adiabatic behavior of flames. Figure 3.2 presents the general functioning scheme of *Cosilab*. The software firstly determines a system of equations on the basis of input data and conservation equations. Then, the equation system is solved using the *Newton's method* that is an iterative algorithm able to determine roots of a function if an initial guess is provided. The solver therefore requires an initial guess that is sufficiently close to the final solution. This can be achieved by entering the experimental structure of the analyzed flame or by starting the calculation with a known flame that is subsequently converted to the desired flame by step by step modifying its initial com-

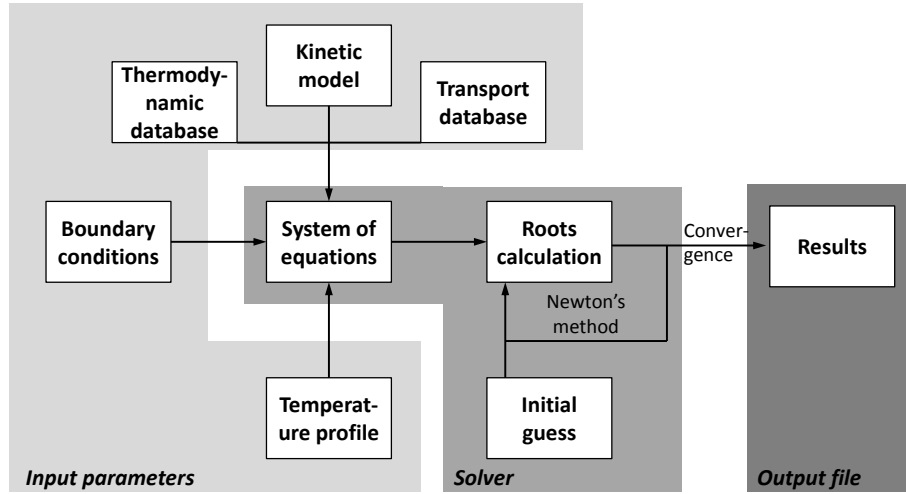


Figure 3.2: general functioning scheme of the Cosilab software

position. The convergence level can be adjusted and highly affects the calculation time, in the same way as the quality of the initial guess, the size of the kinetic model and the number of involved chemical species. Once the solver has converged, an output file is written with the calculated flame structure. Additional information such as rate of chemical reactions as a function of the coordinate z can be stored in the output file. Following sections detail some key points of the general functioning scheme of Cosilab, presented in figure 3.2.

3.3.1 Boundary conditions

The boundary parameters that have to be entered into Cosilab are:

- i the temperature T_f of the fresh gas mixture;
- ii the mass flux ρv of the fresh gas mixture at the output of the burner that is calculated using equation 3.21, where i represents each chemical species of the fresh gas mixture (fuel, oxidizer and dilutant), M_i is the molecular mass of i , R is the ideal gas constant, S_b is the burner surface and Dv_i is the volumetric flow rate of i , which is measured

with the setup described in the previous chapter;

$$\rho v = \sum_i D v_i \frac{P M_i}{R T_f S_b} \quad (3.21)$$

- iii the mole fraction composition of the fresh gas mixture;
- iv the pressure in the combustion chamber.

3.3.2 The kinetic model

From a chemical point of view, the kinetic model is the key input as it identifies chemical species involved in flame chemistry, as well as kinetic parameters of chemical reactions that occur. The size of the kinetic model depends on the considered fuel and on the desired detail level of the calculated flame structure. Indeed, versatile mechanisms that comprehensively describe flame structures and provide reliable predictions for various conditions are generally voluminous. For example, a detailed description of methane and kerosene combustion will respectively require 325 reactions for 53 chemical species [40] and 3500 reactions for 225 chemical species [4]. These large models are generally developed by chemists and allow to analyze in details reaction pathways of fuel consumption and pollutant formation in flames. Such models may be reduced and optimized for specific conditions, as the calculation of flame speeds and ignition delays over small ranges of temperatures, pressures and equivalence ratios. These reduced mechanisms may be finally included by engineers into models describing systems with complex fluid dynamic behaviors, such as those encountered in engines and power plants.

Practically, the kinetic model that is used as input parameter by Cosilab consists of two sections. The first lists all chemical species involved in the mechanism and the second gives elementary chemical reactions that may occur. Each reaction corresponds to one of general forms discussed in the first chapter and is listed with its three Arrhenius parameters (A ,

```

! ***** BENZENE SUBMECHANISM *****

! DECOMPOSITION AND ISOMERIZATION REACTIONS
C6H5+H(+M) = C6H6(+M)      2.200000E+014 0.000000E+000 0.000000E+000
LOW /4.100000E+104 -2.463000E+001 2.150500E+004/
TROE /4.600000E-002 3.520000E+002 6.000000E+004 7.60000E+003/
FULVEN = C6H6              5.620000E+081 -1.936000E+001 1.215000E+005
C3H3+C3H3 = C6H6          1.290000E+069 -1.673000E+001 2.786400E+004
C3H3+C3H3 = C6H6          7.070000E+039 -8.819000E+000 7.049000E+003

! C6H6+H REACTIONS
C6H6+H = C6H5+H2          6.020000E+008 1.805000E+000 1.640000E+004
C6H6+H => C6H7            4.030000E+013 0.000000E+000 4.300000E+003
C6H7 => C6H6+H            1.300000E+016 0.000000E+000 3.320300E+004

! C6H6+O REACTIONS
C6H6+O = C6H5+OH          6.000000E+013 0.000000E+000 1.106400E+004
C6H6+O = C6H5O+H          6.660000E+012 0.000000E+000 2.332000E+003

! C6H6+OH REACTIONS
C6H6+OH = C6H5+H2O        2.386100E+004 2.680000E+000 7.730000E+002
C6H6+OH = C6H5OH+H        1.320000E+002 3.250000E+000 5.590000E+003

```

Figure 3.3: kinetic sub-model used in the present work for benzene reactions

n and Ea). As an example, the kinetic sub-model of benzene is depicted in figure 3.3.

Reactions included into the kinetic model can be either *reversible* (i.e. they can occur in both directions) or *non reversible*. The way these reactions are introduced into Cosilab is described hereafter, together with the method to calculate the mass rate of formation r_i for each chemical species.

Reversible reactions

Elementary and reversible reactions are written in the general form of equation 3.22. Only parameters of the forward rate constant (k_f) are introduced in Cosilab, as the reverse rate constant k_r can be calculated at each temperature T by equation 3.23.



$$\frac{k_f}{k_r} = K_p = e^{-\frac{\Delta H - T\Delta S}{RT}} \quad (3.23)$$

In this equation, K_p is the gas equilibrium constant, expressed in term of partial pressures P_i , as depicted in equation 3.24. Cosilab can easily compute partial pressure P_i of each compound i by using equation 3.25, where R , T , ρ_i and M_i are respectively the ideal gas constant, the temperature, the density of i and its molecular mass.

$$K_p = \frac{P_C P_D}{P_A P_B} \quad (3.24)$$

$$P_i = \frac{\rho_i}{M_i} \times RT \quad (3.25)$$

The ΔH and ΔS involved in reactions 3.23 are respectively the variation in enthalpy and entropy caused by the considered reaction at the temperature T . They can be calculated by equations 3.26 and 3.27, where h_i and s_i are enthalpy and entropy of each compound i at the temperature T . The thermodynamic database, which will be further presented, contains information on h_i and s_i for each compound involved in the kinetic model, as a function of the temperature.

$$\Delta H = (h_C + h_D) - (h_A + h_B) \quad (3.26)$$

$$\Delta S = (s_C + s_D) - (s_A + s_B) \quad (3.27)$$

The net formation rate of a compound i , involved in an elementary and reversible reaction such as that of equation 3.22, can be calculated by subtracting its consumption rate to its formation rate, as depicted in equations 3.28 and 3.29 for i being a product and a reactant, respectively.

$$\forall i \in \text{products}, \frac{d[i]}{dt} = k_f \times \prod_{i=\text{reactants}} [i] - k_r \times \prod_{i=\text{products}} [i] \quad (3.28)$$

$$\forall i \in \text{reactants}, \frac{d[i]}{dt} = k_r \times \prod_{i=\text{products}} [i] - k_f \times \prod_{i=\text{reactants}} [i] \quad (3.29)$$

Non reversible reactions

Non reversible and elementary reactions are entered in the general form of equation 3.30, along with parameters of their forward rate constants k_f . Their reverse rate constants k_r are not taken into account by Cosilab and the net formation rate of i can therefore be calculated according to equation 3.31 and 3.32, for i being a product and a reactant, respectively.



$$\forall i \in \text{products}, \frac{d[i]}{dt} = k_f \times \prod_{i=\text{reactants}} [i] \quad (3.31)$$

$$\forall i \in \text{reactants}, \frac{d[i]}{dt} = -k_f \times \prod_{i=\text{reactants}} [i] \quad (3.32)$$

Non reversible reactions can be used to introduce non elementary processes whose reverse rate constants cannot be calculated using equation 3.23.

Pressure dependent reactions

As discussed in the introduction of this work, dissociation and recombination reactions are not elementary but two steps processes that involve collisions with non reactive partners M . The rate of these reactions therefore depends on the M concentration, which in turn depends on the working pressure. In Cosilab, this pressure dependence is specified by inserting a third body M in the reaction, as depicted in the recombination reaction 3.33.



Each compound M of the gas-phase does not has the same collision efficiency. Consequently, in Cosilab the third body efficiency α_M can be specified for each compound M involved in the kinetic model. If not specified, this factor is 1.

Rate constants k_f and k_r of such reactions have low (k_0) and high (k_∞) pressure limits. In between these two regions, rate constants are said in the fall-off regime and Troe's parameters (a , T^* , T^{**} and T^{***}) [15–17] may be used to model their behavior. In Cosilab, k_0 , k_∞ and the 4 Troe's parameters may be specified in order to account for the pressure dependence of k_f and k_r .

The net formation rate of a compound i , involved in a pressure dependent reaction, can be calculated by multiplying the pressure dependent rate constants k_f and k_r of equations 3.28, 3.29, 3.31 and 3.32 by $\sum_M ([M]\alpha_M)$, in order to account for concentration and efficiency of each third body M .

Calculation of mass rate of formation of a compound i

By summing net formation rates of a compound i , calculated for each reaction where it is involved, Cosilab obtains the global net formation rate of i . This term corresponds to $d[i]/dt$ in equation 3.9 and allows to determine the mass rate of production r_i of a compound i , which is involved in equations 3.12 and 3.18 of species and energy conservation, respectively.

3.3.3 The thermodynamic database

For each chemical species i included into the kinetic model, thermodynamic properties are calculated using a polynomial curve fit of the NASA type [41] that consists in two sets of 7 coefficients ($a_1 - a_7$), corresponding to 2 ranges of temperatures (300 K to 1000 K and 1000 K to 5000 K). These 14 coefficients allow to calculate molar heat capacity $c_{p,i}$, enthalpy h_i and entropy s_i of a compound i at various temperatures, using the following equations.

$$c_{p,i} = R(a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4) \quad (3.34)$$

$$h_i = R(a_6 + a_1T + \frac{a_2}{2}T^2 + \frac{a_3}{3}T^3 + \frac{a_4}{4}T^4 + \frac{a_5}{5}T^5) \quad (3.35)$$

$$s_i = R(a_7 + a_1 \ln(T) + a_2 T + \frac{a_3}{2} T^2 + \frac{a_4}{3} T^3 + \frac{a_5}{4} T^4) \quad (3.36)$$

C6H6	C 6H 6	G	300.000	5000.000	1000.000	1
1.10809576E+01	2.07176746E-02	7.52145991E-06	1.22320984E-09	7.36091279E-14		2
4.30641035E+03	4.00413310E+01	5.04818632E-01	1.85020642E-02	7.38345881E-05		3
-1.18135741E-07	5.07210429E-11	8.55247913E+03	2.16412893E+01			4

Figure 3.4: NASA coefficients used in the present work for benzene

As illustrated for benzene in figure 3.4, NASA coefficients consist in 4 lines. The first gives information on the name of the chemical species used in the kinetic model, as well as its elemental composition and the temperature range of the provided coefficients. The 3 last lines give, from the left to the right, the 7 high and low temperature range coefficients. Specification of the molecular composition allows to calculate the molecular weight M_i of chemical species and to verify the atomic balance for each reaction provided in the kinetic model. Practically, NASA coefficients can be found in databases such as that of Burcat [42] or estimated using the Thergas software [43], based on the method of group additivity proposed by Benson [44].

3.3.4 The transport database

The transport database provides information for calculation of coefficients D_{ij} , D_i^T and λ that are necessary to determine j_i (molecular diffusion) and j_q (heat conduction) in equations 3.19 and 3.20, respectively. In these equations, D_{ij} is the multicomponent diffusion coefficient, D_i^T is the thermal diffusion coefficient and λ represents the heat conductivity of the mixture. These 3 parameters can be calculated by Cosilab by providing into a transport database the Lennard-Jones well depth ϵ , the Lennard-Jones collision diameter σ , the dipole moment δ , the polarizability α and the rotational relaxation collision number Z_{rot} of each chemical species involved into the kinetic model. A comprehensive presentation of the relationships between these properties and D_{ij} , D_i^T and λ can be found in the paper of Kee and co-workers [45].

3.3.5 System of equations

On the basis of boundary conditions, the kinetic model and thermodynamic and transport databases presented in previous sections, Cosilab is able to determine the system of equations to solve for calculating the predicted flame structure. It consists in 1 linear equation, 3 differential equations and 1 constraint stipulating that the sum on w_i coefficients of reaction 3.12 and 3.18 is 1. These equations are discussed hereafter.

Equation of state

The total density of the flow may be calculated from the temperature T , the working pressure P and mass fractions w_i , using the ideal gas law:

$$\rho = \frac{m}{V} = \frac{P \sum_i^N w_i M_i}{RT} \quad (3.37)$$

Equation of the total mass conservation

Since the equation 3.8 describing the total mass conservation stipulates that the product ρv of equation 3.21 is constant all along the flame, the velocity v of the flow can be calculated at any distance z of the burner surface by knowing the corresponding total density ρ .

Equation of species conservation

In the equation 3.12 of chemical species conservation, the only unknowns are ρ , v , w_i and T , as r_i can be calculated with the detailed kinetic model and terms constituting j_i (see equation 3.19) may be calculated from thermodynamical and transport databases and the equation of state 3.37. In addition to the conservation equation of species the constraint that the sum on the N mass coefficients w_i corresponds to the unity can be written.

$$\sum_i^N w_i = 1 \quad (3.38)$$

Equation of energy conservation

The conservation equation of the enthalpy mixture 3.17 has the same unknowns than that of chemical species conservation (ρ , v , w_i and T),

as $c_{p,i}$, h_i , r_i and terms involved in j_i and j_q (see equation 3.19 and 3.20, respectively) can be calculated on the basis of the kinetic model, the thermodynamical and the transport databases, and the equation of state.

3.3.6 The output file

As previously mentioned, Cosilab solves the equation system using the Newton's method. After the calculation, Cosilab writes a text file containing information that have been requested (mole fractions or concentrations of chemical species, reaction rates, etc). This file is in the CSV (Coma Separated Values) format, which means that each line of the file is a table row, where data are separated by comas. The Cosilab output file can be imported into *Excel*[®] for data examination. However, when large kinetic models are used, the importation into *Excel*[®] may become fastidious, as well as the analysis of net reaction rates. Indeed, Cosilab does not save the name of reactions in the output file, but numbers them according to their order in the kinetic model. Moreover, the output file does not allow to compare rate of reactions that involve a definite chemical species, in order to determine the weight of each reaction that consumes or produces it. The development of a post-processing software was therefore required to efficiently analyze output files with a high reaction number, such as in those of this work.

3.4 Postprocessing analysis: contribution calculation

An efficient macro has been developed in *Excel*[®] to import output files generated by Cosilab. It allows to replace reaction numbers by reaction names and to calculate contributions of each reaction to the consumption and formation of every chemical species of the kinetic model. The control panel of the developed macro is depicted in figure 3.5 and consists of three buttons that respectively allow to import an output Cosilab

LIMITATIONS:	1	Dans cette version, l'importation de données est limitée à 5 feuilles excel (+/- 1000 réactions)
PREPARATIONS:	1	Configurer Cosilab pour qu'il fournisse un Output TXT séparé par des points virgules
	2	Faire une copie de l'OUTPUT dans un fichier TXT
	3	Vérifier qu'il n'existe pas de virgules dans votre mécanisme. Au besoin, les enlever ou les remplacer.
	4	Faire une copie du MECANISME dans un fichier TXT
UTILISATION DE L'IMPORTATION:	1	Lancer l'importation de vos données COSILAB en cliquant sur le bouton vert ci-dessous
	2	Vous ne devriez rien changer. Cliquer sur Begin using these parameters
	3	Spécifiez l'emplacement du fichier TXT de l'output de cosilab précédemment enregistré
	4	Si vous voulez remplacer les numéros de réaction par les intitulés, cliquez sur OUI
	5	Spécifiez l'emplacement du fichier TXT de votre mécanisme précédemment enregistré
	6	Attendez l'importation

IMPORTATION

RAZ

UTILISATION DU TRIAGE DE REACTIONS:	1	Cliquez sur le bouton rouge ci-dessous (ou utiliser le raccourci ctrl+q)
	2	Entrez le nom d'une espèce à trier Pour adapter le programme à votre environnement de travail, veuillez ajuster les paramètres ci-dessous

TRIAGE DE REACTIONS

PARAMETRES:	1	Maximum des abscisses	2.0
	2	Ecart entre les graphes	240

Figure 3.5: control panel of the post-processing macro developed in the present work

file into the Excel document, to erase all data contained into the Excel file and to calculate reaction contributions for a definite chemical species.

Concerning the calculation of reaction contributions, after pushing the corresponding button, a dialog box opens and invites the user to enter a chemical species formula. Then, the macro looks for all reactions that contain this compound i and stores their net reaction rate profiles into a separated spreadsheet. In order to assess the relative weight of a reaction j forming or consuming i , the macro compares the surface S_j beyond its curve of net reaction rate to the sum of those involved in formation or consumption of i , respectively. The procedure developed for such calculations is detailed hereafter.

The macro first calculates surfaces S_j delimited by the and the z -axis and curves of each net reaction rate involving i , by summing surfaces A_n of every rectangle n centered on a coordinate z_n , as depicted in figure 3.6 and in equation 3.39. Since the grid used for Cosilab calculations

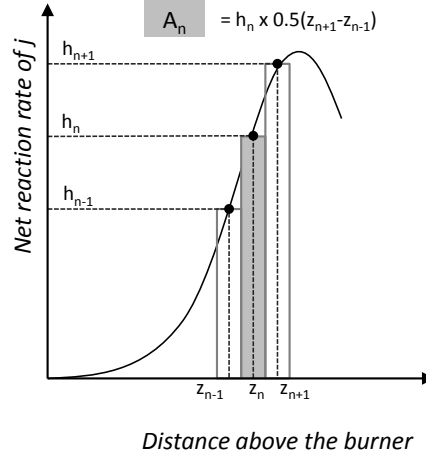


Figure 3.6: calculation of the surface S_j beyond curves of net reaction rates

has about 200 points, homogeneously spread along the 3.5 cm of the considered reaction zone, the distance $z_n - z_{n-1} = z_{n+1} - z_n \approx 0.017$ and equation 3.39 is a good approximation of S_j .

$$S_j = \sum_n A_n = \sum_n h_n \times 0.5(z_{n+1} - z_{n-1}) \quad (3.39)$$

Afterwards, contributions C_j of each reaction j are calculated by dividing their surfaces S_j by the sum on absolute values of all surfaces S_j , according to equation 3.40.

$$C_j = \frac{S_j}{\sum_j |S_j|} \quad (3.40)$$

These general contributions can be either positive or negative, depending on the direction taken by the considered reaction. Based on the sign of each contribution C_j and the position of the chemical species i compared with the arrow in the chemical reaction j , reactions are sorted in two sets: one noted "*formation*" that gathers reactions forming i , and one noted "*consumption*" that gathers reactions consuming i . Then, the sum on absolute values of surfaces S_j are calculated inside each set of reactions

and contributions of j to either i formation (Cf_j) or i consumption (Cc_j) is calculated by equations 3.41 and 3.42.

$$\forall j \in \text{formation}, Cf_j = \frac{|S_j|}{\sum_i |S_i|} \quad (3.41)$$

$$\forall j \in consumption, Cc_j = \frac{|S_j|}{\sum_i |S_i|} \quad (3.42)$$

These contributions Cf_j and Cc_j are positive since absolute values of S_j are used. Practically, the spreadsheet where contributions are calculated has a presentation similar to that of figure 3.7. Reactions consuming and producing i are respectively sorted on the left and the right side of the sheet and net reaction rates of consumption and production are plotted into two specific graphs for an easier analysis. Moreover, values of Cf_j and Cc_j are reported for each reaction in order to perform comparative analyses, allowing to determine main reaction channels for formation and consumption of i . Such comparisons are the basis of dis-

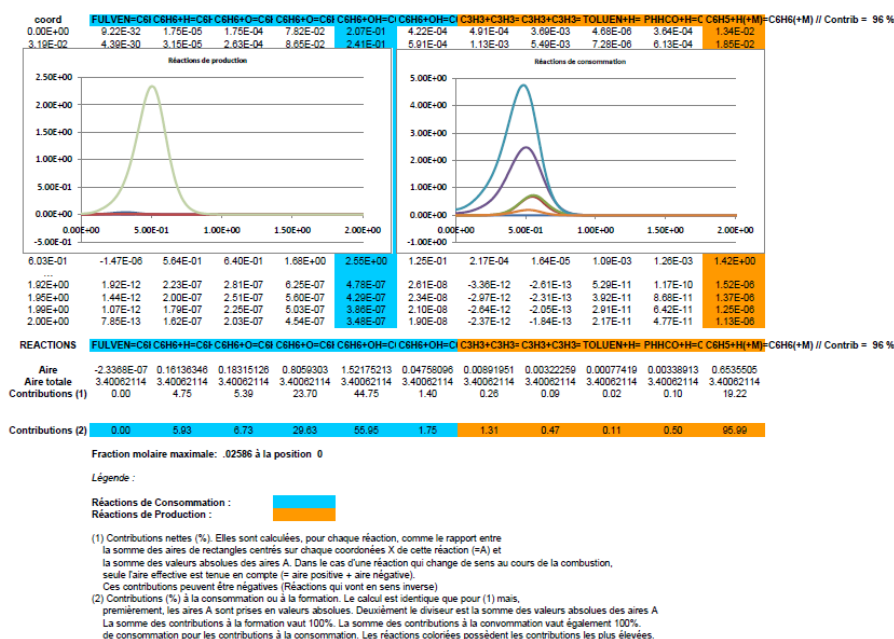


Figure 3.7: illustration of contribution calculations performed with the developed macro

cussions on aromatic combustion proposed in following chapters. The developed macro allows to calculate contributions within a few seconds, compared to several minutes if done manually for small mechanisms. It therefore enables to more efficiently analyze kinetic results issued from Cosilab. This improvement was necessary for dealing with large reaction mechanisms such as that developed in this work.

3.5 Adiabatic flame temperature

Basically, the heat $(Q_P)_{T_1}$ evolved by a flame burning at a constant pressure P and at the temperature T_1 corresponds to the change in enthalpy $(\Delta H_r)_{T_1}$ due to the combustion reaction. Since a fraction of the heat evolved by the reaction may be used to heat up the product gases at a temperature T_2 higher than T_1 , $(Q_P)_{T_1}$ is calculated following equation 3.43. In this equation, T_0 , T_1 and T_2 are respectively the reference, the reactant and the product temperatures, and n , H° and ΔH_f° are the mole number, the standard enthalpy and the standard formation enthalpy of the product i or the reactant j .

$$(Q_P)_{T_1} = (\Delta H_r)_{T_1} = \sum_{i \text{ products}} n_i \left(H_{T_2}^\circ - H_{T_0}^\circ + (\Delta H_f^\circ)_{T_0} \right)_i - \sum_{j \text{ reactants}} n_j \left(H_{T_1}^\circ - H_{T_0}^\circ + (\Delta H_f^\circ)_{T_0} \right)_j \quad (3.43)$$

If all the heat evolved by the combustion reaction is used to heat up the product gases, $(Q_P)_{T_1}$ is zero and the flame is referred to as adiabatic. Therefore, for adiabatic flames equation 3.43 can be written as equation 3.44. If the reactant temperature T_1 and the mole numbers n_i and n_j are known, this equation can be solved and the product temperature T_2 can be deduced. This temperature is called the *adiabatic flame temperature*.

$$\sum_{i \text{ products}} n_i \left(H_{T_2}^\circ - H_{T_0}^\circ + (\Delta H_f^\circ)_{T_0} \right)_i = \sum_{j \text{ reactants}} n_j \left(H_{T_1}^\circ - H_{T_0}^\circ + (\Delta H_f^\circ)_{T_0} \right)_j \quad (3.44)$$

However the product composition is generally not known. Indeed, in addition to carbon dioxide and water, other chemical species may persist in the burnt gases (CO , O_2 , H_2 , H , O , OH , ...) and their nature and mole numbers depend on the equivalence ratio, as well as on the burnt gas temperature. At a definite temperature T_2 , the product composition may be calculated based on the conservation equations of elements and the equilibrium constants between the products.

Consequently, the calculation of an adiabatic flame temperature is an iterative process where the product composition is determined for an initial guess of T_2 and introduced into equation 3.44 to deduce a new burnt gas temperature. The latter is used to calculate a new product composition, which allows to determine a new burned gas temperature, and so on until the iteration converges into the adiabatic flame temperature. In this work, the program called *Stanjan* and developed by W. C. Reynolds [46] is used to perform these calculations.

3.6 Conclusions

This chapter has shown that mass, chemical species and energy conservation equations can be written for laminar, premixed and one-dimensional flat flames investigated in this work. These equations can be solved by knowing the working pressure, boundary conditions and rate parameters of reactions occurring in the flame, along with thermodynamical and transport data of chemical species. The resolution of the equation system gives information on mole fractions of chemical species involved in the flame and on rates of each included reaction. A predicted flame structure can therefore be obtained and main reaction pathways can be determined by comparing reaction rates of included reactions.

In this work, the Cosilab software is used for solving these equation systems and the way the kinetic model and thermodynamical and transport databases have to be provided has been described. A powerful macro has been developed in Excel[®] to post process reaction rates calculated by

Cosilab and to allow calculation of reaction contributions to formation and consumption of each chemical species.

The following chapter describes the development of a comprehensive kinetic model for benzene combustion and compares flame structures predicted by Cosilab to experimental measurements performed with setups presented in the previous chapter. Contributions of reactions to formation and consumption of major chemical species will be calculated in each investigated flame with the developed macro and main reaction channels will be emphasized in order to describe the chemistry of aromatic flames.

Part II

Benzene and toluene flame chemistry: the fuel oxidation

Benzene combustion

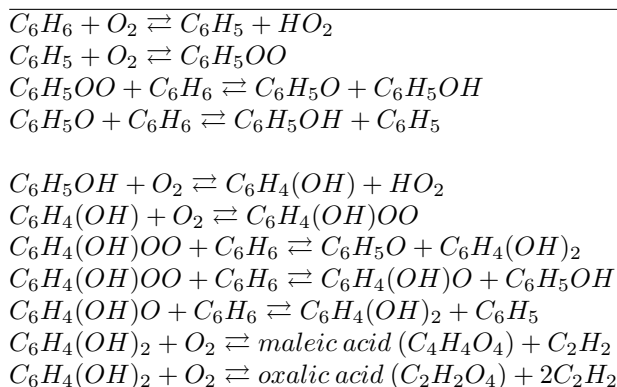
4.1 Introduction

Benzene was discovered by Michael Faraday [47] in 1825 when he succeeded in separating a new compound with a boiling point close to 80 °C from petroleum distillation. Faraday named this new chemical species bi-carburet of hydrogen and tried to characterize it by conducting many physical and chemical experiments. Among his observations, Michael Faraday highlighted that *"It burns with a bright flame and much smoke"*. Although in 1825 the first scientist who burned pure benzene had already noticed its ability to produce large amount of smoke, 185 years later scientists are still trying to understand chemical mechanisms involved in benzene combustion and soot formation.

However, benzene oxidation, combustion and pyrolysis have been investigated by numerous researchers for many years. To the best of our knowledge, the first kinetic study devoted to benzene oxidation was performed in 1930 by Fort and Hinshelwood [48] at temperatures between 507 and 567 °C. They determined that final products of the reaction are steam, carbon monoxide and carbon dioxide and measured the reaction rate over a wide range of initial benzene and oxygen concentrations. In order to explain their kinetic measurements, Fort and Hinshelwood noticed that a chain branching mechanism should occur during benzene

oxidation rather than a molecular one. In 1937, 1940 and 1954 other scientists [49–52] studied benzene oxidation between 550 and 650 °C. These studies mainly demonstrated that co-products of benzene oxidation under moderate temperatures are phenol, formaldehyde, ethylene, acetylene, paraffins, molecular hydrogen and acids, including maleic and formic acids. In 1956, Norrish and Taylor [53] performed benzene oxidation and pyrolysis experiments at higher temperatures (680 and 685 °C). They measured the variation of product yields with different benzene to oxygen ratios and variable reaction times. As Fort and Hinshelwood [48] in 1930, Norrish and Taylor suggested that a chain branching mechanism should occur and proposed the chemical mechanism described in table 4.1 to explain their measurements.

Table 4.1: chemical mechanism proposed by Norrish and Taylor [53]



C_2H_2 oxidation produces CH_2O and chain branching radicals.
 $CH_2O + O_2$ leads to radical formation.

Between 1956 and 1971, several groups performed benzene pyrolysis [54–59] and oxidation [53, 60] experiments at temperatures below 1000 K. Contrarily to previous studies, Hou and Palmer [57] proposed in 1965 that benzene pyrolysis should proceed through the molecular mechanism $2C_6H_6 \rightleftharpoons C_{12}H_{10} + H_2$. In 1971, Asaba and Fujii [61] performed a high temperature (1400 - 1900 K) investigation of the pyrolysis of benzene and highlighted that the molecular mechanism proposed by Hou and Palmer was not able to predict their measurements. Therefore, as Fort

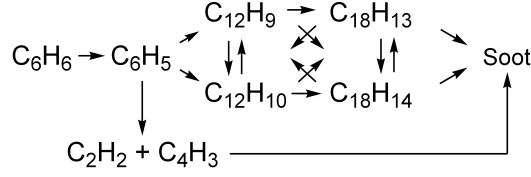
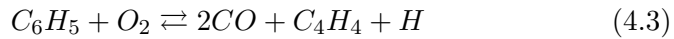
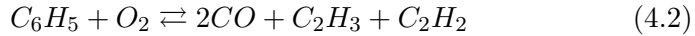
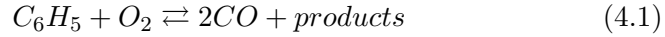


Figure 4.1: kinetic scheme proposed by Asaba and Fujii [61, 63] for benzene pyrolysis.

and Hinshelwood [48] in 1930 and Norrish and Taylor [53] in 1956, they suggested that a chain mechanism should occur and proposed the mechanism summarized in the kinetic scheme of figure 4.1. In this figure, it is interesting to note that, in 1971, Asaba and Fujii already suggested a soot formation mechanism based on phenyl addition reactions, which is now discussed in the literature as the Phenyl Addition Cyclization (PAC) mechanism [62]. After benzene pyrolysis, Fujii and Asaba [63] studied its oxidation in shock-tubes. They extended their kinetic model of figure 4.1 to account for benzene oxidation by including benzene H abstraction reactions with O_2 , O , OH and HO_2 , the chain branching reaction $H + O_2 \rightleftharpoons OH + O$ and the phenyl oxidation reaction 4.1.



By comparing predicted and measured rates of product appearance and reactant disappearance, Fujii and Asaba showed that reaction 4.1 should be responsible of most of CO formation. They proposed 2 possible sets of products for this reaction: $C_2H_3 + C_2H_2$ (reaction 4.2) and $C_4H_4 + H$ (reaction 4.3). In 1979, McLain and co-workers [64] performed similar benzene oxidation experiments behind shock waves and highlighted the importance of reaction 4.2 for properly modeling CO formation.

Beside the understanding of benzene oxidation and pyrolysis, some works [65–69] were devoted to the study of soot formation in flames. These works showed that benzene flames produce large Polycyclic Aromatic

Hydrocarbons (PAHs) and suggested that these chemical species coagulate into soot. The understanding of aromatic and particularly benzene flame chemistry therefore became a central theme of research. In 1963, Homann and co-workers [70] performed such a flame study in a pioneer work, where they measured mole fraction profiles of a few compounds in a rich benzene-oxygen-nitrogen flame by Molecular Beam Mass Spectrometry (MBMS).

In 1981, Bittner and Howard [71, 72] comprehensively investigated rich benzene combustion in a premixed, laminar and one-dimensional benzene-oxygen-argon flame burning at low pressure, near the sooting limit. Authors measured mole fraction profiles of many stable and free radical species using MBMS and based on the observed sequence of species profile maximums, Bittner and Howard postulated a kinetic scheme for benzene combustion (see figure 4.2). Unlike previous studies of Norrish and Taylor [53] and Fujii and Asaba [63], Bittner and Howard expected phenyl radical to be a minor intermediate of benzene oxidation, since they measured a low maximum mole fraction and supposed its consumption paths to be slow. They proposed that benzene should principally react with O atom, forming phenol (C_6H_5OH) that should produce cyclopentadiene (C_5H_6), which had a high maximum mole frac-

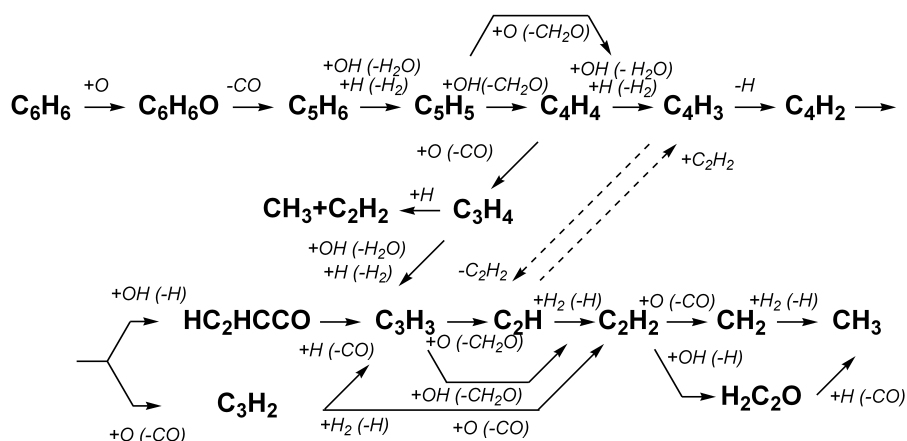


Figure 4.2: kinetic scheme proposed by Bittner and Howard [71] for benzene flame chemistry.

tion. Authors suggested that cyclopentadiene consumption leads to the formation of C_4H_x , C_3H_x , C_2H_x and CH_x hydrocarbons, as illustrated in figure 4.2. Beside benzene consumption towards smaller chemical species, Bittner and Howard investigated the formation of larger compounds. They measured mole fraction profiles of chemical species with masses corresponding to PAHs between 100 and 200 amu and an overall signal for aromatic material with masses higher than 200 amu. They showed that PAHs with masses between 100 and 200 amu disappear at about 10 mm above the burner surface, probably due to their oxidation, whereas those with masses higher than 200 amu continue to grow. They demonstrated that this growth was correlated with the onset of soot formation, confirming the major role of PAHs in soot formation.

In 1982, Venkat and co-workers [73] studied the oxidation of benzene, toluene and ethylbenzene at 1200 K in a turbulent flow reactor, in order to clarify the mechanism of aromatic oxidation. In their work, authors demonstrated that reaction 4.1 would be fast enough to explain the low maximum of phenyl radical mole fraction measured by Bittner and Howard [71], even if phenyl radical is produced from a major benzene consumption path. Therefore, contrarily to Bittner and Howard,

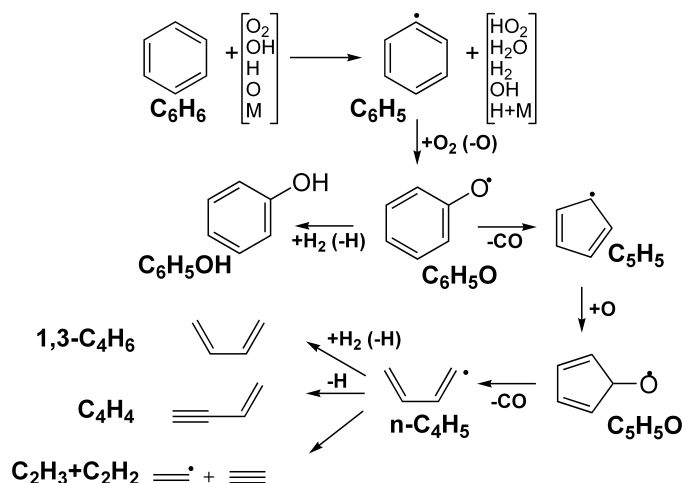


Figure 4.3: kinetic scheme proposed by Venkat and co-workers to describe benzene oxidation in turbulent flow reactors [73].

Venkat and co-workers postulated that benzene consumption into phenol (C_6H_5OH) and phenyl radical (C_6H_5) were respectively minor and major channels. Based on their measurements, Venkat and co-workers proposed the chemical mechanism depicted in figure 4.3. As reported by the authors, phenyl radical can react with molecular oxygen, yielding phenoxy radical (C_6H_5O) and oxygen atom. Then, C_6H_5O can decompose into cyclopentadienyl radical (C_5H_5) and carbon monoxide (CO). The cyclopentadienyl radical can react with O atom forming the cyclopentadienoxy radical (C_5H_5O), which can further dissociate into 1,3-butadien-1-yl radical ($n-C_4H_5$) and CO . $n-C_4H_5$ is a precursor of either 1,3-butadiene (C_4H_6), vinylacetylene (C_4H_4) or acetylene + vinyl radical ($C_2H_2 + C_2H_3$). Venkat and co-workers therefore showed that the overall reaction of such a mechanism corresponds either to reaction 4.2 or to reaction 4.3, confirming previous findings of Fujii and Asaba [63] and McLain and co-workers [64].

In 1984, Hsu and co-workers [74] studied kinetics of the CO formation in lean benzene-oxygen mixtures behind shock-waves. They used the kinetic mechanism proposed by Fujii and Asaba [63] to model the CO production and confirmed by a sensitivity analysis that reaction 4.3 is of particular importance in CO formation. Hsu and co-workers stressed that the pathway linking $C_6H_5 + O_2$ to $C_4H_4 + H + 2CO$ proposed by Venkat and co-workers (see figure 4.3) is not the only reaction route, since the mechanism of figure 4.4 would also occur at combustion temperatures. Hsu and co-workers equally measured significant UV chemiluminescence in their experiments. They attributed these electronic excitation processes to reactions 4.4 and 4.5. Authors concluded that even

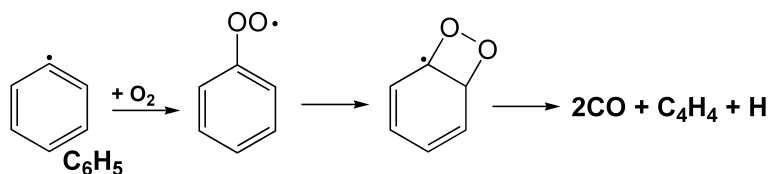
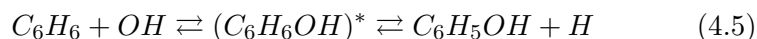
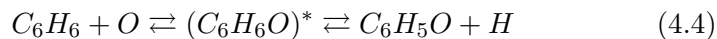


Figure 4.4: mechanism for reaction $C_6H_5 + O_2 \rightleftharpoons 2CO + C_4H_4 + H$, as proposed by Hsu and co-workers [74].

if benzene consumption to phenyl radical is the major pathway, benzene reactions with O atom and OH radical should therefore not be neglected.



In 1985, Rotzoll [75] studied the high temperature oxidation of benzene in a flow reactor using MBMS and detected an important number of chemical species. Based on his observations and on previous studies devoted to benzene oxidation, Rotzoll postulated a kinetic scheme describing benzene consumption until C_2H_x hydrocarbons (see figure 4.5). Rotzoll showed that the reaction of the phenoxy radical via benzoquinone and cyclopentadienone represents an additional pathway for $C_4H_4 + H$ formation, confirming the suggestion of Hsu and co-workers [74].

In 1988, Lovell and co-workers investigated benzene oxidation perturbed by NO_2 addition, in order to change O , H and OH radical concentra-

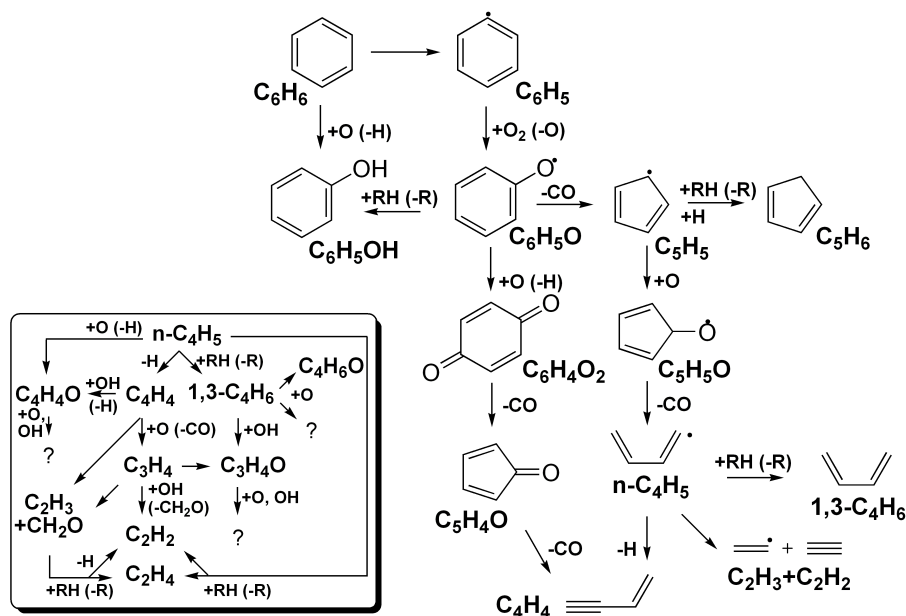


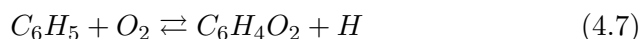
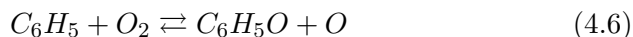
Figure 4.5: kinetic scheme proposed by Rotzoll [75] for benzene oxidation.

tions [76]. They showed that the main route of phenoxy radical formation is the reaction of phenyl radical with molecular oxygen and that O atom addition onto benzene, yielding phenoxy radical and H atom (see reaction 4.4), is only minor.

Based on mechanistic and rate constant information gained over previous years, detailed mechanisms for aromatic oxidation were developed by Bittker in 1990 [77] and Emdee and co-workers in 1992 [78] and compared to experimental data of Lovell and co-workers [76]. Both studies reported a satisfactory agreement for lean and stoichiometric benzene-oxygen-argon mixtures, whereas a poor predictive capability was observed under rich conditions. In 1994, Lindstedt and Skevis [79] extended the kinetic model of Emdee and co-workers [78] to the flame chemistry of small hydrocarbons and compared its predictions to experimental measurements performed by Bittner and Howard [71] in a rich benzene-oxygen-argon flame. Lindstedt and Skevis obtained a good agreement for reactants, products and some main intermediates but highlighted that their C_5H_x submodel was subject to a high uncertainty. However, it was the first time that predictions of a detailed kinetic model were compared to an experimental benzene-oxygen-argon flame structure. In 1995, Zhang and McKinnon [80] also developed a kinetic model to compare with data of Bittner and Howard and only reached a poor agreement for major intermediates, as Lindstedt and co-workers. In the same year, Bermudez and Pfefferle [81] performed an investigation of benzene oxidation at moderate temperatures, using laser ionization Time-of-Flight Mass Spectrometry combined with residual gas analysis. Their experimental observations are consistent with the kinetic scheme previously proposed by Venkat and co-workers but do not give evidences of linear $C_6H_5O_2$ formation, involved in reaction 4.2 proposed by Fujii and Asaba [63] and later by Saikannan and co-workers [82].

In 1996, Shandross and co-workers [83] experimentally analyzed benzene consumption in H_2/O_2 flames and compared their data to predictions of models previously developed by Emdee and co-workers [78], Lindstedt and Skevis [79] and Zhang and McKinnon [80]. They highlighted that phenoxy radical (C_6H_5O) is extraordinarily overpredicted by all

models and that it affects phenol (C_6H_5OH) predictions, as H atom recombination with C_6H_5O radical plays a main role in C_6H_5OH formation. In addition, they stressed that errors in predictions of phenyl radical (C_6H_5) and O atom may exacerbate the overprediction of phenoxy radical mole fractions by kinetic models. The same year, Tan and Frank [84] developed a new kinetic model for benzene combustion, including their measurements on kinetics of the $C_6H_5 + O_2$ reaction performed in 1994 [85]. In their former work, authors found that reaction of phenyl radical and molecular oxygen produces O and H atoms. They measured kinetics of these 2 channels and suggested that they should correspond to overall reactions 4.6 and 4.7, respectively.



Shandross and co-workers obtained a better agreement for phenyl radical predictions than with previous models but experimental mole fractions of other intermediates were still poorly reproduced. At the same time, the group of Brezinsky (Davis and co-workers [86]) measured laminar flame speeds of benzene-air and toluene-air mixtures at room temperature and atmospheric pressure. They improved the model initially developed in their group (Emdee and co-workers [78]) to compare with flame speed measurements and reached a satisfactory predictive capability. Modifications brought to the model mainly consisted in improvements of fall-off behaviors for pressure dependent reactions and the use of rate parameters of Frank and co-workers [85], divided by a factor 2.6, for the reaction of phenyl radical with molecular oxygen giving phenoxy radical and O atom.

In 1998, Chai and Pfefferle [87] investigated benzene oxidation at fuel-lean and stoichiometric conditions in a well mixed reactor over the temperature range 900 - 1300 K. Authors noted that concentrations of main intermediate species of benzene oxidation are significantly affected by changes in the O_2 concentration. Based on their observations, they discussed the dependence of the benzene oxidation mechanism on the

equivalence ratio and highlighted that reactions 4.6 and 4.4, together with reactions of the cyclopentadienyl radical with O_2 and O atom should be of particular importance. Moreover, Chai and Pfefferle reported the measurement of a compound with a mass corresponding to benzoquinone ($C_6H_4O_2$), confirming that reaction 4.7 may play a role in phenyl oxidation, as predicted earlier by Frank and co-workers [85]. However the maximum concentration of $C_6H_4O_2$ measured by Chai and Pfefferle was relatively low and did not give evidence that reaction 4.7 is a major pathway.

In 1999, new experimental data on laminar, premixed, one-dimensional and rich benzene-air flames were obtained by Tregrossi and co-workers [88] at atmospheric pressure, using gas chromatography. High equivalence ratios of these flames prevent significant insights into the understanding of benzene oxidation under combustion conditions. However, flame structures investigated by Tregrossi and co-workers included large PAHs and soot volume fraction measurements, which are of particular importance to validate soot formation models.

Between 2000 and 2003, some groups developed new detailed kinetic models for benzene oxidation. Firstly, Alzueta and co-workers [89] proposed a new mechanism to predict their C_6H_6 , CO , CO_2 , O_2 and NO measurements in benzene oxidation experiments conducted in a flow reactor. This mechanism was based on the previous kinetic model of Emdee and co-workers [78] and included an additional sub-model describing the oxidation of para and ortho benzoquinone isomers [90]. Since benzoquinone has been postulated as an intermediate in phenyl oxidation and observed in benzene oxidation, Alzueta and co-workers stressed that it should be included in kinetic models describing aromatic oxidation. The kinetic model was able to reproduce their product measurements, but authors highlighted that a number of kinetic issues need to be addressed before concentration of intermediate species can be predicted satisfactorily. Secondly, Ristori and co-workers [22] developed in 2001 a new kinetic model for benzene oxidation and compared its predictions to new experiments in jet-stirred reactors. In addition to their experimental data, authors compared their model predictions to

the benzene flame structure measured by Bittner and Howard [71], ignition delays of benzene-oxygen-argon mixtures determined by Burcat [91] and laminar burning velocities of benzene-air flames measured by Davis and co-workers [86]. Contrarily to Alzueta and co-workers, Ristori and co-workers did not include benzoquinone in their kinetic model, as they did not detect it in their experiments. The developed kinetic model satisfactorily predicts experimental data but authors stressed that further improvements were needed to better represent benzene oxidation under flame conditions. Thirdly, Richter and Howard [92] developed a new detailed kinetic model to describe structures of acetylene and ethylene-oxygen-argon flames, together with the benzene flame previously investigated by Bittner and Howard. Similarly to the model of Alzueta and co-workers, that of Richter and Howard includes benzoquinone. Whereas their kinetic model has a satisfactory predictive capability for light hydrocarbons (C_1H_x to C_4H_x), authors pointed up that only a qualitative understanding of benzene oxidation has been achieved. They concluded that further works in the fields of $C_6H_5 + O_2$ reaction and formation and consumption of benzoquinone, cyclopentadienyl radical and cyclopentadienone were necessary. Fourthly, Da Costa and co-workers [93] developed a new kinetic model for benzene oxidation and compared its predictions to experimental measurements performed in a flow reactor, ignition delays of benzene-oxygen-argon mixtures and the flame structure of Bittner and Howard. As previous authors, Da Costa and co-workers concluded that many uncertainties remain in kinetics of benzene combustion.

These 4 kinetic models are all based on the kinetic scheme of aromatic oxidation originally proposed by Venkat and co-workers [73] in 1982 and mainly differ by the choice in rate parameters of some reactions, or by the use of particular sub-models, as that of benzoquinone. All authors stressed that many uncertainties remain in the understanding of benzene oxidation and that only a qualitative prediction of the benzene-oxygen-argon flame studied by Bittner and Howard could be achieved. Therefore, this sudden emergence of numerous detailed kinetic models for aromatic oxidation did not come with significant insights in the un-

derstanding of benzene oxidation. After 2005, reinvestigation of benzene combustion in flames were performed by a few groups in order to enlarge the experimental database used to compare with predictions of kinetic models. In 2005, Defoeux and co-workers [94] determined the structure of a laminar, premixed and one-dimensional benzene-oxygen-argon flame burning at low pressure with an equivalence ratio of two. Whereas this flame had a slightly higher equivalence ratio than the one of Bittner and co-workers (2 instead of 1.8), both flame structures are very close and their comparison did not allow to improve the understanding of benzene oxidation in flames. In 2007, Yang and co-workers [95] used the recent tunable synchrotron photoionization method to reinvestigate the flame structure of Bittner and Howard, with a higher ionization energy resolution, allowing to detect isomeric composition of some hydrocarbon species. One of the main insight of this work was the measurement of the maximum mole fraction of phenoxy radical, which is thought to be a key intermediate of benzene oxidation. Authors showed that its mole fraction is very low ($5.0 \cdot 10^{-5}$), contrarily to predictions of kinetic models used to describe benzene oxidation (about $5.0 \cdot 10^{-3}$).

Surprisingly, recent experimental re-investigations of benzene-oxygen-argon flames [94,95] were all conducted at rich equivalence ratios, whereas low equivalence ratios should help to emphasize kinetic issues concerning reactions with O_2 . In order to fill this lack in experimental data and to throw some light on the kinetic scheme of aromatic combustion, the present chapter reports new measurements in laminar, premixed and one-dimensional benzene-oxygen-argon flames, burning at low pressure with equivalence ratios of 0.7, 1, 1.8, and 2. These flame structures have been measured with experimental setups presented in chapter 2. Beside these measurements, the development of a new detailed kinetic model based on a recent literature survey is presented. According to the method exposed in the previous chapter, this mechanism is used to interpret experimental measurements and determine main reaction channels of benzene flames. A particular attention was paid to benzoquinone and phenoxy radical formation, as their kinetic modeling is a recurrent problem.

4.2 Experimental results

This section presents experimental structures of six laminar, premixed and one-dimensional benzene-oxygen-argon flames, stabilized at low pressure on the flat flame burner of the experimental setup described in chapter three. Table 4.2 summarizes parameters of each investigated flame and introduces flame codes that will be used in the following discussion. A more detailed presentation of the flame characteristics is given in appendix B. Since the literature review has highlighted that premixed, laminar and one-dimensional benzene flames have only been investigated at rich conditions, the chosen range of equivalence ratios ($\phi = 0.7$ to 2) spreads from lean to rich conditions.

The dilution ratio of the richest benzene flame (BF20) has been fixed to 45%. This ratio allows to obtain a large concentration of soot precursors, while keeping the maximum flame temperature below the fusion temperature of the quartz nozzle (about 2000 K). In BF18, the initial mole fraction of C_6H_6 is equal to that in BF20, in order to have a similar carbon content in the flame. The equivalence ratio is adjusted to 1.8 by respectively increasing and decreasing initial mole fractions of O_2 and Ar (see table 4.2). In BF10, the dilution ratio has been increased to 77% as the maximum flame temperature reaches its peak around the stoichiometry. Whereas this ratio leads to lower maximum flame temperatures than in BF18 and BF20, it allows to study the influence of the temperature on the flame chemistry. Similarly to BF20 and BF18, the initial mole fraction of C_6H_6 in BF07 is equal to that in BF10, in order

Table 4.2: investigated benzene flame parameters

Code	ϕ	P mbar	Mass flux ($g\ s^{-1}\ cm^{-2}$)	Fresh gas composition		
				$\chi_{C_6H_6}$	χ_{O_2}	χ_{Ar}
BF07	0.7	45	$2.93\ 10^{-3}$	$2.72\ 10^{-2}$	$2.92\ 10^{-1}$	$6.81\ 10^{-1}$
BF10	1.0	45	$2.98\ 10^{-3}$	$2.72\ 10^{-2}$	$2.04\ 10^{-1}$	$7.68\ 10^{-1}$
BF18	1.8	45	$3.07\ 10^{-3}$	$1.16\ 10^{-1}$	$4.84\ 10^{-1}$	$4.00\ 10^{-1}$
BF20	2.0	45	$3.10\ 10^{-3}$	$1.16\ 10^{-1}$	$4.36\ 10^{-1}$	$4.48\ 10^{-1}$
BF20-35	2.0	35	$3.10\ 10^{-3}$	$1.16\ 10^{-1}$	$4.36\ 10^{-1}$	$4.48\ 10^{-1}$
BF20-65	2.0	65	$3.10\ 10^{-3}$	$1.16\ 10^{-1}$	$4.36\ 10^{-1}$	$4.48\ 10^{-1}$

to have a similar carbon content. The equivalence ratio is decreased by adjusting the mole fraction of O_2 and the dilution ratio (see table 4.2).

These four flames have been investigated at 45 mbar. Moreover, the working pressure of the richest benzene flame (BF20) has been varied to 35, 45 and 65 mbar in order to identify the pressure dependence of its structure.

Flames stabilized at 35, 45 and 65 mbar have a fresh gas velocity v_c of respectively 53, 41 and 28 cm s⁻¹ at 298 K. Lean and stoichiometric benzene flames depict a typical blue color, whereas rich flames are greener and orange in the burnt gas region, as soot emits in this part of the visible spectrum. The soot production of rich benzene flames is confirmed by its deposition on the wall of the combustion chamber and particularly on the quartz nozzle. To avoid blocking the apex of the nozzle, measurements in the sooting region have to be performed rapidly.

Gas chromatography has been used for the measurement of mole fraction profiles of all chemical species, except for benzoquinone ($C_6H_4O_2$), phenoxy radical (C_6H_5O), phenol (C_6H_5OH) and propargyl radical (C_3H_3), which were analyzed by MBMS. These 4 compounds were not followed by GC, as this method cannot detect radical species and because phenol has a considerable eluting time and benzoquinone could not be identified in the chromatogram. For each detected compound, appendix D summarizes the method of measurement and the maximum mole fraction in every investigated flame.

4.2.1 Flame temperatures

Temperature profiles of each investigated flame are depicted in figures 4.6 and 4.7. They all exhibit the three main flame areas described in the first chapter: a preheating zone where temperature slowly increases, the flame front where the heat release is maximum and the burnt gas region where temperature slowly decreases. As shown in figure 4.6,

BF07, BF10, BF18 and BF20 reach their maximum temperatures of respectively 1470, 1495, 1775 and 1715 K at 1.6, 1.15, 0.95 and 1.15 cm from the burner surface, respectively. Although the maximum flame temperature should be theoretically located near the stoichiometry, rich benzene flames BF18 and BF20 have higher temperatures than lean (BF07) and stoichiometric (BF10) flames. This comes from their lower dilution ratios (see table 4.2), chosen to maximize their soot precursor concentrations.

Temperature profiles of flames with an equivalence ratio of two and investigated at 35, 45 and 65 mbar are depicted in figure 4.7. BF20-35, BF20 and BF20-65 respectively reach their maximum temperatures of 1720, 1715 and 1670 K at 1.3, 1.2 and 1 cm from the burner surface, respectively. An increase of the working pressure brings flames closer to the burner, increasing the heat transfer to its surface. The working pressure therefore significantly influences flame temperature profiles and the discrimination between pressure and temperature effects will be difficult.

For each investigated flame, the adiabatic flame temperature has been calculated using *Stanjan* [46]. These data are presented and compared to experimental temperatures in the appendix C.

4.2.2 Influence of equivalence ratio on flame structures

In this section, the influence of equivalence ratio (ϕ) on the 4 benzene-oxygen-argon flame structures measured in this work is discussed. As summarized in table 4.2, these flames have ϕ of 0.7, 1, 1.8 and 2 and will be called BF07, BF10, BF18 and BF20, respectively. Experimental structures of these flames are depicted in figures 4.8, 4.9, 4.10 and 4.11, respectively. Flame structures with equivalence ratios of 0.7, 1 and 2 have been published in 2009 [96], along with a kinetic modeling analysis based on mechanisms proposed by Ristori and co-workers [22] in 2001 and Richter and Howard [92] in 2002. The kinetic modeling of these benzene flames will be discussed in section 4.3 on page 107.

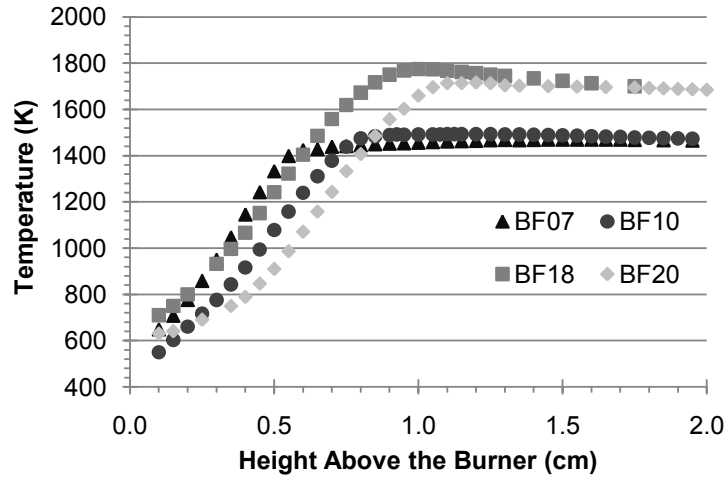


Figure 4.6: experimental temperature profiles of benzene-oxygen-argon flames burning at 45 mbar with equivalence ratios of 0.7, 1, 1.8 and 2.

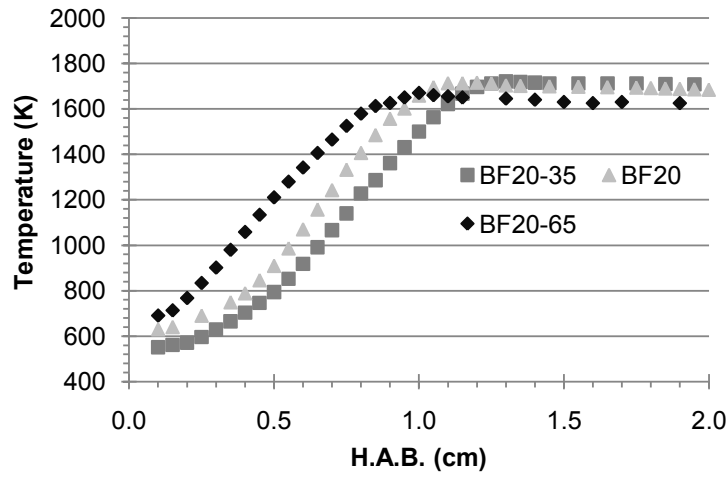
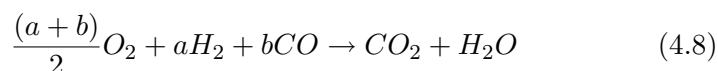


Figure 4.7: experimental temperature profiles of benzene-oxygen-argon flames burning at 35, 45 and 65 mbar with an equivalence ratio of 2.

Basically, at lean conditions molecular oxygen is in excess compared to the fuel and main chain carriers are O atom and OH radical due to the high oxygen content of flames. On the contrary, at rich conditions fuel is in excess and H atom becomes the main chain carrier. Stoichiometric flames have an intermediate behavior, where O atom, OH radical and H atom all play an important role. In addition to a change in equivalence ratio, flame structures presented in this chapter have different temperature profiles, as discussed earlier. Consequently, each trends highlighted in the following discussion comes from a combination of changes in equivalence ratio and flame temperature.

In each investigated flame, reactants (benzene and molecular oxygen) are consumed into products (carbon dioxide, water, carbon monoxide and molecular hydrogen) through the formation of intermediate species such as cyclopentadiene (C_5H_6) or vinylacetylene (C_4H_4). In rich BF18 and BF20 flames, reactants are completely consumed in burnt gases, whereas molecular oxygen subsists in BF07 and BF10. In BF10, this phenomenon can be explained by the presence of molecular hydrogen (H_2) and carbon monoxide (CO) in the burnt gases, indicating that the reaction is not completed. The stoichiometry of BF10 can be verified by comparing remaining mole fractions of CO and H_2 at 2 cm of the burner surface ($3.5 \cdot 10^{-2}$ and $5 \cdot 10^{-3}$, respectively) to the one of molecular oxygen required to fully oxidize them into CO_2 and H_2O , according to reaction 4.8.



The calculated mole fraction of $2 \cdot 10^{-2}$ is very close to the experimental value of $1.9 \cdot 10^{-2}$, confirming the stoichiometry of BF10. A similar calculation for BF07 gives $3.9 \cdot 10^{-2}$. Compared to the experimental value of $5 \cdot 10^{-2}$, it demonstrates the oxygen excess in BF07.

Contrarily to the excess of O_2 in lean benzene flames, that of C_6H_6 goes to zero under rich conditions. This phenomenon can be explained by the persistence of some intermediate species such as acetylene (C_2H_2) and polyacetylenic compounds ($C_{2x}H_2$ with $x \geq 1$) in the burnt gas

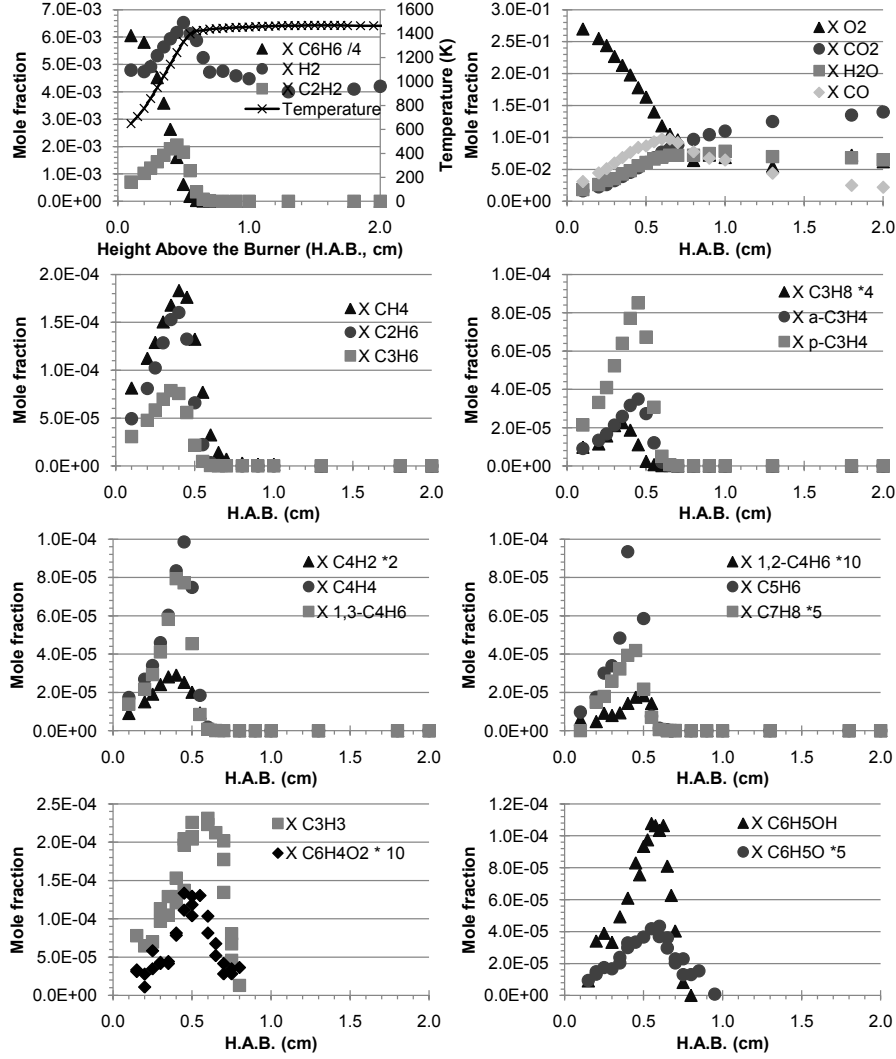


Figure 4.8: experimental structure of the benzene-oxygen-argon flame BF07 ($\phi = 0.7$). X and Y-axes represent the height above the burner in cm and the mole fraction X measured for each chemical species, respectively. When indicated, mole fraction profiles are scaled for more clarity.

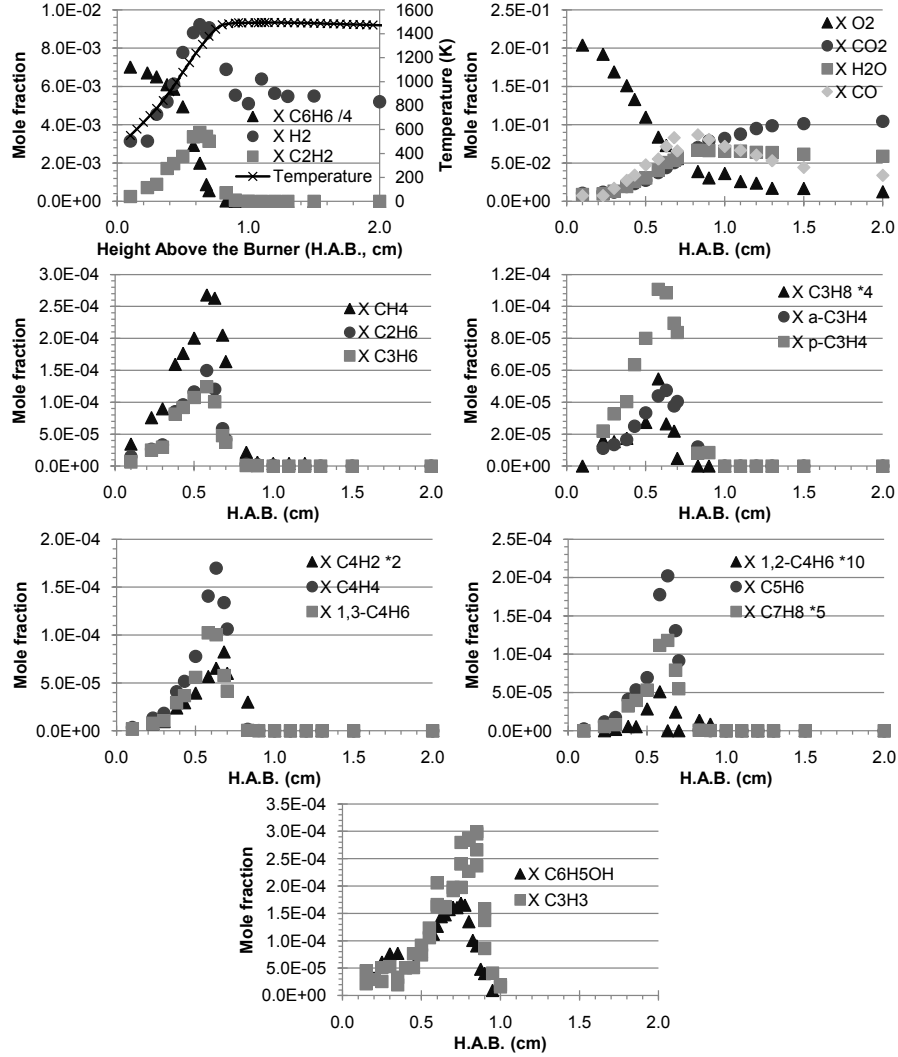


Figure 4.9: experimental structure of the benzene-oxygen-argon flame BF10 ($\phi = 1$). X and Y-axes represent the height above the burner in cm and the mole fraction X measured for each chemical species, respectively. When indicated, mole fraction profiles are scaled for more clarity.

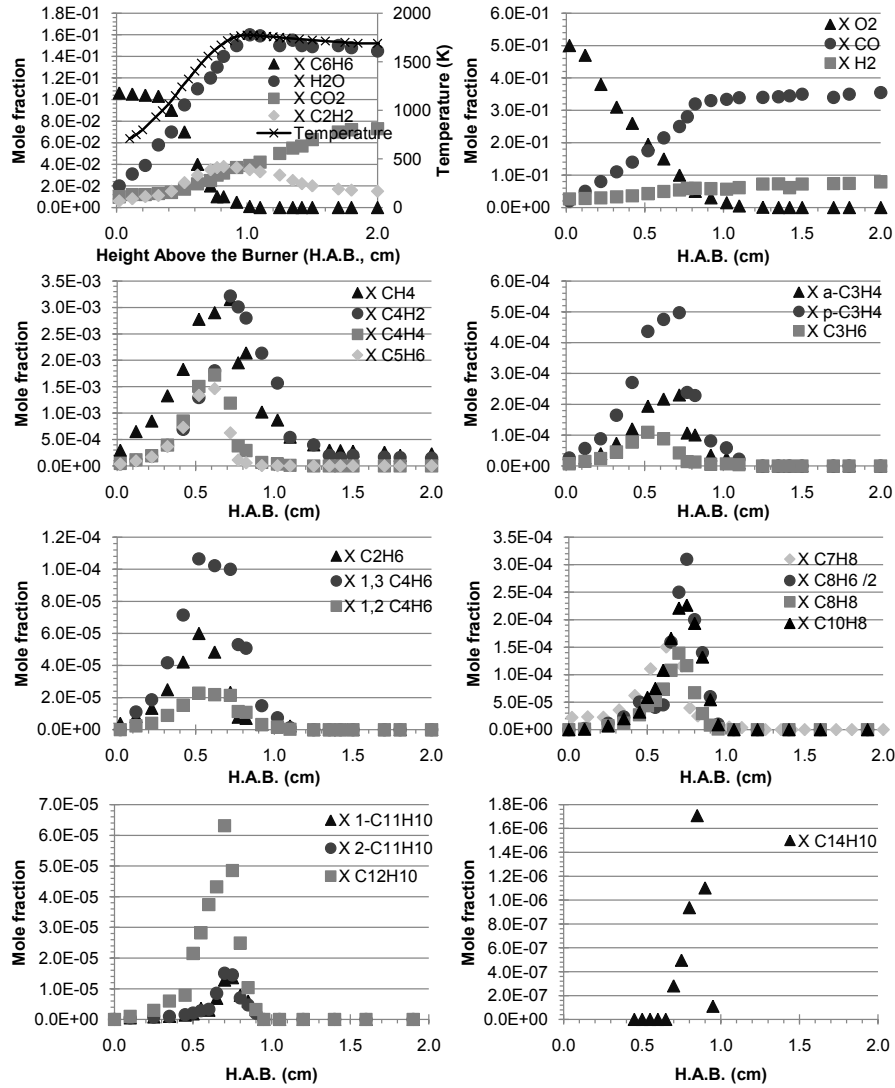


Figure 4.10: experimental structure of the benzene-oxygen-argon flame BF18 ($\phi = 1.8$). X and Y-axes represent the height above the burner in cm and the mole fraction X measured for each chemical species, respectively. When indicated, mole fraction profiles are scaled for more clarity.

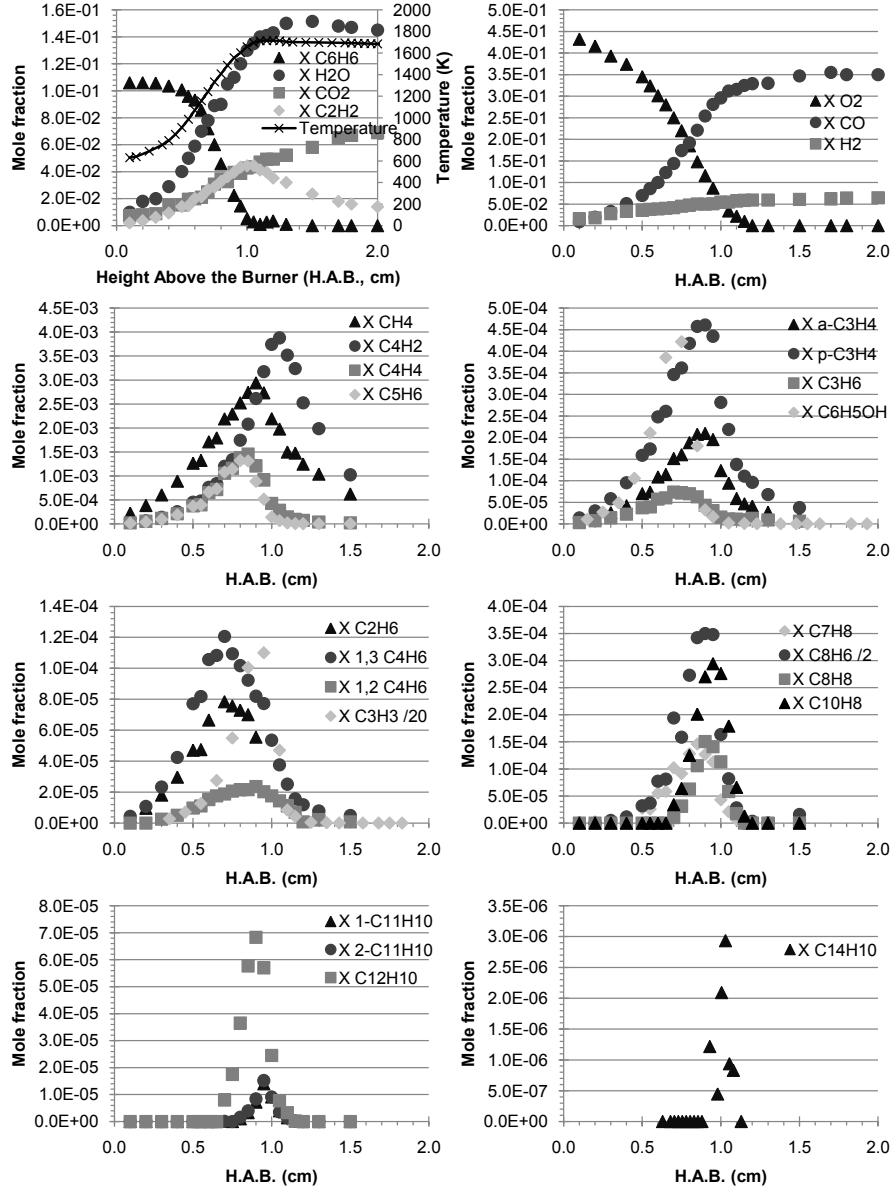


Figure 4.11: experimental structure of the benzene-oxygen-argon flame BF20 ($\phi = 2$). X and Y-axes represent the height above the burner in cm and the mole fraction X measured for each chemical species, respectively. When indicated, mole fraction profiles are scaled for more clarity.

region and by the formation of soot, which is C_xH_y material. A detailed discussion on soot formation will be given in chapter 7. Another difference between rich and lean combustion is the χ_{CO}/χ_{CO_2} mole fraction ratio measured in burnt gases. It is worth 0.25, 0.40, 4.3 and 5 in BF07, BF10, BF18 and BF20, respectively, confirming that it highly depends on the equivalence ratio. This phenomenon is explained by the reaction $CO + OH \rightleftharpoons CO_2 + H$ that is the main CO_2 formation route. As OH concentration is higher in lean flames than in rich flames, this reaction is stimulated in BF07 and BF10, compared to BF18 and BF20.

The mole fraction profile of argon could not be measured by Gas Chromatography. Indeed, the use of He and Ar as carrier gases with the MOLSIEVE 5A column (see appendix A), respectively leads to similar eluting times for oxygen and argon, and prevents to observe the response of Ar present inside the injected sample. Whereas argon is a non reactive compound, its mole fraction should decrease in burned gases, as the total mole number increases in benzene flames ($C_6H_6 + 7.5O_2 \rightarrow 6CO_2 + 3H_2O$, $\Delta n = +0.5$).

Concerning intermediate species, the sole C_1 hydrocarbon measured using gas chromatography is methane (CH_4) and its maximum mole fraction increases with the equivalence ratio. In BF07 and BF10, methane is completely consumed in burnt gases and its maximum mole fractions are respectively $1.8 \cdot 10^{-4}$ and $2.6 \cdot 10^{-4}$. In rich BF18 and BF20 flames, methane slightly persists in burnt gases and measured maximum mole fractions are $2.8 \cdot 10^{-3}$ and $3.0 \cdot 10^{-3}$, respectively.

Two C_2 hydrocarbons have been measured: acetylene (C_2H_2) and ethane (C_2H_6). The measured C_2H_2 profile is the sum on acetylene and ethylene mole fractions, as our chromatographic setup cannot distinguish between these two compounds. However, previous studies [71, 94, 95] on benzene oxidation have shown that ethylene mole fraction is very low compared to acetylene, allowing to assume ethylene signal as negligible. Acetylene maximum mole fraction spreads from 10% of the initial benzene mole fraction in BF07 to 40% in BF20, making it quantitatively the main intermediate of benzene combustion. This observation agrees

with previous findings on benzene oxidation, stressing that acetylene is a key intermediate. As CH_4 , C_2H_2 is completely consumed in burnt gases of BF07 and BF10, whereas it persists in BF18 and BF20. The high acetylene concentration measured in the burnt gas region of rich flames makes it a potential building block of soot formation, as further discussed in chapters 6 and 7. In BF07 and BF10, C_2H_6 and CH_4 mole fraction profiles are of similar magnitude, whereas in BF18 and BF20 C_2H_6 maximum mole fraction is a factor 40 lower than CH_4 . Both these compounds should be formed from methyl radical (CH_3) through reactions such as $CH_3 + CH_3 \rightleftharpoons C_2H_6$ or $CH_3 + H \rightleftharpoons CH_4$. The highest H atom concentration in BF18 and BF20 should therefore explain the stimulation of CH_4 production, compared to that of C_2H_6 .

Four C_3 hydrocarbons were measured using gas chromatography: allene (CH_2CCH_2 , called a- C_3H_4), propyne (CH_3CCH , called p- C_3H_4), propylene (C_3H_6) and propane (C_3H_8). As previous studies [71, 94, 95] reported that propargyl radicals (C_3H_3) may play an important role in benzene oxidation, its mole fraction profiles have been measured in BF07, BF10 and BF20 by Molecular Beam Mass Spectrometry (MBMS). Moreover, it is now well established that a channel linking C_3H_3 to benzene is of particular importance in rich hydrocarbon flames [97] and experimental data on this radical are therefore necessary. Its maximum mole fraction is relatively high in each investigated flame, confirming that it should play a key role in benzene oxidation. Propane has a very low maximum mole fraction in each investigated flame and should not play a significant role in benzene oxidation. In BF18 and BF20, maximum mole fractions of propylene are significantly lower than those of p- C_3H_4 and C_3H_3 . On the contrary, in BF07 and BF10 maximum mole fractions of C_3H_6 are relatively similar to those of other C_3 hydrocarbons, indicating that C_3H_6 formation is favored under oxidation conditions, compared to other C_3 intermediates. Over the entire range of equivalence ratio, propyne has constantly a higher mole fraction than allene. However, mole fraction profiles of these C_3H_4 isomers are very similar and the mole fraction ratio between p- C_3H_4 and a- C_3H_4 seems

constant, suggesting that rapid isomerization reactions should be active.

Four C_4 hydrocarbons were measured by gas chromatography: diacetylene (C_4H_2), vinylacetylene (C_4H_4), 1,3-butadiene ($1,3-C_4H_6$) and 1,2-butadiene ($1,2-C_4H_6$). Compared to other C_4 hydrocarbons, diacetylene is only a minor intermediate species in BF07 and BF10. However, in BF18 and BF20 C_4H_2 is quantitatively the second major intermediate and slightly persists in burnt gases. Since this behavior is similar to C_2H_2 , one can postulate that pathways such as $C_2H + C_2H_2 \rightleftharpoons C_4H_2 + H$ are involved in diacetylene formation. Contrarily to C_4H_2 , vinylacetylene has relatively high maximum mole fractions over the entire range of equivalence ratio. This observation confirms kinetic schemes previously postulated for benzene oxidation (see figures 4.2, 4.3 and 4.5) where its consumption converge towards C_4H_4 formation. $1,3-C_4H_6$ and $1,2-C_4H_6$ are minor intermediates of benzene oxidation as their maximum mole fractions are low in each investigated flame.

The sole C_5 hydrocarbon measured by gas chromatography is cyclopentadiene (C_5H_6). This intermediate has high maximum mole fractions over the entire range of equivalence ratios, confirming the major role played by its parent radical C_5H_5 in kinetic schemes previously postulated by Bittner and co-workers [71], Venkat and co-workers [73] and Rotzoll [75].

Concerning C_6 chemical species, only benzene (C_6H_6) was measured by gas chromatography. Mole fractions of phenol (C_6H_5OH) has been measured in BF07, BF10 and BF20 by MBMS, as well as phenoxy radical (C_6H_5O) and benzoquinone ($C_6H_4O_2$) in BF07. Regarding the high uncertainty surrounding the importance of these compounds in aromatic oxidation, these complementary MBMS measurements are of great interest. Phenol has a maximum mole fraction close to $1.0 \cdot 10^{-4}$ in BF07 and BF10, and close to $5.0 \cdot 10^{-4}$ in BF20, indicating that it is an important intermediate of benzene oxidation. Contrarily to phenol, C_6H_5O and $C_6H_4O_2$ have very low mole fractions in BF07, whereas they are described as principal intermediates of phenyl oxidation in the litera-

ture. Consequently, present measurements tend to disapprove the benzoquinone channel supported by Alzueta and co-workers [89] and indicate that previous kinetic schemes assuming that the only major phenoxy radical decomposition route is cyclopentadienyl and carbon monoxide formation are not reliable. Indeed, if phenoxy radical is really a key intermediate of benzene oxidation, the high activation energy of reaction $C_6H_5O \rightleftharpoons C_5H_5 + CO$ (43.92 kcal mol⁻¹) cannot explain phenoxy radical mole fractions as low as those measured in BF07. The role of phenoxy radical in benzene combustion will be discussed in more details in a following section.

Concerning C_7 hydrocarbons, toluene (C_7H_8) is the only intermediate compound measured by gas chromatography. Its mole fraction is worth about $1 \cdot 10^{-5}$ and $2 \cdot 10^{-4}$ in flames with low and high equivalence ratios, respectively. Compared to other intermediate species, these maximums are relatively low. In present experiments, toluene is the first intermediate having more carbon atoms than benzene and is the largest hydrocarbon detected in BF07 and BF10. Toluene combustion is the subject of the next chapter.

Among C_8 hydrocarbons, phenylacetylene (C_8H_6) and styrene (C_8H_8) have been measured by gas chromatography in rich BF18 and BF20 flames. In these flames, phenylacetylene maximum mole fractions reach $6 \cdot 10^{-4}$ and $7 \cdot 10^{-4}$, highlighting that it may play an important role in hydrocarbon growth towards polycyclic aromatic hydrocarbons. This observation agrees with previous findings of Bockhorn and co-workers [98] and Frenklach and co-workers [99], who proposed a kinetic scheme describing benzene growth to PAHs through H Abstractions and C_2H_2 Additions (later named the HACA mechanism by Frenklach and Wang [100]) where phenylacetylene is a key intermediate. As toluene, styrene mole fractions are close to $1.5 \cdot 10^{-4}$ in BF18 and BF20 flames. Styrene should not play a major role in soot formation.

Three C_{10} hydrocarbons have been measured by gas chromatography in BF18 and BF20: naphthalene ($C_{10}H_8$), 1-methylnaphthalene ($1-C_{11}H_{10}$) and 2-methylnaphthalene ($2-C_{11}H_{10}$). $C_{10}H_8$ is the first polycyclic aro-

matic hydrocarbon and exhibits a higher maximum mole fraction in BF20 than in BF18. Methylnaphthalene isomers have maximum mole fractions close to $1.0 \cdot 10^{-5}$ in both BF18 and BF20. These compounds should be formed through reactions of the methyl radical with naphthalene and naphthyl radicals. The sole C_{12} hydrocarbon that has been measured by gas chromatography is biphenyl ($C_{12}H_{10}$). Its mole fraction is close to $7.0 \cdot 10^{-5}$ in both BF18 and BF20 flames and it should be mainly produced by reactions between phenyl radical and benzene or phenyl radicals self recombination. One C_{14} hydrocarbon has been measured by gas chromatography: phenanthrene ($C_{14}H_{10}$). It could be produced either from HACA reactions on biphenyl or on naphthalene and its mole fraction is in the ppm range in BF18 and BF20. Phenanthrene is the highest hydrocarbon observed in the present study.

4.2.3 Influence of pressure on flame structures

In addition to the influence of the equivalence ratio on benzene flame structures, the influence of pressure has been investigated. The richest flame BF20 has been analyzed at 35 (BF20-35), 45 (BF20) and 65 mbar (BF20-65), as shown on figures 4.12, 4.11 and 4.13, respectively. As discussed previously, the working pressure highly influences temperature profiles of investigated flames and it is therefore very difficult to discriminate between temperature and pressure effects. Consequently, the study of BF20-35 and BF20-65 flame structures has been limited to the measurement of mole fraction profiles of hydrocarbons from C_1H_x to C_7H_x , including small soot precursors as C_2H_2 and C_5H_6 . Table 4.3 summarizes the variation in maximum mole fractions of main hydrocarbons in BF20-35 and BF20-65, compared to BF20. Except for methane, maximum mole fractions of intermediate species measured in BF20 (45 mbar) respectively increase and decrease when decreasing and increasing the working pressure. Compared to BF20, the general increase in consumption reactions of intermediate species observed in BF20-65 seems to produce higher CH_3 radical concentrations, which promote the methane formation. On the contrary, the consumption of

these intermediate species seems slower in BF20-35 and should therefore produce less CH_3 radical, disadvantaging methane formation.

Whereas the pressure increase disadvantages the formation of soot precursors such as C_2H_2 and C_5H_6 , the mean diameter of soot particles may be higher in BF20-65 than in BF20 and BF20-35, as the mean free path between them decreases. This hypothesis agrees with experimental difficulties encountered when analyzing BF20-65. Indeed, the soot produced in this flame blocks the quartz nozzle and the filter of the vacuum pump connected to the combustion chamber more often than in BF20 and BF20-35, indicating that the mean diameter of soot particles may be higher.

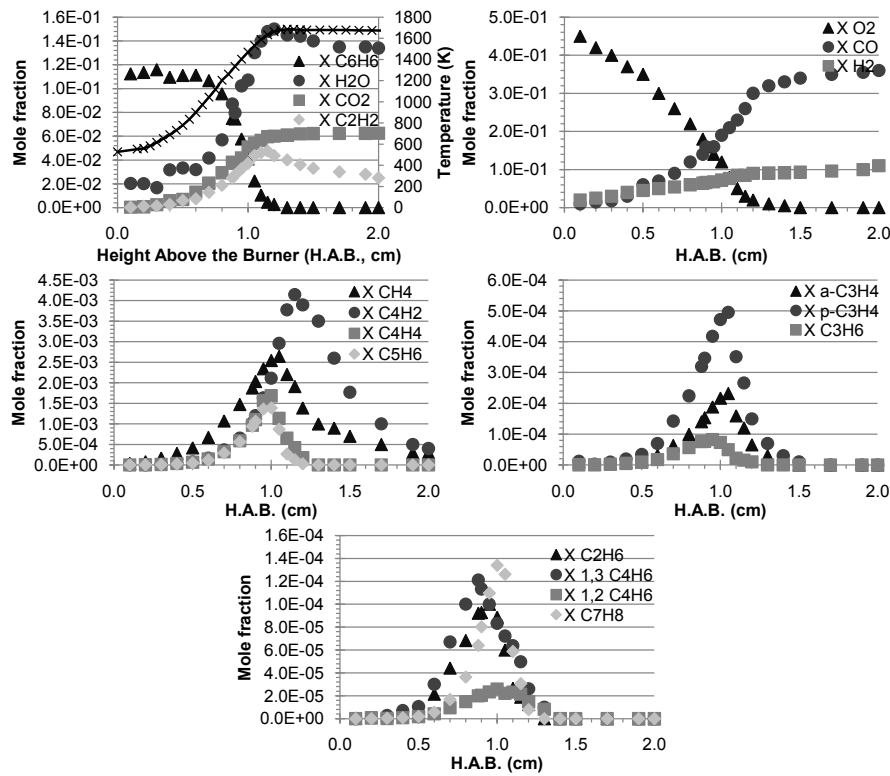


Figure 4.12: Experimental flame structure of the rich benzene-oxygen-argon flame BF20-35 (P = 35 mbar). The X-axis and Y-axis represent the height above the burner in cm and the mole fraction measured for each chemical species, respectively.

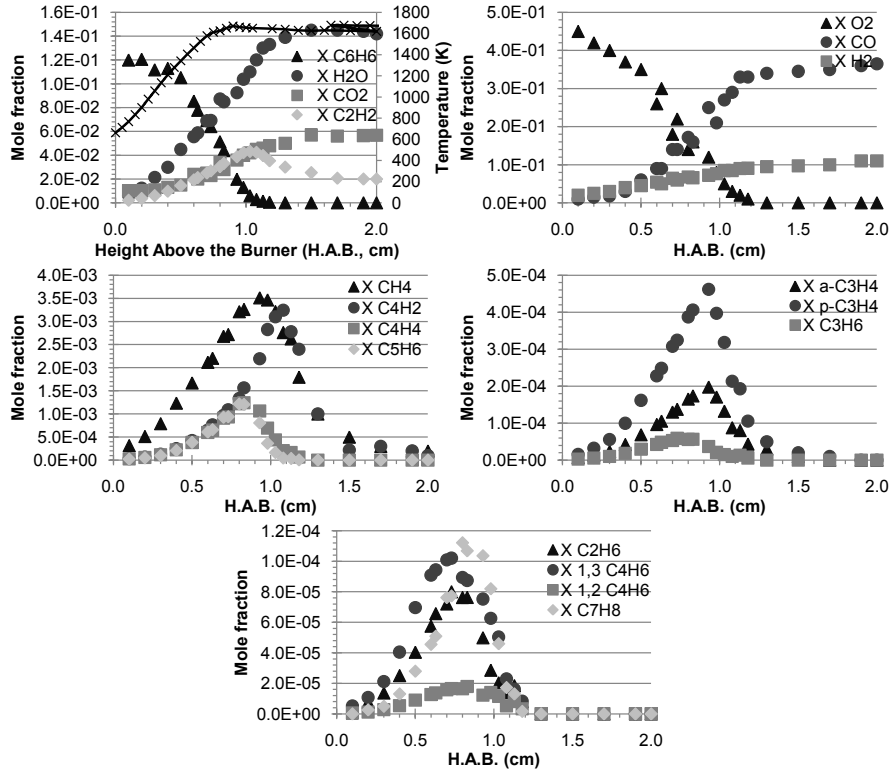


Figure 4.13: Experimental flame structure of the rich benzene-oxygen-argon flame BF20-65 ($P = 65$ mbar). The X-axis and Y-axis represent the height above the burner in cm and the mole fraction measured for each chemical species, respectively.

Table 4.3: variation of maximum mole fractions in BF20-35 and BF20-65, compared to BF20

Species	BF20-35	BF20-65
CH_4	-10%	+19%
C_2H_2	+6%	-3%
C_2H_6	+4%	-16%
C_3H_6	+12%	-20%
a- C_3H_4	+10%	-6%
p- C_3H_4	+7%	-0.2%
C_4H_4	+16%	-15%
C_4H_2	+7%	-19%
1,3- C_4H_6	+0.4%	-15%
C_5H_6	+5%	-8%

4.3 Discussion on benzene flame chemistry

This section presents the development of a detailed kinetic model for benzene combustion and compares its predictions to experimental results previously discussed. The following discussion is divided into several subsections corresponding to chemical intermediates of benzene combustion. For each intermediate compound, reactions leading to its formation are presented and choices in consumption pathways and kinetic parameters are justified by a comprehensive literature survey.

The predictive capability of the developed kinetic model is evaluated for each compound by comparing its predictions to mole fraction profiles measured in BF07, BF10, BF18 and BF20 or to experimental data available in the literature. The comparison with measurements performed for BF20 at 35 and 65 mbar will be briefly discussed at the end of this chapter. In addition to our kinetic model predictions, experimental results are compared to predictions of the mechanism developed by Richter and Howard (the RH model) for benzene combustion [92], in order to assess improvements brought by the present study. In a recent paper [96], we have shown that this mechanism has a predictive capability as bad as that of Ristori and co-workers [22] for lean and stoichiometric benzene flames. However, the RH model has been retained for comparison with the present work since it has been developed for the modeling of a rich benzene flame similar to BF18 and since it includes new calculated data for the pressure dependence of several reactions.

Finally, comparative reaction rate analyses allow to determine the importance of each reaction pathway involved in consumption and formation of every intermediate compound. The discussion begins with benzene, introduced as a reactant in flames described in this chapter.

4.3.1 The benzene sub-model

Benzene (C_6H_6) is a planar and aromatic hexagonal ring, considered as one of the most stable organic compounds. Since the benzene molecule

has a D_{6h} symmetry, its reaction pathways do not depend on the position of the reacting carbon or hydrogen atom and therefore lead to single isomer products. In flames, benzene can be consumed through either decomposition reactions, radical addition reactions or H abstraction reactions by H , O and OH . Since C_6H_6 is a reactant, each chemical pathway connected to it is a potential consumption route and is presented hereafter. Channels that occur backward, producing benzene, will be pointed up later.

Benzene consumption pathways

(i) Benzene isomerization and decomposition routes

Despite its high stability, C_6H_6 undergoes isomerization reactions at high temperature, as experimentally highlighted in 1987 by Scott and co-workers [101]. They showed that the reaction of doubly labeled $1,2\text{-}^{13}C_2$ -benzene in a flow reactor at 1375 K gives a product distribution of 74%, 24% and 4% of 1,2-, 1,3- and 1,4- $^{13}C_2$ -benzene, respectively. In 1998, Bettinger and co-workers [106] theoretically studied the C_6H_6 potential energy surface to elucidate Scott and co-workers findings. They found that a path linking 1,2- $^{13}C_2$ -benzene to 1,3- $^{13}C_2$ -benzene through cyclohexadienecarbene and fulvene ($f\text{-}C_6H_6$) should be involved in benzene topomerization reactions (see figure 4.14). In 1992,

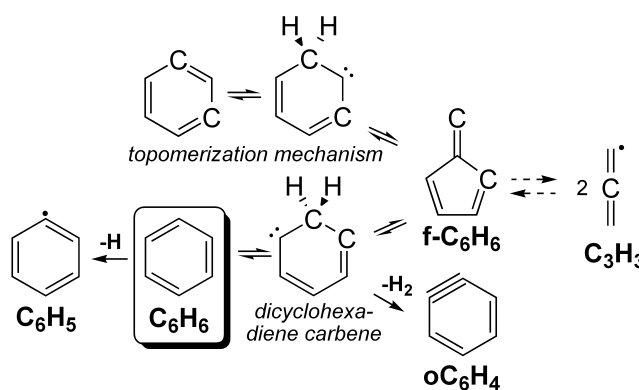


Figure 4.14: main isomerization and decomposition pathways of benzene

Table 4.4: C_6H_6 consumption reactions included into the kinetic model.

Reactions		$k = AT^n e^{-E_a/RT}$			Refs.
		A^a	n	Ea^a	
Isomerization and decomposition reactions.					
R1	$f\text{-}C_6H_6 \rightleftharpoons C_6H_6$	$5.62 \cdot 10^{81}$	-19.4	121.5	[97]
R2	$C_3H_3 + C_3H_3 \rightleftharpoons C_6H_6$	$1.29 \cdot 10^{69}$	-16.7	27.86	[97]
R3	$C_3H_3 + C_3H_3 \rightleftharpoons C_6H_6$	$7.07 \cdot 10^{39}$	-8.8	7.05	[97]
R4	$C_6H_5 + H + M \rightleftharpoons C_6H_6 + M$ (k_∞)	$2.20 \cdot 10^{14}$	0	0	[86]
	$C_6H_5 + H + M \rightleftharpoons C_6H_6 + M$ (k_0)	$4.10 \cdot 10^{104}$	-24.6	21.51	[86]
	Troe's broadening factors: $4.6 \cdot 10^{-2}$ / $3.5 \cdot 10^2$ / $6.0 \cdot 10^4$ / $7.6 \cdot 10^3$				[86]
Reactions with H atom.					
R5	$C_6H_6 + H \rightleftharpoons C_6H_5 + H_2$	$6.02 \cdot 10^8$	1.8	16.4	[102]
R6	$C_6H_6 + H \rightleftharpoons C_6H_7$	$1.12 \cdot 10^{167}$	-45.87	81.8	b
Reactions with O atom.					
R7	$C_6H_6 + O \rightleftharpoons C_6H_5 + OH$	$6 \cdot 10^{13}$	0	11.06	c
R8	$C_6H_6 + O \rightleftharpoons C_6H_5O + H$	$6.66 \cdot 10^{12}$	0	2.33	c
Reactions with OH radical.					
R9	$C_6H_6 + OH \rightleftharpoons C_6H_5 + H_2O$	$2.38 \cdot 10^4$	2.68	0.77	[103]
R10	$C_6H_6 + OH \rightleftharpoons C_6H_5OH + H$	$1.32 \cdot 10^2$	3.25	5.59	[103]

^a A units are s^{-1} and $cm^3 \text{ mol s}^{-1}$ for Unimolecular and bimolecular reactions, respectively. E_a is expressed in kcal mol^{-1} .

^b determined on the basis of data presented at 100 Torr in [102].

^c $k_{R7} + k_{R8}$ comes from [104] and the branching ratio is from [105].

Miller and Melius [107, 108] investigated the potential energy surface of $C_3H_3 + C_3H_3$ systems and found that propargyl radicals (C_3H_3) self-recombination should be an important benzene formation pathway in flames since it can produce $f\text{-}C_6H_6$. As Bettinger and co-workers, they showed that $f\text{-}C_6H_6$ can subsequently isomerize into cyclohexadienecarbene and benzene, as depicted in figure 4.14. Later, Mebel and co-workers [109, 110], Madden and co-workers [111] and Miller and Klippenstein [97] provided additional theoretical studies and investigated new features of the C_6H_6 potential energy surface. In 2001, Mebel and co-workers [110] showed that beside isomerization to fulvene, benzene can undergo decomposition reactions to phenyl radical (C_6H_5) and H atom, to orthobenzynes ($o\text{-}C_6H_4$) and H_2 or can isomerize into vinylacetylene

(C_4H_4) and acetylene (C_2H_2) or into ethylene (C_2H_4) and diacetylene (C_4H_2). They calculated that most favorable pathways were f- C_6H_6 and $C_6H_5 + H$ formation with activation barriers of 104.7 and 115.2 kcal mol⁻¹ relative to benzene, respectively. In 2003 Miller and Klippenstein [97] re-investigated the potential energy surface and calculated rate coefficients of key reactions linking C_6H_6 to f- C_6H_6 , $C_3H_3 + C_3H_3$ and $C_6H_5 + H$ at various pressures.

In our kinetic mechanism, the sub-model connecting benzene to fulvene and $C_3H_3 + C_3H_3$ determined by Miller and Klippenstein at 30 Torr has been included (see reactions R1 to R3 in table 4.4). Benzene decomposition to phenyl radical and hydrogen atom is also considered but its rate constant is taken from the work of Davis and co-workers [86] (see reaction R4) who calculated the detailed fall-off behavior of this reaction.

(ii) Benzene reactions with H atom

Hydrogen atom can react with benzene through 2 different pathways (see reactions R5 and R6 in table 4.4 on the previous page). The first consists in an H abstraction reaction yielding C_6H_5 and H_2 , while the second adds an H atom to the C_6H_6 ring forming a cyclohexadienyl radical (C_6H_7). These both reactions have been experimentally studied by numerous researchers including Sauer and Many [112], Kim and co-workers [113], Knutti and Buhler [114] and Nicovich and Ravishankara [115]. The conclusion of these studies is that at temperatures below 1000 K, the addition pathway is faster than the H abstraction route. On the contrary, above 1000 K C_6H_7 fastly dissociates back into $C_6H_6 + H$, allowing the H abstraction route to dominate. In 1997 and 2003, respectively, Mebel and co-workers [102] and Barckholtz and co-workers [116] performed theoretical studies on the $H + C_6H_6$ reaction and confirmed previous experimental findings. Authors calculated a higher activation barrier for the H abstraction pathway than for the H addition route.

Since the temperature range of all investigated flames spreads from 700 K to 1800 K, reactions R5 and R6 have been added into the kinetic

model using rate parameters calculated by Mebel and co-workers at 100 Torr [102], as described in table 4.4 on page 109.

(iii) *Benzene reactions with O atom*

In the same way as *H* atom, *O* atom reacts with benzene either through an *H* abstraction reaction, forming phenyl and hydroxyl radicals, or through an electrophilic addition to the benzene ring, yielding a triplet biradical C_6H_6O . Extensive experimental investigations of the $O + C_6H_6$ reaction, including particularly works of Nicovich and co-workers [117] and Ko and co-workers [104], have led to a general consensus on the overall rate constant of the $O + C_6H_6 \rightarrow products$ reaction, over a temperature range of 300 to 1400 K. Ko and co-workers [104] equally showed that below a pressure of 1 atm, the rate constant of the overall reaction is essentially independent of pressure. In spite of these studies, little information is available on the product distribution of the $O + C_6H_6$ reaction. Indeed, experimental works devoted to product observation have reached different conclusions. In 1977, Sloane [118] performed crossed molecular beam experiments of benzene and oxygen atoms and showed by mass spectrometry that main products should be phenol (C_6H_5OH) and carbon monoxide. In 1980, Sibener and co-workers [119] performed similar experiments at higher collision energies. Unlike Sloane, they did not measure *CO* formation but found that the phenoxy radical (C_6H_5O) and phenol should be main reaction products. Later, Nicovich and co-workers [117] and Bajaj and Fontijn [120] confirmed that *CO* production was a minor reaction pathway by studying the $C_6H_6 + O$ reaction in flow reactors. Moreover, as Sibener and co-workers, Bajaj and Fontijn showed that the phenoxy radical was the main reaction product. In 1999 and 2004, Parker and Davis [121] and Berndt and Boge [122] identify for the first time different C_6H_6O isomers in flash photolysis and flow reactor experiments of the $C_6H_6 + O$ reaction: cyclohexadienone, butadienylketene and benzene oxide/oxepin.

Recently, Nguyen and co-workers [105] have theoretically studied the potential energy surface of the $C_6H_6 + O$ system and have calculated the branching ratio between *H* atom abstraction and *O* atom addition chan-

nels, along with the product distribution of the C_6H_6O diradical isomerization and decomposition, as a function of temperature and pressure. They showed that the O atom addition pathway dominates until 2000 K, but competes with the H atom abstraction channel above 1000 K and predicted that the C_6H_6O diradical mainly decomposes into the resonantly stabilized phenoxy radical (C_6H_5O) and H atom in flames. Very recently, Taatjes and co-workers [123] have experimentally and theoretically examined the branching ratio between products of the $C_6H_6 + O$ reaction, over the temperature range 300 to 1000 K and pressure range 1 to 10 Torr. They have found that $C_6H_5O + H$, phenol and cyclopentadiene + CO are major products and have calculated rate parameters and branching ratios representative of their measurements. Taatjes and co-workers and Nguyen and co-workers have shown that the $C_6H_6 + O$ reaction mechanism is extremely complex and highly dependent on temperature and pressure, explaining contradictory conclusions of previous experimental works [105, 123]. Even if the uncertainty on the product distribution is still significant, up to now phenoxy radical and H atom formation seems to be globally considered as the main reaction products.

Consequently, reactions R7 and R8 of table 4.4 on page 109, respectively describing H abstraction on benzene by O atom and oxygen atom addition to benzene, giving phenoxy radical and hydrogen atom, have been included in the developed kinetic model. The total rate constant ($k_{R7} + k_{R8}$) has been taken from the work of Ko and co-workers [104] and individual rate parameters have been deduced from the branching ratio calculated by Nguyen and co-workers [105].

(iv) Benzene reactions with OH radical

Similarly to H and O atoms, hydroxyl radical (OH) can either perform an H abstraction reaction or an electrophilic addition onto the benzene ring. Numerous experimental and theoretical kinetic studies have been devoted to reactions of hydroxyl radical with benzene, but have been essentially carried out at room temperature, as they play a significant role in atmospheric chemistry. These studies have been well

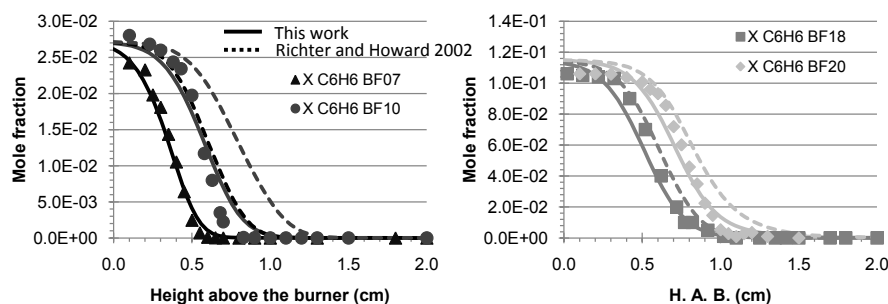


Figure 4.15: experimental and predicted mole fraction profiles of benzene (C_6H_6). Gray scale symbols represent experiment ($\triangle$ BF07, $\circ$ BF10, $\square$ BF18, $\diamond$ BF20) and solid and dashed curves stand for predictions of present and Richter and Howard [92] models, respectively.

summarized as part of recent reviews of Barckholtz and co-workers [116], Chen and co-workers [124], and Seta and co-workers [103]. Under atmospheric conditions, they are known to proceed mainly via the formation of a C_6H_6OH adduct, and the H abstraction channel is reported as minor.

Recently, Seta and co-workers [103] have measured rate constants for reactions of OH radicals with benzene and toluene, in shock tubes and at high temperature. Authors have calculated the product distribution by a quantum chemical analysis. They have shown that the H abstraction channel (reaction R9 of table 4.4 on page 109) dominates under flame conditions, whereas OH addition followed by an H atom elimination, forming phenol (reaction R10), can significantly compete at elevated temperatures. Reactions R9 and R10 have been included into our kinetic model using rate constant parameters determined by Seta and co-workers.

Comparison between predicted and experimental results

Figure 4.15 compares experimental C_6H_6 measurements performed in BF07, BF10, BF18 and BF20 to predictions of the present model and that developed by Richter and Howard [92] (further called the RH model). Over the entire range of equivalence ratios, the present model well pre-

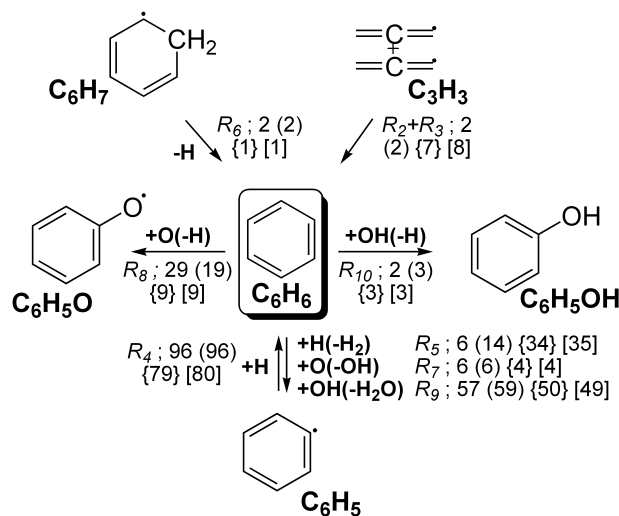


Figure 4.16: summary of benzene consumption pathways included into the developed kinetic model. Percentages represent contribution of each reaction in BF07, (BF10), {BF18} and [BF20].

dicts the rate of benzene consumption. The RH model well reproduces BF18 and BF20 measurements, but is unable to predict the shape of benzene mole fraction profiles in stoichiometric and lean flames. This underestimation of the benzene consumption rate mainly comes from a loop between phenoxy radical and phenol formations, which will be discussed further. Figure 4.15 indicates that our mechanism improves the modeling of the benzene mole fraction profiles in BF07 and BF10.

A comparative reaction rate analysis has been carried out to determine contribution of each reaction pathway to benzene consumption. Figure 4.16 presents reactions significantly active and gives percentages of their contributions to C_6H_6 consumption or formation. This figure shows that among all investigated pathways, only H abstraction reactions giving phenyl radical (reactions R_5 , R_7 and R_9 of table 4.4 on page 109 and figure 4.16) and reactions of O atom and OH radical with benzene, yielding phenoxy radical (reaction R_8) and phenol (reaction R_{10}), consume C_6H_6 . Other reactions (R_2 , R_3 , R_4 and R_6) proceed backward, forming benzene.

Over the entire range of equivalence ratio, the main benzene consumption route is phenyl radical formation through H atom abstraction by OH radical, by H atom and by O atom (reactions R9, R5 and R7, respectively). The contribution of reaction R7 is minor (about 5%) in all investigated flames, compared to reactions R9 and R5. Whereas H atom contribution is always lower than that of OH radical, it increases when moving towards higher equivalence ratios, contrarily to contributions of OH radical and O atom. This observation can be explained by the highest H atom concentration in rich flames, due to their lowest oxygen content. Another major benzene consumption channel is phenoxy radical production through reaction R8. Since this reaction involves O atom, its contribution is highest under lean conditions and decreases when increasing the equivalence ratio. The last pathway that consumes benzene is reaction with OH radical, yielding phenol and H atom (R10). Its contribution remains essentially constant over the investigated range of equivalence ratio.

Benzene is slightly produced by reactions R2, R3, R4 and R6 in all investigated flames. However, the molar flux of these reactions is significantly smaller than that of consumption routes and no benzene formation is experimentally observed (see figure 4.15). Phenyl radical recombination to H atom (reaction R4) and propargyl radical self-recombination (reaction R2 and R3) are main benzene formation channels. The chemical pathway leading to cyclohexadienyl radical (C_6H_7) formation will be discussed in section 4.3.6. The three following sections present chemical reactions involved in consumption of main benzene consumption products: phenyl radical, phenoxy radical and phenol.

4.3.2 The phenyl radical sub-model

Phenyl radical formation pathways

Phenyl radical is principally produced through H abstraction reactions on benzene and is quantitatively the most important product of benzene consumption, as depicted in figure 4.16.

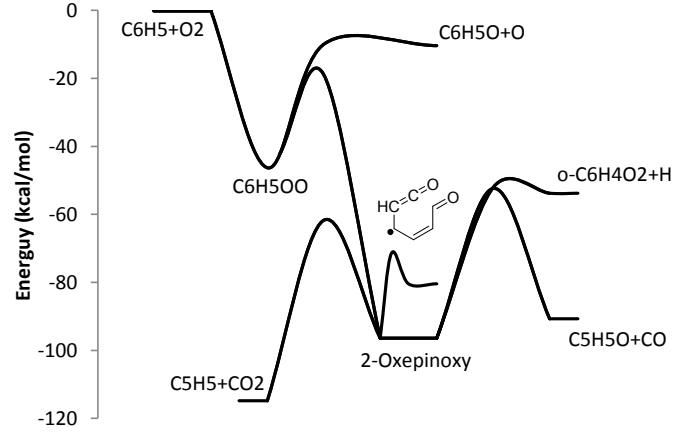
Phenyl radical consumption pathways

As discussed in the introduction of this chapter, phenyl radical reaction with O_2 is thought to be a major consumption channel. However, C_6H_5 dissociation and recombination with H atom, with O atom and with OH radical are other potential pathways that are equally discussed hereafter.

(i) Phenyl radical reactions with O_2

For many years, phenyl radical (C_6H_5) reaction with O_2 is thought to be of particular importance in aromatic oxidation. There are experimental evidences that this reaction proceeds through two different pathways, giving either H or O atom [85, 125] and co-products are generally assumed to be benzoquinone ($C_6H_4O_2$) and phenoxy radical (C_6H_5O), respectively. However, our MBMS measurements performed in BF07 at m/z ratios corresponding to phenoxy radical and benzoquinone (see figure 4.8 on page 96) have revealed that their mole fractions are very low in benzene flames. Consequently, if phenoxy radical and benzoquinone are really major products of the $C_6H_5 + O_2$ reaction, their degradation channels should be fast enough to explain such low maximum mole fractions. Otherwise, new reaction products should be postulated in order to agree with experimental measurements.

In the past decade, many researchers theoretically studied the $C_6H_5 + O_2$ reaction and showed that molecular oxygen addition to phenyl radical, forming the phenylperoxy radical (C_6H_5OO), is exothermic by about 45 kcal mol⁻¹ and fast since it is barrierless [126, 128, 129], as described in figure 4.17. Moreover, these studies highlighted that $C_6H_5O + O$ should be a main product channel of subsequent C_6H_5OO decomposition, because phenylperoxy radical has gained enough energy to eliminate an O atom. This theoretical finding has been recently confirmed by an experimental investigation of the $C_6H_5 + O_2$ reaction, showing that phenoxy radical is formed in high concentration [130]. Regarding these theoretical and experimental evidences, our kinetic model considers that phenoxy radical is the co-product of O atom formation from $C_6H_5 + O_2$ reac-

**Figure 4.17:** potential energy surface of the $C_6H_5 + O_2$ reaction [126]**Table 4.5:** C_6H_5 consumption reactions included into the kinetic model.

Reactions		$k = AT^n e^{-Ea/RT}$			Refs.
		A^a	n	Ea^a	
Reactions with O_2 .					
R11	$C_6H_5+O_2 \rightleftharpoons C_6H_5O+O$	$1.02 \cdot 10^{13}$	0	3.58	[125]
R12	$C_6H_5+O_2 \rightleftharpoons C_6H_4O_2+H$	$8.1 \cdot 10^{10}$	0	3.6	^b
R13	$C_6H_5+O_2 \rightleftharpoons n-C_4H_5+2CO$	$4.44 \cdot 10^{12}$	0	3.6	^b
Reactions with O atom and OH radical.					
R14	$C_6H_5+O \rightleftharpoons C_5H_5+CO$	$1 \cdot 10^{14}$	0	0	[85]
R15	$C_6H_5+OH \rightleftharpoons C_6H_5O+H$	$5 \cdot 10^{13}$	0	0	[107]
Isomerization and decomposition reactions: Lories sub-model [127].					
R16	$C_6H_5 \rightleftharpoons o-C_6H_4+H$	$8.75 \cdot 10^{14}$	0	86.1	[127]
R17	$C_6H_5 \rightarrow n-C_4H_3+C_2H_2$	$1.67 \cdot 10^{19}$	0	110.72	[127]
	$n-C_4H_3+C_2H_2 \rightarrow C_6H_5$	$1.02 \cdot 10^{15}$	-0.8	13.32	[127]
R18	$C_6H_5 \rightarrow l-C_6H_4+H$	$9.74 \cdot 10^{17}$	0	107.37	[127]
	$l-C_6H_4+H \rightarrow C_6H_5$	$2.25 \cdot 10^{12}$	0.5	11.12	[127]
R19	$C_6H_5 \rightarrow f-C_6H_5$	$2.03 \cdot 10^{14}$	0	59.84	[127]
	$f-C_6H_5 \rightarrow C_6H_5$	$1.17 \cdot 10^{13}$	0	29.96	[127]

^a A units are s^{-1} and $cm^3 mol s^{-1}$ for Unimolecular and bimolecular reactions, respectively. Ea is expressed in $kcal mol^{-1}$.

^b $k_{R12} + k_{R13}$ comes from [125] and the branching ratio is estimated to 0.017.

tion (see reaction R11 of table 4.5). Since this reaction is predicted to fastly produce phenoxy radical, C_6H_5O consumption routes should be fast enough to explain low maximum mole fractions measured in the present work, as discussed in the next section.

More uncertainties remain on the identification of the co-product of the H atom formation channel. Whereas it is generally assumed to be ortho-benzoquinone ($o\text{-}C_6H_4O_2$), a kinetic model considering C_6H_5OO dissociation into $o\text{-}C_6H_4O_2 + H$ and including an experimentally validated sub-mechanism for the consumption of benzoquinone isomers [90] overestimates $C_6H_4O_2$ measurements performed in our benzene flames by a factor close to 100 (see the dashed curve of figure 4.18). As indicated in appendix C, the total benzoquinone mole fraction has been measured by MBMS. The use of this technique is particularly justified for the detection of $o\text{-}C_6H_4O_2$, as it decomposes at temperatures higher than 80°C . To the best of our knowledge, it is the first time that benzoquinone measurements are performed into benzene flames and compared to kinetic modeling. This comparison clearly highlights that mechanisms using benzoquinone as a major intermediate of phenyl radical oxidation [89, 92, 93] are not reliable.

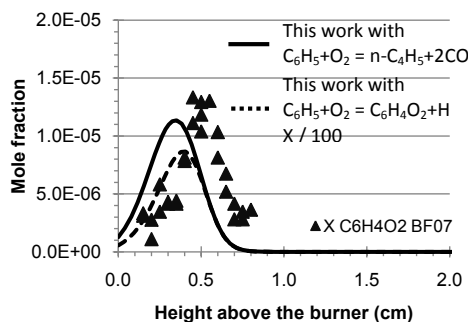


Figure 4.18: experimental and predicted mole fraction profiles of $C_6H_4O_2$. Symbols represent experiment (BF07) and solid and dashed curves stand for predictions of the present model considering either $C_6H_5 + O_2 \rightleftharpoons C_6H_4O_2 + H$ or $C_6H_5 + O_2 \rightleftharpoons n\text{-}C_4H_5 + 2CO$ as the major route, respectively. Mole fractions represented by the dashed curves are divided by a factor 100.

Benzoquinone formation through reaction of phenyl radical with O_2 should therefore be minor and another pathway should be responsible of most of the experimentally observed H atom formation. Several theoretical investigations of the $C_6H_5 + O_2$ reaction have recently showed that beside phenoxy radical + O atom, 2-oxepinoxy radical formation may be a major product [126, 128, 129] and that this radical may have enough energy to further dissociate into either n-1,3-butadienyl radical and CO , cyclopentadienyl radical and CO_2 , $C_5H_5O + CO$, or ortho-benzoquinone and H atom, as depicted in figure 4.17. Our study has shown that dissociation into ortho-benzoquinone + H atom is irrelevant in this work. Moreover, the C_5H_5 channel of figure 4.17 will yield an early CO_2 formation that is not observed in flames. Therefore, by the process of elimination, H atom formation from $C_6H_5 + O_2$ reaction should mainly be due to $C_5H_5O + CO$ or n-1,3-butadienyl radical formation. As it will be presented further, C_5H_5O is mainly consumed into n- $C_4H_5 + CO$. It is therefore assumed that products of the H atom formation channel of the $C_6H_5 + O_2$ reaction are n- $C_4H_5 + 2CO$. This hypothesis is plausible since n- C_4H_5 can subsequently decompose into C_4H_4 and H atom, explaining hydrogen atom formation.

Consequently, two reactions are included into our kinetic model for H atom production from the $C_6H_5 + O_2$ reaction: one leading to benzoquinone (reaction R12, see table 4.5) and one yielding n- $C_4H_5 + CO$ (reaction R13). The sum on $k_{R12} + k_{R13}$ is set to the rate constant experimentally measured by Kumaran and Michael [125] for $C_6H_5 + O_2 \rightleftharpoons H + products$ and the branching ratio between these two channels has been fitted to 0.017 in order to properly predict benzoquinone measurements of this work. However, the reaction of phenyl radical with molecular oxygen is particularly complex and its poor understanding is responsible of most of uncertainties surrounding benzene combustion. Further experimental and theoretical studies analyzing reaction channels of $C_6H_5 + O_2$ and their dependence on pressure and temperature are obviously needed.

(ii) Phenyl radical reactions with O atom, OH radical and H atom

In addition to molecular oxygen, phenyl radical can react with O atom (R14, see table 4.5 on page 117), with OH radical (reaction R15) and with H atom (reaction R4 of table 4.4 on page 109), yielding respectively cyclopentadienyl radical + CO , phenoxy radical + H and benzene. Reaction R14 is an overall process involving phenoxy radical, whose consumption will be discussed in the next section. The rate constant of reaction R14 has been estimated by Frank and co-workers to $1.0 \cdot 10^{14}$ [85]. Reaction R15 is equally an overall process that goes through phenol formation. Its rate constant has been estimated to $5.0 \cdot 10^{13}$ by Miller and Melius in 1992 [107].

(iii) Phenyl radical isomerization and decomposition routes

Many kinetic models consider that phenyl radical decomposition occurs by decyclization to a linear open chain radical ($l-C_6H_5$), followed by a rapid fragmentation into $n-C_4H_3 + C_2H_2$. However, Madden and co-workers [131] showed in 1997 that the barrier for fragmentation of $l-C_6H_5$ is significantly higher than that for recyclization into C_6H_5 . Moreover, authors demonstrated that the overall energy required for phenyl radical decomposition into $n-C_4H_3 + C_2H_2$ is greater than that for formation of ortho benzyne ($o-C_6H_4$) + H or linear 1,5 hexadiyn-3-ene ($l-C_6H_4$) + H , as depicted in figure 4.19. In 2010, Lories [127] extensively investigated the C_6H_5 potential energy surface and demonstrated that beside $n-C_4H_3 + C_2H_2$, $o-C_6H_4 + H$ and $l-C_6H_4 + H$, phenyl radical can produce

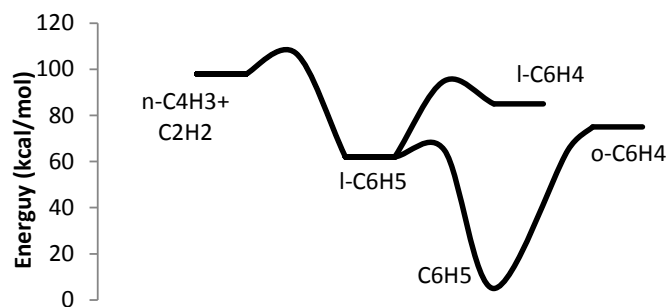


Figure 4.19: potential energy surface of C_6H_5 decomposition [131]

$i\text{-C}_4\text{H}_3 + \text{C}_2\text{H}_2$ or the fulvenyl radical ($\text{f-C}_6\text{H}_5$). The $\text{f-C}_6\text{H}_5$ radical can subsequently recombine with H atom forming fulvene ($\text{f-C}_6\text{H}_6$), whose reactions are discussed later. Lories calculated kinetic parameters of each reaction involved in phenyl radical decomposition and summarized them into a C_6H_5 sub-model which is used in the present kinetic mechanism. Some key reactions of this sub-model are presented in table 4.5 on page 117 (reactions R16 to R19).

Comparison between predicted and experimental results

Unfortunately, phenyl radical mole fraction profiles could not be measured by MBMS in this work, due to the high perturbation of C_6H_6 , introduced as a reactant. However, Yang and co-workers [95] recently detected this radical with a tunable synchrotron device in a benzene-oxygen-argon flame with a composition close to BF18 ($\phi = 1.78$ and dilution = 50%, compared to 1.8 and 40% in BF18) and our model predictions will therefore be compared to these experimental data. As shown on the left of figure 4.20, whereas C_6H_5 predictions of RH and present models differ by a factor 2, they are of the same magnitude than measurements performed by Yang and co-workers. Phenyl radical is predicted to be the main benzene consumption product, whereas its modeled maximum mole fraction is low. This indicates that its degradation

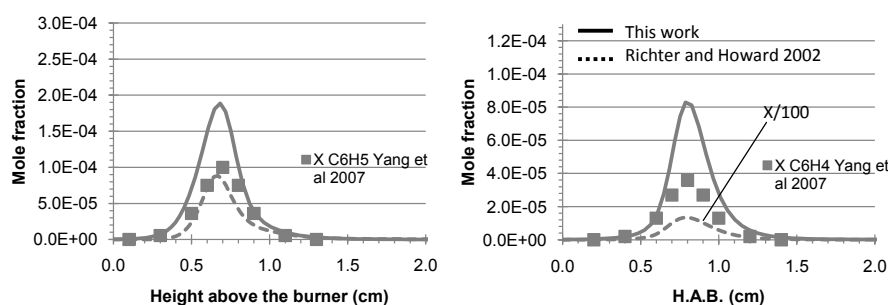


Figure 4.20: comparison between Yang and co-workers [95] measurements (symbols) with predictions of present and Richter and Howard [92] models (solid and dashed curves, respectively). For C_6H_4 , Richter and Howard's predictions are divided by a factor 100.

routes are fast enough to balance its quick formation. A comparative reaction rate analysis has therefore been carried out to determine contributions of each reaction pathway to phenyl radical consumption.

Figure 4.21 presents significantly active reactions and gives percentages of their contribution to C_6H_5 consumption or formation. In each investigated flame, phenyl radical is principally consumed through reactions with O_2 giving $C_6H_5O + H$ and $n-C_4H_5 + 2CO$ (reaction R11 and R13 of table, respectively). Under lean and stoichiometric conditions, the high O atom concentration allows reaction R14 to play a significant role whereas it is negligible in BF18 and BF20. Decomposition reactions R17 and R18 are inactive in BF07 and BF10 but contribute to about 25% of phenyl consumption in BF18 and BF20. This can be explained by their highest temperatures, allowing to easily cross activation barriers of these reactions. Whereas present and RH models give close predictions of phenyl radical measurements, the mechanisms differ in the contributions of each consumption route [96]. Since $l-C_6H_4$ and $o-C_6H_4$ are only produced from phenyl decomposition in present and RH models,

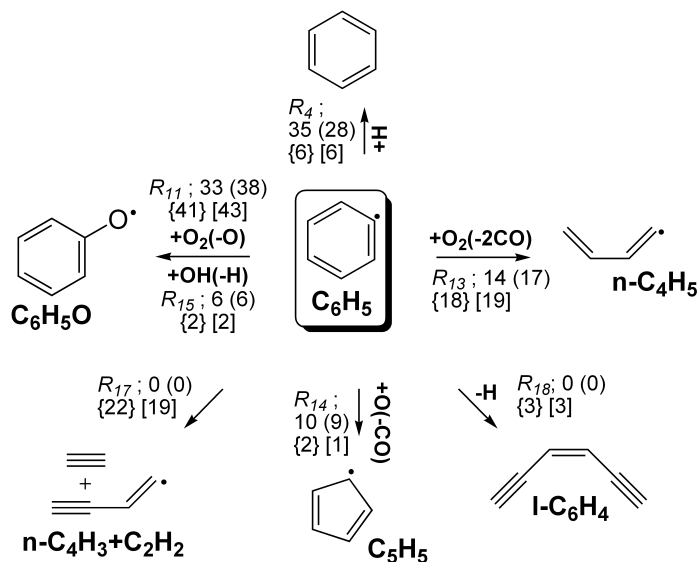


Figure 4.21: summary of phenyl radical consumption pathways included into the developed kinetic model. Percentages represent contribution of each reaction in BF07, (BF10), {BF18} and [BF20].

the comparison of total C_6H_4 measurements performed by Yang and co-workers to predictions of both mechanisms allows to assess the weight given to this channel in both models (see the right part of figure 4.20). Present and RH mechanisms respectively well predict and hugely overestimate C_6H_4 maximum mole fraction, indicating that RH model reactions that decompose phenyl radical into C_6H_4 species are not reliable. Contrarily to this mechanism, the sub-model of Lories [127] included in this work for the modeling of the unimolecular decomposition of phenyl radical has a good predictive capability.

4.3.3 The phenoxy radical sub-model

Phenoxy radical formation pathways

In 1956, Norrish and Taylor [53] already suggested that phenoxy radical might play an important role in benzene oxidation. Later, Venkat and co-workers [73] developed a general kinetic scheme for benzene combustion, including phenoxy radical for linking C_6H_x to C_5H_x hydrocarbons. Nowadays, kinetic models representing aromatic oxidation are still based on the pioneer study of Venkat and co-workers. In the present work, two reactions principally produce phenoxy radical (C_6H_5O). The first is reaction R8 of table 4.4 on page 109 that consumes benzene through O atom addition, yielding a C_6H_6O adduct that subsequently decomposes into $C_6H_5O + H$. The second is reaction R11 of table 4.5 on page 117 that converts $C_6H_5 + O_2$ into $C_6H_5O + O$. These two reactions are of particular importance since they produce flame propagating radicals (O atom and H atom), which have a significant impact on the entire kinetic scheme. Reactions R8 and R11 are fast and bring a significant mole flux towards phenoxy radical formation that needs to be balanced by fast consumption channels in order to reproduce low C_6H_5O maximum mole fractions observed experimentally in BF07 (see figure 4.8 on page 96).

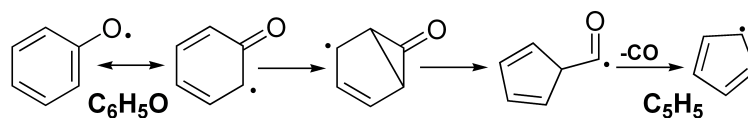


Figure 4.22: mechanism of phenoxy radical dissociation into cyclopentadienyl radical and CO [136]

Phenoxy radical consumption pathways

(i) Phenoxy radical isomerization and decomposition routes

In the nineties, researchers [132–134] experimentally observed that primary products of the high temperature dissociation of phenoxy radical are carbon monoxide and cyclopentadienyl radical (C_5H_5). Moreover, Lin and Lin [134] experimentally determined that the high pressure rate constant of this reaction could be fitted to $k = 2.51 \cdot 10^{11} e^{-22100/T} \text{ s}^{-1}$ (see reaction R20 in table 4.6). Further theoretical calculations of Olivella and co-workers [135] and Liu and co-workers [136] have confirmed these rate parameters and identified the mechanism involved in the phenoxy radical decomposition (see figure 4.22). This mechanism involves the formation of a bicycle intermediate from a carbon-centered phenoxy radical, followed by two subsequent CC bond cleavages, giving $C_5H_5 + CO$.

Table 4.6: C_6H_5O consumption reactions included into the kinetic model.

Reactions		$k = AT^n e^{-E_a/RT}$			Refs.
		A^a	n	E_a^a	
Isomerization and decomposition reactions.					
R20	$C_6H_5O \rightleftharpoons C_5H_5+CO$	$2.51 \cdot 10^{11}$	0	43.9	[134]
Reactions with O atom and OH radical.					
R21	$C_6H_5O+H \rightarrow C_3H_3+C_2H_3+CO$	$4.5 \cdot 10^{13}$	0	0	[137], ^b
R22	$C_6H_5O+O \rightarrow C_2H_2+C_2H_3+2CO$	$1.68 \cdot 10^{14}$	0	0	[137], ^b

^a A units are s^{-1} and $\text{cm}^3 \text{ mol s}^{-1}$ for Unimolecular and bimolecular reactions, respectively. Ea is expressed in kcal mol^{-1} .

^b Reaction products have been changed, see text

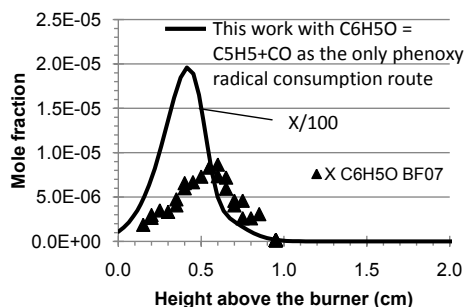


Figure 4.23: experimental and predicted mole fraction profiles for the phenoxy radical in BF07. Symbols represent the experiment and the curve stand for predictions ($\chi/100$) of the present model considering $C_6H_5O \rightleftharpoons C_5H_5 + CO$ as the only consumption route.

The significant activation energy of this decomposition reaction (about 44 kcal mol^{-1}) contrasts with fast reactions expected for phenoxy radical consumption. A kinetic model considering phenoxy radical consumption only through reaction R20 hugely overestimates C_6H_5O maximum mole fraction, as depicted in figure 4.23. To the best of our knowledge, it is the first time that phenoxy radical predictions are compared to experimental measurements in lean benzene flames. These measurements confirm the hypothesis of Shandross and co-workers [83], stressing that phenoxy radical may be overestimated by current kinetic models. This comparison obviously demonstrates that additional consumption routes should compete with phenoxy radical decomposition into $C_5H_5 + CO$. Similarly to propargyl, cyclopentadienyl and benzyl radicals, C_6H_5O is resonantly stabilized and is therefore less reactive to non radical compounds such as O_2 . Consequently, its additional consumption channels should mainly include reactions with radical species present in significant concentrations, as H and O atoms or OH radical.

(ii) *Phenoxy radical reaction with H atoms*

To the best of our knowledge, the study of Buth and co-workers [137] is the only devoted to experimental analysis of phenoxy radical reactions with H and O atoms. In 1994, authors experimentally investigated these reactions at low pressure and room temperature, and studied reaction

products and rate constants of each channel. Since these experiments focus on recombination reactions which are temperature independent and were conducted at low pressure, results are to some extent quantitatively and qualitatively applicable to the present work.

Concerning the $C_6H_5O + H$ recombination reaction, Buth and co-workers pointed up that it might produce either phenol (C_6H_5OH) or cyclohexadienone (C_6H_6O), because phenoxy radical has 4 resonant forms: one oxygen centered radical and three carbon centered radicals. Authors measured a global value for the $C_6H_5O + H$ reaction but were unable to determine the exact branching ratio between both product channels. However, many experimental and theoretical studies (see [136] and references therein) demonstrated that the unpaired electron is significantly delocalized from the oxygen atom onto the carbon ring. Consequently, one postulates that reaction $C_6H_5O + H$ forms cyclohexadienone rather than phenol.

This assumption agrees with the low maximum mole fraction measured by MBMS at an m/z ratio corresponding to C_6H_5OH in BF07. Indeed, if one considers that reaction $C_6H_5O + H$ produces C_6H_5OH as do many other kinetic models, its mole fraction is about 20 times overestimated. Moreover, since phenol consumption mainly yields back the phenoxy radical, a loop between phenoxy radical and phenol formation would appear, decreasing the rate of benzene consumption. This phenomenon occurs in the RH model and the underestimation of the benzene consumption rate has been presented in figure 4.15 on page 113. Nevertheless, substituting phenol by C_6H_6O in the $C_6H_5O + H$ reaction still yields to an overestimation of mole fraction measurements at $m/z = C_6H_5OH$, as both compounds have the same mass. Therefore, the fast C_6H_6O production by $C_6H_5O + H$ reaction should be balanced by rapid cyclohexadienone consumption reactions, forming other compounds than phenol or phenoxy radical.

To the best of our knowledge, no experimental investigation on high temperature cyclohexadienone reactions have been reported into the literature. Consequently, in figure 4.24 one proposes three potential channels

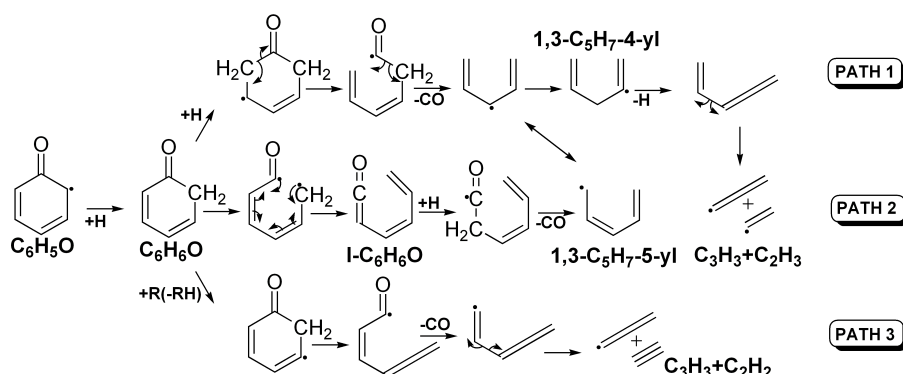


Figure 4.24: Potential pathways of cyclohexadienone consumption

to consume C_6H_6O . The first involves an H atom addition onto the sp^2 carbon atom vicinal to the CO group of cyclohexadienone, followed by a CC bond cleavage and a carbon monoxide expulsion, forming a linear and resonantly stabilized C_5H_7 radical. After an H atom migration, this radical can perform a beta scission, forming a linear C_5H_6 hydrocarbon that might dissociate into propargyl and vinyl radicals. This C_5H_7 radical is already suspected to be a key intermediate of propargyl radicals formation in cyclopentene combustion [138, 139]. Moreover, it is a resonantly stabilized radical and these compounds are generally admitted to play an important role in combustion chemistry. This first path of figure 4.24 has already been suggested to properly model C_2H_4 formation in anisole thermolysis experiments by Arends and co-workers [140].

The second route involves cyclohexadienone isomerization to cis-1,3-butadienyl-4-ketene. Hydrogen atom addition on the sp^2 carbon atom of the ketene group, followed by a CC bond cleavage, produces the same linear C_5H_7 radical as in the first route of figure 4.24. Therefore, the second path may produce propargyl and vinyl radicals, as the first channel. Cyclohexadienone isomerization to 1,3-butadienyl-4-ketene has been shown to be energetically achievable by a few groups [105, 141, 142] and butadienylketene has been experimentally observed in benzene oxidation experiments by Parker and co-workers [121].

Finally, the last path of figure 4.24 involves an H atom abstraction reaction in beta of the sp^3 carbon atom of cyclohexadienone, followed

by the ring opening and the loss of a carbon monoxide forming a linear C_5H_5 radical. Then, this radical might dissociate into acetylene and propargyl radicals. This last dissociation process is already known to play a key role in cyclopentadienyl radical dissociation to acetylene and propargyl radicals [143, 144].

Each channel presented above yields propargyl radical that is underestimated in both BF07 and BF10. Consequently, their inclusion into the kinetic model might improve both propargyl and phenoxy radicals predictions. As kinetic parameters of these 3 pathways are mostly unknown, the overall reaction R21 ($C_6H_5O + H \rightleftharpoons C_3H_3 + C_2H_3 + CO$, see table 4.6 on page 124) has been introduced in our kinetic model. It corresponds to paths 1 and 2 of figure 4.24 and considers that cyclohexadienone consumption is faster than its production from phenoxy radical recombination to H atom, as discussed above. Rate parameters of reaction R21 are fixed to measurements of Buth and co-workers for phenoxy radical reaction with hydrogen atom [137]. Whereas reaction R21 is non elementary, one shows that pathways linking phenoxy radical to propargyl radical might exist and that further studies on cyclohexadienone consumption are clearly needed in order to throw light on kinetics of the phenoxy radical in flames.

(iii) Phenoxy radical reaction with O atoms

Concerning the $C_6H_5O + O$ recombination reaction, Buth and co-workers [137] expected two different product channels, as for the recombination with an H atom. They suggested that carbon and oxygen centered forms of phenoxy radical react with oxygen atom forming benzoquinone + H and $C_5H_5 + CO_2$, respectively. Since they did not observed significant carbon dioxide formation, authors concluded that the benzoquinone channel should dominate. This assumption is confirmed by studies on the localization of the unpaired electron of phenoxy radical, as mentioned above. However, as discussed previously, benzoquinone mole fraction is low in benzene flames and its degradation paths, experimentally determined by Alzueta and co-workers [90], are not fast enough to consume a formation flux coming from $C_6H_5 + O_2$ or $C_6H_5O + O$. This observa-

tion is confirmed by the theoretical investigation of Lin and Mebel [145] who calculated a rate constant for $C_6H_5O + O \rightleftharpoons C_6H_4O_2 + H$ about 100 times slower than that measured experimentally by Butth and co-workers [137]. Benzoquinone is therefore not the main product of this reaction and other pathways should exist. Reaction $C_6H_5O + O$ may be connected to the potential energy surface of the $C_6H_5 + O_2$ reaction described in section 4.3.2 and postulated to give $n\text{-}C_4H_5 + 2CO$. Considering that $n\text{-}C_4H_5$ may undergo a beta scission into $C_2H_2 + C_2H_3$, the reaction R22 ($C_6H_5O + O \rightleftharpoons C_2H_2 + C_2H_3 + 2CO$, see table 4.6 on page 124) has been introduced into the kinetic model. This overall process is similar to reaction 4.2 on page 81, whose importance has been highlighted by Fujii and co-workers [63] and McLain and co-workers [64].

Comparison between predicted and experimental results

Figure 4.25 compares predictions of present and RH models to C_6H_5O measurements performed in BF07 and in the flame of Yang and co-workers [95], which has a composition close to BF18. The model developed in this work, as well as that of Richter and Howard [92], overestimates maximum mole fractions of phenoxy radical by a factor equal to or greater than 10. As both models include C_6H_5O dissociation into

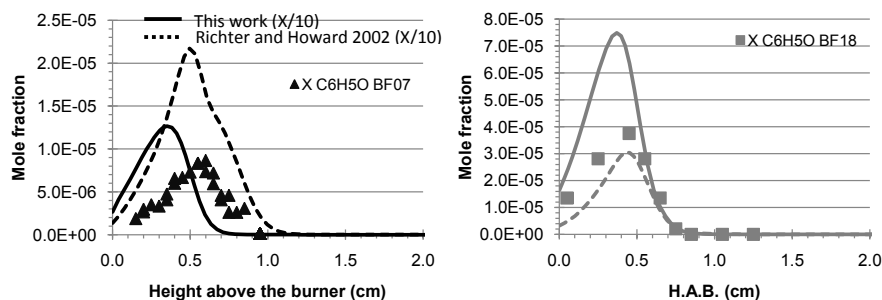


Figure 4.25: experimental and predicted mole fraction profiles at m/z corresponding to C_6H_5O . Gray scale symbols represent experiment (Δ BF07 (this work), $\square$ BF18 (Yang and co-workers [95])). Solid and dashed curves stand for predictions of the present and the Richter and Howard [92] models, respectively.

$C_5H_5 + CO$ and C_6H_5O reactions with H and O atoms, with same kinetic parameters, predicted results are of similar magnitude. In BF07, the position of the C_6H_5O maximum mole fraction predicted by the kinetic model developed in this work is shifted towards the burner surface. This observation indicates that phenoxy radical formation pathways may still be overestimated in the present model.

A comparative reaction rate analysis allows to detect reactions that are significantly involved in phenoxy radical consumption. Results are summarized in figure 4.26 that indicate contributions of each major channel. In lean and stoichiometric flames, C_6H_5O is mainly consumed through reactions R21 and R22, giving $C_2H_3 + C_3H_3 + CO$ and $C_2H_2 + C_2H_3 + 2CO$, respectively. The high contribution of reactions R21 and R22 stresses the importance of their inclusion into kinetic models devoted to aromatic oxidation. Mechanisms that do not consider them overestimate phenoxy radical mole fraction far more than our model or that of Richter and Howard [92]. For example, the model of Ristori and co-workers [22] overestimates C_6H_5O by a factor close to 100 in BF07. In BF18 and BF20, phenoxy radical decomposition into cyclopentadienyl radical and carbon monoxide becomes the main reaction channel. This change is due to higher flame temperatures in BF18 and BF20, com-

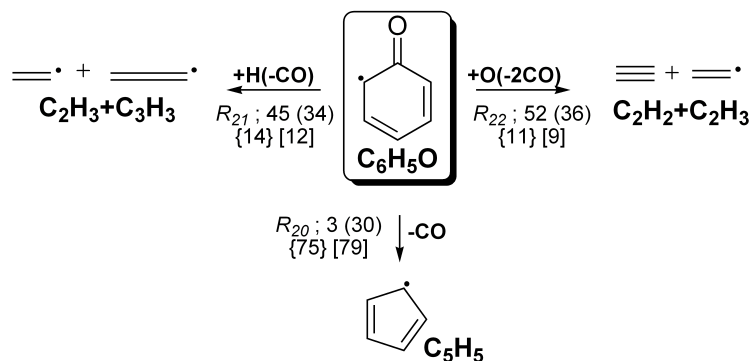


Figure 4.26: summary of phenoxy radical consumption pathways included into the developed kinetic model. Percentages represent contribution of each reaction in BF07, (BF10), {BF18} and [BF20]

pared to BF10 and BF07, which allow to more easily cross its activation barrier.

In the RH model, products of the $C_6H_5O + H$ and the $C_6H_5O + O$ reactions are respectively C_6H_5OH and $C_6H_4O_2$, rather than $C_3H_3 + C_2H_3 + CO$ and $C_2H_3 + C_2H_2 + 2CO$ in this work. The new set of products proposed in this study seems more convenient for kinetic modeling of phenoxy radical consumption in flames, as the C_6H_5O mole fraction profile is a factor 2 lower than that of Richter and Howard in BF07 (see figure 4.25). Moreover, reactions used in the RH model lead to a huge overestimation of the benzoquinone maximum mole fraction, similar to that presented in figure 4.18. As mentioned previously, a loop between phenoxy radical and phenol formation equally occurs in the RH model. It is responsible of the slow decrease of the C_6H_5O mole fraction depicted in figure 4.25. Compared to the present mechanism, the better prediction of C_6H_5O by the RH model in BF18 (see the right part of figure 4.25) comes from the high overestimation of phenyl radical consumption into $C_6H_4 + H$, highlighted in the previous section. This overestimation decreases the phenoxy radical formation through $C_6H_5 + O_2 \rightleftharpoons C_6H_5O + O$ and therefore artificially leads to a better C_6H_5O prediction in BF18.

4.3.4 The phenol sub-model

Phenol formation pathways

In benzene flames, phenol is only produced from OH addition onto the benzene ring, followed by a hydrogen atom elimination, giving $C_6H_5OH + H$ (reaction R10, see table 4.4 on page 109). Compared to other kinetic models, the present work considers that reactions of O atom with benzene and H atom with phenoxy radical do not produce phenol, but $C_6H_5O + H$ and $C_3H_3 + C_2H_3 + CO$, respectively. These reaction channels have been presented in previous sections (see reactions R8 and R21 in table 4.4 on page 109 and table 4.6 on page 124, respectively).

Phenol consumption pathways

A few high temperature investigations on phenol reactions have been reported into the literature. C_6H_5OH can either isomerize, decompose or undergo H abstraction reactions, as presented hereafter.

(i) Phenol isomerization and decomposition routes

In 1998, Horn and co-workers [147] investigated phenol decomposition in shock tubes and found that H , CO and C_5H_6 are major products. Since the breaking of the phenol OH bond through reaction R23 of table 4.7 gives H atom and phenoxy radical, which in turn can dissociate into $C_5H_5 + CO$, authors concluded that this reaction should play a key role in phenol decomposition. However, they noticed that CO formation was faster than H atom production and therefore assumed that phenol undergoes another decomposition reaction R24.

In 2003 and 2006, Zhu and Bozzelli [141] and Xu and Lin [142] theoretically investigated phenol decomposition and confirmed the previous assumption of Horn and co-workers. By studying the potential energy surface of C_6H_5OH (see figure 4.27), authors showed that phenol can either break its OH bond yielding phenoxy radical and H atom or tautomerize to cyclohexadienone (C_6H_6O) which can open into cis-1,3-butadienyl-4-

Table 4.7: C_6H_5OH consumption reactions included into the kinetic model.

Reactions		$k = AT^n e^{-E_a/RT}$			Refs.
		A^a	n	Ea^a	
Isomerization and decomposition reactions					
R23	$C_6H_5OH+M \rightarrow C_6H_5O+H+M$ (k_∞)	$3.33 \cdot 10^{17}$	-0.5	91.6	[142]
	$C_6H_5OH+M \rightarrow C_6H_5O+H+M$ (k_0)	$1.54 \cdot 10^{118}$	-28.2	125.9	[142]
R24	$C_6H_5OH \rightleftharpoons C_5H_6+CO$	$8.62 \cdot 10^{15}$	-0.6	74.1	[142]
Reactions with O atom, H atom and OH radical					
R25	$C_6H_5OH+H \rightleftharpoons C_6H_5O+H_2$	$1.15 \cdot 10^{14}$	0	12.4	[146]
R26	$C_6H_5OH+OH \rightleftharpoons C_6H_5O+H_2O$	$6 \cdot 10^{12}$	0	0	[146]
R27	$C_6H_5OH+O \rightleftharpoons C_6H_5O+OH$	$2.81 \cdot 10^{13}$	0	7.3	[78]

^a A units are s^{-1} and $cm^3 \text{ mol}^{-1} s^{-1}$ for Unimolecular and bimolecular reactions, respectively. E_a is expressed in kcal mol^{-1} .

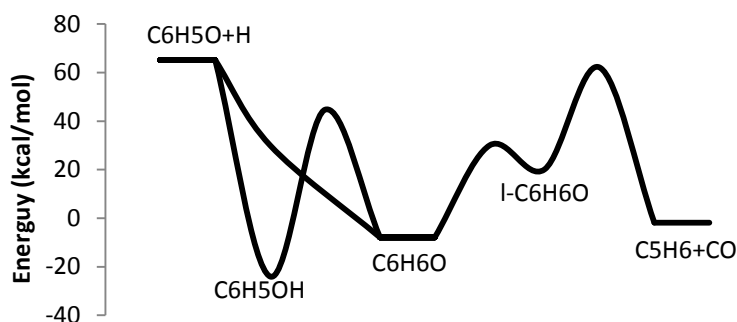


Figure 4.27: potential energy surface of the $C_6H_5O + H$ reaction [142]

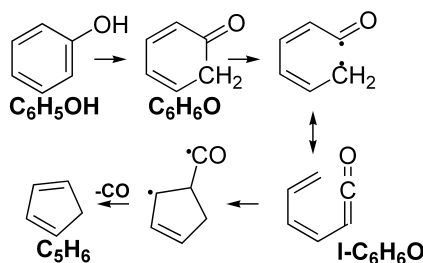


Figure 4.28: mechanism of phenol dissociation into $C_5H_6 + CO$

ketene ($l-C_6H_6O$). Subsequently, $l-C_6H_6O$ can form a 5 membered ring and eliminate a carbon monoxide molecule, yielding cyclopentadiene as depicted in figure 4.28. Rate constants calculated by Xu and Lin have been included into the kinetic model for both decomposition pathways (reactions R23 and R24 of table 4.7 on the facing page).

Concerning the potential energy surface of phenol depicted in 4.27, it first confirms that the previously hypothesized cyclohexadienone formation from phenoxy radical recombination with H atom is achievable from an energy point of view. Secondly, it shows that cyclohexadienone is a key intermediate of phenol isomerization to cyclopentadiene and CO and that this reaction should be included into kinetic models. However combustion conditions are somewhat different than pyrolysis conditions and the radical pool may react with cyclohexadienone or cis-1,3-butadienyl-4-ketene before they isomerize into cyclopentadiene and CO , forming $C_3H_3 + C_2H_3 + CO$ as postulated in the previous section.

(ii) *Phenol reactions with H atom, with O atom and with OH radical*

In 1988, He and co-workers found that H atom and OH radical react with phenol either via abstraction of the phenolic hydrogen atom or the displacement of the OH group [146]. Rate constant measurements of He and co-workers have been added into the present kinetic scheme for H abstractions with H and OH (reactions R25 and R26 of table 4.7 on page 132, respectively). The hydroxyl radical displacement by H atom, giving benzene+ OH , has not been previously included since it is the reverse of reaction R10 (see table 4.4 on page 109). The rate constant estimated by Emdee and co-workers [78] for phenolic H abstraction by O atom (reaction R27) is used in the present study.

Comparison between predicted and experimental results

Figure 4.29 compares numerical predictions of present and RH models to experimental measurements of this work. In BF07, BF10 and BF20, the RH model overestimates phenol maximum mole fraction by a factor comprised between 5 and 10. Moreover, the RH model is unable to reproduce phenol consumption in burnt gases of BF07 and BF10, due to the loop between phenoxy radical and phenol formation discussed earlier. Compared to the RH model, the mechanism developed in this work therefore brings a significant improvement. The better predictive capability of our kinetic model gives evidence that reactions between phenoxy radical and H atom and between O atom and benzene should not produce phenol, as their inclusion into a kinetic model leads to a high overestimation of its maximum mole fraction over a wide range of equivalence ratios. This observation agrees with the recent work of Taatjes and co-workers [123] who stressed that whereas contribution of $C_6H_6 + O \rightleftharpoons C_6H_5OH$ is prevalent between 300 and 900K, it becomes lower than that of $C_6H_6 + O \rightleftharpoons C_6H_5O + H$ at higher temperatures, such as those measured in our flames.

Reactions significantly active in phenol consumption have been determined by a comparative reaction rate analysis and percentages of their

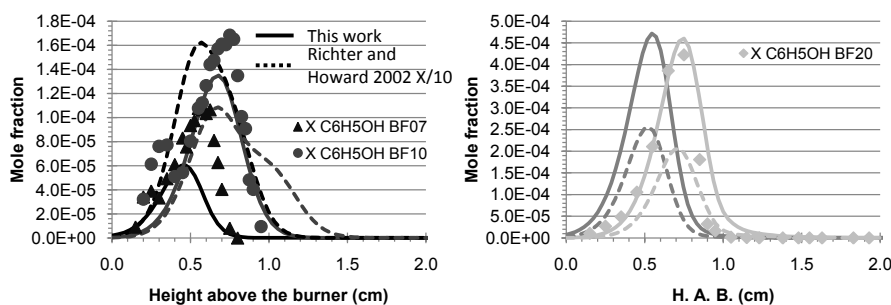


Figure 4.29: experimental and predicted mole fraction profiles of phenol (C_6H_5OH). Gray scale symbols represent experiments ($\triangle$ BF07, $\circ$ BF10, $\diamond$ BF20). Solid and dashed curves stand for predictions of present and Richter and Howard [92] models, respectively. Predictions of the RH model are divided by a factor 10.

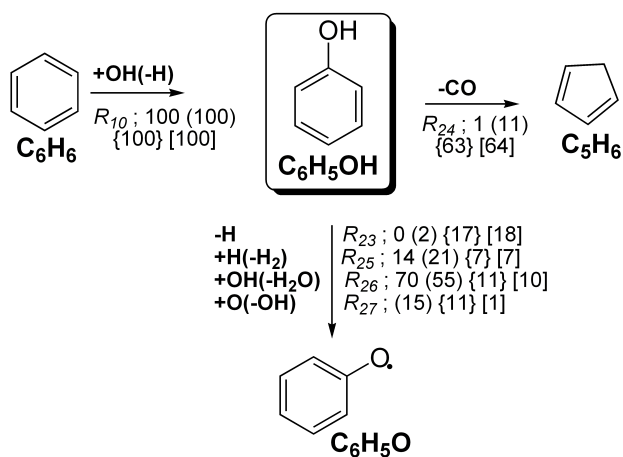


Figure 4.30: summary of phenol consumption pathways included into the developed kinetic model. Percentages represent contribution of each reaction in BF07, (BF10), {BF18} and [BF20]

contributions are summarized into figure 4.30. Since H atom displacement on benzene by OH radical, giving $C_6H_5OH + H$, is the only phenol formation route of the kinetic model, reaction R10 has a contribution of 100% in each investigated flame. In BF07 and BF10, phenol is mainly consumed through abstraction of the phenolic hydrogen atom, giving phenoxy radical (reactions R25, R26 and R27). The overall contribution of decomposition routes are only 1 and 13%, respectively. Compared to BF07 and BF10, contributions of these channels become major in BF18 and BF20, as highest flame temperatures allow to easily overcome their significant activation barriers. Contribution of phenol decomposition into cyclopentadiene and CO (reaction R24) is always greater than dissociation to phenoxy radical and H atom (reaction R23), confirming experimental findings of Horn and co-workers [147].

4.3.5 The fulvene sub-model

Fulvene formation pathways

As discussed in previous sections, benzene isomerization can produce fulvene ($f\text{-}C_6H_6$) that can decompose into propargyl radicals (see reactions R1, R2 and R3 of table 4.4 on page 109). By analyzing contributions of all benzene consumption channels, we pointed up that reactions R1, R2 and R3 were all proceeding backward, indicating that under experimental conditions of this work, fulvene is formed by propargyl radicals (C_3H_3) self-recombination and isomerizes into benzene.

Fulvene consumption pathways

They are numerous fulvene decomposition pathways leading to various C_5 , C_4 , C_3 , C_2 and C_1 chemical species, as depicted in figure 4.31. In 1990 Yokoyama and co-workers showed that one of primary fragmentation channels of benzene photodissociation is $C_5H_3 + CH_3$ [148] and in 1997 Mebel and co-workers theoretically studied the mechanism of benzene dissociation into these fragments [109]. They found that fulvene is

a key intermediate of benzene photodissociation and that 2 isomers of C_5H_3 can be formed: $n-C_5H_3$ and $i-C_5H_3$, as shown in the lower part of figure 4.31. In 1992, Miller and Melius proposed that propargyl radicals (C_3H_3) self recombination can produce fulvene, isomerizing to benzene. Later, Miller and Klippenstein in 2003 calculated the potential energy surface linking C_6H_6 to $f-C_6H_6$ and C_3H_3 , along with kinetic parameters of major reaction channels [97].

Pathways connecting fulvene to C_3H_3 are summarized into the highest part of figure 4.31. In 2000 Pope and Miller developed a kinetic sub-model summarizing reactions linking fulvene to $i-C_5H_3$, $n-C_5H_3$ and C_3H_3 radicals and proposed new channels connecting some intermediates to isomers of C_4H_3 and C_4H_5 radicals [149], as described in figure

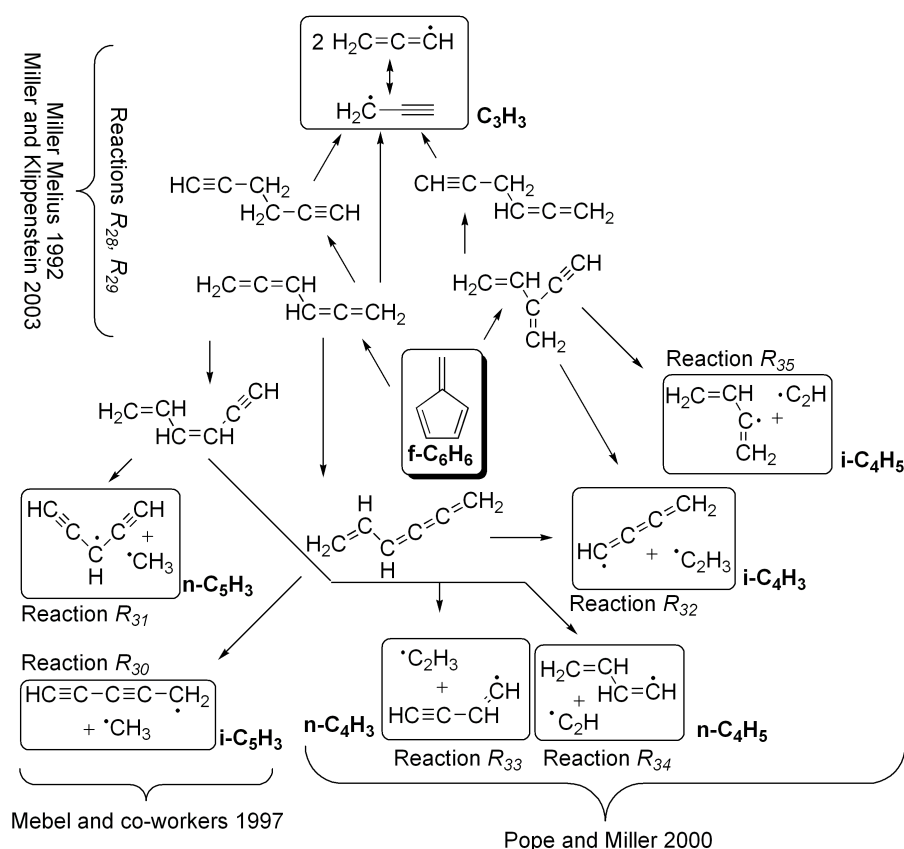


Figure 4.31: Main decomposition pathways of fulvene ($f-C_6H_6$).

Table 4.8: f- C_6H_6 consumption reactions included into the kinetic model.

Reactions		$k = AT^n e^{-Ea/RT}$			
		A^a	n	Ea^a	Refs.
Isomerization and decomposition reactions.					
R28	$C_3H_3 + C_3H_3 \rightleftharpoons f\text{-}C_6H_6$	$2.34 \cdot 10^{69}$	-17.02	25.8	[97] ^b
R29	$C_3H_3 + C_3H_3 \rightleftharpoons f\text{-}C_6H_6$	$1.74 \cdot 10^{44}$	-10.31	8	[97] ^b
R30	$i\text{-}C_5H_3 + CH_3 \rightleftharpoons f\text{-}C_6H_6$	$1.4 \cdot 10^{13}$	0	0	[149]
R31	$n\text{-}C_5H_3 + CH_3 \rightleftharpoons f\text{-}C_6H_6$	$1.0 \cdot 10^{13}$	0	0	[149]
R32	$i\text{-}C_4H_3 + C_2H_3 \rightleftharpoons f\text{-}C_6H_6$	$5.0 \cdot 10^{12}$	0	0	[149]
R33	$n\text{-}C_4H_3 + C_2H_3 \rightleftharpoons f\text{-}C_6H_6$	$4.0 \cdot 10^{12}$	0	0	[149]
R34	$n\text{-}C_4H_5 + C_2H \rightleftharpoons f\text{-}C_6H_6$	$4.0 \cdot 10^{12}$	0	0	[149]
R35	$i\text{-}C_4H_5 + C_2H \rightleftharpoons f\text{-}C_6H_6$	$1.0 \cdot 10^{13}$	0	0	[149]
R36	$f\text{-}C_6H_5(1) + H \rightleftharpoons f\text{-}C_6H_6$	$3.88 \cdot 10^{13}$	0.2	0	[127]
R37	$f\text{-}C_6H_5(2) + H \rightleftharpoons f\text{-}C_6H_6$	$9.79 \cdot 10^{13}$	0.15	0	[127]
Reactions with <i>H</i> atom.					
R38	$f\text{-}C_6H_5(1) + H_2 \rightleftharpoons f\text{-}C_6H_6 + H$	$2.14 \cdot 10^4$	2.5	6.9	[127]
R39	$f\text{-}C_6H_5(2) + H_2 \rightleftharpoons f\text{-}C_6H_6 + H$	$1.31 \cdot 10^4$	-1.3	30.8	[127]
R40	$f\text{-}C_6H_6 + H \rightleftharpoons C_5H_5CH_2$	$1.52 \cdot 10^{14}$	0	6.4	[127]
R41	$f\text{-}C_6H_6 + H \rightleftharpoons C_5H_4CH_3$	$1.7 \cdot 10^{12}$	2	0	[127]
R42	$f\text{-}C_6H_5(1) \rightleftharpoons C_6H_5$	$1.17 \cdot 10^{13}$	0	30.0	[127]

^a A units are s^{-1} and $cm^3 \text{ mol}^{-1} s^{-1}$ for Unimolecular and bimolecular reactions, respectively. Ea is expressed in kcal mol^{-1} .

^b These two reactions correspond to the two pathways linking fulvene to C_3H_3 presented in figure 4.31.

4.31. In 2006, the presence of C_4H_3 , C_4H_5 and C_5H_3 isomers in flames has been demonstrated by Hansen and co-workers and Yang and co-workers [150–152], confirming that channels proposed by Pope and Miller might be active [149]. Very recently, Lories and co-workers developed a kinetic sub-mechanism for phenyl decomposition (see paragraph 4.3.2 on page 115) and showed that C_6H_5 can isomerize into a dehydrofulvene radical that can subsequently abstract a hydrogen atom to another compound forming fulvene.

The developed kinetic model uses rate parameters of Miller and Klippenstein for fulvene decomposition into C_3H_3 radicals and isomerization to benzene [97] (see reactions R28 and R29 of table 4.8 and reaction R1 of table 4.4 on page 109). The kinetic sub-models of Pope and Miller [149] is used for fulvene degradation into C_4 and C_5 hydrocarbons, as depicted

in reactions R30 to R35 of table 4.8 on the facing page). Reactions connecting fulvene to either dehydrofulvene isomers (reactions R36 to R39) or C_6H_7 isomers (reactions R40 and R41) come from the sub-model developed by Lories [127]. Chemistry of C_6H_7 isomers will be discussed in the following section.

Comparison between predicted and experimental results

As fulvene is highly reactive, its observation by Gas Chromatography was not possible. Moreover, since it has the same mass than benzene, the measurement of its mole fraction profile using MBMS could equally not be achieved. Fortunately, Yang and co-workers have recently estimated the maximum mole fraction of fulvene to $5.0 \cdot 10^{-5}$ by studying a benzene-oxygen-argon flame with a composition close to BF18 using a tunable synchrotron [95]. Figure 4.32 compares this value to fulvene mole fraction profiles predicted for BF18 using present and RH kinetic models. It shows that our mechanism has a better predictive capability than that of Richter and Howard. Nevertheless, more reliable fulvene mole fraction measurements are necessary to assess improvements brought by the developed kinetic model. A comparative reaction rate analysis allows to identify major reaction pathways involved in fulvene flame chemistry and to determine their contributions to its formation or consumption (see figure 4.33).

Over the entire range of equivalence ratio, fulvene is formed through propargyl recombination (see reactions R28 and R29 of table 4.8). In the lean BF07 and the stoichiometric BF10 flames, reaction R41 that involves an H atom addition onto fulvene, giving 5-methylcyclopentadiene ($C_5H_4CH_3$), is the most important consumption channel. However, fulvene maximum mole fraction is very low (about $1 \cdot 10^{-7}$) and its reactions should not highly influence benzene combustion. In BF18 and BF20, reactions R41, R40, R32 and R38 compete and produce $C_5H_4CH_3$, 5-methylenecyclopentadiene ($C_5H_5CH_2$), $i-C_4H_3 + C_2H_3$ and dehydrofulvene (f- $C_6H_5(1)$), respectively. Whereas fulvene maximum mole fraction is somewhat higher than in BF07 and BF10, fulvene is still a minor

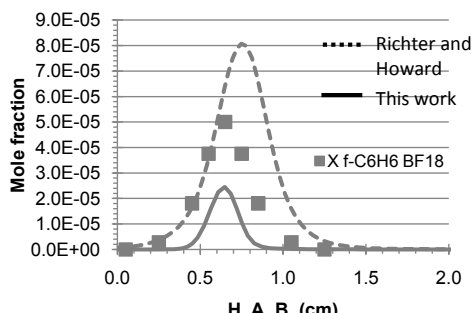


Figure 4.32: predicted and experimentally estimated fulvene maximum mole fraction of Yang and co-workers in a benzene-oxygen-argon flame with a composition close to BF18 [95]. The gray scale symbol represents experiment and solid and dashed curves stand for predictions of present and Richter and Howard [92] models, respectively.

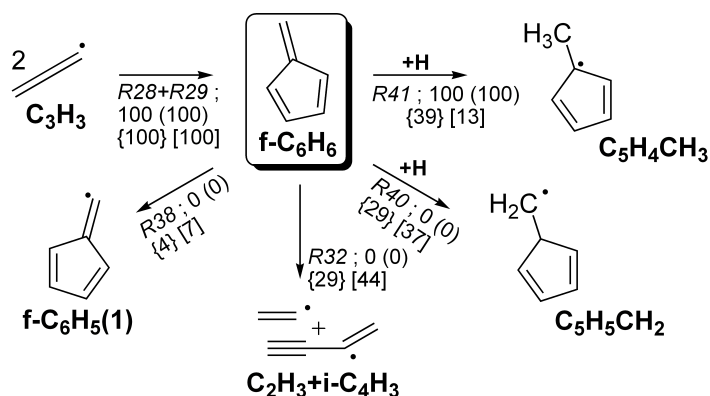


Figure 4.33: summary of fulvene consumption pathways included into the developed kinetic model. Percentages represent contribution of each reaction in BF07, (BF10), {BF18} and [BF20]

intermediate of benzene combustion. This observation contrasts with the key role played by fulvene for benzene formation in other hydrocarbon flames. $f\text{-C}_6\text{H}_5(1)$ isomerizes into phenyl radical through reaction R42. $\text{C}_5\text{H}_4\text{CH}_3$ and $\text{C}_5\text{H}_5\text{CH}_2$ radicals are intermediates of the cyclohexadienyl radical (C_6H_7) consumption, which will be discussed hereafter.

Figure 4.34: main decomposition pathways of cyclohexadienyl radical (c- C_6H_7).

their work, authors successfully developed a kinetic mechanism based on their previous rate coefficient calculations to model their measurements. In 1984 and 2001, Louw and co-workers [159] and van Scheppingen [160] and co-workers experimentally investigated benzene hydrogenolysis at high pressure and showed that methane is a major product, indicating that the route forming benzene from cyclopentadienyl and methyl radicals can proceed backward under certain conditions. From figure 4.34 summarizing reactions of the C_6H_7 potential energy surface, it is clear that if not produced from benzene, cyclohexadienyl radical should be formed from 5-methylenecyclopentadiene ($C_5H_5CH_2$) isomerization. This last radical may either be formed by the H atom addition to fulvene, discussed in the previous section, or by dehydrogenation reactions of methylcyclopentadiene. In the present kinetic model, rate coefficients of the reactions between cyclopentadienyl and methyl radicals, giving methylcyclopentadiene and 5-methylcyclopentadiene radical ($C_5H_4CH_3$) + H atom, as well as their subsequent reactions towards $C_5H_5CH_2$ formation, have been added from the theoretical work of Sharma and Green [157] (see reactions R44 to R46 of table 4.9). Kinetic parameters of the isomerization of $C_5H_5CH_2$ and $C_5H_4CH_3$ radicals into c- C_6H_7 are taken from the work of Dubnikova and Lifshitz [154] (see reactions R43 and R47). Finally, rate constants of Lories and co-

Table 4.9: c- C_6H_7 formation reactions included into the kinetic model.

Reactions		$k = AT^n e^{-E_a/RT}$			Refs.
		A^a	n	Ea^a	
Reactions linking $C_5H_5CH_2$ to $C_5H_5 + CH_3$.					
R43	$C_5H_4CH_3 \rightleftharpoons C_5H_5CH_2$	$3.0 \cdot 10^{12}$	0	50.4	[154]
R44	$C_5H_5+CH_3 \rightarrow C_5H_5CH_3$	$1.11 \cdot 10^{-51}$	16	-74.1	[157]
-R44	$C_5H_5CH_3 \rightarrow C_5H_5 + CH_3$	$5.21 \cdot 10^{76}$	-19	88.8	[157]
R45	$C_5H_5CH_3 \rightleftharpoons C_5H_4CH_3+H$	$6.5 \cdot 10^{77}$	-20	93.2	[157]
R46	$C_5H_5+CH_3 \rightleftharpoons C_5H_4CH_3+H$	$6.4 \cdot 10^{15}$	-0.5	10.7	[157]
Isomerization reactions.					
R47	$C_5H_5CH_2 \rightleftharpoons C_6H_7$	$1.4 \cdot 10^{13}$	0	17.4	[154]

^a A units are s^{-1} and $cm^3 \text{ mol } s^{-1}$ for unimolecular and bimolecular reactions, respectively. E_a is expressed in kcal mol^{-1} .

workers [127] were taken for H addition to fulvene, as discussed in previous section (see reactions R38 and R39 of table 4.8 on page 138).

Cyclohexadienyl radical consumption pathways

As discussed in section 4.3.1 devoted to benzene reactions, cyclohexadienyl radical is decomposed into benzene and H atom through reaction -R6 of table 4.4 on page 109.

Comparison between predicted and experimental results

Unfortunately, cyclohexadienyl radical has not been detected using our experimental setup and no measurements are available into the literature. A comparative reaction rate analysis of reaction channels presented into figure 4.34 shows that H atom addition to fulvene producing $C_5H_5CH_2$ and $C_5H_4CH_3$ radicals, followed by isomerization into cyclohexadienyl radical are the main formation pathways. In flames presented in this chapter, methyl and cyclopentadienyl radicals recombination is found to be insignificant. Although benzene formation through this pathway is negligible in BF07, BF10, BF18 and BF20, it will be interesting to determine its contribution into toluene-oxygen-argon flames presented in the following chapter.

4.3.7 The cyclopentadienyl radical sub-model

In previous sections we have examined benzene consumption into C_6H_x intermediates and found that three main channels consume benzene: phenyl radical formation, phenoxy radical production and conversion to phenol (see paths 1, 2 and 3 of figure 4.35). We have stressed that C_5H_5 is a product of all these routes and that it might also be involved in benzene formation through recombination with methyl radical. Therefore, C_5H_5 is a central intermediate of benzene combustion and kinetics of its consumption is of particular importance in models describing aromatic oxidation.

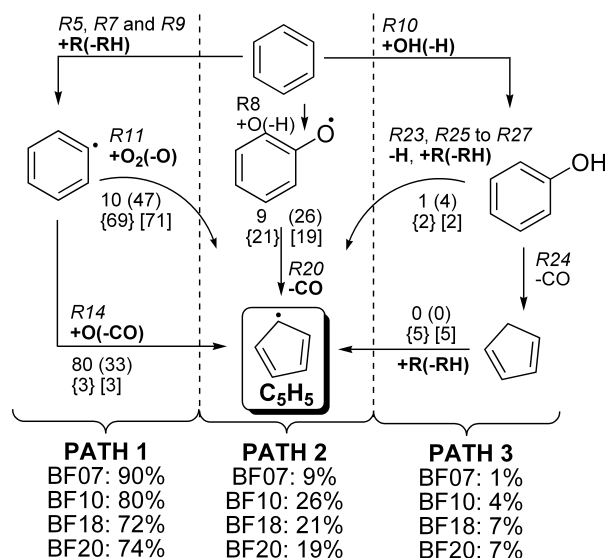


Figure 4.35: the three main cyclopentadienyl radical formation routes that compete over the investigated range of equivalence ratios. Percentages represent contribution of each pathway in BF07, (BF10), {BF18} and [BF20]

Cyclopentadienyl formation pathways

Figure 4.35 highlights that the 3 pathways cited above compete in cyclopentadienyl radical formation and that path 1 is prevalent on path 2 and 3 over the investigated range of equivalence ratio. Whereas *O* atom concentrations are highest in BF07, path 2 involving *O* atom addition on benzene is not stimulated compares to higher equivalence ratios. The reason is the lowest flame temperature of BF07 which prevents an easy crossing of the energy barrier of the decomposition reaction R20 (see figure 4.35 and table 4.6 on page 124). Since BF10 has a lower oxygen atom content and a higher flame temperatures than BF07, contribution of path 1 and 2 respectively decreases from 90 to 80% and increases from 9 to 26%. Under rich conditions, the lowest oxygen atom content causes contribution of path 2 to decrease until 21 and 19% in BF18 and BF20, respectively. Over the investigated range of equivalence ratios, contribution of path 3 to cyclopentadienyl formation is always minor. It is maximal in BF20 where highest flame temperatures stimulate reaction

R24, decomposing phenol into cyclopentadiene and CO (see figure 4.35 and table 4.7 on page 132).

Cyclopentadienyl consumption pathways

To the best of our knowledge there are only few works devoted to cyclopentadienyl radical consumption in the literature. However, kinetics of pyrolysis and oxidation of its parent molecule C_5H_6 have been experimentally investigated by several researchers [143, 144, 161–164] and theoretically studied by a few groups [165–168]. As depicted in figure 4.36, it is now well admitted that C_5H_5 consumption is mainly achieved through its recombination with H atom giving C_5H_6 , its dissociation into acetylene and propargyl radicals (C_3H_3) and its reaction with O atom yielding cyclopentadienoxo radical (C_5H_5O). These pathways are described hereafter.

(i) Cyclopentadienyl radical isomerization and decomposition

In 1998 Roy and co-workers [143] and Kern and co-workers [144] experimentally investigated cyclopentadiene pyrolysis in shock tubes and found that major products are propargyl radicals and acetylene. They measured reaction rates of cyclopentadiene decomposition into $C_5H_5 + H$

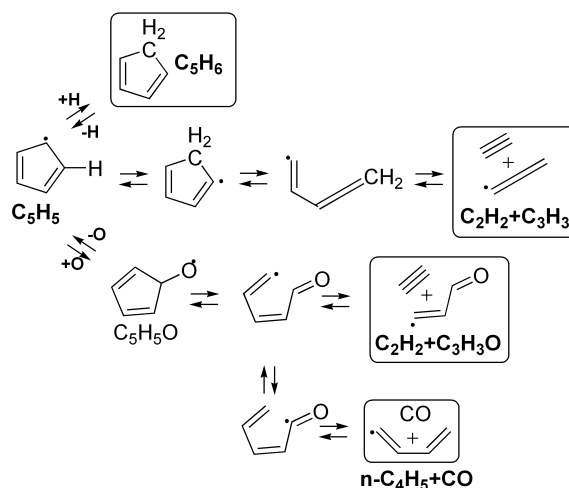


Figure 4.36: Mechanism of cyclopentadienyl radical decomposition

and further dissociation reactions of C_5H_5 . Both groups proposed that C_5H_5 decomposition occurs through an H atom migration reaction, followed by the ring opening and a CC bond fission giving acetylene and propargyl radicals, as depicted in figure 4.36 and summarized by reaction R48 of table 4.10.

Since only Kern and co-workers measured the rate of C_5H_5 decomposition at various pressure and determined k_0 and k_∞ , one has chosen to include their rate parameters into the present kinetic model. This reaction is not considered as reversible in our mechanism because it is not elementary and its reverse reaction cannot be calculated using its equilibrium constant. Therefore, one included a rate expression calculated by Moskaleva and Lin [169] at 133 mbar for the $C_2H_2 + C_3H_3$ recombination giving cyclopentadienyl radical (see reaction -R48).

(ii) *Cyclopentadienyl radical reaction with H atom*

Beside this dissociation channel, C_5H_5 can recombine with H atom forming cyclopentadiene (C_5H_6) (see reaction R49). Together with reaction R24 (see table 4.7 on page 132) of phenol decomposition, reaction R49 is the only cyclopentadiene formation route. Rate constants k_0 and k_∞

Table 4.10: C_5H_5 consumption reactions included into the kinetic model.

Reactions		$k = AT^n e^{-Ea/RT}$			Refs.
		A^a	n	Ea^a	
Isomerization and decomposition reactions.					
R48	$C_5H_5+M \rightarrow C_2H_2+C_3H_3+M$ (k_∞)	$6.3 \cdot 10^{13}$	0.1	62.3	[144]
	$C_5H_5+M \rightarrow C_2H_2+C_3H_3+M$ (k_0)	$1.0 \cdot 10^{45}$	-8.4	47.5	[144]
-R48	$C_2H_2+C_3H_3 \rightarrow C_5H_5$	$6.17 \cdot 10^{66}$	-15.7	47.8	[169]
Reactions with H , O and O_2 .					
R49	$C_5H_6+M \rightleftharpoons C_5H_5+H+M$ (k_∞)	$7.7 \cdot 10^{19}$	-1.2	84.5	[167]
	$C_5H_6+M \rightleftharpoons C_5H_5+H+M$ (k_0)	$1.1 \cdot 10^{80}$	-16.8	16.9	[167]
R50	$C_5H_5+O \rightleftharpoons C_5H_5O$	$1.00 \cdot 10^{14}$	0	0	^b
R51	$C_5H_5+O_2 \rightleftharpoons C_5H_5O+O$	$8.50 \cdot 10^{14}$	0	28	[163]

^a A units are s^{-1} and $cm^3 \text{ mol}^{-1} s^{-1}$ for Unimolecular and bimolecular reactions, respectively. Ea is expressed in kcal mol^{-1} .

^b Reaction rate is estimated, see text.

calculated by Roy and co-workers [167] in 2001 have been included into the developed kinetic model.

(iii) Cyclopentadienyl radical reaction with O atom and O₂

In 1998, Zhong and Bozzelli [165] theoretically investigated reactions of H , OH , O and O_2 with cyclopentadienyl radical and found that the $O + C_5H_5$ reaction giving cyclopentadienone (C_5H_4O) and H atom should have an important contribution to cyclopentadienyl radical consumption under combustion conditions. However, C_5H_4O has never been observed in significant concentration in flames whereas kinetic models including reactions calculated by Zhong and Bozzelli predict large maximum mole fractions.

Recently, Butler and Glassman [164] have investigated cyclopentadiene oxidation in a plug flow reactor and have not detected cyclopentadienone, demonstrating that it is not a key intermediate of the $C_5H_5 + O$ reaction. Instead of C_5H_4O formation, authors proposed that the cyclopentadienoxo radical intermediate is directly converted into $n-C_4H_5 + CO$, as described in figure 4.36. Since theoretical predictions of the $C_5H_5 + O$ rate constant disagree with experimental evidences and no experimental measurements are available in the literature, we have estimated the rate constant of reaction R50 ($C_5H_5 + O \rightleftharpoons C_5H_5O$) to $1.0 \cdot 10^{14}$. This value is consistent with measurements performed by Buth and co-workers [137] in 1994 for the rate of O atom reaction with the phenoxy radical (see reaction R22 of table 4.6 on page 124), which is resonantly stabilized as C_5H_5 . Moreover, our estimation is more plausible than the exceptionally high value of $5.0 \cdot 10^{14}$ proposed by Ristori and co-workers [22].

In addition to $C_5H_5 + O$, Murakami and co-workers [163] showed that reaction of molecular oxygen with cyclopentadienyl radical can produce C_5H_5O and an O atom (see reaction R51 of table 4.10). However, as previously mentioned for $C_6H_5O + O_2$, reactions of resonantly stabilized radicals with non radical compounds are slow and do not play a significant role in their consumption.

Comparison between predicted and experimental results

Unfortunately, cyclopentadienyl radical mole fraction was not measured in the present work. However, figure 4.37 compares BF18 predictions of present and RH models to the maximum mole fraction of C_5H_5 measured by Yang and co-workers [95] in a benzene-oxygen-argon flame with a composition close to BF18. Whereas the RH model significantly overestimates Yang et al. measurements, the kinetic mechanism developed in this work has a good predictive capability. This observation is of particular importance because cyclopentadienyl radical is a key intermediate that links C_6 to C_4 hydrocarbons and is thought to play a role in naphthalene formation through its self recombination [156,170]. The good agreement between our prediction and experiment demonstrates that our kinetic model brings significant improvement in kinetic modeling of C_5H_5 formation and consumption.

A comparative reaction rate analysis allows to determine the contribution of each C_5H_5 consumption pathway included into the kinetic model, as depicted into figure 4.38. In BF07 and BF10, recombination reactions with H and O atoms (reactions R49 and R50 of table 4.10)

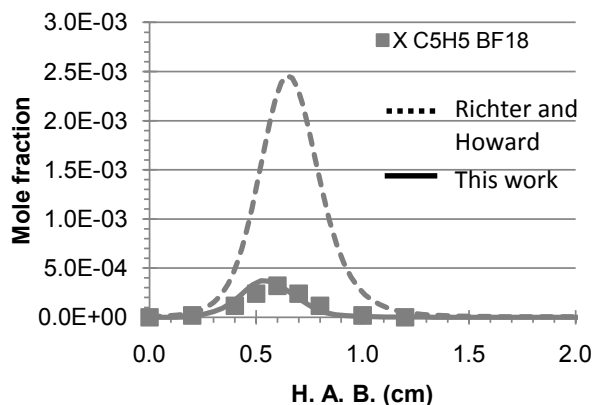


Figure 4.37: predicted and experimentally measured cyclopentadienyl radical maximum mole fraction of Yang and co-workers in a benzene-oxygen-argon flame with a composition close to BF18 [95]. The gray scale symbol represents experiment and solid and dashed curves stand for predictions of present and Richter and Howard [92] models, respectively.

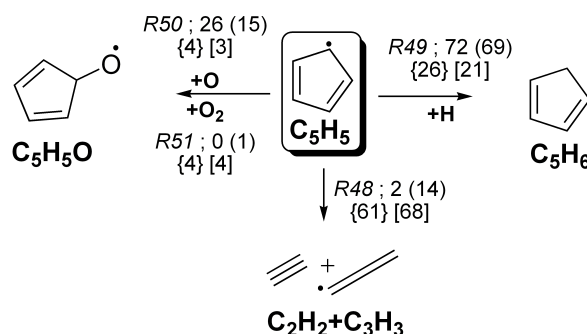


Figure 4.38: summary of cyclopentadienyl radical consumption pathways included into the developed kinetic model. Percentages represent contribution of each reaction in BF07, (BF10), {BF18} and [BF20]

are prevalent and contribute to 98 and 94% of the C_5H_5 consumption, respectively. Compared to BF10 and BF07, contribution of reaction R50 falls to 4.3 % in BF18 and BF20. This drop is due to the lower oxygen atom concentration and to the higher flame temperatures of BF18 and BF20 increasing the contribution of reaction R48 that dissociates C_5H_5 into acetylene and propargyl radicals. As previously postulated, reaction R51 involving O_2 reaction with the resonantly stabilized radical C_5H_5 is slow and does not significantly contribute to cyclopentadienyl radical consumption under flame conditions investigated in this work.

In addition to these consumption channels, the self recombination of cyclopentadienyl radicals produces naphthalene and two hydrogen atoms. This channel contributes to 4% of C_5H_5 consumption in BF18 and BF20 and will be discussed in much details in chapter 6, devoted to PAHs formation.

4.3.8 The cyclopentadiene sub-model

Cyclopentadiene formation pathways

In all investigated benzene flames, cyclopentadiene (C_5H_6) is mainly produced from H atom recombination with the cyclopentadienyl radical (reaction R49 of table 4.10 on page 146). In addition, under high tem-

perature conditions phenol decomposition to $C_5H_6 + CO$ significantly contributes to cyclopentadiene formation (reaction R24 of table 4.7 on page 132).

Cyclopentadiene consumption pathways

C_5H_6 can undergo H abstraction reactions giving back the C_5H_5 radical or can react with O atom, H atom and OH radical, yielding C_5H_6O , C_5H_7 and C_5H_6OH , respectively. To the best of our knowledge, theoretical works of Zhong and Bozzelli [171] and Bacskay and co-workers [166, 172] are the only in the field of rate constant determination of cyclopentadiene reactions. Zhong and Bozzelli investigated kinetics of H , O , OH and HO_2 addition reactions to cyclopentadiene, while Bacskay and co-workers focused on H abstraction by H atom [172] and cyclopentadiene decomposition to C_3H_4 isomers and acetylene [166].

(i) Cyclopentadiene isomerization and decomposition routes

In 2001, Bacskay and Mackie found that migration of hydrogen atoms connected to sp^2 carbons of cyclopentadiene, followed by the ring opening, can form linear C_5H_6 compounds that might subsequently decompose into propyne (p- C_3H_4) or allene (a- C_3H_4) and acetylene, as presented in figure 4.39. Authors calculated rate parameters of these reactions pathways and demonstrated that they can compete with other cyclopentadiene reactions at combustion temperatures. These reactions

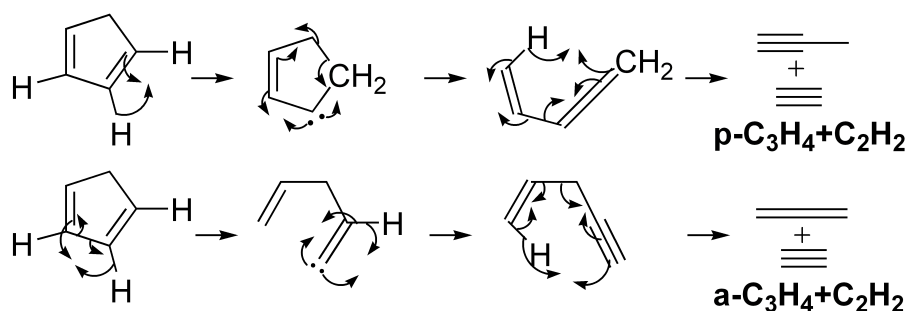


Figure 4.39: mechanism of cyclopentadiene decomposition into C_3H_4 isomers and acetylene

Table 4.11: C_5H_6 consumption reactions included into the kinetic model.

Reactions		$k = AT^n e^{-Ea/RT}$			Refs.
		A^a	n	Ea^a	
Isomerization and decomposition reactions.					
R52	$C_5H_6 \rightleftharpoons CH_2CHCHCCH_2$	$1.3 \cdot 10^{15}$	0	80.4	[166]
R53	$CH_2CHCHCCH_2 \rightleftharpoons p\text{-}C_3H_4 + C_2H_2$	$2.9 \cdot 10^{13}$	0	66.6	[166]
R54	$C_5H_6 \rightleftharpoons a\text{-}C_3H_4 + C_2H_2$	$3.8 \cdot 10^{17}$	0	104	[166]
R55	$C_5H_6 \rightleftharpoons CH_2CHCH_2CCH$	$8.5 \cdot 10^{14}$	0	90.5	[166]
R56	$CH_2CHCH_2CCH \rightleftharpoons a\text{-}C_3H_4 + C_2H_2$	$3.55 \cdot 10^{13}$	0	63.4	[166]
Reactions with H , O and OH .					
R57	$C_5H_6 + H \rightleftharpoons C_5H_7(A)$	$3.2 \cdot 10^{13}$	0	2.7	[171]
R58	$C_5H_6 + H \rightleftharpoons C_5H_7(B)$	$6.1 \cdot 10^{13}$	0	2.7	[171]
R59	$C_5H_6 + H \rightleftharpoons C_5H_5 + H_2$	$3 \cdot 10^{14}$	0	6.6	[172]
R60	$C_5H_6 + O \rightleftharpoons C_5H_5 + OH$	$1.8 \cdot 10^{14}$	0	3.1	[78]
R61	$C_5H_6 + OH \rightleftharpoons C_5H_5 + H_2O$	$3.4 \cdot 10^9$	1.2	-0.5	[78]

^a A units are s^{-1} and $cm^3 \text{ mol } s^{-1}$ for Unimolecular and bimolecular reactions, respectively. E_a is expressed in kcal mol^{-1} .

have been added into the developed kinetic model (see reactions R52 to R56 of table 4.11).

(ii) *Cyclopentadiene reactions with O atom, OH radical and H atom*

H atom addition onto the double bond of cyclopentadiene forms either cyclopent-2-en-1-yl (noted $C_5H_7(A)$) or cyclopent-3-en-1-yl (noted $C_5H_7(B)$) radicals (see reactions R57 and R58 of table 4.11). Subsequent reactions of these radicals will be presented in the following section. Rate constants calculated by Zhong and Bozzelli [171] for H atom addition to cyclopentadiene have been included into the present kinetic model. In addition to these reactions, abstraction of the hydrogen atom connected to the sp^3 carbon by an H atom, forming $C_5H_5 + H_2$, has been implemented into the kinetic model using rate parameters calculated by Bacskey and co-workers [172] in 1998 (see reaction 59). Zhong and Bozzelli found that O atom addition to cyclopentadiene can form cyclic or linear cyclopentenyl-carbonyl products + H atom. However, in a recent study on cyclopentadiene oxidation, Butler and Glassmann [164] were unable to give evidences of such pathways and stressed that ab-

straction of the H atom connected to the sp^3 carbon of cyclopentadiene by O atom should be the most important $O + C_5H_6$ reaction (see reaction R60). Therefore, no reactions of O atom addition onto C_5H_6 have been included into the present model. As for O atom, OH addition to cyclopentadiene double bounds are expected to be slower than the H abstraction reaction by OH . Consequently, no OH atom addition onto C_5H_6 is considered. Rate parameters estimated by Emdee and co-workers [78] for C_5H_6 hydrogen atom abstraction by O atom and OH radical, giving C_5H_5 are included into the present model (see reactions R60 and R61).

Comparison between predicted and experimental results

Figure 4.40 compares predictions of present and RH models to experimental measurements of C_5H_6 in BF07, BF10, BF18 and BF20. Although our model exhibits a good agreement for all investigated flames, the RH mechanism highly overestimates C_5H_6 mole fractions in BF07 and BF10. The large discrepancy between the RH predictions and those of our kinetic model comes from the use of a different set of products for the reaction between C_6H_5O and H . As discussed previously, Richter and Howard consider that this reaction produces phenol, which then gives back the phenoxy radical by dissociation and by H abstraction reactions. Therefore, in the RH model the $C_6H_5O + H$ reaction does not allow a net consumption of the phenoxy radical. As a result, the decomposition of the phenoxy radical into $C_5H_5 + CO$ and the subsequent recombination of C_5H_5 and H atom into C_5H_6 are overestimated. Contrarily to the RH model, we consider that the reaction between the C_6H_5O radical and H atom gives $C_3H_3 + C_2H_3 + CO$. Consequently, in our mechanism the C_6H_5O radical is partly consumed through another channel than the C_5H_5 formation and the cyclopentadiene mole fraction is better predicted.

Figure 4.41 gives contributions of each reaction channel to cyclopentadiene consumption. Abstraction of a H atom bounded to the sp^3 carbon atom of C_5H_6 dominates over the entire range of equivalence

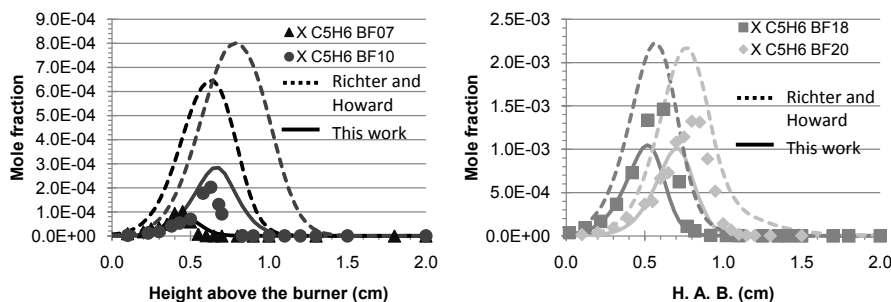


Figure 4.40: experimental and predicted profiles of cyclopentadiene (C_5H_6) mole fractions. Gray scale symbols represent experiments (Δ BF07, $\circ$ BF10, $\square$ BF18, $\diamond$ BF20). Solid and dashed curves in corresponding gray scale stand for predictions of present and Richter and Howard [92] models, respectively.

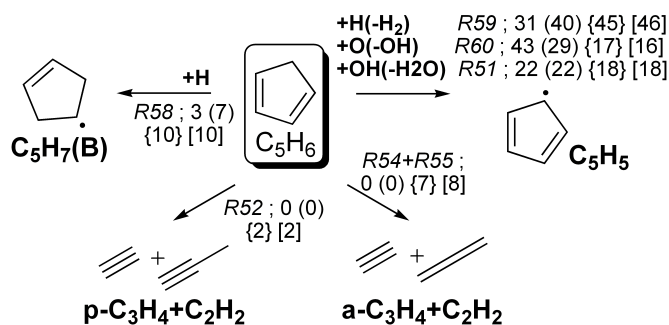


Figure 4.41: summary of cyclopentadiene consumption pathways included into the developed kinetic model. Percentages represent contributions in BF07, (BF10), {BF18} and [BF20].

ratio. Contributions of reactions R59 and R60 respectively decrease and increase with the drop in equivalence ratio, as they respectively depend on hydrogen and oxygen atom concentrations. Decomposition pathways proposed by Bacskey and Mackie [166] have only a significant contribution in BF18 and BF20 that have highest flame temperatures, since they have high energy barriers. Finally, hydrogen atom addition onto cyclopentadiene play a minor role in all investigated flames and further reactions of the $C_5H_7(B)$ radical will be examined in the following section.

4.3.9 The C_5H_7 radicals sub-model

C_5H_7 radicals formation pathways

In benzene flames $C_5H_7(A)$ and $C_5H_7(B)$ are produced by H atom addition to cyclopentadiene, as discussed previously.

C_5H_7 radicals consumption pathways

Kinetics of C_5H_7 radicals consumption has been investigated by Gueniche and co-workers [138] in 2008. In their work devoted to cyclopentene (C_5H_8) combustion, authors proposed the kinetic scheme summarized in figure 4.42 for C_5H_8 consumption and validated it against an experimental methane-cyclopentene-oxygen-argon flame. In this mechanism, cyclopentene is converted to 3 cyclopentenyl isomers ($C_5H_7(A)$, $C_5H_7(B)$ and $C_5H_7(C)$, see figure 4.42) that can subsequently decompose into cyclopentadiene and H atom or open into linear isomers, decomposing into various products such as CH_3 , C_3H_3 , $a-C_3H_4$ or $p-C_3H_4$. Since this kinetic scheme includes each C_5H_7 intermediate produced from H atom addition to cyclopentadiene and links these radicals to other important chemical species, the mechanism of Gueniche and co-workers [138] has been included into the present kinetic model.

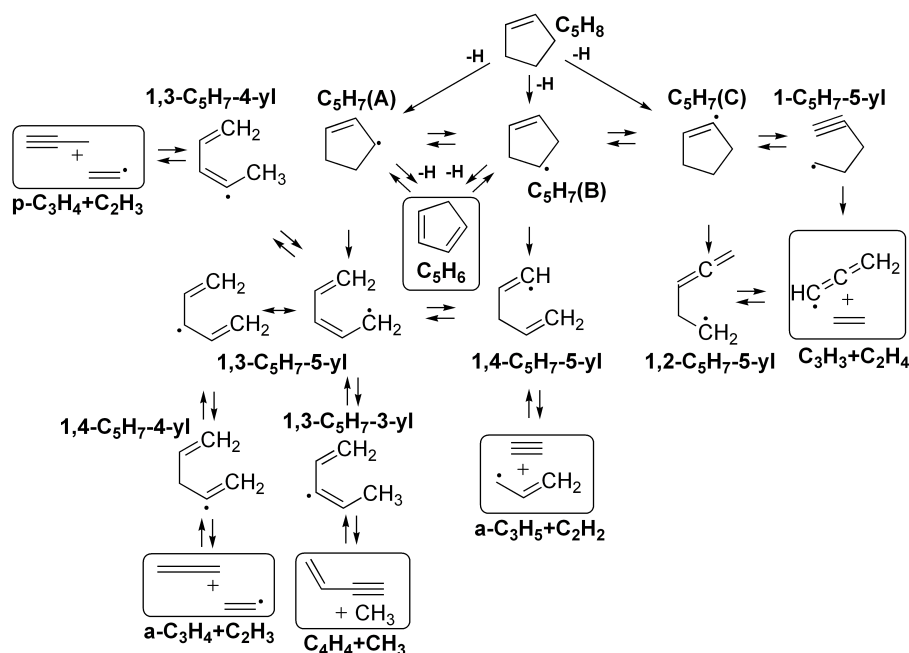


Figure 4.42: decomposition pathways considered by Gueniche and co-workers [138] for C_5H_7 radicals .

Comparison between predicted and experimental results

The present kinetic model predicts an overall maximum mole fraction of $8.0 \cdot 10^{-5}$ for C_5H_7 radicals, which is relatively close to the value of $1.3 \cdot 10^{-4}$ measured by Yang and co-workers [95]. The RH model does not include C_5H_7 formation and only has an overall $C_5H_6 + H \rightleftharpoons a-C_3H_5 + C_2H_2$ reaction. The inclusion of the sub-mechanism developed by Gueniche and co-workers into our kinetic model shows that the main products of C_5H_7 decomposition should be C_4H_4 and CH_3 . Therefore, the RH model may be wrong and further studies are needed to clarify kinetics of the C_5H_7 decomposition routes.

Since cyclopentene consumption can produce high concentrations of C_5H_5 radical, which is thought to be involved in PAHs formation, cyclopentene flames will be investigated in chapter 6. The sub-model developed by Gueniche and co-workers [138] will be presented in this chapter

and compared to experimental measurements performed in these cyclopentene flames.

4.3.10 The cyclopentadienoxo radical sub-model

Cyclopentadienoxo radical formation pathways

In the present kinetic model, the cyclopentadienoxo radical (C_5H_5O) is produced through O atom and O_2 reactions with cyclopentadienyl radical (C_5H_5).

Cyclopentadienoxo radical consumption pathways

In 1982, Venkat and co-workers [73] proposed that C_5H_5O consumption yields $n-C_4H_5$ and carbon monoxide. Rate constant of this reaction was estimated to $2.51 \cdot 10^{11} e^{-22094/T} \text{ s}^{-1}$ by Emdee and Brezinsky [78] in 1992. In 1998, Zhong and Bozzelli [165] calculated that C_5H_5O can dissociate through three major channels: (i) hydrogen atom and cyclopentadienone, (ii) $n-C_4H_5 + CO$ and (iii) $C_2H_2 + C_3H_3O$. They calculated rate constants of each reaction channel and found that the first and the third should dominate in flames. Recently, Butler and Glassman [164] studied cyclopentadiene oxidation and did not observe cyclopentadienone formation. Consequently, they ruled out this reaction pathway and proposed the kinetic sub-model composed of reactions R62, R63 and R64 of table 4.12.

Comparison between predicted and experimental results

Unfortunately, no experimental data on C_5H_5O formation in flames are available in the literature. Our kinetic model predicts maximum mole fractions spreading from $3.5 \cdot 10^{-4}$ to $1.5 \cdot 10^{-4}$ in BF07 and BF20, respectively. Further experimental studies on C_5H_5O flame chemistry are needed to compare with kinetic models and improve the understanding of C_6 to C_5 conversion. In our kinetic scheme, C_5H_5O conversion into

Table 4.12: C_5H_6 consumption reactions included into the kinetic model.

Reactions		$k = AT^n e^{-E_a/RT}$			Refs.
		A^a	n	E_a^a	
Isomerization and decomposition reactions.					
R62	$C_5H_5O \rightleftharpoons n-C_4H_5+CO$	$2.5 \cdot 10^{11}$	0	29.7	[164]
R63	$C_5H_5O \rightleftharpoons n-C_4H_5+CO$	$2.5 \cdot 10^{11}$	0	37.4	[164]
R64	$C_5H_5O \rightleftharpoons C_3H_3O+C_2H_2$	$2.0 \cdot 10^{13}$	0	104	[164]

^a A units are s^{-1} and $cm^3 \text{ mol } s^{-1}$ for Unimolecular and bimolecular reactions, respectively. E_a is expressed in kcal mol^{-1} .

$C_3H_3O + C_2H_2$ (see reaction R64) is negligible and the main channel is $n-C_4H_5 + CO$ formation from reactions R62 and R63. Reactions linking C_4 to C_1 hydrocarbons are summarized in the following section, together with a comparison of predicted results with experimental measurements performed in BF07, BF10, BF18 and BF20.

4.3.11 Further reactions of C_4H_x and smaller hydrocarbons

Previous sections have described the development of a new kinetic model for C_6H_6 based on a comprehensive literature survey. The model has a good predictive capability for main chemical species, C_6H_5OH , C_6H_5 , C_6H_4 , C_5H_5 and C_5H_6 but still overestimates phenoxy radical mole fraction, whereas its prediction is globally improved, compared to other models available in the literature. One has shown that consumption of C_6 and C_5 intermediates principally leads to C_2 , C_3 and C_4 hydrocarbon formation through chemical pathways summarized in figure 4.43.

Formation of C_2 , C_3 and C_4 hydrocarbons

A comparative reaction rate analysis shows that in BF07 and BF10, benzene consumption is dominated by path 1 and 2 of figure 4.43, which produce C_2H_2 , C_2H_3 and C_3H_3 from phenoxy radical reactions with H and O atoms. In BF18 and BF20 that have higher flame tempera-

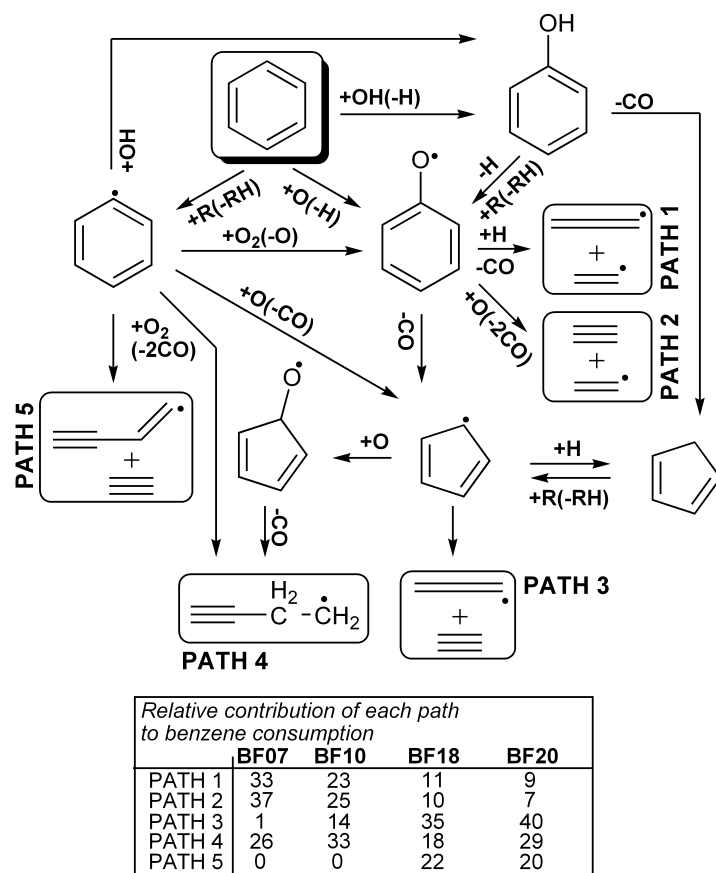


Figure 4.43: summary of chemical pathways involved in C_6 and C_5 conversion to C_2 , C_3 and C_4 . The table in the lowest part of this figure gives contribution percentage of each route to benzene consumption in BF07, BF10, BF18 and BF20.

tures than BF07 and BF10, the rate of phenoxy radical dissociation into $C_5H_5 + CO$ significantly increases, diminishing contributions of path 1 and 2 and increasing that of path 3, which becomes the main benzene consumption channel. Whereas cyclopentadienyl radical formation is stimulated in BF18 and BF20, contribution of path 4 that involves $C_5H_5 + O \rightleftharpoons C_5H_5O$ decreases, as it necessitates an O atom which is present in lower concentrations, compared to BF07 and BF10. Path 5 is not active in BF07 and BF10 but converts about 20% of benzene into $n-C_4H_3 + C_2H_2$ in BF18 and BF20, due to their high flame tem-

peratures that allow to more easily cross the activation barrier of this reaction.

As shown in figure 4.43, the developed kinetic model must contain reactions describing C_4H_x to C_1H_x combustion chemistry and a H_2/O_2 sub-mechanism in order to fully model benzene flames. Since a comprehensive investigation of these reactions was beyond the scope of this work, our kinetic model has been completed with sub-mechanisms carefully selected from the literature. Reactions describing C_4H_x hydrocarbon combustion have been taken from the work of Wang and Frenklach [173], who developed a detailed kinetic model to predict aromatic formation in ethylene and acetylene flames. Authors gave a particular attention to C_4H_x reactions, as they play a major role in benzene formation. Reactions of C_3H_x to C_1H_x and the H_2/O_2 sub-mechanism have been taken from the work of Leplat and co-workers [174,175], who comprehensively investigated various oxygenated C_2 hydrocarbons and ethylene flames. Authors developed a kinetic model, successfully validated over an impressive set of experimental data, including low-pressure flames, jet-stirred reactor studies conducted at 1 and 10 bars, laminar flame velocities and ignition delay times. The complete kinetic model used in this work is provided as supplementary information in appendix E. The following discussion describes a comparative reaction rate analysis performed for BF07, BF10, BF18 and BF20, in order to highlight major chemical pathways involved in C_4 , C_3 and C_2 hydrocarbon consumption. Predicted mole fraction profiles of these intermediates and of main chemical species are equally compared to measurements.

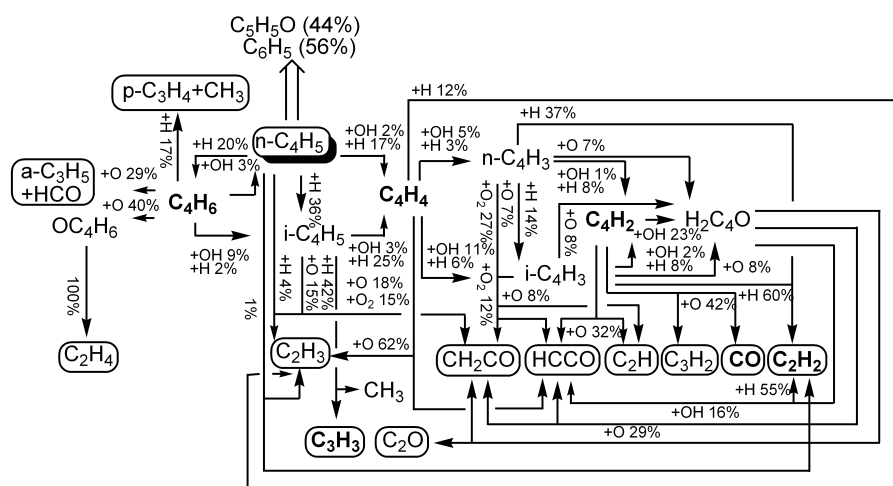
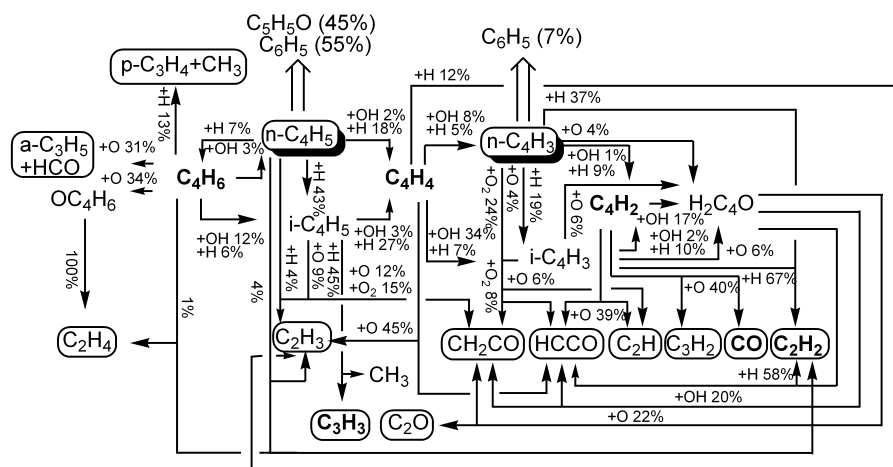
Consumption of C_4H_x hydrocarbons

As shown in figure 4.43, cyclopentadienoxo radical (C_5H_5O) decomposition and phenyl radical reaction with O_2 are the only C_4 production route from benzene in BF07. In BF10, these channels compete with phenyl radical decomposition, giving the n- C_4H_3 radical. Contributions of kinetic pathways converting n- C_4H_5 and n- C_4H_3 radicals into smaller

hydrocarbons are presented in figures 4.44 and 4.45 for BF07 and BF10, respectively.

In BF07, 36% of $n\text{-C}_4\text{H}_5$ is converted to $i\text{-C}_4\text{H}_5$ by an isomerization reaction catalyzed by an H atom, 20% recombines with H atom forming 1,3-butadiene, 18% reacts with O atom forming C_2H_3 and ketene (CH_2CO) and 19% yields vinylacetylene (C_4H_4) through H abstraction reactions. While contributions of reactions forming vinylacetylene are similar in BF07 and BF10, the highest equivalence ratio and flame temperature of BF10 promote $n\text{-C}_4\text{H}_5$ isomerization into $i\text{-C}_4\text{H}_5$, which reaches a contribution of 43% in BF10. The highest contribution of this reaction disadvantages H atom recombination with $n\text{-C}_4\text{H}_5$ yielding 1,3- C_4H_6 , whose contribution decreases in BF10, compared to BF07. The lowest O atom concentration in BF10, compared to BF07, disadvantages the reaction forming $C_2H_3 + CH_2CO$, whose contribution decreases to 12%. As $n\text{-C}_4\text{H}_5$, $i\text{-C}_4\text{H}_5$ produces C_4H_4 by H abstraction reactions or reacts with O atom forming $C_2H_3 + CH_2CO$. Contributions of these reactions are affected by the equivalence ratio in the same way as $n\text{-C}_4\text{H}_5$.

In addition to these chemical pathways, $i\text{-C}_4\text{H}_5$ reacts with H atom yielding $CH_3 + C_3H_3$. This reaction contributes to 42% and 45% of $i\text{-C}_4\text{H}_5$ consumption in BF07 and BF10, respectively. In BF07 and BF10, C_4H_6 either yields $i\text{-C}_4\text{H}_5$ and $n\text{-C}_4\text{H}_5$ by H abstraction reactions or reacts with O atom, giving ethylene + ketene and $a\text{-C}_3\text{H}_5 + CO$. Compared to BF07, the overall C_4H_6 reaction with O atom less important in BF10, as O atom concentration is lower. In BF07 and BF10, vinylacetylene (C_4H_4) is mainly consumed by reaction with O atom, forming $C_2H_3 + HCCO$. Other reaction pathways produce either $n\text{-C}_4H_3$ or $i\text{-C}_4H_3$ through H abstraction reactions. Contribution of reactions forming the resonantly stabilized $i\text{-C}_4H_3$ radical are always higher than those forming $n\text{-C}_4H_3$. C_4H_3 isomers are consumed either (i) by reaction with H atom forming two acetylene molecules, (ii) by reaction with O_2 yielding ketene and $HCCO$, (iii) by recombination with O atom followed by decomposition into ketene and C_2H , (iv) by H abstraction reactions giving diacetylene (C_4H_2) or (v) by reaction OH radical giving $H_2C_4O + H$.

Figure 4.44: kinetic scheme of C_4H_x hydrocarbons in BF07Figure 4.45: kinetic scheme of C_4H_x hydrocarbons in BF10

Moreover, $n\text{-C}_4\text{H}_3$ is converted into $i\text{-C}_4\text{H}_3$ by an isomerization reaction catalyzed by a hydrogen atom. As previously discussed, reactions depending on oxygenated compounds and hydrogen atom are respectively disadvantaged and favored in BF10, compared to BF07. Consequently, contributions of reactions converting $n\text{-C}_4\text{H}_3$ into $i\text{-C}_4\text{H}_3$ and both isomers into two acetylene molecules increase in BF10, compared to BF07. Diacetylene reacts either with O atom forming $HCCO + C_2H$ and $C_3H_2 + CO$, or with OH radical giving H_2C_4O , which is in turn converted to *ketene* + C_2O , *ketene* + $HCCO$ and $C_2H_2 + HCCO$ by reactions with O , OH and H atom, respectively.

As discussed previously, in BF18 and BF20 phenyl dissociation into $n\text{-C}_4\text{H}_3 + C_2H_2$ highly competes with $n\text{-C}_4\text{H}_5$ formation from $C_6H_5 + O_2$ and C_5H_5O decomposition (see path 4 and 5 of figure 4.43). Contributions of kinetic pathways converting $n\text{-C}_4\text{H}_5$ and $n\text{-C}_4\text{H}_3$ into smaller hydrocarbons are presented in figures 4.46 and 4.47 for BF18 and BF20, respectively. These kinetic schemes are similar to those of BF07 and BF10, excepted that reactions depending on H and O atoms are respectively favored and disadvantaged, due to highest equivalence ratios. Since BF18 and BF20 are less diluted than BF07 and BF10, they have highest flame temperatures, which equally increase the contribution of dissociation reactions. In BF18 and BF20, $n\text{-C}_4\text{H}_5$ is still principally converted into $i\text{-C}_4\text{H}_5$ but its dissociation reactions into $C_2H_3 + C_2H_2$ and $C_4H_4 + H$ begin to compete, as they contribute to about 10% and 6% of its consumption in BF20. Consumption channels of $i\text{-C}_4\text{H}_5$ in BF18 and BF20 are similar to those in BF07 and BF10, except that reactions with hydrogen atom dominate and that the decomposition into $C_4H_4 + H$ competes. As in BF07 and BF10, in BF18 and BF20 the C_4H_4 consumption is performed through $i\text{-C}_4\text{H}_3$ formation, which is equally produced from $n\text{-C}_4\text{H}_3$ isomerization. Both $C_4\text{H}_3$ isomers are consumed through H abstraction reactions, giving diacetylene (C_4H_2). Since in BF18 and BF20 the $n\text{-C}_4\text{H}_3$ radical is directly produced from phenyl radical dissociation, C_4H_2 formation is highly promoted, compared to BF07 and BF10. Whereas reactions consuming C_4H_2 into C_4H are not significantly active in BF07 and BF10, they contribute to about 15%

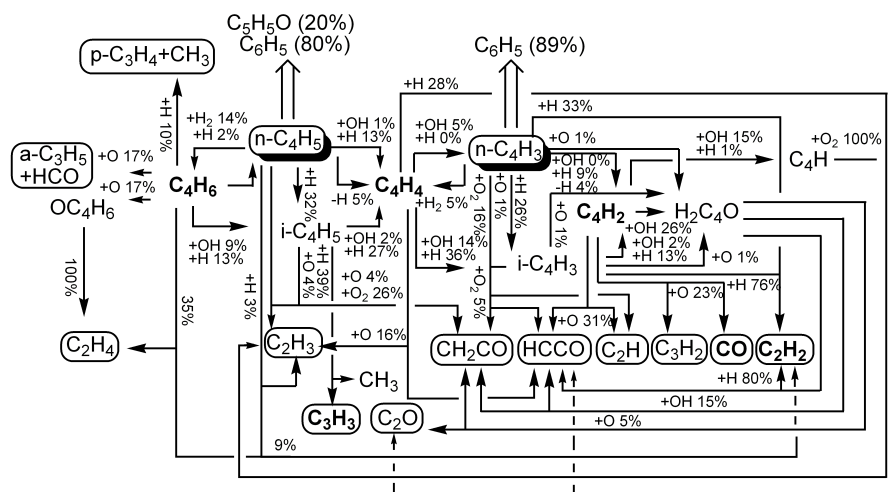


Figure 4.46: kinetic scheme of C_4H_x hydrocarbons in BF18

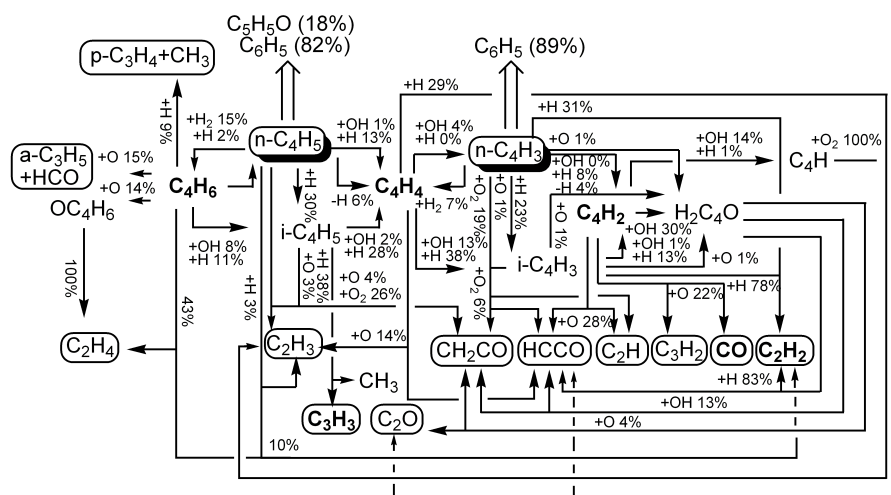


Figure 4.47: kinetic scheme of C_4H_x hydrocarbons in BF20

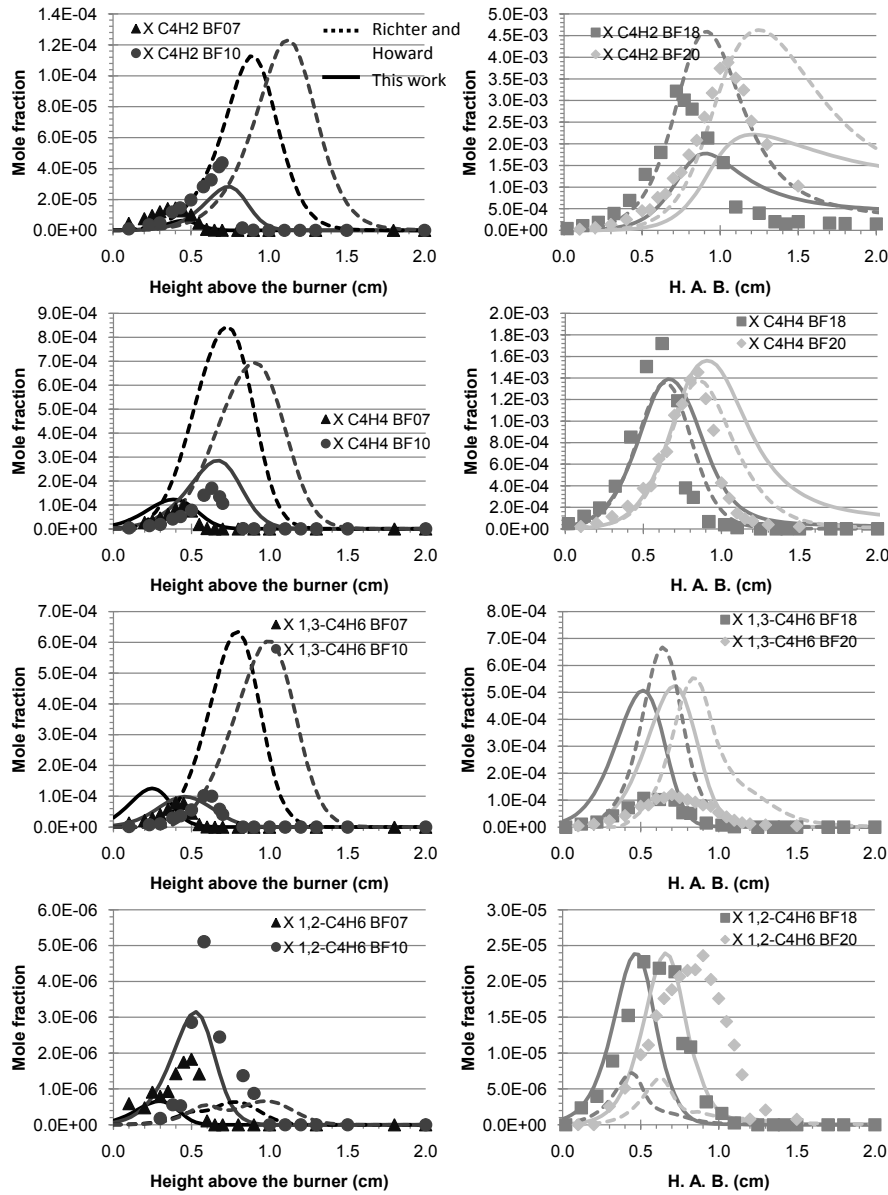


Figure 4.48: experimental and predicted mole fraction profiles of diacetylene (C_4H_2), vinylacetylene (C_4H_4) and 1,3-butadiene (C_4H_6). Gray scale symbols represent experiments ($\triangle$ BF07, $\circ$ BF10, $\square$ BF18, $\diamond$ BF20). Solid and dashed curves in corresponding gray scale stand for predictions of present and Richter and Howard [92] models, respectively.

of diacetylene consumption in BF18 and BF20 and C_4H reacts with molecular oxygen giving $C_2O + HCCO$.

Figure 4.48 compares experimental and predicted mole fraction profiles of C_4H_x compounds measured in this work. Vinylacetylene (C_4H_4), which is principally produced from H abstraction reactions on C_4H_5 radicals, is well predicted in BF18 and BF20 but slightly overestimated by the kinetic model in BF07 and BF10. However our predictions are significantly better than those of Richter and Howard that highly overestimate C_4H_4 and are unable to reproduce the effect of the equivalence ratio on its maximum mole fraction. As the RH model, 1,3- C_4H_6 is overestimated by our kinetic mechanism in BF18 and BF20. However, a better predictive capability is reached in BF07 and BF10, whereas a slight overestimation is observed. The 1,2- C_4H_6 is predicted to be formed from the recombination between C_3H_3 and CH_3 . Its mole fraction profile is well predicted in each investigated benzene flame. The C_4H_2 predictions are close to experimental measurements over the entire range of equivalence ratio, whereas the RH model overestimates its maximum mole fraction in BF07 and BF10. Compared to the Richter and Howard model, our mechanism therefore significantly improves the predictive capability of C_4H_x hydrocarbons. This improvement is due to the better understanding of the C_6H_6 consumption pathways brought by this work and by the use of the comprehensive model of Wang and Frenklach for C_4H_x combustion chemistry.

Consumption of C_3H_x hydrocarbons.

In each investigated benzene flame, propargyl radicals (C_3H_3) are produced from benzene consumption, through phenoxy radical reaction with H atom and cyclopentadienyl radical decomposition (see path 1 and path 2 of figure 4.43 on page 158). In BF07 and BF10, $C_6H_5O + H \rightleftharpoons C_3H_3 + C_2H_3 + CO$ dominates propargyl radicals formation, as the dissociation of cyclopentadienyl radical is slower than its reaction with O atom giving C_5H_5O . In the previous section, one has shown that C_3H_3 is equally produced from H atom reaction with $i-C_4H_5$. Beside

C_3H_3 , minor benzene consumption routes produce a- C_3H_4 , p- C_3H_4 and a- C_3H_5 (CH_2CHCH_2 . radical) through the dissociation of cyclopentadiene or its reaction with a hydrogen atom. Contributions of kinetic pathways converting C_3H_3 , C_3H_4 and C_3H_5 compounds into smaller hydrocarbons are presented into figures 4.49 and 4.50 for BF07 and BF10, respectively.

In BF07 and BF10, a- C_3H_5 consumption is dominated by recombination with H atom producing propylene (C_3H_6), which is subsequently consumed either (i) by H atom abstraction reactions giving C_3H_5 radicals, (ii) by reactions with O atom yielding $C_2H_5 + HCO$ and *ketene* + CH_3 and (iii) by H atom addition, followed by a CC bond fission forming $CH_3 + C_2H_4$. H abstraction reactions giving a- C_3H_5 dominate propylene consumption in all investigated benzene flames. In addition to the recombination with an H atom, a- C_3H_5 is consumed through H abstraction reactions forming allene (a- C_3H_4) or by reaction with O atom producing $CH_2CHCHO + H$. p- C_3H_5 ($CH_2C.CH_3$) undergoes H abstraction reactions giving propyne (p- C_3H_4), reacts with O atom producing $CH_3CHCO + H$ or is converted into $CH_3CHCO + OH$ and $CH_3CHO + HCO$ through reaction with O_2 . s- C_3H_5 ($.CHCHCH_3$) forms p- C_3H_4 and a- C_3H_4 by H abstraction reactions. It equally reacts with O_2 forming $CH_2O + CH_3CO$ and with HO_2 , OH and O atom giving $CH_2CO + CH_3$. Moreover, p- C_3H_5 and s- C_3H_5 give a- C_3H_5 through isomerization reactions.

Contributions of consumption pathways depending on oxygen atom decrease in BF10, compared to BF07. Allene and propyne can react with H and O atoms, respectively giving $C_2H_2 + CH_3$ and $C_2H_4 + CO$. Beside these reactions, propyne reacts with H atom producing either a- $C_3H_4 + H$, s- C_3H_5 or a- C_3H_5 and reacts by H atom abstraction reactions, giving C_3H_3 radicals. Allene reacts either with H atom forming a- C_3H_5 and $C_2H_2 + CH_3$, with O atom forming $C_2H_4 + CO$ and by H abstraction reactions producing the C_3H_3 radical. C_3H_3 is mainly consumed into propargylene (C_3H_2) by H abstraction reaction. It equally reacts with O atom and O_2 , giving $CH_2O + C_2H$ and $CH_2CO + HCO$, respectively. Propargylene gives back C_3H_3 by recombination with an

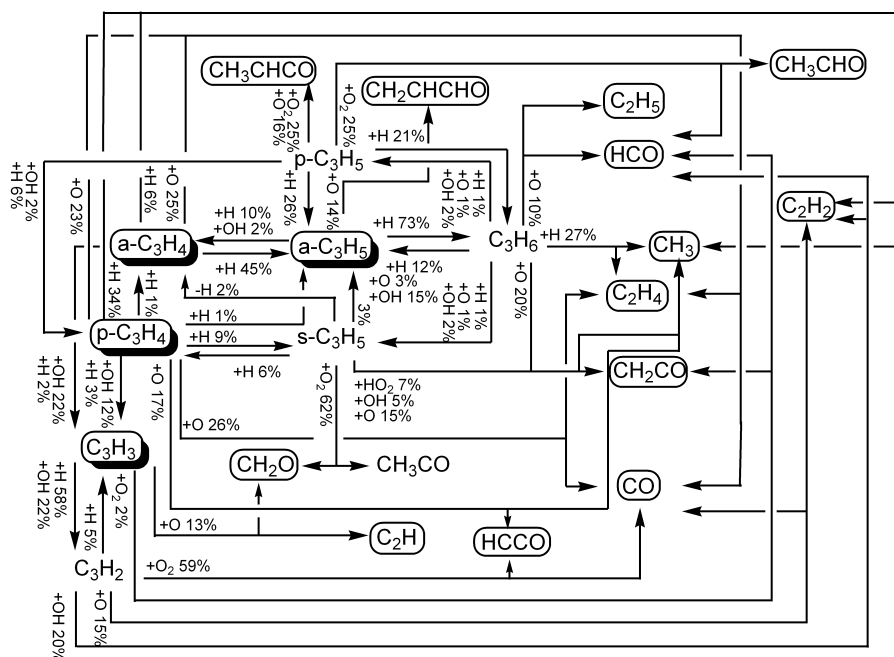


Figure 4.49: kinetic scheme of C_3H_x hydrocarbons in BF07

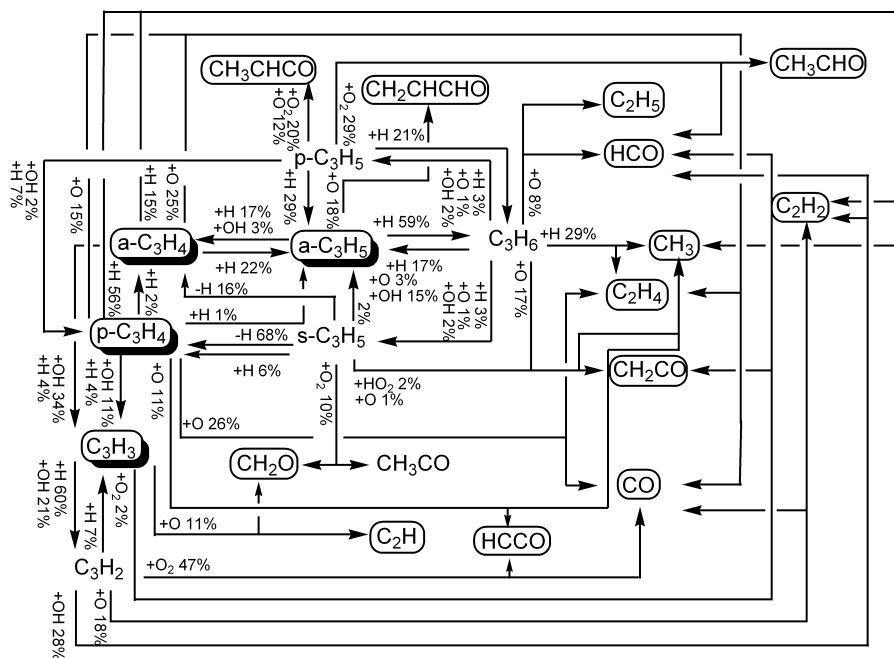


Figure 4.50: kinetic scheme of C_3H_x hydrocarbons in BF10

H atom or reacts with O , OH and O_2 to yield $C_2H_2 + CO$, $C_2H_2 + HCO$ and $HCCO + CO$, respectively.

Contrarily to BF07 and BF10, in BF18 and BF20 the reaction $C_5H_5 \rightleftharpoons C_2H_2 + C_3H_3$ dominates propargyl radicals formation. As in BF07 and BF10, minor benzene consumption routes form a- C_3H_4 , p- C_3H_4 and a- C_3H_5 through cyclopentadiene dissociation or reaction with a hydrogen atom. Contributions of kinetic pathways converting C_3H_3 , C_3H_4 and C_3H_5 compounds into smaller hydrocarbons are presented into figures 4.51 and 4.52 for BF18 and BF20, respectively. The kinetic scheme of C_3 hydrocarbon consumption is similar to BF07 and BF10, except that reactions depending on H atom are promoted and those depending on oxygenated compounds are disadvantaged, due to the increase of the equivalence ratio. Highest flame temperatures of BF18 and BF20, compared to BF07 and BF10, allow some dissociation reactions to compete with pathways previously discussed.

Figure 4.53 compares experimental and predicted mole fraction profiles of C_3H_x compounds measured in this work. The mole fraction profile of C_3H_3 is well predicted in BF10 and BF20, but is slightly underestimated in BF07. However, our mechanism significantly improves propargyl radical prediction in stoichiometric and lean conditions, compared to the model of Richter and Howard [92]. This observation supports our hypothesis that additional consumption pathways connecting the phenoxy radical to propargyl radicals should be active in benzene flames. The developed kinetic model well predicts mole fraction profiles of a- C_3H_4 and p- C_3H_4 over the entire range of equivalence ratios. Although the kinetic model of Richter and Howard is unable to reproduce the allene/propyne mole fraction ratio, figure 4.53 shows that our mechanism achieves good predictions. The C_3H_6 is underestimated in BF07 and BF10 by our kinetic model, whereas in BF18 and BF20 it is well reproduced. The Richter and Howard has a bad predictive capability over the entire range of equivalence ratios. All considered, one concludes that the developed kinetic model brings significant improvements to the modeling of C_3H_x hydrocarbons in benzene flames.

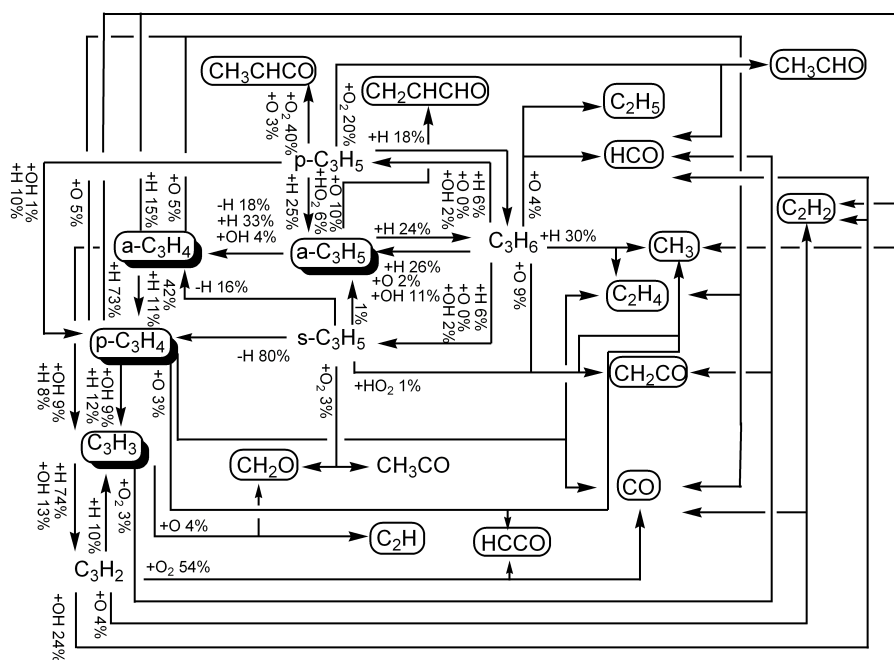


Figure 4.51: kinetic scheme of C_3H_x hydrocarbons in BF18

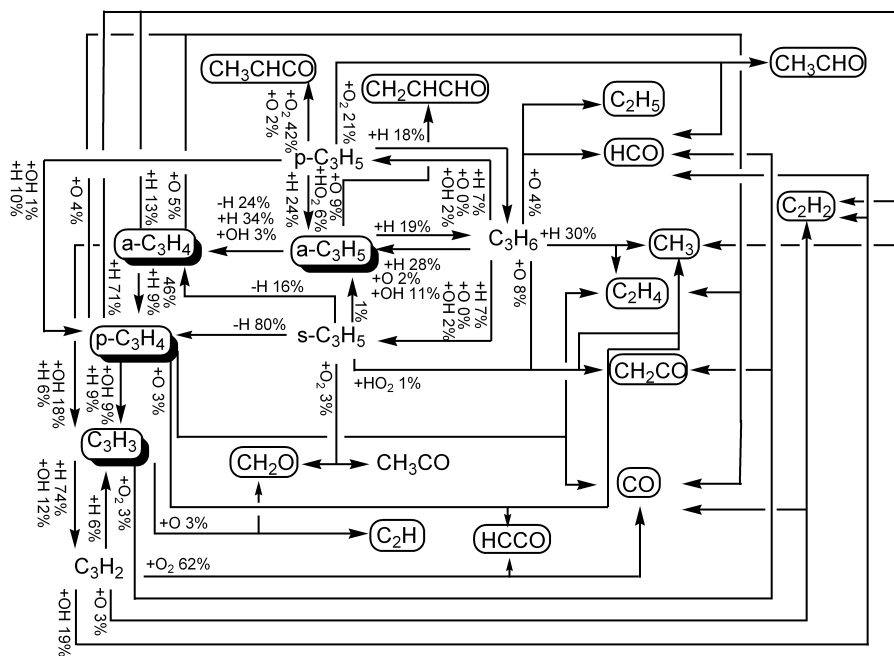


Figure 4.52: kinetic scheme of C_3H_x hydrocarbons in BF20

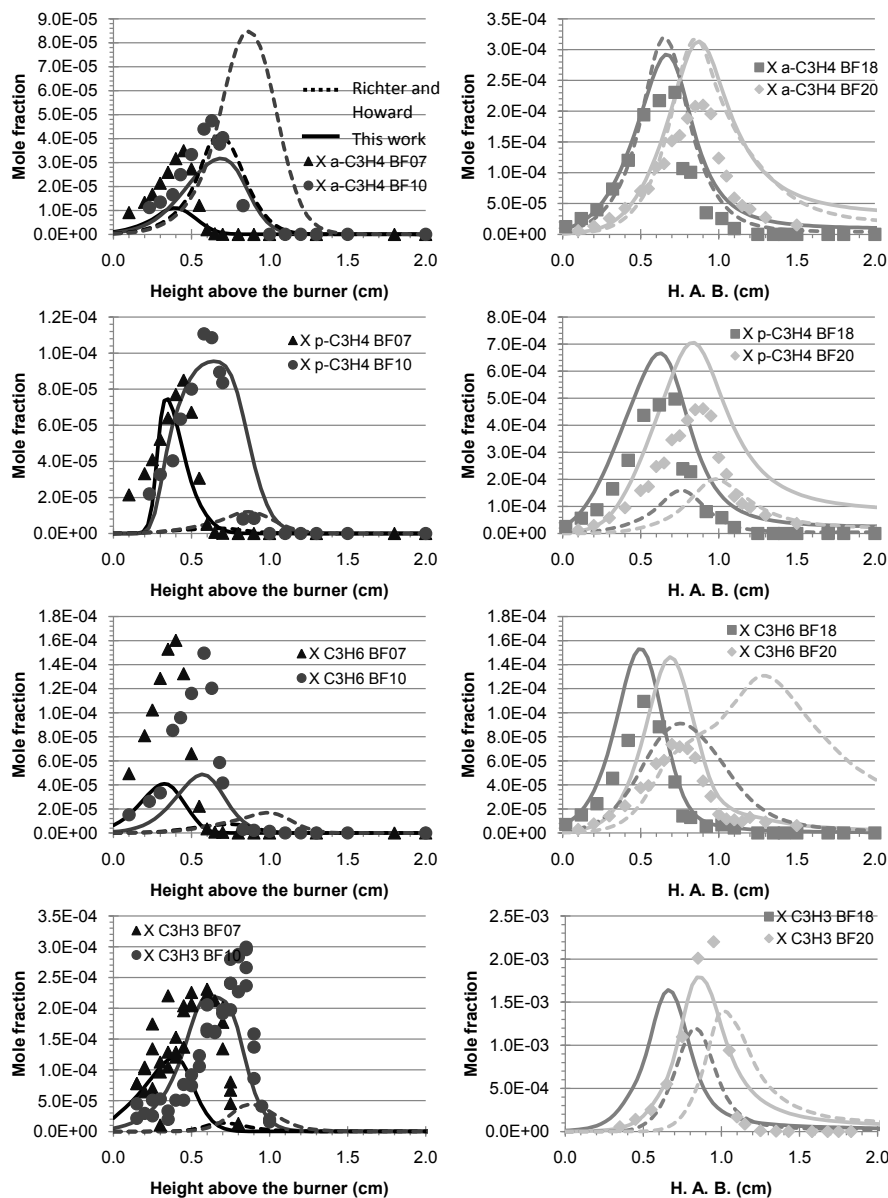


Figure 4.53: experimental and predicted mole fraction profiles of propargyl radicals (C_3H_3), allene ($\alpha\text{-C}_3\text{H}_4$), propyne ($\text{p-C}_3\text{H}_4$) and propylene (C_3H_6). Gray scale symbols represent experiments ($\triangle$ BF07, $\circ$ BF10, $\square$ BF18, $\diamond$ BF20). Solid and dashed curves in corresponding gray scale stand for predictions of present and Richter and Howard [92] models, respectively.

Consumption of C_2H_x and C_1H_x hydrocarbons.

As depicted in figure 4.43 on page 158, benzene consumption produces C_2 hydrocarbons from paths 1, 2, 3 and 4. In BF07 and BF10, paths 1 and 2 involving phenoxy radical consumption into $C_3H_3 + C_2H_3$ and $C_2H_2 + C_2H_3$ dominate the C_2 hydrocarbon formation. In BF18 and BF20, the highest flame temperatures promote dissociation reactions. Therefore, paths 3 and 5 become major C_2 formation channels. In addition to these pathways, C_4H_x and C_3H_x consumption routes equally produce C_2 hydrocarbons, as depicted in figures of previous sections.

Figures 4.54 and 4.55 present main consumption routes of C_2H_x and C_1H_x hydrocarbons in BF07 and BF10, respectively. Vinyl radical (C_2H_3) is principally consumed through H abstraction reactions giving acetylene (C_2H_2), which in turn mainly reacts with O atom, forming $HCCO + H$ and $CH_2 + CO$. In addition to C_2H_2 , vinyl radical consumption produces $CH_2CO + H$ and $CH_2CHO + O$ through reactions with O atom and O_2 , respectively. In addition to the $C_2H_3 + O$ reaction, ketene (CH_2CO) is produced from C_4H_x and C_3H_x consumption, as discussed previously. Consequently, ketene seems to be an important intermediate species in benzene flames. It is mainly consumed into $HCCO$ by H abstraction reactions, and into $CH_3 + CO$ and $CH_2 + CO$ by reactions with H and O atoms, respectively. CH_2CHO is principally converted to $CH_3 + CO$ and $CH_3 + HCO$ by decomposition reaction and reaction with H atom, respectively. These reactions, together with $CH_2CO + H \rightleftharpoons CH_3 + CO$ and $i-C_4H_5 + H \rightleftharpoons CH_3 + C_3H_3$, dominates methyl radical formation in BF07 and BF10. CH_3 principally produces CH_2O and $CH_2(S)$ (methylene singlet radical) through reactions with O atom and OH radical. Minor consumption channels lead to CH_4 , C_2H_6 and C_2H_5 formation. Ethane (C_2H_6) is consumed by H abstraction reactions giving C_2H_5 , which subsequently reacts with H atom and OH radical, respectively forming methyl radical and ethanol (C_2H_5OH). Ethanol is converted by H abstraction reactions to CH_3CHOH , which in turn gives CH_3CHO . Its consumption either produces the CH_2CHO radical previously discussed or the CH_3CO radical that decomposes into

methyl radical and carbon monoxide. $HCCO$ consumption yields CO , CO_2 and $CH_2(S)$. $CH_2(S)$ isomerizes into the methylene triplet (CH_2) radical or reacts with O_2 , giving carbon monoxide. The consumption of the methylene triplet radical produces CO , CO_2 , CH_2O , CH and HCO . CH_2O and CH are consumed into HCO that is converted into carbon monoxide.

In BF18 and BF20, kinetic schemes of C_2H_x are globally similar to those of BF07 and BF10, except that reactions depending on O atom are disadvantaged, compared to reactions involving H atom. Moreover, decomposition reactions are promoted due to the highest flame temperatures. Whereas in BF07 C_2H_5 decomposition into $C_2H_4 + H$ is negligible, it accounts for 40%, 84% and 87% of C_2H_5 consumption in BF10, BF18 and BF20, respectively. The same phenomenon occurs for $C_2H_3 \rightleftharpoons C_2H_2 + H$, $CH_2CHO \rightleftharpoons CH_2CO + H$ and $CH_2OH \rightleftharpoons CH_2O + H$.

In BF07, the most important CO production channels are $HCO + O_2 \rightleftharpoons CO + HO_2$, $HCCO + H \rightleftharpoons CO + CH_2(S)$ and $C_2H_2 + O \rightleftharpoons CH_2 + CO$ that are responsible of 23%, 10% and 8% of its formation, respectively. In BF20 these channels are $HCCO + H \rightleftharpoons CO + CH_2(S)$, $C_3H_2 + O_2 \rightleftharpoons CO + HCCO + H$ and $C_6H_5O \rightleftharpoons C_5H_5 + CO$ that contributes to 17%, 12% and 10% of carbon monoxide formation, respectively. This change in primary CO formation channels between BF07 and BF20 can be explained by the highest flame temperature of BF20, compared to BF07, which promotes dissociation reactions such as $C_6H_5O \rightleftharpoons C_5H_5 + CO$ and $C_5H_5 \rightleftharpoons C_3H_3 + C_2H_2$. As depicted in figure 4.52 on page 169, propargyl radicals (C_3H_3) formed by this last reaction are mainly consumed into C_3H_2 , which is a major CO precursor. The increase in the contribution of the $HCCO + H \rightleftharpoons CO + CH_2(S)$ reaction comes from the highest equivalence ratio of BF20, compared to BF07, advantaging reactions depending on H atoms. Carbon monoxide is only consumed through reaction with OH radical, forming $CO_2 + H$. Therefore, the CO consumption rate is slow compared to its production rate and its mole fraction persists in burnt gases. In flames with low

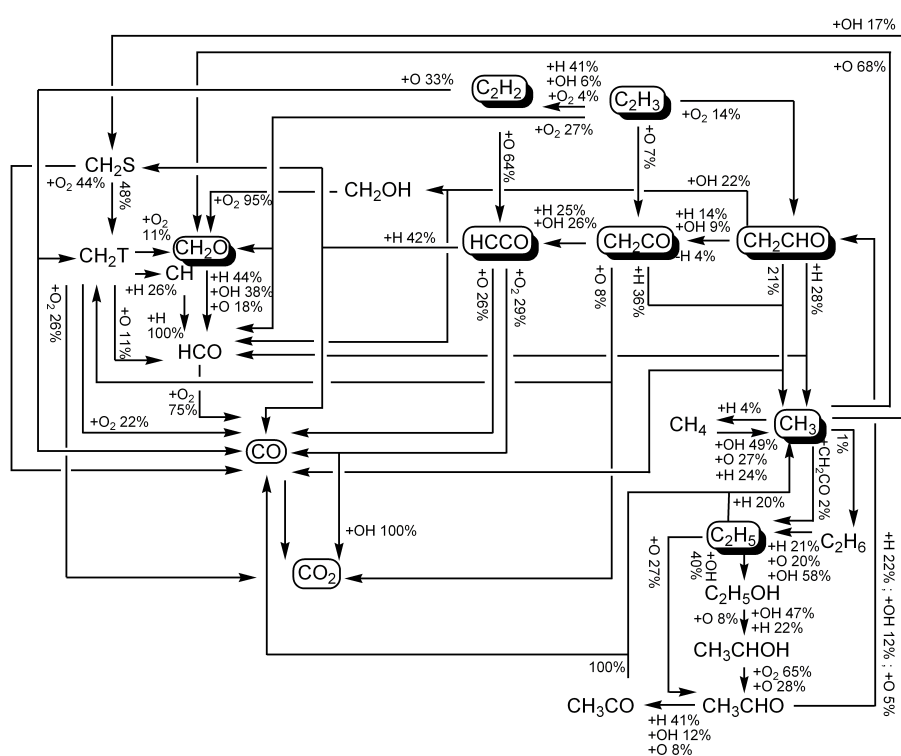


Figure 4.54: kinetic scheme of C_2H_x and C_1H_x hydrocarbons in BF07.

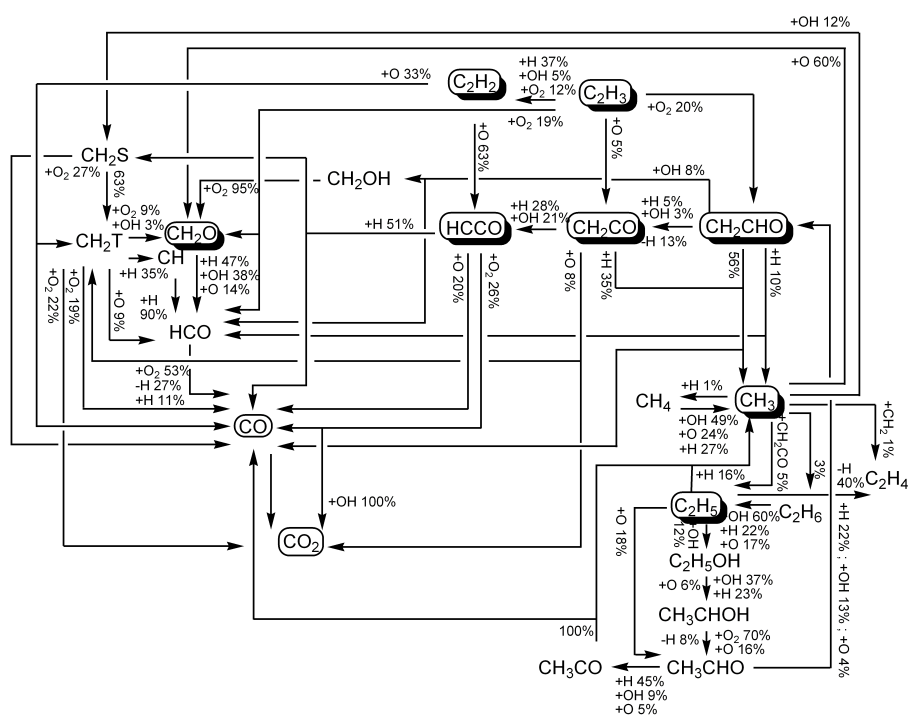


Figure 4.55: kinetic scheme of C_2H_x and C_1H_x hydrocarbons in BF10.

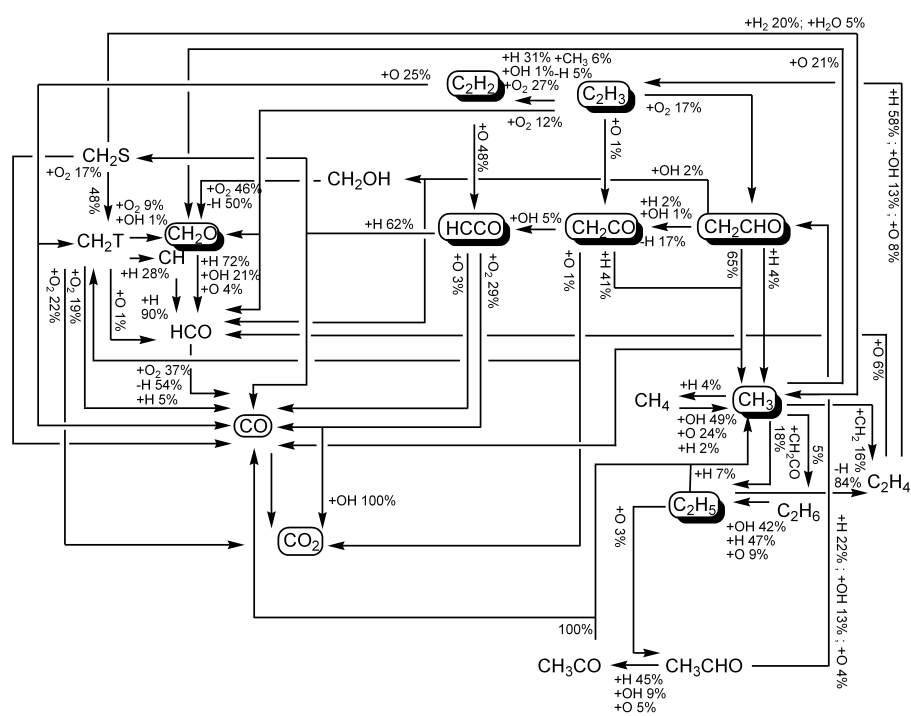
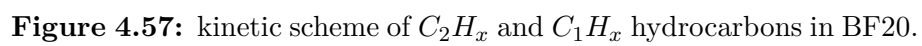


Figure 4.56: kinetic scheme of C_2H_x and C_1H_x hydrocarbons in BF18.



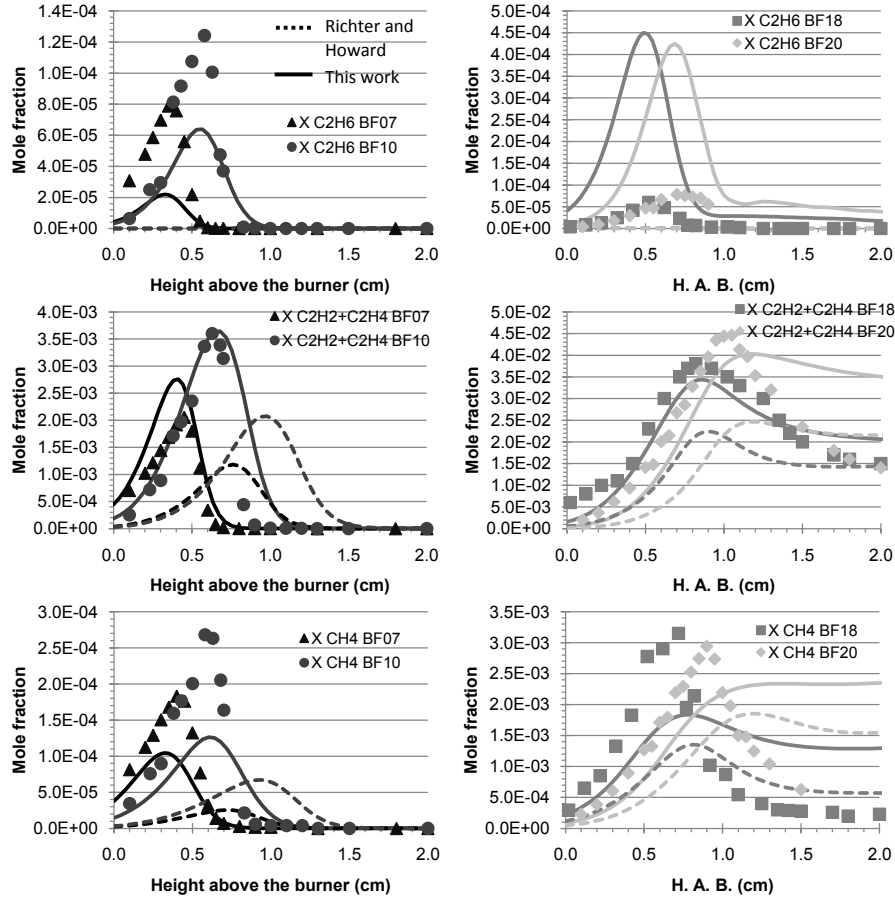


Figure 4.58: experimental and predicted mole fraction profiles of ethane (C_2H_6), acetylene (C_2H_2) and methane (CH_4). Gray scale symbols represent experiments ($\triangle$ BF07, $\circ$ BF10, $\square$ BF18, $\diamond$ BF20). Solid and dashed curves in corresponding gray scale stand for predictions of present and Richter and Howard [92] models, respectively.

equivalence ratios, such as BF07 and BF10, OH concentration are high and CO_2 formation is stimulated, compared to BF18 and BF20.

Over the entire range of equivalence ratios, main H_2O formation routes are $OH + H_2 \rightleftharpoons H_2O + H$ and $C_6H_6 + OH \rightleftharpoons C_6H_5 + H_2O$. The OH radical is formed from the chain branching reactions $H + O_2 \rightleftharpoons OH + O$ and $O + H_2 \rightleftharpoons OH + H$. In BF07, molecular hydrogen is formed from H abstraction reactions on vinyl and propargyl radicals, yielding acetylene and propargylene, respectively. In BF20, high concentration of H atom stimulates $C_6H_6 + H \rightleftharpoons C_6H_5 + H_2$ that become the principal H_2 formation route, whereas $C_3H_3 + H \rightleftharpoons C_3H_2 + H_2$ is still the second most important channel.

Figure 4.58 on the previous page compares mole fraction profiles of C_2H_6 , C_2H_2 and CH_4 predicted by present and RH models to measurements performed in benzene flames of this work. Whereas acetylene mole fraction profile is accurately reproduced in all investigated flames, C_2H_6 and CH_4 are underestimated in BF07 and BF10 and C_2H_6 is overestimated in BF18 and BF10. Since ethane and methane are produced from methyl radical recombination reactions, underestimation of their maximum mole fractions in BF07 and BF10 should be due to an underestimation of CH_3 radical concentrations. However, compared to the model of Richter and Howard, the developed model significantly improves predictions of ethane and methane mole fractions. The nice fit between C_2H_2 measurements and predictions over the investigated range of equivalence ratios supports the hypothesis of phenoxy radical consumption into C_2H_3 and C_2H_2 . All considered, we conclude that the developed mechanism brings significant improvement to the prediction of C_2 hydrocarbons in benzene flames.

4.3.12 The main chemical species

Finally, figures 4.59 and 4.60 compare mole fraction profiles of main chemical species predicted by the present and the RH models to measurements performed in benzene flames of this work. In the present work, a general good agreement is obtained for these main species. The

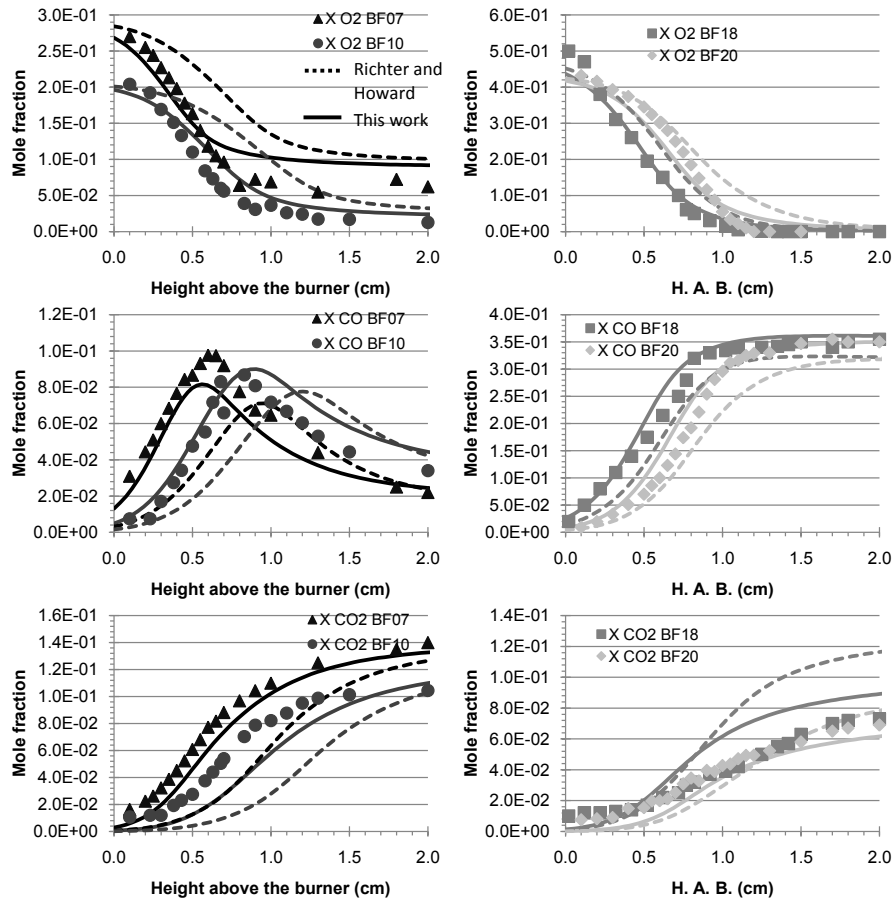


Figure 4.59: experimental and predicted mole fraction profiles of carbon monoxide (CO), carbon dioxide (CO_2) and molecular oxygen (O_2). Gray scale symbols represent experiments ($\triangle$ BF07, $\circ$ BF10, $\square$ BF18, $\diamond$ BF20). Solid and dashed curves in corresponding gray scale stand for predictions of present and Richter and Howard [92] models, respectively.

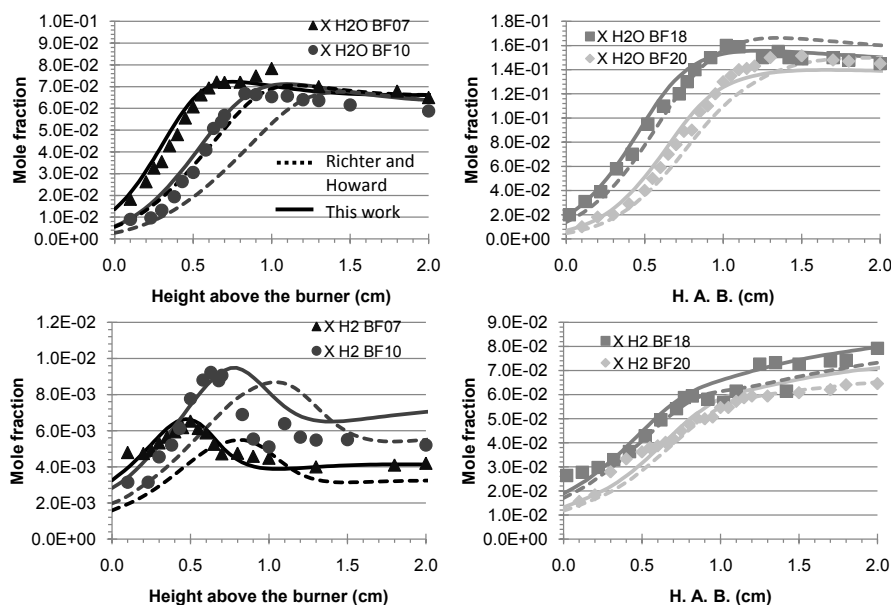


Figure 4.60: experimental and predicted mole fraction profiles of water (H_2O) and molecular hydrogen (H_2). Gray scale symbols represent experiments ($\triangle$ BF07, $\circ$ BF10, $\square$ BF18, $\diamond$ BF20). Solid and dashed curves in corresponding gray scale stand for predictions of present and Richter and Howard [92] models, respectively.

position of their mole fraction profiles is better predicted in BF07 and BF10 with the developed mechanism than with that of Richter and Howard [92].

4.3.13 Kinetic modeling of the pressure dependence of BF20

The kinetic model whose development has been presented in previous sections has been used to predict the influence of pressure on the richest benzene flame structure. As depicted in table 4.2 on page 91, this benzene flame with an equivalence ratio of 2 has been analyzed at 35 mbar (noted the BF20-35 flame), 45 mbar (BF20) and 65 mbar (BF20-65) in order to determine the effect of pressure on its structure. Unfortunately, one has shown that the impact of pressure could not be distinguished

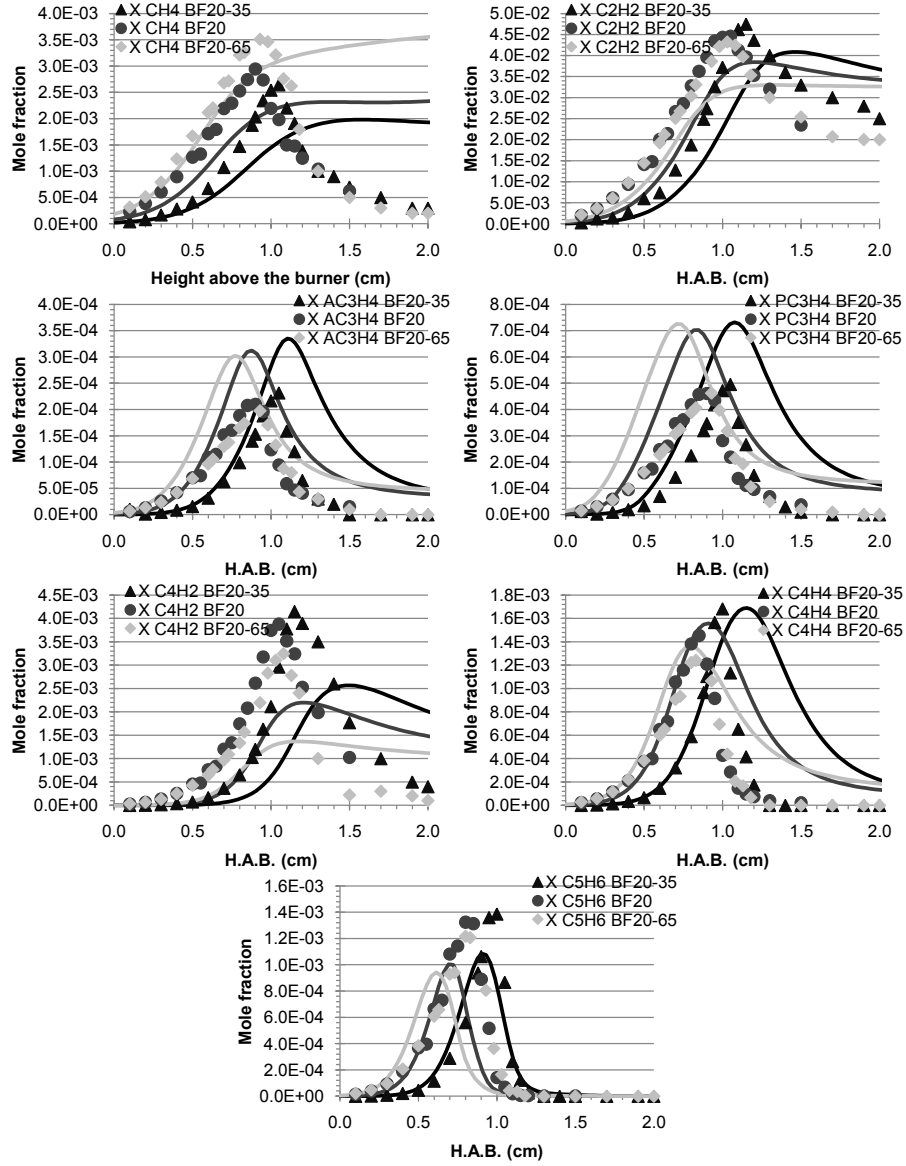


Figure 4.61: experimental and predicted mole fraction profiles of CH_4 , C_2H_2 , $a-C_3H_4$, $p-C_3H_4$, C_4H_2 , C_4H_4 and C_5H_6 in the richest benzene flame, at 35 mbar (BF20-35), 45 mbar (BF20) and 65 mbar (BF20-65). Gray scale symbols represent experiments ($\triangle$ BF20-35, $\square$ BF20, $\diamond$ BF20-65). Solid curves in corresponding gray scale stand for predictions of the model developed in this work.

of that of temperature, as the flame temperature is closely linked to the working pressure. Indeed, the increase in pressure brings the flame closer to the burner, increasing the heat transfer to its surface and therefore decreases the flame temperature. Consequently, this section does not discuss how the pressure influences the flame structure but only validates experimental mole fraction profiles of some major intermediates against predictions of the developed kinetic model (see figure 4.61). Such a validation shows that the developed kinetic model well represents small pressure and temperature perturbations, demonstrating its reliability.

Whereas the maximum mole fraction and the shape of methane mole fraction profiles are not well reproduced, the increase in methane maximum with that of the working pressure is properly predicted by the kinetic model. Concerning acetylene, the maximum mole fraction decreases with the pressure increase. Whereas this trend contrasts with that observed for methane, it is well reproduced by the kinetic model. Other main intermediates exhibit a pressure dependence similar to that of acetylene. For each chemical species depicted in figure 4.61, the variation in maximum mole fractions are generally well predicted by the kinetic model. Since these compounds are all important intermediates of the benzene kinetic scheme, one can conclude that the developed mechanism is well representative of slight pressure perturbations under rich conditions.

4.4 Conclusions

Benzene oxidation has been experimentally investigated for many years by several researchers. However one have shown that many uncertainties remain on chemical pathways involved in its consumption. Among them, roles of benzoquinone and phenoxy radical in aromatic oxidation are important points that have required some clarification. Whereas benzene oxidation has been extensively investigated in chemical reactors, studies devoted to its combustion are scarce, as to the best of our knowledge only

three works describing premixed, laminar and one-dimensional benzene-oxygen-argon flames have been published in the literature. These works have been performed to acquire experimental data on PAH and soot formation in flames, and have consequently only focused on rich aromatic flames. However, the experimental investigation of lean and stoichiometric benzene-oxygen-argon flames should provide new experimental data to guide the kinetic model development and should throw some light on recurrent problems surrounding aromatic oxidation. We think that a reliable kinetic modeling of benzene combustion under lean conditions is the first step of PAH and soot modeling in rich hydrocarbon flames, as their building blocks are produced during the fuel oxidation.

All things considered, experimental structures of six laminar, premixed and one-dimensional benzene-oxygen-argon flames with equivalence ratios spreading from 0.7 to 2 have been stabilized at low pressure on the movable burner described in chapter 2. Their structures have been principally investigated by Gas Chromatography, whereas Molecular Beam Mass Spectrometry has been used to measure mole fraction profiles of some key intermediates, undetected by GC. A particular attention has been paid to mole fractions of phenoxy radical and benzoquinone in order to help the kinetic model development. Experimental measurements have shown that chemical species such as phenol, cyclopentadiene, vinylacetylene, propargyl radicals and acetylene are present in significant concentration over the entire range of equivalence ratio, suggesting that they should play a key role in benzene combustion. However, maximum mole fractions of phenol, phenoxy radical and benzoquinone were found to be relatively low, compared to other intermediates, indicating that if they are important intermediates, their consumption routes should be fast. These observations are inconsistent with results of kinetic modeling studies on aromatic oxidation described in the literature, which predict high concentrations of phenol, phenoxy radical and benzoquinone. To the best of our knowledge, among these oxygenated compounds only phenol and phenoxy radical were previously measured under rich benzene flame conditions. Therefore, our experimental measurements bring very new and pertinent data on aromatic oxidation, which are expected

to help the understanding of reactions involved in benzene consumption.

Predictions of the most recent kinetic model developed for benzene flame chemistry have been compared with our flame measurements, in order to assess its validity. Under rich conditions, one found that even if mole fraction profiles of reactants, products and some intermediates are well predicted, several discrepancies remain. Under lean and stoichiometric conditions, that kinetic model is unable to predict the rate of fuel consumption, shifting positions of maximum mole fractions towards burnt gases. A comparative reaction rate analysis has shown that this underestimation of benzene consumption rate was due to a loop between phenoxy radical and phenol formation. Indeed, that model considers that at lean and stoichiometric equivalence ratios, phenoxy radical principally recombines with H atom, giving huge phenol concentrations that mainly yield back the phenoxy radical through H abstraction reactions. This kinetic model equally has a poor predictive capability for benzoquinone and other main intermediates maximum mole fractions. Therefore, we have developed a new kinetic sub-mechanism for benzene combustion, able to better reproduce measurements of this work.

This new sub-model has been developed by performing a comprehensive literature survey on high temperature reactions of each intermediate of benzene oxidation. The model therefore includes recent insights performed in reaction pathways and rate parameters of aromatic combustion. For some years, theoretical calculations have become a powerful tool in studying combustion reactions. When available, these investigations were taken into consideration for the kinetic model construction. One has shown that benzene is mainly consumed either through H abstraction reactions giving phenyl radical, by reaction with an O atom yielding phenoxy radical and H atom, or by a metathesis reaction with the OH radical, producing phenol and H atom. Whereas phenoxy radical formation is most important under fuel lean conditions, which exhibit a higher O atom concentration compared to rich flames, H abstraction reactions dominate benzene consumption over the entire range of equivalence ratios. The phenyl radical reaction with molecular oxygen is fast

and accounts for the vast majority of phenyl radical consumption in flames. However, one has shown that this reaction is highly complex and that many uncertainties remain on the branching ratio between its potential products. Previous experimental investigations have shown that two main channels should be active and that one produces phenoxy radical and O atom. Consequently, this channel has been included into our kinetic model. It is known that the second channel produces H atom and many researchers suggested that benzoquinone is the co-product. However, when this channel is considered our kinetic model cannot reproduce the low maximum mole fraction of benzoquinone that has been measured in this work, even using a sub-mechanism experimentally validated for benzoquinone consumption. Therefore, based on theoretical investigations of phenyl radical reaction with molecular oxygen, it is suggested that the second channel of this reaction forms $n\text{-}C_4H_5$ and CO , instead of benzoquinone and H atom. This change allows to well predict benzoquinone measurements. Under rich conditions, phenyl radical decomposition into $n\text{-}C_4H_3 + C_2H_2$ and $l\text{-}C_6H_4 + H$ are found to compete with reactions involving O_2 . The predictions of the phenyl radical mole fraction profile in BF18 has been successfully compared to experimental data from the literature. As discussed previously, phenoxy radical reactions are badly reproduced by the kinetic model taken in the literature and improvements were therefore needed. We have suggested that the reaction of phenoxy radical and H atom does not produce phenol but cyclohexadienone and that cyclohexadienone might reacts with H atom forming propargyl and vinyl radicals. Whereas this overall reaction pathway is hypothetical, one has shown that some evidences support this assumption. Moreover, this new channel allows to prevent the loop appearing in other kinetic models and to better predict propargyl radicals and acetylene formation under lean conditions. Concerning cyclopentadienyl radical, one has taken into account recent works on its oxidation, showing that cyclopentadienone formation does not occur, as generally postulated by other kinetic models. Our fruitless tentatives to measure this compound confirm this recent finding and one has considered that cyclopentadienyl radical react with O atom forming cyclopentadienoxy radical. Cyclopentadienoxy radical subsequently de-

composes into $n\text{-}C_4H_5$ radical and CO. Kinetic sub-mechanisms found in the literature and developed in the lab have been used for C_4 and C_3 to C_1 reactions, respectively. The whole kinetic model has a better predictive capability than previous mechanisms published into the literature. Intermediates such as phenyl radical, phenol, benzoquinone, cyclopentadienyl radical, cyclopentadiene and propargyl radicals, known to play an important role in aromatic oxidation are well reproduced by the developed model.

The benzene flame structure with an equivalence ratio of 2 has been measured at 35, 45 and 65 mbar in order to assess the influence of pressure on soot precursors formation. Unfortunately, pressure and temperature effects cannot be distinguished as the pressure variation implies a change in flame position, and thus in the heat transfer towards the burner surface. The increase of the working pressure therefore decreases the flame temperature. Whereas the pressure influence on the kinetic model has not been determined, predictions of the kinetic model have been compared to experimental measurements. The developed model well predict the changes in the working pressure, showing that the model may be used for the modeling of benzene flames analyzed at higher pressures. However, the investigated pressure range is small and should be enlarged prior to predict benzene combustion at atmospheric conditions.

Finally, our work has brought valuable experimental data on benzene combustion that should help to improve the current understanding of aromatic oxidation. Since no kinetic models were able to reproduce all our measurements, we developed a new mechanism that has allowed us to test some recent results on kinetics of certain reactions and to throw some light on recurrent uncertainties, as benzoquinone or phenol formation. However, many uncertainties remain and further works are still needed, especially on phenyl radical reaction with O_2 and phenoxy radical reactions with the radical pool in order to verify assumptions performed in this work.

5.1 Introduction

In the same way as benzene, high temperature reactions of toluene have been investigated under many different conditions. Many groups investigated toluene pyrolysis in order to focus on its decomposition reactions, whose understanding is essential to determine mechanism of toluene oxidation in chemical reactors and flames. To our best knowledge, toluene pyrolysis was firstly investigated in 1939 by Tilicheev [176], who found that toluene decomposition has an activation energy of 70 kcal mol^{-1} and is about 13 times faster than that of benzene. In 1943, Hein and Messee [177] studied toluene pyrolysis in presence of mercury vapor and succeeded in isolating mercury-di-benzyl as a product of the reaction. Authors postulated from the detection of this chemical species that the first step of toluene pyrolysis should be the rupture of a methyl CH bond, giving the resonantly stabilized benzyl radical. In 1948, Szwarc [178] equally investigated toluene pyrolysis and measured the formation of molecular hydrogen, methane and dibenzyl. The author proposed a mechanism explaining the formation of these products, which has been extensively reviewed between 1948 and 1962 [179–182].

The model proposed by Price [182] in 1962 is depicted in table 5.1. It consists in toluene dissociation into benzyl radical ($\text{b-C}_7\text{H}_7$) and H

Table 5.1: mechanism of toluene pyrolysis proposed by Price [182] in 1962.

Reactions	
R1	$C_7H_8 \rightleftharpoons b - C_7H_7 + H$
R2	$H + C_7H_8 \rightleftharpoons b - C_7H_7 + H_2$
R3	$H + C_7H_8 \rightleftharpoons C_6H_6 + CH_3$
R4	$CH_3 + C_7H_8 \rightleftharpoons b - C_7H_7 + CH_4$
R5	$H + C_7H_8 \rightleftharpoons C_6H_4CH_3 + H_2$
R6	$CH_3 + C_7H_8 \rightleftharpoons C_6H_4CH_3 + CH_4$
R7	$C_7H_8 \rightleftharpoons C_6H_5 + CH_3$
R8	$2CH_3 \rightleftharpoons C_2H_6$

atom (see reaction R1 of table 5.1), followed by H atom reactions with toluene, giving either benzyl radical and H_2 or methyl radical and benzene, through reactions R2 and R3, respectively. The reaction between methyl radical and toluene can form benzyl radical and methane, as depicted by reaction R4. Beside H abstraction reactions on the methyl group of toluene, Price highlighted that abstraction of hydrogen atom onto the phenyl ring may play a significant role at high temperatures, as summarized by reactions R5 and R6. The author equally postulated that the dissociation of toluene into phenyl and methyl radicals (see reaction R7) should play a negligible role, compared to that forming benzyl radical and H atom.

After the Price's study, the appearance of new experimental techniques has allowed to identify additional reaction products such as C_7H_7 , C_7H_6 , C_7H_5 , C_6H_6 , C_5H_5 , C_4H_4 , C_4H_3 , C_3H_3 and C_2H_2 [183, 184]. Further studies were therefore devoted to the mechanism of toluene pyrolysis in order to extend the Price's mechanism to the formation of C_2 , C_3 , C_4 and C_5 hydrocarbons. The decomposition of benzyl radical has been rapidly postulated as responsible of such chemical species formation and various chemical pathways have been proposed by Rao and Skinner [185], Benson [186] and Colket and Seery [187]. These decomposition channels are quite complex and were surrounded by a high uncertainty until recently, as further discussed in this chapter. In addition to C_1 to C_7 hydrocarbons, in 1994 Colket and Seery [187] equally detected the formation of polycyclic aromatic hydrocarbons in toluene pyrolysis experiments and

consequently proposed an updated mechanism to reproduce their measurements. Authors postulated that an overall reaction between benzyl and propargyl radicals might yield naphthalene and two hydrogen atoms, explaining the significant levels of naphthalene and other observed PAHs. This naphthalene formation pathway will be further discussed in chapter 6, dealing with PAH formation in our benzene and toluene flames. Beside these insights performed in toluene pyrolysis, first experiments on its oxidation began in 1979 when McLain and co-workers [64] measured ignition delay times of toluene-oxygen-argon mixtures under shock waves. Authors developed a simplified kinetic model based on findings derived from pyrolysis experiments, and added reactions involving oxygenated compounds, such as H abstraction reactions on toluene by O_2 and O atom and overall reactions of the benzyl radical with O_2 and O atom, forming $2CO + C_3H_5 + C_2H_2$ and $CH_2O + C_6H_5$, respectively.

One had to wait the pioneer works of the Brezinsky's group [78, 188] in 1984 and 1992 to better understand the high temperature oxidation of the methyl side chain of toluene. In these studies, this group performed a turbulent flow reactor analysis of toluene oxidation and proposed that benzyl radical reacts faster with radicals than with the molecular oxygen. Consequently, authors developed a detailed kinetic model where benzyl radical reacts with O atom and HO_2 radical, respectively forming benzaldehyde + H or + OH . Then, they suggested that benzaldehyde can undergo H abstraction reactions forming the benzoyl radical, which subsequently decomposes into phenyl radical and carbon monoxide. This kinetic scheme contrasts with previous hypothesis of McLain and co-workers [64], who considered a direct CC bond fission after the O atom addition on the benzyl radical, forming $C_6H_5 + CH_2O$. Brezinsky and co-workers equally mentioned that benzyl radical can recombine with OH radical forming benzylalcohol, which can subsequently produce benzaldehyde through H atom abstraction reactions, followed by the loss of a hydrogen atom. In 1996 and 1998, the Brezinsky's group respectively determined laminar burning velocities of toluene-air flames [86] and experimentally investigated oxidation of toluene-butane blends in

a flow reactor [189]. Authors updated their kinetic model in order to reproduce all these new measurements.

In addition to shock tubes and turbulent flow reactors, toluene oxidation was equally investigated in flames. In 1987, Hamins and Seshadri [190] performed an experimental analysis of toluene combustion in diffusion flames and measured mole fraction profiles of numerous compounds by gas chromatography. In 1990, Hamins and co-workers [191] compared a pure methane diffusion flame to a methane-toluene one, in order to deduce some mechanistic indications. Authors showed that benzene formation should be one of the main toluene consumption routes in flames, confirming pyrolysis mechanisms previously postulated (see reaction R3 of table 5.1). In 1996, Lindstedt and Maurice [192] developed a more detailed kinetic model whose predictions satisfactorily compare with reactor data of Brezinsky and co-workers [188], diffusion flame measurements of Hamins and Seshadri [190] and flame speed measurements of the Brezinsky's group [86]. Comparatively to the kinetic scheme outlined by Brezinsky and co-workers [78, 188], the mechanism of Lindstedt and Maurice contains additional toluene consumption pathways, including benzyl radical decomposition reactions [192].

Surprisingly, one has to wait 2007 for new investigations devoted to toluene oxidation in flames. El Bakali and co-workers [23] investigated a laminar, premixed and one-dimensional methane flame, seeded with toluene and burning at low pressure. Measurements satisfactorily compared to predictions of a new kinetic model, whose toluene sub-mechanism was based on the work of Lindstedt and Maurice [192]. In the mean time, Dagaut and co-workers [21] investigated toluene oxidation in a jet stirred reactor, at various temperatures and equivalence ratios. Authors measured concentration profiles of 20 chemical species and satisfactorily compared these data to predictions of their model developed for benzene oxidation in 2001 [22]. In 2005, Bounaceur and co-workers [193] performed new flow reactor and shock tube measurements on toluene oxidation and developed a detailed kinetic model to compare with their measurements. In 2004, 2005 and 2006, the Brezinsky's group investigated toluene oxidation and pyrolysis under high pressure conditions [194–197].

Authors updated their kinetic model to reproduce their experiments and reached a good fit between measurements and predictions.

Since 2007, important insights were performed into the understanding of toluene combustion. These improvements were allowed by the contribution of theoretical chemistry to analyze complex reaction pathways. As an example example, Klippenstein and co-workers [198] have theoretically determined the fall-off behavior and branching ratios of toluene decomposition through CH and CC bond fissions (see reactions R1 and R7 of table 5.1) and successfully compared their calculations to measurements performed by Eng and co-workers [199] in 2002. The work of Klippenstein has thrown light on uncertainties that remained since 1939 and its introduction into new kinetic models should be of particular importance. Recently, da Silva and co-workers [200–202] and Cavallotti and co-workers [203] have theoretically investigated reactions involving benzyl radical and methylphenyl radicals, whose consumptions involve complex channels that were still misunderstood. They found that benzyl radical may decompose into H atom and fulvenallene (C_7H_6), which can subsequently react with hydrogen atom, decomposing into cyclopentadienyl radical and acetylene. Moreover, authors calculated kinetic parameters of these reactions in order to help detailed kinetic model developments. At the same time of our work, Li and co-workers [204] have used the new tunable synchrotron technique to investigate the first laminar, premixed and one-dimensional toluene-oxygen-argon flame. In this rich flame, authors have measured a significant concentration of the C_7H_6 compound, previously predicted by theoretical investigations, but did not provide an update kinetic model to interpret their measurements. As presented in this chapter, such a kinetic model has been developed in this work and published in 2009 [24]. The model confirms that fulvenallene formation is an important pathway of toluene combustion chemistry.

Very recently, Tian and co-workers have published a new kinetic model that well predicts a rich toluene flame [205]. The same year, we have published new structures of toluene flames burning at lean and stoichiometric conditions, together with an updated kinetic model [25]. There-

fore, the model presented in this work is the first validated over a wide range of equivalence ratios. Li and co-workers equally published lean and stoichiometric toluene flame structures in 2011 [206], demonstrating that toluene combustion has really become a central theme of research.

The present chapter exposes the experimental structures of laminar, premixed and one-dimensional toluene-oxygen-argon flames partly published in [24] and [25]. In addition, it provides new measurements performed at an equivalence ratio of 1.8. The kinetic model developed in the previous chapter has been extended to toluene combustion, in order to compare its predictions with experimental flame structures. The main toluene consumption channels are highlighted by comparative reaction rate analyses and the dependence of these pathways to the equivalence ratio and the flame temperature is investigated.

5.2 Experimental results

This section presents the experimental measurements performed in laminar, premixed and one-dimensional toluene-oxygen-argon flames in this work. Similarly to benzene flames discussed in the previous chapter, toluene flames have been stabilized at low pressure on the experimental setup presented in chapter 2 and have been investigated with equivalence ratios (ϕ) spreading from 0.7 to 2. This wide range of ϕ should allow to identify its influence on main reaction pathways of toluene combustion. Table 5.2 summarizes flame parameters and provides flame codes that will be used throughout this chapter. A more detailed descrip-

Table 5.2: toluene flame parameters

Code	ϕ	P mbar	Mass flux ($\text{g s}^{-1} \text{ cm}^{-2}$)	Fresh gas composition		
				$\chi_{C_7H_8}$	χ_{O_2}	χ_{Ar}
TF07	0.7	45	$2.94 \cdot 10^{-3}$	$2.26 \cdot 10^{-2}$	$2.9 \cdot 10^{-1}$	$6.87 \cdot 10^{-1}$
TF10	1.0	45	$2.99 \cdot 10^{-3}$	$2.26 \cdot 10^{-2}$	$2.03 \cdot 10^{-1}$	$7.74 \cdot 10^{-1}$
TF18	1.8	45	$3.12 \cdot 10^{-3}$	$9.89 \cdot 10^{-2}$	$4.94 \cdot 10^{-1}$	$4.07 \cdot 10^{-1}$
TF20	2.0	45	$3.15 \cdot 10^{-3}$	$9.89 \cdot 10^{-2}$	$4.45 \cdot 10^{-1}$	$4.56 \cdot 10^{-1}$

tion of flame characteristics and parameters is proposed in the appendix B.

Similarly to benzene flames of the previous chapter, the dilution ratios of rich toluene flames have been chosen to maximize the soot precursor concentrations, while preventing the occurrence of excessive temperatures in the burnt gases. As the maximum flame temperature increases near the stoichiometry, lean and stoichiometric toluene flames have been investigated at higher dilution ratios. Initial mole fractions of toluene in TF20 and TF18 have been chosen to keep the total carbon content similar to that of rich benzene flames, according to equation 5.1.

$$\chi_{C_7H_8} = \chi_{C_6H_6} \times \frac{6}{7} \quad (5.1)$$

The working pressure and fresh gas velocity v_c of each investigated flame is respectively 45 mbar and 41 cm s⁻¹ at 298 K. Lean and stoichiometric toluene flames depict a typical blue color, whereas rich flames are greener and orange in the burnt gas region, as soot emits in this part of the visible spectrum. As Benzene flames, the soot production of rich toluene flames is confirmed by its deposition on the wall of the combustion chamber, and particularly on the quartz nozzle. To avoid blocking the hole of the quartz nozzle, measurements in the sooting region have to be rapidly performed.

5.2.1 Investigated flame temperatures

Figure 5.1 presents temperature profiles of toluene-oxygen-argon flames investigated in this work. Each flame depicts a preheating zone where temperature rises slowly, a flame front where the heat exchange is maximum, and a burnt gas region where temperature slightly decreases. Figure 5.1 shows that TF18 and TF20 have maximum temperatures close to 1800 K, higher than those measured in TF10 and TF07 (about 1650 K). This observation contrasts with the theory that predicts occurrence of maximum flame temperatures around the stoichiometry. The lowest

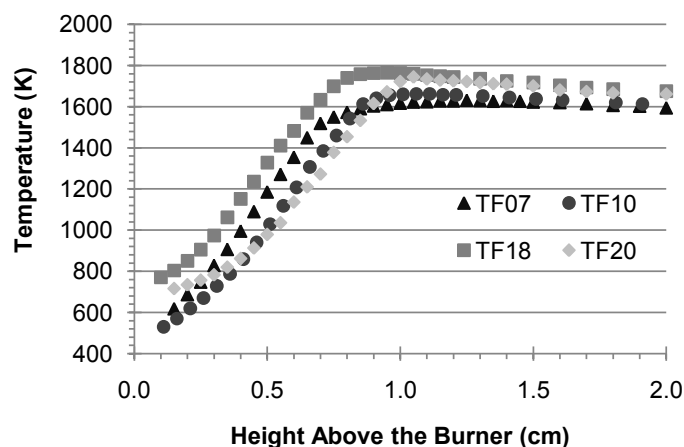


Figure 5.1: experimental temperature profiles of toluene-oxygen-argon flames. X-axis and Y-axis respectively represent the height above the burner in cm and the measured temperature in K. Flame codes refer to table 5.2.

dilution ratios of TF18 and TF20 (see table 5.2), compared to TF10 and TF07, fully explains this behavior.

Adiabatic flame temperatures have been calculated for toluene flames presented in table 5.2 and are summarized in the appendix C.

5.2.2 Influence of equivalence ratio on flame structures

This section presents measurements performed in the toluene flames of this work. Since many chemical species are common with benzene flames exposed in the previous chapter, the following discussion focuses on a comparison between experimental toluene and benzene flame structures. These observations bring important clues to understand the impact of the methyl group of toluene on its flame chemistry, which will be discussed in more details in the following sections.

Figures 5.2, 5.3, 5.4 and 5.5 respectively present measurements performed in TF07, TF10, TF18 and TF20. In TF07 and TF10, toluene is fully consumed at 0.6 and 0.8 cm of the burner surface, respectively. On the contrary, molecular oxygen remains in burnt gases of TF07 and

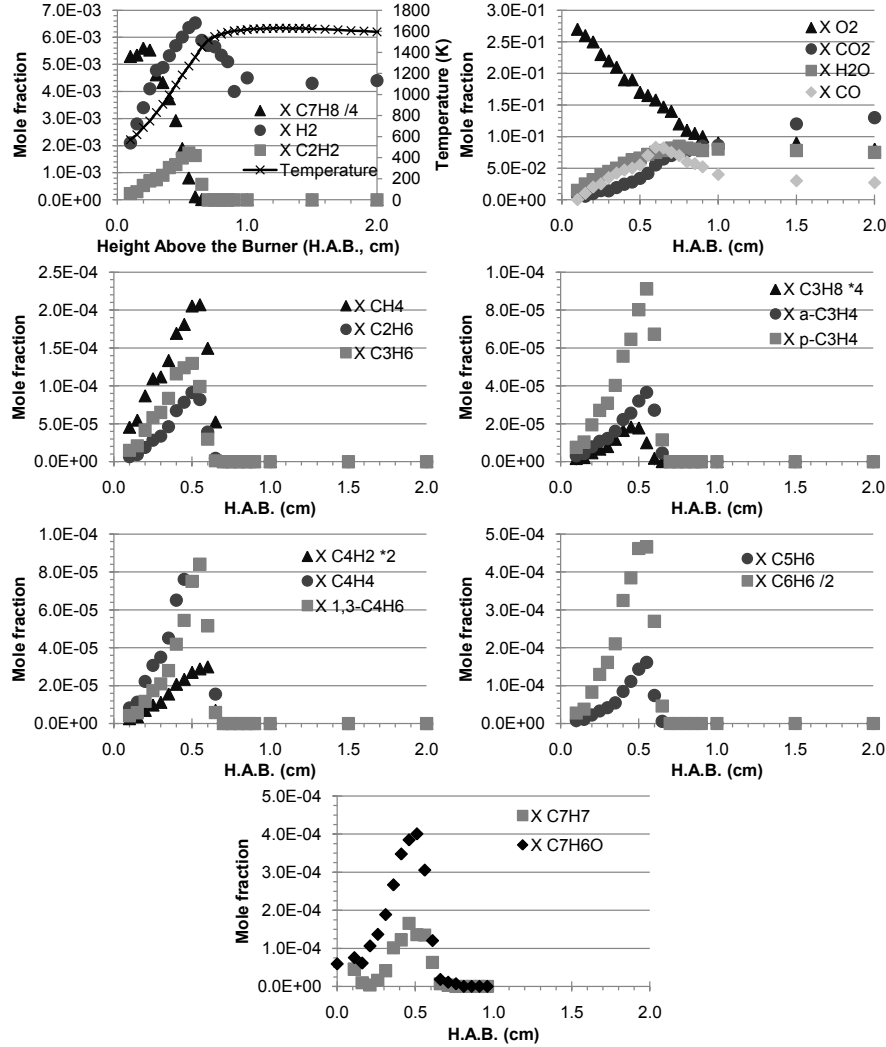


Figure 5.2: experimental flame structure of the lean toluene-oxygen-argon flame TF07. The X-axis and Y-axis represent the height above the burner in cm and the mole fraction measured for each chemical species, respectively. If indicated, mole fraction profiles are multiplied or divided by a factor allowing its fit in the graph.

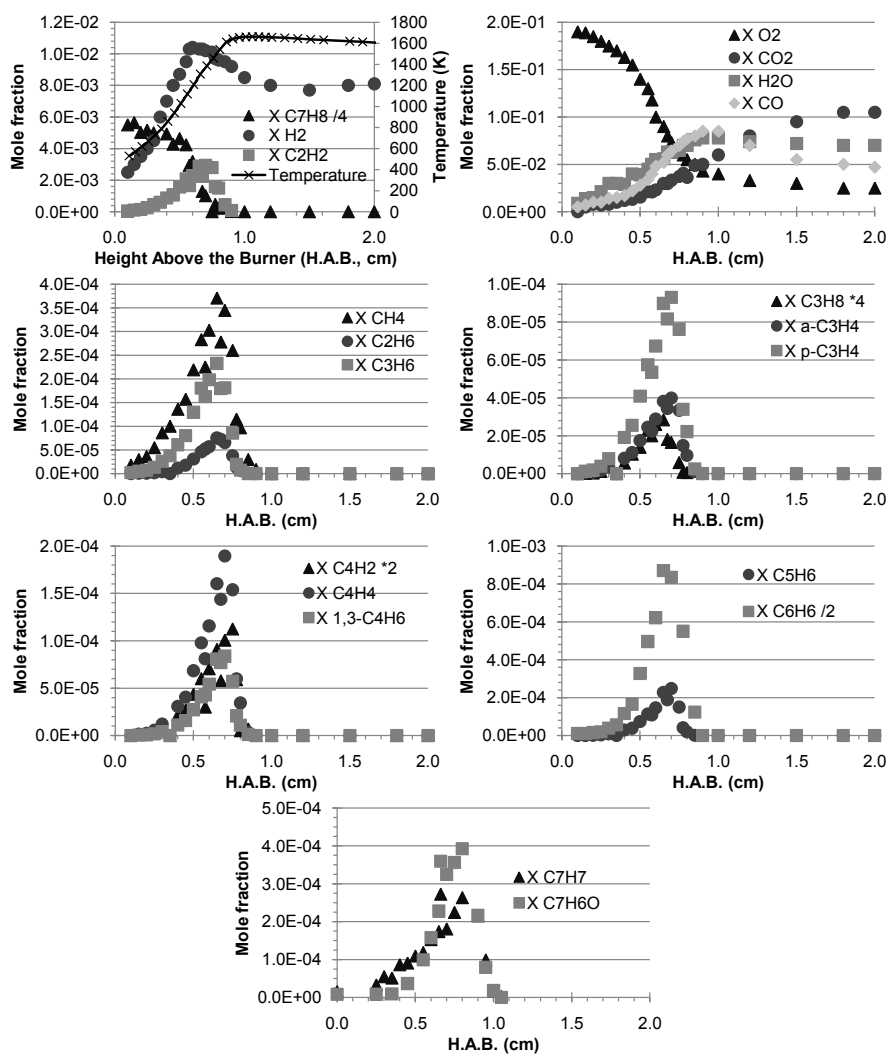


Figure 5.3: experimental flame structure of the stoichiometric toluene-oxygen-argon flame TF10. X-axis and Y-axis respectively represent the height above the burner in cm and the mole fraction measured for each chemical species. If indicated, mole fraction profiles are multiplied or divided by a factor allowing its fit in the graph.

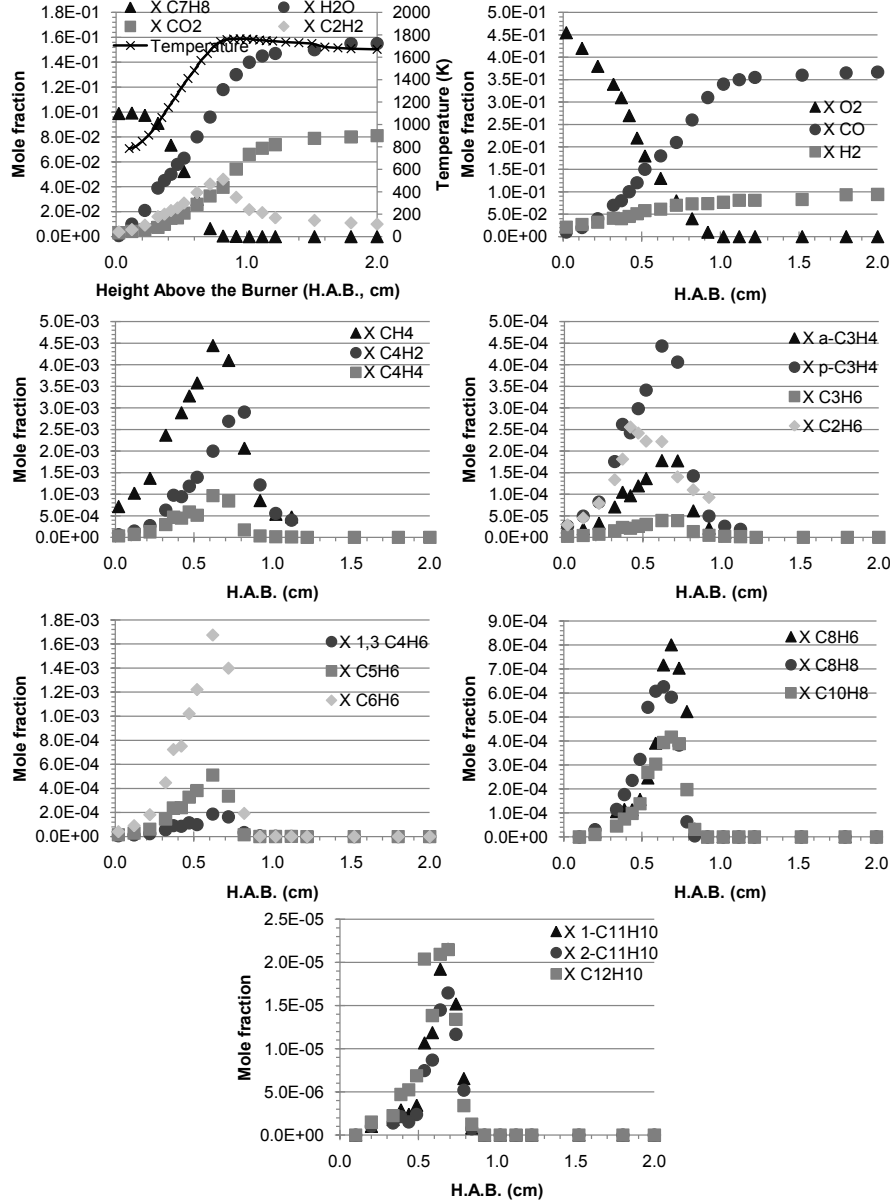


Figure 5.4: experimental flame structure of the rich toluene-oxygen-argon flame TF18. X-axis and Y-axis respectively represent the height above the burner in cm and the mole fraction measured for each chemical species. If indicated, mole fraction profiles are multiplied or divided by a factor allowing its fit in the graph..

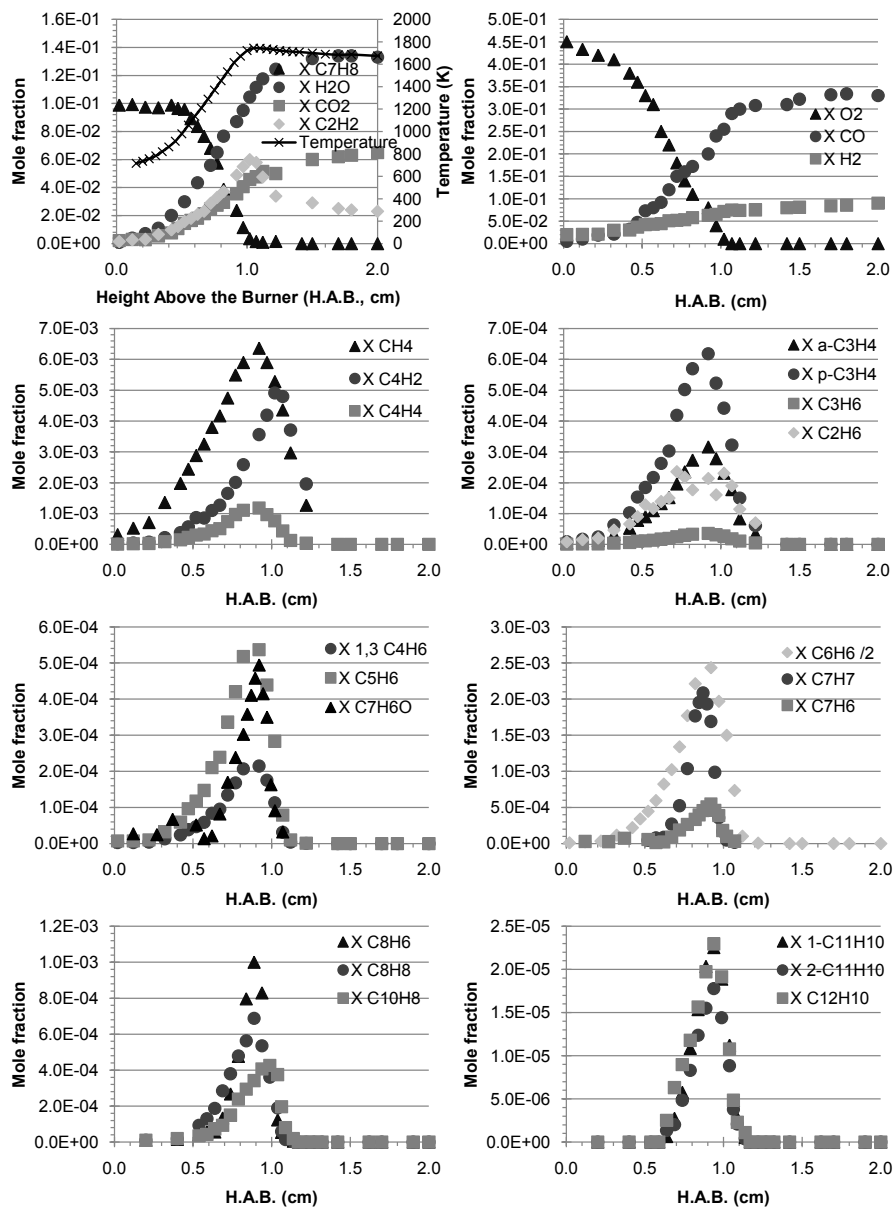


Figure 5.5: experimental flame structure of the rich toluene-oxygen-argon flame TF20. X-axis and Y-axis respectively represent the height above the burner in cm and the mole fraction measured for each chemical species. If indicated, mole fraction profiles are multiplied or divided by a factor allowing its fit in the graph..

TF10, with mole fractions of $1 \cdot 10^{-1}$ and $2.5 \cdot 10^{-2}$, respectively. Since TF10 is a stoichiometric flame, O_2 should theoretically be completely consumed in burnt gases, in the same way as toluene. However, carbon monoxide and molecular hydrogen are still present in burnt gases, indicating that the combustion reaction is not fully completed. Considering that experimental mole fractions of CO and H_2 persisting in burnt gases of TF10 still have to be consumed through the overall reaction $O_2 + H_2 + CO \rightleftharpoons CO_2 + H_2O$, O_2 mole fraction in burnt gases should be of $2.2 \cdot 10^{-2}$, which is very close to the measured value of $2.5 \cdot 10^{-2}$. The increase of the χ_{CO}/χ_{CO_2} ratio in TF10, compared to TF07, can be explained by the main CO consumption route $CO + OH \rightleftharpoons CO_2 + H$, which is disadvantaged under rich conditions, depicting lower OH concentrations. In TF18 and TF20, toluene and molecular oxygen are fully consumed around 0.8 and 1 cm, respectively. This obviously demonstrates that contrarily to O_2 in lean flames, the excess of fuel is fully consumed in rich flames. It is converted to H_2 , some hydrocarbons such as polyacetylenic compounds and soot, which all persist in the burnt gas region.

Compared to benzene flames, methane (CH_4) is an important intermediate of rich toluene combustion. This may be explained either by reactions substituting the methyl group of toluene by a H atom, yielding methane and benzene, or by toluene decomposition into phenyl and methyl radicals, which can subsequently recombine with a hydrogen atom into CH_4 . In the same way as CH_4 , maximum mole fractions of ethane (C_2H_6) significantly increase in toluene flames. Since methyl radical is a major methane precursor and CH_3 recombination yields C_2H_6 , this observation is consistent with higher methane mole fractions measured in toluene flames, compared to benzene flames. Acetylene (C_2H_2) maximum mole fractions are significant over the entire range of equivalence ratios and are close to those measured in corresponding benzene flames. This observation suggests that acetylene formation routes in toluene flames might be analogous to those of benzene flames. As in benzene flames, the main C_3 and C_4 hydrocarbons detected are allene (a- C_3H_4), propyne (p- C_3H_4), propylene (C_3H_6), propane (C_3H_8),

diacetylene (C_4H_2), vinylacetylene (C_4H_4) and butadiene (1,3- C_4H_6). Similarly to acetylene, their maximum mole fractions are close to those measured in benzene flames with similar equivalence ratios, indicating that C_2 , C_3 and C_4 hydrocarbons may be formed through reaction pathways which are common to benzene and toluene combustion. The only C_5 hydrocarbon that has been identified is cyclopentadiene (C_5H_6) and its maximum mole fractions in TF07 and TF10 are similar to those measured in BF07 and BF10. Under rich conditions, toluene flames exhibit lower C_5H_6 mole fractions than corresponding benzene flames, whereas cyclopentadiene is still present in high concentrations. As in benzene combustion, the parent radical of C_5H_6 (cyclopentadienyl radical, C_5H_5) might therefore be a central intermediate of toluene consumption, connected to C_4 and C_3 hydrocarbons. This assumption could explain similarities observed between mole fraction profiles of several C_4 , C_3 and C_2 hydrocarbons in benzene and toluene flames, and is coherent with previous pyrolysis studies on toluene which demonstrated that C_5H_5 is a key intermediate of its thermal decomposition [187]. Benzene (C_6H_6) maximum mole fractions are significant over the entire range of equivalence ratios. This suggests that benzene is a key intermediate of toluene combustion and that a significant overlap between toluene and benzene flame chemistry should exist. This assumption confirms analogies observed between benzene and toluene flames and may explain important cyclopentadiene concentrations, since it is an important intermediate of benzene combustion. In the same way as methane, significant benzene mole fractions support that substitution of the methyl group of toluene by a H atom may play an important role in the toluene combustion.

In order to throw some light on toluene decomposition into benzyl radical + H atom and its subsequent degradation into C_7H_6 intermediates, MBMS measurements at m/z ratios corresponding to C_7H_7 and C_7H_6 have been performed. Surprisingly, in TF20 the maximum mole fraction of benzyl radical is 10 times higher than that of the phenyl radical in BF20. This significant difference should come from the resonant stabilization of the benzyl radical, which makes it less reactive to O_2 than

phenyl radical. The measurement of a C_7H_6 maximum mole fraction as high as $5 \cdot 10^{-4}$ in TF20 and below the detection limit in TF07 and TF10 is an interesting finding which indicates that C_7H_6 may only be an important decomposition product of benzyl radical at temperatures as high as those measured in TF20. This confirms previous theoretical studies showing that the decomposition of benzyl radical into $C_7H_6 + H$ might be an important consumption route [200–203]. Measurements performed in this chapter provide relevant experimental data that will allow to compare with recent rate parameters proposed for the kinetic modeling of benzyl radical decomposition. MBMS measurements have equally been performed at an m/z ratio corresponding to benzaldehyde (C_7H_6O), as it is thought to be an important intermediate of the benzyl radical oxidation. C_7H_6O is present in significant mole fractions in all investigated toluene flames and the ratio between benzyl radical and benzaldehyde mole fractions increases towards lean conditions, confirming that this pathway plays a key role in toluene and benzyl radical oxidation.

The measurement of mole fraction profiles of larger chemical species has equally been achieved. Phenylacetylene (C_8H_6), styrene (C_8H_8), naphthalene ($C_{10}H_8$), methylnaphthalene isomers (1- $C_{11}H_{10}$ and 2- $C_{11}H_{10}$) and biphenyl ($C_{12}H_{10}$) have been detected in rich toluene flames. Phenanthrene mole fraction was close to the detection limit but its maximum mole fraction is estimated to $5 \cdot 10^{-6}$. Styrene formation is highly stimulated in toluene flames, compared to benzene flames, indicating that its formation could depend on the benzyl radical. Phenylacetylene mole fractions are similar in benzene and toluene flames, whereas naphthalene mole fractions are higher in toluene flames. This suggests that phenylacetylene may not be an important intermediate of naphthalene formation in aromatic flames, whereas its formation pathways are favored in toluene combustion. Biphenyl maximum mole fraction is three times lower in toluene flames than in benzene flames. This observation demonstrates that reactions such as the phenyl radical self recombination or the phenyl radical addition to benzene, followed by the loss of an H atom may play an important role in its formation. The development

of a kinetic sub-model devoted to molecular growth and PAH formation will be the subject of the next chapter. The present chapter only focuses on toluene oxidation in flames.

5.3 Discussion on toluene combustion chemistry

This section presents the development of a detailed kinetic sub-model for toluene combustion and compares its predictions to the experimental results. The following discussion is divided into several subsections that each corresponds to flame chemistry of specific intermediates of toluene combustion. For each intermediate compound, reactions leading to its formation are presented and choices in consumption pathways and kinetic parameters are justified by a comprehensive literature survey on its flame chemistry. The predictive capability of the developed kinetic sub-model is evaluated for each compound by comparing its predictions to mole fraction profiles measured in TF07, TF10, TF18 and TF20 or to experimental data available in the literature. In addition to our kinetic model predictions, experimental results are compared to predictions of the mechanism developed by Richter and Howard for benzene combustion [92], called the RH model, in order to assess improvements brought by the present study. Finally, comparative reaction rate analyses allow to determine the importance of each reaction pathway in consumption or formation of every intermediate compound. The discussion begins with toluene, introduced as a reactant in flames described in this chapter.

5.3.1 The toluene sub-model

The toluene molecule consists in a benzene ring with a hydrogen atom replaced by a methyl group. This slight difference has a deep impact on toluene combustion, as H abstraction reactions may now react with this new CH_3 group, yielding the benzyl radical which is not an important intermediate of benzene combustion. Moreover, the methyl group

transforms the D_{6h} symmetry of benzene into C_{2v} . Consequently, all hydrogen atoms are no more equivalent and H abstraction reactions onto the phenyl ring can lead to ortho, meta and para isomers. In addition to these H abstraction reactions, toluene can undergo decomposition and electrophilic addition reactions, as discussed hereafter.

Toluene consumption pathways

(i) Unimolecular dissociation reactions

The thermal decomposition of toluene has been investigated by many researchers [183,184,187,199,207–212] who found that its main products are H atom, methyl, phenyl and benzyl radicals. These compounds are produced by reactions breaking either the CC bond between the phenyl ring and the methyl group or a CH bond of the CH_3 , as respectively summarized by reactions R1 and R2 of table 5.3. Whereas these works provide kinetic measurements of these two reaction routes at various pressures, no experimental studies fully describe the fall-off behavior of toluene decomposition. In 2007, Klippenstein and co-workers [198] performed a theoretical investigation of these reactions and calculated their high and low pressure rate constants, together with their fall-off parameters. Authors equally calculated that the recombination of benzyl radical with an H atom can give toluene with an excess of energy, which subsequently decomposes into phenyl and methyl radicals (see reaction R3). Since Klippenstein and co-workers comprehensively investigated toluene decomposition and successfully validated their calculations against several experiments, their rate parameters have been included into the present kinetic model.

(ii) Reactions with OH radical

The toluene reaction with OH radical has been investigated by two groups at high temperature [103,216]. These works showed that H abstraction reactions on the methyl group of toluene (see reaction R4 of table 5.3) is dominant above 500 K. Nevertheless, Seta and co-workers highlighted that the H abstraction of a hydrogen atom onto the phenyl

Table 5.3: C_7H_8 consumption reactions included into the kinetic model.

Reactions		$k = AT^n e^{-E_a/RT}$			Refs.
		A^a	n	E_a^a	
Decomposition reactions.					
R1	$b\text{-}C_7H_7 + H + M \rightleftharpoons C_7H_8 + M$ (k_∞)	$7.23 \cdot 10^{13}$	0.06	0	[198]
	$b\text{-}C_7H_7 + H + M \rightleftharpoons C_7H_8 + M$ (k_0)	$3.03 \cdot 10^{136}$	-33.35	55.6	[198]
	Troe's broadening factors: $1.63 \cdot 10^{-1} / 7.14 \cdot 10^2 / 7.28 \cdot 10^2 / 5.11 \cdot 10^3$				[198] ^b
R2	$C_6H_5 + CH_3 + M \rightleftharpoons C_7H_8 + M$ (k_∞)	$2.33 \cdot 10^{14}$	-0.283	-0.2	[198]
	$C_6H_5 + CH_3 + M \rightleftharpoons C_7H_8 + M$ (k_0)	$6.74 \cdot 10^{83}$	-19.22	15	[198]
	Troe's broadening factors: $7.35 \cdot 10^{-1} / 6.00 \cdot 10^4 / 5.13 \cdot 10^2 / 1.00 \cdot 10^5$				[198] ^b
R3	$b\text{-}C_7H_7 + H \rightleftharpoons C_6H_5 + CH_3$	$4.5 \cdot 10^{58}$	-11.9	51.9	[198]
Reactions with OH radical.					
R4	$C_7H_8 + OH \rightleftharpoons b\text{-}C_7H_7 + H_2O$	$1.31 \cdot 10^5$	2.39	-0.6	[103]
R5	$C_7H_8 + OH \rightleftharpoons o\text{-}C_6H_4CH_3 + H_2O$	$5.22 \cdot 10^3$	2.61	0.3	[103]
R6	$C_7H_8 + OH \rightleftharpoons m\text{-}C_6H_4CH_3 + H_2O$	$7.4 \cdot 10^3$	2.69	0.9	[103]
R7	$C_7H_8 + OH \rightleftharpoons p\text{-}C_6H_4CH_3 + H_2O$	$4.43 \cdot 10^3$	2.66	0.6	[103]
R8	$C_7H_8 + OH \rightleftharpoons HOC_6H_4CH_3 + H$	$1.32 \cdot 10^2$	3.25	5.6	[103]
R9	$C_7H_8 + OH \rightleftharpoons C_6H_5OH + CH_3$	$7.82 \cdot 10^2$	2.88	3.2	[103]
Reactions with H atom.					
R10	$C_7H_8 + H \rightleftharpoons b\text{-}C_7H_7 + H_2$	6.47	3.98	3.4	[213]
R11	$C_7H_8 + H \rightleftharpoons o\text{-}C_6H_4CH_3 + H_2$	$1.02 \cdot 10^8$	1.8	15.9	c
R12	$C_7H_8 + H \rightleftharpoons m\text{-}C_6H_4CH_3 + H_2$	$2.73 \cdot 10^8$	1.8	16.7	c
R13	$C_7H_8 + H \rightleftharpoons p\text{-}C_6H_4CH_3 + H_2$	$1.33 \cdot 10^8$	1.8	16.3	c
R14	$C_7H_8 + H \rightleftharpoons C_6H_6 + CH_3$	$9.50 \cdot 10^5$	2	0.9	[214]
Reactions with O atom.					
R15	$C_7H_8 + O \rightleftharpoons b\text{-}C_7H_7 + OH$	$6.3 \cdot 10^{11}$	0	0	[215]
R16	$C_7H_8 + O \rightleftharpoons o\text{-}C_6H_4CH_3 + OH$	$1.02 \cdot 10^{13}$	0	10.6	c
R17	$C_7H_8 + O \rightleftharpoons m\text{-}C_6H_4CH_3 + OH$	$2.73 \cdot 10^{13}$	0	11.4	c
R18	$C_7H_8 + O \rightleftharpoons p\text{-}C_6H_4CH_3 + OH$	$1.33 \cdot 10^{13}$	0	11	c
R19	$C_7H_8 + O \rightleftharpoons OC_6H_4CH_3 + H$	$5.55 \cdot 10^{12}$	0	2.3	d

^a A units are s^{-1} and $cm^3 \text{ mol}^{-1} s^{-1}$ for Unimolecular and bimolecular reactions, respectively. Ea is expressed in kcal mol^{-1} . ^b These parameters were calculated by Enoch Dames and communicated by Klippenstein. ^c These rate constants have been estimated by analogy with benzene (pre-exponential factors times by 5/6) and branching ratios for ortho, meta and para isomers formations correspond to H abstraction reaction with OH (reactions R5 to R7), investigated by Seta and co-workers [103]. ^d This rate constant has been estimated by analogy with benzene (pre-exponential factor times by 5/6). This reaction is not considered isomer specific (see text).

ring, as well as the substitution of the methyl group and that of a H atom of the ring by OH radical, can compete at higher temperatures. These latter reaction channels can yield three isomers of the methylphenyl radical, through reactions R5 to R7 or give phenol and cresol ($HOC_6H_4CH_3$) by reactions R8 and R9. All these reactions have been introduced into the kinetic model using rate parameters from the work of Seta and co-workers [103]. In order to simplify the developed kinetic model and since the specific consumption of isomers of $HOC_6H_4CH_3$ are poorly known, our mechanism does not differentiate between its ortho, meta and para isomers. This simplification will be discussed in more details further. In figures of the following discussion, $HOC_6H_4CH_3$ and $OC_6H_4CH_3$ will be represented as meta isomers, as Seta and co-workers found that its formation dominates over the investigated temperature range.

(iii) *Reactions with H atom*

The toluene reaction with H atom can basically occur through four different pathways. The first abstracts a H atom on the methyl group, yielding the resonantly stabilized benzyl radical, and was particularly investigated by Ellis and co-workers [214] and Oehlschlaeger and co-workers [213]. Authors found that this reaction is fast and should be the dominant path under rich flame conditions. Rate parameters calculated by Oehlschlaeger and co-workers have been used in the developed kinetic model for this reaction (see R10 of table 5.3). The second path abstracts a hydrogen atom from the benzene ring, forming ortho, meta and para methylphenyl radical isomers ($C_6H_4CH_3$) through reactions R11 to R13, respectively. These rate constants have been estimated using branching ratios determined by Seta and co-workers for the similar reaction with the OH radical [103]. The overall rate constant has been determined by analogy with H atom abstraction on benzene by hydrogen atom, whose pre exponential factor has been multiplied by a factor 5/6 to account for the replacement of a hydrogen atom by the methyl group. The third path involves a H atom addition onto the carbon of the benzene ring that is connected to the methyl group, followed by the CC bond rupture giving benzene and methyl radical. High benzene con-

centrations measured in this work over the entire range of equivalence ratios indicates that this reaction should be important under combustion conditions. The kinetics of this channel has equally been investigated by Ellis and co-workers [214] and their rate constant parameters have been used for reaction R14. The last reaction channel involves an H atom addition onto a CH carbon atom of the toluene ring, giving various methylcyclohexadienyl radicals. To our best knowledge, no studies were devoted to this reaction. Since the previous chapter showed that H atom addition onto the benzene ring does not compete with H atom abstraction reactions, this reaction was not included into the toluene sub-mechanism.

(iv) Reactions with O atom

The toluene reaction with O atom has been investigated in 1990 at high temperature by Hoffmann and co-workers [215]. Authors measured the overall rate of reaction $C_7H_8 + O \rightarrow products$ and estimated the overall rate constant of reaction R15 which abstracts an H atom of methyl group of toluene, giving $b-C_7H_7 + OH$. In the previous chapter devoted to benzene combustion, we showed that O atom can abstract an H atom from the ring as well as perform an electrophilic addition, followed by a CH bond fission giving phenoxy radical. In the same way as benzene, O atom should be able to react with toluene forming methylphenyl ($C_6H_4CH_3$) or methylphenoxy ($OC_6H_4CH_3$) radicals. Reaction parameters of these channels have been introduced into the chemical model by analogy with benzene and pre exponential factors were multiplied by 5/6 in order to account for the replacement of a H atom by CH_3 in toluene (see reactions R16 and R19). As for reactions R11 to R13, branching ratios determined by Seta and co-workers for the same reaction with OH radical have been used [103]. The sum on rate constants introduced for $C_7H_8 + O$ reactions in our kinetic model only differs by a factor comprised between 0.7 and 1.5 from the expression of Homann and co-workers, proving that our estimated rates are satisfactory. Our kinetic model does not differentiate between ortho, meta and para isomers of $OC_6H_4CH_3$. However, it will be further demonstrated that these radicals have common consumption pathways, allowing to use, as a first

approximation, an overall rate constant rather than a detailed mechanism including all isomers.

Comparison between predicted and experimental results

Figure 5.6 compares experimental toluene mole fraction profiles with predictions of the present and RH models. Both kinetic mechanisms depict a good predictive capability. Compared to the RH model, the mechanism developed in this work improves the rate of toluene consumption under lean conditions. The underestimation of the RH model principally comes from the lack in benzyl radical consumption routes involving oxygenated compounds, causing an overestimation of benzyl radical concentration that speeds up toluene formation from the reverse of reaction R1 (see table 5.3).

A comparative reaction rate analysis has been carried out to determine contribution of each reaction channel to toluene consumption and formation. Results are summarized in figure 5.7 and show that the H abstraction of a hydrogen atom from the methyl group of toluene is the dominant pathway over the entire range of investigated equivalence ratios. This observation confirms previous studies that identified the benzyl radical as the major product of the toluene reaction with H , O and OH radicals at high temperature.

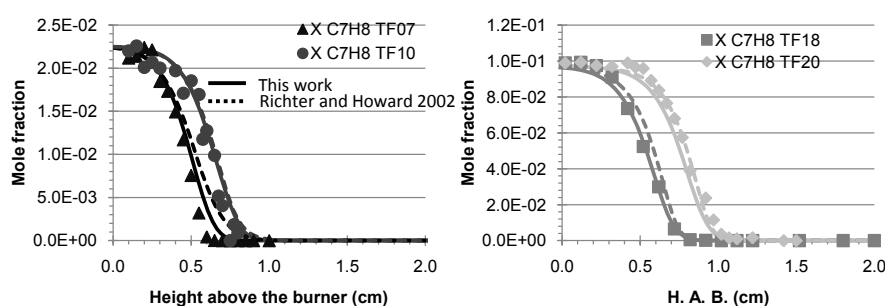


Figure 5.6: experimental and predicted mole fraction profiles of toluene (C_7H_8). Gray scale symbols represent experiments ($\triangle$ TF07, $\circ$ TF10, $\square$ TF18, $\diamond$ TF20). Solid and dashed curves stand for predictions of present and Richter and Howard [92] models, respectively.

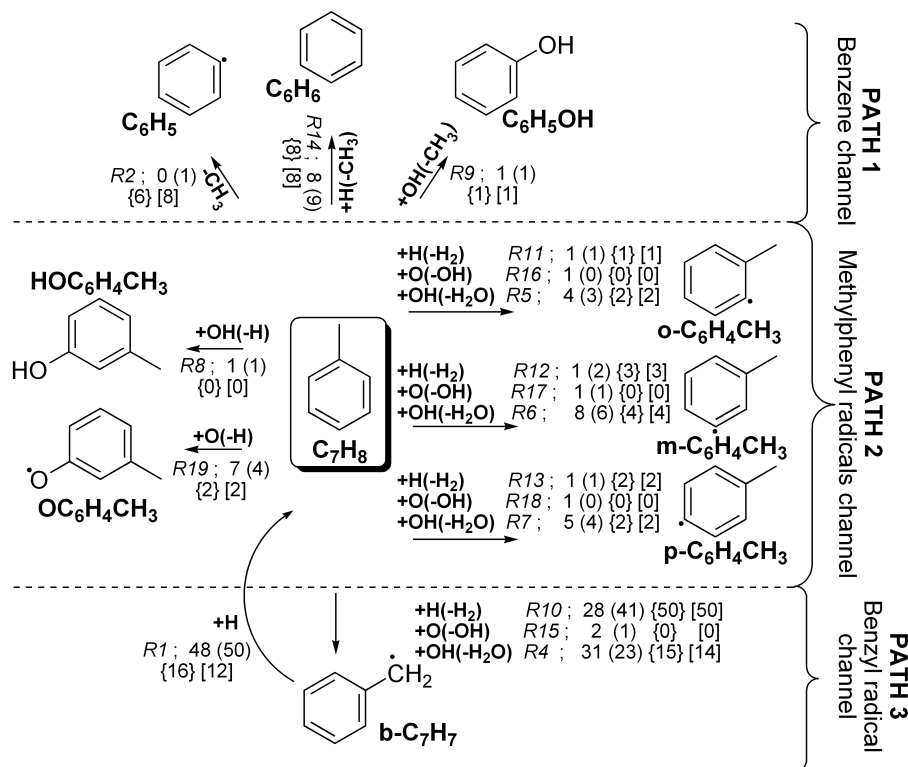


Figure 5.7: summary of toluene consumption pathways included into the developed kinetic model. Percentages represent contributions in TF07, (TF10), {TF18} and [TF20]

However, figure 5.7 demonstrates that minor reaction routes including H abstraction onto the phenyl ring and substitution reactions should not be neglected, as they respectively contribute to 40% and 34% of toluene consumption in TF07 and TF20. Toluene decomposition into benzyl radical and H atom is found to proceed backward, forming toluene. Since the loop involving H abstraction reactions on toluene forming benzyl radical and its recombination with a H atom into toluene globally neutralizes two chain carrier radicals, the use of accurate rate parameters for these reactions is of particular importance for the modeling of the fuel consumption rate. The second toluene decomposition reaction forming phenyl and methyl radicals is not significantly active in TF07 and TF10. However, it is accelerated by higher temperatures of TF18

and TF20, where it respectively contributes to 6 and 8% of toluene consumption.

Whereas the previous chapter has shown that benzene consumption only yields four different products (phenol, phenyl, phenoxy and cyclohexadienyl radicals), the toluene combustion appears to be more complex as nine different products are involved. For more convenience, toluene consumption into these nine intermediate species will be divided into three main pathways, as illustrated in figure 5.7. The first channel gathers phenol, phenyl radical and benzene formations, which are directly connected to the kinetic scheme of benzene combustion already discussed. This first path shows that a significant overlap exists between benzene and toluene chemistry, highlighting the importance of developing reliable benzene combustion mechanisms prior to model toluene combustion. The second channel contains reactions occurring onto CH groups of the toluene ring, forming cresol, methylphenyl and methylphenoxy radicals. Whereas most of previous kinetic models devoted to aromatic oxidation only consider reactions taking place on the side chain of toluene, our work demonstrates that H abstraction and electrophilic O atom addition onto the ring of toluene play a significant role and should not be neglected. Finally, the third path involves benzyl radical formation and is a key channel of toluene combustion, as it dominates over the entire range of equivalence ratios. The following discussion examines further reactions of these three overall channels.

5.3.2 Path 1: the benzene channel

In the previous section, we have shown that reactions R2, R9 and R14 of table 5.3 on page 204 consume toluene into phenyl radical, phenol and benzene, respectively. These reactions form what we have called the first path of toluene consumption, which is connected to the kinetic scheme of benzene. This path accounts for 9, 11, 15 and 17% of toluene consumption in TF07, TF10, TF18 and TF20, respectively. The increase of its contribution with the equivalence ratio and the flame temperature comes from reaction R14 that involves H atom and reaction R2 that

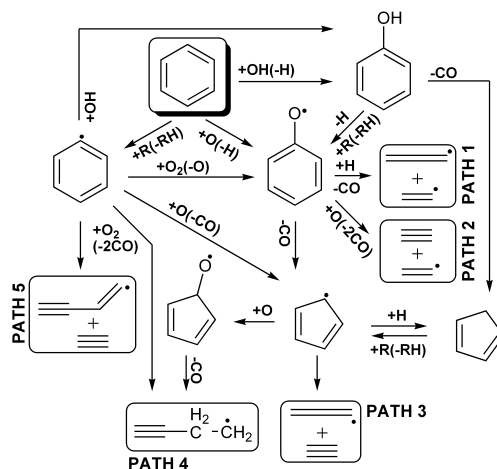


Figure 5.8: summary of benzene consumption pathways included into the developed kinetic model.

has a high activation barrier, respectively. Since intermediate species of path 1 are common with those of benzene combustion, further reactions will be very similar to those discussed in the previous chapter and will consequently not be discussed in much details here.

As summarized and illustrated in figure 5.8, benzene is consumed into phenyl radical, phenoxy radical and phenol, through H abstraction reactions and electrophilic additions of O atom and OH radicals, followed by an H atom elimination. Phenyl radical can recombine with an H atom forming benzene or react with molecular oxygen, giving $n\text{-C}_4\text{H}_5 + \text{CO}$ or phenoxy radical + O atom. Then, phenoxy radical either decomposes into cyclopentadienyl radical and CO or reacts with H and O atoms, respectively giving $\text{C}_2\text{H}_3 + \text{C}_3\text{H}_3 + \text{CO}$ and $\text{C}_2\text{H}_2 + \text{C}_2\text{H}_3 + 2\text{CO}$. In that kinetic scheme, cyclopentadienyl radical plays a key role since it links C_6 to C_4 chemistry through cyclopentadienyl peroxy radical formation. Cyclopentadienyl radical equally recombines with H atom forming cyclopentadiene, which has been detected in high concentration in benzene flames of this work. The high maximum mole fraction of C_5H_6 measured in toluene flames suggests that it may also play an important role in toluene combustion. This hypothesis will be verified in the following

sections, devoted to reactions of intermediates formed in path 2 and 3 of figure 5.7.

5.3.3 Path 2: the methylphenyl radicals channel

The second path of toluene consumption (see figure 5.7) gathers the formation of methylphenyl radicals, methylphenoxy radicals and cresols, which are respectively produced from H abstraction reactions and electrophilic additions of O and OH onto CH groups of the toluene ring. Whereas this path is generally not considered by kinetic models devoted to toluene oxidation [21, 78, 192], our study shows that it should not be neglected since it accounts for 31, 21, 16 and 16% of toluene consumption in TF07, TF10, TF18 and TF20. Contrarily to benzene, positions of carbon and hydrogen atoms of the toluene ring are not equivalent and intermediates formed in path 2 may be either ortho, meta or para isomers. Consumption pathways of these intermediates are discussed hereafter, beginning with methylphenyl radicals.

Methylphenyl radicals consumption pathways

In the previous chapter, we have shown that phenyl radical mainly reacts with molecular oxygen forming phenylperoxy radical, which either dissociates into phenoxy radical and O atom or rearranges into the 2-oxepynoxy radical. Ortho, meta and para isomers of methylphenyl radicals, which have chemical structures close to that of phenyl radical, should react in the same way with O_2 , forming ortho, meta and para methylphenylperoxy radicals, which will either dissociate into corresponding methylphenoxy radicals + O atom or rearrange into various methyloxepynoxy radicals, as illustrated in figure 5.9.

This hypothesis has been confirmed by da Silva and co-workers [200] who have recently theoretically investigated the potential energy surface of the $C_6H_4CH_3 + O_2$ reaction and have calculated kinetic parameters of each reaction channel presented in figure 5.9. Similarly to

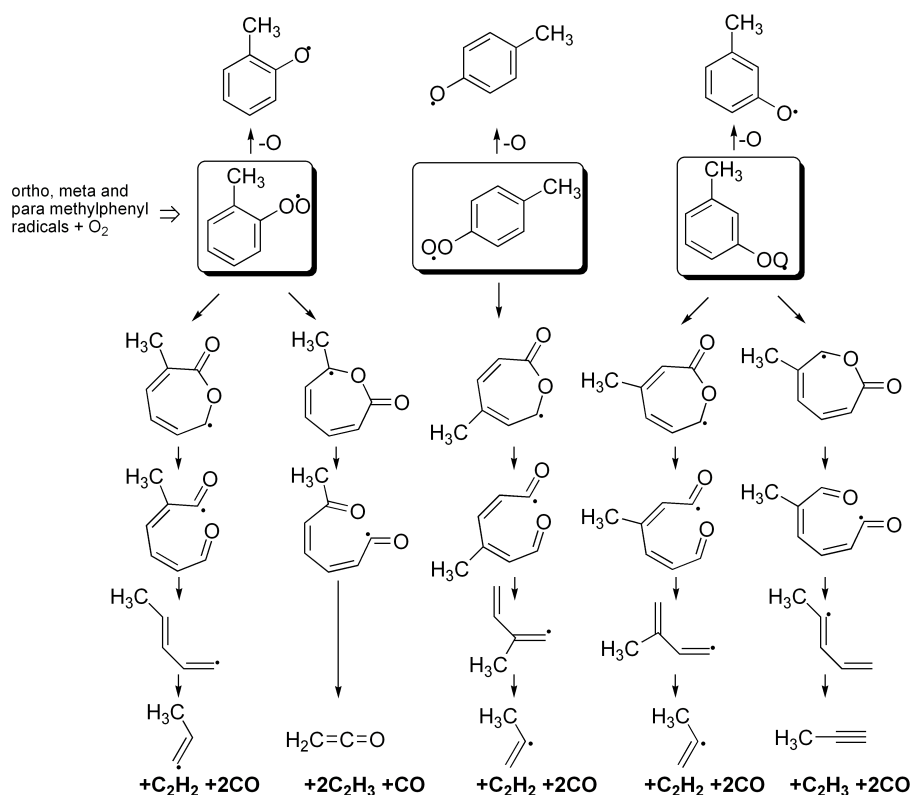


Figure 5.9: mechanism postulated for reaction of molecular oxygen with methylphenyl radicals.

the 2-oxepinoxy radical formed in the phenyl reaction with O_2 , methyloxepinoxy radicals can expel two carbon monoxide molecules, forming various C_5H_7 radicals. Since high temperature reactions of these C_5H_7 radicals are still unknown, we have postulated that they principally dissociate into C_2 and C_3 hydrocarbons, as depicted in figure 5.9. Overall reactions linking ortho, meta and para isomers of methylphenyl radicals to these C_2 and C_3 hydrocarbons have been included into the developed kinetic model using kinetic parameters calculated by da Silva and co-workers for the formation of corresponding methyloxepinoxy radicals (see reactions R20 to R24 of table 5.4).

Beside methyloxepinoxy radicals, other products of the $C_6H_4CH_3 + O_2$ reaction are ortho, meta and para methylphenoxy radicals. By analogy with the phenoxy radical, whose dissociation into cyclopentadienyl

Table 5.4: $C_6H_4CH_3$, $OC_6H_4CH_3$ and $HOC_6H_4CH_3$ consumption reactions included into the kinetic model.

Reactions		$k = AT^n e^{-Ea/RT}$			Refs.
		A^a	n	Ea^a	
Methylphenyl radicals ($C_6H_4CH_3$) reactions with O_2 .					
R20	$o-C_6H_4CH_3 + O_2 \rightleftharpoons 2C_2H_2 + CH_3CO + CO$	$6.95 \cdot 10^9$	0.5	-4.5	^b
R21	$o-C_6H_4CH_3 + O_2 \rightleftharpoons C_2H_2 + p-C_3H_5 + 2CO$	$6.95 \cdot 10^9$	0.5	-4.5	^b
R22	$m-C_6H_4CH_3 + O_2 \rightleftharpoons C_2H_2 + s-C_3H_5 + 2CO$	$2.82 \cdot 10^9$	0.6	-5.1	^b
R23	$m-C_6H_4CH_3 + O_2 \rightleftharpoons C_2H_2 + p-C_3H_4 + 2CO$	$2.82 \cdot 10^9$	0.6	-5.1	^b
R24	$p-C_6H_4CH_3 + O_2 \rightleftharpoons C_2H_2 + s-C_3H_5 + 2CO$	$5.64 \cdot 10^9$	0.6	-5.1	^b
R25	$o-C_6H_4CH_3 + O_2 \rightleftharpoons OC_6H_4CH_3 + O$	$4.99 \cdot 10^{18}$	-1.7	5.3	^d
R26	$m-C_6H_4CH_3 + O_2 \rightleftharpoons OC_6H_4CH_3 + O$	$9.82 \cdot 10^{17}$	-1.5	4.5	^d
R27	$p-C_6H_4CH_3 + O_2 \rightleftharpoons OC_6H_4CH_3 + O$	$9.82 \cdot 10^{17}$	-1.5	4.5	^d
R28	$o-C_6H_4CH_3 + O_2 \rightleftharpoons C_6H_6 + CO + OH$	$4.99 \cdot 10^{18}$	-1.7	5.3	^d
Methylphenyl radicals ($C_6H_4CH_3$) reactions with O and H atoms.					
R29	$o-C_6H_4CH_3 + O \rightleftharpoons C_5H_4CH_3 + CO$	$1 \cdot 10^{14}$	0	0	^c
R30	$m-C_6H_4CH_3 + O \rightleftharpoons C_5H_4CH_3 + CO$	Considered equal to R29			
R31	$p-C_6H_4CH_3 + O \rightleftharpoons C_5H_4CH_3 + CO$	Considered equal to R29			
R32	$o-C_6H_4CH_3 + H + M \rightleftharpoons C_7H_8 + M$ (k_∞)	$2.2 \cdot 10^{14}$	0	0	^c
	$o-C_6H_4CH_3 + H + M \rightleftharpoons C_7H_8 + M$ (k_0)	$4.1 \cdot 10^{104}$	-24.6	21.5	^c
	Troee's broadening factors: $4.6 \cdot 10^{-2} / 3.52 \cdot 10^2 / 6.0 \cdot 10^4 / 7.6 \cdot 10^3$				^c
R33	$m-C_6H_4CH_3 + H + M \rightleftharpoons C_7H_8 + M$	Considered equal to R32			
R34	$p-C_6H_4CH_3 + H + M \rightleftharpoons C_7H_8 + M$	Considered equal to R32			
Methylphenoxy ($OC_6H_4CH_3$) radical reactions.					
R35	$OC_6H_4CH_3 \rightleftharpoons C_5H_4CH_3 + CO$	$2.51 \cdot 10^{11}$	0	43.9	^d
Cresol ($HOC_6H_4CH_3$) radical reactions.					
R36	$HOC_6H_4CH_3 + H \rightleftharpoons OC_6H_4CH_3 + H_2$	$1.15 \cdot 10^{14}$	0	12.4	^e
R37	$HOC_6H_4CH_3 + O \rightleftharpoons OC_6H_4CH_3 + OH$	$2.81 \cdot 10^{13}$	0	7.4	^e
R38	$HOC_6H_4CH_3 + OH \rightleftharpoons OC_6H_4CH_3 + H_2O$	$6 \cdot 10^{12}$	0	0	^e

^a A units are s^{-1} and $cm^3 \text{ mol}^{-1} s^{-1}$ for Unimolecular and bimolecular reactions, respectively. Ea is expressed in kcal mol^{-1} . ^b Rate parameters taken from [200] but products are hypothesized, as discussed in the text. ^c Rate parameters determined by analogy with phenyl radical. ^d Rate parameters determined by analogy with phenoxy radical. ^e Rate parameters determined by analogy with phenol.

radical and CO is a major consumption channel, we have postulated that decomposition of ortho, meta and para methylphenoxy radicals into carbon monoxide and $C_5H_4CH_3$ radicals should be an important consumption path. Figure 5.10 shows that whatever the methylphenoxy isomer that decomposes, it always yields to resonant forms of the same $C_5H_4CH_3$ molecule. Considering this observation, our kinetic model has been simplified by substituting ortho, meta and para methylphenoxy radicals by an overall $OC_6H_4CH_3$ intermediate, which can decompose into carbon monoxide and the $C_5H_4CH_3$ radical of figure 5.10. Kinetic parameters of methylphenyl radicals reactions with O_2 forming the overall $OC_6H_4CH_3$ radical (see reactions R25 to R27 of tabe 5.4) have been taken from the work of da Silva and co-workers [200] and the rate constant of the $OC_6H_4CH_3$ decomposition into $C_5H_4CH_3 + CO$ is estimated by analogy with that of the phenoxy radical (see reaction R35).

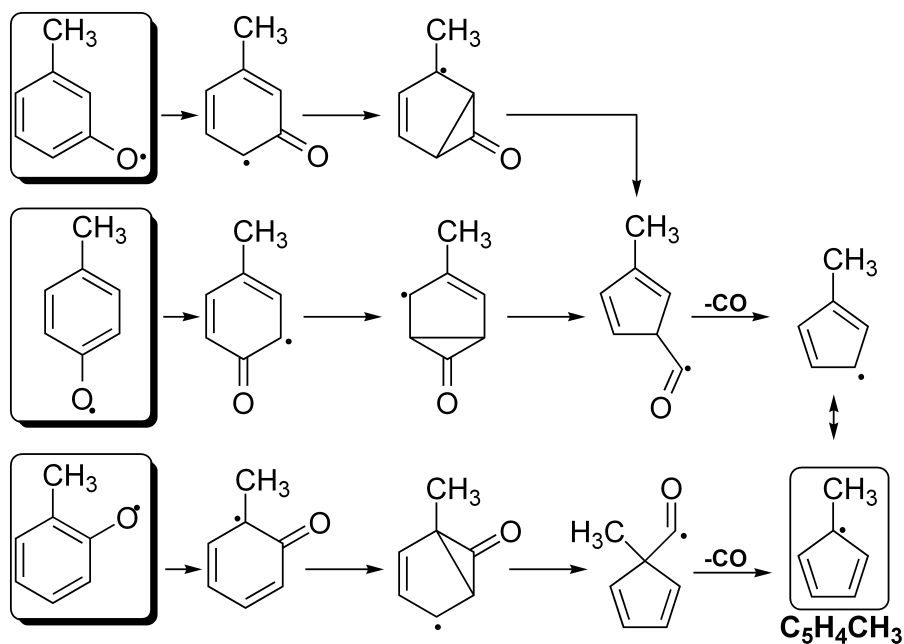


Figure 5.10: mechanism postulated for decomposition of methylphenoxy radicals.

The previous chapter has demonstrated that in addition to the phenoxy radical decomposition into $C_5H_5 + CO$, other reactions channels such as $C_6H_5O + H$ or $C_6H_5O + O$ should be considered. Contrarily to $OC_6H_4CH_3$ decomposition, products of its reaction with O and H atoms will depend on the position of the methyl group onto the ring. Since methylphenyl radicals formation is not the major consumption route of toluene (its contribution is 23% in FT07), we have considered that the introduction of these reactions into the kinetic model was not necessary and that the sole use of reaction R35 of table 5.4, forming $C_5H_4CH_3$ is a good approximation.

The previous chapter has equally highlighted that the $C_5H_4CH_3$ radical is a key intermediate of the C_6H_7 potential energy surface, linking benzene + H atom to cyclopentadienyl en methyl radicals. Therefore, $C_5H_4CH_3$ consumption might contribute to either cyclopentadienyl or benzene formation, detected in high concentration in toluene flames of this work. In their theoretical analysis of the $C_6H_4CH_3 + O_2$ reaction, da Silva and co-workers highlighted that contrarily to meta and para methylphenyl radicals, the ortho isomer can equally react with O_2 forming hydroxyl radical and ortho-quinone methide. The pyrolysis of the latter has been experimentally investigated and was found to principally yield benzene + CO [217]. Consequently, the overall reaction R28 of table 5.4 has been included into the kinetic model.

Similarly to phenyl radical, methylphenyl radicals can also react with O atom forming energized $OC_6H_4CH_3$ radicals, which could have enough energy to decompose into carbon monoxide and the $C_5H_4CH_3$ radical of figure 5.10. Rate constants of these reactions have been estimated by analogy with those of phenyl radical and were included into the kinetic model (see reactions R29 to R31 of table 5.4). In addition to reactions with O atom, methylphenyl radicals can recombine with a hydrogen atom, giving toluene back. Rate parameters are equally estimated by analogy with the phenyl radical, as depicted in reactions R32 to R34. Cresol ($HOC_6H_4CH_3$), which is produced by substitution of an H atom of the toluene ring by a hydroxyl radical, should react similarly to phenol that principally yields phenoxy radical through H abstraction reactions.

As illustrated in reactions R36 to R38, rate parameters of alcoholic H abstraction reactions on cresol, forming methylphenoxy radical, have been supposed identical to those of phenol. Since ortho, meta and para isomers of cresol should all yield to corresponding methylphenoxy isomers, which mainly dissociate into the same $C_5H_4CH_3$ radical, our kinetic model considers an overall cresol compound that is the sum on ortho, meta and para forms, in the same way as methylphenoxy radicals.

In summary, we have shown that similarly to phenyl radical, methylphenyl radicals can undergo reactions with O_2 that could form either methylphe-

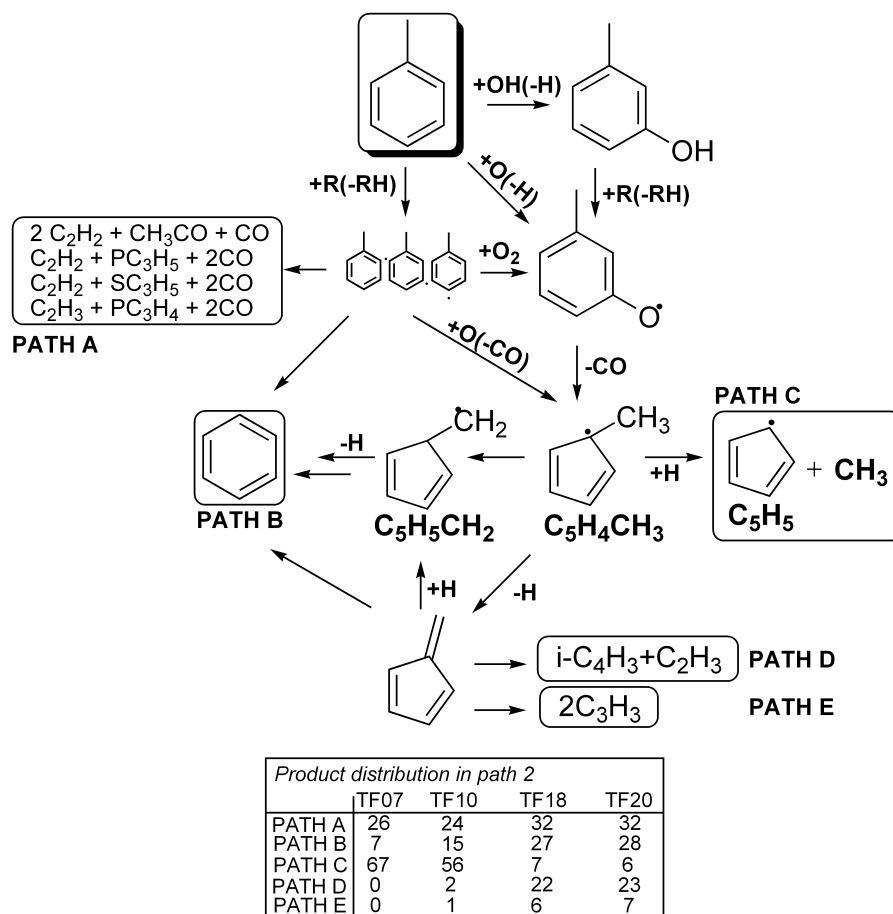


Figure 5.11: product distribution of Path 2 in TF07, TF10, TF18 and TF20.

noxy radicals or various C_2 and C_3 hydrocarbons, which are already considered in the kinetic model developed for benzene combustion. We have demonstrated that the decomposition reactions of ortho, meta and para methylphenoxy radicals yield to resonant forms of the same $C_5H_4CH_3$ radical, which is an intermediate compound of benzene combustion. Moreover, we have shown that cresol, equally formed in toluene consumption through path 2, principally leads to methylphenoxy radical formation. Therefore, path 2 globally leads to $C_5H_4CH_3$ production.

The $C_5H_4CH_3$ is an intermediate of benzene combustion that links cyclopentadienyl and methyl radicals to benzene and fulvene, as illustrated in figure 5.11. Fulvene can either rearrange into benzene or reacts with H atom forming $C_5H_5CH_2$, which subsequently gives benzene or decomposes into propargyl radicals and $i-C_4H_3 + C_2H_3$. Figure 5.11 summarizes contributions of each reaction channel in the path 2. Formation of methyloxepinoxy and their opening in C_2 and C_3 hydrocarbons (PATH A) in figure 5.11 accounts for about 30 % of path 2 in all investigated flames. In TF07, cyclopentadienyl and methane radicals formation (PATH C) dominates in TF07 whereas benzene (PATH B) and $i-C_4H_3 + C_2H_3$ (PATH D) productions prevail into TF20. The increase in contribution of these last channels with a higher flame temperature is consistent with high activation barriers of their entrance reactions, involving isomerization and decomposition of $C_5H_4CH_3$ into $C_5H_5CH_2$ and fulvene, respectively. On the whole, the second path of toluene consumption, involving methylphenyl radicals, methylphenoxy radicals and cresol, mainly produces benzene, cyclopentadienyl radicals and $i-C_4H_3 + C_2H_3$, which are all intermediates of the kinetic scheme developed for benzene combustion.

5.3.4 Path 3: the benzyl channel

Benzyl radical belongs to the third path of toluene consumption, as depicted in figure 5.7. It is formed by H atom abstraction reactions on the methyl group of toluene and it is the main product of toluene consump-

tion. As many other important intermediates of aromatic combustion (phenoxy, cyclopentadienyl or propargyl radicals), benzyl radical is resonantly stabilized. Its is therefore less reactive with stable compounds and its major consumption routes should be isomerization, decomposition and reactions with H , O and OH , rather than reactions with O_2 , as phenyl and methylphenyl radicals. Whereas the investigation of toluene pyrolysis began many years ago, only very recent theoretical findings have allowed significant insights in the understanding of the benzyl radical consumption at high temperatures, as discussed below.

(i) *Benzyl radical isomerization and decomposition routes*

In 1979, Simth [183,184] investigated toluene pyrolysis and found that C_5H_5 , C_2H_2 , C_3H_3 and C_4H_4 fragments are produced. He consequently suggested that benzyl radical decomposition is connected to these chemical species. Since this finding, many researchers have proposed reaction channels linking benzyl radical to these fragments, as summarized in

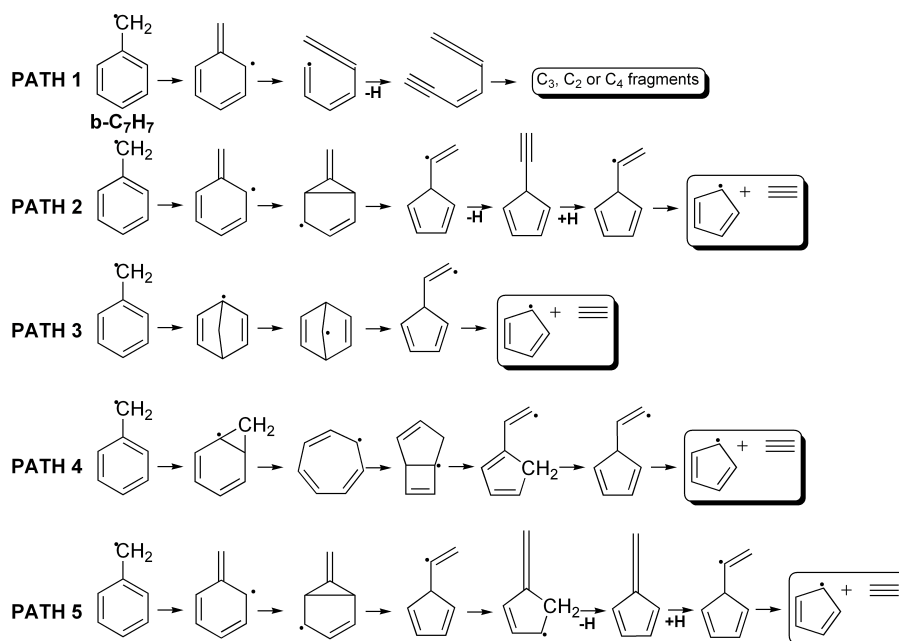


Figure 5.12: benzyl decomposition pathways proposed in the literature.

figure 5.12. In 1990, Braun-Unkhoff and co-workers [218] suggested two alternative pathways based on the 1:1 H atom formation that they measured in the pyrolysis of benzyl iodide. The first is based on early works of Rao and Skinner [185] and involves the ring opening into a linear C_7H_7 radical, followed by a beta scission forming a linear C_7H_6 compound and a hydrogen atom, as depicted in path 1 of figure 5.12. The second followed a Benson's suggestion [186] and involves the benzyl radical rearrangement into a bicycle intermediate that can subsequently isomerize into a 1,3-cyclopentadiene-5-vinyl radical, as shown in path 2 of figure 5.12.

In 1994, Colket and Seery [187] proposed a new route involving benzyl radical isomerization into the norboradienyl radical, followed by its rearrangement into the 1,3-cyclopentadiene-5-vinyl radical and the decomposition into cyclopentadienyl radical and acetylene, as described in path 3 of figure 5.12. In 1997, Jones and co-workers [219] proposed another channel (path 4), forming cyclopentadienyl radical and acetylene through norcaradienyl radical formation. Moreover, authors performed a theoretical investigation of decomposition routes previously suggested in order to determine their kinetic parameters. They concluded that the formation of 1,3-cyclopentadiene-5-vinyl + H atom from path 2 should be dominant at combustion temperatures. In 2006, Oehlschaeger and co-workers [220] experimentally measured rate constant of benzyl decomposition into $C_7H_6 + H$, confirming that it should be the most important route under combustion conditions. However, uncertainties remained on the structure of this C_7H_6 compound. Very recently, Cavallotti and co-workers [203] and da Silva and co-workers [201] have theoretically demonstrated that another decomposition route was faster than those previously proposed. They have suggested that benzyl radical decomposition forms fulvenallene and hydrogen atom instead of 1,3-cyclopentadiene-5-vinyl, as described in path 5 of figure 5.12. Their mechanism involves benzyl radical isomerization into 1,3-cyclopentadiene-5-vinyl radical, followed by a migration of the tertiary hydrogen atom of the C_5 ring to a vicinal CH group. Then, the new C_7H_7 radical expels a hydrogen atom producing fulvenallene. Both

groups have showed that fulvenallene might react with H atom yielding cyclopentadienyl radical and acetylene, demonstrating that the overall benzyl decomposition reaction yields $C_5H_5 + C_2H_2$, as initially proposed by Smith [183,184] 31 years ago. Additional C_4H_4 and C_3H_3 fragments identified by Smith can be formed by cyclopentadienyl radical consumption, as discussed in the previous chapter.

Based on these recent theoretical insights, the kinetic model developed in this work considers C_7H_6 as fulvenallene. Thermodynamical data of C_7H_6 have been calculated using quantum chemistry. Rate constant of benzyl radical decomposition into $C_7H_6 + H$ calculated by Cavallotti and co-workers has been included into the mechanism (see reactions R39 and -R39 of table 5.5).

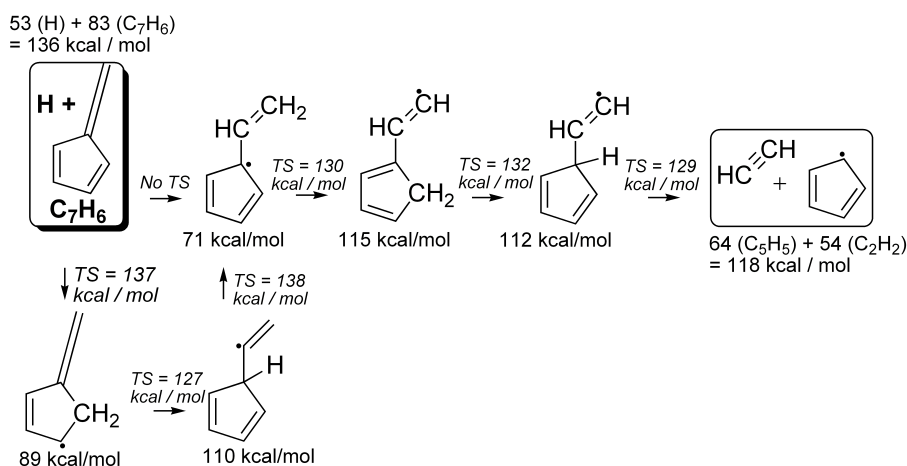


Figure 5.13: mechanism of H atom addition onto fulvenallene proposed by da Silva and co-workers [202].

Only 2 works were devoted to the reaction between fulvenallene and hydrogen atom giving cyclopentadienyl radical and acetylene [202,203] since it has been only very recently suggested. Both studies are theoretical and propose the mechanism that is depicted in figure 5.13, together with enthalpies of intermediates and transition states calculated by da Silva and co-workers [202]. According to these studies, the overall reaction is exothermic by 18 kcal mol^{-1} . H atom addition to fulvenallene occurs either on the C_5 ring or on the allene group, respectively

Table 5.5: b- C_7H_7 and fulvenallene consumption reactions included into the kinetic model.

Reactions		$k = AT^n e^{-E_a/RT}$			Refs.
		A^a	n	Ea^a	
Benzyl radical (b- C_7H_7) reactions.					
R39	$b\text{-}C_7H_7 \rightarrow C_7H_6 + H$	$1.44 \cdot 10^{13}$	0.45	76.3	[203]
-R39	$C_7H_6 + H \rightarrow b\text{-}C_7H_7$	$8.82 \cdot 10^8$	1.2	-2	[203]
R40	$b\text{-}C_7H_7 + O \rightleftharpoons C_7H_6O + H$	$2 \cdot 10^{14}$	0	0.0	[221]
R41	$b\text{-}C_7H_7 + OH \rightleftharpoons C_7H_7OH$	$6.3 \cdot 10^{11}$	0	0	[222]
R42	$b\text{-}C_7H_7 + HO_2 \rightleftharpoons C_7H_7O + OH$	$3.16 \cdot 10^{12}$	0	0	[223]
Fulvenallene (C_7H_6) reactions.					
R43	$C_7H_6 + H \rightleftharpoons C_5H_5 + C_2H_2$	$3 \cdot 10^{14}$	0	0	[24]

^a A units are s^{-1} and $cm^3 \text{ mol}^{-1} s^{-1}$ for Unimolecular and bimolecular reactions, respectively. Ea is expressed in kcal mol^{-1} .

without and with a small activation barrier of 3 kcal mol^{-1} , forming 2 C_7H_7 adducts. Then these intermediates rearrange and dissociate into $C_5H_5 + C_2H_2$ in a few steps whose activation barrier is only 2 kcal mol^{-1} . Therefore, this reaction is expected to be fast under combustion conditions. Both groups calculated rate constants scattered by a factor close to 6. The fastest is that determined by da Silva and co-workers, which reaches $6 \cdot 10^{12} \text{ cm}^3 \text{ mol}^{-1} s^{-1}$ at 1800 K. Unfortunately, this rate constant is too slow to explain fulvenallene and cyclopentadiene mole fractions experimentally observed in toluene flames of this work. By fitting the rate constant of this reaction to $3 \cdot 10^{14} \text{ cm}^3 \text{ mol}^{-1} s^{-1}$ (see reaction R43 of table 5.5) we observed that our kinetic model has a good predictive capability of experimental mole fraction profiles of fulvenallene and cyclopentadienyl radical in each toluene flame of this work [24]. In addition to the present work, this rate approximation has been recently used to successfully model fulvenallene formation in toluene pyrolysis by Zhang and co-workers [224]. Therefore, the submechanism developed for benzyl radical decomposition into $C_5H_5 + C_2H_2$ seems relevant for kinetic modeling of high temperature reactions of toluene. The large discrepancy between our rate approximation and theoretical calculations might come from the lack of direct benzyl decomposition channels into $C_5H_5 + C_2H_2$. Indeed, da Silva and co-workers highlighted that such

pathways exist and that the reaction of fulvenallene with H atom, giving benzyl radical, may proceed faster than that forming cyclopentadienyl radical and acetylene. Therefore, one may think that our kinetic model has to compensate the absence of a direct benzyl decomposition channel into $C_5H_5 + C_2H_2$ by an empirical increase of the rate constant of the reaction R43. However, kinetic studies devoted to benzyl radical decomposition into $C_5H_5 + C_2H_2$ through fulvenallene have only been recently suggested and further studies should throw light on these remaining uncertainties.

(ii) Benzyl radical reactions with H , O , OH , HO_2 and O_2

Benzyl radical reaction with H atom has been discussed in the section devoted to toluene reactions since it corresponds to reaction R1 and R3 of table 5.3 on page 204. The comparative rate analysis of reactions involved in C_7H_8 flame chemistry has showed that reactions R1 and R3 do not consume toluene but are involved in benzyl radical consumption. In 1990, Hippler and co-worker [222] performed a shock-tube study of benzyl radical oxidation and demonstrated that benzyl alcohol and benzaldehyde were important intermediates. This finding explains high maximum mole fractions detected at an m/z ratio corresponding to benzaldehyde in all toluene flames. Rate constant of the benzyl radical reaction with O atom producing benzaldehyde and H atom has been recently reviewed by Baulch and co-workers [221] and fixed to $2 \cdot 10^{14}$, which has been introduced into our mechanism (see reaction R40). Benzyl radical can equally react with the HO_2 radical, forming $C_7H_7O + OH$ (see reaction R42), as suggested by Brezinsky and co-workers [188] and recently theoretically demonstrated by da Silva and Bozzelli [223]. Hippler and co-workers equally demonstrated that benzyl radical reaction with O_2 is very slow as it is stabilized by resonance. Rate constant suggested by authors for $b-C_7H_7$ reaction with OH radical has been introduced into our kinetic model.

(iii) Further reactions of benzaldehyde and benzylalcohol

To our best knowledge, only a few kinetic studies were devoted to high temperature reactions of benzaldehyde and benzylalcohol, including

benzaldehyde decomposition into benzoyl radical + H and benzylalcohol reaction with OH radical, giving $C_6H_5CH_2O + H_2O$. Reaction parameters of other reactions involving these compounds are only estimated in kinetic models of the literature describing the oxidation of aromatics. Therefore, to be integrated rate constants of benzaldehyde and benzylalcohol reactions have been determined by analogy with acetaldehyde and ethanol reactions, as depicted in table 5.6. Only reactions involving the side chain of benzylaldehyde and benzylalcohol have been considered, as reactions on the aromatic ring have been shown to proceed slower [188]. Their addition to the kinetic scheme would lead to a significant increase of considered chemical species, with rate constants of their consumption pathways remaining unknown. Benzaldehyde (C_7H_6O) can react with free radicals through H abstraction reactions (see reaction R44 to R46) forming the benzoyl radical that can subsequently decompose into phenyl and carbon monoxide (see reaction R59). Beside H abstraction reactions, C_7H_6O may react with H atom and OH radical to respectively produce benzene + HCO and phenol + HCO (see reactions R47 to R48). Finally, benzaldehyde can decompose into phenyl radical and HCO through reaction R49 that has a high activation barrier of 79 kcal mol⁻¹, suggesting that it will principally occur at high temperatures. Benzyl alcohol (C_7H_7OH) can undergo H abstraction reactions on its alcoholic hydrogen or on its $-CH_2-$ group, respectively giving C_7H_7O and C_7H_6OH . Whereas all these reactions have been included into the kinetic model, only those involving the $-CH_2-$ group are summarized into table 5.6 (see reactions R50 to R52) because others only play a minor role in C_7H_7OH consumption, as described further. Benzyl alcohol can equally react with H atom yielding benzene + CH_2OH and decomposes into phenyl and CH_2OH through reactions R53 and R54, respectively. C_7H_6OH should mainly react through H abstraction reactions forming benzaldehyde through reactions R55 to R57. Consequently, benzaldehyde and benzylalcohol consumption routes enter into the benzene kinetic scheme discussed in the previous chapter. As benzaldehyde formation is favored under lean conditions, it should significantly contribute to benzene formation at low equivalence ratios.

Table 5.6: C_7H_7OH and C_7H_6O consumption reactions included into the kinetic model.

Reactions		$k = AT^n e^{-Ea/RT}$ A^a	n	Ea^a	Refs.
Benzaldehyde reactions (C_7H_6O).					
R44	$C_7H_6O + H \rightleftharpoons C_7H_5O + H_2$	$1.2 \cdot 10^{14}$	0	7	<i>b</i>
R45	$C_7H_6O + O \rightleftharpoons C_7H_5O + OH$	$5.84 \cdot 10^{12}$	0	1.8	<i>b</i>
R46	$C_7H_6O + OH \rightleftharpoons C_7H_5O + H_2O$	$2.34 \cdot 10^{10}$	0.7	1.1	<i>b</i>
R47	$C_7H_6O + H \rightleftharpoons C_6H_6 + HCO$	$1.2 \cdot 10^{13}$	0	5.1	<i>b</i>
R48	$C_7H_6O + OH \rightleftharpoons C_6H_5OH + HCO$	$1.2 \cdot 10^{13}$	0	5.1	<i>b</i>
R49	$C_7H_6O \rightleftharpoons C_6H_5 + HCO$	$6 \cdot 10^{14}$	0	79.1	<i>b</i>
Benzyl alcohol reactions (C_7H_7OH).					
R50	$C_7H_7OH + H \rightleftharpoons C_7H_6OH + H_2$	$1.79 \cdot 10^5$	2.53	3.42	<i>c</i>
R51	$C_7H_7OH + O \rightleftharpoons C_7H_6OH + OH$	$1.45 \cdot 10^5$	2.41	0.9	<i>c</i>
R52	$C_7H_7OH + OH \rightleftharpoons C_7H_6OH + H_2O$	$1.31 \cdot 10^5$	2.43	-1.5	<i>c</i>
R53	$C_7H_7OH + H \rightleftharpoons C_6H_6 + CH_2OH$	$2 \cdot 10^{14}$	0	0.0	<i>c</i>
R54	$C_7H_7OH + M \rightleftharpoons$ $C_6H_5 + CH_2OH + M$ (k_∞)	$5.94 \cdot 10^{23}$	-1.68	91.1	<i>c</i>
	$C_7H_7OH + M \rightleftharpoons$ $C_6H_5 + CH_2OH + M$ (k_0)	$2.88 \cdot 10^{85}$	-18.9	109.9	<i>c</i>
Troie's broadening factors: $5 \cdot 10^{-1} / 2 \cdot 10^2 / 8.9 \cdot 10^2 / 4.6 \cdot 10^3$					<i>c</i>
C_7H_6OH reactions.					
R55	$C_7H_6OH + O \rightleftharpoons C_7H_6O + OH$	$1 \cdot 10^{14}$	0	0	<i>d</i>
R56	$C_7H_6OH + OH \rightleftharpoons C_7H_6O + H_2O$	$5 \cdot 10^{12}$	0	0	<i>d</i>
R57	$C_7H_6OH + HO_2 \rightleftharpoons C_7H_6O + 2OH$	$4 \cdot 10^{13}$	0	0	<i>d</i>
R58	$C_7H_6OH + M \rightleftharpoons C_7H_6O + H$	$5 \cdot 10^{13}$	0	21.9	<i>d</i>
Benzoyl radical reactions (C_7H_5O).					
R59	$C_7H_5O + M \rightleftharpoons C_6H_5 + CO + M$ (k_∞)	$1.07 \cdot 10^{12}$	0.63	16.8	<i>e</i>
	$C_7H_5O + M \rightleftharpoons C_6H_5 + CO + M$ (k_0)	$2.78 \cdot 10^{18}$	-0.85	14.4	<i>e</i>
Troie's broadening factors: $6 \cdot 10^{-1} / -1 \cdot 10^{15} / 1 \cdot 10^{-15} / 1 \cdot 10^{15}$					<i>e</i>

^a A units are s^{-1} and $cm^3 \text{ mol}^{-1} s^{-1}$ for Unimolecular and bimolecular reactions, respectively. Ea is expressed in kcal mol^{-1} . ^b Rate parameters determined by analogy with acetaldehyde reactions of kinetic model of appendix E. ^c Rate parameters determined by analogy with ethanol reactions of kinetic model of appendix E. ^d Rate parameters determined by analogy with CH_3CH_2O reactions of kinetic model of appendix E. ^e Rate parameters determined by analogy with CH_2CO reactions of kinetic model of appendix E.

Comparison between predicted and experimental results

Figure 5.14 compares predictions of current and RH models to mole fraction profiles measured by MBMS at m/z ratios corresponding to benzyl radical, fulvenallene and benzaldehyde, respectively. Our kinetic model well reproduces mole fraction profiles of benzyl radical measured in TF20 and slightly overestimates measurements performed in TF10 and TF07. However, the present mechanism significantly improves benzyl radical predictions and better represents the dependence of its maximum mole fraction on the equivalence ratio than the RH model. Concerning benzaldehyde, our kinetic model overestimates C_7H_6O mole fraction. However, the overprediction of benzaldehyde is consistent with that of the benzyl radical, which is the main benzaldehyde precursor. Richter and Howard's model well reproduces C_7H_6O mole fraction profiles in TF07 and TF10, but underestimates its maximum mole fraction in TF20. Since this model respectively well predicts and overestimates benzyl radical mole fraction in TF20 and both TF07 and TF10, its good predictive capability observed for benzaldehyde in TF07 and TF10 should be fortuitous. Fulvenallene is well predicted by our kinetic model in TF20. In TF07 and TF10, C_7H_6 mole fractions were beyond the detection limit of our MBMS device that is estimated to $5 \cdot 10^{-5}$, as predicted by the developed model. Richter and Howard model does not consider any C_7H_6 intermediate in toluene consumption.

A comparative rate analysis of reactions involved in benzyl radical, fulvenallene, benzaldehyde and benzylalcohol flame chemistry has allowed to calculate their contributions to consumption of these compounds, as depicted in figure 5.15 for benzyl radical and in figure 5.16 for benzaldehyde and benzylalcohol. Under lean and stoichiometric conditions reaction of benzyl radical with O atom forming benzaldehyde and hydrogen atom (see reaction R40 of table 5.5) respectively accounts for 33 and 24% of b- C_7H_7 consumption. Reaction R41 involving the OH radical recombination with b- C_7H_7 , giving benzylalcohol, contributes to 9 and 4% of b- C_7H_7 consumption in TF07 and TF10. The reaction R42 forming C_7H_7O consumes 1% of benzyl radical under all investigated flame

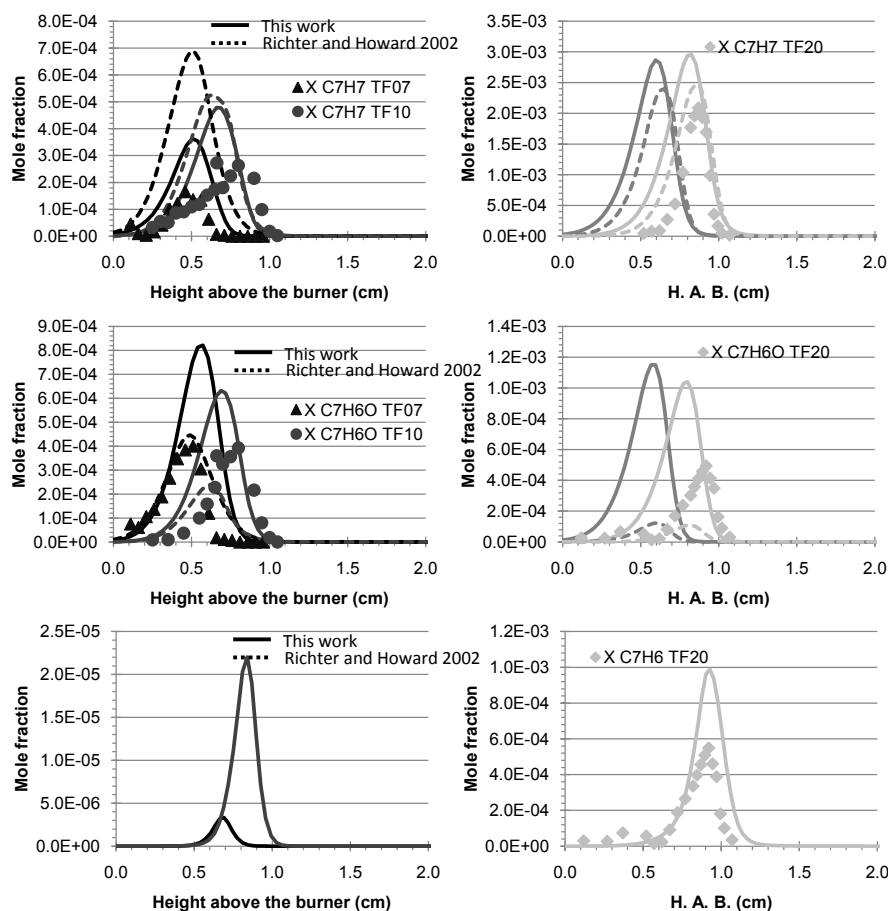


Figure 5.14: experimental and predicted mole fraction profiles of for m/z ratios corresponding to benzyl radical ($\text{b-C}_7\text{H}_7$), benzaldehyde ($\text{C}_7\text{H}_6\text{O}$) and fulvenallene (C_7H_6). Gray scale symbols represent experiments ($\triangle$ TF07, $\circ$ TF10, $\diamond$ TF20). Solid and dashed curves stand for predictions of present and Richter and Howard [92] models, respectively.

conditions. Therefore, oxidation of the side chain of benzyl radical play an important role in toluene combustion chemistry at low equivalence ratios. Benzyl radical recombination with H atom yielding toluene or phenyl and methyl radicals is equally an important route of $\text{b-C}_7\text{H}_7$ consumption over the entire range of equivalence ratio and dominates in FT10. In flames with the highest temperatures (TF18 and TF20), reaction R39 of table 5.5 forming fulvenallene becomes the main con-

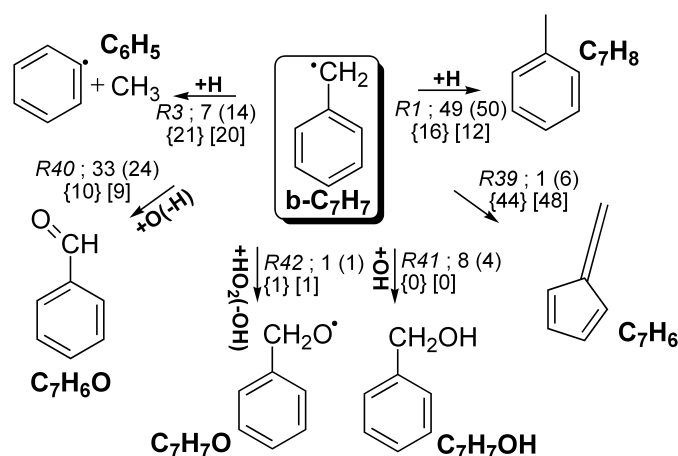


Figure 5.15: summary of benzene consumption pathways included into the developed kinetic model. Percentages represent contribution in TF07, (TF10), {TF18} and [TF20]

sumption route of benzyl radical. Indeed, its activation barrier is more easily overcome. Fulvenallene reacts with H atom through reaction R43, yielding cyclopentadienyl radical and acetylene. From figure 5.15 it is clear that benzyl radical consumption is highly dependent on the equivalence ratio and the flame temperature. High equivalence ratios favor the recombination with an H atom, yielding toluene or $\text{C}_6\text{H}_5 + \text{CH}_3$, and low equivalence ratios stimulate the reaction with an O atom forming benzaldehyde and hydrogen atom. Flame temperature essentially controls the benzyl radical decomposition into fulvenallene and H atom, as this reaction has a high activation energy. Figure 5.16 shows contributions of reactions involved in benzaldehyde and benzyl alcohol consumption. In TF07 and TF10, H abstraction reactions on benzaldehyde (see reactions R44 to R46 of table 5.6) dominate, whereas the dissociation into phenyl and formyl radicals (reaction R49) becomes the major route in TF18 and TF20. This observation is explained by the higher flame temperatures of TF18 and TF20, allowing to more easily overcome the reaction barriers. Consumption routes forming benzene and phenol significantly contribute to benzaldehyde consumption into TF07 and TF10, but are consigned into a minor role in TF20 and TF18. All the benzoyl radical formed from reactions R44 to R46 is consumed into phenyl radical

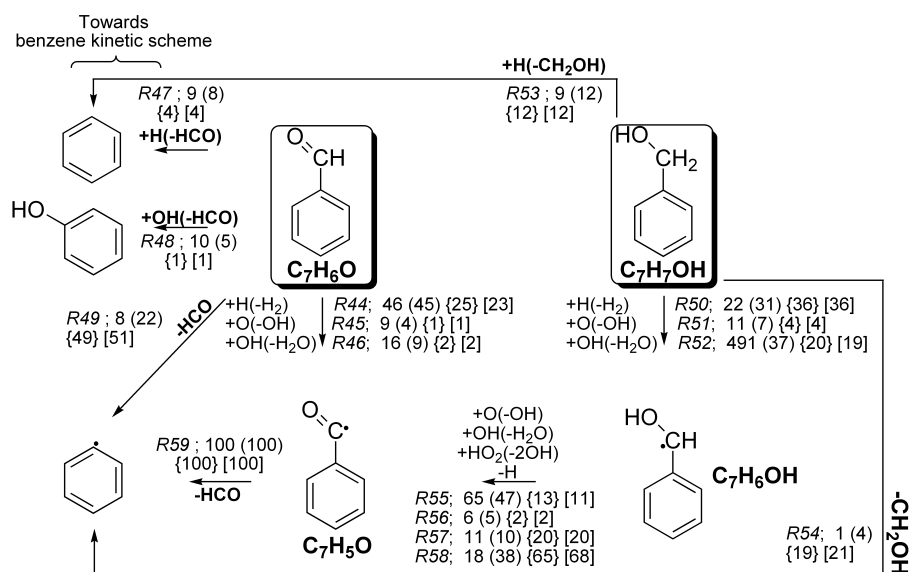


Figure 5.16: summary of benzaldehyde and benzylalcohol consumption pathways included into the developed kinetic model. Percentages represent contribution in TF07, (TF10), {TF18} and [TF20]

and CO through the dissociation reaction R59, over the entire range of equivalence ratios. Benzyl alcohol (C_7H_7OH) consumption mainly gives C_7H_6OH through H abstraction reactions R50 to R52 and reaction R53 with H atom yielding benzene and CH_2OH equally plays a significant role over the entire range of equivalence ratios. C_7H_6OH undergoes H abstraction reactions forming the benzoyl radical that is converted to phenyl radical and CO , as previously discussed. As for benzaldehyde, a dissociation reaction forming phenyl radical directly from benzyl alcohol plays an important role under high temperature conditions of TF18 and TF20.

In summary, benzyl radical consumption either leads to cyclopentadienyl radical and acetylene formation through the fulvenallene pathway or produces phenyl radical, benzene and phenol through benzaldehyde or benzylalcohol formation. Thus, final products of benzyl radical consumption all belong to the kinetic scheme of benzene combustion, discussed in the previous chapter.

5.3.5 Benzene and cyclopentadienyl radical formation

In previous sections, we have shown that three main reaction pathways compete in toluene consumption: the benzene path (path 1), the methylphenyl radical route (path 2) and the benzyl radical channel (path 3). This section analyzes the evolution of their respective contributions to benzene and cyclopentadienyl radical formations, which are their main products. These intermediates belong to the kinetic scheme developed in the previous chapter.

Cyclopentadienyl radical formation

Figure 5.17 presents contributions of main toluene consumption paths to cyclopentadienyl radical formation. Over the investigated range of equivalence ratios, path 3 is the major C_5H_5 formation channel and can proceed either through benzyl radical oxidation into benzaldehyde or fulvenallene formation. Since benzaldehyde and fulvenallene formations respectively depend on the O atom concentration and the temperature,

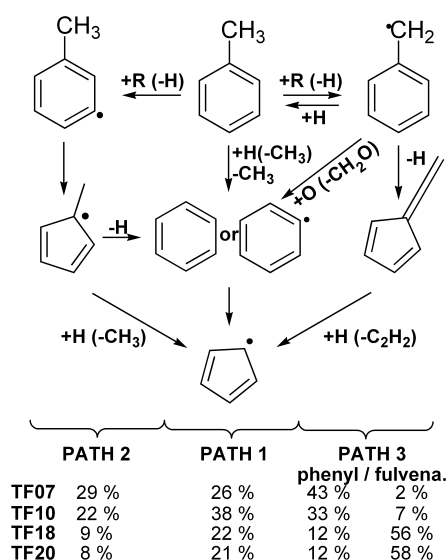


Figure 5.17: contribution of 3 main pathways of toluene consumption to cyclopentadienyl radical formation

their contributions to C_5H_5 radical formation respectively go down and up when the equivalence ratio increases. The overall contribution of path 3 worths 45 % in TF07 and slightly decreases to 40 % in TF10, as the flame temperature increase is unable to balance the drop in O atom concentration, disadvantaging the C_5H_5 radical formation through benzaldehyde. Compared to TF07, the contribution of path 1 in TF10 is favored by the decrease in that of path 3 and by the higher H atom concentration, accelerating the metathesis reaction between toluene and H atom, forming benzene and methyl radical. In TF20, the increase in flame temperature is sufficient to compensate the drop in O atom concentration and the overall contribution of path 3 reaches 70 %. Consequently, contributions of path 1 and path 2 decrease to 21 and 8 %, respectively.

Cyclopentadienyl radical formation in toluene combustion therefore highly depends on the equivalence ratio and the temperature. Each reaction channel in figure 5.17 significantly contributes to its production and should be included in kinetic models devoted to aromatic combustion. As demonstrated in the previous chapter, the cyclopentadiene (C_5H_6) formation is closely linked to that of cyclopentadienyl radical as it is principally formed by the recombination reaction $C_5H_5 + H + M = C_5H_6 + M$. Consequently, the comparison of the experimental cyclopent-

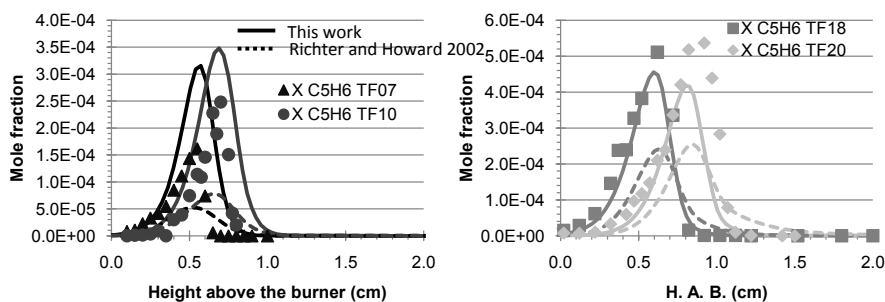


Figure 5.18: experimental and predicted mole fraction profiles of cyclopentadiene (C_5H_6). Gray scale symbols represent experiments ($\triangle$ TF07, $\circ$ TF10, $\diamond$ TF20). Solid and dashed curves stand for predictions of present and Richter and Howard [92] models, respectively.

tadiene mole fraction profile with that predicted by the current model illustrates the validity of the developed mechanism.

As shown in figure 5.18, model predictions are generally close to experimental measurements performed in all investigated flames. Compared to the model developed by Richter and Howard [92], the present mechanism provides a better predictive capability and figure 5.18 attests that significant improvements have been done in the understanding of toluene combustion chemistry. Nevertheless, the model tends to overestimate cyclopentadiene formation under lean conditions. This is caused by the overestimation of the benzaldehyde mole fraction (see figure 5.14), which stimulates the contribution of path 3 in figure 5.17. Rate parameters of the main benzaldehyde formation reaction (reaction R40 in table 5.5) consists in only a pre exponential factor, as its temperature dependence has not been investigated until now. Therefore, the rate of this reaction may not well reproduce the temperature drop observed between TF10 and TF07, respectively. Further studies on the kinetics of benzyl oxidation into benzaldehyde should improve cyclopentadiene predictions under lean conditions.

Benzene formation

Figure 5.19 presents contributions of main toluene consumption paths to the benzene formation. In TF07 and TF10, path 3 involving the benzyl radical is the main benzene formation route. Compared to $C_7H_8 + H \rightleftharpoons C_6H_6 + CH_3$, rate constant of $b-C_7H_7 + H \rightleftharpoons C_6H_5 + CH_3$ increases more than 20 times faster with temperature. Consequently, contribution of path 3 increases by 10 % when moving from TF07 to TF10 that has a maximum flame temperature 50 K higher than TF07. Although TF18 and TF20 have higher flame temperatures and H atom concentrations than TF07 and TF10, the contribution of path 3 suddenly drops to 8 %. Under flame temperatures of TF18 and TF20, the benzyl radical dissociation into fulvenallene and H atom has a high contribution, which consumes most of the benzyl radical into cyclopentadienyl radical and acetylene, instead of benzene. This drop allows path 1 and 2 to become

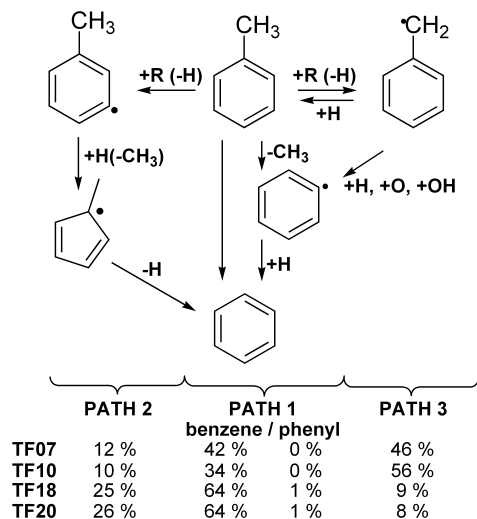


Figure 5.19: contribution to the benzene formation of the 3 main pathways of toluene consumption

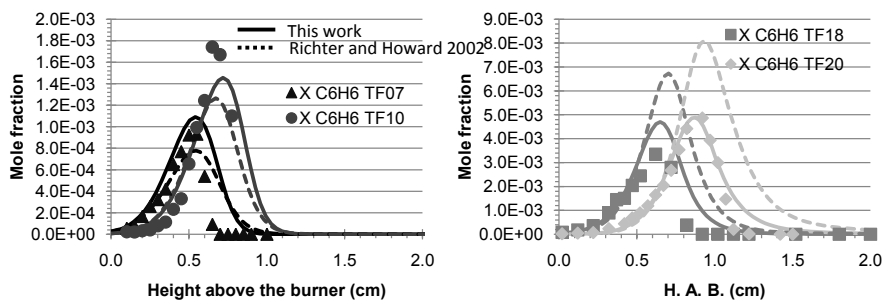


Figure 5.20: experimental and predicted mole fraction profiles of benzene (C_6H_6). Gray scale symbols represent experiments ($\triangle$ TF07, $\circ$ TF10, $\diamond$ TF20). Solid and dashed curves stand for predictions of present and Richter and Howard [92] models, respectively.

main benzene formation channels and path 2 that highly depends on H atom is the most important pathway, contributing to 64% of benzene formation in TF20.

As shown in figure 5.20, this kinetic scheme is able to well reproduce experimental measurements performed in all toluene flames investigated in this work. Compared to the RH model, the present model significantly improves benzene predictions. The good predictive capability of benzene mole fractions is important for the prediction of the molecular growth and soot formation, as it will be discussed in the following chapters.

5.3.6 Further reactions of C_4H_x and smaller hydrocarbons

Formation of C_2 , C_3 and C_4 hydrocarbons

In previous sections, we have demonstrated that toluene consumption is achieved through 3 main channels, which produce various C_2 , C_3 and C_4 hydrocarbons. The contribution of each pathway contributing to the formation of these hydrocarbons is summarized in figure 5.21 for each toluene flame. Most active channels are those connected to benzene and cyclopentadienyl radical (paths 1 to 5 in figure 5.21), as main pathways of toluene combustion converge towards these intermediates. Since these routes have been comprehensively described in the previous chapter, they will not be presented here. Path 6 of figure 5.21 requires high temperatures to overcome the activation barrier of the benzyl radical decomposition into fulvenallene + H . Consequently, acetylene and cyclopentadienyl radical formation from the reaction of fulvenallene with an H atom (path 6) is only important into TF18 and TF20. This additional channel of cyclopentadienyl radical formation increases the propargyl radical production through path 3 in TF18 and TF20, compared to TF07 and TF10. The reaction of methylphenyl radicals with molecular oxygen, forming various C_2 and C_3 hydrocarbons through path 7, accounts for 8%, 6%, 5% and 5% of toluene consump-

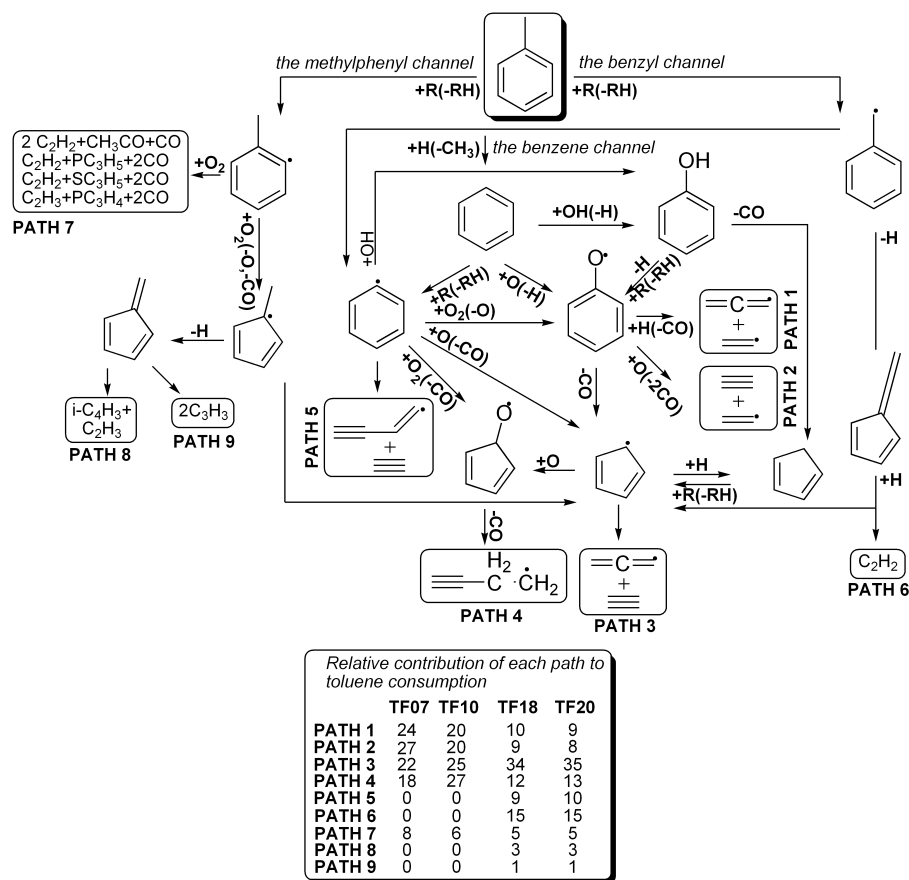


Figure 5.21: summary of chemical pathways involved in C_7 , C_6 and C_5 conversion to C_2 , C_3 and C_4 . The table in the lowest part of this figure gives contribution percentages of each route involved in toluene consumption in TF07, TF10, TF18 and TF20.

tion in TF07, TF10, TF18 and TF20, respectively. The decrease of this channel contribution, observed in flames with larger equivalence ratios, comes from the decrease of the whole contribution of the methylphenyl channel to toluene consumption, which has been discussed in previous sections. Finally, pathways 8 and 9 respectively form $i\text{-C}_4\text{H}_3 + \text{C}_2\text{H}_3$ and $2\text{C}_3\text{H}_3$ from fulvene, which is equally produced from methylphenyl radicals. Paths 8 and 9 only account for 4% of toluene consumption in TF18 and TF20, where the temperature is sufficient to overcome activation barriers of these decomposition reactions. Major reaction channels

involved in the consumption of C_2 , C_3 and C_4 hydrocarbons produced from pathways presented in figure 5.21 are discussed hereafter. The kinetic model for C_4 to C_1 flame chemistry is identical to that of the previous chapter and can be found in appendix E.

Consumption of C_4H_x hydrocarbons

The main C_4H_x hydrocarbons produced in the kinetic scheme proposed for toluene combustion are n- C_4H_5 , n- C_4H_3 and i- C_4H_3 , as depicted in paths 4, 5 and 8 of figure 5.21. The contribution of each major reaction consuming C_4H_x hydrocarbons in TF07, TF10, TF18 and TF20 are respectively presented in figures 5.22, 5.23, 5.24 and 5.25. In TF07 and TF10, the n- C_4H_5 radical is mainly consumed through an isomerization reaction, forming i- C_4H_5 and catalyzed by an H atom. Other major consumption routes involve the reaction with an O atom forming $CH_2CO + C_2H_3$ and H abstraction reactions giving vinylacetylene (C_4H_4). In TF18 and TF20, the isomerization into i- C_4H_5 is still the main consumption route and in addition to C_4H_4 formation, n- C_4H_5 reaction with H_2 forming 1,3-butadiene (C_4H_6) becomes significant due to the highest H_2 mole fractions. The reaction of n- C_4H_5 with O atom is negligible in TF18 and TF20, as the oxygen content of these flames is lower than in TF07 and TF10. In TF07 and TF10, the consumption of C_4H_6 is mainly performed through the addition of an O atom, giving a- $C_3H_5 + HCO$ or forming an OC_4H_6 adduct, which is subsequently decomposed into $C_2H_4 + CH_2CO$. Other major pathways involve either the dissociation of C_4H_6 into $C_2H_4 + C_2H_2$, the formation of $C_2H_4 + C_2H_3$ through reaction with an H atom, or the abstraction of an H atom producing i- C_4H_5 . In TF18 and TF20, which have higher flame temperatures than TF07 and TF10, the C_4H_6 dissociation into $C_2H_4 + C_2H_2$ becomes the most important consumption route, as the reaction barrier is overcome easily. Concerning i- C_4H_5 , in TF07 and TF10 its consumption is mainly achieved through reaction with H atom forming propargyl and methyl radicals. Additional channels produce C_4H_4 and $CH_2CO + C_2H_3$ by H abstraction reactions and reactions

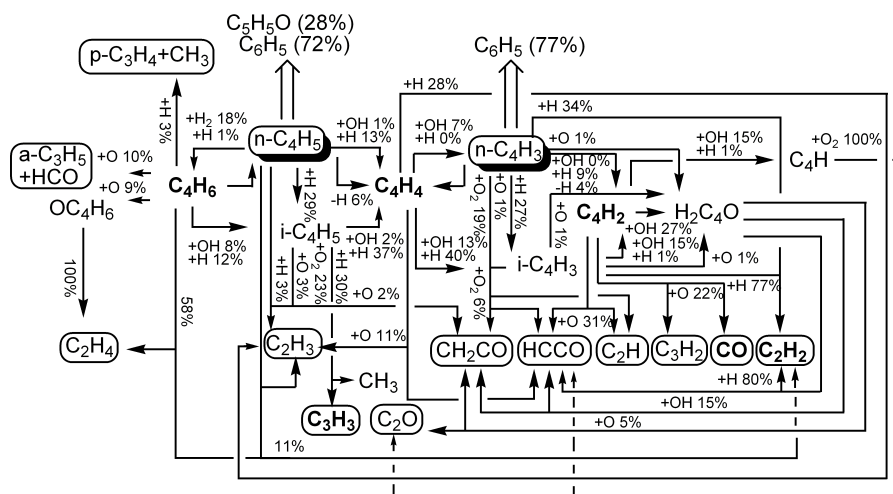


Figure 5.24: kinetic scheme of C_4H_x hydrocarbons in TF18.

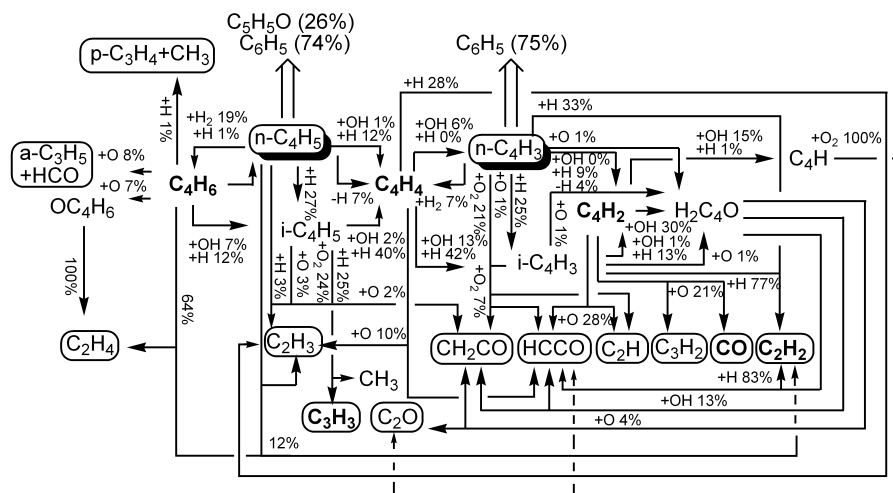


Figure 5.25: kinetic scheme of C_4H_x hydrocarbons in TF20.

with H and O atoms, respectively. In TF18 and TF20, the main consumption route becomes vinylacetylene production through H abstraction reactions. In all toluene flames, $n\text{-}C_4H_5$ and $i\text{-}C_4H_5$ consumption routes are therefore involved in vinylacetylene formation. Over the entire range of equivalence ratio, the main C_4H_4 consumption channel is the abstraction of an H atom forming the $i\text{-}C_4H_3$ radical, which is equally produced from fulvene dissociation in TF18 and TF20, as depicted into path 8 of figure 5.21. Other pathways of C_4H_4 consumption produce $C_2H_3 + HCCO$ and $n\text{-}C_4H_3$ through reaction with O atom and H abstraction reactions, respectively. $i\text{-}C_4H_3$ is mainly consumed into 2 C_2H_2 , through reaction with an H atom. Additional channels are the reaction with O atom forming H_2C_4O and H abstraction reactions producing diacetylene (C_4H_2). Reactions with O atom are mainly active in TF07 and TF10, which have a higher oxygen content than TF18 and TF20. The $n\text{-}C_4H_3$ is connected to $i\text{-}C_4H_3$ through an isomerization reaction catalyzed by an H atom and can form C_4H_2 , similarly to $i\text{-}C_4H_3$. In all investigated flames, the main C_4H_2 consumption route is the reaction with an O atom forming $HCCO + C_2H$. Additional pathways produce $C_3H_2 + CO$ or C_4H and H_2C_4O , which are both consumed into C_2 intermediates, as depicted in figures 5.22, 5.23, 5.24, 5.25. The consumption of C_4H_x hydrocarbons therefore principally converges towards the formation of C_3H_3 , C_3H_2 , C_2H_3 , C_2H_2 , CH_2CO and $HCCO$, whose consumption pathways will be examined in following sections.

In figure 5.26, predicted mole fraction profiles of C_4H_2 , C_4H_4 and 1,3- C_4H_6 are compared to experimental measurements in order to assess the predictive capability of the developed kinetic model. The present model generally well reproduces C_4H_2 and C_4H_4 measurements. The persistence of C_4H_2 in burnt gases is well predicted and comes from a formation route involving C_2H_2 and C_2H , which are equally present in burnt gases. Vinylacetylene predictions are reliable in all investigated flames, contrarily to predictions of the model developed by Richter and Howard [92] which overestimates its mole fraction in all conditions. This last model equally overestimates mole fraction profiles of C_4H_2 but gives better predictions for 1,3- C_4H_6 than the model developed in this

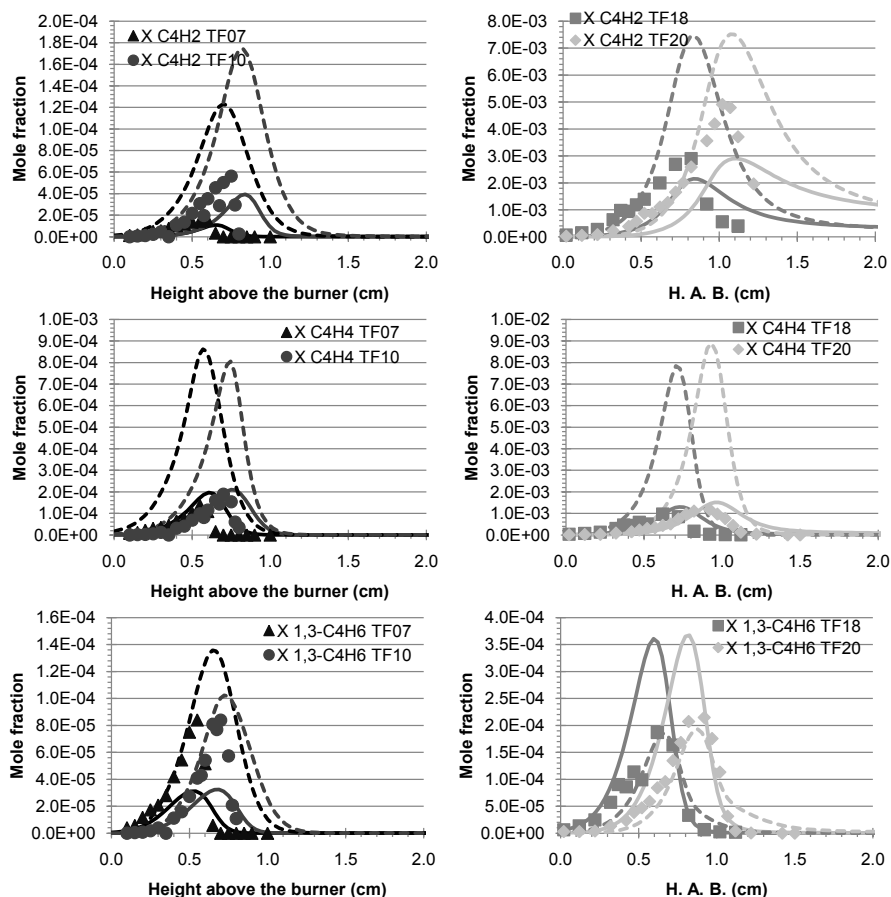


Figure 5.26: experimental and predicted mole fraction profiles of diacetylene (C_4H_2), vinylacetylene (C_4H_4) and 1,3-butadiene (C_4H_6). Gray scale symbols represent experiments ($\triangle$ TF07, $\circ$ TF10, $\square$ TF18, $\diamond$ TF20). Solid and dashed curves in corresponding gray scale stand for predictions of present and Richter and Howard [92] models, respectively.

work. Indeed, our mechanism respectively underestimates and overestimates 1,3 butadiene measurements performed in flames with low and high equivalence ratios. This discrepancy between our model and that developed by Richter and Howard comes from the absence of the reaction $1,3-C_4H_6 + H \rightleftharpoons n-C_4H_5 + H_2$ in the RH model. In our model, this H abstraction reaction proceed backward and is a main pathway of 1,3-butadiene formation. The absence of this reaction from the RH

model is surprising and further studies are therefore required to clarify this point.

Consumption of C_3H_x hydrocarbons.

As depicted in figure 5.21, toluene combustion produces p- C_3H_5 , s- C_3H_5 , p- C_3H_4 and C_3H_3 . Moreover, the consumption of C_4H_x intermediates form C_3H_3 and C_3H_2 , as discussed in the previous section. Figures 5.27, 5.28, 5.29 and 5.30 summarize consumption channels of these C_3H_x species and present contributions of main reactions, calculated by comparative reaction rate analyses. In TF07 and TF10, the consumption of the p- C_3H_5 radical is mainly achieved through reaction with molecular oxygen, forming either $CH_3CHCO + H + O$ or $CH_3CHO + HCO$. Minor channels lead to a- C_3H_5 , propylene and propyne formation, through isomerization, recombination with H atom and H abstraction reactions, respectively. In TF18 and TF20, the contribution of consumption routes depending on molecular oxygen decreases and that of channels forming propyne, propylene and a- C_3H_5 is of greater importance. In TF07 and TF10 a- C_3H_5 principally reacts with O , forming $CH_2CHCHO + OH$. Additional pathways lead to propylene and allene formation through recombination with H atom and H abstraction reactions, respectively. In TF07 and TF10, propylene is mainly consumed through reaction with O atom forming either $C_2H_5 + HCO$ or $CH_2CO + CH_3$. Other pathways produce $CH_3 + C_2H_4$ or p-, a- and s- C_3H_5 by reaction with H atom and H abstraction reactions, respectively. In TF18 and TF20, the contribution of reactions involving O atom are less important than in TF07 and TF10 and the formation of $CH_3 + C_2H_4$ and C_3H_5 isomers is therefore more important. In all investigated flames, s- C_3H_5 is principally converted into allene and propyne through unimolecular dissociations or H abstraction reactions. Then, allene and propyne are mainly converted into $C_2H_2 + CH_3$, $C_2H_4 + CO$ and the propargyl radical (C_3H_3), respectively through reactions with H atom, O atom and H abstraction reactions. Propyne and allene recombination with an H atom can equally produce C_3H_5 radicals. The C_3H_3 radical is a major intermedi-

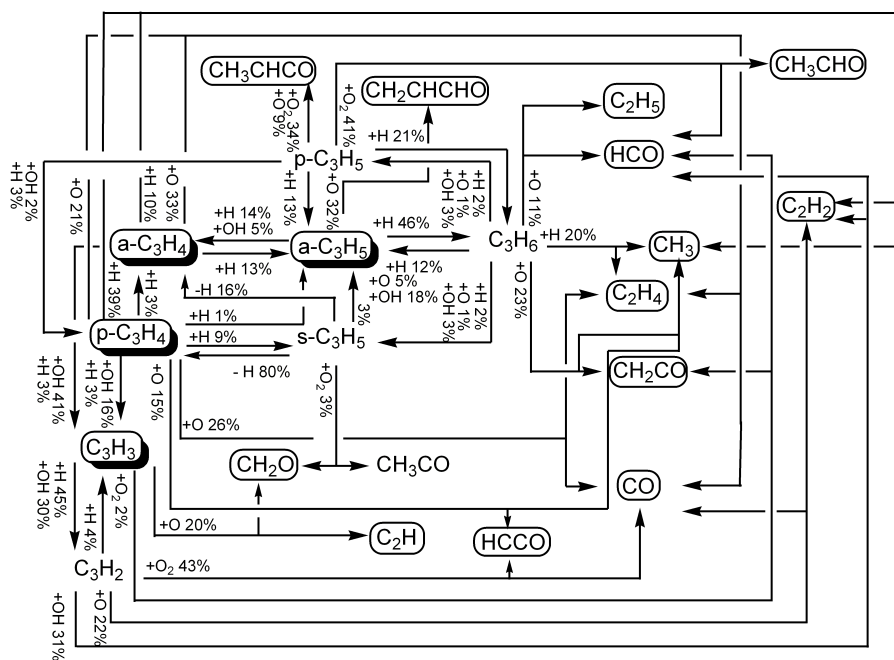


Figure 5.27: kinetic scheme of C_3H_x hydrocarbons in TF07.

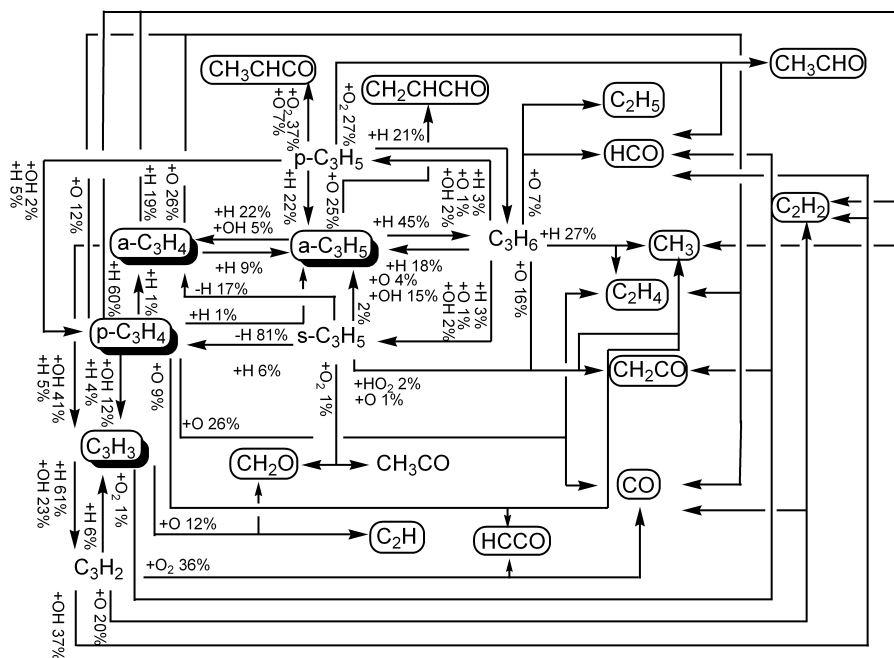
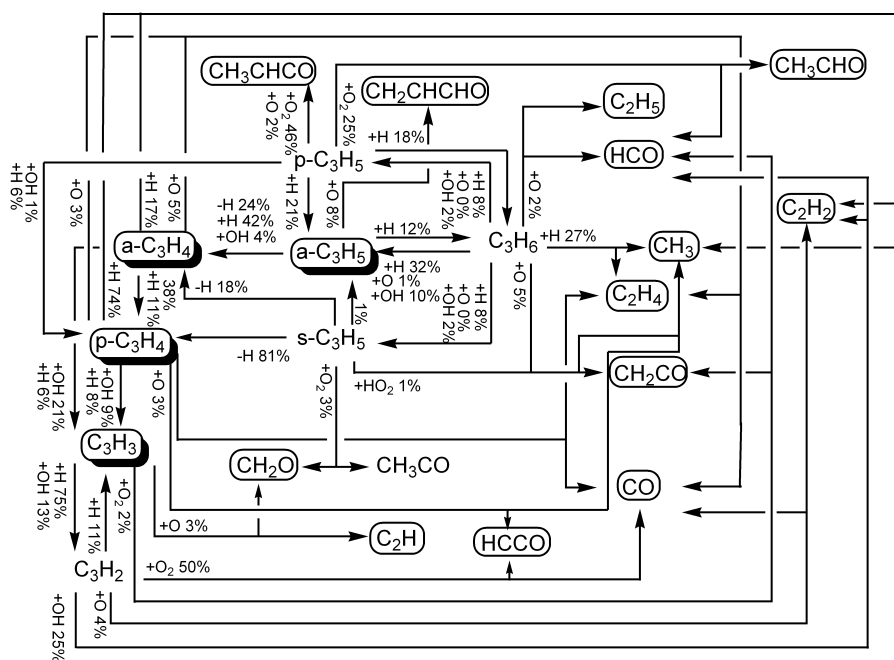
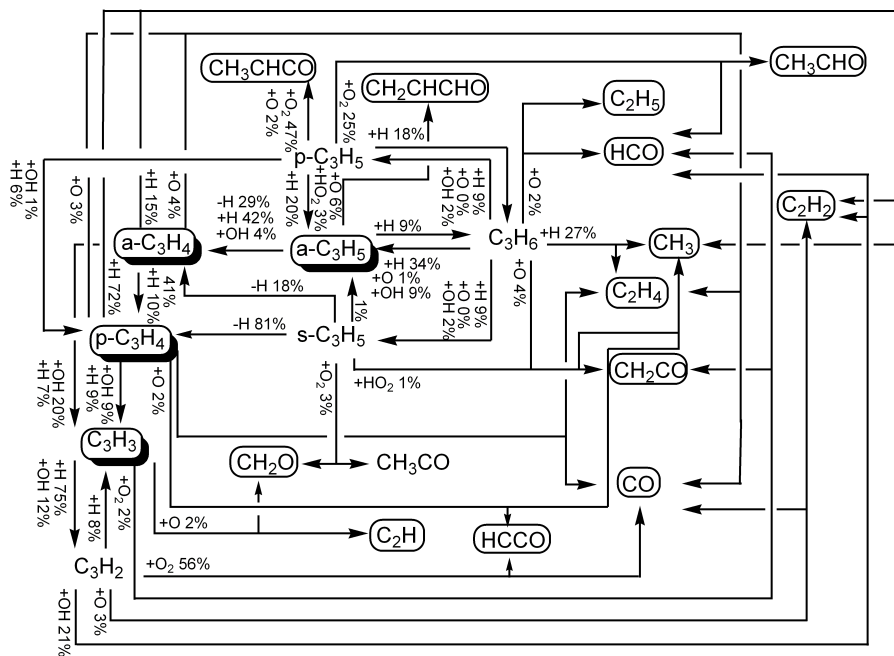


Figure 5.28: kinetic scheme of C_3H_x hydrocarbons in TF10.

Figure 5.29: kinetic scheme of C_3H_x hydrocarbons in TF18.Figure 5.30: kinetic scheme of C_3H_x hydrocarbons in TF20.

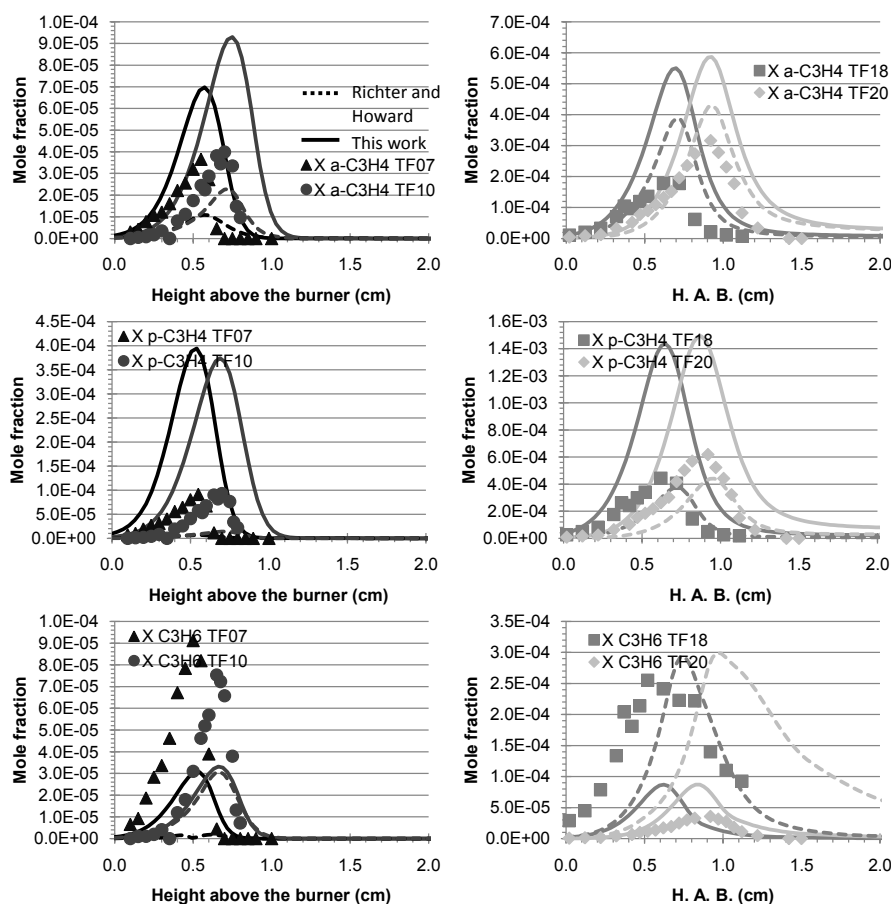


Figure 5.31: experimental and predicted mole fraction profiles of propargyl radicals (C_3H_3), allene (a- C_3H_4), propyne (p- C_3H_4) and propylene (C_3H_6). Gray scale symbols represent experiments ($\triangle$ TF07, $\circ$ TF10, $\square$ TF18, $\diamond$ TF20). Solid and dashed curves in corresponding gray scale stand for predictions of present and Richter and Howard [92] models, respectively.

ate in benzene and toluene flames since it is produced directly from the dissociation of cyclopentadienyl radical, which has been previously identified as a central intermediate species. Moreover, consumption of C_4H_x and C_3H_x hydrocarbons are found to converge towards C_3H_3 formation. This radical mainly undergoes H abstraction reactions producing propargylene (C_3H_2) or reacts with O and O_2 , giving $C_2H + CH_2O$ and $CH_2CO + HCO$, respectively. As previously highlighted, reactions involving O and O_2 are mainly important in TF07 and TF10, compared to TF18 and TF20. The C_3H_2 radical principally reacts with O , OH and O_2 , forming $C_2H_2 + CO$, $C_2H_2 + HCO$ and $HCCO + CO$, respectively. An additional pathway involves the recombination with an H atom, producing the propargyl radical back. Since acetylene is an important product of C_3H_3 consumption and is equally formed in various consumption channels of benzene and toluene combustion, it is therefore a central intermediate that is present in high mole fractions in flames of this work.

Figure 5.31 compares experimental measurements to predictions of the model presented in this chapter and those of the RH mechanism. Predicted mole fractions of a- C_3H_4 and p- C_3H_4 overestimate measurements by factors 2 and 3, respectively and the model of Richter and Howard has a better predictive capability. This overestimation might come from the highest C_3H_5 production with the present model, due to path 7 of figure 5.21. In the present model, methylphenyl reactions with O_2 producing $C_3H_x + C_2H_x$ have been included as overall pathways, whereas they have linear C_5H_7 intermediates. Since no reliable rate constants exist for reactions of linear C_5H_7 hydrocarbons, they are therefore supposed to fully dissociate into $C_3H_x + C_2H_x$ intermediates. This may explain highest predictions of C_3H_4 mole fractions, depicted in figure 5.31. Concerning C_3H_6 , predicted maximum mole fractions of the developed model are slightly better than those of the Richter and Howard's model.

Consumption of C_2H_x and C_1H_x hydrocarbons.

The consumption of toluene, C_4H_x hydrocarbons and C_3H_x hydrocarbons converges towards C_2H_x and CH_x formations, whose principal intermediates are C_2H_2 , C_2H_3 and CH_3 . Figures 5.32, 5.33, 5.34 and 5.35 present main consumption reactions of these hydrocarbons in TF07, TF10, TF18 and TF20, respectively, together with their contributions calculated by comparative reaction rate analyses. The C_2H_3 radical principally reacts with O_2 through three different channels, producing $C_2H_2 + HO_2$, CH_2CHO and $HCO + CH_2O$. The two latter routes are principally active in TF07 and TF10 and the first competes with H abstraction reactions by H and OH radical. In addition to these reactions, in TF07 and TF10 C_2H_3 reacts with O atom, forming $CH_2CO + H$. Acetylene principally reacts with O atom, forming either the triplet radical of CH_2 and CO or $HCCO + H$. Acetylene conversion into $HCCO$ prevails on $CH_2 + CO$ formation in all investigated flames. The $HCCO$ radical can equally be formed through H abstraction reactions on CH_2CO , which is produced from H abstraction reactions on CH_2CHO . In addition to H abstraction reactions, CH_2CHO and CH_2CO reacts with H atom, forming methyl radical, which leads to methane formation through its recombination with an H atom. Methane is only consumed through H abstraction reactions, giving methyl radical back. Methyl radical is a key intermediate in hydrocarbon combustion, as it is responsible of ethylene, ethane, ethyl radical and CH_2O formation. In TF18 and TF20, ethyl radical (C_2H_5) is mainly decomposed into ethylene and H atom, whereas in TF07 and TF10 it principally reacts with O atom and OH radical, forming acetaldehyde and ethanol, respectively. Ethanol is mainly converted into acetaldehyde, which produces CH_2CHO and CH_3CO through H abstraction reactions.

Then, CH_2CO dissociates into CO and methyl radical. In the same way as $HCCO$, methyl radical produces the singlet radical of CH_2 , which is oxidized in CO and CO_2 through H abstraction, O addition and dissociation reactions.

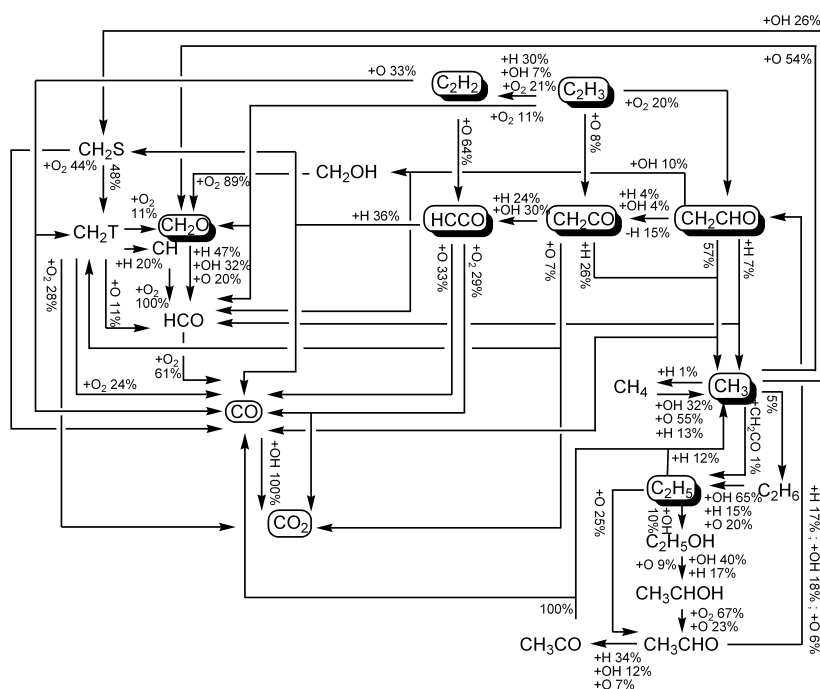


Figure 5.32: kinetic scheme of C_2H_x and C_1H_x hydrocarbons in TF07.

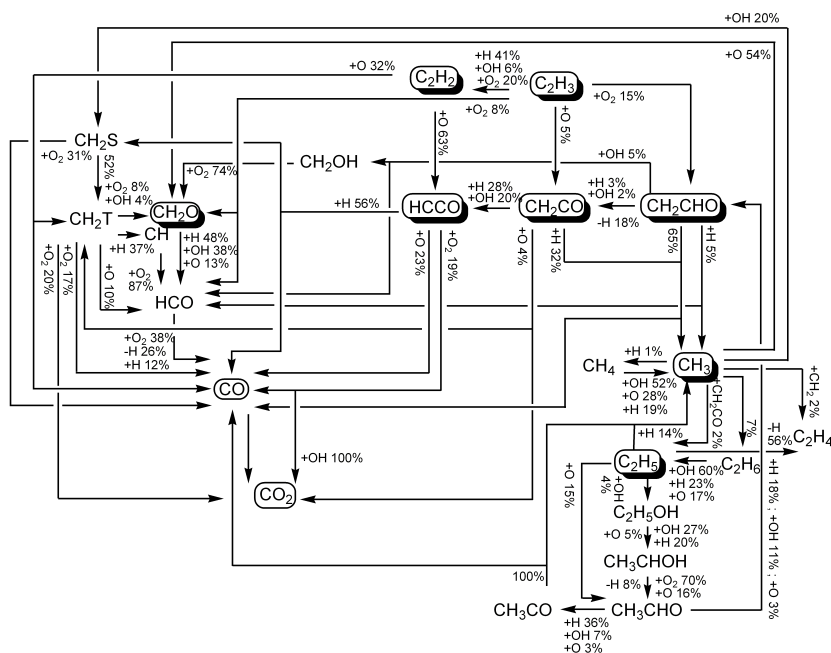
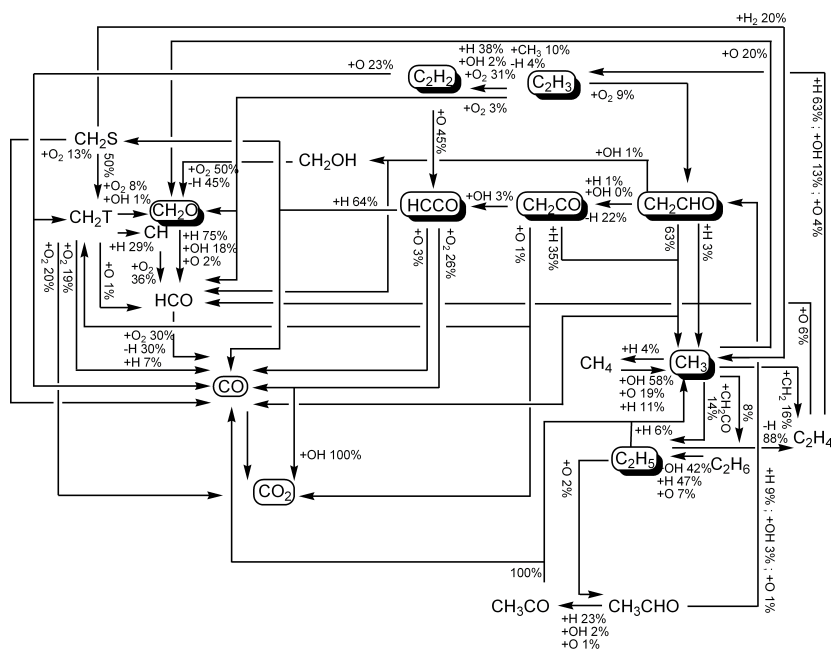
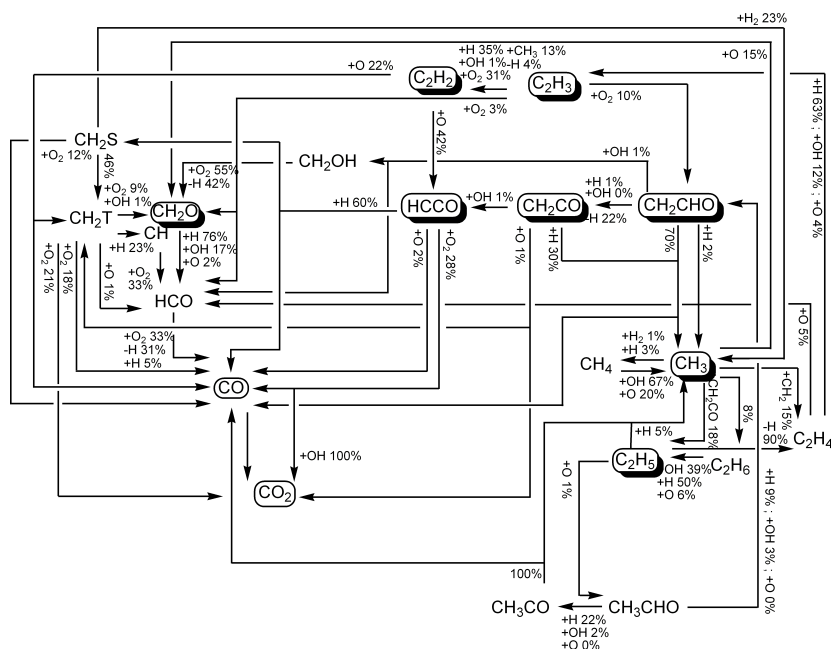


Figure 5.33: kinetic scheme of C_2H_x and C_1H_x hydrocarbons in TF10.

Figure 5.34: kinetic scheme of C_2H_x and C_1H_x hydrocarbons in TF18.Figure 5.35: kinetic scheme of C_2H_x and C_1H_x hydrocarbons in TF20.

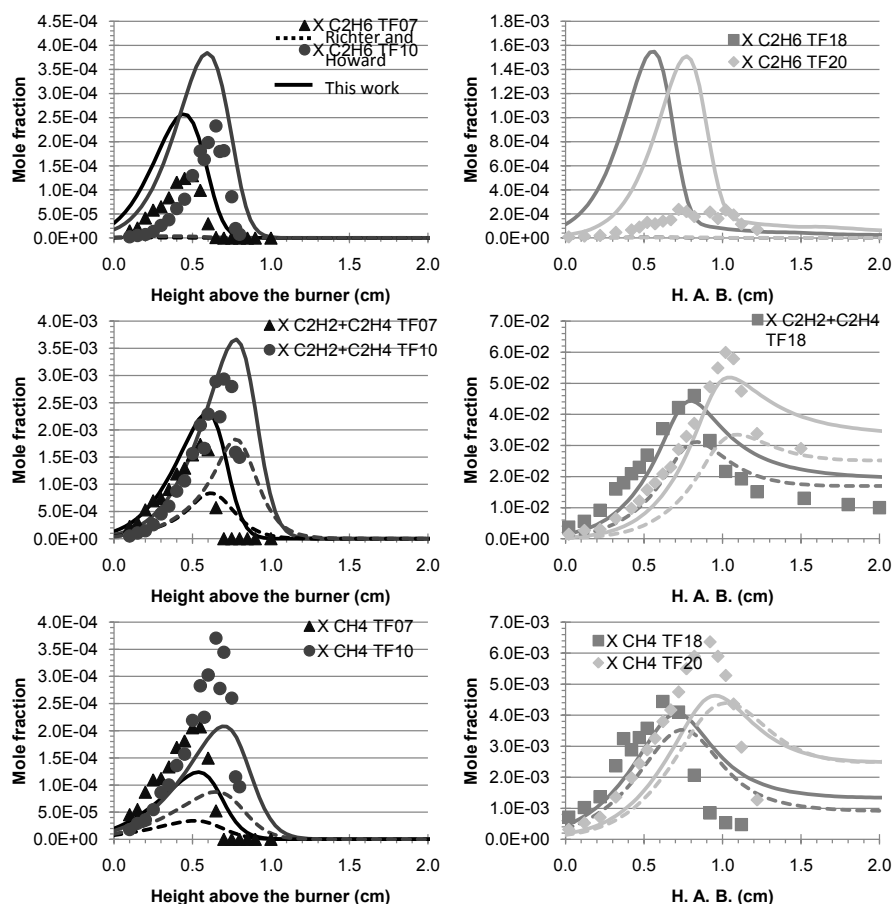


Figure 5.36: experimental and predicted mole fraction profiles of ethane (C_2H_6), acetylene (C_2H_2) and methane (CH_4). Gray scale symbols represent experiments ($\triangle$ TF07, $\circ$ TF10, $\square$ TF18, $\diamond$ TF20). Solid and dashed curves in corresponding gray scale stand for predictions of present and Richter and Howard [92] models, respectively.

Figure 5.36 compares experimental results to predictions of C_2H_2 , C_2H_6 and CH_4 obtained with the developed kinetic model and that of Richter and co-workers [92]. A general good predictive capability is observed. Since C_2H_2 is a key intermediate of toluene consumption, the good agreement obtained demonstrates the relevance of the developed mechanism. Moreover, the good prediction of C_2H_2 is of particular importance in soot formation since it is a major building block of PAH material, as presented in the following chapter. The good methane prediction

equally demonstrates the consistence of the toluene kinetic sub-model, as it is formed from methyl radical, which is principally produced from the substitution of the methyl group of toluene by a hydrogen atom. The distribution between contributions of the 3 main paths of toluene consumption is therefore consistent with methane formation in all investigated flames.

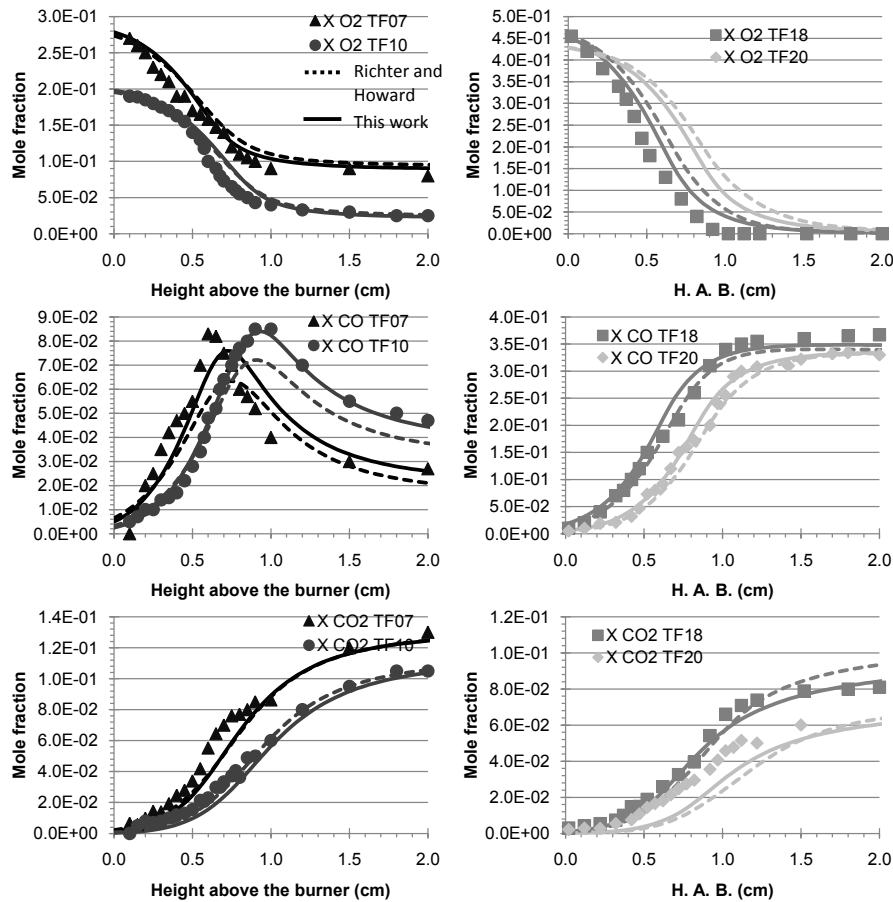


Figure 5.37: experimental and predicted mole fraction profiles of carbon monoxide (CO), carbon dioxide (CO_2) and molecular oxygen (O_2). Gray scale symbols represent experiments ($\triangle$ TF07, O TF10, $\square$ TF18, $\diamond$ TF20). Solid and dashed curves in corresponding gray scale stand for predictions of present and Richter and Howard [92] models, respectively.

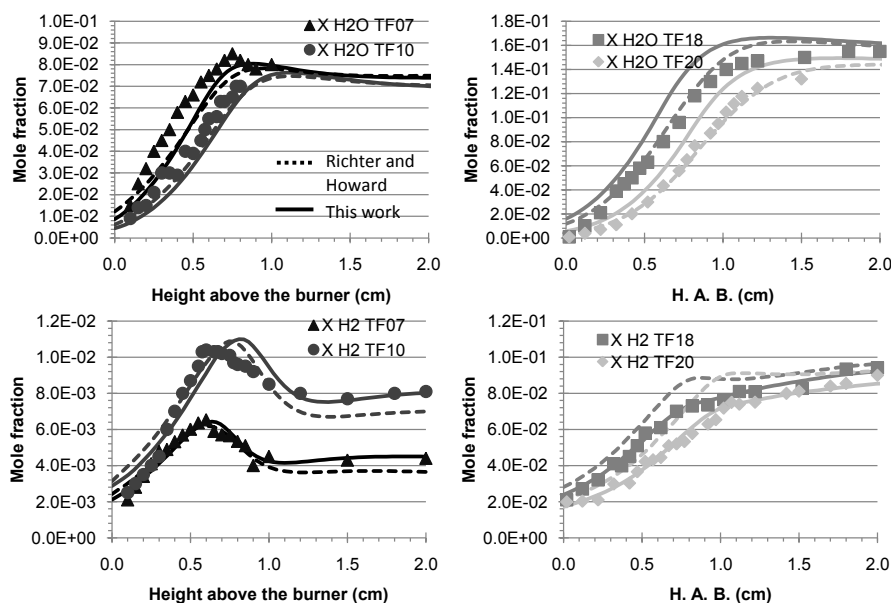


Figure 5.38: experimental and predicted mole fraction profiles of water (H_2O) and molecular hydrogen (H_2). Gray scale symbols represent experiments ($\triangle$ TF07, $\circ$ TF10, $\square$ TF18, $\diamond$ TF20). Solid and dashed curves in corresponding gray scale stand for predictions of present and Richter and Howard [92] models, respectively.

5.3.7 The main chemical species

Figure 5.38 and 5.37 compare experimental mole fraction profiles of main chemical species detected in toluene flames to model predictions. A good agreement is reached for all reactants and products, showing that the developed kinetic model of toluene combustion reliably represent the overall combustion reaction of toluene, over the investigated range of equivalence ratios.

5.4 Conclusions

In this chapter, experimental structures of one-dimensional, laminar and premixed toluene-oxygen-argon flames, burning at 45 mbar and at equivalence ratios of 0.7, 1, 1.8 and 2 have been discussed. To our best knowl-

edge, experimental structures at equivalence ratios of 0.7, 1 and 2 are the first to be investigated. This work is therefore of a great interest for researchers working in the field of oxidation of aromatic hydrocarbons. It has been showed that chemical species detected in toluene flames are very similar to those previously measured in benzene flames. Consequently, it has been suggested that an important overlap between benzene and toluene combustion chemistry should exist. As highlighted in the introduction, a significant uncertainty still surrounds benzyl radical formation and consumption in toluene combustion. Indeed, its consumption is thought to occur through dissociation into fulvenallene (C_7H_6) intermediate and an H atom, or by reaction with an O atom forming benzaldehyde. The measurement of mole fraction profiles of these intermediates is therefore of particular concern and the gas chromatography investigation has been completed by a molecular beam mass spectrometry study at m/z ratios corresponding to benzyl radical, fulvenallene and benzaldehyde.

In parallel to this experimental study, toluene combustion has been investigated by kinetic modeling. A detailed kinetic sub-model has therefore been developed on the basis of a comprehensive literature survey, in order to complete the benzene combustion mechanism presented in the previous chapter. Comparative reaction rate analyses have allowed to determine the contribution of each reaction to the consumption of every chemical species involved in toluene combustion. It has been shown that toluene is mainly consumed through three different pathways consisting of (i) the benzyl radical formation through H abstraction reactions from its methyl group, (ii) benzene and phenyl radical formation through toluene dissociation or substitution of the methyl group by a H atom and (iii) ortho, meta and para-methylphenyl radical production by H abstraction reactions on the phenyl ring. Most of kinetic models describing toluene combustion does not include the latter channel, assuming that its contribution is negligible. However, our study demonstrates that at low temperature and equivalence ratio, this pathway must be taken into account to properly model toluene combustion. The developed kinetic scheme considers the consumption of methylphenyl radicals through re-

actions with molecular oxygen, forming either methylphenoxy radicals or various C_2H_x and C_3H_x intermediates. This reaction is thought to proceed similarly to that involving phenyl radical and O_2 , discussed in the previous chapter. It is shown that methylphenoxy radicals decompose into CO and methylcyclopentadienyl radical, which is further consumed into benzene and cyclopentadienyl+methyl radicals. The benzyl radical produced in the first path of toluene combustion is found to oxidize into benzaldehyde at low equivalence ratios and low temperatures and to decompose into fulvenallene and H atom at higher equivalence ratios and temperatures. Mole fraction profiles measured by MBMS at m/z ratios corresponding to benzyl radical, fulvenallene and benzaldehyde are globally in good agreement with the kinetic modeling. Benzaldehyde is principally converted into benzoyl radical, which subsequently decomposes into phenyl radical and CO . In order to reliably predict the cyclopentadiene mole fraction, it is demonstrated that the reaction of fulvenallene with H atom has to produce cyclopentadienyl radical and C_2H_2 , as recently proposed by some theoretical studies. The present study therefore provides experimental and numerical evidences that this pathway should exist in flames and proposes an estimate of its rate constant, which has been successfully used in recent studies devoted to high temperatures reactions of toluene. The kinetic modeling study predicts that toluene is principally consumed into benzene, phenyl radical and cyclopentadienyl radicals, which are important intermediates of the kinetic scheme of benzene combustion presented in the previous chapter. This confirms the overlap between toluene and benzene flame chemistry, assumed on the basis of similarities observed between benzene and toluene experimental flame structures.

Whereas the developed kinetic sub-model has a general good predictive capability, some improvements are still needed in methylphenyl radical reactions with O_2 forming $C_3H_x + C_2H_x$ hydrocarbons. Indeed, these reactions result in high C_3H_5 formation rates that cause the overestimation of mole fractions of C_3H_4 intermediates. The reaction of benzyl radical with O atom should be equally further addressed, as its rate constant does not account for dependence on pressure and temperature.

Moreover, the rate constant proposed for fulvenallene reaction with H atom is an assumption based on the current kinetic model and more fundamental theoretical and experimental works should be performed to confirm this hypothesis.

This chapter presents valuable toluene-oxygen-argon flames structures, together with a detailed kinetic modeling study that improves the understanding of toluene combustion chemistry and will be helpful for researchers working in the field of oxidation of aromatic hydrocarbons. In the next chapters, the kinetic model developed for combustion of aromatic fuels will be extended to molecular growth towards PAH and soot.

Part III

Benzene and toluene flame chemistry: the molecular growth

Molecular growth: PAH formation

6.1 Introduction

In previous chapters experimental structures of benzene and toluene-oxygen-argon flames have been presented at various equivalence ratios. We have shown that under rich conditions chemical species larger than reactants appear in significant concentrations, demonstrating that a molecular growth process operates simultaneously to the fuel oxidation. As it will be discussed in the following chapter, the soot production process is a complex phenomenon based on particles formation from these large hydrocarbons. The development of a kinetic sub-model able to reproduce mole fraction profiles of these larger hydrocarbons is therefore necessary to extend the model to soot formation. The PAH sub-model development and the comparison of its predictions to experimental measurements will be described in this chapter. The addition of a sub-model allowing to predict soot formation will be the subject of the next chapter. For many years, several reaction pathways have been proposed to explain molecular growth towards large PAHs and most of them are presented below.

6.1.1 The acetylene pathway

In 1981, Bittner and Howard [71] investigated a laminar, premixed and one-dimensional benzene-oxygen-argon flame under rich conditions. Authors measured mole fraction profiles of several intermediate species, including PAHs with masses until 228 uma, and postulated that the molecular growth may operate through reactions depending on acetylene, as illustrated in route 1 of figure 6.1. The involvement of acetylene in PAH formation is supported by its high concentration observed in burnt gases of rich aromatic flames, where PAH growth and soot formation occur. The mechanism proposed by Bittner and Howard consists in phenyl formation from benzene through H abstraction reactions, followed by two successive acetylene additions, a cyclization step and a H atom elimination reaction, forming naphthalene. Based on the pioneer

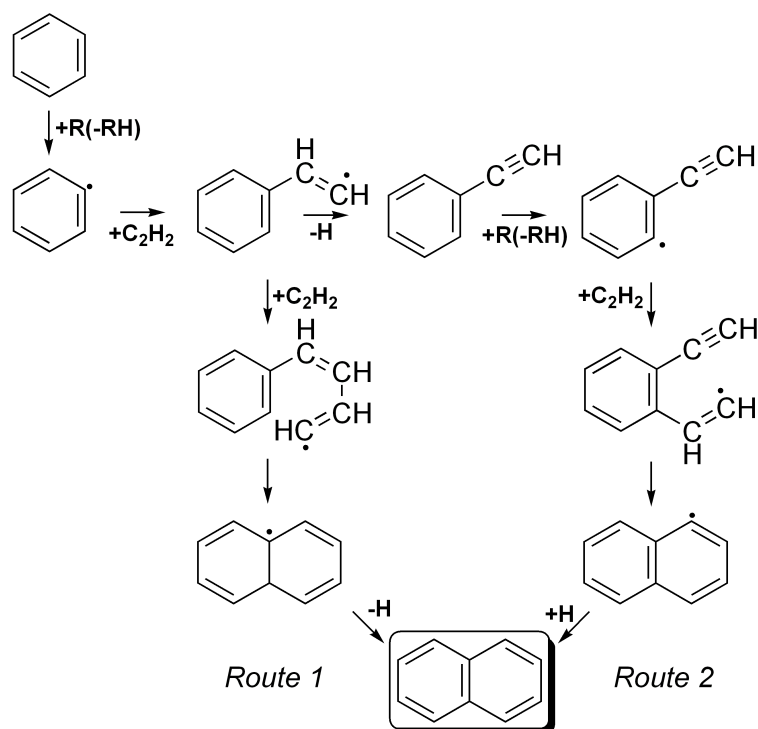


Figure 6.1: the two routes of naphthalene formation from benzene through acetylene addition

study of Bittner and Howard, Frenklach and co-workers [99] later developed a kinetic model for soot formation, using acetylene addition to describe the hydrocarbon growth. In addition to route 1 of figure 6.1, authors included many variant mechanisms and performed a sensitivity analysis to determine which chemical pathway dominates PAH formation in acetylene pyrolysis. They found that route 1 of figure 6.1 is minor and that route 2 is the most important channel of naphthalene formation, since the C_8H_7 adduct formed by acetylene addition on the phenyl radical is unstable and rapidly decomposes into phenylacetylene and H atom. Then phenylacetylene can be reactivated by H abstraction reactions and further react with acetylene to form naphthalene, as depicted in route 2 of figure 6.1. In 1991, Frenklach and Wang [100] introduced the name HACA (Hydrogen Abstraction C_2H_2 Addition) to refer to this mechanism of molecular growth based on acetylene addition reactions. Frenklach and co-workers highlighted that in addition to naphthalene formation, the HACA mechanism can explain the growth towards larger compounds, as depicted in figure 6.2. The HACA mechanism has rapidly

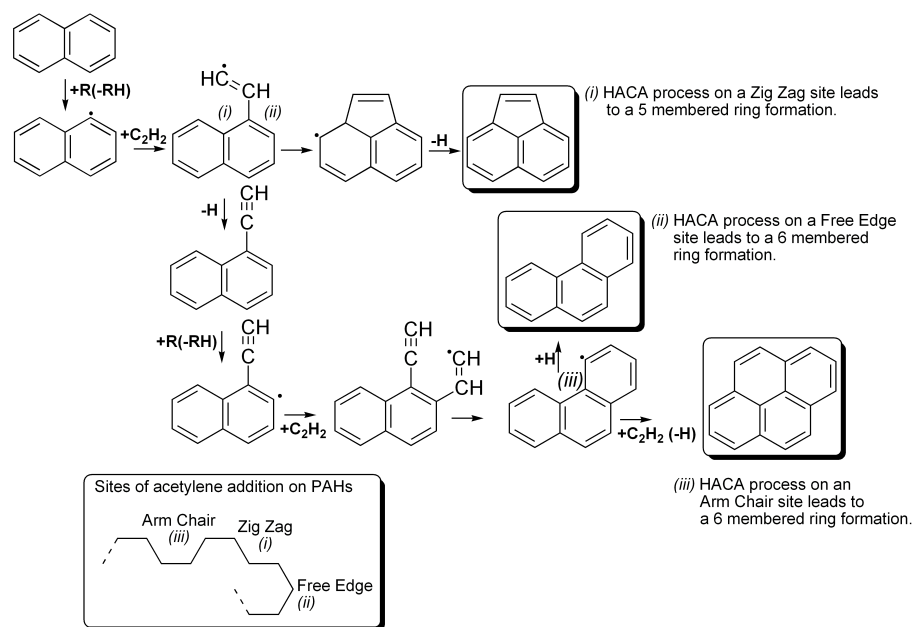


Figure 6.2: further growth of naphthalene through HACA reactions

become very popular and is now widely used to explain PAH and soot formations in hydrocarbon flames. Recently, Celnik and co-workers [225] theoretically investigated PAH growth through the HACA mechanism and stressed that it can lead to various products, depending on the environment of the starting CH group. Basically, they suggested that each PAH surface can be divided into different reacting sites that they called zig zag, free edge, arm chair and bay, which will react through HACA reactions forming determined structures. The HACA process on a zig zag site always produces a five membered ring, while it leads to six membered ring formation if occurring on other sites. Formation of five membered rings are very important because if bordered on all sides by hexagons, they provide a bowl-shaped structure that is specific to some non planar compounds observed in soot, such as corranulene and fullerenes. Figure 6.2 depicts the application of the site governed approach of Celnik and co-workers on naphthalene growth through HACA reactions.

6.1.2 The benzyl pathway

In addition to propose acetylene as a main building block for PAH formation, Bittner and Howard [71] observed high levels of indene (C_9H_8) in their rich benzene-oxygen-argon flames and suggested that a mechanism involving acetylene addition on the benzyl radical, followed by a cyclization step and a hydrogen atom elimination, can explain its formation (see the top of figure 6.3). This mechanism has been theoretically analyzed by Vereecken and Peeters in 2003 [226] and Kislov and Mebel in 2007 [227], who demonstrated that it should contribute to indene formation under combustion conditions. As further discussed, indene can be involved into PAH formation through reactions of cyclopentadienyl and methyl radicals on its C_5 ring, forming phenanthrene and naphthalene, respectively. In addition to these pathways converting the C_5 ring into a C_6 ring, indene can growth by reactions forming PAH containing a five membered ring, needed to explain the bowl-shaped structures of some large PAHs observed in soot. In 1994, Colket and Seery performed a py-

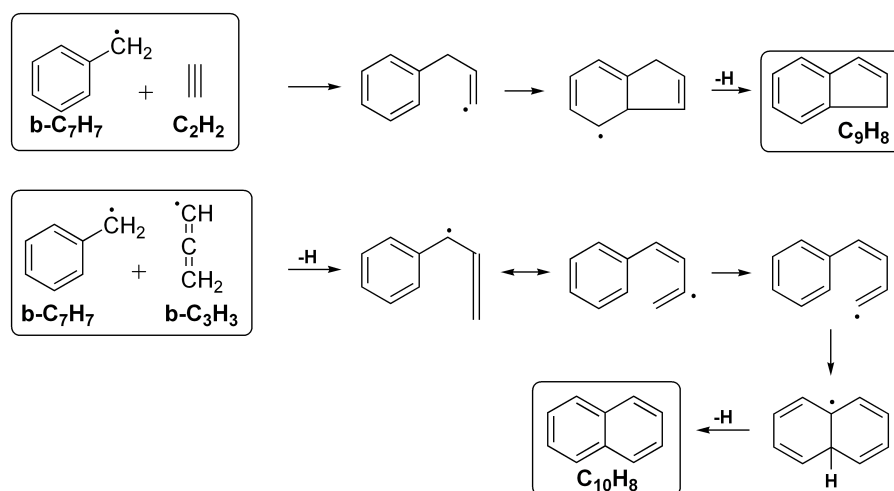


Figure 6.3: naphthalene formation through benzyl and propargyl radicals recombination

rolysis study of toluene in shock tubes [187] and measured high concentrations of several PAHs. Authors highlighted that the HACA process could not explain alone these PAH levels and proposed a new reaction channel for naphthalene formation, involving benzyl and propargyl radical recombination. The mechanism of this chemical pathway is depicted at the bottom of figure 6.3 and involves two main reaction sequences. The first includes the $\text{b-C}_7\text{H}_7 + \text{C}_3\text{H}_3$ recombination, followed by an H atom elimination forming the C_{10}H_9 intermediate of figure 6.3. The second involves a series of isomerization reactions, a cyclization step and an H atom elimination finally forming naphthalene. Until now, this reaction channel has not been theoretically investigated and energy barriers related to its different steps are still unknown. In addition to these two reaction channels forming indene and naphthalene, benzyl radical can react with methyl radical, producing ethylbenzene (C_8H_{10}) that may give styrene (C_8H_8) and phenylacetylene (C_8H_6) through dehydrogenation of the ethyl side chain.

6.1.3 The cyclopentadienyl pathway

In 1996, Marinov and co-workers [170] performed experimental and kinetic modeling studies on PAH formation in methane and ethylene flames. They highlighted that the HACA mechanism was unable to predict the observed levels of PAHs and that additional pathways leading to their formation should compete. Authors proposed that beside the HACA process, self recombination of cyclopentadienyl radicals may significantly contribute to naphthalene formation. The same year, Melius and co-workers [156] performed theoretical calculation on the $C_5H_5 + C_5H_5$ potential energy surface and demonstrated that this new naphthalene formation channel may compete under flame temperatures. The mechanism proposed by Melius and co-workers is depicted in figure 6.4 and consists of 2 main reaction sequences. The first involves the self recombination of two cyclopentadienyl radicals, forming 9,10-dihydrofulvalene that subsequently isomerizes into 1,10-dihydrofulvalene, which finally eliminates a hydrogen atom giving the $C_{10}H_9$ radical of figure 6.4. According to Melius and co-workers, the overall $2C_5H_5 \rightleftharpoons C_{10}H_9 + H$ reaction is only slightly endothermic by 4 kcal mol⁻¹. The second reaction sequence involves a series of ring

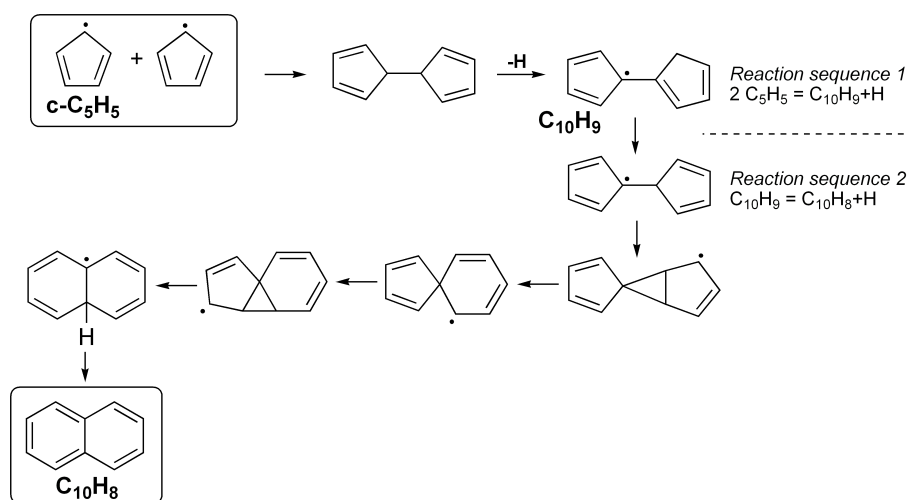


Figure 6.4: naphthalene formation through cyclopentadienyl radical self recombination

closure and opening reactions on the previous $C_{10}H_9$ radical, and finally the loss of a hydrogen atom forming naphthalene, as shown in figure 6.4. Authors calculated that the overall reaction $C_{10}H_9 \rightleftharpoons C_{10}H_8 + H$ would have a maximum energy barrier of 47 kcal mol⁻¹. Consequently, this second reaction sequence should be the rate determining step of naphthalene formation through the self recombination of C_5H_5 radicals. Melius and co-workers stressed that this reaction scheme can equally be applied to compounds having a cyclopentadienyl ring on their chemical structure, such as the indenyl radical (C_9H_7) formed by H abstraction reactions on indene (C_9H_8), whose formation has been discussed previously. As an example, the reaction between C_9H_7 and C_5H_5 will convert the five membered ring of indenyl radical into two six membered rings, forming phenanthrene and two hydrogen atoms. Recently, Kislov and Mebel [228] have comprehensively investigated the potential energy surface of the $C_5H_5 + C_5H_5$ reaction and have highlighted that beside naphthalene, this recombination may result into indene formation through a complex mechanism involving an H atom addition, various isomerization reactions and the loss of a methyl group.

6.1.4 The ring ring condensation pathway

In 1998, Bohm and co-workers [229] investigated PAH growth and soot formation during the pyrolysis of acetylene and benzene and performed a kinetic modeling study of their experiments. Authors showed that soot formation starts much earlier in benzene pyrolysis than in acetylene systems, demonstrating that the HACA mechanism could not explain PAH formation and growth alone. Consequently, Bohm and co-workers considered an additional PAH formation route, initially proposed by Frenklach and co-workers in 1986 [230], which is based on ring ring condensations followed by HACA reactions, as depicted in at the bottom of figure 6.5. Bohm and co-workers determined relative contributions of this new channel, the HACA mechanism and the cyclopentadienyl radical route. Authors found that the ring ring condensation process and the cyclopentadienyl radical route dominate small PAH formation in ben-

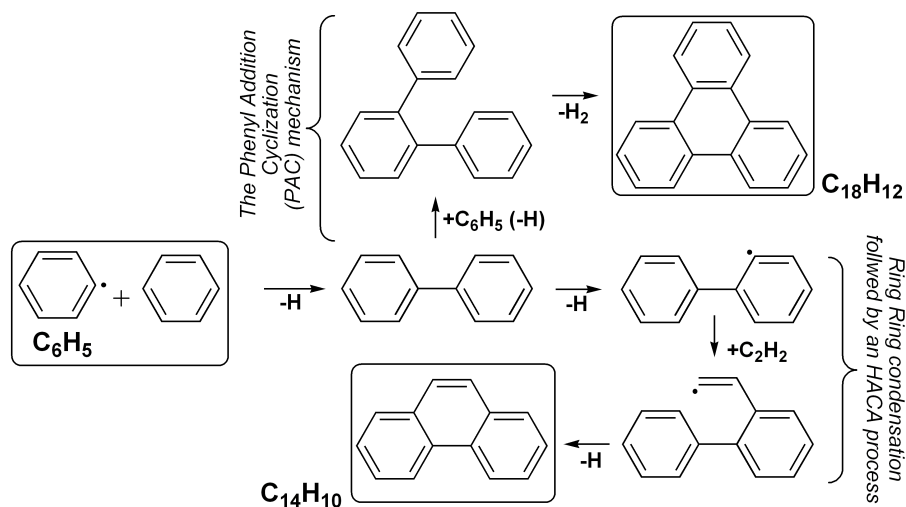


Figure 6.5: PAH formation and growth through ring ring condensation reactions.

zene and acetylene pyrolysis, although the HACA mechanism is mainly responsible of these PAH growth into larger compounds, which will ultimately form soot. The ring ring condensation mechanism proposed by Frenklach and co-workers [230] and used by Bohm and co-workers [229] has been recently reinvestigated by Shukla and co-workers [62] by studying toluene pyrolysis with and without benzene. Authors introduced the Phenyl Addition Cyclization (PAC) mechanism to explain the observation of regular sequences of 74 uma in PAH masses, corresponding to the phenyl addition, followed by H atom elimination and cyclization through H_2 ejection. The top of figure 6.5 illustrates the condensation of three phenyl rings into triphenylene through this PAC mechanism.

6.1.5 Other pathways of PAH formation and growth

The four previous sections present major PAH formation pathways currently described in the literature. However, these four channels are obviously not the only that can be envisioned to propagate the growth of aromatic rings. Several other proposals have appeared, including those involving reactions of vinylacetylene, methyl radical, allene and propyne.

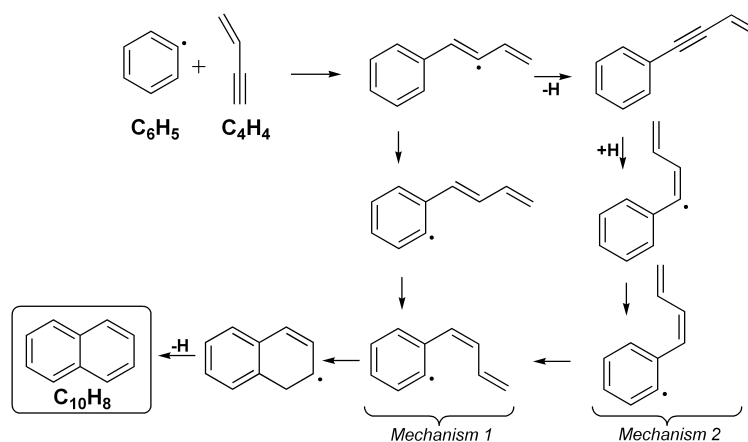


Figure 6.6: naphthalene formation through vinylacetylene reaction with phenyl radical

Naphthalene formation from vinylacetylene addition to phenyl radical was first introduced by Bittner and Howard [71] in 1981, who proposed the isomerization mechanism depicted in mechanism 1 of figure 6.6. In 2000, Moriarty and Frenklach [231] performed a theoretical analysis of this reaction pathway and stressed that the mechanism initially proposed by Bittner and Howard should be significantly slower than that involving an H atom elimination and addition, presented as mechanism 2 in figure 6.6.

Molecular growth mechanisms depending on methyl radical have been suggested by Shulka and co-workers in 2007 [232] and 2010 [233], who performed a mass spectrometry study on PAH formation in toluene pyrolysis. Authors detected mass sequences corresponding to methyl addition on PAHs and proposed a mechanism involving series of dehydrogenation and methyl radical addition reactions to explain their measurements. This general scheme is illustrated for the phenanthrene formation in figure 6.7. Unfortunately, up to now no kinetic studies have been conducted to assess the kinetic viability of such a PAH growth channel. However, it is well admitted that methyl addition on benzyl radical is a key reaction forming ethylbenzene, which is a precursor of styrene and phenylacetylene. The methyl radical channel is a good candidate to explain PAH growth since CH_3 radical is present in relatively

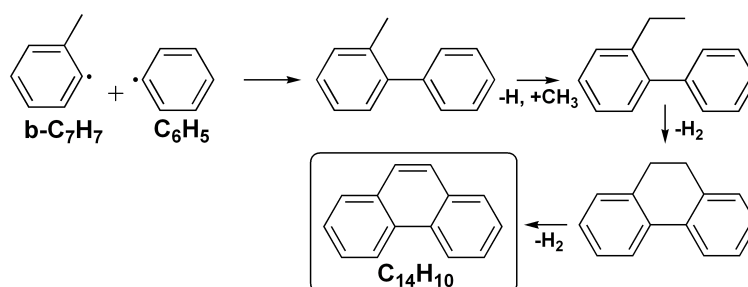


Figure 6.7: phenanthrene formation through methyl addition reactions

high concentrations in burnt gases of hydrocarbon flames. Reactions between phenyl radical and C_3H_4 isomers such as allene and propyne have equally been suggested by Vereecken and Peeters in 2003 [226]. However, authors theoretically showed that these reaction pathways are too slow and should consequently not compete with other PAH formation channels in flames.

Whereas the HACA mechanism explaining PAH formation and their growth has been initially considered as the main source of molecular growth in hydrocarbon flames, this introduction demonstrates that several additional reaction pathways may compete with this acetylene based model. These supplementary channels mainly involve resonantly stabilized radicals such as cyclopentadienyl or benzyl radicals, demonstrating that they do not only play a key role in fuel oxidation but may be highly active in PAH formation. Aromatic flames investigated in this work contain significant concentrations of building blocks involved in all mechanisms presented above. Whereas the development of a detailed kinetic model to predict PAH formation in these flames should include each of these pathways, kinetic parameters of the vinylacetylene and the methyl radical channels are not available in the literature. Consequently, these mechanisms cannot be included into the present model, which will only contain the three main routes discussed above.

In addition to compare model predictions to experimental measurements of PAHs detected in this work, this chapter presents rich flame structures of cyclopentene-oxygen-argon, cyclopentene-benzene-oxygen-

argon and propyne-toluene-oxygen-argon flames. Indeed, cyclopentene and propyne are respectively precursors of cyclopentadienyl and propargyl radicals, two intermediates that are thought to produce naphthalene through the cyclopentadienyl radicals channel or the benzyl + propargyl reaction route. The investigated fuel blends are therefore suspected to influence the naphthalene formation and the validation of the mechanism on these flame structures is therefore important to determine the validity of naphthalene formation routes presented above. Consequently, a kinetic sub-model representing cyclopentene and propyne combustion chemistry is equally presented in the following discussion.

6.2 Discussion on the mechanism of molecular growth

The previous section has introduced mechanisms proposed in the literature for the molecular growth in hydrocarbon flames. The present section examines how these schemes are included into the kinetic model developed for benzene and toluene flames and compares predictions to experimental measurements. PAH formation in stoichiometric and lean flames will not be discussed in this chapter as a significant molecular growth has only been observed in flames with equivalence ratios of 1.8 and 2. The further discussion is divided into subsections, each describing the formation and the consumption of a compound having a molecular mass higher than reactants. Choices of rate parameters are discussed and a contribution analysis is provided to determine how various reaction channels compete.

6.2.1 The toluene sub-model

Toluene has been detected as an intermediate compound in all benzene flames of this work and its formation and consumption involve chemical pathways presented in chapter 5. In benzene flames, toluene is mainly produced through recombination reactions between (i) phenyl

and methyl radicals and (ii) benzyl radical and hydrogen atom. Since benzyl radical is mainly produced from H abstraction reactions on toluene, the channel (ii) consists in a loop between toluene and benzyl radical. Consequently, the key reaction for toluene formation in benzene flames is $C_6H_5 + CH_3 + M \rightleftharpoons C_7H_8 + M$, whose rate parameters have been discussed in table 5.3 on page 204. It is interesting to note that the fulvenallene pathway does not proceed backward in benzene flames, producing benzyl radical through acetylene recombination with cyclopentadienyl radical. However, in hydrocarbon flames having low phenyl and methyl radicals maximum mole fractions, this pathway is a potential toluene formation route. The contribution of reactions involved in consumption of the toluene formed in benzene flames are very similar to those presented in chapter 5. The reader should therefore refer to that chapter for more information on toluene consumption in benzene flames. In addition to these consumption routes, minor pathways lead to molecular growth through recombination reactions of the benzyl radical with various hydrocarbons. These reactions will be discussed further in this chapter.

Figure 6.8 compares toluene mole fraction profiles measured in BF07, BF10, BF18 and BF20 to predictions of kinetic models developed in this work and published by Richter and Howard [92]. Our predictions are close to experimental measurements in all investigated flames and

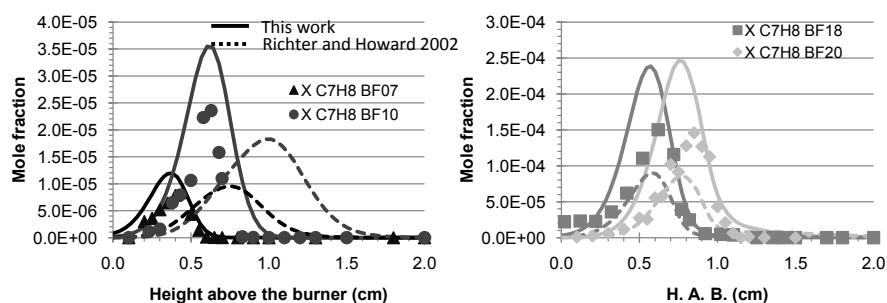


Figure 6.8: experimental and predicted mole fraction profiles of toluene (C_7H_8). Gray scale symbols represent experiments ($\triangle$ TF07, $\circ$ TF10, $\square$ TF18, $\diamond$ TF20). Solid and dashed curves stand for predictions of present and Richter and Howard [92] models, respectively.

a significant improvement of maximum positions is achieved in BF07 and BF10. The good predictive capability of our kinetic model for these toluene mole fraction profiles demonstrates the validity of the sub-model developed for toluene combustion in chapter 5.

6.2.2 The naphthalene sub-model

The development of the naphthalene sub-model

As discussed in the introduction of this chapter, several mechanisms have been postulated to explain naphthalene formation in hydrocarbon

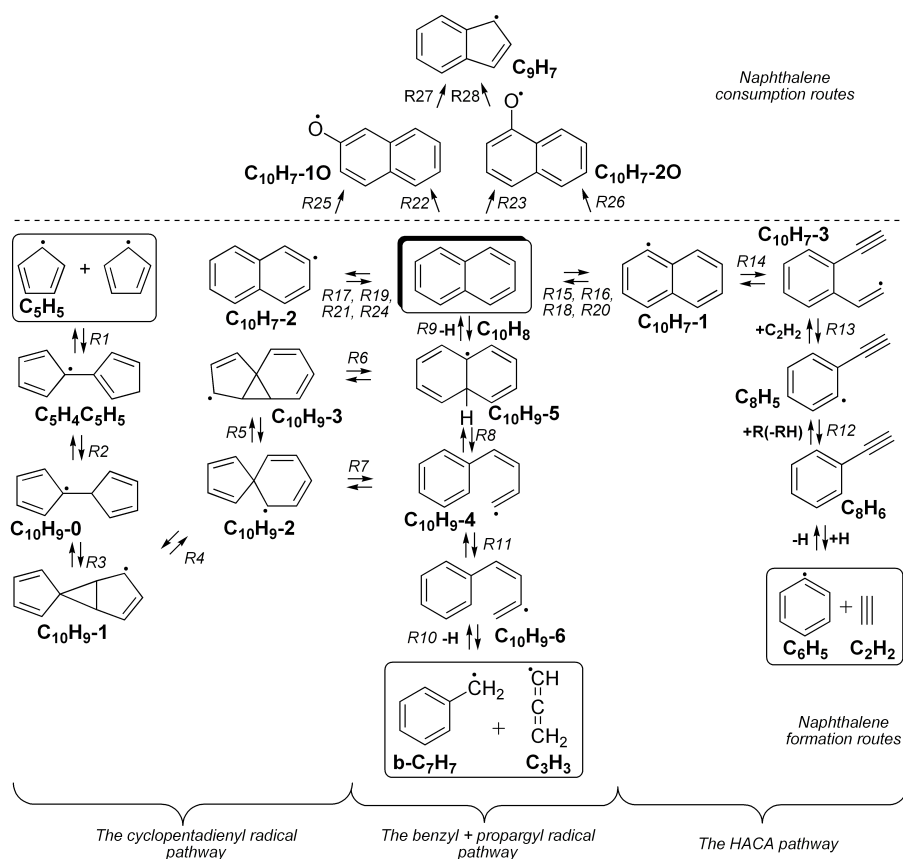


Figure 6.9: reactions pathways considered for naphthalene formation and consumption in the developed kinetic model.

flames. Since this work is devoted to aromatic flames that exhibit significant concentrations of acetylene, cyclopentadiene, benzyl radicals and propargyl radicals, one can suggest that the HACA pathway, the cyclopentadienyl radical recombination route and the benzyl + propargyl radical channel will be key naphthalene formation channels.

These three reaction pathways are usually included in the form of three overall reactions in kinetic models available in the literature [22, 92], whereas they consist in complex mechanisms that involve numerous reaction steps and share common intermediates, as depicted in figure 6.9. Recently, theoretical studies have been conducted in order to determine potential energy surfaces of the HACA mechanism and the cyclopentadienyl radical pathway [168, 228, 234]. These works equally provide rate constant calculations for many individual steps of those two naphthalene formation routes. Concerning the benzyl + propargyl radicals channel, it may be linked to the reaction scheme presented in figure 6.9 by inserting two additional reactions whose kinetic parameters are estimated, as explained further. Consequently, instead of using three overall reactions, a new detailed sub-model for naphthalene formation has been developed. It is depicted in figure 6.9 and rate parameters of each reaction are summarized in table 6.1 and discussed hereafter.

Figure 6.9 shows that the cyclopentadienyl radicals route and the benzyl + propargyl radicals pathway produce naphthalene through reactions belonging to the $C_{10}H_9$ potential energy surface. These two pathways share two intermediate compounds: $C_{10}H_9 - 4$ and $C_{10}H_9 - 5$ (see figure 6.9). When available, rate constant parameters of table 6.1 have been taken from the recent theoretical works of Kislov and co-workers [228, 234]. Rate parameters of reactions that were not calculated in those works (reactions R1, R2, R10 and R11) have been estimated.

Table 6.1: $C_{10}H_8$ production and consumption reactions included into the kinetic model.

Reactions		$k = AT^n e^{-E_a/RT}$ A^a	n	E_a^a	Refs.
Reactions of the C_5 pathway.					
R1	$C_5H_5 + C_5H_5 \rightarrow C_5H_4C_5H_5 + H$	$8.0 \cdot 10^{13}$	0	8	a
	$C_5H_5 + C_5H_5 \leftarrow C_5H_4C_5H_5 + H$	$3 \cdot 10^{13}$	0	0	b
R2	$C_5H_4C_5H_5 \rightleftharpoons C_{10}H_9 - 0$	$3.6 \cdot 10^{10}$	0.9	37	c
R3	$C_{10}H_9 - 0 \rightarrow C_{10}H_9 - 1$	$3.8 \cdot 10^{12}$	-1.92	6	d
	$C_{10}H_9 - 0 \leftarrow C_{10}H_9 - 1$	$5.1 \cdot 10^{13}$	-3.38	-3.4	d
R4	$C_{10}H_9 - 1 \rightarrow C_{10}H_9 - 2$	$3.5 \cdot 10^{22}$	-4.77	14.7	d
	$C_{10}H_9 - 1 \leftarrow C_{10}H_9 - 2$	$6.7 \cdot 10^{21}$	-4.65	29.5	d
R5	$C_{10}H_9 - 2 \rightarrow C_{10}H_9 - 3$	$1.4 \cdot 10^{14}$	-2.37	7.5	d
	$C_{10}H_9 - 2 \leftarrow C_{10}H_9 - 3$	$7.1 \cdot 10^{14}$	-2.4	-0.3	d
R6	$C_{10}H_9 - 3 \rightarrow C_{10}H_9 - 5$	$5.5 \cdot 10^{11}$	-1.67	5.1	d
	$C_{10}H_9 - 3 \leftarrow C_{10}H_9 - 5$	$2.1 \cdot 10^{11}$	-1.52	29.9	d
R7	$C_{10}H_9 - 2 \rightarrow C_{10}H_9 - 4$	$1.7 \cdot 10^{15}$	-4.7	12.3	d
	$C_{10}H_9 - 2 \leftarrow C_{10}H_9 - 4$	$1.2 \cdot 10^{13}$	-4.7	-7.9	d
R8	$C_{10}H_9 - 4 \rightarrow C_{10}H_9 - 5$	$2.2 \cdot 10^9$	-0.8	1.6	d
	$C_{10}H_9 - 4 \leftarrow C_{10}H_9 - 5$	$1.3 \cdot 10^{11}$	-0.5	38.5	d
R9	$C_{10}H_9 - 5 \rightarrow C_{10}H_8 + H$	$7.2 \cdot 10^{10}$	0.8	15.1	d
	$C_{10}H_9 - 5 \leftarrow C_{10}H_8 + H$	$4.4 \cdot 10^8$	1.5	11.1	d
Reactions of $C_7 + C_3$ pathway.					
R10	$b\text{-}C_7H_7 + C_3H_3 \rightarrow C_{10}H_9 - 6 + H$	$6.0 \cdot 10^{11}$	0	0	[187]
	$b\text{-}C_7H_7 + C_3H_3 \leftarrow C_{10}H_9 - 6 + H$	$3.0 \cdot 10^{13}$	0	0	b
R11	$C_{10}H_9 - 4 \rightleftharpoons C_{10}H_9 - 6$	$3.6 \cdot 10^{10}$	0.9	37.3	e
Reactions of the HACA pathway.					
R12	$C_8H_6 + H \rightarrow C_8H_5 + H_2$	$1.3 \cdot 10^8$	1.9	17.6	f
	$C_8H_6 + H \leftarrow C_8H_5 + H_2$	$9.1 \cdot 10^4$	2.4	5.6	f
R13	$C_8H_5 + C_2H_2 \rightarrow C_{10}H_7 - 3$	$1.3 \cdot 10^4$	2.5	1.3	f
	$C_8H_5 + C_2H_2 \leftarrow C_{10}H_7 - 3$	$7.6 \cdot 10^{13}$	0.4	46	f
R14	$C_{10}H_7 - 3 \rightarrow C_{10}H_7 - 1$	$1.3 \cdot 10^9$	-0.7	1.5	f
	$C_{10}H_7 - 3 \leftarrow C_{10}H_7 - 1$	$9.6 \cdot 10^9$	-0.2	71.1	f
R15	$C_{10}H_7 - 1 + H + M \rightleftharpoons C_{10}H_8 + M$ (k_∞)	$2.2 \cdot 10^{14}$	0	0	f
	$C_{10}H_7 - 1 + H + M \rightleftharpoons C_{10}H_8 + M$ (k_0)	$4.1 \cdot 10^{104}$	-24.6	21.5	f
Troe's broadening factors: $4.6 \cdot 10^{-2} / 3.52 \cdot 10^2 / 6 \cdot 10^4 / 7.6 \cdot 10^3$					f
Reactions of naphthalene consumption.					

Continued on next page

Reactions		$k = AT^n e^{-E_a/RT}$			Refs.
		A^a	n	E_a^a	
R16	$C_{10}H_8 + H \rightleftharpoons C_{10}H_7 - 1 + H_2$	$2.3 \cdot 10^8$	1.9	17.1	[234]
R17	$C_{10}H_8 + H \rightleftharpoons C_{10}H_7 - 2 + H_2$	$2.3 \cdot 10^8$	1.9	17.1	g
R18	$C_{10}H_8 + OH \rightleftharpoons C_{10}H_7 - 1 + H_2O$	$9.7 \cdot 10^2$	3.0	4.4	[234]
R19	$C_{10}H_8 + OH \rightleftharpoons C_{10}H_7 - 2 + H_2O$	$8.3 \cdot 10^2$	3.0	4.4	g
R20	$C_{10}H_8 + O \rightleftharpoons C_{10}H_7 - 1 + OH$	$6.0 \cdot 10^{13}$	0	11.1	g
R21	$C_{10}H_8 + O \rightleftharpoons C_{10}H_7 - 2 + OH$	$6.0 \cdot 10^{13}$	0	11.1	g
R22	$C_{10}H_8 + O \rightleftharpoons C_{10}H_7 - 1O + H$	$6.7 \cdot 10^{12}$	0	2.3	g
R23	$C_{10}H_8 + O \rightleftharpoons C_{10}H_7 - 2O + H$	$6.7 \cdot 10^{12}$	0	2.3	g
R24	$C_{10}H_7 - 2 + H + M \rightleftharpoons C_{10}H_8 + M$ (k_∞)	$2.2 \cdot 10^{14}$	0	0	g
	$C_{10}H_7 - 2 + H + M \rightleftharpoons C_{10}H_8 + M$ (k_0)	$4.1 \cdot 10^{104}$	-24.6	21.5	g
	Troe's broadening factors: $4.6 \cdot 10^{-2} / 3.52 \cdot 10^2 / 6 \cdot 10^4 / 7.6 \cdot 10^3$				g
R25	$C_{10}H_7 - 1 + O_2 \rightleftharpoons C_{10}H_7 - 1O + O$	$1.0 \cdot 10^{13}$	0	3.6	g
R26	$C_{10}H_7 - 2 + O_2 \rightleftharpoons C_{10}H_7 - 2O + O$	$1.0 \cdot 10^{13}$	0	3.6	g
R27	$C_{10}H_7 - 1O \rightleftharpoons C_9H_7 + CO$	$3.6 \cdot 10^{11}$	0	43.9	g
R28	$C_{10}H_7 - 2O \rightleftharpoons C_9H_7 + CO$	$3.6 \cdot 10^{11}$	0	43.9	g

^a rate parameters from [235] with pre exponential factor times by 4

^b by analogy with $C_2H_5 + H = 2CH_3$

^c by analogy with $n-C_3H_7 \rightleftharpoons i-C_3H_7$ [236]

^d QRRK calculations on Kislov and Mebel 2008 [228]

^e by analogy with $n-C_3H_7 \rightleftharpoons i-C_3H_7$ from [236]

^f QRRK calculations on Kislov et al. 2005 [234]

^g by analogy with reactions of benzene combustion (see chapter 4)

Kinetic parameters of reaction R1 have been taken from the work of Lindstedt and Maurice [235] and the pre exponential factor has been increased by a factor 4. This adjustment is necessary to obtain a good naphthalene prediction and can be justified by imprecisions on the predicted cyclopentadienyl radical mole fractions, which have a high influence on the rate of cyclopentadienyl radical self recombination. An adjustment of a factor 4 has equally been proposed by Richter and co-workers, demonstrating that a high uncertainty still surrounds rate parameters of that reaction. Kinetic parameters of the reverse reaction have been determined by analogy with the H atom addition onto ethyl radical, giving $2CH_3$ radicals. Theoretical investigations of reactions R1 and -R1 of table 6.1, together with a fall off analysis are utterly needed in order to model naphthalene formation more accurately. The reaction R2 involves the migration of a hydrogen atom and its rate parameters

have been estimated on the basis of a similar H atom isomerization. Concerning the benzyl + propargyl radicals channel, rate constant of reaction R10 has been deduced from the work of Colket and Seery [187] and rate parameters of the reverse reaction have been taken by analogy with the reaction $C_2H_5 + H \rightleftharpoons 2CH_3$, in the same way as reaction -R1. Kinetic parameters of the reaction R10 have been taken by analogy with another H atom migration reaction. Beside the cyclopentadienyl and the benzyl + propargyl radicals channels, the HACA route, forming naphthalene from acetylene addition on the phenyl radical, has been added using kinetic parameters proposed by Tokmakov and Lin [168] in 2004. A second HACA channel, linking $C_6H_5 + C_2H_2$ to $C_{10}H_9 - 4$ exists but necessitates an acetylene addition onto the C_6H_5CHCH adduct that has been demonstrated by Frenklach and co-workers [99] to be substantially slower than the adduct decomposition into phenylacetylene and H atom. Therefore, this second HACA pathway is not included into our kinetic model.

In 2007, Kislov and Mebel predicted that the conversion of $C_{10}H_9 - 2$ into $C_{10}H_9 - 5$ through $C_{10}H_9 - 3$ formation has a lower activation barrier than through $C_{10}H_9 - 4$ production. Authors equally showed that $C_{10}H_9 - 4$ isomerization into $C_{10}H_9 - 5$ is faster than $C_{10}H_9 - 2$ formation. Therefore, one can expect that the C_5 and the $C_7 + C_3$ pathways will converge into $C_{10}H_9 - 5$, rather than into $C_{10}H_9 - 4$.

Comparison with experimental data

Figure 6.10 compares experimental measurements of naphthalene mole fraction profiles to model predictions. Composition of toluene and benzene flames have been chosen in order to have the same total carbon content in BF18 and TF18, and in BF20 and TF20, respectively. Therefore, the highest maximum mole fraction of naphthalene measured in TF20 (500 ppm), compared to that measured in BF20 (300 ppm), indicates that in similar conditions, toluene flames have a higher propensity for $C_{10}H_8$ formation than benzene flames. This observation suggests that, in similar conditions, toluene flames may produce more soot than

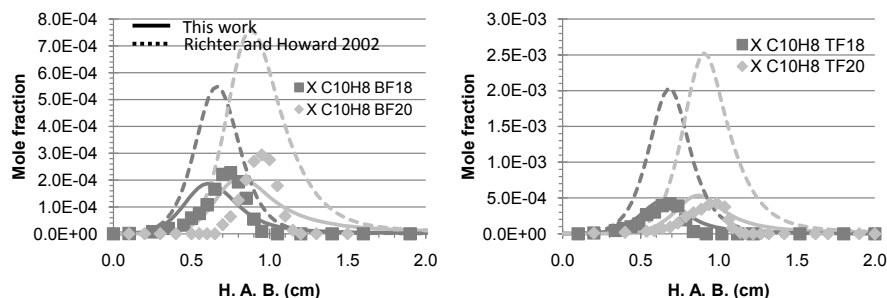


Figure 6.10: experimental and predicted mole fraction profiles of naphthalene ($C_{10}H_8$). Gray scale symbols represent experiments (Δ TF07, $\circ$ TF10, $\square$ TF18, $\diamond$ TF20). Solid and dashed curves stand for predictions of present and Richter and Howard [92] models, respectively.

benzene flames. This assumption will be addressed in the following chapter, devoted to the measurement and to the modeling of soot formation. The developed kinetic model well reproduces naphthalene measurements performed in BF18, BF20, TF18 and TF20. Highest naphthalene levels detected in toluene flames, compared to benzene flames, suggest that its formation depends on the reactant structure and that different pathways should be involved. This hypothesis may be verified by the calculation of relative contributions of each path presented in figure 6.9. Such a calculation shows that in rich benzene flames, 97% of naphthalene formation is achieved through the cyclopentadienyl radical self recombination channel and that only 3% comes from the benzyl + propargyl radicals channel. This prediction is consistent with high cyclopentadiene maximum mole fractions measured in BF18 and BF20, demonstrating that cyclopentadienyl radical could be a key intermediate. Surprisingly, it is found that the HACA mechanism does not participate to naphthalene formation but consumes naphthalene into phenylacetylene. This finding could be explained by the important naphthalene formation through the C_5 route, which yields high $C_{10}H_7 - 1$ formation by H abstraction reactions on naphthalene. This high 1-naphthyl formation forces reactions R14, R13 and R12 to go backward, towards decomposition into phenyl radical and acetylene. This is an important finding that shows that if additional naphthalene formation pathways exist, they will prevent

the HACA mechanism to compete and even force it to go backward, consuming naphthalene.

Our study confirms that the main naphthalene formation channel is different in toluene flames. Indeed, it is found that the benzyl + propargyl radicals pathway is responsible of 60% and 70% of naphthalene formation in TF18 and TF20, respectively. Compared to benzene combustion, the C_5 channel becomes minor and only produces the remaining 40% and 30% of naphthalene. This change in the main $C_{10}H_8$ formation pathway might be explained by the lowest cyclopentadiene mole fractions and the highest benzyl radical levels measured in toluene flames, compared to benzene flames. These changes in maximum mole fractions disadvantage the cyclopentadienyl radical channel and highly promote the benzyl radical route in toluene flames. Our study thus demonstrates that the formation of naphthalene is highly dependent on reactant structure, since the substitution of a hydrogen atom on the benzene ring by a methyl radical leads to a deep modification of the main naphthalene formation route. In the same way as benzene combustion, in toluene flames the HACA mechanism consumes naphthalene rather than producing it.

Concerning naphthalene consumption, rate constants of reactions that might consume it are still uncertain. Consequently, in this work we have postulated that naphthalene reacts similarly to benzene and its reactions with H , O and OH radicals have been determined by analogy. However, contrarily to benzene, positions of CH groups of naphthalene are not all similar and depending on the position where reactions take place, two different isomers can always be formed. 86% of naphthalene consumption is achieved through H abstraction reactions (reactions R16 to R21 of table 6.1), producing 1-naphthyl ($C_{10}H_7 - 1$) and 2-naphthyl ($C_{10}H_7 - 2$) radicals. The 1-naphthyl radical can decompose into phenyl radical and acetylene by the HACA mechanism. However, this channel represents less than 1% of 1 naphthyl consumption and main reaction routes of 1 and 2-naphthyl radicals involve reaction with O_2 producing 1-naphthoxy ($C_{10}H_7 - 1O$) and 2-naphthoxy ($C_{10}H_7 - 2O$) radicals + O atom, through reactions R25 and R26, similarly to the reaction of phenyl

radical with O_2 forming phenoxy radical + O atom. In the same way as phenoxy radical, high temperature reactions of naphthoxy radicals principally consist in ejection of a CO molecule, converting naphthoxy radicals into the indenyl radical (C_9H_7), as depicted at the top of figure 6.9 and in reactions R27 and R28 of table 6.1. Then, this indenyl radical might form indene (C_9H_8) through recombination reactions with H atom, in the same way as cyclopentadienyl radical forms cyclopentadiene.

6.2.3 The indene sub-model

The development of the indene sub-model

In the introduction of this chapter, one mentioned that two main channels can produce indene (C_9H_8). The first involves the reaction between benzyl radical and acetylene and the second consists in the recombination between two cyclopentadienyl radicals. In addition to those pathways, one has shown in the previous section that the $C_{10}H_8$ oxidation equally produces indene in significant levels, bringing the number of indene formation routes to three. Unfortunately, rate parameters of indene formation from benzyl and cyclopentadienyl radicals are still unknown and consequently have to be estimated. The $C_5H_5 + C_5H_5$ channel has been included in the kinetic model thanks to reactions R29 and R30 of table 6.2. Since no rate constant have been proposed for the recombination of two cyclopentadienyl radicals, they have been deduced by analogy with that of two propargyl radicals. The reverse rate constant is taken equal to that of the CC bond breaking in ethane. Then, we have fitted the rate constant of the H atom addition onto $C_{10}H_{10}$ yielding indene and a methyl radical to $2.0 \cdot 10^{13}$, in order to reach the indene maximum mole fraction observed in our benzene flames. Benzene flames have been taken as reference since the indene formation pathway involving benzyl radical and acetylene is supposed to be negligible. Further investigation on the rate constant of reaction R10 are required in order to assess the validity of our rate constant fit. Concerning the benzyl radical recombination with acetylene, we have deduced rate constant pa-

Table 6.2: C_9H_8 production and consumption reactions included into the kinetic model.

Reactions		$k = AT^n e^{-E_a/RT}$			Refs.
		A^a	n	Ea^a	
Reactions of Indene.					
R29	$C_5H_5 + C_5H_5 \rightarrow C_{10}H_{10}$	$2.0 \cdot 10^{13}$	0	0	a
	$C_5H_5 + C_5H_5 \leftarrow C_{10}H_{10}$	$1.1 \cdot 10^{25}$	-8.24	93.6	b
R30	$C_{10}H_{10} + H \rightleftharpoons C_9H_8 + CH_3$	$2.0 \cdot 10^{13}$	0	0	c
R31	$b\text{-}C_7H_7 + C_2H_2 \rightarrow C_9H_8 + H$	$1.71 \cdot 10^{13}$	0	16.9	d
	$b\text{-}C_7H_7 + C_2H_2 \leftarrow C_9H_8 + H$	$3.56 \cdot 10^{13}$	0	28.4	d
R32	$C_9H_8 + M \rightleftharpoons C_9H_7 + H + M$ (k_∞)	$7.7 \cdot 10^{19}$	-1.2	84.5	e
	$C_9H_8 + M \rightleftharpoons C_9H_7 + H + M$ (k_0)	$1.1 \cdot 10^{80}$	-16.8	16.9	e
R33	$C_9H_8 + H \rightleftharpoons C_9H_7 + H_2$	$3 \cdot 10^{14}$	0	6.6	e
R34	$C_9H_8 + O \rightleftharpoons C_9H_7 + OH$	$1.8 \cdot 10^{14}$	0	3.1	e
R35	$C_9H_8 + OH \rightleftharpoons C_9H_7 + H_2O$	$3.4 \cdot 10^9$	1.2	-0.5	e
R36	$C_9H_7 + O \rightarrow C_6H_5CHCH + CO$	$1.0 \cdot 10^{14}$	0	0	[235]

^a Taken equal to propargyl radical recombination calculated by Georgievskii et al. [237]. ^b by analogy with ethane dissociation. ^c Estimated, no rate data available. ^d based on Kislov et al. [227]. ^e by analogy with reactions of cyclopentadiene.

rameters from the theoretical work of Kislov and Mebel in 2007. Further reactions of indene have been introduced by analogy with cyclopentadiene. Rate parameters of O addition on the indenyl radical, forming $C_6H_5CHCH + CO$, come from the work of Lindstedt and Maurice [235].

Comparison with experimental data

Indene was not detected by gas chromatography in this work but our previous MBMS study of BF20 reported a maximum mole fraction of $1.5 \cdot 10^{-4}$ [238] that well compares with the value of $2 \cdot 10^{-4}$ recently reported by Yang and co-workers [95] in a similar flame. A comparative rate constant analysis of reactions included in table 6.2 shows that H atom recombination with the indenyl radical produced from naphthalene oxidation is a minor C_9H_8 formation route and that the $C_5H_5 + C_5H_5$ pathway is responsible of most of indene formation in rich benzene flames. Figure 6.11 shows that indene mole fraction is well predicted in BF20, whereas this observation is evident since rate constant of R30 has been

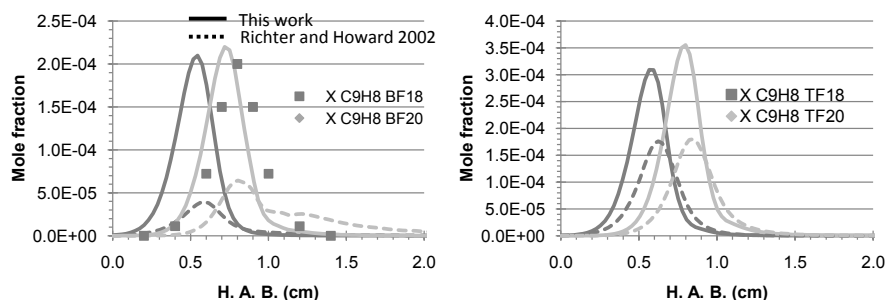


Figure 6.11: experimental and predicted mole fraction profiles of indene (C_9H_8). Gray scale symbols represent experiments (Δ TF07, $\circ$ TF10, $\square$ TF18, $\diamond$ TF20). Solid and dashed curves stand for predictions of present and Richter and Howard [92] models, respectively.

fitted to obtain a good predictive capability. However, this curve fitting is necessary to model soot formation on a firm foundation.

We did not measure indene formation in our toluene flames but Li and co-workers [204] measured a maximum mole fraction of $8/10^{-4}$ in a flame similar to TF18. This indicate that in the same way as naphthalene, toluene flames have a higher propensity for indene formation. The kinetic modeling study also predicts an increase of the indene maximum mole fraction, compared to benzene flames, whereas it underestimates the maximum (see figure 6.11). A comparative reaction rate analysis shows that the increase in naphthalene formation observed in toluene flames comes from the benzyl radical + acetylene channel. This can be compared to the key role played by the benzyl + propargyl radicals route for naphthalene formation in toluene flames, indicating that benzyl radical is of particular importance for the molecular growth.

6.2.4 Styrene and phenylacetylene sub-models

The development of the styrene and phenylacetylene sub-model

Styrene formation can be achieved from several reaction routes, including the recombination of C_4 hydrocarbons, a side chain formation on benzene or the growth of the toluene side chain. The flame chemistry of

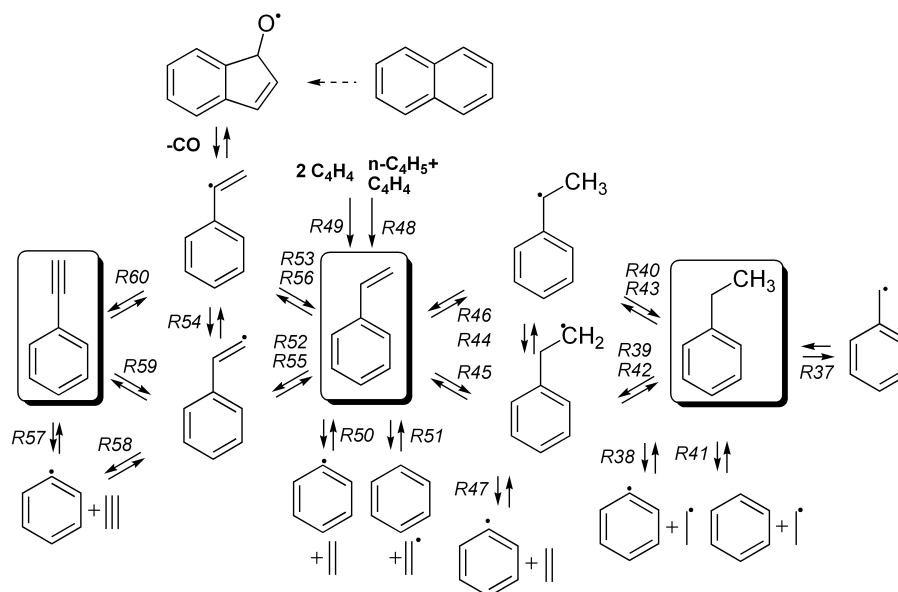


Figure 6.12: reactions pathways considered for ethynylbenzene, styrene and phenylacetylene formation and consumption in the developed kinetic model.

styrene is linked to those of ethylbenzene and phenylacetylene, through its side chain hydrogenation and dehydrogenation, respectively. Figure 6.12 depicts these reaction channels and table 6.3 summarizes rate parameters of corresponding reactions. In the previous section devoted to indene formation, we pointed up that C_6H_5CHCH is a product of indene oxidation in flames. This compound might be involved in C_8H_6 formation through a beta scission reaction, expelling a hydrogen atom from the side chain. In 2004 and 2003, Tokmakov and Lin [168, 239] comprehensively investigated potential energy surfaces of phenyl + acetylene, phenyl + ethylene, benzene + vinyl radical and styrene + H atom reactions. Authors equally calculated rate coefficients of each reaction step that has been included into our kinetic model. In 2003, Ellis and co-workers [214] investigated reactions of hydrogen atom with ethylbenzene and measured the rate parameters that have been used in this work.

Table 6.3: C_8H_{10} , C_8H_8 and C_8H_6 production and consumption reactions included into the kinetic model.

Reactions		$k = AT^n e^{-Ea/RT}$			Refs.
		A^a	n	Ea^a	
Reactions of Ethylbenzene.					
R37	$C_8H_{10}+M \rightleftharpoons b\text{-}C_7H_7+CH_3+M$ (k_∞)	$1.9 \cdot 10^{50}$	-9.72	107.3	a
	$C_8H_{10}+M \rightleftharpoons b\text{-}C_7H_7+CH_3+M$ (k_0)	$3.7 \cdot 10^{65}$	-13.14	101.6	a
	Troe's broadening factors: $3.9 \cdot 10^{-1} / 1.00 \cdot 10^2 / 1.9 \cdot 10^3 / 6 \cdot 10^3$				a
R38	$C_8H_{10}+M \rightleftharpoons C_6H_5+C_2H_5$ (k_∞)	$1.3 \cdot 10^{37}$	-5.84	97.4	a
	$C_8H_{10}+M \rightleftharpoons b\text{-}C_7H_7+CH_3$ (k_0)	$5.6 \cdot 10^{74}$	-15.74	98.7	a
	Troe's broadening factors: $3.1 \cdot 10^{-1} / 5.00 \cdot 10^1 / 3 \cdot 10^3 / 9 \cdot 10^3$				a
R39	$C_6H_5CH_2CH_2+H+M \rightleftharpoons C_8H_{10}+M$ (k_∞)	$1.8 \cdot 10^{13}$	0	0	b
	$C_6H_5CH_2CH_2+H+M \rightleftharpoons C_8H_{10}+M$ (k_0)	$1.5 \cdot 10^{48}$	-9.32	5.8	b
	Troe's broadening factors: $5.0 \cdot 10^{-1} / 1.314 \cdot 10^3 / 1.314 \cdot 10^3 / 5 \cdot 10^4$				b
R40	$C_6H_5CHCH_3+H+M \rightleftharpoons C_8H_{10}+M$ (k_∞)	$2.4 \cdot 10^{13}$	0	0	b
	$C_6H_5CHCH_3+H+M \rightleftharpoons C_8H_{10}+M$ (k_0)	$1.7 \cdot 10^{58}$	-12.1	11.3	b
	Troe's broadening factors: $6.5 \cdot 10^{-1} / 1.213 \cdot 10^3 / 1.213 \cdot 10^3 / 1.337 \cdot 10^4$				b
R41	$C_8H_{10}+H \rightleftharpoons C_2H_5+C_6H_6$	$1.0 \cdot 10^6$	-2	0.9	[214]
R42	$C_8H_{10}+H \rightleftharpoons C_6H_5CH_2CH_2+H_2$	$7.2 \cdot 10^8$	1.5	7.4	[214]
R43	$C_8H_{10}+H \rightleftharpoons C_6H_5CHCH_3+H_2$	$3.3 \cdot 10^7$	2	5.6	[214]
R44	$C_6H_5CH_2CH_2 \rightarrow C_6H_5CHCH_3$	$5.9 \cdot 10^5$	2.07	29.6	[242]
	$C_6H_5CH_2CH_2 \leftarrow C_6H_5CHCH_3$	$2.3 \cdot 10^7$	1.74	44.5	[242]
R45	$C_6H_5CH_2CH_2 \rightleftharpoons C_8H_8+H$	$3.8 \cdot 10^6$	2	32.1	[242]
R46	$C_6H_5CHCH_3 \rightleftharpoons C_8H_8+H$	$3.7 \cdot 10^8$	1.55	44.6	[242]
R47	$C_6H_5+C_2H_4 \rightarrow C_6H_5CH_2CH_2$	$4 \cdot 10^3$	2.6	1.5	[242]
	$C_6H_5+C_2H_4 \leftarrow C_6H_5CH_2CH_2$	$1.7 \cdot 10^{11}$	0.78	38.7	[242]
Reactions of styrene.					
R48	$n\text{-}C_4H_5+C_4H_4 \rightleftharpoons C_8H_8+H$	$3.2 \cdot 10^{11}$	0	0.6	[243]
R49	$C_4H_4+C_4H_4 \rightleftharpoons C_8H_8$	$1.5 \cdot 10^{14}$	0	38	[244]
R50	$C_8H_8+H \rightleftharpoons C_6H_5+C_2H_4$	$1.6 \cdot 10^{37}$	-6.31	31.7	[242]
R51	$C_8H_8+H \rightleftharpoons C_6H_6+C_2H_3$	$5.62 \cdot 10^{24}$	-3	19.8	[242]
R52	$C_8H_8 \rightarrow C_6H_5CHCH+H$	$4.6 \cdot 10^9$	0.81	26.3	[239]
	$C_8H_8 \leftarrow C_6H_5CHCH+H$	$2.0 \cdot 10^{10}$	0.7	27.5	[239]
R53	$C_8H_8 \rightarrow C_6H_5CCH_2+H$	$4.6 \cdot 10^9$	0.81	32	[239]
	$C_8H_8 \leftarrow C_6H_5CCH_2+H$	$2.0 \cdot 10^{10}$	0.7	32	[239]
R54	$C_6H_5CHCH \rightarrow C_6H_5CCH_2$	$4.9 \cdot 10^{12}$	0.45	45.7	[239]
	$C_6H_5CHCH \leftarrow C_6H_5CCH_2$	$6.6 \cdot 10^{13}$	0.14	53	[239]
R55	$C_8H_8+H \rightleftharpoons C_6H_5CHCH+H_2$	$6.6 \cdot 10^5$	2.5	12.2	[235]
R56	$C_8H_8+H \rightleftharpoons C_6H_5CCH_2+H_2$	$3.3 \cdot 10^5$	2.5	12.2	[235]

Continued on next page

Reactions		$k = AT^n e^{-E_a/RT}$			Refs.
		A^a	n	Ea^a	
Reactions of phenylacetylene.					
R57	$C_6H_5 + C_2H_2 \rightleftharpoons C_8H_6 + H$	$2.93 \cdot 10^{12}$	0.18	6.5	[239]
R58	$C_6H_5 + C_2H_2 \rightarrow C_6H_5CHCH$	$2.7 \cdot 10^6$	2.05	3.7	[239]
	$C_6H_5 + C_2H_2 \leftarrow C_6H_5CHCH$	$1.4 \cdot 10^{14}$	0.34	45.7	[239]
R59	$C_6H_5CHCH \rightleftharpoons C_8H_6 + H$	$3.8 \cdot 10^{11}$	0.82	38.91	[239]
R60	$C_6H_5CCH_2 \rightleftharpoons C_8H_6 + H$	$1.2 \cdot 10^{13}$	0.55	42.6	[239]

^a by analogy with propane dissociation [240]

^b by analogy with propane dissociation [241]

In 1984, Cole and co-workers [243] and Lundgard and co-workers [244] suggested that pathways involving C_4 hydrocarbons might participate to styrene formation. These reaction channels, together with their rate parameters, have been included into the model.

Comparison with experimental data

Figure 6.13 compares experimental measurements performed in BF18, BF20, TF18 and TF20 to predictions of the present kinetic model. Experimental phenylacetylene mole fraction in benzene and toluene flames are well reproduced by the kinetic model. The main C_8H_6 formation route in benzene and toluene flames is indenyl radical reaction with O atom, forming CO and the C_6H_5CHCH radical (see reaction R36 in table 6.2), which subsequently gives phenylacetylene + hydrogen atom, as depicted in reaction R59 in table 6.3. Phenylacetylene is mainly consumed through reaction with H atom forming phenyl radical and acetylene (reaction R57). The experimental increase in phenylacetylene mole fraction observed in TF18 and TF20, compared to BF18 and BF20, is not reproduced by the kinetic model. This may be explained by the underestimation of indene mole fraction in TF20, which disadvantages the C_6H_5CHCH and the phenylacetylene productions. Compared to the kinetic model developed by Richter and Howard, this work significantly improves maximum positions of phenylacetylene mole fraction profiles.

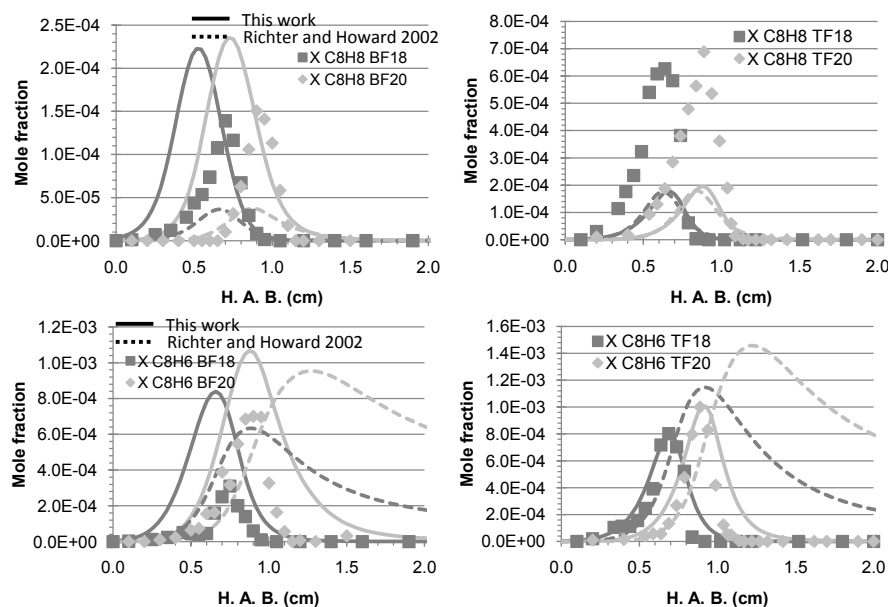


Figure 6.13: Experimental and predicted mole fraction profiles of styrene (C_8H_8) and phenylacetylene (C_8H_6). Gray scale symbols represent experiments ($\triangle$ TF07, $\circ$ TF10, $\square$ TF18, $\diamond$ TF20). Solid and dashed curves stand for predictions of present and Richter and Howard [92] models, respectively.

Concerning styrene formation, our mechanism has a good predictive capability in benzene flames of this work and underestimates mole fraction profiles measured in toluene flames. A comparative reaction rate analysis shows that reaction R51 of table 6.3 proceeds backward and is the main styrene formation route in benzene flames. In toluene flames, benzene concentration are significantly lower and this reaction becomes insignificant. The main channel forming styrene is benzyl radical reaction with methylene triplet radical, followed by the loss of a hydrogen atom. An additional channel for styrene formation from toluene is the reaction with vinyl radical, producing styrene and methyl radical. Unfortunately, rate parameters of this reaction are unknown and their determination should therefore help to better predict styrene formation in toluene flames. It is interesting to note that reaction R37 involving benzyl and methyl radicals recombination forming ethylbenzene is negligi-

ble. Consequently, styrene formation from C_8H_{10} dehydrogenation does not compete with the pathway coming from the indenyl radical.

6.2.5 The biphenyl sub-model

The development of the biphenyl sub-model

Kinetics of the phenyl radical self recombination has been experimentally investigated by Park and Lin [245] in 1997 at high pressure and in the temperature range of 300 - 500 K. Since this rate constant could not be applied to our experimental conditions, we have chosen rate parameters calculated by Richter and Howard [92] in 2002 for the same reaction. The reaction between phenyl radical and benzene giving biphenyl + H atom has also been taken from the work of Richter and Howard. Then, other rate constants have been deduced by analogy with benzene. Table 6.4 summarizes rate parameters used for the $C_{12}H_{10}$ chemistry.

Comparison with experimental data

Figure 6.14 compares experimental measurements of biphenyl performed in benzene and toluene flames to predictions of the kinetic model developed in this work. In benzene flames, maximum mole fractions of

Table 6.4: $C_{12}H_{10}$ production and consumption reactions included into the kinetic model.

Reactions		$k = AT^n e^{-E_a/RT}$			Refs.
		A^a	n	Ea^a	
Reactions of biphenyl.					
R61	$C_6H_5 + C_6H_5 \rightleftharpoons C_{12}H_{10}$	$5.9 \cdot 10^{42}$	-8.83	13.8	[92]
R62	$C_6H_5 + C_6H_6 \rightleftharpoons C_{12}H_{10} + H$	$1.4 \cdot 10^{13}$	0	0.1	[92]
R63	$C_{12}H_{10} + H \rightleftharpoons C_{12}H_9 + H_2$	$3.2 \cdot 10^7$	2.1	15.84	a
R64	$C_{12}H_{10} + OH \rightleftharpoons C_{12}H_9 + H_2O$	$2.11 \cdot 10^{13}$	0	4.57	a
R65	$C_{12}H_9 + H + M \rightleftharpoons C_{12}H_{10} + M$ (k_∞)	$2.20 \cdot 10^{14}$	0	0	a
	$C_{12}H_9 + H + M \rightleftharpoons C_{12}H_{10} + M$ (k_0)	$4.10 \cdot 10^{104}$	-24.6	21.51	a
Troe's broadening factors: $4.6 \cdot 10^{-2} / 3.5 \cdot 10^2 / 6.0 \cdot 10^4 / 7.6 \cdot 10^3$					a

^a by analogy with benzene.

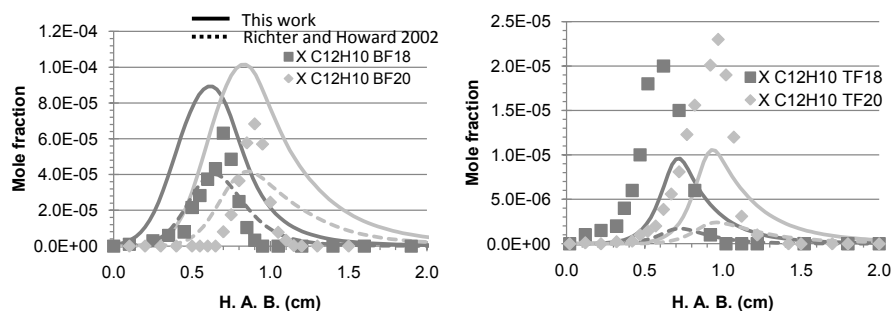


Figure 6.14: Experimental and predicted mole fraction profiles of biphenyl ($C_{12}H_{10}$). Gray scale symbols represent experiments ($\triangle$ TF07, $\circ$ TF10, $\square$ TF18, $\diamond$ TF20). Solid and dashed curves stand for predictions of present and Richter and Howard [92] models, respectively.

biphenyl are well predicted by the kinetic model. The main biphenyl formation pathway is the phenyl radical reaction with benzene (reaction R62). In toluene flames, reaction R61 involving the recombination of two phenyl radicals becomes the main biphenyl formation route, as benzene mole fractions are lower. Biphenyl is principally consumed by reactions R63 and R64 in the $C_{12}H_9$ radical. As discussed in the introduction, this radical may react through a HACA mechanism forming phenanthrene.

6.2.6 Summary on PAH formation and further growth into phenanthrene and pyrene

At this stage, largest hydrocarbons considered in the developed kinetic model are biphenyl, indene and naphthalene. Figure 6.15 summarizes their main formation pathways, which have been comprehensively discussed in previous sections. In flames investigated in this work, naphthalene is predicted to be produced from two major channels, which consist in the recombination either between two cyclopentadienyl radicals or between benzyl and propargyl radicals. The later route is predicted to only contributes to 3% of the naphthalene formation in BF20, whereas it is the main formation channel (71%) in TF20. According to the kinetic modeling analysis, the HACA pathway is not competitive for naphtha-

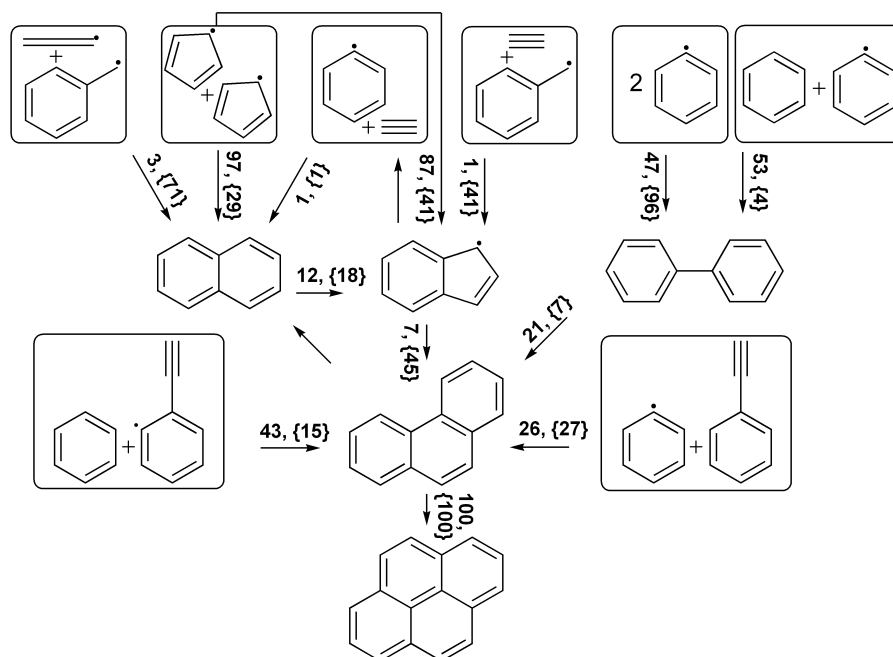


Figure 6.15: summary on PAH formation in BF20 and TF20. Contributions to the formation of chemical species are indicated for BF20 and {TF20}.

lene formation in rich benzene and toluene flames. Indene is predicted to be mainly formed through cyclopentadienyl radical recombination in BF20 (87%), whereas in TF20 a second channel based on acetylene reaction with benzyl radical highly competes (41%) with the cyclopentadienyl radical route (41%). Naphthalene consumption is predicted to produce 12 and 18% of indene in BF20 and TF20, respectively. Finally, the biphenyl formation is achieved through phenyl radical recombination and phenyl radical reaction with benzene in BF20, whereas the recombination route is dominant in TF20.

As described in figure 6.15, naphthalene, indene and biphenyl are starting points of further growth into PAHs having three and four fused aromatic rings, which are respectively called phenanthrene and pyrene. These reactions have been introduced using the kinetic model proposed by D'Anna and co-workers [246]. Whereas pyrene has not been detected by Gas Chromatography due to the detection limit of our apparatus,

its inclusion is necessary to model soot formation, as described in the following chapter.

The reaction pathways considered by D'Anna and co-workers for phenanthrene formation includes (i) the recombination between phenylacetylene (C_8H_6) and phenyl radical or that between C_8H_5 and benzene, (ii) HACA reactions on naphthalene, (iii) HACA reactions on biphenyl and (iv) the cyclopentadienyl radical addition onto the indenyl radical. In rich benzene flames, the first channel accounts for 69 % of phenanthrene formation while routes (iii) and (iv) represent 21 and 7%, respectively. The channel (ii) is not predicted to compete in phenanthrene formation using the mechanism of D'Anna and co-workers. The predicted maximum mole fraction of phenanthrene in BF20 is $1.6 \cdot 10^{-5}$. This prediction is a factor 10 times higher than our measurement. However, we have highlighted that the phenanthrene mole fraction was close to the detection limit of our Gas Chromatograph and that a significant error should therefore be considered. Contrarily to our measurements, that of Yang and co-workers [95] ($1 \cdot 10^{-5}$) achieved in a similar benzene flame well compares with the prediction.

Pyrene formation is considered by D'Anna and co-workers through HACA reactions on phenanthrene and a maximum mole fraction of $7 \cdot 10^{-7}$ is predicted. Compared to the $1 \cdot 10^{-5}$ mole fraction measured by Yang and co-workers, this predicted value seems too low. This discrepancy might come from the uncertainty on the rate parameters of HACA reactions on phenanthrene that are still an important topic of research. In toluene flames, phenanthrene formation is mainly achieved through the reaction between cyclopentadienyl and indenyl radicals (45 %). Compared to the benzene flame, the change in the main reaction route comes from the decrease in benzene and phenyl radical mole fractions. This decrease disadvantages pathways (i) and (iii), whose phenyl radical and benzene are main building blocks. In the same way as in benzene flames, pyrene formation occurs through HACA reactions on phenanthrene.

6.3 Study of naphthalene formation by propyne and cyclopentene seeding into benzene and toluene flames

As discussed in previous sections and summarized in figure 6.15, the main naphthalene formation pathways are based on the recombination between two cyclopentadienyl radicals or propargyl and benzyl radicals. The naphthalene formation rate should consequently depends on mole fractions of cyclopentadienyl and propargyl radicals. In order to verify this hypothesis, precursors of cyclopentadienyl and propargyl radicals have been added into BF20 and TF20 and the resulting flame structures have been measured. The chosen precursors are cyclopentene (C_5H_8) and propyne (C_3H_4) and kinetic sub-models representing cyclopentene and propyne reactions in flames have been developed. The following sections first briefly introduce propyne and cyclopentene combustion by presenting their experimental studies described in the literature and the current understanding of their flame chemistry. Then, experimental measurements are exposed and their comparison to predicted flame structures is presented. The effect of the propyne and the cyclopentene seeding on naphthalene formation is equally discussed.

6.3.1 Introduction

The cyclopentene combustion

To our best knowledge, Lamprecht and co-workers [139] are the first who investigated cyclopentene combustion. In 2000, they measured structures of laminar, premixed and one-dimensional cyclopentene-oxygen-argon flames, burning at 50 mbar and with C/O ratios of 0.6, 0.77 and 0.94, by electron impact MBMS. From their measurements, authors suggested that H abstraction reactions on cyclopentene, forming cyclopentenyl radicals and their subsequent dissociation through pathways presented in section 4.3.9 on page 154 should be main cyclopentene consumption channels. In addition, authors performed a reaction

flow analysis of benzene formation and determined that several reaction pathways should compete, including the recombination of two propargyl radicals and that of cyclopentadienyl and methyl radicals (see sections 4.3.5 on page 136 and 4.3.6 on page 141, respectively). In 2002, Lindstedt and Rizos [247] developed a kinetic model of cyclopentene combustion to predict experimental measurements performed by Lamprecht and co-workers [139]. The model consists in two main cyclopentene consumption pathways: (i) H atom addition onto cyclopentene, followed by the dissociation into $a\text{-}C_3H_5$ (CH_2CHCH_2) + C_2H_4 and (ii) H abstraction reactions on cyclopentene, forming an overall C_5H_7 radical that further decomposes into cyclopentadiene and hydrogen atom. For most of measured species, their model has a good predictive capability and authors demonstrated that both C_3H_3 recombination and cyclopentadienyl and methyl radical recombination routes should form benzene, as previously postulated by Lamprecht and co-workers [139]. Nevertheless, the model overpredicts propargyl radical mole fractions and authors pointed up that it should explain the benzene overestimation equally recorded. Concerning naphthalene formation, Lindstedt and Rizos showed that the overall rate constant proposed by Marinov and co-workers for C_5H_5 recombination ($k = 210^{13} \exp(-2013/T) \text{ cm}^3 \text{ mol}^{-1}$, [170]) leads to naphthalene predictions 35 times higher than the experiment [247]. They consequently proposed a new kinetic description of this pathway, based on a two-steps sequence with estimated rate parameters that better represent naphthalene mole fraction measurements performed by Lamprecht and co-workers [139].

In 2007, Hansen and co-workers reinvestigated the $C/O = 0.77$ cyclopentene flame structure of Lamprecht and co-workers using photoionization molecular beam mass spectrometry and they resolved isomeric composition for most chemical species [248]. In 2008, Kamphus and co-workers [249] compared these new measurements with predictions of models developed by Richter and Howard [92] and by Bakali and co-workers [250]. Since these mechanisms do not include cyclopentene chemistry, they added a set of 11 reactions to each of them, involving (i) H abstraction on the C_5H_8 forming an overall C_5H_7 radical that dis-

sociate into cyclopentadiene and (ii) molecular dehydrogenation of cyclopentene forming cyclopentadiene and H_2 . Therefore, contrarily to the former mechanism of Lindstedt and Rizos [247], the sub-model of Kamphus and co-workers does not consider H atom addition on cyclopentene and involves an additional molecular H_2 elimination process.

Rate parameters of the latter reaction have been investigated by many authors in the past, including [251, 252], and it was found to compete with H abstraction reactions under combustion conditions [249]. Authors performed reaction flux analysis and concluded that this dehydrogenation reaction is the main cyclopentene consumption route in the investigated flame. In addition, they confirmed previous findings of Lindstedt and Rizos by showing that propargyl radicals recombination is a major benzene formation route and that naphthalene is highly overestimated by models considering the C_5H_5 radicals recombination proposed by Marinov and co-workers [170].

The same year, Gueniche and co-workers [138] performed an experimental analysis of a methane flame doped by cyclopentene and developed a detailed mechanism of cyclopentene oxidation. This new sub-model is far more detailed than previous submodels of Lindstedt and Rizos and Kamphus and co-workers, as it takes into account (i) different C_5H_7 radicals formation and their following dissociations, (ii) cyclopentene dehydrogenation into cyclopentadiene and (iii) H atom addition on cyclopentene forming C_5H_9 , which can subsequently dissociates into $a-C_3H_5 + C_2H_4$. This model has an overall good predictive capability and one takes it as a basis for our C_5H_8 and C_5H_7 kinetic sub-model development, as explained in section 4.3.9 on page 154. In addition to the investigation of the naphthalene formation from the recombination of two cyclopentadienyl radicals, the present study should therefore allow to throw some light on consumption pathways of cyclopentene and to study the contribution of the different benzene formation channels.

The propyne combustion

The first comprehensive kinetic modeling study whose we are aware is that of Dagaut and co-workers [253] who developed a detailed kinetic model to predict mole fraction profiles of chemical species measured in perfectly stirred reactors. In 1998, Davis and co-workers [254] studied propyne flame speeds, ignition delays and oxidation in a flow reactor. Authors developed a kinetic model to compare with these measurements and determined that propyne reactions with H atom forming propargyl radicals + H_2 or CH_3CHCH radical, which subsequently decomposes into $CH_3 + C_2H_2$, are major consumption routes. Moreover, authors stressed that propyne isomerization into allene should play a key role in high temperature reactions. Other kinetic models of propyne oxidation have also been developed by Fournet and co-workers [255] and Ranzi and co-workers [256], who have reached the same conclusions concerning main consumption route. To our best knowledge, the influence of propyne addition on naphthalene formation has never been investigated.

6.3.2 Experimental results and discussion

The cyclopentene combustion

The main goal of these measurements is to provide new experimental data to test the predictive capability of the developed model in conditions that should influence naphthalene formation. Consequently, our attention was focused on small hydrocarbons and on naphthalene formation. Mole fraction profiles of main chemical species such as permanent gases of combustion were therefore not measured. Since cyclopentene combustion is a hot topic of the current literature [138, 248, 249], the analysis of a pure cyclopentene-oxygen-argon flame has been performed in order to compare with results previously obtained.

Table 6.5 presents flame parameters of each investigated flame that has been stabilized at 45 mbar on the same apparatus than our ben-

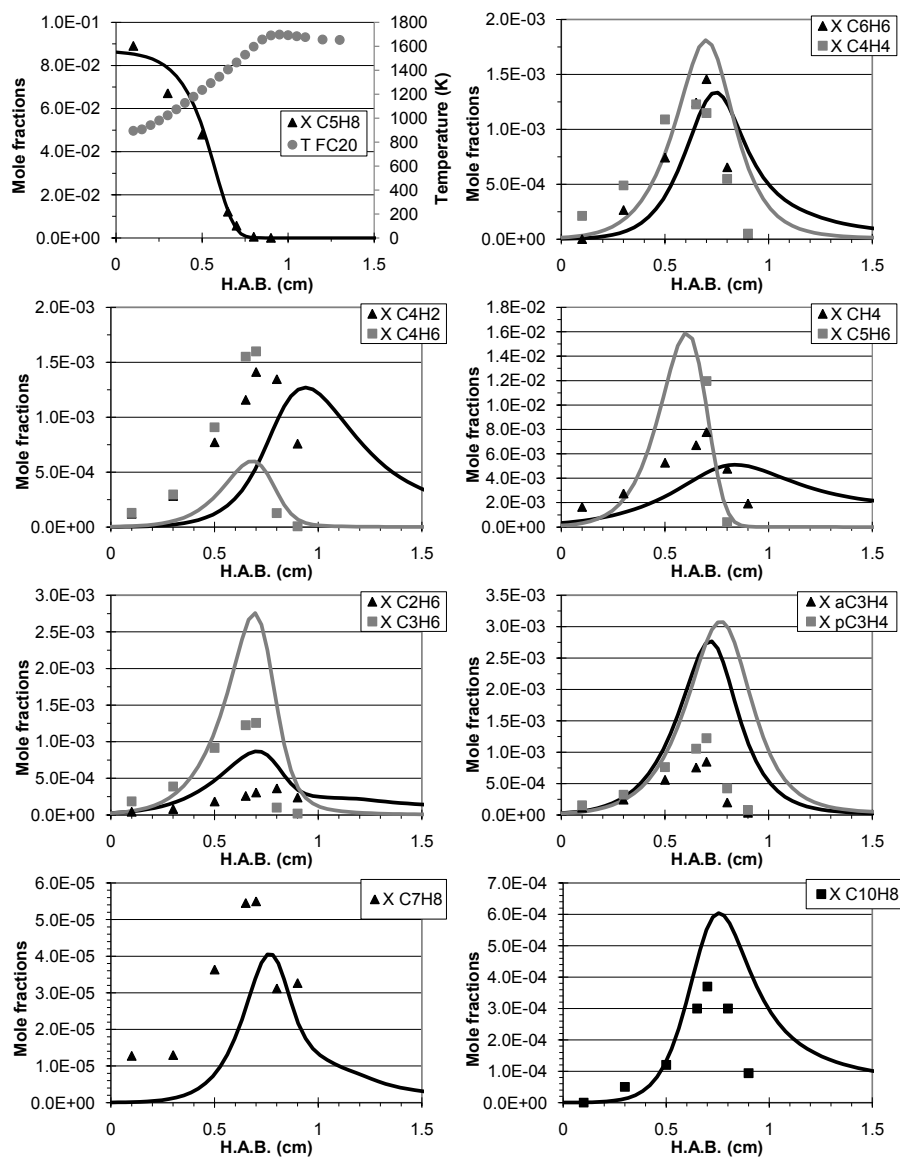


Figure 6.16: Experimental and predicted mole fraction profiles of some key intermediates measured in CF20. Gray scale symbols represent experiments and solid curves in corresponding gray scale stand for predictions of present model.

Table 6.5: Parameters of cyclopentene and propyne flames

<i>Benzene-cyclopentene-oxygen-argon flames :</i>						
Code	ϕ	Mass flux ($\text{g s}^{-1} \text{ cm}^{-2}$)	$\chi_{C_6H_6}$	Fresh gas composition		
				$\chi_{C_5H_8}$	χ_{O_2}	χ_{Ar}
CF20	1.7	$3.38 \cdot 10^{-3}$	0	$8.91 \cdot 10^{-2}$	$3.67 \cdot 10^{-1}$	$5.44 \cdot 10^{-1}$
BCF20	2.0	$3.04 \cdot 10^{-3}$	$8.84 \cdot 10^{-2}$	$3.11 \cdot 10^{-2}$	$4.47 \cdot 10^{-1}$	$4.33 \cdot 10^{-1}$

<i>Toluene-propyne-oxygen-argon flames :</i>						
Code	ϕ	Mass flux ($\text{g s}^{-1} \text{ cm}^{-2}$)	$\chi_{C_7H_8}$	Fresh gas composition		
				$\chi_{C_3H_4}$	χ_{O_2}	χ_{Ar}
TPF21	2.1	$3.15 \cdot 10^{-3}$	$9.89 \cdot 10^{-2}$	$1.11 \cdot 10^{-2}$	$4.45 \cdot 10^{-1}$	$4.45 \cdot 10^{-1}$
TPF22	2.2	$3.15 \cdot 10^{-3}$	$9.89 \cdot 10^{-2}$	$2.22 \cdot 10^{-2}$	$4.45 \cdot 10^{-1}$	$4.34 \cdot 10^{-1}$

zene and toluene flames. The experimental flame structure of the pure cyclopentene-oxygen-argon flame (CF20) is described in figure 6.16. Cyclopentene is fully consumed at 0.75 cm from the burner surface and the maximum flame temperature reaches 1697 K at 0.95 cm. Compared to benzene and toluene flames of this work, cyclopentene combustion forms very high quantities of cyclopentadiene. This observation supports occurrence of a direct dehydrogenation reaction of cyclopentene into cyclopentadiene + H_2 , as discussed previously. Measurements also demonstrate that C_4 , C_3 and C_1 hydrocarbons reach significant mole fractions, suggesting that they might be key intermediates of cyclopentene consumption. This hypothesis is supported the work of Gueniche and co-workers [138] on cyclopentene combustion, which has demonstrated that cyclopentenyl radicals formation and decomposition into $C_3 + C_2$ or $C_4 + C_1$ hydrocarbons can play a significant role in cyclopentene flames. Maximum mole fractions measured for toluene and naphthalene are $5.5 \cdot 10^{-5}$ and $3.9 \cdot 10^{-4}$, respectively. Table 6.6 compares maximum mole fractions measured in the present study with those reported in works of Lamprecht and co-workers [139] and Hansen and co-workers [248]. It appears that discrepancies as high as a factor of 2.25 appears between both previous published works whereas they investigated a flame with an identical cold mixture composition. Authors justified these differences by the presence of fragmentation processes in the electron impact molecular beam mass spectrometry analysis. It is

Table 6.6: Maximum mole fraction measured in CF20.

Species	EI MBMS [139]	UV MBMS [248]	GC - present work
	C/O = 0.77	C/O = 0.77	C/O = 0.65
	$\chi_{Ar} = 25\%$	$\chi_{Ar} = 25\%$	$\chi_{Ar} = 54\%$
CH_4	$2.0 \cdot 10^{-3}$	$4.5 \cdot 10^{-3}$	$8.0 \cdot 10^{-3}$
a- C_3H_4	$3.4 \cdot 10^{-3}$	$1.0 \cdot 10^{-3}$	$8.0 \cdot 10^{-4}$
p- C_3H_4		$2.5 \cdot 10^{-3}$	$1.3 \cdot 10^{-4}$
C_4H_2	$2.3 \cdot 10^{-3}$	$2.8 \cdot 10^{-3}$	$1.4 \cdot 10^{-3}$
C_4H_4	$1.7 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	$1.2 \cdot 10^{-3}$
C_4H_6	$1.2 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	$1.6 \cdot 10^{-3}$
C_5H_6	$1.1 \cdot 10^{-2}$	$1.8 \cdot 10^{-2}$	$1.6 \cdot 10^{-2}$
C_6H_6	$1.8 \cdot 10^{-3}$	$1.3 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$
C_7H_8		$5.0 \cdot 10^{-5}$	$5.5 \cdot 10^{-5}$
$C_{10}H_8$	$2.2 \cdot 10^{-5}$		$3.8 \cdot 10^{-4}$

difficult to compare our measurements with these former works as dilution and C/O ratios are substantially different.

Indeed, in this work CF20 has been stabilized with a dilution ratio of 54% and a C/O ratio of 0.65. However, one can note that maximum mole fractions of our measurements are close to those of previous studies, except for naphthalene which is about 15 times higher than in the work of Lamprecht and co-workers [139]. Unfortunately, Hansen and co-workers [248] did not perform naphthalene measurements in their work of 2007 and this important discrepancy between the present study and that of Lamprecht and co-workers should be addressed in the future. The kinetic sub-model used for the modeling of cyclopentene combustion is detailed in table 6.7, together with references of kinetic parameters for each reaction. It is mainly based on the recent work of Gueniche and co-workers [138] described in a previous section. Predictions of the kinetic model are presented by solid curves in figure 6.16 and comparative reaction rate analyses have been performed to determine main reaction pathways of cyclopentene combustion.

Table 6.7: C_5H_8 consumption reactions included into the kinetic model (see also section 4.3.9).

Reactions		$k = AT^n e^{-Ea/RT}$			Refs.
		A^a	n	Ea^a	
Dehydrogenation reaction.					
R66	$C_5H_8 \rightleftharpoons C_5H_6 + H_2$	$1 \cdot 10^{13}$	0	60.0	[251]
Reactions with H atom.					
R67	$a-C_3H_5 + C_2H_4 \rightleftharpoons C_5H_8 + H$	$1.2 \cdot 10^{10}$	0	11.5	[247]
R68	$C_5H_8 + H \rightleftharpoons C_5H_7(B) + H_2$	$9.0 \cdot 10^6$	2	5	[138]
R69	$C_5H_8 + H \rightleftharpoons C_5H_7(A) + H_2$	$1.1 \cdot 10^5$	2.5	-1.9	[138]
R70	$C_5H_8 + H \rightleftharpoons C_5H_7(C) + H_2$	$8.2 \cdot 10^5$	2	9.8	[138]
Reactions with OH atom.					
R71	$C_5H_8 + OH \rightleftharpoons C_5H_7(B) + H_2O$	$2.6 \cdot 10^6$	2	-0.8	[138]
R72	$C_5H_8 + OH \rightleftharpoons C_5H_7(A) + H_2O$	$2.0 \cdot 10^6$	2	-1.5	[138]
R73	$C_5H_8 + OH \rightleftharpoons C_5H_7(C) + H_2O$	$2.2 \cdot 10^6$	2	1.4	[138]
Reactions with O atom.					
R74	$C_5H_8 + O \rightleftharpoons C_5H_7(B) + OH$	$2.6 \cdot 10^{13}$	2	5.2	[138]
R75	$C_5H_8 + O \rightleftharpoons C_5H_7(A) + OH$	$1.7 \cdot 10^{11}$	0.7	3.2	[138]
R76	$C_5H_8 + O \rightleftharpoons C_5H_7(C) + OH$	$1.2 \cdot 10^{11}$	0.7	7.6	[138]
Reactions of $C_5H_7(A)$.					
R77	$C_5H_7(A) \rightleftharpoons C_5H_6 + H$	$3 \cdot 10^{13}$	0	50.5	[138]
R78	$C_5H_7(A) \rightleftharpoons 1,3-C_5H_7-5-yl$	$1.3 \cdot 10^{13}$	0	35	[138]
R79	$1,3-C_5H_7-3-yl \rightleftharpoons 1,3-C_5H_7-5-yl$	$5 \cdot 10^{13}$	0	37	[138]
R80	$1,4-C_5H_7-5-yl \rightleftharpoons 1,3-C_5H_7-5-yl$	$3.4 \cdot 10^{13}$	0	34.5	[138]
R81	$1,3-C_5H_7-4-yl \rightleftharpoons 1,3-C_5H_7-5-yl$	$2 \cdot 10^{13}$	0	47	[138]
R82	$1,4-C_5H_7-4-yl \rightleftharpoons 1,3-C_5H_7-5-yl$	$1.3 \cdot 10^{13}$	0	44.5	[138]
R83	$1,3-C_5H_7-3-yl \rightleftharpoons CH_3 + C_4H_4$	$3.3 \cdot 10^{12}$	0	31.5	[138]
R84	$1,3-C_5H_7-4-yl \rightleftharpoons p-C_3H_4 + C_2H_3$	$2 \cdot 10^{13}$	0	31	[138]
R85	$1,4-C_5H_7-4-yl \rightleftharpoons a-C_3H_4 + C_2H_3$	$2 \cdot 10^{13}$	0	35.5	[138]
Reactions of $C_5H_7(B)$.					
R86	$C_5H_7(B) \rightleftharpoons C_5H_6 + H$	$6.4 \cdot 10^{13}$	0	34.8	[138]
R87	$C_5H_7(B) \rightleftharpoons C_5H_7(A)$	$2.3 \cdot 10^{11}$	1	44.1	[138]
R88	$C_5H_7(B) \rightleftharpoons 1,4-C_5H_7-5-yl$	$2 \cdot 10^{13}$	0	35.5	[138]
R89	$1,4-C_5H_7-5-yl \rightarrow C_2H_2 + a-C_3H_5$	$4.42 \cdot 10^{12}$	0	16.7	[165]
	$1,4-C_5H_7-5-yl \leftarrow C_2H_2 + a-C_3H_5$	$6.3 \cdot 10^{11}$	0	7.7	[165]

Continued on next page

Reactions		$k = AT^n e^{-E_a/RT}$			Refs.
		A^a	n	Ea^a	
Reactions of $C_5H_7(C)$.					
R90	$C_5H_7(C) \rightleftharpoons C_5H_7(B)$	$6.7 \cdot 10^{12}$	1	49.5	[138]
R91	$C_5H_7(C) \rightleftharpoons 1\text{-}C_5H_7\text{-}5\text{-yl}$	$2 \cdot 10^{13}$	0	33	[138]
R92	$C_5H_7(C) \rightleftharpoons 1,2\text{-}C_5H_7\text{-}5\text{-yl}$	$2 \cdot 10^{13}$	0	31	[138]
R93	$1\text{-}C_5H_7\text{-}5\text{-yl} \rightleftharpoons C_2H_4 + C_3H_3$	$2 \cdot 10^{13}$	0	22.5	[138]
R94	$1,2\text{-}C_5H_7\text{-}5\text{-yl} \rightleftharpoons C_2H_4 + C_3H_3$	$2 \cdot 10^{13}$	0	35.5	[138]

As depicted in figure 6.17, it is found that under conditions of this work three main pathways consume cyclopentene: (i) 62% of cyclopentene undergoes a molecular dehydrogenation reaction forming cyclopentadiene, (ii) 32% reacts with H atom forming a C_5H_9 adduct that subsequently decomposes into $CH_2CHCH_2 + C_2H_4$ and (iii) 6% reacts through H abstraction reactions forming a C_5H_7 radical that is principally decomposed into $C_4H_4 + CH_3$. Qualitatively, the fact that pathways (i), (ii) and (iii) lead to CH_3 , $a-C_3H_5$, C_4H_4 and C_5H_6 intermediate formations agrees with experimental measurements discussed above. Moreover, as shown in figure 6.16, mole fraction profiles of CH_4 , C_4H_4 and C_5H_6 are quantitatively well reproduced by the kinetic model, indicating that paths (i) and (iii) are well described by the mechanism. The significant discrepancy between C_3H_6 measurements and predictions suggests that path (ii) is overestimated by the model. Since 63% of cyclopentene consumption goes through the cyclopentadienyl radical formation, pathways depending on this intermediates should be significantly stimulated. This observation confirms our choice of adding cyclopentene in benzene flames to favor naphthalene formation through the recombination of 2 C_5H_5 radicals.

Before discussing naphthalene formation, we will focus on the first aromatic ring formation in cyclopentene flames. As presented in the previous chapter, benzene formation might occur from a chemical pathway going through the methylcyclopentadiene radical formation. Since this compound can be formed by cyclopentadienyl and methyl radicals recombination, followed by the loss of a hydrogen atom, one can expect

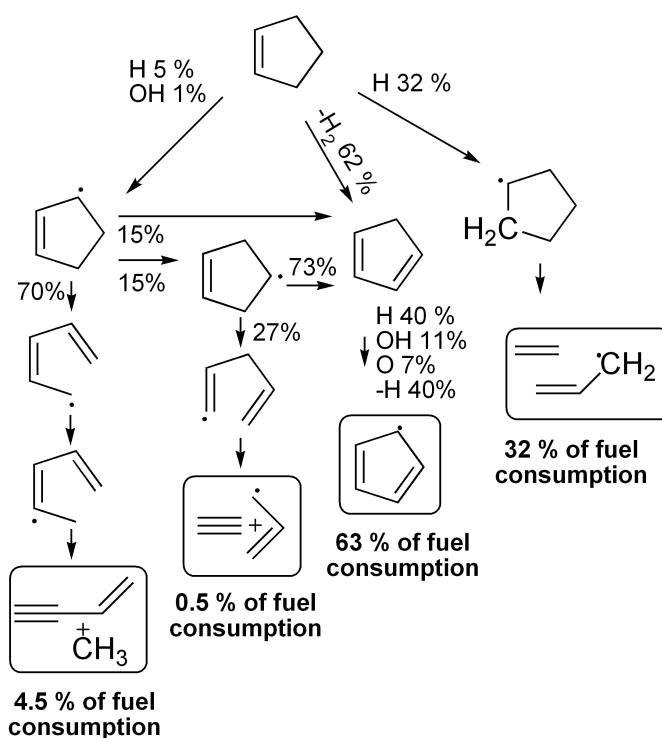


Figure 6.17: Comparative reaction analysis of cyclopentene consumption in the flame investigated in this work.

that this route will play a key role in the cyclopentene flame. This hypothesis has already been made by Lamprecht and co-workers [139] and Kamphus and co-workers [249]. As shown in figure 6.18, a comparative reaction rate analysis reveals that whereas the C_3H_3 recombination channel is the main formation route (77 %), the $C_5H_5 + CH_3$ recombination channel accounts for 23 %. This high contribution confirms that the pathway involving the methylcyclopentadiene radical intermediate is an important benzene formation route. Figure 6.16 shows that the present kinetic model has a good predictive capability of the benzene mole fraction profile.

Concerning naphthalene, an experimental maximum mole fraction of $3.8 \cdot 10^{-4}$ has been measured in CF20. As mentioned previously, this value is about 15 times larger than that measured by Lamprecht and co-workers using MBMS in a flame with a close composition (see table

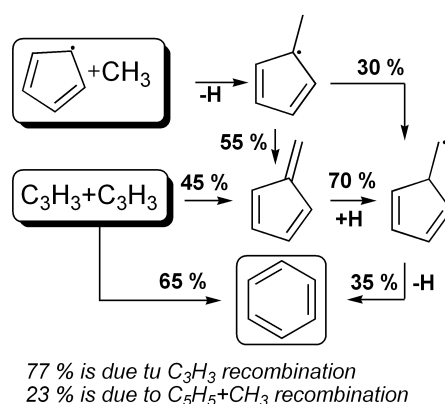


Figure 6.18: Comparative reaction analysis of benzene formation in CF20.

6.6). Therefore, no definitive conclusion about naphthalene formation in cyclopentene flames can be drawn in this work and further experiments devoted to $C_{10}H_8$ measurements are necessary. In 2002 and 2008, Lindstedt and Rizos [247] and Kamphus and co-workers [249] developed a kinetic model for cyclopentene combustion and compared their naphthalene predictions to measurements of Lamprecht and co-workers. They stressed that the C_5H_5 recombination pathway was the main $C_{10}H_8$ formation route but that it overestimates naphthalene formation by a factor close to 35. Even if our naphthalene measurements are higher than those of Lamprecht and co-workers, it is found that our prediction overestimates $C_{10}H_8$ maximum mole fraction by a factor close to 2. Compared to Kamphus and co-workers, our predictions only overestimates Lamprecht and co-workers measurements by a factor of 10. Therefore, our study improves naphthalene predictions in cyclopentene flames, whereas it equally confirms previous observations stressing that kinetics of the C_5H_5 channel might be overestimated in current kinetic models. However, the C_5H_5 concentration in cyclopentene flames is highly sensitive to consumption reactions of cyclopentene, which are still not well understood. Therefore, the observed overestimation might comes from overprediction of the C_5H_5 mole fraction, rather than from kinetic parameters of the C_5H_5 recombination channel.

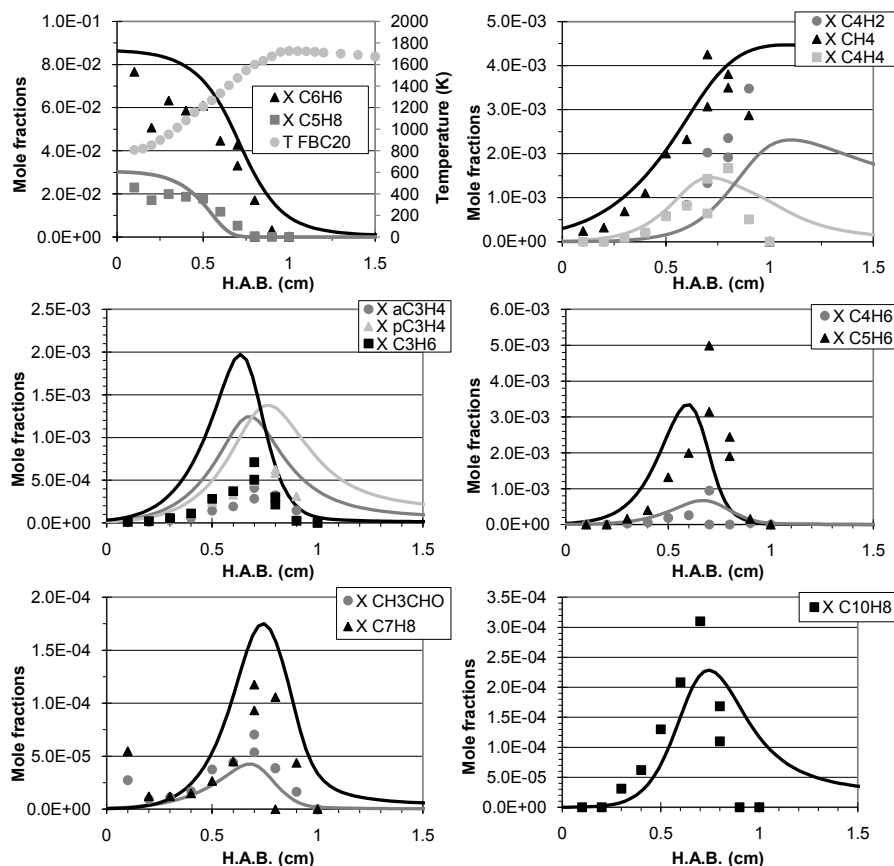


Figure 6.19: Experimental and predicted mole fraction profiles of some key intermediates measured in BCF20. Gray scale symbols represent experiments and solid curves in corresponding gray scale stand for predictions of present model.

In addition to the cyclopentene-oxygen-argon flame, predictions of the kinetic model have been compared to a benzene-cyclopentene-oxygen-argon flame, in order to assess the influence of C_5H_5 precursor addition in BF20. Experimental measurements and predictions obtained by the current model are depicted into figure 6.19. Main differences between the pure BF20 flame and the one seeded with cyclopentene (BCF20) is the increase in cyclopentadiene, methane, vinylacetylene and C_3H_6 maximum mole fractions. This observation agrees with that performed in the cyclopentene-oxygen-argon flame and once again demonstrates

that main cyclopentene consumption routes should correspond to those presented in figure 6.17. Experimentally, the impact of cyclopentene seeding on naphthalene formation is negligible as its maximum mole fraction is similar to that measured in the pure benzene flame. Compared to BF20, the kinetic model predicts a slight increase of the naphthalene mole fraction, whereas the prediction remains close to the experiment 6.19. The predicted increase comes from that in cyclopentadienyl radicals mole fraction. In BCF20, 22% of cyclopentadienyl radical is produced from cyclopentadiene, directly formed through cyclopentene dehydrogenation. The remaining 78% of C_5H_6 formation comes from the phenoxy radical decomposition. This modification in C_5H_5 production channels leads to an increase of 10% in its maximum mole fraction that produces a 12.5% increase in the predicted naphthalene maximum mole fraction. This predicted increase, which is not experimentally reproduced, and the overestimation of the naphthalene maximum mole fraction in CF20 suggest that the C_5H_5 channel might be overestimated in our kinetic model.

However, in benzene flames the benzyl + propargyl pathway and the HACA route could not explain alone levels of naphthalene that have been measured. Therefore, if the C_5H_5 channel is overestimated, additional naphthalene formation routes should exist or the rate of the HACA pathway and the benzyl + propargyl route are underestimated. Recently, Lories and co-workers proposed that the HACA route forming naphthalene might be underestimated since they identified new transition states that are lower in energy. This suggestion should be further addressed to better predict naphthalene formation in benzene and cyclopentene flames. Finally, consumption channels of cyclopentene are still surrounded by a large uncertainty and errors on the C_5H_5 mole fraction profiles could not be rejected. Indeed, naphthalene formation is highly sensitive to the molecular dehydrogenation of cyclopentene forming C_5H_6 , which subsequently gives C_5H_5 , and new measurements of the rate constant of this reaction, at pressure and temperatures corresponding to our flame conditions are necessary.

The propyne combustion

Beside the seeding of benzene flames by cyclopentene, the effect of propyne addition to toluene-oxygen-argon flames has equally been investigated. Since propyne oxidation and combustion has been largely investigated for many years, a pure propyne-oxygen-argon flame has not been analyzed. Contrarily to cyclopentene, we did not compensate the additive introduction by a decrease of the main fuel concentration and the equivalence ratios of toluene-propyne-oxygen-argon flames are therefore different, as depicted in table 6.5.

Figure 6.20 shows that propyne addition to a rich toluene flame increases maximum mole fractions of allene, methane, vinylacetylene and benzene. However, maximum mole fraction of cyclopentadiene is not highly affected by the propyne addition. The kinetic model well reproduces mole fraction variations experimentally recorded for these intermediate compounds. A comparative reaction rate analysis shows that reaction of propyne with an H atom, forming a C_3H_5 adduct that subsequently decomposes into acetylene and methyl radical, is the main propyne consumption route. This explains the important methane increase in TPF21 and TPF22, compared to TF20.

Indeed, this reaction only forms 7% of methyl radical in TF20 whereas it respectively produces 13 and 18% in TPF21 and TPF22. The increase in vinylacetylene maximum mole fraction is mainly caused by the decrease in the contribution of the H abstraction reactions by OH radical at higher equivalence ratios. Concerning cyclopentadiene, the decrease predicted by the kinetic model principally comes from the lower flame temperatures of TPF21 and TPF22, compared to TF20. Indeed, they decrease the contribution of the benzyl radical decomposition into fulvenallene, which subsequently produces cyclopentadienyl radical and acetylene by reaction with a hydrogen atom. Concerning benzene, the observed increase of its maximum mole fraction is mainly due to the stimulation of the propargyl radical recombination, whose formation is favored by H abstraction reactions on propyne. Indeed, the maximum

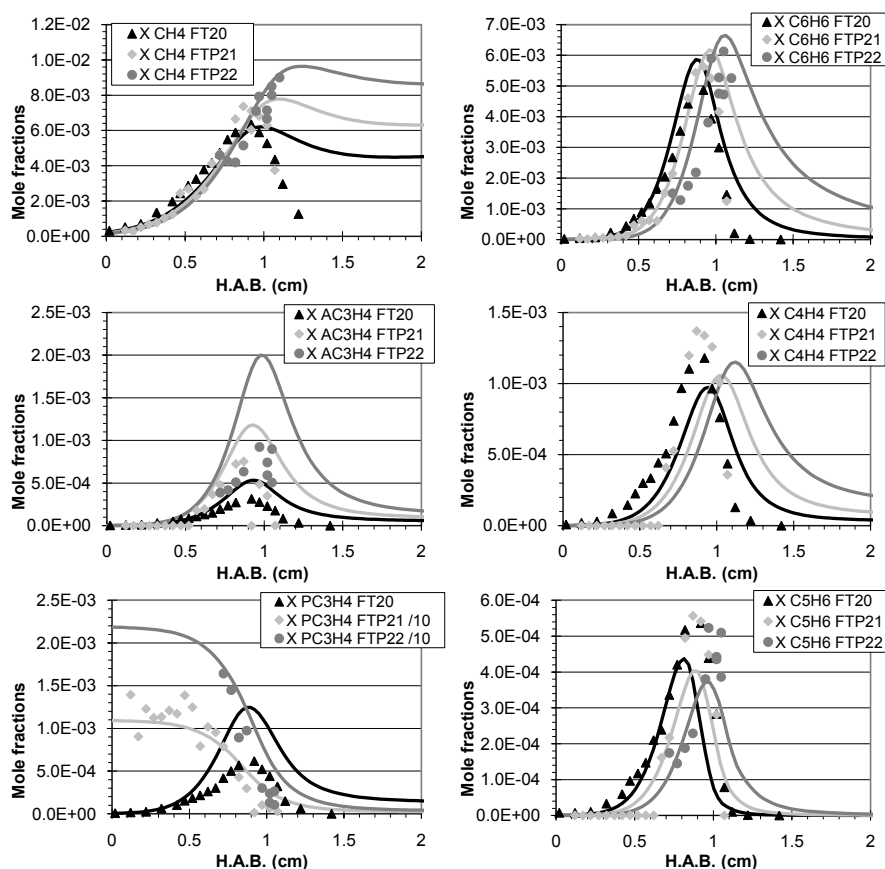


Figure 6.20: Experimental and predicted mole fraction profiles of some key intermediates measured in TF20, TPF21 and TPF22. Gray scale symbols represent experiments and solid curves in corresponding gray scale stand for predictions of present model.

mole fraction of C_3H_3 increases by 8% in TPF22 and in TPF21, compared to TPF21 and TF20, respectively.

Concerning naphthalene formation, figure 6.21 shows that its maximum mole fraction increases by 8 and 9 % in TPF21 and TPF22, respectively compared to TF20 and TPF21. These increases are qualitatively well predicted by the kinetic model but quantitatively slightly overestimated. Indeed, the kinetic modeling predicts increases of 14 and 21%, compared to experimental values of 8 and 9 %. A comparative reaction rate analysis has revealed that the benzyl + propargyl radicals chan-

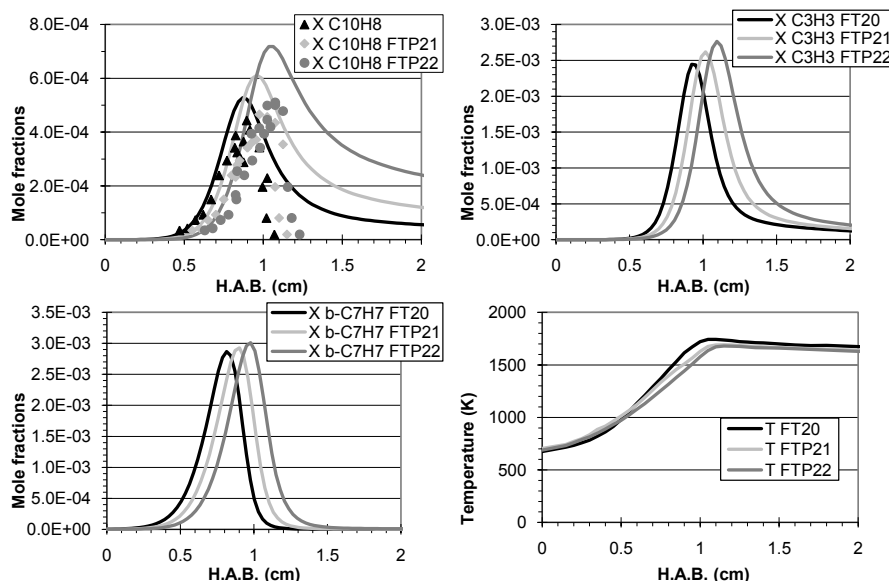


Figure 6.21: Experimental and predicted mole fraction profiles of some key intermediates measured in TF20, TPF21 and TPF22. Gray scale symbols represent experiments and solid curves in corresponding gray scale stand for predictions of present model.

nel is stimulated by the propyne addition as it increases the propargyl mole fraction, as depicted in figure 6.21. This observation confirms the assumption that the benzyl + propargyl radical reaction is a major naphthalene formation route in toluene flames. The overestimation of the naphthalene increase by the kinetic model may come from uncertainties in the C_3H_3/C_3H_4 sub-model, which might overestimate the propargyl radical mole fraction.

6.4 Conclusions

In this chapter the state of the art on molecular growth towards PAH formation in hydrocarbon flames has been presented. Three main pathways are thought to compete in naphthalene formation. The first is called the HACA pathway and is based on the addition of six membered rings through H abstraction and acetylene addition reactions. The second is

named the cyclopentadienyl radical pathway and involves the recombination of two C_5H_5 radicals, forming a $C_{10}H_{10}$ intermediate that subsequently rearranges into naphthalene and two hydrogen atoms. The third route is the benzyl + propargyl pathway, which equally forms a $C_{10}H_{10}$ intermediate that rearranges into naphthalene and two hydrogen atoms. Naphthalene can further grow by HACA reactions into phenanthrene, which can in turn produce pyrene or larger PAHs through HACA reactions. The recombination of phenyl radicals has equally been proposed as an important PAH formation channel. It produces biphenyl, which can subsequently react by HACA reactions, forming phenanthrene.

All these pathways were introduced into the developed kinetic model in order to predict their mole fractions profiles in rich hydrocarbon flames investigated in this work. The three channels suspected to form naphthalene were found to share common intermediates and were included as detailed mechanisms in the present model. It is found that the recombination of cyclopentadienyl radicals is responsible for the majority of naphthalene production in rich benzene flames and that the benzyl + propargyl pathway becomes the main channel in rich toluene flames, competing with C_5H_5 recombination. Naphthalene formation through the HACA pathway is negligible in all investigated flames. Naphthalene is predicted to be consumed by H abstraction reactions, forming 1 and 2-methylnaphthalene isomers. These radicals are mainly consumed in the same way as benzene, forming the indenyl radical. The latter principally reacts with either an O atom, forming the C_6H_5CHCH radical, or with a C_5H_5 radical, producing phenanthrene through a mechanism similar to that of two C_5H_5 recombination forming naphthalene and 2 hydrogen atoms. As suggested in the literature, biphenyl is formed through the recombination of two phenyl radicals and is involved in phenanthrene formation through HACA reactions. Since phenyl radical mole fraction is higher in benzene flame than in toluene flames, this phenanthrene formation pathway is principally active in benzene flames.

Finally, the dependence of naphthalene formation channels on cyclopentadienyl radicals and propargyl radicals has been verified by seeding benzene and toluene flames with cyclopentene and propyne, respectively.

Cyclopentene and propyne are respectively precursors of cyclopentadienyl and propargyl radicals and their addition into benzene and toluene flames were suspected to increase naphthalene mole fractions. A kinetic model has been developed for cyclopentene combustion that was not considered in the model presented in previous chapters. As the flame chemistry of cyclopentene is still not well understood, a pure cyclopentene flame has been experimentally and numerically investigated. The developed model has a good predictive capability in pure cyclopentene and seeded flames but slightly overestimates naphthalene mole fraction. Similar observations were previously made in the literature and indicate that kinetic parameters of the C_5H_5 channel may be overestimated in current models. However, rate parameters of many reactions of the cyclopentene consumption are still assumed and the predicted C_5H_5 mole fraction profile is therefore surrounded by a large uncertainty. Consequently, this study shows that the C_5H_5 channel may not be so competitive than generally considered and that further works on cyclopentene combustion are necessary to throw light on cyclopentene combustion and naphthalene formation. Concerning propyne addition into toluene flames, the experiment showed that naphthalene mole fraction slightly increases compared to pure toluene flames. The kinetic modeling study revealed that this increase is due to the stimulation of the benzyl + propargyl channel, confirming its key role in naphthalene formation in rich toluene flames.

The kinetic model developed in this chapter for the formation of first PAHs will be completed in the following chapter by a soot formation mechanism, in order to predict soot concentration in burnt gases of rich hydrocarbon flames.

Molecular growth: soot formation

7.1 Introduction

At the end of their flame fronts, rich benzene and toluene flames of this work depict a highly luminous region, where carbonaceous particles are formed. Those are characterized by a high C/H ratio and generally referred to as soot. These fine particles can be formed in engines or in several industrial processes involving combustion. Soot may absorb carcinogenic PAHs, whose emission into the atmosphere may pose a health hazard, as demonstrated in 1993 by Dockery and co-workers [257], who showed that fine particle air pollution contributes to excess mortality in six cities of the United States. In addition, soot can be compared to a black body and may therefore contribute to atmospheric solar heating, as suggested by Ramanathan and co-workers [10], who showed that brown clouds containing soot may contribute as much as the recent increase in anthropogenic greenhouse gases to lower atmospheric warming trends in Asia. Beside atmospheric warming, Xu and co-workers [11] have recently suggested that soot deposit on Tibetan glaciers may also be a significant contributing factor to their observed rapid retreat. Finally, soot may also cause technical damages in the industry, such as coating of combustion chambers or damaging of gas turbines in power plants. Soot formation in flames has therefore several disadvantages and is generally avoided. However, its formation may be necessary in certain

industrial processes. For example, furnaces of the glass industry require a high soot concentration in order to significantly increase the radiative heat transfer of flames, allowing to reach a high furnace temperatures. Indeed, rich hydrocarbon flames have a high luminosity, which is due to carbon particles that radiate strongly at the high combustion gas temperature. The solid phase cloud has a very high emissivity, compared to a pure gaseous system, as it can approach the black-body conditions. Beside industrial furnaces, soot formation is also used for fullerene synthesis [258], as these carbon containing compounds are byproducts of reactions leading to soot production. Since depending on the considered setup, soot formation has to be either avoided or maximized, it is very important to understand chemical pathways that control its production in hydrocarbon flames. Such a comprehension can be reached by developing kinetic models able to reproduce experimental evidences. The following sections first expose the current understanding of the soot formation process. Then, some available models of soot formation are presented and the application of two detailed kinetic models to rich benzene and toluene flames of this work is finally discussed.

7.2 The current understanding of soot formation

The study of soot formation in hydrocarbon flames is a central theme of research for many years. In the present work, this vast literature will not be presented in much details, as several review articles have been recently written [8, 259, 260]. However, one will briefly expose the consensus that has been reached by the scientific community concerning the general process of soot formation.

Basically, it is thought to proceed through two different steps. The first is called the **nucleation of soot particles** and consists in the formation of small particle-like structures that have molecular masses between 500 and 2000 uma. As depicted in figure 7.1, this step represents the transition between gas-phase species to solid particles. Nowadays, this

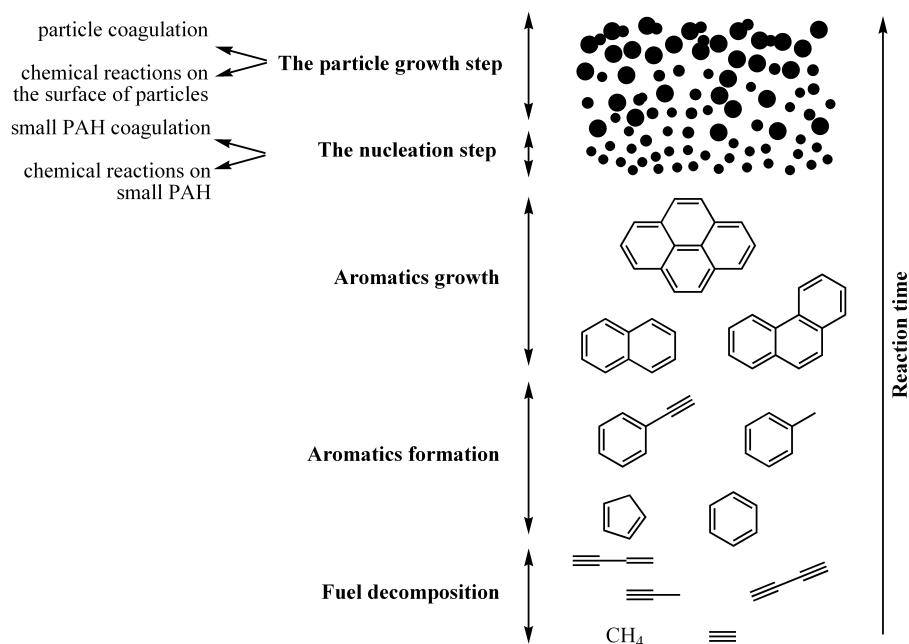


Figure 7.1: scheme of soot formation in hydrocarbon flames [261]

step is probably the least understood part of the soot formation process. Initially, the chemical growth mechanisms were thought to be the only responsible of the nucleation phenomenon. However, it has been shown that this chemical growth alone is not sufficient to explain the time scale of soot inception phenomena and underpredicts particle size. Therefore, it has been proposed that a physical process, which can take place simultaneously, should participate to soot particle nucleation: the coagulation of PAHs. Once PAH have reached a sufficient size, they are thought to form PAH dimers by collision. Then, these PAH dimers may collide with other PAHs, forming PAH trimers or with other dimers forming PAH tetramers, and so on, all while individual PAH species keep increasing in size via molecular chemical growth reactions. Nowadays, authors developing kinetic models of soot formation consider that pyrene dimerization could be the soot nucleation step, whereas many uncertainties still surround this subject. Moreover, the collision efficiency of reactions forming PAH dimers are still uncertain. In summary, soot nucleation is currently thought to proceed through two different phenomena occur-

ring simultaneously: PAH coagulation (physical) and molecular growth (chemical). Soot nucleation determines the density of soot nuclei that will further growth into mature soot.

The second step of soot formation is the **growth of soot particles**. The surface of soot particles may growth by chemical reactions involving compounds available in the surrounding gas phase. Several studies have shown that acetylene is the main co-reactant of PAH surface growth and these observations are consistent with high acetylene concentrations that persist in burnt gases of flames investigated in this work. Simultaneously to surface growth reactions, oxidation of soot particles occurs and tends to decrease their size. All reactions taking place on soot particles are thought to proceed similarly to those occurring on PAH molecules. This assumption has provided a way to describe the rate of surface growth and oxidation in terms of elementary chemical reactions. The surface of soot particles is assumed to look like a PAH edge and thus presents various reacting sites including zig-zag, armchair, free-edge or bay that can be activated by an H abstraction reaction on a CH group. Once activated, the surface radical can react through the HACA mechanism, forming structures that depend on the kind of reaction site involved. Therefore, it is possible to develop stochastic models that are able to predict the structure of growing soot particles, by recording the sequence of sites on its outer edge. The development of such models is currently a hot topic of kinetic modeling of soot formation in flames [262, 263]. The surface growth of soot particles influences soot concentration, but does not change the soot particle density. Similarly to the nucleation step, the chemical growth of soot occurs simultaneously to the particle coagulation phenomenon. It is a physical process that allows soot particles to readily increase their diameter by collision between each other.

In summary, soot formation occurs through two different steps being the nucleation and the growth of soot particles. These two steps involve chemical (the growth of PAH and soot particles by chemical reactions) and physical (the coagulation of PAH and soot particles) phenomenons. The two steps of soot production should be included in any detailed kinetic models describing soot formation.

7.3 Available models of soot formation

Since the industrial control of soot formation in flames is of particular importance, many researchers have tried to model carbonaceous particle formation in combustion processes. These models can be divided into two main categories. The first gathers models that predict soot yield based on one or several empirical parameters, such as the equivalence ratio of the flame, the temperature or the dilution. The second category consists of models that are not based on empirical relations, but on the detailed kinetic modeling of flame structures described in previous chapters.

7.3.1 Empirical models

Many authors have measured the critical equivalence ratio (ϕ_c) at which the onset of some yellow flame luminosity is observed, in order to determine a general fuel sooting tendency. Fuels that exhibit high ϕ_c have low tendency to form soot. It has been shown that sooting tendency does not depend on fuel structure but on its C/H ratio and its number of C atoms [264]. Authors showed that for a similar C/H ratio and temperature, sooting tendency increases with the total C atom number in the fuel and that molecules with similar C atom numbers and C/H ratios have identical sooting tendencies. Moreover, authors showed that in premixed flames, at a constant temperature, the logarithm of this critical sooting equivalence ratio linearly decreases with the number of CC bonds in hydrocarbon fuels, with a double and a triple CC bond counting for two and three CC bonds, respectively. This correlation may be explained by the fact that the CC bond number is an indicator of the total C carbon number and C/H ratio. One should note that according to these observations, benzene has a lower sooting tendency than toluene, resulting in a higher sooting equivalence ratio for benzene, compared to toluene.

In diffusion flames, the sooting tendency of a hydrocarbon is traditionally characterized by the smoke height H , which is the height of that

hydrocarbon jet flames at the smoke point. These smoke heights measured in a particular setup may be converted into setup-independent threshold sooting index (TSI), by the following equation:

$$TSI = A \times \frac{MW_i}{H} + B \quad (7.1)$$

In this equation, MW_i is the molecular weight of the investigated hydrocarbon i and A and B are apparatus specific constants, chosen so that $TSI_{\text{ethane}} = 0$ and $TSI_{\text{naphthalene}} = 100$. These TSI have been measured by McEnally and Pfefferle [265] for about 100 hydrocarbons, and a quantitative relationship between TSI and molecular structure has been derived, allowing to predict TSIs for some other hydrocarbons. Since the H parameter depends inversely on sooting tendency, it is small and difficult to measure for heavily sooting hydrocarbons, such as aromatics.

Consequently, McEnally and Pfefferle recently proposed a new measure of sooting tendency: the maximum soot volume fraction $f_{v,max}$, measured on the centerline of a co-flow and non-premixed flame of methane/air, whose fuel is doped with 400 ppm of the test hydrocarbon. Similarly to smoke points, these soot volume fractions can be converted into apparatus-independent yield sooting indexes (YSI) by the equation:

$$YSI = C \times f_{v,max} + D \quad (7.2)$$

In this equation, C and D are apparatus-specific parameters, chosen so that $YSI_{\text{benzene}} = 30$ and $YSI_{\text{1,2-dihydronaphthalene}} = 100$. According to measurements performed by McEnally and Pfefferle, toluene has an YSI of 43.5, compared to 30 for benzene. Compared to benzene, this higher toluene propensity for soot formation is coherent with the finding of Takahashi and Glassmann [264] discussed above. However, authors showed that compounds having similar C/H ratios and identical total C atom number may have highly different YSI, demonstrating that the fuel structure may play a role in soot formation.

7.3.2 Detailed models: the sectional approach

Beside empirical models that determine the general trend of sooting in hydrocarbons, some authors have developed detailed kinetic models that are able to predict soot concentration in hydrocarbon flames, based on their predicted flame structures. Until now two major concepts have been applied: the method of moments, essentially developed by Frenklach and co-workers [266, 267] and the sectional approach developed by Howard and co-workers [268, 269] and D’Anna and Kent [270]. The model proposed by Frenklach and co-workers consists in 2 sub routines: (i) a kinetic model of 531 reactions for 99 chemical species, allowing the calculation of soot precursors mole fraction profiles and (ii) a mathematical model that post processes mole fraction profiles of soot precursors in order to compute the soot volume fraction. This model will not be presented here since it cannot be integrated directly into the software used to predict flame structures investigated in this work. The modification of the Cosilab code for integration of the Frenklach and co-workers model might be the subject of a future work, devoted to kinetic modeling of soot formation in flames.

In this work, the sectional approach used by Richter and co-workers [269] and D’Anna and Kent [270] is preferred, as it is fully integrable into Cosilab. Moreover, the work of Richter and co-workers is focused on a laminar, premixed and one-dimensional benzene-oxygen-argon flame, burning at low pressure, and is therefore well adapted to aromatic flames investigated in the present work. Consequently, the sectional approach will be discussed in more details hereafter.

Contrarily to the method of moments proposed by Frenklach and co-workers [266], the sectional approach gathers gas-phase and aerosol chemistry into an unique kinetic model, which is written in the common form $A + B \rightarrow C + D$, already used in this work. Models of Richter and co-workers [269] and D’Anna and Kent [270] are available in the Chemkin format, which may be imported into the Cosilab software after some adaptations that will be presented below. These models respectively consist of 295 species for 6654 reactions and 90 species for 1901 re-

actions. Chemical reactions of these models are divided into 2 main sets that consist of (i) a mechanism that describes reactions of chemical species present into the gas-phase and (ii) a mechanism devoted to particle nucleation and growth. The important reaction number of the model developed by Richter and Howard [269] is due to the detailed description of formation of several large PAHs until corranulene ($C_{20}H_{10}$). Particle nucleation is then included by considering PAH dimerization and growth by the HACA mechanism. However, most of kinetic parameters of these large PAH reactions are deduced by analogy, as they are still unknown. Consequently, a very large uncertainty still surrounds formation of PAHs as large as those included into their kinetic model. D'Anna and Kent [270] have limited PAHs of their kinetic model to pyrene ($C_{16}H_{10}$), whose rate constants of formation channels are better known. The exclusion of pathways leading to larger PAH formation explains the smallest reaction number of their kinetic model. The nucleation process is included in the same way as in the work Richter and co-workers, as described hereafter.

In 2006 Wen and co-workers [271] have developed a hybrid kinetic model for soot formation. It consists of a sectional approach for the modeling of soot nuclei formation, combined with an advanced aerosol dynamic model for the growth of soot particles. In this work we only focus on the addition of a soot formation model that is compatible with the chemical model described in previous chapters. Therefore, only the sectional models developed by Richter and co-workers [269] and D'Anna and Kent [270] will be considered. However, the addition of comprehensive models of Frenklach and co-workers [266,267] and Wen and co-workers [271] to our gas phase mechanism may be the subject of future works.

The nucleation process

As the number of mass isomers increases significantly with mass of hydrocarbons, it is practically impossible to write a comprehensive model that includes reactions of all hydrocarbon species involved in the soot

formation. The idea proposed by Richter and co-workers is to describe nuclei formation and their further growth into larger soot particles by using reactions between classes of hydrocarbons, covering certain mass ranges and having mean properties, rather than considering reactions of all possible intermediates. These classes of molecules are called BINs and their characteristics are depicted in table 7.1, for the model proposed by Richter and co-workers [269]. They are 20 BINs and 20 corresponding radicals, which cover the mass range 201 to 2.1×10^8 amu and have a mean diameter σ that spreads from 0.85 nm to 68 nm. For each BIN compound, this mean diameter is calculated by considering a spherical carbonaceous particle, having a density of 1.8 g cm^{-3} .

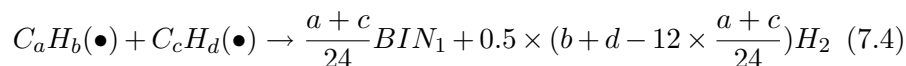
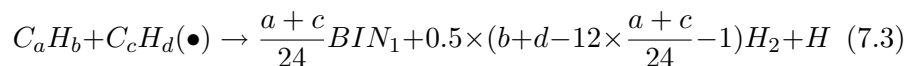
The model co-authored by D’Anna [246, 270] uses the same approach as that of Richter and co-workers but considers six supplementary BINs to cover a higher mass range. Practically, in the present work only 4 of these 6 supplementary BINs will be used for computations (see table 7.1), as experiments are conducted at low pressure and soot cannot grow so rapidly into compounds represented by BIN_{26} than in atmospheric investigations of D’Anna and co-workers.

In order to include the nucleation step in their kinetic model, Richter and co-workers [269] have added formation reactions of several PAHs until corranulene and have considered that radicals of these PAHs can either recombine with other PAH radicals or react with PAHs forming compounds belonging to the first class of molecule, called BIN1 (see table 7.1). This set of nucleation reactions is represented by 610 reactions that are written in the form of equations 7.3 and 7.4, for reactions between a PAH and a PAH radical and 2 PAH radicals, respectively. In these equations, numbers 24 and 12 respectively represent carbon and hydrogen contents of the hydrocarbon $C_{24}H_{12}$, which corresponds to the mean structure of BIN1. For PAH reactions with PAH radicals, Richter and co-workers consider that they produce an H atom and H_2 , whereas for PAH radical recombination only H_2 is produced. This hydrogen production allows to account for the decrease in the C/H ratio

Table 7.1: definition of classes of molecules (BINs) describing large PAH and soot particles.

BIN	Mass range (amu)	C_xH_y	σ (nm)	C/H
<i>BINs proposed by Richter and co-workers [269]</i>				
1	201-400	$C_{24}H_{12}$	0.85	2
2	401-800	$C_{48}H_{24}$	1.07	2
3	801-1600	$C_{96}H_{48}$	1.34	2
4	1601-3200	$C_{193}H_{84}$	1.69	2.3
5	3201-6400	$C_{388}H_{144}$	2.13	2.7
6	6401-12800	$C_{778}H_{264}$	2.68	2.9
7	12801-25600	$C_{1560}H_{480}$	3.37	3.2
8	25601-51200	$C_{3124}H_{912}$	4.24	3.4
9	51201-102400	$C_{6256}H_{1728}$	5.35	3.6
10	102401-204800	$C_{12528}H_{3264}$	6.73	3.8
11	204801-409600	$C_{25088}H_{6144}$	8.48	4.1
12	409601-819200	$C_{50240}H_{11520}$	10.69	4.4
13	819201-1638400	$C_{100608}H_{21504}$	13.46	4.7
14	1638401-3276800	$C_{201472}H_{39936}$	16.96	5.0
15	3276801-6553600	$C_{403456}H_{73728}$	21.36	5.5
16	6553601-13107200	$C_{807936}H_{135168}$	26.91	6.0
17	13107201-26214400	$C_{1617920}H_{245760}$	33.91	6.6
18	26214401-52428800	$C_{3239936}H_{442368}$	42.72	7.3
19	52428801-104857600	$C_{6483968}H_{835584}$	53.83	7.8
20	104857601-209715200	$C_{12972032}H_{1622016}$	67.82	8
<i>Additional BINs proposed by D'Anna [246]</i>				
21	209715201-419430400	$C_{25944593}H_{2464719}$	82.11	10.5
22	419430401-838860800	$C_{51889738}H_{4773836}$	103.44	10.9
23	838860801-1677721600	$C_{103780027}H_{9028841}$	130.31	11.5
24	1677721601-3355443200	$C_{207560605}H_{17019965}$	164.16	12.2

characterizing soot formation.



These reactions do not represent a single step but a sequence of elementary reactions. Richter and co-workers have used rate constants of phenyl + benzene and phenyl + phenyl reactions as references for PAH radical + PAH and PAH radical + PAH radical reactions. Activation

energies have been kept constant for both types of reactions and pre-exponential factors have been scaled based on the change in collision frequencies k_f (see equation 7.5), relative to those of benzene/phenyl + phenyl to take into account the increase in reactive sites. In the following equation, N is the molecular concentration, d is the sum of radii, and μ is the reduced mass.

$$k_f = Nd^2 \sqrt{\frac{8\pi kT}{\mu}} \quad (7.5)$$

The formation of the first class BIN_1 through reactions 7.3 and 7.4 consists in the nucleation step of the soot formation process.

The model co-authored by D'Anna follows the same approach as that of Richter and co-workers. However, since the highest considered PAH is pyrene ($C_{16}H_{10}$), compared to corranulene ($C_{20}H_{10}$) in the model of Richter and co-workers, the number of nucleation reactions is considerably reduced. Another important difference is that, contrarily to Richter and co-workers, D'Anna and co-workers consider coagulation reactions between non radical PAHs. As previously mentioned, these reactions are thought to play a key role in the soot nucleation phenomenon.

The molecular growth phenomena

All further reactions that involve either the first BIN produced by the nucleation process or following BINs consist in the molecular growth section of the kinetic mechanism developed by Richter and co-workers. They proposed that BIN_1 can react through H abstraction reactions by an H atom and an OH radical, forming its corresponding radical BIN_1J , as depicted by reactions R1 to R4 in table 7.2.

As the maximum mole fraction of oxygen atom is significantly lower than that of H atom and OH radical in burnt gases of rich hydrocarbon flames, one can assume that O atom will not be involved in H abstraction reactions of BIN classes. In addition to H abstraction reactions, BIN_1 can decompose forming a hydrogen atom and its parent radical

Table 7.2: reactions considered by Richter and Howard and D’Anna for BINs chemistry.

Considered reactions	
R1	$BIN_i + H \rightarrow BINJ_i + H_2$
R2	$BINJ_i + H_2 \rightarrow BIN_i + H$
R3	$BIN_i + OH \rightarrow BINJ_i + H_2O$
R4	$BINJ_i + H_2O \rightarrow BIN_i + OH$
R5	$BIN_i \rightarrow BINJ_i + H$
R6	$BINJ_i + H \rightarrow BIN_i$
R7	$BIN_i + OH \rightarrow BIN_i + BIN_{i-1} + HCO$
R8	$BINJ_i + O_2 \rightarrow BIN_i + BIN_{i-1} + 2CO$
R9	$BINJ_i + C_2H_2 \rightarrow BIN_i + BIN_{i+1} + H$
R10	$BINJ_i + BIN_j \rightarrow BIN_{i+j} + H$
R11	$BINJ_i + BINJ_j \rightarrow BIN_{i+j}$
R12	$BINJ_i + PAH \rightarrow BIN_i + BIN_{i+1} + H_2 + H$
R13	$BIN_i + PAHJ \rightarrow BIN_i + BIN_{i+1} + H_2 + H$
R14	$BIN_i + BIN_j \rightarrow BIN_{i+j}$

BIN1J, as represented by reactions R5 and R6 of table 7.2. BIN_1 and its radical BIN_1J can equally be oxidized by reaction with OH and O_2 , respectively, as depicted in reactions R7 and R8. All these reactions are included into the Richter and co-workers model and their rate parameters have been taken by analogy with benzene and phenyl radical, by scaling for the number of hydrogen atoms available. The model co-authored by D’Anna considers the same reactions than those of Richter and co-workers, but uses a different method to determine their rate parameters, as described in their studies [246,270].

In addition to reactions R1 to R8 of table 7.2, Richter and co-workers consider that BIN_1 can react through a HACA process with C_2H_2 , which persists in significant concentrations in burnt gases of rich hydrocarbon flames. These reactions are symbolized by reaction R9 that allows BIN_1 to growth into the next class BIN_2 . Then, reactions R1 to R9 are also written for this second class BIN_2 that may growth into BIN_3 , and so on until formation of BIN_{20} . The model of Richter and co-workers equally considers that a radical BIN_iJ can react either with a BIN_j or another BIN_jJ radical through reactions R10 and R11 of table 7.2, forming $BIN_{i+j} + H$ or BIN_{i+j} , respectively. In addition, it

considers reactions of BIN_i and radicals BIN_iJ with PAH radicals and PAHs through reactions R12 and R13, respectively. Reactions R9 to R13 are equally included into the model co-authored by D’Anna, using different kinetic parameters than those proposed by Richter and co-workers. Another major difference between both models is the presence in that of D’Anna and co-workers of reactions that involve the sticking of a BIN_i and a BIN_j molecules, forming dimers that have the molecular composition of BIN_{i+j} (see reaction R14).

As described by reactions R1 and R14 of table 7.2, the total number of reactions describing the chemical growth of BINs is closely linked to the number of considered BINs and the number of PAHs involved in the developed kinetic model. Compared to the model co-authored by D’Anna, that of Richter and Howard includes the formation of a huge number of PAHs. Consequently, the latter is much more complex, as it includes reactions R12 and R13 for each BIN, BINJ radical, PAH and PAH radical.

7.4 Development of a detailed model including soot formation

The development of such a model was not the main objective of this work and since two detailed kinetic models already exist in the literature, one has decided to import their PAH formation chemistry and BIN reactions into the model developed for reactions of gas-phase species in previous

Table 7.3: kinetic models considered for soot formation.

Kinetic model	Species	Reactions	Range
This work	144	757	C1 to C12
Richter et al.	166	6454	C12 to BIN20
Model 1	310	6598	C1 to BIN20
This work	144	757	C1 to C12
D’Anna	61	1683	C12 to BIN24
Model 2	205	2440	C1 to BIN24

chapters. The resulting mechanisms used for the calculation of soot concentrations are called model 1 and model 2 and their characteristics are briefly presented in table 7.3. The first model consists in 310 chemical species and 6598 reactions that describe chemistry from C_1 to BIN_{20} . The model 2 has 205 chemical species and 2440 reactions that describe chemistry from C_1 to BIN_{24} . Consequently, model 2 is smaller than model 1 and requires less calculation time for a larger range of chemical species. However, PAH formation reactions are included in less details than in model 1 and the further discussion will examine the impact on the modeling of the soot nucleation.

7.4.1 Thermodynamic and transport databases

Mean thermodynamic data of each class of molecules presented in table 7.1 were not calculated neither by Richter and co-workers nor by D’Anna. In both mechanisms, these data are assumed to be equal to those of benzene and all forward and reverse reactions involving BIN molecules are considered as irreversible in order to avoid calculation of the reverse rate constant on the basis of erroneous thermodynamic parameters. Transport properties have been deduced by similarity with benzene for each involved BINs by Richter and co-workers. Consequently, thermodynamic and transport databases available in supporting information of the article published by Richter and co-workers [269] are used in the present work.

7.4.2 Modifications required to the Cosilab software

Unfortunately, the use of such large mechanisms in Cosilab has required some modifications of the software that have been achieved by the developers upon our request. The personalized version of Cosilab allows to introduce compounds with a very high number of carbon and hydrogen atoms in the thermodynamic database. In addition, since models are based on reactions involving compounds that have mean molecular compositions, stoichiometric coefficients might not be integer numbers

and the element preservation check performed by Cosilab on reactions of the provided model may not be strictly equal. Consequently, an option allowing to define a tolerance for the element preservation check has been added to the Cosilab software. Finally, the way Cosilab stores calculation results has been modified to support very large files containing information on rate of thousands of reactions and concentrations or mole fractions of hundreds of species.

7.5 Discussion on soot formation

7.5.1 General comments on soot formation

Soot concentration measurements have been performed using the setup presented in chapter 2 inside the rich benzene and toluene flames (equivalence ratios of 1.8 and 2), as depicted in figure 7.2. The residence time of the filter inside the flame has been fixed to 30 min. Measurements below 1 cm of the burner surface have not been conducted as the filter has been found to perturb the flame or to cause its extinction. Measurements beyond 2 cm above the burner surface have not been carried out as an important deformation of the flame has been observed, avoiding reliable soot concentration measurements. Indeed, the burner is placed horizontally and at high heights of the burner surface, hot gases tend to move

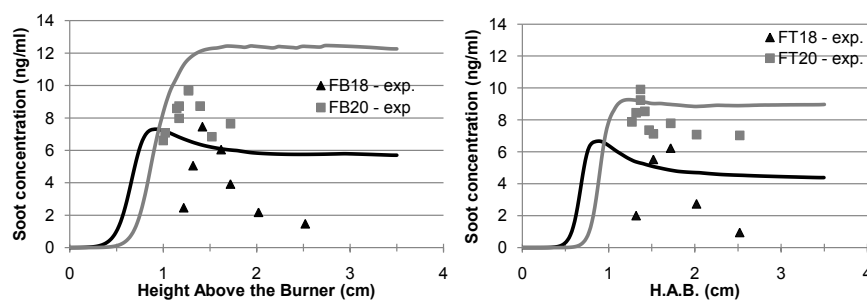


Figure 7.2: Soot concentration profiles in rich benzene and toluene flames. Experiments are represented by symbols and predictions of model 2 by curves.

upside, deforming the flame. When the filter is placed between 1 and 2 cm above the burner surface, the flame is stable and one-dimensional, allowing to perform reliable soot concentration measurements.

However, all particles may not pass through the soot filter and a certain quantity of soot may re-circulate inside the whole combustion chamber. Soot deposition on the backside of the filter, which is not in contact with the flame, confirms this hypothesis. Unfortunately, the error on soot concentration measurements is unknown and profiles depicted in figure 7.2 should be considered with care.

Moreover, since the soot collected with the filter stays at high temperature inside the flame for several minutes, subsequent reactions may not be avoided. These reactions include (i) the chemical growth of the collected soot with compounds from the surrounding gas-phase and (ii) the coagulation of the trapped soot with new particles passing through the filter. Since first reactions might artificially increase the mass of soot collected inside the filter, and therefore invalidate soot concentration measurements discussed in following sections, it has been verified that the measured soot concentration linearly depends on the residence time of the filter in the flame. A perfectly linear behavior has been obtained, demonstrating that the accumulation rate of soot on the filter does not depend on the collected mass of soot, and therefore on its growth through reactions with chemical species in the surrounding gas-phase. Consequently, it is assumed that the chemical growth of soot trapped inside the mass filter is negligible.

Coagulation reactions that may occur during the residence of the filter inside the flame does not introduce errors on the measured soot concentration, but might change the morphology of the collected soot, as discussed in the section devoted to its structural analysis. In the laboratory, the developed method is a first attempt to measure soot inside hydrocarbon flames and should utterly be improved in the future. Nevertheless, measurements presented in figure 7.2 allow to know the magnitude of soot concentration in flames of this work and to discuss the effect of the equivalence ratio and the fuel structure on the soot concen-

tration profiles. Moreover, these effects may be compared to predictions of models presented above and the predicted magnitude of measured soot concentrations can be compared to experiment.

Each soot concentration profile is characterized by a rapid increase, reaching a maximum before slightly decreasing. This shape is unexpected as soot is supposed to continue to grow in burnt gases, from surface reactions with acetylene. This is confirmed by the work of Grieco and co-workers, who analyzed a rich benzene-oxygen-argon flame with an equivalence ratio of 2.4 at low pressure [272] and showed that soot concentration in such a flame continues to increase in burnt gases. The concentration decrease observed in our work should be linked to the lowest efficiency of the filter at higher distances above the burner, as previously discussed. The equivalence ratio has an important impact on soot concentration as its decrease from 2 to 1.8 causes a diminution of about 30% of the soot concentration in benzene and toluene flames. This observation is consistent with the highest oxygen content of flames with lowest equivalence ratios, allowing a larger oxidation of soot and its precursors.

In burnt gases, the decrease observed in soot concentrations is much more pronounced at equivalence ratio of 1.8 than 2. The soot concentrations in toluene flames are found to be similar to those measured in benzene flames with corresponding equivalence ratios. Therefore, the substitution of a hydrogen atom from the benzene ring with a methyl group seems to only have a limited impact on the soot yield, whereas it has an important effect on the combustion chemistry, as described in previous chapters. In the present work, the equivalence ratio seems to be the main parameter that affects the soot concentration. However, a more reliable setup should be developed for the measurement of soot concentrations in order to verify this hypothesis.

7.5.2 Model predictions

Figure 7.2 only presents model predictions of D'Anna and co-workers [246, 270] as the model of Richter and co-workers has been found to

highly underestimate experimental measurements. Regarding the good predictive capability presented in their article of 2005 [269], this underprediction is surprising. Therefore, comparative reaction rate analyses have been performed on predicted results obtained for BF20, with the model provided in their study and with that developed in this work. The analyses have revealed that the major nucleation route of the model developed by Richter and co-workers begins with the recombination of two ortho benzyne ($o\text{-}C_6H_4$) molecules into biphenylene ($C_{12}H_8$). However, in chapter 4 we have shown that the model of Richter and co-workers highly overestimates the $o\text{-}C_6H_4$ maximum mole fraction. In our kinetic model we have therefore included a new sub-model for phenyl decomposition, developed by Lories [127], which gives more reliable predictions of ortho benzyne, significantly decreasing the biphenylene formation rate. Consequently, the use of the sub-model of soot formation developed by Richter and co-workers in combination with the model developed in this work for the gas-phase chemistry causes a significant underestimation of the soot yield.

In contrast with the model developed by Richter and co-workers, the one co-authored by D’Anna gives very encouraging results, for each investigated flame, as depicted in figure 7.2. Since the model of D’Anna gives significantly better predictions and requires less calculation time than that of Richter and co-workers, only that of D’Anna has been used for soot modeling in this work. In following sections, prediction of the different steps of soot formation with this mechanism will be examined.

7.5.3 Soot nucleation

Figure 7.3 compares derivatives of predicted soot concentrations measured in BF20 and TF20, which indicate the growth rate of soot particles. The nucleation zone is defined as the range of height above the burner surface spreading from the beginning of the growth until the reach of a constant growth rate. In BF20, this nucleation zone is worth 0.4 cm and begins around 0.18 cm of the burner surface. In TF20, this zone is smaller than in BF20 and begins at 0.36 cm of the burner surface, which

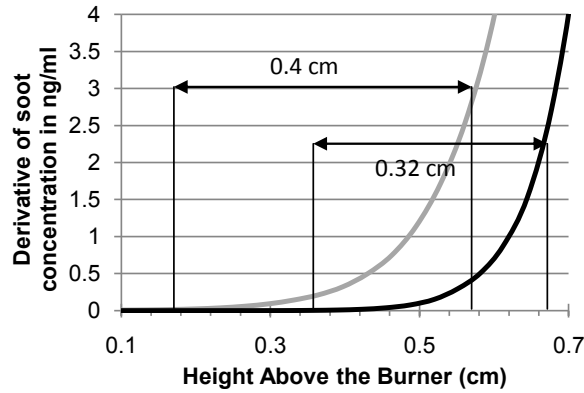


Figure 7.3: derivative of predicted soot concentration curves of BF20 (the gray curve) and TF20 (the black curve). Indicated distances represent the spreading of the nucleation zone.

is 0.18 cm above the beginning position of BF20. This gap of 0.18 cm is consistent with that of about 0.12 cm predicted between maximum of mole fraction profiles of chemical species measured in TF20 and BF20. These predicted gaps are experimentally confirmed and comes from the difference in the position of the flame above the burner. Whereas particle nucleation in TF20 begins later than in BF20, its zone is the narrowest, indicating that the nucleation occurs faster in TF20 than in BF20.

A comparative reaction rate analysis has been performed on predicted data of BF20 and TF20, in order to identify reactions involved in the nucleation process and to examine how the change in the fuel struc-

Table 7.4: Contributions of main reactions involved in particle nucleation in BF20 and TF20.

	Reactions	BF20	TF20
R1	$C_6H_5 + C_{10}H_8 \rightarrow 0.6667BIN_1 + 2H_2 + H$	0.24	0.32
R2	$C_6H_5 + C_{10}H_7 - 2 \rightarrow 0.6667BIN_1 + 2H_2$	0.18	0.24
R3	$C_6H_5 + C_{10}H_7 - 1 \rightarrow 0.6667BIN_1 + 2H_2$	0.17	0.22
R4	$C_6H_6 + C_{10}H_7 - 2 \rightarrow 0.6667BIN_1 + 2H_2 + H$	0.10	0.06
R5	$C_6H_6 + C_{10}H_7 - 1 \rightarrow 0.6667BIN_1 + 2H_2 + H$	0.10	0.05
R6	$C_6H_5 + C_{14}H_{10} \rightarrow 0.8333BIN_1 + 2H_2 + H$	0.08	0.02

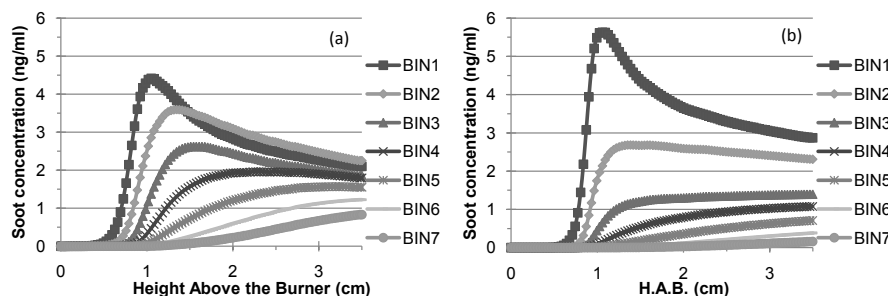


Figure 7.4: (a) Concentration of the first 7 BINs molecules predicted in BF20 (a) and TF20 (b).

ture affects their contributions (see table 7.4). The principal reaction which produces BIN_1 from PAHs is that between phenyl radical and naphthalene. It accounts for 24% and 32% of BIN_1 formation in BF20 and TF20, respectively. Recombination reactions of phenyl radical with isomers of naphthyl radical ($C_{10}H_7J1$ and $C_{10}H_7J2$) are also major nucleation pathways, as they have contributions of respectively 18% and 17 % in BF20, and 24% and 22% in TF20. The contribution increase observed for these three reactions in TF20, compared to BF20, is due to the important increase of naphthalene and naphthyl radicals mole fractions in TF20, compared to BF20. These increases largely compensate for the slight decrease in phenyl radical mole fraction observed in TF20, compared to BF20, allowing to speed up the rate of BIN_1 production through these reactions.

The stimulation of these three main nucleation reactions in TF20 explains the shortest nucleation zone predicted for this flame, compared to BF20. Moreover, as depicted in figure 7.4, the concentration of BIN_1 in TF20 is about 25% higher than in BF20, demonstrating that the nucleation step in TF20 is predicted to be more efficient. The major role played by reactions 1 to 3 in the soot nucleation process equally explains the large drop in soot concentrations observed in BF18 and TF18, compared to BF20 and TF20. Indeed, at lower equivalence ratios, naphthalene and naphthyl radicals mole fractions are lower and therefore significantly decrease the nucleation rate.

Whereas the phenyl radical mole fraction only slightly decreases in TF20, compared to BF20, the maximum mole fraction of benzene considerably drops off in TF20, as it is no longer a reactant. This causes the decrease in contributions of nucleation reactions R4 and R5, which involve C_6H_6 . The last important nucleation route is reaction R6 of table 7.4 that involves phenyl radical and phenanthrene ($C_{14}H_{10}$). As previously discussed, phenyl radical mole fraction decreases in TF20, compared to BF20. Since the mechanism of D’Anna and co-workers mainly predicts phenanthrene formation through HACA reactions on biphenyl, which is principally formed from phenyl radical recombination, phenanthrene mole fraction decreases in TF20, compared to BF20. The combination of decreases in phenyl radical and phenanthrene mole fractions in TF20 causes the drop in the contribution of reaction R6 to BIN_1 formation in TF20, compared to BF20.

From table 7.4 it emerges that mole fractions of naphthalene, naphthyl radicals, benzene and phenyl radical play a determining role in soot nucleation. It is found that reactions involving dimerization of PAHs such as pyrene ($C_{16}H_{10}$) are not significantly involved in particle formation, contrarily to pathways proposed by Frenklach [260]. However, reactions R1 to R6 of table 7.4 are not elementary and they may include pyrene formation and its dimerization. The mechanism of D’Anna is thus statistical and does not allow to precisely determine reaction pathways involved in the nucleation process.

7.5.4 Chemical growth of BIN material

The BIN_1 class of molecules produced during the nucleation process is mainly consumed through H abstraction reactions by H atom, forming the corresponding radical BIN_1J . The further chemical growth of soot nuclei occurs either through HACA reactions on this radical or by reactions involving aromatic chemical species present in the gas phase and BIN_1 molecules or its radical BIN_1J . Concerning the chemical growth of BINs through HACA reactions, it involves acetylene that is a main product of both BF20 and TF20. As presented in figure 7.5 (a), the

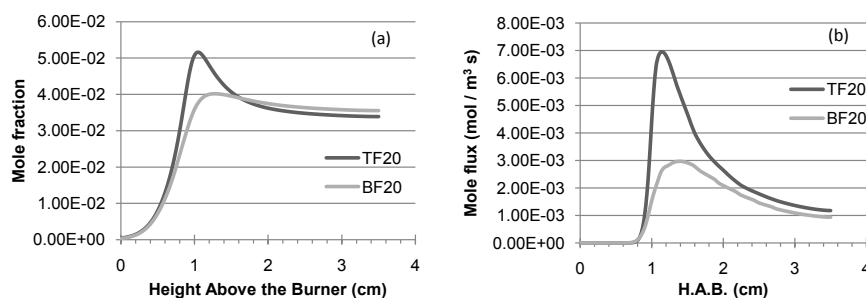


Figure 7.5: (a) Mole fraction profiles of acetylene in BF20 and TF20 (b) Net mole flux of $BIN_1J + C_2H_2 \rightarrow 0.9167BIN_1 + 0.0833BIN_2$ in BF20 and TF20.

mole fraction profile of C_2H_2 depicts different shapes in these flames.

In TF20, the increase of the acetylene mole fraction is sharper and reaches a higher maximum than in BF20. Then, the mole fraction decrease is more pronounced in TF20 and finally reaches a similar mole fraction than in BF20. The sharpest acetylene increase in TF20 speeds up HACA reactions of BIN_1 molecules, as shown in figure 7.5 (b) that depicts the net reaction rate of BIN_2 formation from reaction R7 of table 7.5 in BF20 and TF20. Similar reactions than those discussed for BIN_1 are included in the mechanism to represent the growth of larger BINs until BIN_{24} . The acceleration of HACA reactions is equally observed for reactions of BIN_2J radicals and higher with acetylene. Since these particle growth reactions, as well as the nucleation step, are stimulated in TF20, compared to BF20, one can expect that concentrations of BIN_2 and higher will be greater in TF20 than those predicted in BF20.

However, figure 7.4, which depicts mass concentrations of BINs in BF20 and TF20, shows that the kinetic model exactly predicts the opposite. Moreover, figure 7.2 indicates that the maximum soot concentration is lower in TF20 than in BF20. These predictions can be explained by the high contribution of another chemical growth pathway, which involves reactions of aromatic chemical species of the surrounding gas phase with

BIN molecules or their radicals. As an example, in BF20 and TF20 the growth of BIN_1 through the HACA pathway is predicted to have contributions of only 21 and 39 %, respectively (see table 7.5), whereas the growth through reactions with aromatic compounds, principally represented by reactions R8 to R12, respectively accounts for 77 and 57 %. In TF20, the 20 % drop in contribution of this second channel is due to the lowest benzene and phenyl radical mole fractions, compared to BF20, where benzene is a reactant. Since in TF20 this second channel is still the major BINs formation route, the stimulation of the HACA pathway previously discussed cannot result in higher BINs concentrations than in BF20, as depicted in figure 7.4.

According to the model prediction of the distribution of various BINs concentrations, the soot produced in TF20 should be structurally different than that formed in BF20. Indeed, in TF20, BIN_1 in one hand, and BIN_2 to BIN_{24} in the other hand, respectively have higher and lower concentrations than in BF20. Consequently, particles in TF20 are predicted to have a structure closer to BIN_1 , which has a small mean molecular diameter, whereas particles in BF20 are predicted to have a larger size distribution and thus a higher mean diameter than those in TF20. This is confirmed by calculating the mean particle diameter $\bar{\sigma}_z$ at $z = 3$ cm of the burner surface, by using equation 7.6, where σ_i and C_i are the diameter of BIN i and its mole concentration, respectively. In BF20 and TF20, the model predicts a mean particle diameter of 1.02

Table 7.5: Contributions of main reactions involved in particle growth in BF20 and TF20.

	Reactions	BF20	TF20
	HACA pathway	0.21	0.39
R7	$BIN_1J + C_2H_2 \rightarrow 0.9167BIN_1 + 0.8333BIN_2$	0.21	0.39
	Reactions with aromatic species	0.77	0.57
R8	$C_6H_6 + BIN_1J \rightarrow 0.75BIN_1 + 0.25BIN_2 + 0.5H_2 + H$	0.30	0.15
R9	$C_6H_5 + BIN_1J \rightarrow 0.75BIN_1 + 0.25BIN_2 + 0.5H_2$	0.29	0.28
R10	$C_6H_5 + BIN_1 \rightarrow 0.75BIN_1 + 0.25BIN_2 + 0.5H_2 + H$	0.15	0.11
R11	$C_6H_6 + BIN_1 \rightarrow 0.75BIN_1 + 0.25BIN_2 + 1.5H_2$	0.03	0.01
R12	$C_{10}H_8 + BIN_1J \rightarrow 0.5833BIN_1 + 0.4167BIN_2 + 0.5H_2 + H$	0	0.02

and 0.93 nm, respectively.

$$\bar{\sigma}_z = \frac{\sum_{i=1}^{24} C_i \times \sigma_i}{\sum_{i=1}^{24} C_i} \quad (7.6)$$

Nevertheless, the kinetic model of D'Anna and co-workers does not consider reactions of BINs molecules and their radicals with toluene or benzyl radical that are present in high concentration in TF20. Contrarily to phenyl and benzene addition on PAHs through the PAC mechanism, these reactions have never been proposed in the literature. Their addition into the kinetic model highly increases the rate of BINs growth in TF20 and thus the predicted mean diameter of particles. However, their addition also leads to the overestimation of the maximum soot concentration predicted in TF20 and should results in BINs having several methyl groups that contrast with regular PAHs generally detected in soot samples. The molecular growth through toluene and benzyl radical addition is thus a topic of research that should be addressed in the future, in order to model soot formation in toluene flames with a higher accuracy.

A last channel involving the growth of BIN material is the recombination of two BIN radicals or the reaction of a BIN molecule with a bin radical, followed by the loss of an H atom. The kinetic model predicts that the contribution of these reactions to the formation of small BIN molecules is insignificant and progressively becomes important for larger compounds. For molecules greater than BIN_9 , these reactions reach a contribution of formation close to 15%.

The lowest soot concentration observed in BF18 and TF18, compared to BF20 and TF20, can be explained by the drop in the equivalence ratio, yielding a decrease in mole fractions of acetylene, benzene, phenyl radical, BIN_1 and BIN_1J radical. Consequently, reactions of table 7.5 are disadvantaged and the chemical growth is slower.

7.5.5 Physical growth of bin material

The physical growth of BIN material is included into the kinetic model of D'Anna and co-workers by reactions R14 of table 7.2. In the present work, these reactions are found to have an insignificant contribution to the growth of soot particles, compared to reactions of the chemical growth presented above. However, these reactions may have a more important role at higher distances of the burner surface than those considered here, where concentrations of chemical species involved in the chemical growth of BIN compounds become sufficiently low to make their rate negligible. These distances may be relatively high considering the low pressure of flames investigated in this work. On the contrary, literature studies devoted to atmospheric flames showed that coagulation of soot particles plays a determining role in soot formation, even at close distances of the burner surface.

7.5.6 Oxidation of Bins

The oxidation of BIN molecules and radicals is achieved through reactions R7 and R8 of table 7.2, which respectively involve hydroxyl radical reaction with a BIN molecule and molecular oxygen reaction on a BIN radical. Due to the low concentrations of hydroxyl and molecular oxygen in the region where soot formation occurs, reactions R7 and R8 only account for about 5 % and 1% of BIN consumption, respectively. Compared to BF20 and TF20, these contributions increase in BF18 and TF18, reaching 10 % and 3%, respectively. These increases are due to the decrease of the equivalence ratio, increasing the availability of hydroxyl radical and molecular oxygen in the burnt gases.

7.5.7 Structural analysis of soot

Figure 7.6 shows a Scanning Electron Microscopy picture of the soot collected in BF20, at 8 cm of the burner surface. Since no isolated particles can be found, this picture demonstrates that particle coagulation

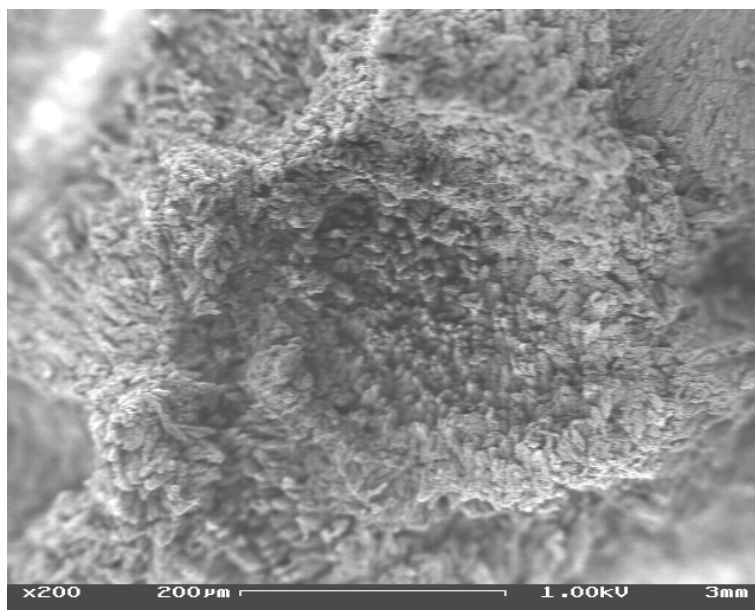


Figure 7.6: SEM picture of soot collected in BF20.

occurs inside the filter, changing the observed morphology, as previously discussed. Consequently, SEM pictures that are presented in this chapter are not representative of the exact structure of particles that have been sampled inside the flame, but show coagulation patterns of them. However, these pictures give information on the soot morphology that deposit on the wall of a combustion chamber that is in contact with a flame, such as in industrial or domestic burners. Moreover, considering that at investigated height above the burner, coagulation reactions are negligible inside the flame (see model predictions discussed above), following figures will allow to define a maximum size for primary soot particles that have been sampled inside the flame. Figure 7.7 represents an enlargement of a factor 10 on a section of figure 7.6, showing that the fine structure of soot is equally composed of small aggregates stucked together. The largest pattern of figure 7.7 has a diameter of about 20 micrometers and is composed by several smaller particles that depict a diameter of about 8 micrometers, which are in turn composed by smaller aggregates of 3 micrometers in diameter. Figure 7.8 presents an enlargement of such a small structure, showing that it is equally

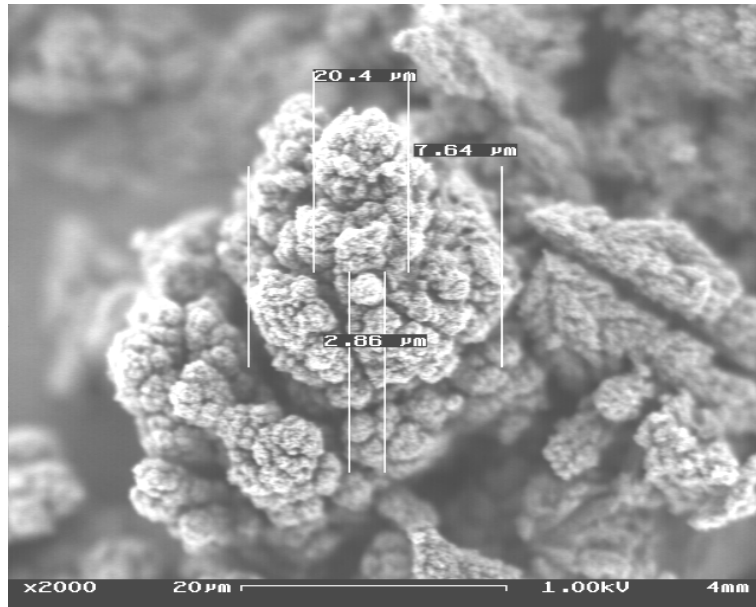


Figure 7.7: SEM picture of soot collected in BF20.

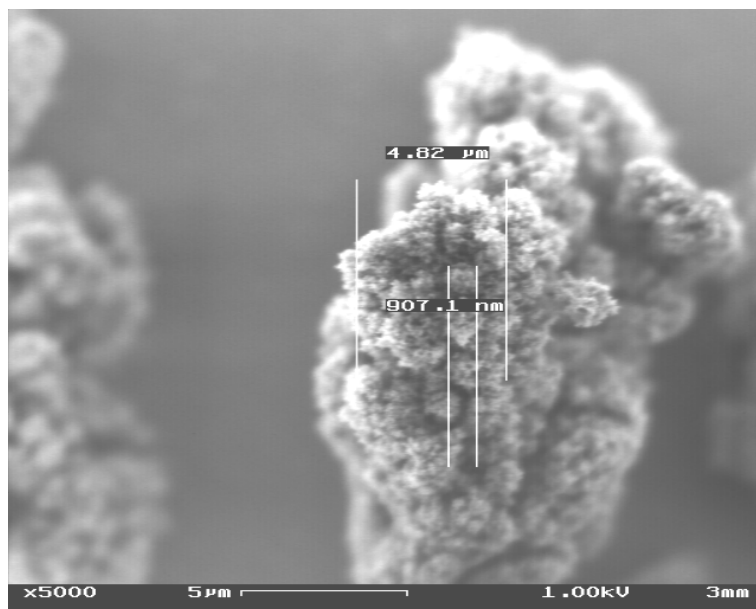


Figure 7.8: SEM picture of soot collected in BF20.

composed by many smaller similar aggregates that have diameters of hundreds of nanometers. Finally, these structures also seem to be composed by several smaller aggregates, and so on. Figures 7.6, 7.7 and 7.8 therefore clearly demonstrate that primary soot particles should have a mean diameter lower than hundreds of nanometers and prove that these primary structures should coagulate together, forming larger patterns of several micrometers, which can in turn coagulate together or with primary particles, and so on until soot particles of a few millimeters are produced. The soot trapped inside the filter can therefore be defined as an irregularly object that is "self-similar" and "scale invariant" over certain length scales. These properties are typical of a *fractal morphology* that has already been observed by several researchers investigating soot formation [273,274]. The maximum limit deduced at 8 cm of the burner surface for the diameter of primary soot particles (less than hundreds of nanometers) is consistent with that predicted at 3 cm by the kinetic model in BF20 and TF20 (about 1 nm). The significant gap between these 2 values can be explained by the region of 5 cm that separates them, where several reaction growth should still occur.

7.6 Conclusions

This chapter has presented the current general consensus that has been reached by scientists on the understanding of the soot formation process. Basically it can be divided into 2 main steps, whose the first is the *soot particle nucleation* forming soot nuclei by chemical reactions between species from the gas-phase and by the coagulation of small PAH. The second is the *growth of soot particles* through chemical reactions with compounds from the surrounding gas-phase and by coagulation with other particles. Since the control of soot formation is of particular health and industrial concerns, we have shown that for many years researchers have developed models to predict carbonaceous particles formation in hydrocarbon flames. These models are empirical if they consists in a relation between a flame parameter such as the equivalence ratio and the soot concentration, or detailed if they are based on predicted flame

structures that are calculated in the same way as those presented in previous chapters.

Since this work is devoted to the development of a detailed kinetic model for benzene and toluene combustion, one has decided to complete it with a detailed model of soot formation. Among the literature, only models of Richter and co-workers and D'Anna and co-workers may be easily added into the software used for the calculation of flame structures in this work. These models consider classes of molecules that cover defined mass ranges from large PAHs until that of soot particles. Then, these models include reactions between these classes of molecules instead of considering reactions between all possible intermediate species that may link PAHs to soot. The formation of the first class of molecule is defined as the nucleation step and consists of reactions between aromatic species of the gas-phase. Then, the first class may growth into larger classes of compounds, through soot growth reactions, and the different classes are allowed to coagulate together, producing larger particles. The two well admitted steps of soot formation are therefore included in these detailed models.

Experimental measurements of the soot concentration were performed in rich hydrocarbon flames of this work in order to compare with predicted data. A simple setup consisting in a filter that is inserted inside the flame has been developed. This intrusive method is the first apparatus allowing to collect soot that has been developed in the laboratory. It therefore presents many disadvantages that should be addressed in further studies, as the small sampling spatial range due to the flame perturbation, or the long residence time of the collected soot inside the flame, altering its morphological properties. Nevertheless, the present apparatus allows to measure the magnitude of the soot concentration in flames of this work and to compare them in order to determine the effect of the equivalence ratio and the fuel structure on particles formation. Moreover, concentration profiles can be compared to predicted results to assess the predictive capability of the developed models.

It has been found that the model of Richter and co-workers significantly underpredicts soot concentrations, whereas that of D'Anna and co-workers gives predictions of similar magnitude as experimental measurements. The underprediction of the model of Richter and co-workers comes from the better prediction of ortho benzyne mole fraction with the gas-phase kinetic model developed in this work, which disadvantage biphenylene formation that is a major nucleation channel in their detailed soot formation model. Since the model of Richter and co-workers requires an important computation time, compared to that of D'Anna and co-workers, it has not been further considered.

Comparative reaction rate analysis have been achieved on predicted results of the model developed by D'Anna and co-workers. The most important nucleation reactions involve benzene, phenyl radical, naphthalene and naphthyl radical. Since the toluene flames have higher naphthalene mole fractions than benzene flames, they are predicted to undergo a faster nucleation process than corresponding benzene flames. This observation agrees with studies of the literature, demonstrating that toluene has a larger propensity to form soot than benzene. However, the analysis of predicted results has shown that the chemical growth of soot nuclei is mainly achieved through reactions with benzene and phenyl radicals from the surrounding gas-phase, which are in lower concentration in toluene flames, compared to benzene flames. Consequently, toluene flames depict a slower particle growth than benzene flames and are predicted to produce lower soot concentrations. This prediction disagree with experimental results of this work and those of the literature, which respectively show that toluene flames should produce similar or higher soot concentrations than benzene flames. This might be explained by the lack of growth reactions involving toluene and benzyl radicals, which are present in high concentrations in toluene flames.

The improvement of the soot formation model may be the subject of a future work and should address this hypothesis. Until a distance of 3.5 cm above the burner surface, coagulation reactions are predicted to be negligible compared to the chemical growth phenomenon. The mean diameter of soot particles in benzene and toluene flames having

an equivalence ratio of 2 are therefore predicted to be as small as 1.02 and 0.93 nanometer, respectively. The highest diameter of particles formed in benzene flames is due to the highest rate of chemical growth reactions. According to experiments, the soot concentration is found to depend on the flame equivalence ratios and this observation is well reproduced by the kinetic model. A comparative reaction rate analysis reveals that the higher oxygen content of these flames promotes oxidation of soot particles. In addition, the lowest naphthalene mole fractions of these flames decrease their nucleation rate.

Scanning Electron Microscopy has been used to analyze the morphological properties of the collected soot, obtained in the richest benzene flame at a distance of 8 cm from the burner surface. Since no isolated particle has been detected, it is supposed that soot highly coagulates inside the mass filter during the residence in the flame. However, the SEM analysis reveals that soot depicts a fractal morphology, confirming previous findings described in the literature. Moreover, it is found that at 8 cm of the burner surface, the primary soot particle diameter should be lower than hundreds of nanometers, which is consistent with that of 1 nm predicted by the kinetic model at 3 cm from the burner surface.

The kinetic model developed for the gas-phase chemistry of benzene and toluene combustion has been successfully completed with a soot formation sub-model available in the literature. The analysis of predicted data allows to discuss the contribution of chemical reactions involved in the different steps of the general soot formation process and the effect of the fuel and equivalence ratio on the soot concentration. Finally, SEM analysis have allowed to analysis the morphology of the produced soot and verify the magnitude of the predicted primary soot particle diameter. This chapter describes the first attempt to measure and predict soot concentration in the laboratory. Both the apparatus developed for soot concentration measurement and the kinetic model assembled should be improved in further studies.

Conclusions and perspectives

Conclusions

The present work consists in an experimental and a kinetic modeling study of laminar, premixed and one-dimensional benzene-oxygen-argon and toluene-oxygen-argon flames, burning at low pressure. The investigation has been conducted over a large range of equivalence ratios, including lean, stoichiometric and rich conditions. Experimental mole fraction profiles of several chemical species occurring in the investigated flames have been measured by Gas Chromatography (GC). Molecular Beam Mass Spectrometry (MBMS) measurements have equally been achieved for some radicals and hydrocarbons of interest, which could not be detected by GC. An experimental setup for the measurement of soot concentrations in flames has been developed and profiles have been determined in rich benzene and toluene flames. To the best of our knowledge, such experimental flame structure studies of lean and stoichiometric benzene and toluene flames have never been published in the literature. Moreover, this work provides soot concentration measurements for 4 rich premixed, laminar and one-dimensional aromatic flames. Consequently, it provides valuable experimental data that will be useful for the scientific community working on the understanding of aromatic oxidation, as well as on that of PAHs and soot formation.

Experimental structures of benzene-oxygen-argon flames have shown that some hydrocarbons such as cyclopentadiene, vinylacetylene and acetylene are produced in high concentrations over the entire range of equivalence ratios, demonstrating that these compounds play a central role in benzene combustion. Other chemical species have been detected in lower concentrations, as allene, propyne and methane. Chemical species heavier than benzene have been detected in rich benzene-oxygen-argon flames, including toluene, styrene, phenylacetylene, naphthalene, biphenyl and phenanthrene. PAHs above phenanthrene could not be detected using the Gas Chromatography setup. The improvement of the detection limit of this apparatus is an interesting perspective, which should allow to close the gap between small PAHs and soot formation.

Based on a recent literature survey, a detailed kinetic model with a good predictive capability has been developed for benzene combustion. A comparative reaction rate analysis has revealed that in the investigated flames benzene is mainly consumed into the phenyl radical through H abstraction reactions. It is now well admitted that phenyl radical principally reacts with O_2 through two different pathways. The first consists in the O_2 addition, followed by the break of the O-O bond, giving oxygen atom and phenoxy radical. As highlighted in this work, the second pathway is still surrounded by a large uncertainty. Many kinetic models consider that it consists in O_2 addition on the phenyl radical, followed by a complex rearrangement yielding benzoquinone and a hydrogen atom, whereas no previous experimental evidence exists for the benzoquinone formation in benzene flames. Consequently, measurements at a m/z ratio corresponding to benzoquinone have been performed by MBMS in a lean benzene flame, demonstrating that its maximum mole fraction is very low compared to other species. This value is highly overestimated by kinetic models considering that phenyl radical reacts with O_2 giving benzoquinone. The present study clearly demonstrates that other reaction pathways should exist and that kinetic models that consider the conversion of phenyl radical into benzoquinone have to be improved. In the developed kinetic model, we have suggested that this reaction rather

produces n-1,3-butadienyl radical and two CO. This assumption is coherent with other experimental studies on this reaction and gives better predictions of experimental structures of benzene flames. Since models of the literature equally predict large mole fractions for phenoxy radical, MBMS measurements have equally been performed. Our study confirms that its maximum mole fraction is significantly lower than usually predicted and we have therefore conducted a kinetic modeling analysis of pathways involved in its formation and consumption. We have shown that its recombination with an H atom giving phenol causes an important overestimation of the latter and equally significantly slows down the flame speed, as phenol gives back the phenoxy radical, leading to a loop. Based on studies published in the literature, we have proposed that the reaction between the phenoxy radical and a H atom should rather produce acetylene, vinyl and two CO. This reaction allows to better predict the speed of benzene consumption, as well as the phenoxy radical mole fraction. Our study has confirmed that at high temperature, the phenoxy radical mainly decomposes into the cyclopentadienyl radical and CO, explaining the significant mole fractions of cyclopentadiene observed experimentally. The cyclopentadienyl radical is predicted to be a key intermediate, as it links C_6 chemistry to C_4 , C_3 and C_2 formations, through reactions with O atom and dissociation into propargyl radicals and acetylene. Acetylene is therefore equally a central intermediate of benzene consumption, explaining its large experimental mole fraction. The developed kinetic model well reproduces most of measurements performed in benzene-oxygen-argon flames, over the entire range of equivalence ratio. The kinetic modeling study, together with experimental measurements, have therefore allowed to improve the understanding of benzene oxidation, by throwing some light on certain remaining uncertainties. However, some hypotheses take in this work still have to be further examined, by theoretical and experimental studies on definite reactions.

The measurement of toluene-oxygen-argon flame structures has equally been performed over a large range of equivalence ratios. These flame structures involve chemical species similar to those observed in benzene

flames. Indeed, high mole fractions of intermediates such as benzene, cyclopentadiene, vinylacetylene and acetylene have been detected. We have therefore postulated that an important overlap between benzene and toluene flame chemistry should exist. This hypothesis has been verified by the development of a kinetic model with a good predictive capability for toluene combustion. Comparative reaction rate analyses have demonstrated that toluene is principally consumed through three main pathways, converging towards benzene and cyclopentadienyl radical formation. This explains the significant overlap observed between benzene and toluene flame structures. The first channel of toluene consumption consists in forming the benzyl radical through H abstraction reactions on its methyl group. Reactions of benzyl radical at high temperature are currently a central theme of research. According to most recent insights on this topic, its decomposition into fulvenallene and H atom has been included into the kinetic model. Concerning the consumption of fulvenallene, it has been demonstrated that a good predictive capability of cyclopentadiene could only be achieved if a pathway involving H atom addition and decomposition into cyclopentadienyl radical and acetylene, is included. Such a pathway has been recently proposed in the literature and we have demonstrated that its consideration gives reliable predictions of mole fraction profiles measured by MBMS at m/z ratios corresponding to fulvenallene and benzyl radical. However, compared to theoretical predictions, the rate constant proposed for the H atom reaction with fulvenallene is larger. Then, further works on this subject are necessary to fully elucidate the mechanism of benzyl radical decomposition in cyclopentadienyl radical. Beside this decomposition route, the side chain of the benzyl radical can be oxidized, forming the phenyl radical that is consumed in the same way as in benzene flames. The second route of toluene consumption produces benzene and phenyl radical, respectively through the substitution of the methyl group by an H atom and through toluene dissociation. This path is very important since it is responsible of most of methyl radical formation, whose in turn gives methane that is observed in large concentrations in toluene flames. The last toluene consumption channel consists in H abstraction reactions onto the phenyl ring. Whereas this pathway is generally not included

into kinetic models devoted to toluene oxidation, our study has shown that it plays a significant role at low equivalence ratios and low temperatures. Contrarily to benzene, this path can produce different isomers that have to be taken into account, as their consumption may give various products. Methylphenyl radicals are expected to react similarly to phenyl radicals and their consumption are therefore equally uncertain. Based on the literature, we have proposed that methylphenyl radicals react with O_2 , forming two CO and various C_3H_x and C_2H_x compounds. Beside this channel, methylphenoxy radicals can equally be formed and we have demonstrated that their decompositions at high temperature should produce resonant forms of the $C_5H_4CH_3$ radical. This radical is converted to cyclopentadienyl radical and CH_3 by reaction with H atom, and may also produce benzene through a complex isomerization pathway, followed by the loss of an H atom. The benzene formation in toluene flames has been demonstrated to occur from the second route of toluene consumption, as well as from the isomerization of $C_5H_4CH_3$ and the recombination of propargyl radicals, which has been widely discussed in the literature these last years. Formation of C_4 and smaller hydrocarbons have been showed to proceed similarly to benzene flames. The developed mechanism well reproduces most of the measurements performed in toluene flames, over the entire range of investigated equivalence ratios. Mole fractions of C_3H_4 hydrocarbons are overestimated by the model, due to the significant formation of C_3 intermediates through reactions of methylphenyl radicals with O_2 . In the same way as phenyl radical reaction with O_2 , this reaction is still uncertain and should therefore be further investigated. Phenyl and methylphenyl radicals reactions with O_2 are complicated pathways, whose products and kinetics are difficult to interpret. It is very interesting to note that similar uncertainties still surround O_2 reaction with the vinyl radical, which has a reacting site somewhat similar to that of phenyl and methylphenyl radicals. This problem seems therefore recurrent in combustion of hydrocarbons and should be utterly addressed in further studies.

The measurement of PAH mole fraction profiles in benzene and toluene flames has shown that toluene flames generally exhibit larger naphtha-

lene mole fractions than corresponding benzene flames. Based on this observation, we have postulated that it should exist naphthalene formation routes highly dependent on toluene. A detailed kinetic model for PAH formation has been developed based on major reaction pathways described in the literature, including the HACA route, the cyclopentadienyl radical self-recombination channel and the benzyl+propargyl radicals pathway. The comparative reaction rate analysis has confirmed that the benzyl+propargyl channel plays a key role in the naphthalene formation in toluene flames. In benzene flames, this route is not active and naphthalene is only produced from cyclopentadienyl radicals self-recombination. This work shows that the HACA mechanism should not produce naphthalene in benzene and toluene flames, whereas it may be responsible of the further growth of large PAHs and soot. Concerning biphenyl, we have shown that its formation is disadvantaged in toluene flames, as it principally depends on the phenyl radical. Biphenyl is found to form phenanthrene through HACA reactions. Other compounds such as phenylacetylene and styrene have been included into the kinetic model and an overall good predictive capability of their mole fraction profiles has been obtained.

Cyclopentene and propyne have been respectively added to benzene and toluene flames, in order to further investigate the naphthalene formation. Indeed, cyclopentene and propyne are respectively cyclopentadienyl and propargyl radicals precursors, which should respectively promote the cyclopentadienyl radicals and the benzyl + propargyl radicals pathways producing naphthalene. The kinetic model has been extended to cyclopentene flame chemistry and experimental flame structures have been compared to predictions. It is found that the cyclopentadienyl radicals pathway slightly overestimates naphthalene formation, highlighting that further studies on this mechanism should be conducted. However, as stressed in this work, cyclopentene flame chemistry is still uncertain and the overestimation of consumption routes forming cyclopentadienyl radicals could equally be responsible of the naphthalene overestimation. The addition of propyne to rich toluene flames is better reproduced by

the kinetic model, confirming the key role played by the benzyl + propargyl pathway in the formation of naphthalene in toluene flames.

Finally, the developed kinetic model has been completed by a soot formation mechanism available in the literature. This model considers the formation of classes of molecules (BIN) having mean properties, rather than describing all chemical species linking PAHs to soot. The mechanism used for soot formation has a reasonable number of reactions and performs calculations within a reasonable time. The model includes the main soot formation steps admitted by the scientific community: nucleation, chemical growth and coagulation. It well predicts the magnitude of soot concentration measured in all investigated flames and the effect of the equivalence ratio. It is found that main nucleation routes depend on naphthalene in both benzene and toluene flames. Therefore a reliable prediction of naphthalene formation is crucial to obtain a good predictive capability of soot concentration. The molecular growth of soot is found to occur through HACA reactions and reactions with aromatic species subsisting into the gas phase. Scanning Electron Microscopy has been used to characterize the collected soot. However, the long residence time of the filter inside the flame allows soot coagulation and subsequent reactions that alter its morphology. Consequently, no direct information could be obtained on the structure of initial soot particles. Nevertheless, this analysis confirms the fractal morphology of soot and indicated that the primary soot particle diameter should be smaller than few hundreds of nanometers, which is consistent with model predictions.

In conclusion, the objectives presented at the beginning of this work have been fulfilled and the developed strategy therefore seems relevant to the understanding of hydrocarbon flame chemistry. The present study brings valuable experimental data on oxidation of aromatics, as well as on PAH and soot formations in flames. It therefore helps to close the gap towards soot formation. The developed kinetic model has allowed to assess the validity of certain hypotheses recently proposed in the literature, and consequently contributes to a better understanding of aromatic flame chemistry. However, the road towards the development of a versatile mechanism, working for most of hydrocarbons, is still long.

Indeed, the number of possible structures and reaction pathways significantly increases with the molecular weight and the detailed modeling of large PAH and soot formation therefore appears to be very difficult. Fortunately, recent statistical methods allow to predict the soot concentration and its morphology without including such a detailed modeling. These statistical methods are very promising and their development will certainly be a central theme of research for the coming years.

Perspectives

In addition to elucidate the remaining uncertainties that have been highlighted in this work, the developed kinetic model should be validated under different conditions. Since the addition of oxygenated species to hydrocarbon flames is thought to reduce the soot formation, the study of flames burning blends of aromatic and oxygenated hydrocarbons is an interesting perspective. Moreover, the kinetic model of this work is well appropriated for such conditions, as it includes the sub-model for ethanol, acetaldehyde and acetic acid combustion developed by Lepat [174]. The kinetic model should equally be validated at higher pressures, using flame structures of Tregrossi and co-workers [88] or flame speed measurements of Davis and co-workers [86]. As the work of Tregrossi and co-workers includes soot concentration measurements, the sub-model for soot formation may equally be validated at higher pressures.

Beside these additional validations, the kinetic model should be reduced as much as possible in order to be used as an input database by engineers working on the modeling of industrial combustion processes. Since the sub-model for soot formation consists of thousand of reactions, other sub-models should be tested. The one of Frenklach and co-workers is interesting as it consists of an algorithm that may be more easily included into codes developed for the modeling of combustion phenomena.

Concerning the experimental setup, it should be adapted to the detection of larger PAHs, by using new chromatographic detectors, such as UV or Mass Spectrometry detectors. The apparatus of soot sampling should be improved in order to avoid flame perturbations, as well as the

residence of the collected soot inside the flame. The sampling method proposed by Abid and co-workers [37] or non intrusive techniques are good candidates. The development of such setups is very important to close the gap between PAH and soot formation.

The measurement of mole fraction profiles of H and O atoms, as well as that of the OH radical is equally an interesting perspective. Indeed, these chemical species play a key role in hydrocarbon flames and the validation of the kinetic model against such experimental data is of particular importance.

Appendix A

Experimental parameters of chromatographic separations.

This appendix summarizes parameters used for chromatographic separations carried out with the setup presented in chapter 2. Table 1 presents the four configurations that have been discussed. Parameters associated to these configurations are given hereafter and eluting times of detected compounds are presented in table 2.

Table 1: chromatographic configurations used in the present work

Configuration	Injection setup ¹	Column	Carrier Gas	Detectors
A	A	MOLSIEVE 5A	He	TCD
B	A	MOLSIEVE 5A	Ar	TCD
C	A	PORAPLOT Q	He	FID + TCD
D	B	CPSILPAH CB	He	FID

¹ Setups A and B are those described in figures 2.4 on page 27 and 2.6 on page 29, respectively.

Parameters of configurations A and B:

Flow rate: 10 ml/min

TCD temperature: 30°C

Oven temperature:

1. 35°C for 5 minutes
2. first increase: 10°C / min

3. 110°C for 10 min

Parameters of configuration C:

Flow rate: 8 ml/min

FID temperature: 200°C

TCD temperature: 30°C

Oven temperature:

1. 60°C for 10 minutes
2. first increase: 40°C / min
3. 120°C for 5 min
4. second increase: 40°C / min
5. 200°C for 50 min

Parameters of configuration D:

Flow rate: 2.4 ml/min

FID temperature: 380°C

Oven temperature:

1. 55°C for 5 minutes
2. first increase: 20°C / min
3. 70°C for 10 min
4. second increase: 2°C / min
5. 150°C for 1 min
6. third increase: 10°C / min
7. 300°C for 10 min

Table 2: Eluting times of detected chemical species

Chemical species	Name	Eluting times (min.)
Configuration A		
H_2	molecular hydrogen	2.5
O_2	molecular oxygen	3.4
Ar	argon	3.6
CO	carbon monoxide	11.7
Configuration B		
H_2	molecular hydrogen	3.0
Configuration C		
CH_4	methane	3.6
CO_2	carbon dioxide	3.9
C_2H_4, C_2H_2	ethylene, acetylene	4.4
C_2H_6	ethane	5.2
H_2O	water	5.2
C_3H_6	propylene	11.2
C_3H_8	propane	11.6
a- C_3H_4	allene	11.8
p- C_3H_4	propyne	11.9
C_4H_4	vinylacetylene	16
1,3- C_4H_6	1,3-butadiene	16.2
C_4H_2	diacetylene	16.9
C_5H_6	cyclopentadiene	19.6
C_6H_6	benzene	22.6
C_7H_8	toluene	27.2
Configuration D		
C_8H_6	phenylacetylene	10.2
C_8H_8	styrene	11
$C_{10}H_8$	naphthalene	23.4
1 - $C_{11}H_{10}$	1-methylnaphthalene	25.4
2 - $C_{11}H_{10}$	2-methylnaphthalene	25.7
$C_{12}H_{10}$	biphenyl	26.7
$C_{14}H_{10}$	phenanthrene	31.1

Appendix B

Composition and characteristics of investigated flames

Table 3 summarizes the code and the fresh gas composition of each flame presented in this work. Table 4 gives detailed characteristics of these flames, including the equivalence ratio ϕ , the C/O ratio, the working pressure P , the mass flux at the output of the burner, the total volumetric flow rate Dv_T measured at 298K and 1 atm, and the cold gas velocity v_c at the working pressure P and 298 K.

Table 3: code and fresh gas composition of each investigated flame

Code	Fresh gas composition					
	$\chi_{C_6H_6}$	$\chi_{C_7H_8}$	$\chi_{C_5H_8}$	$\chi_{C_3H_4}$	χ_{O_2}	χ_{Ar}
BF07	$2.72 \cdot 10^{-2}$				$2.92 \cdot 10^{-1}$	$6.81 \cdot 10^{-1}$
BF10	$2.72 \cdot 10^{-2}$				$2.04 \cdot 10^{-1}$	$7.68 \cdot 10^{-1}$
BF18	$1.16 \cdot 10^{-1}$				$4.84 \cdot 10^{-1}$	$4.00 \cdot 10^{-1}$
BF20	$1.16 \cdot 10^{-1}$				$4.36 \cdot 10^{-1}$	$4.48 \cdot 10^{-1}$
BF20-35	$1.16 \cdot 10^{-1}$				$4.36 \cdot 10^{-1}$	$4.48 \cdot 10^{-1}$
BF20-65	$1.16 \cdot 10^{-1}$				$4.36 \cdot 10^{-1}$	$4.48 \cdot 10^{-1}$
TF07		$2.26 \cdot 10^{-2}$			$2.9 \cdot 10^{-1}$	$6.87 \cdot 10^{-1}$
TF10		$2.26 \cdot 10^{-2}$			$2.03 \cdot 10^{-1}$	$7.74 \cdot 10^{-1}$
TF18		$9.89 \cdot 10^{-2}$			$4.94 \cdot 10^{-1}$	$4.07 \cdot 10^{-1}$
TF20		$9.89 \cdot 10^{-2}$			$4.45 \cdot 10^{-1}$	$4.56 \cdot 10^{-1}$
CF20			$8.91 \cdot 10^{-2}$		$3.67 \cdot 10^{-1}$	$5.44 \cdot 10^{-1}$
BCF20	$8.84 \cdot 10^{-2}$		$3.11 \cdot 10^{-2}$		$4.47 \cdot 10^{-1}$	$4.33 \cdot 10^{-1}$
TPF21		$9.89 \cdot 10^{-2}$		$1.11 \cdot 10^{-2}$	$4.45 \cdot 10^{-1}$	$4.45 \cdot 10^{-1}$
TPF22		$9.89 \cdot 10^{-2}$		$2.22 \cdot 10^{-2}$	$4.45 \cdot 10^{-1}$	$4.34 \cdot 10^{-1}$

Table 4: codes and detailed characteristics of each investigated flame.

Code	ϕ	C/O	P mbar	Mass flux (g s ⁻¹ cm ⁻²)	Dv_T l/min [†]	v_c cm/s [‡]
BF07	0.7	0.28	45	2.93 10 ⁻³	5.5	41
BF10	1.0	0.40	45	2.98 10 ⁻³	5.5	41
BF18	1.8	0.72	45	3.07 10 ⁻³	5.5	41
BF20	2.0	0.80	45	3.10 10 ⁻³	5.5	41
BF20-35	2.0	0.80	35	3.10 10 ⁻³	5.5	53
BF20-65	2.0	0.80	65	3.10 10 ⁻³	5.5	28
TF07	0.7	0.27	45	2.94 10 ⁻³	5.5	41
TF10	1.0	0.39	45	2.99 10 ⁻³	5.5	41
TF18	1.8	0.70	45	3.12 10 ⁻³	5.5	41
TF20	2.0	0.78	45	3.15 10 ⁻³	5.5	41
CF20	1.7	0.61	45	3.38 10 ⁻³	6.2	46
BCF20	2.0	0.77	45	3.04 10 ⁻³	5.5	41
TPF21	2.1	0.82	45	3.15 10 ⁻³	5.5	41
TPF22	2.2	0.85	45	3.15 10 ⁻³	5.5	41

[†] Measured at 298K and 1 atm

[‡] At the working pressure P and 298K

Appendix C

Experimental and adiabatic flame temperatures

As presented in table 5, adiabatic flame temperatures T_{sta} have been calculated for each investigated flame using the software *Stanjan* [46]. Adiabatic flame temperatures T_{cos} have been calculated using *Cosilab* [39] at 3.5 cm from the burner surface for BF07, BF10, TF07 and TF10, in

Table 5: Experimental and adiabatic flame temperatures of each investigated flame

Code	z_{exp} [†] cm	Tm_{exp} [‡] K	T_{sta} [*] K	T_{cos} [*] K
BF07	1.6	1470	2432	2095
BF10	1.15	1495	2414	2146
BF18	0.95	1775	2670	
BF20	1.15	1715	2564	
BF20-35	1.3	1720	2545	
BF20-65	1	1670	2592	
TF07	1.25	1630	2418	2106
TF10	1.06	1660	2400	2141
TF18	0.85	1765	2643	
TF20	1.05	1745	2530	
CF20	0.95	1700	2579	
BCF20	1.0	1725	2574	
TPF21	1.1	1690	2489	
TPF22	1.15	1680	2446	

[†] Position of the maximum of experimental flame temperature.

[‡] Tm_{exp} , stands for the maximum flame temperatures measured using the thermocouple.

^{*} These adiabatic flame temperatures have been calculated using *Stanjan* (T_{sta}) [46] and *Cosilab* (T_{cos}) [39]. T_{cos} are taken at 3.5 cm from the burner surface.

order to compare with Stanjan calculations. The input temperature of reactants has been fixed to 300 K in Cosilab and Stanjan. In Stanjan, the products involved in the equilibrium are CO_2 , H_2O , CO , H_2 , O_2 , H , O , OH and C_s . The calculated adiabatic flame temperatures T_{sta} and T_{cos} are systematically higher than those measured in our flames. This highlights that flames investigated in this work should significantly transfer heat to the burner surface, to the walls of the combustion chamber, and to the quartz nozzle.

As presented in chapter 3, the adiabatic flame temperature depends on the product distribution in the burnt gases. Since Cosilab and Stanjan calculate this distribution based on the chemical kinetics and on the thermodynamic equilibrium, respectively, the predicted temperatures are significantly different. Indeed, the equilibrium composition of the burnt gases is an ideal case that the system tends to reach, in a time that depends on the chemical kinetics. Therefore, at 3.5 cm from the burner surface, the product composition and the adiabatic flame temperature predicted by Cosilab contrast with the equilibrium distribution and the adiabatic temperature calculated with Stanjan.

The amount of heat transferred by a flame to the burner surface depends on its position above it. In this work, since lean benzene and toluene flames stabilize closer to the burner surface than rich flames, the heat transfer should decrease when the equivalence ratio increases. This phenomenon causes experimental flame temperatures of BF10 and TF10 to be larger than those respectively measured in BF07 and TF07, whereas adiabatic flame temperatures T_{sta} predict the opposite.

Although adiabatic temperatures of lean and stoichiometric benzene and toluene flames are similar (see table 5), experimental toluene flame temperatures are larger than those corresponding to benzene flames. As toluene flames stabilize further of the burner surface than benzene flames, this phenomenon can equally be explained by a decrease of the heat transfer.

According to adiabatic temperature calculations, the substitution of some benzene by cyclopentene in BCF20 should not significantly change

the temperature in the burnt gases. Experimental temperatures confirm this hypothesis, as their maxima in BF20 and BCF20 only differ by 10 K. Concerning the seeding of TF20 by propyne, the drop of the flame temperature predicted by adiabatic calculations is consistent with that measured in TPF21 and TPF22.

Appendix D

Method of measurement and maximum mole fractions of compounds detected in investigated flames

Table 6 and 7 summarize experimental maximum mole fractions of compounds detected in flames presented in this work. White and gray background colors indicate chemical species measured by Gas Chromatography and Molecular Beam Mass Spectrometry, respectively. Flame codes refer to table 3 of appendix B.

Table 6: maximum mole fraction and method of measurement of each compound detected in *benzene*- and *toluene*-*oxygen*-*argon* flames. White and gray background colors indicate compounds measured by Gas Chromatography and Molecular Beam Mass Spectrometry, respectively.

species	BF07	BF10	BF18	BF20	BF20-35	BF20-65	TF07	TF10	TF18	TF20
O_2	$2.7 \cdot 10^{-1}$	$2.04 \cdot 10^{-1}$	$4.7 \cdot 10^{-1}$	$4.32 \cdot 10^{-1}$	$4.3 \cdot 10^{-1}$	$4.3 \cdot 10^{-1}$	$2.9 \cdot 10^{-1}$	$1.91 \cdot 10^{-1}$	$4.29 \cdot 10^{-1}$	$4.55 \cdot 10^{-1}$
H_2	$6.53 \cdot 10^{-3}$	$9.22 \cdot 10^{-3}$	$7.92 \cdot 10^{-2}$	$6.07 \cdot 10^{-2}$	$1.1 \cdot 10^{-1}$	$1.1 \cdot 10^{-1}$	$6.6 \cdot 10^{-3}$	$1.1 \cdot 10^{-2}$	$9.0 \cdot 10^{-2}$	$9.7 \cdot 10^{-2}$
H_2O	$7.84 \cdot 10^{-2}$	$6.68 \cdot 10^{-2}$	$1.62 \cdot 10^{-1}$	$1.52 \cdot 10^{-1}$	$1.5 \cdot 10^{-1}$	$1.45 \cdot 10^{-1}$	$8.5 \cdot 10^{-2}$	$7.8 \cdot 10^{-2}$	$1.5 \cdot 10^{-1}$	$1.34 \cdot 10^{-1}$
CO	$9.77 \cdot 10^{-2}$	$8.68 \cdot 10^{-2}$	$3.6 \cdot 10^{-1}$	$3.51 \cdot 10^{-1}$	$3.6 \cdot 10^{-1}$	$3.65 \cdot 10^{-1}$	$8.68 \cdot 10^{-2}$	$9.05 \cdot 10^{-2}$	$3.68 \cdot 10^{-1}$	$3.41 \cdot 10^{-1}$
CO_2	$1.4 \cdot 10^{-1}$	$1.04 \cdot 10^{-1}$	$6.1 \cdot 10^{-2}$	$6.9 \cdot 10^{-2}$	$6.25 \cdot 10^{-2}$	$5.7 \cdot 10^{-2}$	$1.3 \cdot 10^{-1}$	$1.05 \cdot 10^{-1}$	$7.88 \cdot 10^{-2}$	$6.5 \cdot 10^{-2}$
CH_4	$1.83 \cdot 10^{-4}$	$2.68 \cdot 10^{-4}$	$3.15 \cdot 10^{-3}$	$2.94 \cdot 10^{-3}$	$2.64 \cdot 10^{-3}$	$3.51 \cdot 10^{-3}$	$2.07 \cdot 10^{-4}$	$3.71 \cdot 10^{-4}$	$4.44 \cdot 10^{-3}$	$6.36 \cdot 10^{-3}$
C_2H_2	$2.06 \cdot 10^{-3}$	$3.6 \cdot 10^{-3}$	$3.8 \cdot 10^{-2}$	$4.46 \cdot 10^{-2}$	$4.75 \cdot 10^{-2}$	$4.32 \cdot 10^{-2}$	$1.73 \cdot 10^{-3}$	$2.94 \cdot 10^{-3}$	$4.6 \cdot 10^{-2}$	$5.99 \cdot 10^{-2}$
C_2H_6	$7.88 \cdot 10^{-5}$	$1.24 \cdot 10^{-4}$	$1.6 \cdot 10^{-4}$	$7.83 \cdot 10^{-5}$	$1.00 \cdot 10^{-4}$	$8.00 \cdot 10^{-5}$	$1.3 \cdot 10^{-4}$	$2.33 \cdot 10^{-4}$	$2.5 \cdot 10^{-4}$	$2.36 \cdot 10^{-4}$
C_3H_3	$2.31 \cdot 10^{-4}$	$2.99 \cdot 10^{-4}$		$2.2 \cdot 10^{-3}$						
a- C_3H_4	$3.49 \cdot 10^{-5}$	$4.74 \cdot 10^{-5}$	$2.31 \cdot 10^{-4}$	$2.1 \cdot 10^{-4}$	$2.32 \cdot 10^{-4}$	$1.97 \cdot 10^{-4}$	$3.66 \cdot 10^{-5}$	$3.99 \cdot 10^{-5}$	$1.78 \cdot 10^{-4}$	$3.16 \cdot 10^{-4}$
p- C_3H_4	$8.51 \cdot 10^{-5}$	$1.11 \cdot 10^{-4}$	$4.97 \cdot 10^{-4}$	$4.61 \cdot 10^{-4}$	$4.95 \cdot 10^{-4}$	$4.62 \cdot 10^{-4}$	$9.11 \cdot 10^{-5}$	$9.3 \cdot 10^{-5}$	$4.43 \cdot 10^{-4}$	$6.18 \cdot 10^{-4}$
C_3H_6	$1.6 \cdot 10^{-4}$	$1.5 \cdot 10^{-4}$	$1.09 \cdot 10^{-4}$	$7.37 \cdot 10^{-5}$	$8.26 \cdot 10^{-5}$	$5.91 \cdot 10^{-5}$	$9.11 \cdot 10^{-5}$	$7.53 \cdot 10^{-5}$	$2.55 \cdot 10^{-4}$	$3.56 \cdot 10^{-5}$
C_4H_2	$1.45 \cdot 10^{-5}$	$4.37 \cdot 10^{-5}$	$3.22 \cdot 10^{-3}$	$3.88 \cdot 10^{-3}$	$4.15 \cdot 10^{-3}$	$3.24 \cdot 10^{-3}$	$1.5 \cdot 10^{-5}$	$5.62 \cdot 10^{-5}$	$2.9 \cdot 10^{-3}$	$4.91 \cdot 10^{-3}$
C_4H_4	$9.85 \cdot 10^{-5}$	$1.7 \cdot 10^{-4}$	$1.72 \cdot 10^{-3}$	$1.45 \cdot 10^{-3}$	$1.68 \cdot 10^{-3}$	$1.24 \cdot 10^{-3}$	$1.37 \cdot 10^{-4}$	$1.89 \cdot 10^{-4}$	$9.67 \cdot 10^{-4}$	$1.18 \cdot 10^{-3}$
1,2- C_4H_6	$1.83 \cdot 10^{-6}$	$5.11 \cdot 10^{-6}$	$2.27 \cdot 10^{-5}$	$2.36 \cdot 10^{-5}$	$2.59 \cdot 10^{-5}$	$1.8 \cdot 10^{-5}$				
1,3- C_4H_6	$7.94 \cdot 10^{-5}$	$1.02 \cdot 10^{-4}$	$1.07 \cdot 10^{-4}$	$1.21 \cdot 10^{-4}$	$1.21 \cdot 10^{-4}$	$1.02 \cdot 10^{-4}$	$8.41 \cdot 10^{-5}$	$8.38 \cdot 10^{-5}$	$1.67 \cdot 10^{-4}$	$2.15 \cdot 10^{-4}$
C_5H_6	$1.01 \cdot 10^{-4}$	$2.02 \cdot 10^{-4}$	$1.46 \cdot 10^{-3}$	$1.32 \cdot 10^{-3}$	$1.39 \cdot 10^{-3}$	$1.22 \cdot 10^{-3}$	$1.61 \cdot 10^{-4}$	$2.28 \cdot 10^{-4}$	$5.11 \cdot 10^{-4}$	$5.37 \cdot 10^{-4}$
$C_6H_4O_2$	$1.63 \cdot 10^{-5}$									
C_6H_5O	$8.35 \cdot 10^{-6}$									
C_6H_5OH	$1.08 \cdot 10^{-4}$	$1.68 \cdot 10^{-4}$		$4.22 \cdot 10^{-4}$						

Continued on next page

species	BF07	BF10	BF18	BF20	BF20-35	BF20-65	TF07	TF10	TF18	TF20
C_6H_6	$2.42 \cdot 10^{-2}$	$2.8 \cdot 10^{-2}$	$1.07 \cdot 10^{-1}$	$1.06 \cdot 10^{-1}$	$1.12 \cdot 10^{-1}$	$1.2 \cdot 10^{-1}$	$9.32 \cdot 10^{-4}$	$1.74 \cdot 10^{-3}$	$3.35 \cdot 10^{-3}$	$4.87 \cdot 10^{-3}$
C_7H_6							$< 1 \cdot 10^{-6\dagger}$	$< 1 \cdot 10^{-6\dagger}$		$5.49 \cdot 10^{-4}$
C_7H_6O							$4.01 \cdot 10^{-4}$	$3.92 \cdot 10^{-4}$		$4.94 \cdot 10^{-4}$
C_7H_7							$1.66 \cdot 10^{-4}$	$2.72 \cdot 10^{-4}$		$2.09 \cdot 10^{-3}$
C_7H_8	$8.37 \cdot 10^{-6}$	$2.36 \cdot 10^{-5}$	$1.5 \cdot 10^{-4}$	$1.46 \cdot 10^{-4}$	$1.34 \cdot 10^{-4}$	$1.12 \cdot 10^{-4}$	$2.12 \cdot 10^{-2}$	$2.2 \cdot 10^{-2}$	$9.89 \cdot 10^{-2}$	$9.9 \cdot 10^{-2}$
C_8H_6			$6.20 \cdot 10^{-4}$	$7.00 \cdot 10^{-4}$					$7.95 \cdot 10^{-4}$	$1.00 \cdot 10^{-3}$
C_8H_8			$1.39 \cdot 10^{-4}$	$1.51 \cdot 10^{-4}$					$6.26 \cdot 10^{-4}$	$6.88 \cdot 10^{-4}$
$C_{10}H_8$			$2.27 \cdot 10^{-4}$	$2.94 \cdot 10^{-4}$					$4.16 \cdot 10^{-5}$	$4.26 \cdot 10^{-4}$
$1-C_{11}H_{10}$			$1.36 \cdot 10^{-5}$	$1.4 \cdot 10^{-5}$					$2.15 \cdot 10^{-5}$	$2.25 \cdot 10^{-5}$
$2-C_{11}H_{10}$			$1.5 \cdot 10^{-5}$	$1.52 \cdot 10^{-5}$					$1.65 \cdot 10^{-5}$	$1.78 \cdot 10^{-5}$
$C_{12}H_{10}$			$6.31 \cdot 10^{-5}$	$6.83 \cdot 10^{-5}$					$2.15 \cdot 10^{-5}$	$2.3 \cdot 10^{-5}$
$C_{14}H_{10}$			$1.6 \cdot 10^{-6}$	$3.0 \cdot 10^{-6}$						$\simeq 5.0 \cdot 10^{-6}$

[†] An upper limit of the maximum mole fraction has been determined whereas this compound could not be detected.

Table 7: maximum mole fraction and method of measurement of each compound detected in *cyclopentene*-, *benzene*-, *cyclopentene*- and *toluene-propyne-oxygen-argon* flames. White and gray background colors indicate compounds measured by Gas Chromatography and Molecular Beam Mass Spectrometry, respectively.

species	CF20	BF20	BCF20	TF20	TPF21	TPF22
CH_4	$7.77 \cdot 10^{-3}$	$2.94 \cdot 10^{-3}$	$4.25 \cdot 10^{-3}$	$6.36 \cdot 10^{-3}$	$7.36 \cdot 10^{-3}$	$9.0 \cdot 10^{-3}$
C_2H_6	$3.64 \cdot 10^{-4}$	$7.83 \cdot 10^{-5}$	$1.93 \cdot 10^{-4}$	$2.36 \cdot 10^{-4}$	$2.84 \cdot 10^{-4}$	$3.01 \cdot 10^{-4}$
a- C_3H_4	$8.48 \cdot 10^{-4}$	$2.1 \cdot 10^{-4}$	$4.08 \cdot 10^{-4}$	$3.16 \cdot 10^{-4}$	$7.24 \cdot 10^{-4}$	$9.23 \cdot 10^{-4}$
p- C_3H_4	$1.22 \cdot 10^{-3}$	$4.61 \cdot 10^{-4}$	$7.12 \cdot 10^{-4}$	$6.18 \cdot 10^{-4}$	$1.23 \cdot 10^{-2}$	$2.1 \cdot 10^{-2}$
C_3H_6	$1.26 \cdot 10^{-3}$	$7.37 \cdot 10^{-5}$	$7.11 \cdot 10^{-4}$	$3.56 \cdot 10^{-5}$	$5.28 \cdot 10^{-5}$	$6.03 \cdot 10^{-5}$
C_4H_2	$1.45 \cdot 10^{-5}$	$3.88 \cdot 10^{-3}$	$2.35 \cdot 10^{-3}$	$4.91 \cdot 10^{-3}$	$4.91 \cdot 10^{-3}$	$4.98 \cdot 10^{-3}$
C_4H_4	$1.41 \cdot 10^{-3}$	$1.45 \cdot 10^{-3}$	$1.67 \cdot 10^{-3}$	$1.18 \cdot 10^{-3}$	$1.37 \cdot 10^{-3}$	$1.52 \cdot 10^{-3}$
1,3- C_4H_6	$1.6 \cdot 10^{-3}$	$1.21 \cdot 10^{-4}$	$9.45 \cdot 10^{-4}$	$2.15 \cdot 10^{-4}$	$5.57 \cdot 10^{-4}$	$5.23 \cdot 10^{-4}$
C_5H_6	$1.2 \cdot 10^{-2}$	$1.32 \cdot 10^{-3}$	$4.9 \cdot 10^{-3}$	$5.37 \cdot 10^{-4}$	$5.57 \cdot 10^{-4}$	$5.23 \cdot 10^{-4}$
C_6H_6	$1.46 \cdot 10^{-3}$	$1.06 \cdot 10^{-1}$	$7.67 \cdot 10^{-2}$	$4.87 \cdot 10^{-3}$	$5.63 \cdot 10^{-3}$	$6.13 \cdot 10^{-3}$
C_7H_8	$5.5 \cdot 10^{-5}$	$1.46 \cdot 10^{-4}$	$1.18 \cdot 10^{-4}$	$9.9 \cdot 10^{-2}$	$9.84 \cdot 10^{-2}$	$9.86 \cdot 10^{-2}$
$C_{10}H_8$	$3.7 \cdot 10^{-4}$	$2.94 \cdot 10^{-4}$		$4.26 \cdot 10^{-4}$	$4.66 \cdot 10^{-4}$	$5.01 \cdot 10^{-4}$

Appendix E

Detailed kinetic model presented in this work

This appendix presents the whole kinetic model used in this work. All references included in this appendix report to the end of the table presented on following pages. The whole kinetic scheme may be divided into as follows.

1. The sub-model that includes reactions of the H_2/O_2 system and those of C_1H_x and C_2H_x hydrocarbons. It comes from the PhD Thesis of Leplat. This model is mainly based on the GRI mechanism [14] and on models of Marinov [1], Yasunaga et al. [8] and Gasnot et al. [17] for ethanol, acetaldehyde and acetic acid, respectively.
2. The sub-model for reactions of C_3H_x hydrocarbons, which comes from mechanisms of Davis et al. [38] and Marinov et al. [15].
3. The sub-model for reactions of C_4 intermediates, which is based on the kinetic model of Wang and Frenklach [45].
4. The sub-model for C_6H_x to $C_{14}H_x$ flame chemistry, which has been discussed in chapters 4, 5 and 6.
5. The sub-model for soot formation, which comes from the work of D’Anna and co-workers. It is not presented in the following table but may be found in supporting information of their paper.

The table on the following pages presents the kinetic model. Rate constant are expressed in the form $k = AT^n e^{-\frac{E_a}{RT}}$, with the units cm^3 , mol, s and cal.

	Reactions	A	n	E _a	Refs
C₂H₅OH Reactions					
1	C ₂ H ₅ OH(+M)=CH ₃ +CH ₂ OH(+M)	5.94E+23	-1.68	91163	[1]
	LOW PRESSURE LIMIT:	2.88E+85	-18.90	109914	
	TROE PARAMETERS: a = 0.5, T*** = 200, T* = 890, T** = 4600				
	Enhanced Third Body Efficiencies: H ₂ O = 5.0 H ₂ = 2.0 CO ₂ = 3.0 CO = 2.0				
2	C ₂ H ₅ OH(+M)=C ₂ H ₄ +H ₂ O(+M)	2.79E+13	0.09	66136	[1]
	LOW PRESSURE LIMIT:	2.57E+83	-18.85	86452	
	TROE PARAMETERS: a = 0.7, T*** = 350, T* = 800, T** = 3800				
	Enhanced Third Body Efficiencies: H ₂ O = 5.0				
3	C ₂ H ₅ OH(+M)=CH ₃ HCO+H ₂ (+M)	7.24E+11	0.10	91007	[1]
	LOW PRESSURE LIMIT:	4.46E+87	-19.42	115586	
	TROE PARAMETERS: a = 0.9, T*** = 900, T* = 1100, T** = 3500				
	Enhanced Third Body Efficiencies: H ₂ O = 5.0				
4	C ₂ H ₅ OH(+M)=C ₂ H ₅ +OH(+M)	1.25E+23	-1.54	96005	[1]
	LOW PRESSURE LIMIT:	3.25E+85	-18.81	114930	
	TROE PARAMETERS: a = 0.5, T*** = 300, T* = 900, T** = 5000				
	Enhanced Third Body Efficiencies: H ₂ O = 5.0 H ₂ = 2.0 CO ₂ = 3.0				
5	C ₂ H ₅ OH+OH=C ₂ H ₄ OH+H ₂ O	6.20E+03	2.68	-576	[2]
6	C ₂ H ₅ OH+OH=CH ₃ CHOH+H ₂ O	1.31E+05	2.43	-1457	[2]
7	C ₂ H ₅ OH+OH=CH ₃ CH ₂ O+H ₂ O	2.81E+02	2.97	-580	[2]
8	C ₂ H ₅ OH+H=C ₂ H ₄ OH+H ₂	1.88E+03	3.20	7150	[3]
9	C ₂ H ₅ OH+H=CH ₃ CHOH+H ₂	1.79E+05	2.53	3420	[3]
10	C ₂ H ₅ OH+H=CH ₃ CH ₂ O+H ₂	5.55E-23	10.60	-4459	[3]
11	C ₂ H ₅ OH+O=C ₂ H ₄ OH+OH	9.69E+02	3.23	4658	[4]
12	C ₂ H ₅ OH+O=CH ₃ CHOH+OH	1.45E+05	2.41	876	[4]
13	C ₂ H ₅ OH+O=CH ₃ CH ₂ O+OH	1.46E-03	4.73	1727	[4]
14	C ₂ H ₅ OH+CH ₃ =C ₂ H ₄ OH+CH ₄	9.90E+02	3.30	12291	[5], ^b
15	C ₂ H ₅ OH+CH ₃ =CH ₃ CHOH+CH ₄	5.97E+01	3.37	7635	[5]], ^b
16	C ₂ H ₅ OH+CH ₃ =CH ₃ CH ₂ O+CH ₄	6.11E+00	3.57	7722	[5], ^b
17	C ₂ H ₅ OH+HO ₂ =CH ₃ CHOH+H ₂ O ₂	8.20E+03	2.55	10750	[1]
18	C ₂ H ₅ OH+HO ₂ =C ₂ H ₄ OH+H ₂ O ₂	1.23E+04	2.55	15750	[1]
19	C ₂ H ₅ OH+HO ₂ =CH ₃ CH ₂ O+H ₂ O ₂	2.50E+12	0.00	24000	[1]
CH₃CH₂O Reactions					
20	CH ₃ CH ₂ O+M=CH ₃ HCO+H+M	1.16E+35	-5.89	25274	[1]
21	CH ₃ CH ₂ O+M=CH ₃ +CH ₂ O+M	1.35E+38	-6.96	23800	[1]
22	CH ₃ CH ₂ O+O ₂ =CH ₃ HCO+HO ₂	4.00E+10	0.00	1100	[1, 6]
23	CH ₃ CH ₂ O+CO=C ₂ H ₅ +CO ₂	4.68E+02	3.16	5380	[1]

24	$\text{CH}_3\text{CH}_2\text{O} + \text{H} = \text{CH}_3 + \text{CH}_2\text{OH}$	3.00E+13	0.00	0	[1]
25	$\text{CH}_3\text{CH}_2\text{O} + \text{H} = \text{C}_2\text{H}_4 + \text{H}_2\text{O}$	3.00E+13	0.00	0	[1]
26	$\text{CH}_3\text{CH}_2\text{O} + \text{OH} = \text{CH}_3\text{HCO} + \text{H}_2\text{O}$	1.00E+13	0.00	0	[1]

CH₃CHOH Reactions

27	$\text{CH}_3\text{CHOH} + \text{M} = \text{CH}_3\text{HCO} + \text{H} + \text{M}$	5.00E+13	0.00	21877	[7]
28	$\text{CH}_3\text{CHOH} + \text{O}_2 = \text{CH}_3\text{HCO} + \text{HO}_2$	1.00E+13	0.00	5569	[7]
29	$\text{CH}_3\text{CHOH} + \text{O} = \text{CH}_3\text{HCO} + \text{OH}$	1.00E+14	0.00	0	[1]
30	$\text{CH}_3\text{CHOH} + \text{HO}_2 = \text{CH}_3\text{HCO} + \text{OH} + \text{OH}$	4.00E+13	0.00	0	[1]
31	$\text{CH}_3\text{CHOH} + \text{OH} = \text{CH}_3\text{HCO} + \text{H}_2\text{O}$	5.00E+12	0.00	0	[1]

CH₃HCO Reactions

32	$\text{CH}_3\text{HCO} = \text{CH}_3 + \text{HCO}$	6.00E+14	0.00	79100	[8]
33	$\text{CH}_3\text{HCO} = \text{CH}_3\text{CO} + \text{H}$	5.00E+14	0.00	87900	[9]
34	$\text{CH}_3\text{HCO} = \text{CH}_4 + \text{CO}$	1.00E+15	0.00	85000	[8]
35	$\text{CH}_3\text{HCO} = \text{CH}_2\text{CO} + \text{H}_2$	3.00E+14	0.00	84000	[8]
36	$\text{CH}_3\text{HCO} + \text{OH} = \text{CH}_3\text{CO} + \text{H}_2\text{O}$	2.34E+10	0.73	1100	[10]
37	$\text{CH}_3\text{HCO} + \text{OH} = \text{CH}_2\text{HCO} + \text{H}_2\text{O}$	1.55E+06	2.20	1000	[11]
38	$\text{CH}_3\text{HCO} + \text{OH} = \text{CH}_3 + \text{HCOOH}$	3.00E+15	-1.08	0	[11]
39	$\text{CH}_3\text{HCO} + \text{O} = \text{CH}_3\text{CO} + \text{OH}$	5.84E+12	0.00	1810	[10]
40	$\text{CH}_3\text{HCO} + \text{O} = \text{CH}_2\text{HCO} + \text{OH}$	1.50E+13	0.00	5000	[8]
41	$\text{CH}_3\text{HCO} + \text{H} = \text{CH}_3\text{CO} + \text{H}_2$	1.20E+14	0.00	7000	[8]
42	$\text{CH}_3\text{HCO} + \text{H} = \text{CH}_2\text{HCO} + \text{H}_2$	1.85E+12	0.40	5359	[1]
43	$\text{CH}_3\text{HCO} + \text{CH}_3 = \text{CH}_3\text{CO} + \text{CH}_4$	1.60E+12	0.00	8000	[8]
44	$\text{CH}_3\text{HCO} + \text{CH}_3 = \text{CH}_2\text{HCO} + \text{CH}_4$	6.00E+12	0.00	11000	[8]
45	$\text{CH}_3\text{HCO} + \text{HO}_2 = \text{CH}_3\text{CO} + \text{H}_2\text{O}_2$	3.00E+12	0.00	11900	[10]
46	$\text{CH}_3\text{HCO} + \text{HO}_2 = \text{CH}_2\text{HCO} + \text{H}_2\text{O}_2$	1.00E+12	0.00	14000	[8]
47	$\text{CH}_3\text{HCO} + \text{O}_2 = \text{CH}_3\text{CO} + \text{HO}_2$	2.00E+13	0.50	42200	[12]

CH₂HCO et CH₃CO Reactions

48	$\text{CH}_3\text{CO} (+\text{M}) = \text{CH}_3 + \text{CO} (+\text{M})$	1.07E+12	0.63	16835	[13], ^b
	LOW PRESSURE LIMIT:	2.78E+18	-0.85	14425	
	TROE PARAMETERS: a = 0.6, T*** = 1E+15, T* = 1E-15, T** = 1E+15				
49	$\text{CH}_2\text{HCO} (+\text{M}) = \text{CH}_3 + \text{CO} (+\text{M})$	2.93E+12	0.29	40161	[13], ^b
	LOW PRESSURE LIMIT:	6.55E+37	-6.11	42436	
	TROE PARAMETERS: a = 1.8, T*** = 10, T* = 500, T** = 5200				
50	$\text{CH}_2\text{HCO} (+\text{M}) = \text{CH}_2\text{CO} + \text{H} (+\text{M})$	1.43E+15	-0.15	45605	[13], ^b
	LOW PRESSURE LIMIT:	1.96E+32	-4.67	43398	
	TROE PARAMETERS: a = 0.55, T*** = 1E+15, T* = 1E-15, T** = 1E+15				
51	$\text{CH}_2\text{HCO} + \text{H} = \text{CH}_3 + \text{HCO}$	2.20E+13	0.00	0	[14]
52	$\text{CH}_2\text{HCO} + \text{H} = \text{CH}_2\text{CO} + \text{H}_2$	1.10E+13	0.00	0	[14]

53	$\text{CH}_2\text{HCO} + \text{OH} = \text{CH}_2\text{CO} + \text{H}_2\text{O}$	1.20E+13	0.00	0	[14]
54	$\text{CH}_2\text{HCO} + \text{OH} = \text{CH}_2\text{OH} + \text{HCO}$	3.01E+13	0.00	0	[14]
55	$\text{CH}_2\text{HCO} + \text{CH}_3 = \text{C}_2\text{H}_5 + \text{CO} + \text{H}$	4.90E+14	-0.50	0	[1, 15]
56	$\text{CH}_2\text{HCO} + \text{HO}_2 = \text{CH}_2\text{O} + \text{HCO} + \text{OH}$	7.00E+12	0.00	0	[1]
57	$\text{CH}_2\text{HCO} + \text{HO}_2 = \text{CH}_3\text{HCO} + \text{O}_2$	3.00E+12	0.00	0	[1]

CH₃COOH Reactions

58	$\text{CH}_3\text{COOH} = \text{CH}_2\text{CO} + \text{H}_2\text{O}$	4.47E+14	0.00	79800	[16]
59	$\text{CH}_3\text{COOH} = \text{CH}_4 + \text{CO}_2$	7.08E+13	0.00	74600	[16]
60	$\text{CH}_3\text{CO} + \text{OH} = \text{CH}_3\text{COOH}$	1.00E+14	0.00	0	[16]
61	$\text{CH}_3\text{COOH} + \text{OH} = \text{CH}_3\text{CO}_2 + \text{H}_2\text{O}$	2.40E+11	0.00	-400	[16]
62	$\text{CH}_3\text{COOH} + \text{H} = \text{CH}_3\text{CO}_2 + \text{H}_2$	5.55E-23	10.60	-4459	[3], ^b
63	$\text{CH}_3\text{COOH} + \text{O} = \text{CH}_3\text{CO}_2 + \text{OH}$	1.46E-03	4.73	1727	[4], ^b
64	$\text{CH}_3\text{COOH} + \text{HO}_2 = \text{CH}_3\text{CO}_2 + \text{H}_2\text{O}_2$	2.50E+12	0.00	24000	[1], ^b
65	$\text{CH}_3\text{COOH} + \text{CH}_3 = \text{CH}_3\text{CO}_2 + \text{CH}_4$	6.11E+00	3.57	7722	[5], ^b
66	$\text{CH}_3\text{COOH} + \text{H} = \text{CH}_2\text{COOH} + \text{H}_2$	8.40E+07	2.00	7703	[17]
67	$\text{CH}_3\text{COOH} + \text{OH} = \text{CH}_2\text{COOH} + \text{H}_2\text{O}$	1.29E+10	1.10	1813	[17]
68	$\text{CH}_3\text{COOH} + \text{O} = \text{CH}_2\text{COOH} + \text{OH}$	5.01E+13	0.00	7871	[17]
69	$\text{CH}_3\text{COOH} + \text{HO}_2 = \text{CH}_2\text{COOH} + \text{H}_2\text{O}_2$	5.61E+12	0.00	19426	[17]
70	$\text{CH}_3\text{COOH} + \text{O}_2 = \text{CH}_2\text{COOH} + \text{HO}_2$	1.26E+13	0.00	49043	[17]
71	$\text{CH}_3\text{COOH} + \text{CH}_3 = \text{CH}_2\text{COOH} + \text{CH}_4$	6.60E+11	0.00	2781	[17]

CH₂COOH et CH₃CO₂ Reactions

72	$\text{CH}_3\text{CO}_2 + \text{M} = \text{CH}_3 + \text{CO}_2 + \text{M}$	8.70E+15	0.00	14400	[16]
73	$\text{CH}_2\text{COOH} = \text{CH}_2\text{CO} + \text{OH}$	4.00E+13	0.00	49043	[17], ^b

CH₂CO Reactions

74	$\text{CH}_2 + \text{CO}(+\text{M}) = \text{CH}_2\text{CO}(+\text{M})$	8.10E+11	0.50	4510	[14]
LOW PRESSURE LIMIT:					
TROE PARAMETERS: $\alpha = 0.576$, $T^{***} = 237$, $T^* = 1652$, $T^{**} = 5069$					
Enhanced Third Body Efficiencies:					
Ar = 0.7 H ₂ = 2.0 H ₂ O = 6.0 CH ₄ = 2.0 CO = 1.5 CO ₂ = 2.0 C ₂ H ₆ = 3.0					
75	$\text{CH}_2\text{CO} + \text{O} = \text{CO}_2 + \text{CH}_2$	1.75E+12	0.00	1350	[14]
76	$\text{CH}_2\text{CO} + \text{H} = \text{CH}_3 + \text{CO}$	1.13E+13	0.00	3428	[14]
77	$\text{CH}_2\text{CO} + \text{H} = \text{HCCO} + \text{H}_2$	5.00E+13	0.00	8000	[14]
78	$\text{CH}_2\text{CO} + \text{O} = \text{HCCO} + \text{OH}$	1.00E+13	0.00	8000	[14]
79	$\text{CH}_2\text{CO} + \text{OH} = \text{HCCO} + \text{H}_2\text{O}$	7.50E+12	0.00	2000	[14]
80	$\text{CH} + \text{CH}_2\text{O} = \text{CH}_2\text{CO} + \text{H}$	9.46E+13	0.00	-515	[14]
81	$\text{CH}_2\text{CO} + \text{CH}_3 = \text{C}_2\text{H}_5 + \text{CO}$	5.00E+12	0.00	0	[18]
82	$\text{CH}_2\text{CO} + \text{CH}_2(\text{s}) = \text{C}_2\text{H}_4 + \text{CO}$	1.60E+14	0.00	0	[19]

HCCO Reactions

83	CH+CO(+M)=HCCO(+M)	5.00E+13	0.00	0	[14]
	LOW PRESSURE LIMIT:	2.69E+28	-3.74	1936	
	TROE PARAMETERS: a = 0.576, T*** = 237, T* = 1652, T** = 5069				
	Enhanced Third Body Efficiencies:				
	Ar = 0.7 H ₂ = 2.0 H ₂ O = 6.0 CH ₄ = 2.0 CO = 1.5 CO ₂ = 2.0 C ₂ H ₆ = 3.0				
84	HCCO+H=CH ₂ (s)+CO	1.00E+14	0.00	0	[14]
85	HCCO+O=H+CO+CO	1.00E+14	0.00	0	[14]
86	HCCO+CH=C ₂ H ₂ +CO	5.00E+13	0.00	0	[14]
87	HCCO+CH ₂ =C ₂ H ₃ +CO	3.00E+13	0.00	0	[14]
88	HCCO+HCCO=C ₂ H ₂ +CO+CO	1.00E+13	0.00	0	[14]
89	HCCO+O ₂ =CO+CO+OH	3.20E+12	0.00	854	[14]

C₂H₆ Reactions

90	CH ₃ +CH ₃ (+M)=C ₂ H ₆ (+M)	9.61E+16	-1.20	586.16	[20]
	LOW PRESSURE LIMIT:	6.16E+42	-7.25	4315	
	TROE PARAMETERS: a = 0.0, T*** = 506, T* = 1, T** = 0				
	H ₂ O = 5.0 H ₂ = 2.0 CO ₂ = 3.0 CO = 2.0				
91	C ₂ H ₅ +H(+M)=C ₂ H ₆ (+M)	5.21E+17	-0.99	1580	[14]
	LOW PRESSURE LIMIT:	1.99E+41	-7.08	6685	
	TROE PARAMETERS: a = 0.842, T*** = 125, T* = 2219, T** = 6882				
92	C ₂ H ₆ +CH ₃ =C ₂ H ₅ +CH ₄	6.14E+06	1.74	10450	[14]
93	C ₂ H ₆ +H=C ₂ H ₅ +H ₂	5.72E+13	0.00	8577	[21]
94	C ₂ H ₆ +O=C ₂ H ₅ +OH	9.99E+08	1.50	5803	[10]
95	C ₂ H ₆ +OH=C ₂ H ₅ +H ₂ O	1.76E+14	0.00	7651	[22]
96	C ₂ H ₆ +HO ₂ =C ₂ H ₅ +H ₂ O ₂	8.70E+04	2.69	18900	[23]
97	C ₂ H ₅ +HO ₂ =C ₂ H ₆ +O ₂	3.00E+12	0.00	0	[15]

C₂H₅ Reactions

98	C ₂ H ₄ +H(+M)=C ₂ H ₅ (+M)	5.40E+11	0.45	1820	[14]
	LOW PRESSURE LIMIT:	6.00E+41	-7.62	6970	
	TROE PARAMETERS: a = 0.975, T*** = 210, T* = 984, T** = 4374				
	Enhanced Third Body Efficiencies:				
	H ₂ O = 6.0 H ₂ = 2.0 CO ₂ = 2.0 CO = 1.5 CH ₄ = 2.0 C ₂ H ₆ = 3.0 Ar = 0.7				
99	C ₂ H ₅ +H=C ₂ H ₄ +H ₂	2.00E+12	0.00	0	[14]
100	C ₂ H ₅ +H=CH ₃ +CH ₃	3.00E+13	0.00	0	[24]
101	C ₂ H ₅ +O=CH ₃ +CH ₂ O	2.24E+13	0.00	0	[14]
102	C ₂ H ₅ +O ₂ =C ₂ H ₄ +HO ₂	2.89E+28	-5.40	7585	[25]

C₂H₄ Reactions

103	$\text{C}_2\text{H}_4(+\text{M})=\text{C}_2\text{H}_2+\text{H}_2(+\text{M})$	8.00E+12	0.44	86770	[14]
	LOW PRESSURE LIMIT:	1.58E+51	-9.30	97800	
	TROE PARAMETERS: $a = 0.735$, $T^{***} = 180$, $T^* = 1035$, $T^{**} = 5417$				
	Enhanced Third Body Efficiencies:				
	$\text{H}_2 = 2.0$ $\text{H}_2\text{O} = 6.0$ $\text{CH}_4 = 2.0$ $\text{CO} = 1.5$ $\text{CO}_2 = 2.0$ $\text{C}_2\text{H}_6 = 3.0$ $\text{Ar} = 0.7$				
104	$\text{C}_2\text{H}_3+\text{H}(+\text{M})=\text{C}_2\text{H}_4(+\text{M})$	6.08E+12	0.27	280	[14]
	LOW PRESSURE LIMIT:	1.40E+30	-3.86	3320	
	TROE PARAMETERS: $a = 0.782$, $T^{***} = 207$, $T^* = 2663$, $T^{**} = 6095$				
	Enhanced Third Body Efficiencies:				
	$\text{H}_2 = 2.0$ $\text{H}_2\text{O} = 6.0$ $\text{CH}_4 = 2.0$ $\text{CO} = 1.5$ $\text{CO}_2 = 2.0$ $\text{C}_2\text{H}_6 = 3.0$ $\text{Ar} = 0.7$				
105	$\text{C}_2\text{H}_4+\text{OH}=\text{C}_2\text{H}_4\text{OH}$	1.29E+12	0.00	-817	[1]
106	$\text{C}_2\text{H}_4+\text{OH}=\text{C}_2\text{H}_3+\text{H}_2\text{O}$	3.60E+06	2.00	2500	[14]
107	$\text{C}_2\text{H}_4+\text{O}=\text{C}_2\text{H}_3+\text{OH}$	1.51E+07	1.91	3739	[26]
108	$\text{C}_2\text{H}_4+\text{O}=\text{CH}_3+\text{HCO}$	1.25E+07	1.83	220	[14]
109	$\text{C}_2\text{H}_4+\text{O}=\text{CH}_2\text{HCO}+\text{H}$	6.70E+06	1.83	220	[14]
110	$\text{C}_2\text{H}_4+\text{CH}_3=\text{C}_2\text{H}_3+\text{CH}_4$	4.16E+12	0.00	11100	[10]
111	$\text{C}_2\text{H}_4+\text{H}=\text{C}_2\text{H}_3+\text{H}_2$	1.33E+06	2.53	12240	[14]

C₂H₃ Reactions

112	$\text{C}_2\text{H}_3(+\text{M})=\text{C}_2\text{H}_2+\text{H}(+\text{M})$	6.38E+09	1.00	37609	[27-28]
	LOW PRESSURE LIMIT:	1.51E+14	0.10	32670	
	TROE PARAMETERS: $a = 0.7$, $T^{***} = 1\text{E-}15$, $T^* = 1\text{E+}15$, $T^{**} = 1\text{E+}15$				
	Enhanced Third Body Efficiencies:				
	$\text{H}_2 = 2.0$ $\text{H}_2\text{O} = 6.0$ $\text{CH}_4 = 2.0$ $\text{CO} = 1.5$ $\text{CO}_2 = 2.0$ $\text{Ar} = 0.7$				
113	$\text{C}_2\text{H}_3+\text{H}=\text{C}_2\text{H}_2+\text{H}_2$	9.00E+13	0.00	0	[15]
114	$\text{C}_2\text{H}_3+\text{O}=\text{CH}_2\text{CO}+\text{H}$	3.00E+13	0.00	0	[15]
115	$\text{C}_2\text{H}_3+\text{O}_2=\text{CH}_2\text{O}+\text{HCO}$	1.70E+29	-5.31	6500	[29]
116	$\text{C}_2\text{H}_3+\text{O}_2=\text{CH}_2\text{HCO}+\text{O}$	3.50E+14	-0.61	5260	[29]
117	$\text{C}_2\text{H}_3+\text{O}_2=\text{C}_2\text{H}_2+\text{HO}_2$	2.12E-06	6.00	9484	[15, 29]
118	$\text{C}_2\text{H}_3+\text{OH}=\text{C}_2\text{H}_2+\text{H}_2\text{O}$	2.00E+13	0.00	0	[15]
119	$\text{C}_2\text{H}_3+\text{C}_2\text{H}=\text{C}_2\text{H}_2+\text{C}_2\text{H}_2$	3.00E+13	0.00	0	[15]
120	$\text{C}_2\text{H}_3+\text{CH}=\text{CH}_2+\text{C}_2\text{H}_2$	5.00E+13	0.00	0	[15]
121	$\text{C}_2\text{H}_3+\text{CH}_3=\text{C}_2\text{H}_2+\text{CH}_4$	2.00E+13	0.00	0	[15]

C₂H₂ Reactions

122	$\text{C}_2\text{H}+\text{H}(+\text{M})=\text{C}_2\text{H}_2(+\text{M})$	1.00E+17	-1.00	0	[14]
	LOW PRESSURE LIMIT:	3.75E+33	-4.80	1900	
	TROE PARAMETERS: $a = 0.6464$, $T^{***} = 132$, $T^* = 1315$, $T^{**} = 5566$				
	Enhanced Third Body Efficiencies:				
	$\text{H}_2 = 2.0$ $\text{H}_2\text{O} = 6.0$ $\text{CH}_4 = 2.0$ $\text{CO} = 1.5$ $\text{CO}_2 = 2.0$ $\text{C}_2\text{H}_6 = 3.0$ $\text{Ar} = 0.7$				
123	$\text{C}_2\text{H}_2+\text{OH}=\text{C}_2\text{H}+\text{H}_2\text{O}$	3.37E+07	2.00	14000	[14]
124	$\text{C}_2\text{H}_2+\text{OH}=\text{HCCOH}+\text{H}$	5.04E+05	2.30	13500	[14]
125	$\text{HCCOH}+\text{H}=\text{CH}_2\text{CO}+\text{H}$	1.00E+13	0	0	[14]

126	$\text{C}_2\text{H}_2 + \text{OH} = \text{CH}_2\text{CO} + \text{H}$	2.18E-04	4.50	-1000	[14]
	duplicate				
	$\text{C}_2\text{H}_2 + \text{OH} = \text{CH}_2\text{CO} + \text{H}$	2.00E+11	0.00	0	[15]
	duplicate				
127	$\text{C}_2\text{H}_2 + \text{OH} = \text{CH}_3 + \text{CO}$	4.83E-04	4.00	-2000	[14]
128	$\text{C}_2\text{H}_2 + \text{O} = \text{CH}_2 + \text{CO}$	6.94E+06	2.00	1900	[14]
129	$\text{C}_2\text{H}_2 + \text{O} = \text{HCCO} + \text{H}$	1.35E+07	2.00	1900	[14]
130	$\text{C}_2\text{H}_2 + \text{O} = \text{C}_2\text{H} + \text{OH}$	4.60E+19	-1.41	28950	[14]
131	$\text{C}_2\text{H}_2 + \text{O}_2 = \text{HCCO} + \text{OH}$	2.00E+08	1.50	30100	[19]
132	$\text{CH} + \text{CH}_2 = \text{C}_2\text{H}_2 + \text{H}$	4.00E+13	0.00	0	[14]
133	$\text{CH}_2 + \text{CH}_2 = \text{C}_2\text{H}_2 + \text{H}_2$	1.60E+15	0.00	11944	[14]
134	$\text{CH}_2 + \text{CH}_2 = \text{C}_2\text{H}_2 + \text{H} + \text{H}$	2.00E+14	0.00	10989	[14]

C₂H Reactions

135	$\text{C}_2\text{H} + \text{H}_2 = \text{C}_2\text{H}_2 + \text{H}$	5.68E+10	0.90	1993	[14]
136	$\text{C}_2\text{H} + \text{O} = \text{CH} + \text{CO}$	5.00E+13	0.00	0	[14]
137	$\text{C}_2\text{H} + \text{OH} = \text{HCCO} + \text{H}$	2.00E+13	0.00	0	[14]
138	$\text{C}_2\text{H} + \text{O}_2 = \text{CO} + \text{HCO}$	1.00E+13	0.00	-755	[14]

C₂H₂OH Reactions

139	$\text{C}_2\text{H}_2 + \text{OH} (+\text{M}) = \text{C}_2\text{H}_2\text{OH} (+\text{M})$	2.29E+13	0.00	1808	[30]
	LOW PRESSURE LIMIT:	7.44E+26	-3.10	1808	
	TROE PARAMETERS: $a = 0.17$, $T^{***} = 180$, $T^* = 500000$, $T^{**} = 12772$				
140	$\text{C}_2\text{H}_2\text{OH} = \text{CH}_2\text{CO} + \text{H}$	5.00E+15	0.00	28000	[31]
141	$\text{C}_2\text{H}_2\text{OH} + \text{H} = \text{CH}_2\text{CO} + \text{H}_2$	2.00E+13	0.00	4000	[31]
142	$\text{C}_2\text{H}_2\text{OH} + \text{O} = \text{CH}_2\text{CO} + \text{OH}$	2.00E+13	0.00	4000	[31]
143	$\text{C}_2\text{H}_2\text{OH} + \text{OH} = \text{CH}_2\text{CO} + \text{H}_2\text{O}$	1.00E+13	0.00	2000	[31]

CH₄ Reactions

144	$\text{CH}_3 + \text{H} (+\text{M}) = \text{CH}_4 (+\text{M})$	1.39E+16	-0.53	536	[14]
	LOW PRESSURE LIMIT:	2.62E+33	-4.76	2440	
	TROE PARAMETERS: $a = 0.783$, $T^{***} = 74$, $T^* = 2941$, $T^{**} = 6964$				
	Enhanced Third Body Efficiencies:				
	$\text{H}_2\text{O} = 6.0$ $\text{H}_2 = 2.0$ $\text{CO}_2 = 2.0$ $\text{CO} = 1.5$ $\text{CH}_4 = 3.0$ $\text{C}_2\text{H}_6 = 3.0$ $\text{Ar} = 0.7$				
145	$\text{CH}_4 + \text{H} = \text{CH}_3 + \text{H}_2$	6.60E+08	1.62	10840	[14]
146	$\text{CH}_4 + \text{OH} = \text{CH}_3 + \text{H}_2\text{O}$	1.00E+08	1.60	3120	[14]
147	$\text{CH}_4 + \text{O} = \text{CH}_3 + \text{OH}$	1.02E+09	1.50	8600	[14]
148	$\text{CH}_4 + \text{CH}_2 = \text{CH}_3 + \text{CH}_3$	2.46E+06	2.00	8270	[14]

CH₃ Reactions

149	$\text{CH}_3 + \text{H}_2\text{O}_2 = \text{CH}_4 + \text{HO}_2$	2.45E+04	2.47	5180	[14]
150	$\text{CH}_3 + \text{HO}_2 = \text{CH}_3\text{O} + \text{OH}$	8.00E+12	0.00	0	[32]
151	$\text{CH}_3 + \text{HO}_2 = \text{CH}_4 + \text{O}_2$	1.00E+12	0.00	0	[14]
152	$\text{CH}_3 + \text{O} = \text{CH}_2\text{O} + \text{H}$	5.06E+13	0.00	0	[14]
153	$\text{CH}_3 + \text{O}_2 = \text{CH}_3\text{O} + \text{O}$	3.56E+13	0.00	30480	[14]
154	$\text{CH}_3 + \text{O}_2 = \text{CH}_2\text{O} + \text{OH}$	2.31E+12	0.00	20315	[14]
155	$\text{CH}_3 + \text{OH} = \text{CH}_2(\text{s}) + \text{H}_2\text{O}$	6.44E+17	-1.34	1417	[14]
156	$\text{CH}_3 + \text{OH} = \text{CH}_2 + \text{H}_2\text{O}$	5.60E+07	1.60	5422	[14]
157	$\text{CH}_2 + \text{H}_2 = \text{CH}_3 + \text{H}$	5.00E+05	2.00	7230	[14]
158	$\text{CH} + \text{H}_2(+\text{M}) = \text{CH}_3(+\text{M})$	1.97E+12	0.43	-370	[14]
	LOW PRESSURE LIMIT:	4.82E+25	-2.80	590	
	TROE PARAMETERS: $\alpha = 0.578$, $T^{***} = 122$, $T^* = 2535$, $T^{**} = 9365$				
	Enhanced Third Body Efficiencies:				
	$\text{H}_2 = 2.0$ $\text{H}_2\text{O} = 6.0$ $\text{CH}_4 = 2.0$ $\text{CO} = 1.5$ $\text{CO}_2 = 2.0$ $\text{C}_2\text{H}_6 = 3.0$ $\text{Ar} = 0.7$				
159	$\text{CH}_2 + \text{H}(+\text{M}) = \text{CH}_3(+\text{M})$	6.00E+14	0.00	0	[14]
	LOW PRESSURE LIMIT:	1.04E+26	-2.76	1600	
	TROE PARAMETERS: $\alpha = 0.562$, $T^{***} = 91$, $T^* = 5836$, $T^{**} = 8552$				
	Enhanced Third Body Efficiencies:				
	$\text{H}_2 = 2.0$ $\text{H}_2\text{O} = 6.0$ $\text{CH}_4 = 2.0$ $\text{CO} = 1.5$ $\text{CO}_2 = 2.0$ $\text{C}_2\text{H}_6 = 3.0$ $\text{Ar} = 0.7$				

CH₃OH Reactions

160	$\text{CH}_3 + \text{OH}(+\text{M}) = \text{CH}_3\text{OH}(+\text{M})$	2.79E+18	-1.43	1330	[14]
	LOW PRESSURE LIMIT:	4.00E+36	-5.92	3140	
	TROE PARAMETERS: $\alpha = 0.412$, $T^{***} = 195$, $T^* = 5900$, $T^{**} = 6394$				
	$\text{H}_2\text{O} = 6.0$ $\text{H}_2 = 2.0$ $\text{CO}_2 = 2.0$ $\text{CO} = 1.5$ $\text{CH}_4 = 2.0$ $\text{C}_2\text{H}_6 = 3.0$				
161	$\text{CH}_2(\text{s}) + \text{H}_2\text{O}(+\text{M}) = \text{CH}_3\text{OH}(+\text{M})$	4.82E+17	-1.16	1145	[14]
	LOW PRESSURE LIMIT:	1.88E+38	-6.36	5040	
	TROE PARAMETERS: $\alpha = 0.603$, $T^{***} = 208$, $T^* = 3922$, $T^{**} = 10180$				
	$\text{H}_2\text{O} = 6.0$ $\text{H}_2 = 2.0$ $\text{CO}_2 = 2.0$ $\text{CO} = 1.5$ $\text{CH}_4 = 2.0$ $\text{C}_2\text{H}_6 = 3.0$				
162	$\text{H} + \text{CH}_3\text{O}(+\text{M}) = \text{CH}_3\text{OH}(+\text{M})$	2.43E+12	0.52	50	[14]
	LOW PRESSURE LIMIT:	4.66E+41	-7.44	14080	
	TROE PARAMETERS: $\alpha = 0.7$, $T^{***} = 100$, $T^* = 900000$, $T^{**} = 10000$				
	$\text{H}_2 = 2.0$ $\text{H}_2\text{O} = 6.0$ $\text{CH}_4 = 2.0$ $\text{CO} = 1.5$ $\text{CO}_2 = 2.0$ $\text{C}_2\text{H}_6 = 3.0$				
163	$\text{H} + \text{CH}_2\text{OH}(+\text{M}) = \text{CH}_3\text{OH}(+\text{M})$	1.06E+12	0.50	86	[14]
	LOW PRESSURE LIMIT:	4.36E+31	-4.65	5080	
	TROE PARAMETERS: $\alpha = 0.6$, $T^{***} = 100$, $T^* = 900000$, $T^{**} = 10000$				
	Enhanced Third Body Efficiencies:				
	$\text{H}_2 = 2.0$ $\text{H}_2\text{O} = 6.0$ $\text{CH}_4 = 2.0$ $\text{CO} = 1.5$ $\text{CO}_2 = 2.0$ $\text{C}_2\text{H}_6 = 3.0$				
164	$\text{CH}_3\text{OH} + \text{OH} = \text{CH}_2\text{OH} + \text{H}_2\text{O}$	1.44E+06	2.00	-840	[14]
165	$\text{CH}_3\text{OH} + \text{OH} = \text{CH}_3\text{O} + \text{H}_2\text{O}$	6.30E+06	2.00	1500	[14]
166	$\text{CH}_3\text{OH} + \text{O} = \text{CH}_2\text{OH} + \text{OH}$	3.88E+05	2.50	3100	[14]
167	$\text{CH}_3\text{OH} + \text{O} = \text{CH}_3\text{O} + \text{OH}$	1.30E+05	2.50	5000	[14]
168	$\text{CH}_3\text{OH} + \text{H} = \text{CH}_2\text{OH} + \text{H}_2$	1.70E+07	2.10	4870	[14]
169	$\text{CH}_3\text{OH} + \text{H} = \text{CH}_3\text{O} + \text{H}_2$	4.20E+06	2.10	4870	[14]

170	$\text{CH}_3\text{OH} + \text{CH}_3 = \text{CH}_2\text{OH} + \text{CH}_4$	3.00E+07	1.50	9940	[14]
171	$\text{CH}_3\text{OH} + \text{CH}_3 = \text{CH}_3\text{O} + \text{CH}_4$	1.00E+07	1.50	9940	[14]

CH₃O Reactions

172	$\text{CH}_2\text{O} + \text{H}(+\text{M}) = \text{CH}_3\text{O}(+\text{M})$	5.40E+11	0.45	2600	[14]
	LOW PRESSURE LIMIT:	2.20E+30	-4.80	5560	
	TROE PARAMETERS: $a = 0.758$, $T^{***} = 94$, $T^* = 1555$, $T^{**} = 4200$				
	Enhanced Third Body Efficiencies:				
	$\text{H}_2\text{O} = 6.0$ $\text{H}_2 = 2.0$ $\text{CH}_4 = 2.0$ $\text{CO} = 1.5$ $\text{CO}_2 = 2.0$ $\text{C}_2\text{H}_6 = 3.0$				
173	$\text{CH}_3\text{O} + \text{H} = \text{CH}_2\text{O} + \text{H}_2$	2.00E+13	0.00	0	[14]
174	$\text{CH}_3\text{O} + \text{H} = \text{CH}_3 + \text{OH}$	1.50E+12	0.50	-110	[14]
175	$\text{CH}_3\text{O} + \text{H} = \text{CH}_2\text{OH} + \text{H}$	4.15E+07	1.63	1924	[14]
176	$\text{CH}_3\text{O} + \text{H} = \text{CH}_2(\text{s}) + \text{H}_2\text{O}$	2.62E+14	-0.23	1070	[14]
177	$\text{CH}_3\text{O} + \text{OH} = \text{CH}_2\text{O} + \text{H}_2\text{O}$	5.00E+12	0.00	0	[14]
178	$\text{CH}_3\text{O} + \text{O} = \text{CH}_2\text{O} + \text{OH}$	1.00E+13	0.00	0	[14]
179	$\text{CH}_3\text{O} + \text{O}_2 = \text{CH}_2\text{O} + \text{HO}_2$	4.28E-13	7.60	-3530	[14]

CH₂OH Reactions

180	$\text{CH}_2\text{O} + \text{H}(+\text{M}) = \text{CH}_2\text{OH}(+\text{M})$	5.40E+11	0.45	3600	[14]
	LOW PRESSURE LIMIT:	1.27E+32	-4.82	6530	
	TROE PARAMETERS: $a = 0.719$, $T^{***} = 103$, $T^* = 1291$, $T^{**} = 4160$				
	Enhanced Third Body Efficiencies:				
	$\text{H}_2\text{O} = 6.0$ $\text{H}_2 = 2.0$ $\text{CH}_4 = 2.0$ $\text{CO} = 1.5$ $\text{CO}_2 = 2.0$ $\text{C}_2\text{H}_6 = 3.0$				
181	$\text{CH}_2\text{OH} + \text{H} = \text{CH}_2\text{O} + \text{H}_2$	2.00E+13	0.00	0	[14]
182	$\text{CH}_2\text{OH} + \text{H} = \text{CH}_2(\text{s}) + \text{H}_2\text{O}$	3.28E+13	-0.09	610	[14]
183	$\text{CH}_2\text{OH} + \text{H} = \text{CH}_3 + \text{OH}$	1.65E+11	0.65	-284	[14]
184	$\text{CH}_2\text{OH} + \text{OH} = \text{CH}_2\text{O} + \text{H}_2\text{O}$	5.00E+12	0.00	0	[14]
185	$\text{CH}_2\text{OH} + \text{O} = \text{CH}_2\text{O} + \text{OH}$	1.00E+13	0.00	0	[14]
186	$\text{CH}_2\text{OH} + \text{O}_2 = \text{CH}_2\text{O} + \text{HO}_2$	1.80E+13	0.00	900	[14]

CH₂ Reactions

187	$\text{CH}_2 + \text{OH} = \text{CH} + \text{H}_2\text{O}$	1.13E+07	2.00	3000	[14]
188	$\text{CH}_2 + \text{OH} = \text{CH}_2\text{O} + \text{H}$	2.00E+13	0.00	0	[14]
189	$\text{CH}_2 + \text{O} = \text{HCO} + \text{H}$	8.00E+13	0.00	0	[14]
190	$\text{CH}_2 + \text{O}_2 = \text{CH}_2\text{O} + \text{O}$	2.40E+12	0.00	1500	[14]
191	$\text{CH}_2 + \text{O}_2 = \text{CO}_2 + \text{H} + \text{H}$	5.80E+12	0.00	1500	[14]
192	$\text{CH}_2 + \text{O}_2 = \text{CO} + \text{OH} + \text{H}$	5.00E+12	0.00	1500	[14]
193	$\text{CH}_2 + \text{CH}_3 = \text{C}_2\text{H}_4 + \text{H}$	4.00E+13	0.00	0	[14]
194	$\text{CH}_2 + \text{HCCO} = \text{C}_2\text{H}_3 + \text{CO}$	3.00E+13	0.00	0	[14]
195	$\text{CH}_2 + \text{HO}_2 = \text{CH}_2\text{O} + \text{OH}$	2.00E+13	0.00	0	[14]

CH₂(s) Reactions

196	CH ₂ (s)+CH ₄ =CH ₃ +CH ₃	1.60E+13	0.00	-570	[14]
197	CH ₂ (s)+C ₂ H ₆ =CH ₃ +C ₂ H ₅	4.00E+13	0.00	-550	[14]
198	CH ₂ (s)+O ₂ =CO+OH+H	2.80E+13	0.00	0	[14]
199	CH ₂ (s)+H ₂ =CH ₃ +H	7.00E+13	0.00	0	[14]
200	CH ₂ (s)+O=CO+H ₂	1.50E+13	0.00	0	[14]
201	CH ₂ (s)+OH=CH ₂ O+H	3.00E+13	0.00	0	[14]
202	CH ₂ (s)+H=CH+H ₂	3.00E+13	0.00	0	[14]
203	CH ₂ (s)+CO ₂ =CH ₂ O+CO	1.40E+13	0.00	0	[14]
204	CH ₂ (s)+CH ₃ =C ₂ H ₄ +H	1.20E+13	0.00	-570	[14]
205	CH ₂ (s)+N ₂ =CH ₂ +N ₂	1.50E+13	0.00	600	[14]
206	CH ₂ (s)+Ar=CH ₂ +Ar	9.00E+12	0.00	600	[14]
207	CH ₂ (s)+CO=CH ₂ +CO	9.00E+12	0.00	0	[14]
208	CH ₂ (s)+CO ₂ =CH ₂ +CO ₂	7.00E+12	0.00	0	[14]
209	CH ₂ (s)+O ₂ =CO+H ₂ O	1.20E+13	0.00	0	[14]
210	CH ₂ (s)+H ₂ O=CH ₂ O+H ₂	6.82E+10	0.25	-935	[14]
211	CH ₂ (s)+H ₂ O=CH ₂ +H ₂ O	3.00E+13	0.00	0	[14]
212	CH ₂ (s)+O=HCO+H	1.50E+13	0.00	0	[14]

CH Reactions

213	CH+H ₂ =CH ₂ +H	1.08E+14	0.00	3110	[14]
214	CH+O ₂ =HCO+O	6.71E+13	0.00	0	[14]
215	CH+O=CO+H	5.70E+13	0.00	0	[14]
216	CH+OH=HCO+H	3.00E+13	0.00	0	[14]
217	CH+H ₂ O=CH ₂ O+H	5.71E+12	0.00	-755	[14]
218	CH+CH ₃ =C ₂ H ₃ +H	3.00E+13	0.00	0	[14]
219	CH+CH ₄ =C ₂ H ₄ +H	6.00E+13	0.00	0	[14]
220	CH+CO ₂ =HCO+CO	1.90E+14	0.00	15792	[14]

CH₂O Reactions

221	CH ₂ O+M=HCO+H+M Enhanced Third Body Efficiencies: H ₂ O = 16.25 CO = 1.875 CO ₂ = 3.75 CH ₄ = 16.25 C ₂ H ₆ = 16.25	1.26E+16	0.00	77898	[10]
222	CH ₂ O+OH=HCO+H ₂ O	1.72E+09	1.18	-447	[33]
223	CH ₂ O+H=HCO+H ₂	1.26E+08	1.62	2170	[34]
224	CH ₂ O+O=HCO+OH	1.81E+13	0.00	3088	[27]
225	CH ₂ O+CH ₃ =CH ₄ +HCO	4.09E+12	0.00	8843	[10]
226	CH ₂ O+O ₂ =HCO+HO ₂	2.04E+13	0.00	39000	[33]

HCO Reactions

227	HCO+M=H+CO+M	1.86E+17	-1.00	17000	[14]
Enhanced Third Body Efficiencies:					
H ₂ O = 0.0 H ₂ = 2.0 CH ₄ = 2.0 CO ₂ = 2.0 CO = 1.5 C ₂ H ₆ = 3.0					
228	HCO+H ₂ O=H+CO+H ₂ O	1.50E+18	-1.00	17000	[14]
229	HCO+O ₂ =CO+HO ₂	1.35E+13	0.00	400	[14]
230	HCO+OH=H ₂ O+CO	5.02E+13	0.00	0	[14]
231	HCO+H=CO+H ₂	7.34E+13	0.00	0	[14]
232	HCO+O=CO+OH	3.00E+13	0.00	0	[14]
233	HCO+O=CO ₂ +H	3.00E+13	0.00	0	[14]
234	HCO+CH ₃ =CH ₄ +CO	2.65E+13	0.00	0	[14]

CO Reactions

235	CO+OH=CO ₂ +H	4.76E+07	1.23	70	[14]
236	CO+O(+M)=CO ₂ (+M)	1.80E+10	0.00	2385	[14]
LOW PRESSURE LIMIT:					
Enhanced Third Body Efficiencies:					
H ₂ = 2.0 O ₂ = 6.0 H ₂ O = 6.0 CH ₄ = 2.0 CO = 1.5 CO ₂ = 3.5 C ₂ H ₆ = 3.0 = 0.5					
237	CO+O ₂ =CO ₂ +O	2.50E+12	0.00	47800	[14]
238	CO+HO ₂ =CO ₂ +OH	1.57E+05	2.18	17943	[35]

HCOOH Reactions

239	HCOOH+M=CO+H ₂ O+M	2.09E+14	0.00	40400	[36]
240	HCOOH+M=CO ₂ +H ₂ +M	1.35E+15	0.00	60600	[36]
241	HCOOH+OH=CO+H ₂ O+OH	1.85E+07	1.50	-962	[1]
242	HCOOH+H=CO ₂ +H ₂ +H	4.24E+06	2.10	4868	[1]
243	HCOOH+H=CO+H ₂ +OH	6.06E+13	-0.35	2988	[1]
244	HCOOH+CH ₃ =CH ₄ +CO+OH	3.90E-07	5.80	2200	[1]
245	HCOOH+O=CO+OH+OH	1.77E+18	-1.90	2975	[1]

H₂/O₂ Reactions

246	OH+H ₂ =H+H ₂ O	2.16E+08	1.51	3430	[14]
247	O ₂ +H=O+OH	2.65E+16	-0.67	17041	[14]
248	O+H ₂ =OH+H	3.87E+04	2.70	6260	[14]
249	H+O ₂ +M=HO ₂ +M	8.00E+17	-0.80	0	[24]
Enhanced Third Body Efficiencies:					
H ₂ O = 16.25 CO = 1.875 CO ₂ =3.75 CH ₄ = 16.25 C ₂ H ₆ = 16.25 H ₂ =					

2.5					
250	OH+HO ₂ =H ₂ O+O ₂	1.45E+13	0.00	-500	[14]
251	H+HO ₂ =OH+OH	8.40E+13	0.00	635	[14]
252	H+HO ₂ =H ₂ +O ₂	4.48E+13	0.00	1068	[14]
253	H+HO ₂ =O+H ₂ O	3.97E+12	0.00	671	[14]
254	O+HO ₂ =O ₂ +OH	2.00E+13	0.00	0	[14]
255	OH+OH=O+H ₂ O	3.57E+04	2.40	-2110	[14]
256	H+H+M=H ₂ +M	1.00E+18	-1.00	0	[14]
Enhanced Third Body Efficiencies:					
H ₂ O = 0.0 H ₂ = 0.0 CO ₂ = 0.0 Ar = 0.63 CH ₄ = 2.0 C ₂ H ₆ = 3.0					
257	H+H+H ₂ =H ₂ +H ₂	9.00E+16	-0.60	0	[14]
258	H+H+H ₂ O=H ₂ +H ₂ O	6.00E+19	-1.25	0	[14]
259	H+H+CO ₂ =H ₂ +CO ₂	5.50E+20	-2.00	0	[14]
260	H+OH+M=H ₂ O+M	2.20E+22	-2.00	0	[14]
Enhanced Third Body Efficiencies:					
H ₂ O = 3.65 H ₂ = 0.73 CH ₄ = 2.0 C ₂ H ₆ = 3.0 Ar = 0.38					
261	H+O+M=OH+M	5.00E+17	-1.00	0	[14]
Enhanced Third Body Efficiencies:					
H ₂ O = 6.0 H ₂ = 2.0 CH ₄ = 2.0 CO = 1.5 CO ₂ = 2.0 C ₂ H ₆ = 3.0 Ar = 0.7					
262	O+O+M=O ₂ +M	1.20E+17	-1.00	0	[14]
Enhanced Third Body Efficiencies:					
H ₂ = 2.4 H ₂ O = 15.4 CH ₄ = 2.0 CO = 1.75 CO ₂ = 3.6 C ₂ H ₆ = 3.0 Ar = 0.83					
263	HO ₂ +HO ₂ =H ₂ O ₂ +O ₂	1.20E+14	0.00	12000	[14]
duplicate					
	HO ₂ +HO ₂ =H ₂ O ₂ +O ₂	1.30E+11	0.00	-1630	
duplicate					
264	OH+OH(+M)=H ₂ O ₂ (+M)	7.40E+13	-0.37	0	[14]
LOW PRESSURE LIMIT:					
		2.30E+18	-0.90	-1700	
TROE PARAMETERS: a = 0.735, T*** = 94, T* = 1756, T** = 5182					
Enhanced Third Body Efficiencies:					
H ₂ = 2.0 H ₂ O = 6.0 CO = 1.5 CO ₂ = 2.0 Ar = 0.7 CH ₄ = 2.0 C ₂ H ₆ = 3.0					
265	H ₂ O ₂ +H=HO ₂ +H ₂	1.21E+07	2.00	5200	[14]
266	H ₂ O ₂ +H=OH+H ₂ O	1.00E+13	0.00	3600	[14]
267	H ₂ O ₂ +O=OH+HO ₂	9.63E+06	2.00	4000	[14]
268	H ₂ O ₂ +OH=H ₂ O+HO ₂	2.00E+12	0.00	427	[14]
duplicate					
	H ₂ O ₂ +OH=H ₂ O+HO ₂	2.70E+18	0.00	29410	
duplicate					
C₃H₈ Reactions					
269	C ₃ H ₈ (+M)=C ₂ H ₅ +CH ₃ (+M)	1.29E+37	-5.84	97383	[37]
LOW PRESSURE LIMIT:					
		5.64E+74	-15.74	98714	
TROE PARAMETERS: a = 0.31, T*** = 50, T* = 3000, T** = 9000					
270	nC ₃ H ₇ +H(+M)=C ₃ H ₈ (+M)	3.60E+13	0.00	0	[38]

	LOW PRESSURE LIMIT:	3.01E+48	-9.32	5834	
	TROE PARAMETERS: $a = 0.498$, $T^{***} = 1314$, $T^* = 1314$, $T^{**} = 50000$				
271	$iC_3H_7 + H(+M) = C_3H_8(+M)$	2.40E+13	0.00	0	[38]
	LOW PRESSURE LIMIT:	1.70E+58	-12.08	11264	
	TROE PARAMETERS: $a = 0.649$, $T^{***} = 1213$, $T^* = 1213$, $T^{**} = 13370$				
272	$C_3H_8 + O_2 = iC_3H_7 + HO_2$	4.00E+13	0.00	47590	[39]
273	$C_3H_8 + O_2 = nC_3H_7 + HO_2$	4.00E+13	0.00	50930	[39]
274	$C_3H_8 + HO_2 = nC_3H_7 + H_2O_2$	4.76E+04	2.55	16490	[39]
275	$C_3H_8 + HO_2 = iC_3H_7 + H_2O_2$	9.64E+03	2.60	13910	[39]
276	$C_3H_8 + OH = nC_3H_7 + H_2O$	1.40E+03	2.66	527	[39]
277	$C_3H_8 + OH = iC_3H_7 + H_2O$	2.70E+04	2.39	393	[39]
278	$C_3H_8 + O = nC_3H_7 + OH$	1.90E+05	2.68	3716	[39]
279	$C_3H_8 + O = iC_3H_7 + OH$	4.76E+04	2.71	2106	[39]
280	$C_3H_8 + H = iC_3H_7 + H_2$	3.10E+13	0.00	8000	[40]
281	$C_3H_8 + H = nC_3H_7 + H_2$	9.30E+13	0.00	8000	[40]
282	$C_3H_8 + CH_3 = nC_3H_7 + CH_4$	9.04E-01	3.65	7153	[39]
283	$C_3H_8 + CH_3 = iC_3H_7 + CH_4$	1.51E+00	3.46	5480	[39]

 iC_3H_7 Reactions

284	$C_3H_6 + H(+M) = iC_3H_7(+M)$	1.33E+13	0.00	1559	[38]
	LOW PRESSURE LIMIT:	8.70E+42	-7.50	4722	
	TROE PARAMETERS: $a = 1.00$, $T^{***} = 1000$, $T^* = 645$, $T^{**} = 6844$				
285	$iC_3H_7 + H = C_2H_5 + CH_3$	1.40E+28	-3.94	15916.00	[38]
286	$iC_3H_7 + H = C_3H_6 + H_2$	3.20E+12	0.00	0	[39]
287	$iC_3H_7 + O = CH_3HCO + CH_3$	9.60E+13	0.00	0	[39]
288	$iC_3H_7 + OH = C_3H_6 + H_2O$	2.40E+13	-4.44	7724.00	[39]
289	$iC_3H_7 + O_2 = C_3H_6 + HO_2$	1.30E+11	0.00	0	[39]
290	$iC_3H_7 + HO_2 = CH_3HCO + CH_3 + OH$	2.40E+13	0.00	0	[39]
291	$iC_3H_7 + HCO = C_3H_8 + CO$	1.20E+14	0.00	0	[39]
292	$iC_3H_7 + CH_3 = C_3H_6 + CH_4$	2.20E+14	-0.68	0	[39]

 nC_3H_7 Reactions

293	$C_3H_6 + H(+M) = nC_3H_7(+M)$	1.33E+13	0.00	3260.00	[38]
	LOW PRESSURE LIMIT:	6.26E+38	-6.66	7000	
	TROE PARAMETERS: $a = 1.00$, $T^{***} = 1000$, $T^* = 1310$, $T^{**} = 48097$				
294	$C_2H_4 + CH_3 = nC_3H_7$	3.30E+11	0.00	7700	[41]
295	$nC_3H_7 + H = C_2H_5 + CH_3$	3.70E+24	-2.92	12505	[38]
296	$nC_3H_7 + H = C_3H_6 + H_2$	1.80E+12	0.00	0	[39]
297	$nC_3H_7 + O = C_2H_5 + CH_2O$	9.60E+13	0.00	0	[39]
298	$nC_3H_7 + OH = C_3H_6 + H_2O$	2.40E+13	-4.44	7724	[39]
299	$nC_3H_7 + O_2 = C_3H_6 + HO_2$	9.00E+10	0.00	0	[39]
300	$nC_3H_7 + HO_2 = C_2H_5 + CH_2O + OH$	2.40E+13	0.00	0	[39]

301	$\text{nC}_3\text{H}_7 + \text{HCO} = \text{C}_3\text{H}_8 + \text{CO}$	6.00E+13	0.00	0	[39]
302	$\text{nC}_3\text{H}_7 + \text{CH}_3 = \text{C}_3\text{H}_6 + \text{CH}_4$	1.10E+13	0.00	0	[39]

C₃H₆ Reactions

303	$\text{aC}_3\text{H}_5 + \text{H} (+\text{M}) = \text{C}_3\text{H}_6 (+\text{M})$	2.00E+14	0.00	0	[38]
	LOW PRESSURE LIMIT:	1.33E+60	-12	5968	
	TROE PARAMETERS: $\text{a} = 0.02$, $\text{T}^{***} = 1097$, $\text{T}^* = 1097$, $\text{T}^{**} = 6860$				
304	$\text{C}_2\text{H}_3 + \text{CH}_3 (+\text{M}) = \text{C}_3\text{H}_6 (+\text{M})$	2.5E+13	0	0	[38]
	LOW PRESSURE LIMIT:	6.27E+58	-11.94	9770	
	TROE PARAMETERS: $\text{a} = 0.175$, $\text{T}^{***} = 1341$, $\text{T}^* = 60000$, $\text{T}^{**} = 10140$				
305	$\text{C}_3\text{H}_6 + \text{H} = \text{C}_2\text{H}_4 + \text{CH}_3$	1.6E+22	-2.39	11180	[38]
306	$\text{C}_3\text{H}_6 + \text{H} = \text{aC}_3\text{H}_5 + \text{H}_2$	1.70E+05	2.5	2490	[42]
307	$\text{C}_3\text{H}_6 + \text{H} = \text{sC}_3\text{H}_5 + \text{H}_2$	4.00E+05	2.5	9790	[42]
308	$\text{C}_3\text{H}_6 + \text{H} = \text{pC}_3\text{H}_5 + \text{H}_2$	8.04E+05	2.5	12284	[15]
309	$\text{C}_3\text{H}_6 + \text{O} = \text{CH}_2\text{CO} + \text{CH}_3 + \text{H}$	1.20E+08	1.65	327	[42]
310	$\text{C}_3\text{H}_6 + \text{O} = \text{C}_2\text{H}_5 + \text{HCO}$	3.50E+07	1.65	-972	[42]
311	$\text{C}_3\text{H}_6 + \text{O} = \text{aC}_3\text{H}_5 + \text{OH}$	1.75E+11	0.7	5884	[42]
312	$\text{C}_3\text{H}_6 + \text{O} = \text{sC}_3\text{H}_5 + \text{OH}$	6.00E+10	0.7	7630	[42]
313	$\text{C}_3\text{H}_6 + \text{O} = \text{pC}_3\text{H}_5 + \text{OH}$	1.20E+11	0.7	8959	[15]
314	$\text{C}_3\text{H}_6 + \text{OH} = \text{aC}_3\text{H}_5 + \text{H}_2\text{O}$	3.10E+06	2	-298	[42]
315	$\text{C}_3\text{H}_6 + \text{OH} = \text{sC}_3\text{H}_5 + \text{H}_2\text{O}$	1.10E+06	2	1450	[42]
316	$\text{C}_3\text{H}_6 + \text{OH} = \text{pC}_3\text{H}_5 + \text{H}_2\text{O}$	8.04E+05	2.5	12284	[15]
317	$\text{C}_3\text{H}_6 + \text{HO}_2 = \text{aC}_3\text{H}_5 + \text{H}_2\text{O}_2$	9.60E+03	2.6	13910	[42]
318	$\text{C}_3\text{H}_6 + \text{CH}_3 = \text{aC}_3\text{H}_5 + \text{CH}_4$	2.22E+00	3.5	5675	[42]
319	$\text{C}_3\text{H}_6 + \text{CH}_3 = \text{sC}_3\text{H}_5 + \text{CH}_4$	8.40E-01	3.5	11660	[42]
320	$\text{C}_3\text{H}_6 + \text{CH}_3 = \text{pC}_3\text{H}_5 + \text{CH}_4$	1.35E+00	3.5	12848	[15]
321	$\text{CH}_2(\text{s}) + \text{C}_2\text{H}_4 = \text{C}_3\text{H}_6$	6.60E+13	0	0	[43]

aC₃H₅ Reactions

322	$\text{CH}_2(\text{s}) + \text{C}_2\text{H}_4 = \text{aC}_3\text{H}_5 + \text{H}$	1.30E+14	0	0	[15]
323	$\text{C}_2\text{H}_2 + \text{CH}_3 = \text{aC}_3\text{H}_5$	2.68E+53	-12.82	35730	[38]
324	$\text{C}_2\text{H}_3 + \text{CH}_3 = \text{aC}_3\text{H}_5 + \text{H}$	1.50E+24	-2.83	18618	[38]
325	$\text{aC}_3\text{H}_5 + \text{H} = \text{aC}_3\text{H}_4 + \text{H}_2$	1.80E+13	0	0	[42]
326	$\text{aC}_3\text{H}_5 + \text{O} = \text{CH}_2\text{CHCHO} + \text{H}$	6.00E+13	0	0	[42]
327	$\text{aC}_3\text{H}_5 + \text{OH} = \text{aC}_3\text{H}_4 + \text{H}_2\text{O}$	6.00E+12	0	0	[42]
328	$\text{aC}_3\text{H}_5 + \text{O}_2 = \text{aC}_3\text{H}_4 + \text{HO}_2$	4.99E+15	-1.4	22428	[44]
329	$\text{aC}_3\text{H}_5 + \text{O}_2 = \text{CH}_3\text{CO} + \text{CH}_2\text{O}$	1.19E+15	-1.01	20128	[44]
330	$\text{aC}_3\text{H}_5 + \text{O}_2 = \text{CH}_2\text{CHCHO} + \text{OH}$	1.82E+13	-0.41	22859	[44]
331	$\text{aC}_3\text{H}_5 + \text{HO}_2 = \text{C}_3\text{H}_6 + \text{O}_2$	3.00E+12	0	0	[15]
332	$\text{aC}_3\text{H}_5 + \text{HO}_2 = \text{CH}_2\text{CHCH}_2\text{O} + \text{OH}$	1.00E+13	0	0	[15]
333	$\text{aC}_3\text{H}_5 + \text{HCO} = \text{C}_3\text{H}_6 + \text{CO}$	6.00E+13	0	0	[42]
334	$\text{aC}_3\text{H}_5 + \text{CH}_3 = \text{aC}_3\text{H}_4 + \text{CH}_4$	3.02E+12	-0.32	-131	[42]

335	$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_5 = \text{aC}_3\text{H}_5 + \text{CH}_3$	3.90E+32	-5.22	19747	[38]
336	$\text{aC}_3\text{H}_5 = \text{sC}_3\text{H}_5$	7.06E+56	-14.08	75868	[38]

sC₃H₅ Reactions

337	$\text{C}_2\text{H}_2 + \text{CH}_3 = \text{sC}_3\text{H}_5$	4.99E+22	-4.39	18850	[38]
338	$\text{sC}_3\text{H}_5 + \text{H} = \text{pC}_3\text{H}_4 + \text{H}_2$	3.34E+12	0	0	[38]
339	$\text{sC}_3\text{H}_5 + \text{O} = \text{CH}_2\text{CO} + \text{CH}_3$	6.00E+13	0	0	[38]
340	$\text{sC}_3\text{H}_5 + \text{OH} = \text{CH}_2\text{CO} + \text{CH}_3 + \text{H}$	5.00E+12	0	0	[38]
341	$\text{sC}_3\text{H}_5 + \text{O}_2 = \text{CH}_3\text{CO} + \text{CH}_2\text{O}$	1.00E+11	0	0	[38]
342	$\text{sC}_3\text{H}_5 + \text{HO}_2 = \text{CH}_2\text{CO} + \text{CH}_3 + \text{OH}$	2.00E+13	0	0	[38]
343	$\text{sC}_3\text{H}_5 + \text{HCO} = \text{C}_3\text{H}_6 + \text{CO}$	9.00E+13	0	0	[38]
344	$\text{sC}_3\text{H}_5 + \text{CH}_3 = \text{pC}_3\text{H}_4 + \text{CH}_4$	1.00E+11	0	0	[38]

pC₃H₅ Reactions

345	$\text{pC}_3\text{H}_5 + \text{O}_2 = \text{CH}_3\text{HCO} + \text{HCO}$	1.09E+23	-3.29	3892	[15]
346	$\text{pC}_3\text{H}_5 + \text{O}_2 = \text{CH}_3\text{CHCO} + \text{H} + \text{O}$	1.60E+15	-0.78	3135	[15]
347	$\text{pC}_3\text{H}_5 + \text{O} = \text{CH}_3\text{CHCO} + \text{H}$	1.00E+14	0	0	[15]
348	$\text{pC}_3\text{H}_5 + \text{H} = \text{pC}_3\text{H}_4 + \text{H}_2$	2.00E+13	0	0	[15]
349	$\text{pC}_3\text{H}_5 + \text{OH} = \text{pC}_3\text{H}_4 + \text{H}_2\text{O}$	1.00E+13	0	0	[15]
350	$\text{pC}_3\text{H}_5 + \text{H} = \text{aC}_3\text{H}_5 + \text{H}$	1.00E+14	0	0	[15]

CH₂CHCH₂O Reactions

351	$\text{CH}_2\text{CHCH}_2\text{O} + \text{O}_2 = \text{CH}_2\text{CHCHO} + \text{HO}_2$	4.00E+10	0	1100	[1]
352	$\text{CH}_2\text{CHCH}_2\text{O} + \text{CO} = \text{aC}_3\text{H}_5 + \text{CO}_2$	4.68E+02	3.16	5380	[1]
353	$\text{CH}_2\text{CHCHO} + \text{H}(+\text{M}) = \text{CH}_2\text{CHCH}_2\text{O}(+\text{M})$	5.40E+11	0.45	2600	[1]
	LOW PRESSURE LIMIT:	1.50E+30	-4.80	5560	[1]
	TROE PARAMETERS: a = 0.78, T*** = 94, T* = 1555, T** = 4200				
	Enhanced Third Body Efficiencies:				
	$\text{H}_2\text{O} = 5.0$				

CH₂CHCHO Reactions

354	$\text{C}_2\text{H}_3 + \text{HCO} = \text{CH}_2\text{CHCHO}$	1.80E+13	0	0	[42]
355	$\text{CH}_2\text{CHCHO} + \text{H} = \text{C}_2\text{H}_4 + \text{HCO}$	1.08E+12	0.45	1820	[38]
356	$\text{CH}_2\text{CHCHO} + \text{O} = \text{C}_2\text{H}_3 + \text{CO} + \text{OH}$	3.00E+13	0	3540	[38]
357	$\text{CH}_2\text{CHCHO} + \text{O} = \text{CH}_2\text{CO} + \text{CH}_2\text{O}$	1.90E+07	1.8	220	[38]
358	$\text{CH}_2\text{CHCHO} + \text{OH} = \text{C}_2\text{H}_3 + \text{CO} + \text{H}_2\text{O}$	3.43E+09	1.18	-447	[38]
359	$\text{CH}_2\text{CHCHO} + \text{OH} = \text{CH}_2\text{CHCO} + \text{H}_2\text{O}$	1.00E+13	0	0	[15]
360	$\text{CH}_2\text{CHCHO} + \text{O} = \text{CH}_2\text{CHCO} + \text{OH}$	7.24E+12	0	1970	[15]
361	$\text{CH}_2\text{CHCHO} + \text{H} = \text{CH}_2\text{CHCO} + \text{H}_2$	3.98E+13	0	4200	[15]
362	$\text{CH}_2\text{CHCHO} + \text{O}_2 = \text{CH}_2\text{CHCO} + \text{HO}_2$	3.00E+13	0	36000	[15]

CH₃CHCO Reactions

363	CH ₃ CHCO+OH=CH ₂ CHCO+H ₂ O	4.00E+06	2	0	[15]
364	CH ₃ CHCO+O=CH ₂ CHCO+OH	7.60E+08	1.5	8500	[15]
365	CH ₃ CHCO+H=CH ₂ CHCO+H ₂	2.00E+05	2.5	2500	[15]
366	CH ₃ CHCO+H=C ₂ H ₅ +CO	2.00E+13	0	2000	[15]
367	CH ₃ CHCO+O=CH ₃ +HCO+CO	3.00E+07	2	0	[15]

CH₂CHCO Reactions

368	CH ₂ CHCO=C ₂ H ₃ +CO	1.00E+14	0	34000	[15]
369	CH ₂ CHCO+O=C ₂ H ₃ +CO ₂	1.00E+14	0	0	[15]

pC₃H₄ Reactions

370	pC ₃ H ₄ =cC ₃ H ₄	1.20E+44	-9.92	69250	[38]
371	pC ₃ H ₄ =aC ₃ H ₄	5.15E+60	-13.93	91117	[38]
372	C ₃ H ₃ +H=pC ₃ H ₄	1.50E+13	0	0	[38]
373	pC ₃ H ₄ +H=C ₃ H ₃ +H ₂	1.30E+06	2	5500	[38]
374	pC ₃ H ₄ +H=aC ₃ H ₄ +H	6.27E+17	-0.91	10079	[38]
375	pC ₃ H ₄ +H=sC ₃ H ₅	1.66E+47	-10.58	13690	[38]
376	pC ₃ H ₄ +H=aC ₃ H ₅	4.91E+60	-14.37	31644	[38]
377	pC ₃ H ₄ +O=HCCO+CH ₃	7.30E+12	0	2250	[38]
378	pC ₃ H ₄ +O=C ₂ H ₄ +CO	1.00E+13	0	2250	[38]
379	pC ₃ H ₄ +OH=C ₃ H ₃ +H ₂ O	1.00E+06	2	100	[45]
380	pC ₃ H ₄ +CH ₃ =C ₃ H ₃ +CH ₄	1.80E+12	0	7700	[38]
381	pC ₃ H ₄ +C ₂ H=C ₃ H ₃ +C ₂ H ₂	1.00E+13	0	0	[45]

aC₃H₄ Reactions

382	cC ₃ H ₄ =aC ₃ H ₄	4.89E+41	-9.17	49594	[38]
383	C ₃ H ₃ +H(+M)=aC ₃ H ₄ (+M)	2.50E+12	0	0	[38]
384	CH ₃ +C ₂ H ₂ =aC ₃ H ₄ +H	5.14E+09	0.86	22153	[38]
385	aC ₃ H ₄ +H=C ₃ H ₃ +H ₂	1.30E+06	2	5500	[38]
386	aC ₃ H ₄ +H=aC ₃ H ₅	1.52E+59	-13.54	26949	[38]
387	aC ₃ H ₄ +H=sC ₃ H ₅	9.46E+42	-9.43	11190	[38]
388	aC ₃ H ₄ +O=C ₂ H ₄ +CO	2.00E+07	1.8	1000	[38]
389	aC ₃ H ₄ +OH=C ₃ H ₃ +H ₂ O	5.30E+06	2	2000	[45]
390	aC ₃ H ₄ +CH ₃ =C ₃ H ₃ +CH ₄	1.30E+12	0	7700	[38]
391	aC ₃ H ₄ +C ₂ H=C ₃ H ₃ +C ₂ H ₂	1.00E+13	0	0	[45]

C₃H₃ Reactions

392	$\text{C}_3\text{H}_2 + \text{H} = \text{C}_3\text{H}_3$	1.00E+13	0	0	[38]
393	$\text{C}_3\text{H}_3 + \text{H} = \text{C}_3\text{H}_2 + \text{H}_2$	5.00E+13	0	1000	[46]
394	$\text{C}_3\text{H}_3 + \text{O} = \text{CH}_2\text{O} + \text{C}_2\text{H}$	2.00E+13	0	0	[47]
395	$\text{C}_3\text{H}_3 + \text{OH} = \text{C}_3\text{H}_2 + \text{H}_2\text{O}$	2.00E+13	0	0	[47]
396	$\text{C}_3\text{H}_3 + \text{O}_2 = \text{CH}_2\text{CO} + \text{HCO}$	3.00E+10	0	2868	[48]
397	$\text{C}_3\text{H}_3 + \text{HO}_2 = \text{C}_2\text{H}_3 + \text{CO} + \text{OH}$	8.00E+11	0	0	[38]
398	$\text{C}_3\text{H}_3 + \text{HO}_2 = \text{aC}_3\text{H}_4 + \text{O}_2$	3.00E+11	0	0	[38]
399	$\text{C}_3\text{H}_3 + \text{HO}_2 = \text{pC}_3\text{H}_4 + \text{O}_2$	2.50E+12	0	0	[38]
400	$\text{C}_3\text{H}_3 + \text{HCO} = \text{aC}_3\text{H}_4 + \text{CO}$	2.50E+13	0	0	[45]
401	$\text{C}_3\text{H}_3 + \text{HCO} = \text{pC}_3\text{H}_4 + \text{CO}$	2.50E+13	0	0	[45]
402	$\text{C}_2\text{H} + \text{CH}_3 = \text{C}_3\text{H}_3 + \text{H}$	2.41E+13	0	0	[33]
403	$\text{C}_2\text{H}_2 + \text{CH}_2 = \text{C}_3\text{H}_3 + \text{H}$	1.20E+13	0	6620	[49]
404	$\text{C}_2\text{H}_2 + \text{CH}_2(\text{s}) = \text{C}_3\text{H}_3 + \text{H}$	2.00E+13	0	0	[45]
405	$\text{HCCO} + \text{C}_2\text{H}_2 = \text{C}_3\text{H}_3 + \text{CO}$	1.00E+11	0	3000	[47]

C₃H₂ Reactions

406	$\text{C}_3\text{H}_2 + \text{O} = \text{C}_2\text{H}_2 + \text{CO}$	6.80E+13	0	0	[50]
407	$\text{C}_3\text{H}_2 + \text{OH} = \text{C}_2\text{H}_2 + \text{HCO}$	6.80E+13	0	0	[50]
408	$\text{C}_3\text{H}_2 + \text{O}_2 = \text{HCCO} + \text{CO} + \text{H}$	2.00E+12	0	1000	[46]
409	$\text{CH} + \text{C}_2\text{H}_2 = \text{C}_3\text{H}_2 + \text{H}$	3.00E+13	0	0	[50]

1-C₄H₈ Reactions

410	$\text{C}_4\text{H}_7 + \text{H} (+\text{M}) = 1\text{-C}_4\text{H}_8 (+\text{M})$	3.60E+13	0	0	[38]
	LOW PRESSURE LIMIT:	3.01E+48	-9.32	5834	
	TROE PARAMETERS: $\text{a} = 0.498$, $\text{T}^{***} = 1314$, $\text{T}^* = 1314$, $\text{T}^{**} = 5000$				
411	$\text{aC}_3\text{H}_5 + \text{CH}_3 (+\text{M}) = 1\text{-C}_4\text{H}_8 (+\text{M})$	1.00E+14	-0.32	-262	[38]
	LOW PRESSURE LIMIT:	3.51E+60	-12.97	6000	
	TROE PARAMETERS: $\text{a} = 0.896$, $\text{T}^{***} = 60000$, $\text{T}^* = 1606$, $\text{T}^{**} = 6118$				
412	$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_5 (+\text{M}) = 1\text{-C}_4\text{H}_8 (+\text{M})$	1.50E+13	0	0	[38]
	LOW PRESSURE LIMIT:	1.55E+56	-11.79	8985	
	TROE PARAMETERS: $\text{a} = 0.198$, $\text{T}^{***} = 2278$, $\text{T}^* = 60000$, $\text{T}^{**} = 5723$				
413	$1\text{-C}_4\text{H}_8 + \text{H} = \text{C}_2\text{H}_4 + \text{C}_2\text{H}_5$	1.60E+22	-2.39	11180	[38]
414	$1\text{-C}_4\text{H}_8 + \text{H} = \text{C}_3\text{H}_6 + \text{CH}_3$	3.20E+22	-2.39	11180	[38]
415	$1\text{-C}_4\text{H}_8 + \text{H} = \text{C}_4\text{H}_7 + \text{H}_2$	6.50E+05	2.54	6756	[38]
416	$1\text{-C}_4\text{H}_8 + \text{O} = \text{nC}_3\text{H}_7 + \text{HCO}$	3.30E+08	1.45	-402	[38]
417	$1\text{-C}_4\text{H}_8 + \text{O} = \text{C}_4\text{H}_7 + \text{OH}$	1.50E+13	0	5760	[38]
	duplicate				
	$1\text{-C}_4\text{H}_8 + \text{O} = \text{C}_4\text{H}_7 + \text{OH}$	2.60E+13	0	4470	[38]
	duplicate				
418	$1\text{-C}_4\text{H}_8 + \text{OH} = \text{C}_4\text{H}_7 + \text{H}_2\text{O}$	7.00E+02	2.66	527	[38]
419	$1\text{-C}_4\text{H}_8 + \text{O}_2 = \text{C}_4\text{H}_7 + \text{HO}_2$	2.00E+13	0	50930	[38]
420	$1\text{-C}_4\text{H}_8 + \text{HO}_2 = \text{C}_4\text{H}_7 + \text{H}_2\text{O}_2$	1.50E+11	0	14900	[38]

421	$1\text{-C}_4\text{H}_8 + \text{CH}_3 = \text{C}_4\text{H}_7 + \text{CH}_4$	4.50E-01	3.65	7153	[38]
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C₄H₇ Reactions (CH₂CHCH₂CH₂)

422	$\text{C}_4\text{H}_7 = 1,3\text{-C}_4\text{H}_6 + \text{H}$	2.28E+52	-12.01	51230	[38]
423	$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_4 = \text{C}_4\text{H}_7$	7.93E+38	-8.47	14220	[38]
424	$\text{C}_4\text{H}_7 + \text{H} = \text{CH}_3 + \text{aC}_3\text{H}_5$	2.00E+21	-2	11000	[38]
425	$\text{C}_4\text{H}_7 + \text{H} = 1,3\text{-C}_4\text{H}_6 + \text{H}_2$	1.80E+12	0	0	[38]
426	$\text{C}_4\text{H}_7 + \text{O}_2 = 1,3\text{-C}_4\text{H}_6 + \text{HO}_2$	1.00E+11	0	0	[38]
427	$\text{C}_4\text{H}_7 + \text{HO}_2 = \text{CH}_2\text{O} + \text{OH} + \text{aC}_3\text{H}_5$	2.40E+13	0	0	[38]
428	$\text{C}_4\text{H}_7 + \text{HCO} = 1\text{-C}_4\text{H}_8 + \text{CO}$	6.00E+13	0	0	[38]
429	$\text{C}_4\text{H}_7 + \text{CH}_3 = 1,3\text{-C}_4\text{H}_6 + \text{CH}_4$	1.10E+13	0	0	[38]

1,3-C₄H₆ Reactions

430	$\text{C}_2\text{H}_4 + \text{C}_2\text{H}_3 = 1,3\text{-C}_4\text{H}_6 + \text{H}$	5.00E+11	0	7313	[33]
431	$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_3 = 1,3\text{-C}_4\text{H}_6$	7.00E+57	-13.82	17629	[45]
432	$1,3\text{-C}_4\text{H}_6 = \text{iC}_4\text{H}_5 + \text{H}$	8.20E+51	-10.92	118410	[45]
433	$1,3\text{-C}_4\text{H}_6 = \text{nC}_4\text{H}_5 + \text{H}$	3.50E+61	-13.87	129680	[45]
434	$1,3\text{-C}_4\text{H}_6 + \text{H} = \text{nC}_4\text{H}_5 + \text{H}_2$	1.33E+06	2.53	12240	[45]
435	$1,3\text{-C}_4\text{H}_6 + \text{H} = \text{iC}_4\text{H}_5 + \text{H}_2$	6.65E+05	2.53	9240	[45]
436	$1,3\text{-C}_4\text{H}_6 + \text{H} = \text{pC}_3\text{H}_4 + \text{CH}_3$	7.00E+12	0	2000	[51]
437	$1,3\text{-C}_4\text{H}_6 + \text{O} = \text{aC}_3\text{H}_5 + \text{HCO}$	6.00E+08	1.45	-860	[52]
438	$1,3\text{-C}_4\text{H}_6 + \text{OH} = \text{nC}_4\text{H}_5 + \text{H}_2\text{O}$	6.20E+06	2	3430	[45]
439	$1,3\text{-C}_4\text{H}_6 + \text{OH} = \text{iC}_4\text{H}_5 + \text{H}_2\text{O}$	3.10E+06	2	430	[45]
440	$1,3\text{-C}_4\text{H}_6 = \text{C}_2\text{H}_4 + \text{C}_2\text{H}_2$	1.00E+14	0	75000	[32]
441	$1,3\text{-C}_4\text{H}_6 + \text{o} = \text{>OC}_4\text{H}_6$	3.00E+13	0	80	[32]

OC₄H₆ Reactions

442	$\text{OC}_4\text{H}_6 = \text{>CH}_2\text{CO} + \text{C}_2\text{H}_4$	5.00E+14	1	78000	[32]
443	$\text{OC}_4\text{H}_6 = \text{>C}_3\text{H}_6 + \text{CO}$	2.00E+13	0	57000	[32]

1,2-C₄H₆ Reactions

444	$\text{C}_3\text{H}_3 + \text{CH}_3 (+\text{M}) = 1,2\text{-C}_4\text{H}_6 (+\text{M})$	1.50E+12	0	0	[38]
	LOW PRESSURE LIMIT:	2.60E+57	-11.94	9770	
	TROE PARAMETERS: a = 0.175, T*** = 1341, T* = 60000, T** = 9770				
445	$1,2\text{-C}_4\text{H}_6 + \text{H} = 1,3\text{-C}_4\text{H}_6 + \text{H}$	2.00E+13	0	4000	[45]
446	$1,2\text{-C}_4\text{H}_6 + \text{H} = \text{iC}_4\text{H}_5 + \text{H}_2$	1.70E+05	2.5	2490	[45]
447	$1,2\text{-C}_4\text{H}_6 + \text{H} = \text{aC}_3\text{H}_4 + \text{CH}_3$	2.00E+13	0	2000	[45]
448	$1,2\text{-C}_4\text{H}_6 + \text{H} = \text{pC}_3\text{H}_4 + \text{CH}_3$	2.00E+13	0	2000	[51]
449	$1,2\text{-C}_4\text{H}_6 + \text{O} = \text{CH}_2\text{CO} + \text{C}_2\text{H}_4$	1.20E+08	1.65	327	[38]
450	$1,2\text{-C}_4\text{H}_6 + \text{O} = \text{iC}_4\text{H}_5 + \text{OH}$	1.80E+11	0.7	5880	[38]

451	$1,2\text{-C}_4\text{H}_6 + \text{OH} = \text{i-C}_4\text{H}_5 + \text{H}_2\text{O}$	3.10E+06	2	-298	[38]
452	$1,2\text{-C}_4\text{H}_6 = 1,3\text{-C}_4\text{H}_6$	2.50E+13	0	62290	[53]

n-C₄H₅ Reactions

453	$\text{C}_2\text{H}_2 + \text{C}_2\text{H}_3 = \text{n-C}_4\text{H}_5$	1.10E+32	-7.33	6200	[45]
454	$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_3 = \text{n-C}_4\text{H}_5 + \text{H}$	1.10E+24	-3.28	12395	[45]
455	$\text{n-C}_4\text{H}_5 (+\text{M}) = \text{C}_4\text{H}_4 + \text{H} (+\text{M})$	1.00E+14	0	37000	[19]
	LOW PRESSURE LIMIT:	1.00E+14	0	30000	
456	$\text{n-C}_4\text{H}_5 = \text{i-C}_4\text{H}_5$	1.30E+62	-16.38	49600	[54]
457	$\text{n-C}_4\text{H}_5 + \text{H} = \text{i-C}_4\text{H}_5 + \text{H}$	1.00E+36	-6.26	17486	[45]
458	$\text{n-C}_4\text{H}_5 + \text{O}_2 = \text{C}_2\text{H}_4 + \text{CO} + \text{HCO}$	4.16E+10	0	2.50E+03	[55]
459	$\text{n-C}_4\text{H}_5 + \text{H} = \text{C}_4\text{H}_4 + \text{H}_2$	1.50E+13	0	0	[45]
460	$\text{n-C}_4\text{H}_5 + \text{OH} = \text{C}_4\text{H}_4 + \text{H}_2\text{O}$	2.50E+12	0	0	[45]
461	$\text{n-C}_4\text{H}_5 + \text{HCO} = 1,3\text{-C}_4\text{H}_6 + \text{CO}$	9.00E+13	0	0	[45]
462	$\text{n-C}_4\text{H}_5 + \text{O} = \text{CH}_2\text{CO} + \text{C}_2\text{H}_3$	3.00E+13	0	0	^a

i-C₄H₅ Reactions

463	$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_3 = \text{i-C}_4\text{H}_5 + \text{H}$	1.50E+30	-4.95	12958	[45]
464	$\text{C}_2\text{H}_2 + \text{C}_2\text{H}_3 = \text{i-C}_4\text{H}_5$	2.10E+36	-8.78	9100	[45]
465	$\text{i-C}_4\text{H}_5 (+\text{M}) = \text{C}_4\text{H}_4 + \text{H} (+\text{M})$	1.00E+14	0	50000	[19]
	LOW PRESSURE LIMIT:	2.00E+15	0	42000	
466	$\text{i-C}_4\text{H}_5 + \text{O} = \text{CH}_2\text{CO} + \text{C}_2\text{H}_3$	3.00E+13	0	0	^a
467	$\text{i-C}_4\text{H}_5 + \text{H} = \text{C}_4\text{H}_4 + \text{H}_2$	3.00E+13	0	0	[45]
468	$\text{i-C}_4\text{H}_5 + \text{OH} = \text{C}_4\text{H}_4 + \text{H}_2\text{O}$	5.00E+12	0	0	[45]
469	$\text{i-C}_4\text{H}_5 + \text{C}_2\text{H} = \text{C}_3\text{H}_3 + \text{C}_3\text{H}_3$	4.00E+12	0	0	[57]
470	$\text{i-C}_4\text{H}_5 + \text{H} = \text{C}_3\text{H}_3 + \text{CH}_3$	5.00E+13	0	0	^a
471	$\text{i-C}_4\text{H}_5 + \text{O}_2 = \text{CH}_2\text{CO} + \text{CH}_2\text{HCO}$	7.86E+16	-1.8	0	[45]
472	$\text{i-C}_4\text{H}_5 + \text{HCO} = 1,3\text{-C}_4\text{H}_6 + \text{CO}$	9.00E+13	0	0	[45]

C₄H₄ Reactions

473	$\text{C}_4\text{H}_4 + \text{H} = \text{n-C}_4\text{H}_3 + \text{H}_2$	6.65E+05	2.53	12240	[45]
474	$\text{C}_4\text{H}_4 + \text{H} = \text{i-C}_4\text{H}_3 + \text{H}_2$	3.33E+05	2.53	9240	[45]
475	$\text{C}_4\text{H}_4 + \text{OH} = \text{n-C}_4\text{H}_3 + \text{H}_2\text{O}$	3.10E+07	2	3430	[45]
476	$\text{C}_4\text{H}_4 + \text{OH} = \text{i-C}_4\text{H}_3 + \text{H}_2\text{O}$	1.55E+07	2	430	[45]
477	$\text{C}_4\text{H}_4 + \text{O} = \text{C}_2\text{H}_3 + \text{HCCO}$	3.00E+13	0	1808	^a
478	$\text{C}_2\text{H}_2 + \text{C}_2\text{H}_3 = \text{C}_4\text{H}_4 + \text{H}$	5.00E+14	-0.71	6700	[45]
479	$\text{C}_2\text{H}_4 + \text{C}_2\text{H} = \text{C}_4\text{H}_4 + \text{H}$	1.20E+13	0	0	[45]
480	$\text{C}_3\text{H}_3 + \text{CH}_2 = \text{C}_4\text{H}_4 + \text{H}$	2.00E+13	0	0	[45]
481	$\text{C}_3\text{H}_2 + \text{CH}_3 = \text{C}_4\text{H}_4 + \text{H}$	5.00E+12	0	0	[45]

i-C₄H₃ Reactions

482	$\text{C}_2\text{H}_2 + \text{C}_2\text{H} = \text{i-C}_4\text{H}_3$	4.10E+33	-7.31	4600	[45]
483	$\text{C}_3\text{H}_3 + \text{CH} = \text{i-C}_4\text{H}_3 + \text{H}$	5.00E+13	0	0	[45]
484	$\text{i-C}_4\text{H}_3(+\text{M}) = \text{C}_4\text{H}_2 + \text{H}(+\text{M})$	1.00E+14	0	55000	[19]
	LOW PRESSURE LIMIT:	2.00E+15	0	48000	
485	$\text{i-C}_4\text{H}_3 + \text{H} = \text{C}_4\text{H}_2 + \text{H}_2$	1.21E+13	0	0	[10, 56]
486	$\text{i-C}_4\text{H}_3 + \text{H} = \text{C}_4\text{H}_4$	4.20E+44	-10.27	7890	[45]
487	$\text{i-C}_4\text{H}_3 + \text{OH} = \text{C}_4\text{H}_2 + \text{H}_2\text{O}$	5.00E+12	0	0	[45]
488	$\text{i-C}_4\text{H}_3 + \text{O}_2 = \text{HCCO} + \text{CH}_2\text{CO}$	7.86E+16	-1.8	0	[45]
489	$\text{i-C}_4\text{H}_3 + \text{H} = \text{C}_2\text{H}_2 + \text{C}_2\text{H}_2$	2.40E+19	-1.6	2800	[45]
490	$\text{i-C}_4\text{H}_3 + \text{O} = \text{CH}_2\text{CO} + \text{C}_2\text{H}$	2.00E+13	0	0	[19]
491	$\text{i-C}_4\text{H}_3 + \text{O} = \text{H}_2\text{C}_4\text{O} + \text{H}$	2.00E+13	0	0	[19]

n-C₄H₃ Reactions

492	$\text{C}_2\text{H}_2 + \text{C}_2\text{H} = \text{n-C}_4\text{H}_3$	1.10E+30	-6.3	2790	[45]
493	$\text{n-C}_4\text{H}_3 = \text{i-C}_4\text{H}_3$	3.70E+61	-15.81	54890	[45]
494	$\text{n-C}_4\text{H}_3 + \text{H} = \text{i-C}_4\text{H}_3 + \text{H}$	2.40E+11	0.79	2410	[45]
495	$\text{n-C}_4\text{H}_3(+\text{M}) = \text{C}_4\text{H}_2 + \text{H}(+\text{M})$	1.00E+14	0	36000	[19]
	LOW PRESSURE LIMIT:	1.00E+14	0	30000	
496	$\text{n-C}_4\text{H}_3 + \text{H} = \text{C}_4\text{H}_2 + \text{H}_2$	1.50E+13	0	0	[45]
497	$\text{n-C}_4\text{H}_3 + \text{H} = \text{C}_4\text{H}_4$	1.10E+42	-9.65	7000	[45]
498	$\text{n-C}_4\text{H}_3 + \text{OH} = \text{C}_4\text{H}_2 + \text{H}_2\text{O}$	2.50E+12	0	0	[45]
499	$\text{n-C}_4\text{H}_3 + \text{O}_2 = \text{CH}_2\text{CO} + \text{HCCO}$	1.00E+12	0	0	^a
500	$\text{n-C}_4\text{H}_3 + \text{O} = \text{CH}_2\text{CO} + \text{C}_2\text{H}$	2.00E+13	0	0	^a
501	$\text{n-C}_4\text{H}_3 + \text{O} = \text{H}_2\text{C}_4\text{O} + \text{H}$	2.00E+13	0	0	^a
502	$\text{n-C}_4\text{H}_3 + \text{H} = \text{C}_2\text{H}_2 + \text{C}_2\text{H}_2$	1.60E+19	-1.6	2220	[45]
503	$\text{C}_3\text{H}_2 + \text{CH}_2 = \text{n-C}_4\text{H}_3 + \text{H}$	5.00E+13	0	0	[45]
504	$\text{C}_3\text{H}_2 + \text{HCCO} = \text{n-C}_4\text{H}_3 + \text{CO}$	1.00E+13	0	0	[45]

C₄H₂ Reactions

505	$\text{C}_2\text{H}_2 + \text{C}_2\text{H} = \text{C}_4\text{H}_2 + \text{H}$	9.60E+13	0	0	[45]
506	$\text{C}_4\text{H}_2 + \text{H} = \text{C}_4\text{H} + \text{H}_2$	6.03E+13	0	27820	[10, 56]
507	$\text{C}_4\text{H}_2 + \text{OH} = \text{C}_4\text{H} + \text{H}_2\text{O}$	3.37E+07	2	14000	[45]
508	$\text{C}_4\text{H}_2 + \text{O} = \text{C}_3\text{H}_2 + \text{CO}$	2.70E+13	0	1720	[45]
509	$\text{C}_4\text{H}_2 + \text{O} = \text{C}_2\text{H} + \text{HCCO}$	1.35E+07	2	1900	^a
510	$\text{C}_4\text{H}_2 + \text{OH} = \text{H}_2\text{C}_4\text{O} + \text{H}$	6.66E+12	0	-410	[58]
511	$\text{C}_3\text{H}_2 + \text{CH} = \text{C}_4\text{H}_2 + \text{H}$	5.00E+13	0	0	[45]

H₂C₄O Reactions

512	$\text{H}_2\text{C}_4\text{O} + \text{H} = \text{C}_2\text{H}_2 + \text{HCCO}$	5.00E+13	0	3000	[19]
513	$\text{H}_2\text{C}_4\text{O} + \text{OH} = \text{CH}_2\text{CO} + \text{HCCO}$	1.00E+07	2	2000	[19]
514	$\text{H}_2\text{C}_4\text{O} + \text{O} = \text{CH}_2\text{CO} + \text{C}_2\text{O}$	2.10E+07	1.9	200	[45]

C₄H Reactions

515	$\text{C}_4\text{H} + \text{H} (+\text{M}) = \text{C}_4\text{H}_2 (+\text{M})$	1.00E+17	-1	0	[45]
	LOW PRESSURE LIMIT:	3.75E+33	-4.8	1900	
	TROE PARAMETERS: $a = 0.6464$, $T^{***} = 132$, $T^* = 1315$, $T^{**} = 5566$				
	Enhanced Third Body Efficiencies:				
	$\text{H}_2 = 2.0$ $\text{H}_2\text{O} = 6.0$ $\text{CO} = 1.5$ $\text{CO}_2 = 2.0$ $\text{Ar} = 0.7$ $\text{CH}_4 = 2.0$ $\text{C}_2\text{H}_6 = 3.0$				
516	$\text{C}_4\text{H} + \text{O} = \text{C}_2\text{H} + \text{C}_2\text{O}$	5.00E+13	0	0	[45]
517	$\text{C}_4\text{H} + \text{O}_2 = \text{HCCO} + \text{C}_2\text{O}$	5.00E+13	0	1500	[45]

C₅H₈ Reactions

518	$\text{C}_5\text{H}_8 = \text{C}_5\text{H}_6 + \text{H}_2$	1.00E+13	0	60000	[59]
519	$\text{aC}_3\text{H}_5 + \text{C}_2\text{H}_4 = \text{C}_5\text{H}_8 + \text{H}$	1.20E+10	0	11488	[60]
520	$\text{C}_5\text{H}_8 + \text{H} = \text{C}_5\text{H}_7(\text{B}) + \text{H}_2$	9.00E+06	2	5000	[61]
521	$\text{C}_5\text{H}_8 + \text{H} = \text{C}_5\text{H}_7(\text{A}) + \text{H}_2$	1.08E+05	2.5	-1900	[61]
522	$\text{C}_5\text{H}_8 + \text{H} = \text{C}_5\text{H}_7(\text{C}) + \text{H}_2$	8.20E+05	2	9800	[61]
523	$\text{C}_5\text{H}_8 + \text{OH} = \text{C}_5\text{H}_7(\text{B}) + \text{H}_2\text{O}$	2.60E+06	2	-800	[61]
524	$\text{C}_5\text{H}_8 + \text{OH} = \text{C}_5\text{H}_7(\text{A}) + \text{H}_2\text{O}$	2.00E+06	2	-1500	[61]
525	$\text{C}_5\text{H}_8 + \text{OH} = \text{C}_5\text{H}_7(\text{C}) + \text{H}_2\text{O}$	2.20E+06	2	1400	[61]
526	$\text{C}_5\text{H}_8 + \text{O} = \text{C}_5\text{H}_7(\text{B}) + \text{OH}$	2.60E+13	0	5200	[61]
527	$\text{C}_5\text{H}_8 + \text{O} = \text{C}_5\text{H}_7(\text{A}) + \text{OH}$	1.70E+11	0.7	3200	[61]
528	$\text{C}_5\text{H}_8 + \text{O} = \text{C}_5\text{H}_7(\text{C}) + \text{OH}$	1.20E+11	0.7	7600	[61]

C₅H₇(A) Reactions

529	$\text{C}_5\text{H}_7(\text{A}) = \text{C}_5\text{H}_6 + \text{H}$	3.00E+13	0	50500	[61]
530	$\text{C}_5\text{H}_7(\text{A}) = 1,3\text{-C}_5\text{H}_7\text{-5-yl}$	1.30E+13	0	35000	[61]
531	$1,3\text{-C}_5\text{H}_7\text{-3-yl} = 1,3\text{-C}_5\text{H}_7\text{-5-yl}$	5.00E+13	0	37000	[61]
532	$1,4\text{-C}_5\text{H}_7\text{-5-yl} = 1,3\text{-C}_5\text{H}_7\text{-5-yl}$	3.40E+13	0	34500	[61]
533	$1,3\text{-C}_5\text{H}_7\text{-4-yl} = 1,3\text{-C}_5\text{H}_7\text{-5-yl}$	2.00E+13	0	47000	[61]
534	$1,4\text{-C}_5\text{H}_7\text{-4-yl} = 1,3\text{-C}_5\text{H}_7\text{-5-yl}$	1.30E+13	0	44500	[61]
535	$1,3\text{-C}_5\text{H}_7\text{-3-yl} = \text{CH}_3 + \text{C}_4\text{H}_4$	3.30E+12	0	31500	[61]
536	$1,3\text{-C}_5\text{H}_7\text{-4-yl} = \text{pC}_3\text{H}_4 + \text{C}_2\text{H}_3$	2.00E+13	0	31000	[61]
537	$1,4\text{-C}_5\text{H}_7\text{-4-yl} = \text{aC}_3\text{H}_4 + \text{C}_2\text{H}_3$	2.00E+13	0	35500	[61]

C₅H₇(B) Reactions

538	$\text{C}_5\text{H}_7(\text{B}) = \text{C}_5\text{H}_6 + \text{H}$	6.40E+13	0	34800	[61]
539	$\text{C}_5\text{H}_7(\text{B}) = \text{C}_5\text{H}_7(\text{A})$	2.30E+11	1	44100	[61]

540	$\text{C}_5\text{H}_7(\text{B})=1,4\text{-C}_5\text{H}_7\text{-5-yl}$	2.00E+13	0	35500	[61]
541	$1,4\text{-C}_5\text{H}_7\text{-5-yl}=>\text{C}_2\text{H}_2+\text{aC}_3\text{H}_5$	4.42E+12	0	16700	[62]
542	$\text{C}_2\text{H}_2+\text{aC}_3\text{H}_5=>1,4\text{-C}_5\text{H}_7\text{-5-yl}$	6.31E+11	0	7700	[62]

C₅H₇(C) Reactions

543	$\text{C}_5\text{H}_7(\text{C})=\text{C}_5\text{H}_7(\text{A})$	6.70E+12	1	49500	[61]
544	$\text{C}_5\text{H}_7(\text{C})=1\text{-C}_5\text{H}_7\text{-5-yl}$	2.00E+13	0	33000	[61]
545	$\text{C}_5\text{H}_7(\text{C})=1,2\text{-C}_5\text{H}_7\text{-5-yl}$	2.00E+13	0	31000	[61]
546	$1\text{-C}_5\text{H}_7\text{-5-yl}=\text{C}_2\text{H}_4+\text{C}_3\text{H}_3$	2.00E+13	0	22500	[61]
547	$1,2\text{-C}_5\text{H}_7\text{-5-yl}=\text{C}_2\text{H}_4+\text{C}_3\text{H}_3$	2.00E+13	0	35500	[61]

C₅H₆ Reactions

548	$\text{C}_2\text{H}_3+\text{pC}_3\text{H}_4=\text{C}_5\text{H}_6+\text{H}$	1.00E+13	0	1000	[63]
549	$\text{C}_5\text{H}_6+\text{H}=\text{C}_5\text{H}_5+\text{H}_2$	3.00E+14	0	6640	[64]
550	$\text{C}_5\text{H}_6+\text{OH}=\text{C}_5\text{H}_5+\text{H}_2\text{O}$	3.43E+09	1.2	-447	[65]
551	$\text{C}_5\text{H}_6+\text{O}=\text{C}_5\text{H}_5+\text{OH}$	1.81E+14	0	3080	[65]
552	$\text{C}_5\text{H}_6+\text{CH}_3=\text{C}_5\text{H}_5+\text{CH}_4$	4.16E+12	0	11130	^a
553	$\text{C}_5\text{H}_5+\text{O}_2=>\text{C}_5\text{H}_5\text{O}+\text{O}$	8.50E+14	0	28000	[66]
554	$\text{C}_5\text{H}_5+\text{O}=\text{C}_5\text{H}_5\text{O}$	1.00E+14	0	0	^a
555	$\text{C}_5\text{H}_6(+\text{M})=\text{C}_5\text{H}_5+\text{H}(+\text{M})$	7.65E+19	-1.18	84473	[67]
	LOW PRESSURE LIMIT:	1.07E+80	-16.788	16985	
556	$\text{C}_5\text{H}_5(+\text{M})=>\text{C}_2\text{H}_2+\text{C}_3\text{H}_3(+\text{M})$	6.31E+13	0.075	62300	[68]
	LOW PRESSURE LIMIT:	1.00E+45	-8.4	47500	
557	$\text{C}_3\text{H}_3+\text{C}_2\text{H}_2=>\text{C}_5\text{H}_5$	6.17E+66	-15.7	47753	[69]
558	$\text{C}_5\text{H}_6=\text{CH}_2\text{CHCHCCH}_2$	1.35E+15	0	80450	[64]
559	$\text{CH}_2\text{CHCHCCH}_2=\text{pC}_3\text{H}_4+\text{C}_2\text{H}_2$	2.88E+13	0	66550	[64]
560	$\text{C}_5\text{H}_6=\text{C}_2\text{H}_2+\text{aC}_3\text{H}_4$	3.80E+17	0	104000	[64]
561	$\text{C}_5\text{H}_6=\text{CH}_2\text{CHCH}_2\text{CCH}$	8.50E+14	0	90540	[64]
562	$\text{CH}_2\text{CHCH}_2\text{CCH}=\text{C}_2\text{H}_2+\text{aC}_3\text{H}_4$	3.55E+13	0	63360	[64]

C₅H₅O Reactions

563	$\text{C}_5\text{H}_5\text{O}=\text{nC}_4\text{H}_5+\text{CO}$	2.51E+11	0	29740	[70]
564	$\text{C}_5\text{H}_5\text{O}=\text{nC}_4\text{H}_5+\text{CO}$	2.51E+11	0	37433	[70]

C₅H₄O Reactions

565	$\text{C}_5\text{H}_4\text{O}=>\text{CO}+\text{C}_4\text{H}_4$	1.00E+12	0	53000	[71]
566	$\text{C}_5\text{H}_4\text{O}+\text{H}=\text{nC}_4\text{H}_5+\text{CO}$	1.71E+13	0	0	[71]

C₆H₆ Reactions

567	$\text{C}_6\text{H}_5 + \text{H} (+\text{M}) = \text{C}_6\text{H}_6 (+\text{M})$	2.20E+14	0	0	[72]
	LOW PRESSURE LIMIT:	4.10E+104	-24.63	21505	
	TROE PARAMETERS: $a = 0.046$, $T^{***} = 352$, $T^* = 60000$, $T^{**} = 7600$				
568	$\text{f-C}_6\text{H}_6 = \text{C}_6\text{H}_6$	5.62E+81	-19.36	121500	[73]
569	$\text{C}_6\text{H}_6 + \text{H} = \text{C}_6\text{H}_5 + \text{H}_2$	6.02E+08	1.805	16400	[74]
570	$\text{C}_6\text{H}_6 + \text{H} = \text{C}_6\text{H}_7$	1.12E+167	-45.87	81800	[74]
571	$\text{C}_6\text{H}_6 + \text{O} = \text{C}_6\text{H}_5 + \text{OH}$	6.00E+13	0	11064	^a
572	$\text{C}_6\text{H}_6 + \text{O} = \text{C}_6\text{H}_5\text{O} + \text{H}$	6.66E+12	0	2332	^a
573	$\text{C}_6\text{H}_6 + \text{OH} = \text{C}_6\text{H}_5 + \text{H}_2\text{O}$	2.39E+04	2.68	773	[75]
574	$\text{C}_6\text{H}_6 + \text{OH} = \text{C}_6\text{H}_5\text{OH} + \text{H}$	1.32E+02	3.25	5590	[75]
575	$\text{C}_3\text{H}_3 + \text{C}_3\text{H}_3 = \text{C}_6\text{H}_6$	1.29E+69	-16.73	27864	[73]
576	$\text{C}_3\text{H}_3 + \text{C}_3\text{H}_3 = \text{C}_6\text{H}_6$	7.07E+39	-8.819	7049	[73]
577	$\text{n-C}_4\text{H}_5 + \text{C}_2\text{H}_2 = \text{C}_6\text{H}_6 + \text{H}$	2.10E+15	-1.07	4800	[54]
578	$\text{C}_4\text{H}_4 + \text{C}_2\text{H}_3 = \text{C}_6\text{H}_6 + \text{H}$	1.90E+12	0	2510	[76]
579	$\text{n-C}_4\text{H}_5 + \text{C}_2\text{H}_3 = \text{C}_6\text{H}_6 + \text{H}_2$	2.80E-07	5.63	-1890	[77]

f-C₆H₆ Reactions

580	$\text{f-C}_6\text{H}_6 = \text{C}_6\text{H}_5 + \text{H}$	2.57E+97	-23.16	153470	[73]
581	$\text{C}_3\text{H}_3 + \text{C}_3\text{H}_3 = \text{f-C}_6\text{H}_6$	2.34E+69	-17.02	25864	[73]
582	$\text{C}_3\text{H}_3 + \text{C}_3\text{H}_3 = \text{f-C}_6\text{H}_6$	1.74E+44	-10.31	7992	[73]
583	$\text{f-C}_6\text{H}_6 + \text{H} = \text{C}_5\text{H}_5\text{CH}_2$	1.52E+14	0	6406	[78]
584	$\text{f-C}_6\text{H}_6 + \text{H} = \text{C}_5\text{H}_4\text{CH}_3$	1.70E+12	2	0.45	[78]
585	$\text{i-C}_4\text{H}_3 + \text{C}_2\text{H}_3 = \text{f-C}_6\text{H}_6$	5.00E+12	0	0	[57]
586	$\text{n-C}_4\text{H}_3 + \text{C}_2\text{H}_3 = \text{f-C}_6\text{H}_6$	4.00E+12	0	0	[57]
587	$\text{n-C}_4\text{H}_5 + \text{C}_2\text{H} = \text{f-C}_6\text{H}_6$	4.00E+12	0	0	[57]
588	$\text{i-C}_4\text{H}_5 + \text{C}_2\text{H} = \text{f-C}_6\text{H}_6$	1.00E+13	0	0	[57]

b-C₆H₆ Reactions

589	$\text{b-C}_6\text{H}_6 = \text{f-C}_6\text{H}_6$	5.75E+76	-18.67	95531	[73]
590	$\text{b-C}_6\text{H}_6 = \text{C}_6\text{H}_6$	6.76E+98	-24.58	122310	[73]
591	$\text{b-C}_6\text{H}_6 = \text{C}_6\text{H}_5 + \text{H}$	2.69E+84	-20.14	121900	[73]
592	$\text{C}_3\text{H}_3 + \text{C}_3\text{H}_3 = \text{b-C}_6\text{H}_6$	8.31E+71	-17.58	29253	[73]
593	$\text{C}_3\text{H}_3 + \text{C}_3\text{H}_3 = \text{b-C}_6\text{H}_6$	8.70E+40	-9.173	7568	[73]

C₆H₅ Reactions

594	$\text{C}_3\text{H}_3 + \text{C}_3\text{H}_3 = \text{C}_6\text{H}_5 + \text{H}$	1.58E+54	-11.94	28973	[73]
595	$\text{C}_3\text{H}_3 + \text{C}_3\text{H}_3 = \text{C}_6\text{H}_5 + \text{H}$	1.38E+34	-6.722	13799	[73]
596	$\text{C}_6\text{H}_5 + \text{O}_2 = \text{O} + \text{C}_6\text{H}_5\text{O}$	1.02E+13	0	3581	[79]

597	$\text{C}_6\text{H}_5 + \text{O}_2 = \text{n-C}_4\text{H}_5 + \text{CO} + \text{CO}$	4.44E+12	0	3604	[79]
598	$\text{C}_6\text{H}_5 + \text{O}_2 = \text{p-C}_6\text{H}_4\text{O}_2 + \text{H}$	8.00E+10	0	3604	[79]
599	$\text{C}_6\text{H}_5 + \text{O} = \text{C}_5\text{H}_5 + \text{CO}$	1.00E+14	0	0	[80]
609	$\text{C}_6\text{H}_5 + \text{OH} = \text{C}_6\text{H}_5\text{O} + \text{H}$	1.00E+13	0	0	^a
601	$\text{i-C}_4\text{H}_3 + \text{C}_2\text{H}_3 = \text{C}_6\text{H}_5 + \text{H}$	6.00E+12	0	0	[57]
602	$\text{n-C}_4\text{H}_3 + \text{C}_2\text{H}_3 = \text{C}_6\text{H}_5 + \text{H}$	1.60E+13	0	0	[57]
603	$\text{n-C}_4\text{H}_5 + \text{C}_2\text{H} = \text{C}_6\text{H}_5 + \text{H}$	1.60E+13	0	0	[57]
604	$\text{i-C}_4\text{H}_5 + \text{C}_2\text{H} = \text{C}_6\text{H}_5 + \text{H}$	6.00E+12	0	0	[57]
605	$\text{C}_6\text{H}_5 = >\text{l-C}_6\text{H}_4 + \text{H}$	9.74E+17	0	107370	[78]
606	$\text{C}_6\text{H}_5 = >\text{n-C}_4\text{H}_3 + \text{C}_2\text{H}_2$	1.67E+19	0	110720	[78]
607	$\text{n-C}_4\text{H}_3 + \text{C}_2\text{H}_2 = >\text{C}_6\text{H}_5$	1.02E+15	-0.84	13320	[78]

C₅H₅CH₃, C₅H₅CH₂ et C₅H₄CH₃ Reactions

608	$\text{C}_5\text{H}_5\text{CH}_2$	1.40E+13	0	17400	[81]
609	$\text{C}_5\text{H}_4\text{CH}_3 = \text{C}_5\text{H}_5\text{CH}_2$	3.00E+12	0	50400	[81]
610	$\text{C}_5\text{H}_5 + \text{CH}_3 = >\text{C}_5\text{H}_5\text{CH}_3$	1.11E-51	16	-74100	[82]
611	$\text{C}_5\text{H}_5\text{CH}_3 = >\text{C}_5\text{H}_5 + \text{CH}_3$	5.21E+76	-19	88800	[82]
612	$\text{C}_5\text{H}_5\text{CH}_3 = \text{C}_5\text{H}_4\text{CH}_3 + \text{H}$	6.47E+77	-20	93200	[82]
613	$\text{C}_5\text{H}_5 + \text{CH}_3 = \text{C}_5\text{H}_4\text{CH}_3 + \text{H}$	6.40E+15	-0.5	10700	[82]

C₆H₅OH Reactions

614	$\text{C}_6\text{H}_5\text{OH} = >\text{C}_6\text{H}_5\text{O} + \text{H}$	3.33E+17	-0.51	91600	[83]
	LOW PRESSURE LIMIT:	1.54E+118	-28.21	125976	
615	$\text{C}_6\text{H}_5\text{OH} = \text{C}_5\text{H}_6 + \text{CO}$	8.62E+15	-0.61	74115	[83]
616	$\text{C}_6\text{H}_5\text{OH} + \text{OH} = \text{C}_6\text{H}_5\text{O} + \text{H}_2\text{O}$	6.00E+12	0	0	[84]
617	$\text{C}_6\text{H}_5\text{OH} + \text{H} = \text{C}_6\text{H}_5\text{O} + \text{H}_2$	1.15E+14	0	12400	[84]
618	$\text{C}_6\text{H}_5\text{OH} + \text{O} = \text{C}_6\text{H}_5\text{O} + \text{OH}$	2.81E+13	0	7352	[65]

C₆H₅O Reactions

619	$\text{C}_6\text{H}_5\text{O} = \text{C}_5\text{H}_5 + \text{CO}$	2.51E+11	0	43900	[85]
620	$\text{C}_6\text{H}_5\text{O} + \text{O} = >\text{C}_2\text{H}_2 + \text{C}_2\text{H}_3 + 2\text{CO}$	1.68E+14	0	0	[86]
621	$\text{C}_6\text{H}_5\text{O} + \text{H} = >\text{C}_2\text{H}_3 + \text{C}_3\text{H}_3 + \text{CO}$	4.50E+13	0	0	[86]

p-C₆H₄O₂, C₆H₃O₂ et C₆H₃O₃ Reactions

622	$\text{p-C}_6\text{H}_4\text{O}_2 = \text{C}_5\text{H}_4\text{O} + \text{CO}$	3.70E+11	0	58972	[80]
623	$\text{p-C}_6\text{H}_4\text{O}_2 + \text{H} = >\text{C}_5\text{H}_5\text{O} + \text{CO}$	2.50E+13	0	4698	[87]
624	$\text{p-C}_6\text{H}_4\text{O}_2 + \text{O} = \text{C}_6\text{H}_3\text{O}_3 + \text{H}$	1.50E+13	0	4528	[87]
625	$\text{p-C}_6\text{H}_4\text{O}_2 + \text{OH} = \text{C}_6\text{H}_3\text{O}_2 + \text{H}_2\text{O}$	1.00E+06	2	3998	[87]
626	$\text{C}_6\text{H}_3\text{O}_2 + \text{H} = >_2\text{C}_2\text{H}_2 + 2\text{CO}$	1.00E+14	0	0	[87]
627	$\text{C}_6\text{H}_3\text{O}_2 + \text{O} = >\text{C}_2\text{H}_2 + \text{HCCO} + 2\text{CO}$	1.00E+14	0	0	[87]

628	$\text{C}_6\text{H}_3\text{O}_3 \Rightarrow \text{C}_2\text{H}_2 + \text{HCCO} + 2\text{CO}$	1.00E+12	0	49976	[87]
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f-C₆H₅(2) Reactions

629	$\text{i-C}_4\text{H}_3 + \text{C}_2\text{H}_2 \Rightarrow \text{f-C}_6\text{H}_5(2)$	2.08E+48	-10.89	33548	[78]
630	$\text{b-C}_6\text{H}_4 + \text{H} \Rightarrow \text{f-C}_6\text{H}_5(2)$	2.50E+54	-11.65	29555	[78]
631	$\text{f-C}_6\text{H}_5(2) + \text{H} = \text{f-C}_6\text{H}_6$	9.79E+13	0.15	0	[78]
632	$\text{f-C}_6\text{H}_5(2) + \text{H}_2 = \text{f-C}_6\text{H}_6 + \text{H}$	1.31E+14	-1.2691	30843	[78]
633	$\text{f-C}_6\text{H}_5(2) \Rightarrow \text{b-C}_6\text{H}_4 + \text{H}$	4.02E+16	0	61948	[78]

f-C₆H₅(1) Reactions

634	$\text{C}_6\text{H}_5 \Rightarrow \text{f-C}_6\text{H}_5(1)$	2.01E+15	0	71176	[78]
	duplicate				
	$\text{C}_6\text{H}_5 \Rightarrow \text{f-C}_6\text{H}_5(1)$	2.03E+14	0	59840	[78]
	duplicate				
635	$\text{f-C}_6\text{H}_5(1) \Rightarrow \text{C}_6\text{H}_5$	1.16E+14	0	41016	[78]
	duplicate				
	$\text{f-C}_6\text{H}_5(1) \Rightarrow \text{C}_6\text{H}_5$	1.17E+13	0	29959	[78]
	duplicate				
636	$\text{f-C}_6\text{H}_5(1) = \text{f-C}_6\text{H}_5(2)$	1.54E-18	8.7552	36703	[78]
637	$\text{f-C}_6\text{H}_5(1) + \text{H} = \text{f-C}_6\text{H}_6$	3.88E+13	0.2	0	[78]
638	$\text{f-C}_6\text{H}_5(1) + \text{H}_2 = \text{f-C}_6\text{H}_6 + \text{H}$	2.14E+04	2.4551	6874.2	[78]
639	$\text{f-C}_6\text{H}_5(1) \Rightarrow \text{l-C}_6\text{H}_4 + \text{H}$	1.00E+15	0	70000	[78]
640	$\text{n-C}_4\text{H}_3 + \text{C}_2\text{H}_2 \Rightarrow \text{f-C}_6\text{H}_5(1)$	1.93E+15	-0.82	10850	[78]

b-C₆H₄ Reactions

641	$\text{i-C}_4\text{H}_3 + \text{C}_2\text{H}_2 \Rightarrow \text{b-C}_6\text{H}_4 + \text{H}$	3.21E+48	-9.96	57340	[78]
	$\text{b-C}_6\text{H}_4 + \text{H} \Rightarrow \text{i-C}_4\text{H}_3 + \text{C}_2\text{H}_2$	5.90E+57	-11.59	54682	[78]

o-C₆H₄ Reactions

643	$\text{C}_6\text{H}_5 = \text{o-C}_6\text{H}_4 + \text{H}$	8.75E+14	0	86100	[78]
644	$\text{n-C}_4\text{H}_3 + \text{C}_2\text{H}_2 = \text{o-C}_6\text{H}_4 + \text{H}$	8.29E+35	-6.91	24629	[88]

l-C₆H₄ Reactions

645	$\text{n-C}_4\text{H}_3 + \text{C}_2\text{H}_2 \Rightarrow \text{l-C}_6\text{H}_4 + \text{H}$	2.67E+16	-0.335	46759	[78]
646	$\text{l-C}_6\text{H}_4 + \text{H} \Rightarrow \text{f-C}_6\text{H}_5(1)$	3.59E+12	0.534	8653.9	[78]
647	$\text{l-C}_6\text{H}_4 + \text{H} \Rightarrow \text{C}_6\text{H}_5$	2.25E+12	0.49475	11195	[78]
648	$\text{l-C}_6\text{H}_4 + \text{H} \Rightarrow \text{n-C}_4\text{H}_3 + \text{C}_2\text{H}_2$	3.90E+14	1.1182	47759	[78]
659	$\text{l-C}_6\text{H}_4 + \text{OH} = \text{l-C}_6\text{H}_3 + \text{H}_2\text{O}$	3.10E+06	2	430	[89]
650	$\text{l-C}_6\text{H}_4 + \text{H} = \text{l-C}_6\text{H}_3 + \text{H}_2$	6.65E+06	2.53	9240	[89]

I-C₆H₃ Reactions

651	$\text{l-C}_6\text{H}_3 + \text{H} = \text{l-C}_6\text{H}_2 + \text{H}_2$	2.00E+13	0	0	[89]
652	$\text{C}_4\text{H}_2 + \text{C}_2\text{H} = \text{l-I-C}_6\text{H}_3$	3.76E+63	-14.722	27250	[90]
653	$\text{l-C}_6\text{H}_2 + \text{H} = \text{l-C}_6\text{H}_3$	2.74E+56	-12.585	29690	[90]

I-C₆H₂ Reactions

654	$2\text{C}_3\text{H}_2 = \text{l-C}_6\text{H}_2 + \text{H}_2$	2.00E+13	0	85000	[91]
655	$\text{l-C}_6\text{H}_2 + \text{C}_2\text{H} = \text{C}_4\text{H} + \text{C}_4\text{H}_2$	1.00E+13	0	0	[89]
656	$\text{C}_4\text{H}_2 + \text{C}_2\text{H} = \text{l-C}_6\text{H}_2 + \text{H}$	4.98E+40	-7.66	21910	[90]

C₇H₈ Reactions

657	$\text{b-C}_7\text{H}_7 + \text{H} (+\text{M}) = \text{C}_7\text{H}_8 (+\text{M})$	7.23E+13	0.062	-44	[92]
	LOW PRESSURE LIMIT:	3.03E+136	-33.35	55600	
	TROE PARAMETERS: $a = 0.163$, $T^{***} = 714$, $T^* = 728$, $T^{**} = 5112$				
658	$\text{C}_6\text{H}_5 + \text{CH}_3 (+\text{M}) = \text{C}_7\text{H}_8 (+\text{M})$	2.33E+14	-0.283	-191	[92]
	LOW PRESSURE LIMIT:	6.74E+83	-19.22	15000	
	TROE PARAMETERS: $a = 0.735$, $T^{***} = 60000$, $T^* = 513$, $T^{**} = 100000$				
659	$\text{C}_7\text{H}_8 + \text{H} = \text{o-C}_6\text{H}_4\text{CH}_3 + \text{H}_2$	1.02E+08	1.805	15900	[93]
660	$\text{C}_7\text{H}_8 + \text{H} = \text{m-C}_6\text{H}_4\text{CH}_3 + \text{H}_2$	2.73E+08	1.805	16700	[93]
661	$\text{C}_7\text{H}_8 + \text{H} = \text{p-C}_6\text{H}_4\text{CH}_3 + \text{H}_2$	1.33E+08	1.805	16300	[93]
662	$\text{C}_7\text{H}_8 + \text{H} = \text{b-C}_7\text{H}_7 + \text{H}_2$	6.47E+00	3.98	3384	[94]
663	$\text{C}_7\text{H}_8 + \text{H} = \text{C}_6\text{H}_6 + \text{CH}_3$	9.50E+05	2	940	[95]
664	$\text{C}_7\text{H}_8 + \text{O} = \text{o-C}_6\text{H}_4\text{CH}_3 + \text{OH}$	1.02E+13	0	10600	[93]
665	$\text{C}_7\text{H}_8 + \text{O} = \text{m-C}_6\text{H}_4\text{CH}_3 + \text{OH}$	2.73E+13	0	11400	[93]
666	$\text{C}_7\text{H}_8 + \text{O} = \text{p-C}_6\text{H}_4\text{CH}_3 + \text{OH}$	1.33E+13	0	11000	[93]
667	$\text{C}_7\text{H}_8 + \text{O} = \text{b-C}_7\text{H}_7 + \text{OH}$	6.30E+11	0	0	[96]
668	$\text{C}_7\text{H}_8 + \text{O} = \text{OC}_6\text{H}_4\text{CH}_3 + \text{H}$	5.55E+12	0	2332	[93]
669	$\text{C}_7\text{H}_8 + \text{OH} = \text{b-C}_7\text{H}_7 + \text{H}_2\text{O}$	1.31E+05	2.394	-602	[75]
670	$\text{C}_7\text{H}_8 + \text{OH} = \text{C}_6\text{H}_5\text{OH} + \text{CH}_3$	7.82E+02	2.884	3221	[75]
671	$\text{C}_7\text{H}_8 + \text{OH} = \text{HOC}_6\text{H}_4\text{CH}_3 + \text{H}$	1.32E+02	3.25	5590	[75]
672	$\text{C}_7\text{H}_8 + \text{OH} = \text{o-C}_6\text{H}_4\text{CH}_3 + \text{H}_2\text{O}$	5.22E+03	2.611	309	[75]
673	$\text{C}_7\text{H}_8 + \text{OH} = \text{m-C}_6\text{H}_4\text{CH}_3 + \text{H}_2\text{O}$	7.40E+03	2.691	921	[75]
674	$\text{C}_7\text{H}_8 + \text{OH} = \text{p-C}_6\text{H}_4\text{CH}_3 + \text{H}_2\text{O}$	4.43E+03	2.665	606	[75]
675	$\text{C}_7\text{H}_8 + \text{O}_2 = \text{b-C}_7\text{H}_7 + \text{HO}_2$	2.18E+07	2.5	46050	[97]
676	$\text{C}_7\text{H}_8 + \text{HO}_2 = \text{b-C}_7\text{H}_7 + \text{H}_2\text{O}_2$	3.00E+14	0	22010	[98]
677	$\text{C}_7\text{H}_8 + \text{CH}_3 = \text{b-C}_7\text{H}_7 + \text{CH}_4$	1.17E+11	0	8010	[99]
678	$\text{C}_7\text{H}_8 + \text{C}_6\text{H}_5 = \text{b-C}_7\text{H}_7 + \text{C}_6\text{H}_6$	2.10E+12	0	4400	[65]
679	$\text{b-C}_7\text{H}_7 + \text{C}_6\text{H}_5\text{OH} = \text{C}_7\text{H}_8 + \text{C}_6\text{H}_5\text{O}$	1.05E+11	0	9500	[65]
680	$\text{C}_7\text{H}_8 + \text{C}_2\text{H}_3 = \text{b-C}_7\text{H}_7 + \text{C}_2\text{H}_4$	3.98E+12	0	8000	[100]
681	$a\text{C}_3\text{H}_4 + n\text{-C}_4\text{H}_5 = \text{C}_7\text{H}_8 + \text{H}$	2.00E+11	0	3696	[101]

682	$\text{p-C}_3\text{H}_4 + \text{n-C}_4\text{H}_5 = \text{C}_7\text{H}_8 + \text{H}$	3.12E+11	3696	[102]
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o-C₆H₄CH₃, m-C₆H₄CH₃ et p-C₆H₄CH₃ Reactions

683	o-C ₆ H ₄ CH ₃ +H(+M)= C ₇ H ₈ (+M)	2.20E+14	0	0	a
	LOW PRESSURE LIMIT:	4.10E+104	-24.63	21505	
	TROE PARAMETERS: a = 0.046, T*** = 352, T* = 60000, T** = 7600				
684	m-C ₆ H ₄ CH ₃ +H(+M)= C ₇ H ₈ (+M)	2.20E+14	0	0	a
	LOW PRESSURE LIMIT:	4.10E+104	-24.63	21505	
	TROE PARAMETERS: a = 0.046, T*** = 352, T* = 60000, T** = 7600				
685	p-C ₆ H ₄ CH ₃ +H(+M)= C ₇ H ₈ (+M)	2.20E+14	0	0	a
	LOW PRESSURE LIMIT:	4.10E+104	-24.63	21505	
	TROE PARAMETERS: a = 0.046, T*** = 352, T* = 60000, T** = 7600				
686	o-C ₆ H ₄ CH ₃ +O ₂ =OC ₆ H ₄ CH ₃ +O	4.99E+18	-1.68	5320	[103]
687	m-C ₆ H ₄ CH ₃ +O ₂ =OC ₆ H ₄ CH ₃ +O	9.82E+17	-1.47	4530	[103]
688	p-C ₆ H ₄ CH ₃ +O ₂ =OC ₆ H ₄ CH ₃ +O	9.82E+17	-1.47	4530	[103]
689	o-C ₆ H ₄ CH ₃ +O ₂ =C ₆ H ₆ +CO+OH	4.98E+09	0.6	-4060	a
	o-				
690	C ₆ H ₄ CH ₃ +O ₂ =C ₂ H ₂ +C ₂ H ₂ +CH ₃ CO+CO	6.95E+09	0.52	-4500	a
691	o-C ₆ H ₄ CH ₃ +O ₂ =C ₂ H ₂ +p-C ₃ H ₅ +2CO	6.95E+09	0.52	-4500	a
692	m-C ₆ H ₄ CH ₃ +O ₂ =C ₂ H ₂ +s-C ₃ H ₅ +2CO	2.82E+09	0.64	-5135	a
693	m-C ₆ H ₄ CH ₃ +O ₂ =C ₂ H ₂ +p-C ₃ H ₄ +2CO	2.82E+09	0.64	-5135	a
694	p-C ₆ H ₄ CH ₃ +O ₂ =C ₂ H ₂ +s-C ₃ H ₅ +2CO	5.64E+09	0.64	-5135	a
695	o-C ₆ H ₄ CH ₃ +O=C ₅ H ₄ CH ₃ +CO	1.00E+14	0	0	a
696	m-C ₆ H ₄ CH ₃ +O=C ₅ H ₄ CH ₃ +CO	1.00E+14	0	0	a
697	p-C ₆ H ₄ CH ₃ +O=C ₅ H ₄ CH ₃ +CO	1.00E+14	0	0	a

HO-C₆H₄CH₃ et OC₆H₄CH₃ Reactions

698	HO-C ₆ H ₄ CH ₃ +OH=OC ₆ H ₄ CH ₃ +H ₂ O	6.00E+12	0	0	a
699	HO-C ₆ H ₄ CH ₃ +H=OC ₆ H ₄ CH ₃ +H ₂	1.15E+14	0	12400	a
700	HO-C ₆ H ₄ CH ₃ +O=OC ₆ H ₄ CH ₃ +OH	2.81E+13	0	7352	a
701	OC ₆ H ₄ CH ₃ =C ₅ H ₄ CH ₃ +CO	2.51E+11	0	43900	a

f-C₇H₈ Reactions

702	b-C ₇ H ₇ =>C ₇ H ₆ +H	1.44E+13	0.453	76300	[104]
703	C ₇ H ₆ +H=> b-C ₇ H ₇	8.82E+08	1.2	-2018	[104]
704	C ₇ H ₆ +H=>C ₅ H ₅ +C ₂ H ₂	1.00E+14	0	0	a
705	C ₅ H ₅ +C ₂ H ₂ =>C ₇ H ₆ +H	1.58E-01	4.18	29670	[105]

b-C₇H₇ Reactions

706	b-C ₇ H ₇ +H=C ₆ H ₅ +CH ₃	4.50E+58	-11.9	51860	[92]
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707	$\text{b-C}_7\text{H}_7 + \text{OH} = \text{b-C}_7\text{H}_7\text{OH}$	2.00E+13	0	0	[106]
708	$\text{b-C}_7\text{H}_7 + \text{O} = \text{C}_7\text{H}_6\text{O} + \text{H}$	1.00E+14	0	0	[107]
709	$\text{b-C}_7\text{H}_7 + \text{O}_2 = \text{O} + \text{C}_7\text{H}_7\text{O}$	6.31E+12	0	43000	[108]
710	$\text{b-C}_7\text{H}_7 + \text{HO}_2 = \text{C}_7\text{H}_7\text{O} + \text{OH}$	1.19E+09	1.03	-2250	[109]
711	$\text{b-C}_7\text{H}_7 = \text{C}_5\text{H}_5 + \text{C}_2\text{H}_2$	6.03E+13	0	70000	[110]
712	$\text{C}_4\text{H}_4 + \text{C}_3\text{H}_3 = \text{b-C}_7\text{H}_7$	5.39E+51	-12.2	7120	[90]

C₇H₇OH Reactions

713	$\text{C}_7\text{H}_7\text{OH} (+\text{M}) = \text{C}_6\text{H}_5 + \text{CH}_2\text{OH} (+\text{M})$	5.94E+23	-1.68	91163	a
	LOW PRESSURE LIMIT:	2.88E+85	-18.9	109914	
	TROE PARAMETERS: $\alpha = 0.5$, $T^{***} = 200$, $T^* = 890$, $T^{**} = 4600$				
	Enhanced Third Body Efficiencies: $\text{H}_2\text{O} = 5.0$ $\text{H}_2 = 2.0$ $\text{CO}_2 = 3.0$ $\text{CO} = 2.0$				
714	$\text{C}_7\text{H}_7\text{OH} (+\text{M}) = \text{C}_7\text{H}_6\text{O} + \text{H}_2 (+\text{M})$	7.24E+11	0.095	91007	a
	LOW PRESSURE LIMIT:	4.46E+87	-19.42	115586	
	TROE PARAMETERS: $\alpha = 0.9$, $T^{***} = 900$, $T^* = 1100$, $T^{**} = 3500$				
	Enhanced Third Body Efficiencies: $\text{H}_2\text{O} = 5.0$				
715	$\text{C}_7\text{H}_7\text{OH} + \text{OH} = \text{C}_7\text{H}_6\text{OH} + \text{H}_2\text{O}$	1.31E+05	2.43	-1457	a
716	$\text{C}_7\text{H}_7\text{OH} + \text{OH} = \text{C}_7\text{H}_7\text{O} + \text{H}_2\text{O}$	2.81E+02	2.97	-580	a
717	$\text{C}_7\text{H}_7\text{OH} + \text{H} = \text{C}_7\text{H}_6\text{OH} + \text{H}_2$	1.79E+05	2.53	3420	a
718	$\text{C}_7\text{H}_7\text{OH} + \text{H} = \text{C}_7\text{H}_7\text{O} + \text{H}_2$	5.55E-23	10.6	-4459	a
719	$\text{C}_7\text{H}_7\text{OH} + \text{O} = \text{C}_7\text{H}_6\text{OH} + \text{OH}$	1.45E+05	2.41	876	a
720	$\text{C}_7\text{H}_7\text{OH} + \text{O} = \text{C}_7\text{H}_7\text{O} + \text{OH}$	1.46E-03	4.73	1727	a
721	$\text{C}_7\text{H}_7\text{OH} (+\text{M}) = \text{b-C}_7\text{H}_7 + \text{OH} (+\text{M})$	1.25E+23	-1.54	96005	
	LOW PRESSURE LIMIT:	3.25E+85	-18.81	114930	
	TROE PARAMETERS: $\alpha = 0.5$, $T^{***} = 300$, $T^* = 900$, $T^{**} = 5000$				
	Enhanced Third Body Efficiencies: $\text{H}_2\text{O} = 5.0$ $\text{H}_2 = 2.0$ $\text{CO}_2 = 3.0$				
722	$\text{C}_7\text{H}_7\text{OH} + \text{H} = \text{C}_6\text{H}_6 + \text{CH}_2\text{OH}$	1.20E+13	0	5148	[65]

C₇H₆OH Reactions

723	$\text{C}_7\text{H}_6\text{OH} + \text{O} = \text{C}_7\text{H}_6\text{O} + \text{OH}$	1.00E+14	0	0	a
724	$\text{C}_7\text{H}_6\text{OH} + \text{HO}_2 = \text{C}_7\text{H}_6\text{O} + \text{OH} + \text{OH}$	4.00E+13	0	0	a
725	$\text{C}_7\text{H}_6\text{OH} + \text{OH} = \text{C}_7\text{H}_6\text{O} + \text{H}_2\text{O}$	5.00E+12	0	0	a
726	$\text{C}_7\text{H}_6\text{OH} + \text{M} = \text{C}_7\text{H}_6\text{O} + \text{H} + \text{M}$	5.00E+13	0	21877	a

C₇H₇O Reactions

727	$\text{C}_7\text{H}_7\text{O} + \text{M} = \text{C}_7\text{H}_6\text{O} + \text{H} + \text{M}$	1.16E+35	-5.89	25274	a
728	$\text{C}_7\text{H}_7\text{O} + \text{M} = \text{C}_6\text{H}_5 + \text{CH}_2\text{O} + \text{M}$	1.35E+38	-6.96	23800	a
729	$\text{C}_7\text{H}_7\text{O} + \text{O}_2 = \text{C}_7\text{H}_6\text{O} + \text{HO}_2$	4.00E+10	0	1100	a
730	$\text{C}_7\text{H}_7\text{O} + \text{H} = \text{C}_6\text{H}_5 + \text{CH}_2\text{OH}$	3.00E+13	0	0	a
731	$\text{C}_7\text{H}_7\text{O} + \text{OH} = \text{C}_7\text{H}_6\text{O} + \text{H}_2\text{O}$	1.00E+13	0	0	a

C₇H₆O et C₇H₅O Reactions

732	C ₇ H ₆ O + H = C ₇ H ₅ O + H ₂	1.20E+14	0	7000	a
733	C ₇ H ₆ O + O = C ₇ H ₅ O + OH	5.84E+12	0	1810	a
734	C ₇ H ₆ O + OH = C ₇ H ₅ O + H ₂ O	2.34E+10	0.73	1100	a
735	C ₇ H ₆ O + CH ₃ = C ₇ H ₅ O + CH ₄	1.60E+12	0	8000	a
736	C ₇ H ₆ O + HO ₂ = C ₇ H ₅ O + H ₂ O ₂	3.00E+12	0	11900	a
737	C ₇ H ₆ O + O ₂ = C ₇ H ₅ O + HO ₂	2.00E+13	0.5	42200	a
738	C ₇ H ₆ O + H = C ₆ H ₆ + HCO	1.20E+13	0	5148	[65]
739	C ₇ H ₆ O + OH = C ₆ H ₅ OH + HCO	1.20E+13	0	5123	[111]
740	C ₇ H ₆ O = C ₆ H ₅ + HCO	6.00E+14	0	79100	a
741	C ₇ H ₆ O = C ₇ H ₅ O + H	5.00E+14	0	87900	a
742	C ₇ H ₆ O = C ₆ H ₆ + CO	1.00E+15	0	85000	a
743	C ₇ H ₅ O (+M) = C ₆ H ₅ + CO(+M)	1.07E+12	0.63	16835	a
			-8.50E-		
	LOW PRESSURE LIMIT:	2.78E+18	01	14425	
	TROE PARAMETERS: a = 0.6, T*** = 1E+15, T* = 1E-15, T** = 1E+15				

C₈H₁₀ Reactions

744	C ₈ H ₁₀ (+M) = b-C ₇ H ₇ + CH ₃ (+M)	1.88E+50	-9.72	107338	a
	LOW PRESSURE LIMIT:	3.72E+65	-13.14	101575	
	TROE PARAMETERS: a = 0.39, T*** = 100, T* = 1900, T** = 6000				
745	C ₈ H ₁₀ (+M) = C ₆ H ₅ + C ₂ H ₅ (+M)	1.29E+37	-5.84	97383	a
	LOW PRESSURE LIMIT:	5.64E+74	-15.74	98714	
	TROE PARAMETERS: a = 0.31, T*** = 50, T* = 3000, T** = 9000				
746	C ₆ H ₅ CH ₂ CH ₂ + H(+M) = C ₈ H ₁₀ (+M)	1.80E+13	0	0	a
	LOW PRESSURE LIMIT:	1.51E+48	-9.32	5834	
	TROE PARAMETERS: a = 0.498, T*** = 1310, T* = 1310, T** = 50000				
747	C ₆ H ₅ CHCH ₃ + H(+M) = C ₈ H ₁₀ (+M)	2.40E+13	0	0	a
	LOW PRESSURE LIMIT:	1.70E+58	-12.08	11264	
	TROE PARAMETERS: a = 0.649, T*** = 1210, T* = 1210, T** = 13370				
748	C ₈ H ₁₀ + H = C ₂ H ₅ + C ₆ H ₆	1.00E+06	2	940	[95]
749	C ₈ H ₁₀ + H = C ₆ H ₅ CH ₂ CH ₂ + H ₂	7.20E+08	1.5	7411	[95]
750	C ₈ H ₁₀ + H = C ₆ H ₅ CHCH ₃ + H ₂	3.30E+07	2	5350	[95]

C₆H₅CH₂CH₂ et C₆H₅CHCH₃ Reactions

751	C ₆ H ₅ CHCH ₃ + H = C ₂ H ₅ + C ₆ H ₅	1.40E+28	-3.94	15916	a
752	C ₆ H ₅ CH ₂ CH ₂ + H = C ₂ H ₅ + C ₆ H ₅	3.70E+24	-2.92	12505	a
753	C ₆ H ₅ CH ₂ CH ₂ = > C ₆ H ₅ CHCH ₃	5.96E+05	2.074	29582	[112]
754	C ₆ H ₅ CHCH ₃ = > C ₆ H ₅ CH ₂ CH ₂	2.30E+07	1.737	44456	[112]
755	C ₆ H ₅ CH ₂ CH ₂ = C ₈ H ₈ + H	3.79E+06	1.991	32106	[112]
756	C ₆ H ₅ CHCH ₃ = C ₈ H ₈ + H	3.74E+08	1.55	44609	[112]

757	$\text{C}_6\text{H}_5 + \text{C}_2\text{H}_4 \Rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2$	4.04E+03	2.64	1459	[112]
758	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2 \Rightarrow \text{C}_6\text{H}_5 + \text{C}_2\text{H}_4$	1.72E+11	0.783	38704	[112]

C₈H₈ Reactions

759	$\text{CH}_2(\text{S}) + \text{b-C}_7\text{H}_7 \Rightarrow \text{C}_8\text{H}_8 + \text{H}$	1.20E+13	0	-570	^a
760	$\text{CH}_2 + \text{b-C}_7\text{H}_7 \Rightarrow \text{C}_8\text{H}_8 + \text{H}$	4.00E+13	0	0	^a
761	$\text{n-C}_4\text{H}_5 + \text{C}_4\text{H}_4 \Rightarrow \text{C}_8\text{H}_8 + \text{H}$	3.16E+11	0	600	[102]
762	$\text{C}_4\text{H}_4 + \text{C}_4\text{H}_4 \Rightarrow \text{C}_8\text{H}_8$	1.48E+14	0	37960	[113]
763	$\text{C}_8\text{H}_8 + \text{H} \Rightarrow \text{C}_6\text{H}_5 + \text{C}_2\text{H}_4$	1.63E+37	-6.31	31672	[112]
764	$\text{C}_8\text{H}_8 + \text{H} \Rightarrow \text{C}_6\text{H}_6 + \text{C}_2\text{H}_3$	5.62E+24	-3	19830	[112]
765	$\text{C}_6\text{H}_5\text{CCH}_2 + \text{H} \Rightarrow \text{C}_8\text{H}_8$	3.87E+13	0.2	0	^a
766	$\text{C}_6\text{H}_5\text{CHCH} + \text{H} \Rightarrow \text{C}_8\text{H}_8$	3.87E+13	0.2	0	^a
767	$\text{C}_8\text{H}_8 + \text{H} \Rightarrow \text{C}_6\text{H}_5\text{CHCH} + \text{H}_2$	6.60E+05	2.53	12240	[114]

C₆H₅CHCH et C₆H₅CCH₂ Reactions

768	$\text{C}_6\text{H}_5\text{CHCH} = \text{C}_6\text{H}_5\text{CCH}_2$	4.90E+12	0.45	45740	[115]
769	$\text{C}_6\text{H}_5 + \text{C}_2\text{H}_2 \Rightarrow \text{C}_6\text{H}_5\text{CHCH}$	2.70E+06	2.05	3720	[115]
770	$\text{C}_6\text{H}_5\text{CHCH} \Rightarrow \text{C}_6\text{H}_5 + \text{C}_2\text{H}_2$	1.35E+14	0.34	45710	[115]
771	$\text{C}_6\text{H}_5\text{CHCH} = \text{C}_8\text{H}_6 + \text{H}$	3.80E+11	0.82	38910	[115]
772	$\text{C}_6\text{H}_5\text{CCH}_2 = \text{C}_8\text{H}_6 + \text{H}$	1.23E+13	0.55	42580	[115]
773	$\text{C}_6\text{H}_5\text{CHCH} + \text{H} \Rightarrow \text{C}_8\text{H}_6 + \text{H}_2$	1.65E+11	0.49	10630	[116]

C₈H₆ et C₈H₅ Reactions

774	$\text{C}_6\text{H}_5 + \text{C}_2\text{H}_2 = \text{C}_8\text{H}_6 + \text{H}$	2.93E+12	0.18	6517	[90]
775	$\text{C}_8\text{H}_6 + \text{H}_2 \Rightarrow \text{C}_6\text{H}_5\text{CHCH} + \text{H}$	6.99E+08	1.319	86997	[116]
776	$\text{C}_8\text{H}_6 + \text{H} \Rightarrow \text{C}_8\text{H}_5 + \text{H}_2$	1.29E+08	1.886	17580	[116]
777	$\text{C}_8\text{H}_5 + \text{H}_2 \Rightarrow \text{C}_8\text{H}_6 + \text{H}$	9.09E+04	2.389	5641	[116]

C₉H₈ Reactions

778	$\text{b-C}_7\text{H}_7 + \text{C}_2\text{H}_2 \Rightarrow \text{C}_9\text{H}_8 + \text{H}$	1.71E+13	0	16900	^a
779	$\text{C}_9\text{H}_8 + \text{H} \Rightarrow \text{b-C}_7\text{H}_7 + \text{C}_2\text{H}_2$	3.56E+13	0	28400	^a
780	$\text{C}_6\text{H}_5 + \text{C}_4\text{H}_6 \Rightarrow \text{C}_9\text{H}_8 + \text{CH}_3$	1.58E+13	-1.35	5167	[117]
781	$\text{C}_9\text{H}_8 + \text{H} = \text{C}_9\text{H}_7 + \text{H}_2$	3.00E+14	0	6640	^a
782	$\text{C}_9\text{H}_8 + \text{OH} = \text{C}_9\text{H}_7 + \text{H}_2\text{O}$	3.43E+09	1.2	-447	[65]
783	$\text{C}_9\text{H}_8 + \text{O} = \text{C}_9\text{H}_7 + \text{OH}$	1.81E+14	0	3080	[65]
784	$\text{C}_9\text{H}_8 + \text{CH}_3 = \text{C}_9\text{H}_7 + \text{CH}_4$	4.16E+12	0	11130	^a
785	$\text{C}_9\text{H}_8(+\text{M}) = \text{C}_9\text{H}_7 + \text{H}(+\text{M})$	7.65E+19	-1.18	84473	^a
	LOW PRESSURE LIMIT:	1.07E+80	-16.788	16985	

C₉H₇ Reactions

786	$\text{C}_9\text{H}_7 + \text{H} \Rightarrow \text{b-C}_7\text{H}_7 + \text{C}_2\text{H}$	1.00E+12	0	0	a
787	$\text{C}_9\text{H}_7 + \text{O} \Rightarrow \text{C}_6\text{H}_5\text{CHCH} + \text{CO}$	1.00E+14	0	0	[114]

C₁₀H₁₀ Reactions

788	$\text{C}_5\text{H}_5 + \text{C}_5\text{H}_5 \Rightarrow \text{C}_{10}\text{H}_{10}$	2.00E+13	0	0	a
789	$\text{C}_{10}\text{H}_{10} \Rightarrow \text{C}_5\text{H}_5 + \text{C}_5\text{H}_5$	1.10E+25	-8.24	93600	a
790	$\text{C}_{10}\text{H}_{10} + \text{H} \Rightarrow \text{C}_9\text{H}_8 + \text{CH}_3$	2.00E+13	0	0	a

C₅H₄C₅H₅ et C₁₀H₉-1, 2, 3, 4, 5 et 6 Reactions

791	$\text{C}_5\text{H}_5 + \text{C}_5\text{H}_5 \Rightarrow \text{C}_5\text{H}_4\text{C}_5\text{H}_5 + \text{H}$	8.00E+13	0	8000	a
792	$\text{C}_5\text{H}_4\text{C}_5\text{H}_5 + \text{H} \Rightarrow \text{C}_5\text{H}_5 + \text{C}_5\text{H}_5$	3.00E+13	0	0	a
793	$\text{C}_5\text{H}_4\text{C}_5\text{H}_5 = \text{C}_{10}\text{H}_9-0$	3.60E+10	0.9	37000	a
794	$\text{C}_{10}\text{H}_9-0 \Rightarrow \text{C}_{10}\text{H}_9-1$	3.82E+12	-1.92	6015	a
795	$\text{C}_{10}\text{H}_9-1 \Rightarrow \text{C}_{10}\text{H}_9-0$	5.13E+13	-3.38	-3386	a
796	$\text{C}_{10}\text{H}_9-1 \Rightarrow \text{C}_{10}\text{H}_9-2$	3.47E+22	-4.77	14773	a
797	$\text{C}_{10}\text{H}_9-2 \Rightarrow \text{C}_{10}\text{H}_9-1$	6.70E+21	-4.65	29528	a
798	$\text{C}_{10}\text{H}_9-2 \Rightarrow \text{C}_{10}\text{H}_9-4$	1.66E+15	-4.7	12281	a
799	$\text{C}_{10}\text{H}_9-4 \Rightarrow \text{C}_{10}\text{H}_9-2$	1.23E+13	-4.67	-7950	a
800	$\text{C}_{10}\text{H}_9-2 \Rightarrow \text{C}_{10}\text{H}_9-3$	1.36E+14	-2.375	7479	a
801	$\text{C}_{10}\text{H}_9-3 \Rightarrow \text{C}_{10}\text{H}_9-2$	7.14E+14	-2.4	-253.8	a
802	$\text{C}_{10}\text{H}_9-3 \Rightarrow \text{C}_{10}\text{H}_9-5$	5.49E+11	-1.67	5136	a
803	$\text{C}_{10}\text{H}_9-5 \Rightarrow \text{C}_{10}\text{H}_9-3$	2.10E+11	-1.52	29884	a
804	$\text{b-C}_7\text{H}_7 + \text{C}_3\text{H}_3 \Rightarrow \text{C}_{10}\text{H}_9-6 + \text{H}$	6.00E+11	0	0	[110]
805	$\text{C}_{10}\text{H}_9-6 + \text{H} \Rightarrow \text{b-C}_7\text{H}_7 + \text{C}_3\text{H}_3$	3.00E+13	0	0	a
806	$\text{C}_{10}\text{H}_9-4 = \text{C}_{10}\text{H}_9-6$	3.56E+10	0.88	37300	a
807	$\text{C}_{10}\text{H}_9-4 \Rightarrow \text{C}_{10}\text{H}_9-5$	2.17E+09	-0.83	1555	a
808	$\text{C}_{10}\text{H}_9-5 \Rightarrow \text{C}_{10}\text{H}_9-4$	1.33E+11	-0.55	38522	a

C₁₀H₈ Reactions

809	$\text{C}_{10}\text{H}_9-5 \Rightarrow \text{C}_{10}\text{H}_8 + \text{H}$	7.16E+10	0.756	15144	a
810	$\text{C}_{10}\text{H}_8 + \text{H} \Rightarrow \text{C}_{10}\text{H}_9-5$	4.43E+08	1.542	11108	a
811	$\text{C}_{10}\text{H}_8 + \text{H} = \text{C}_{10}\text{H}_7-1 + \text{H}_2$	2.28E+08	1.87	17097	[116]
812	$\text{C}_{10}\text{H}_8 + \text{H} = \text{C}_{10}\text{H}_7-2 + \text{H}_2$	2.65E+08	1.87	17097	a
813	$\text{C}_{10}\text{H}_8 + \text{OH} = \text{C}_{10}\text{H}_7-1 + \text{H}_2\text{O}$	9.66E+02	3.016	4374	[116]
814	$\text{C}_{10}\text{H}_8 + \text{OH} = \text{C}_{10}\text{H}_7-2 + \text{H}_2\text{O}$	8.31E+02	3.016	4374	a
815	$\text{C}_{10}\text{H}_8 + \text{O} = \text{C}_{10}\text{H}_7-1\text{O} + \text{H}$	6.66E+12	0	2332	a
816	$\text{C}_{10}\text{H}_8 + \text{O} = \text{C}_{10}\text{H}_7-1 + \text{OH}$	6.00E+13	0	11064	a
817	$\text{C}_{10}\text{H}_8 + \text{O} = \text{C}_{10}\text{H}_7-2\text{O} + \text{H}$	6.66E+12	0	2332	a
818	$\text{C}_{10}\text{H}_8 + \text{O} = \text{C}_{10}\text{H}_7-2 + \text{OH}$	6.00E+13	0	11064	a
819	$\text{C}_{10}\text{H}_8 + \text{CH}_3 = \text{C}_{10}\text{H}_7-1 + \text{CH}_4$	2.00E+12	0	15060	[118]

820	$\text{C}_{10}\text{H}_8 + \text{CH}_3 = \text{C}_{10}\text{H}_7\text{-2} + \text{CH}_4$	1.86E+13	0	19380	[119]
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C₁₀H₇-1, 2 et 3 Reactions

821	$\text{C}_8\text{H}_5 + \text{C}_2\text{H}_2 = >\text{C}_{10}\text{H}_7\text{-3}$	1.34E+04	2.499	1283	a
822	$\text{C}_{10}\text{H}_7\text{-3} = >\text{C}_8\text{H}_5 + \text{C}_2\text{H}_2$	7.64E+13	0.42	45987	a
823	$\text{C}_{10}\text{H}_7\text{-3} = >\text{C}_{10}\text{H}_7\text{-1}$	1.29E+09	-0.73	1474	a
824	$\text{C}_{10}\text{H}_7\text{-1} = >\text{C}_{10}\text{H}_7\text{-3}$	9.61E+09	-0.17	71105	a
825	$\text{C}_{10}\text{H}_7\text{-1} + \text{H} (+\text{M}) = \text{C}_{10}\text{H}_8 (+\text{M})$	2.20E+14	0	0	a
	LOW PRESSURE LIMIT:	4.10E+104	-24.63	21505	
	TROE PARAMETERS: a = 0.046, T*** = 352, T* = 60000, T** = 7600				
826	$\text{C}_{10}\text{H}_7\text{-2} + \text{H} (+\text{M}) = \text{C}_{10}\text{H}_8 (+\text{M})$	2.20E+14	0	0	a
	LOW PRESSURE LIMIT:	4.10E+104	-24.63	21505	
	TROE PARAMETERS: a = 0.046, T*** = 352, T* = 60000, T** = 7600				
827	$\text{C}_{10}\text{H}_7\text{-1} + \text{O}_2 = \text{C}_{10}\text{H}_7\text{-1O} + \text{O}$	1.02E+13	0	3581	a
828	$\text{C}_{10}\text{H}_7\text{-1} + \text{OH} = \text{C}_{10}\text{H}_7\text{-1O} + \text{H}$	5.00E+13	0	0	[90]

C₁₀H₇-1O et 2 Reactions

829	$\text{C}_{10}\text{H}_7\text{-2} + \text{O}_2 = \text{C}_{10}\text{H}_7\text{-2O} + \text{O}$	1.02E+13	0	3581	a
830	$\text{C}_{10}\text{H}_7\text{-2} + \text{OH} = \text{C}_{10}\text{H}_7\text{-2O} + \text{H}$	5.00E+13	0	0	[90]
831	$\text{C}_{10}\text{H}_7\text{-1O} = \text{C}_9\text{H}_7 + \text{CO}$	3.60E+11	0	43943	a
832	$\text{C}_{10}\text{H}_7\text{-2O} = \text{C}_9\text{H}_7 + \text{CO}$	3.60E+11	0	43943	a

1-C₁₁H₁₀ et A₂CH₂-1 Reactions

833	$\text{C}_{10}\text{H}_7\text{-1} + \text{CH}_3 (+\text{M}) = 1\text{-C}_{11}\text{H}_{10} (+\text{M})$	2.33E+14	-0.283	-191	a
	LOW PRESSURE LIMIT:	6.74E+83	-19.22	15000	
	TROE PARAMETERS: a = 0.735, T*** = 60000, T* = 513, T** = 100000				
834	$\text{A}_2\text{CH}_2\text{-1} + \text{H} (+\text{M}) = 1\text{-C}_{11}\text{H}_{10} (+\text{M})$	7.23E+13	0.062	-44	a
	LOW PRESSURE LIMIT:	3.03E+136	-33.35	55600	
	TROE PARAMETERS: a = 0.163, T*** = 714, T* = 728, T** = 5112				
835	$1\text{-C}_{11}\text{H}_{10} + \text{H} = \text{C}_{10}\text{H}_8 + \text{CH}_3$	9.50E+05	2	940	a
836	$1\text{-C}_{11}\text{H}_{10} + \text{H} = \text{A}_2\text{CH}_2\text{-1} + \text{H}_2$	6.47E+00	3.98	3384	a
837	$1\text{-C}_{11}\text{H}_{10} + \text{OH} = \text{A}_2\text{CH}_2\text{-1} + \text{H}_2\text{O}$	1.31E+05	2.394	-602	a
838	$1\text{-C}_{11}\text{H}_{10} + \text{O} = \text{A}_2\text{CH}_2\text{-1} + \text{OH}$	6.30E+11	0	0	a
839	$\text{A}_2\text{CH}_2\text{-1} = >\text{A}_2\text{CH}_2\text{-f} + \text{H}$	1.44E+13	0.453	76300	a
840	$\text{A}_2\text{CH}_2\text{-f} + \text{H} = >\text{A}_2\text{CH}_2\text{-1}$	8.82E+08	1.2	2018	a

2-C₁₁H₁₀ et A₂CH₂-2 Reactions

841	$\text{C}_{10}\text{H}_7\text{-2} + \text{CH}_3 (+\text{M}) = 2\text{-C}_{11}\text{H}_{10} (+\text{M})$	2.33E+14	-0.283	-191	a
	LOW PRESSURE LIMIT:	6.74E+83	-19.22	15000	
	TROE PARAMETERS: a = 0.735, T*** = 60000, T* = 513, T** = 100000				

842	$\text{A}_2\text{CH}_2\text{-2}+\text{H}(+\text{M})=2\text{-C}_{11}\text{H}_{10} (+\text{M})$	7.23E+13	0.062	-44	^a
	LOW PRESSURE LIMIT:	3.03E+136	-33.35	55600	
	TROE PARAMETERS: $a = 0.163$, $T^{***} = 714$, $T^* = 728$, $T^{**} = 5112$				
843	$2\text{-C}_{11}\text{H}_{10}+\text{H}=\text{C}_{10}\text{H}_8+\text{CH}_3$	9.50E+05	2	940	^a
844	$2\text{-C}_{11}\text{H}_{10}+\text{H}=\text{A}_2\text{CH}_2\text{-2}+\text{H}_2$	6.47E+00	3.98	3384	^a
845	$2\text{-C}_{11}\text{H}_{10}+\text{OH}=\text{A}_2\text{CH}_2\text{-2}+\text{H}_2\text{O}$	1.31E+05	2.394	-602	^a
846	$2\text{-C}_{11}\text{H}_{10}+\text{O}=\text{A}_2\text{CH}_2\text{-2}+\text{OH}$	6.30E+11	0	0	^a
847	$\text{A}_2\text{CH}_2\text{-2}=>\text{A}_2\text{CH}_2\text{-f}+\text{H}$	1.44E+13	0.453	76300	^a
848	$\text{A}_2\text{CH}_2\text{-f}+\text{H}=>\text{A}_2\text{CH}_2\text{-2}$	8.82E+08	1.2	2018	^a

A₂CH₃-f Reactions

849	$\text{A}_2\text{CH}_2\text{-f}+\text{H}=>\text{C}_9\text{H}_7+\text{C}_2\text{H}_2$	1.00E+14	0	0	^a
850	$\text{C}_9\text{H}_7+\text{C}_2\text{H}_2=>\text{A}_2\text{CH}_2\text{-f}+\text{H}$	1.58E-01	4.18	29670	^a

C₁₂H₁₀ et C₁₂H₉ Reactions

851	$\text{C}_6\text{H}_5+\text{C}_6\text{H}_5=\text{C}_{12}\text{H}_{10}$	5.94E+42	-8.83	13830	[90]
852	$\text{C}_6\text{H}_5+\text{C}_6\text{H}_6=\text{C}_{12}\text{H}_{10}+\text{H}$	1.90E+76	-18.9	39470	[120]
853	$\text{C}_{12}\text{H}_{10}+\text{H}=\text{C}_{12}\text{H}_9+\text{H}_2$	3.23E+07	2.095	15842	[90]
854	$\text{C}_{12}\text{H}_{10}+\text{OH}=\text{C}_{12}\text{H}_9+\text{H}_2\text{O}$	2.11E+13	0	4571	[90]
855	$\text{C}_6\text{H}_5+\text{C}_3\text{H}_3=\text{C}_6\text{H}_5\text{C}_3\text{H}_2+\text{H}$	3.00E+12	0	0	[121]
856	$\text{C}_6\text{H}_5\text{C}_3\text{H}_2+\text{C}_3\text{H}_3=\text{C}_{12}\text{H}_9+\text{H}$	3.00E+12	0	0	[121]
857	$\text{C}_{12}\text{H}_9+\text{H}=\text{C}_{12}\text{H}_{10}$	1.17E+33	-5.57	8760	[90]

^a This work^b Estimated, see Leplat 2010Units : mol, K, cal, cm³**References of rate parameters :**

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