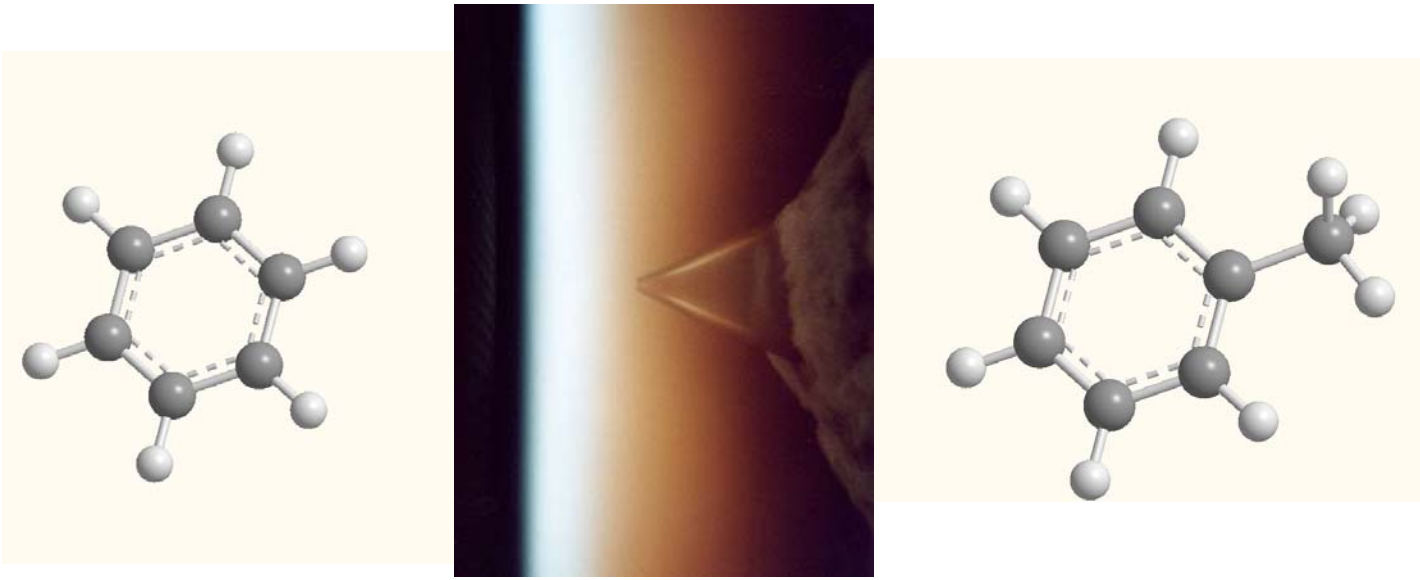
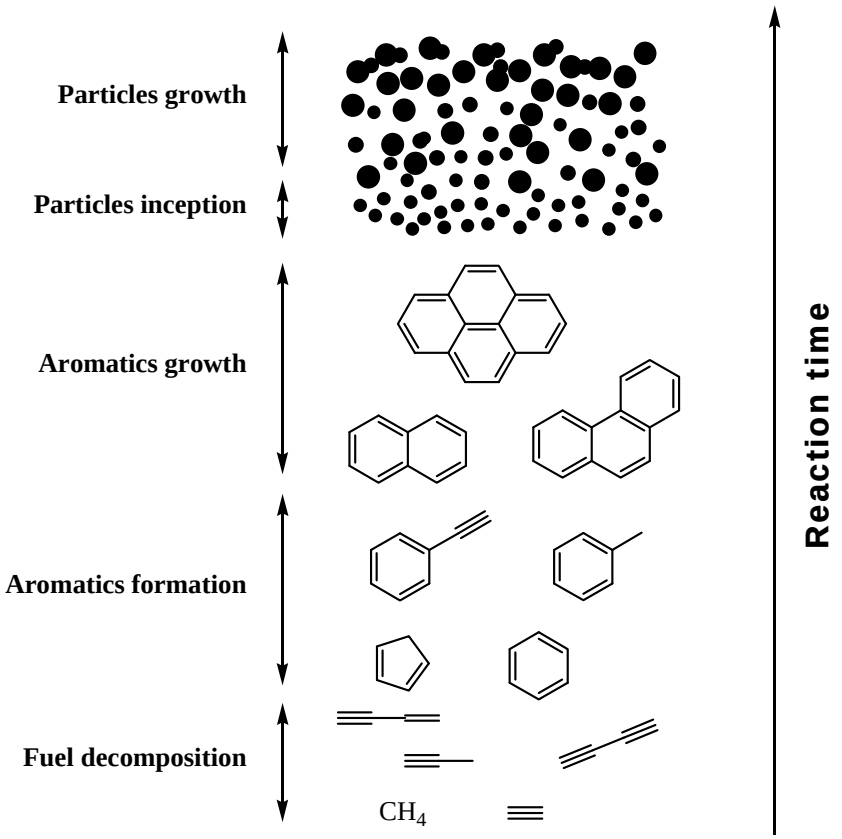
Experimental study and kinetic modeling study of $C_6H_6/O_2/Ar$ and $C_7H_8/O_2/Ar$ flames at ϕ = 2.0



Valéry Detilleux, Véronique Dias, Jacques Vandooren

Rich combustion and soot production



In the present work, we will focus on:

1. Aromatic decomposition and oxidation
2. Small PAH formation

H. Bockhorn, *H. Bockhorn (ed), Soot Formation in Combustion, p.3*

1. Introduction
2. Objectives
3. Experimental procedure and modeling details
4. Results and discussion
5. Conclusions and perspectives

Literature overview

(low pressure, laminar, premixed and 1 dimensional)

C_6H_6 flames

Bittner and Howard, 1981
Defoeux and co-workers, 2005
Yang and co-workers, 2006
Detilleux and co-workers, 2009

C_7H_8 flames

Bakali and co-workers, 2007 (CH_4 + C_7H_8)

Yuyang and co-workers, 2009

Modeling studies

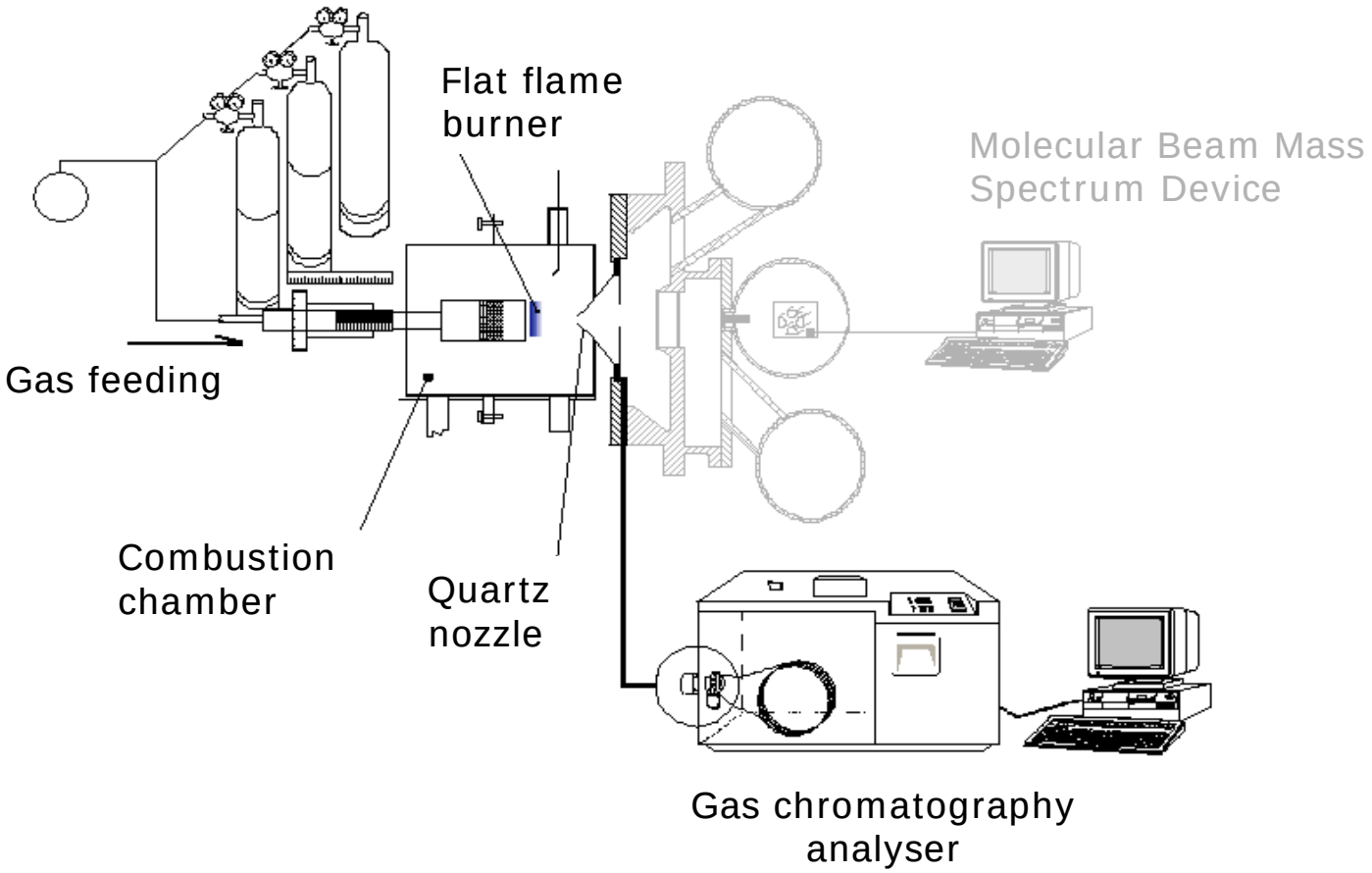
Bittker, 1991
Lindstedt and Skevis, 1994
Tan and Frank, 1996
Ristori and co-workers, 2001
Richter and Howard, 2002
…

Dagaut, 2002
Bounaceur, 2005
…

Objectives of the present work

- To provide **new experimental data** on benzene and toluene combustion (one dimensional and low pressure laminar flat flames) ;
- To understand and **to model benzene and toluene decomposition and oxidation** in such flames ;
- To understand and **to model formation of the first PAH** in rich aromatic hydrocarbon flames ;
- To emphasize **differences between toluene and benzene combustion.**

Experimental setup



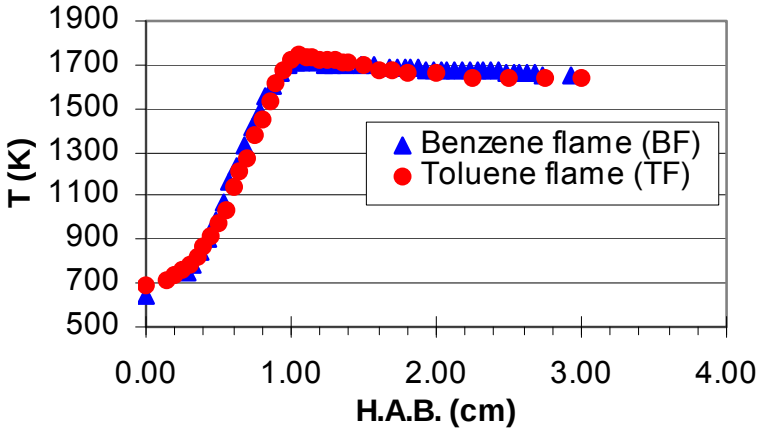
Working pressure = 45 mbar

Kinetic modeling details

Software : Cosilab ®

Models : Developed in the present work
Contain : 174 chemical species
921 reactions

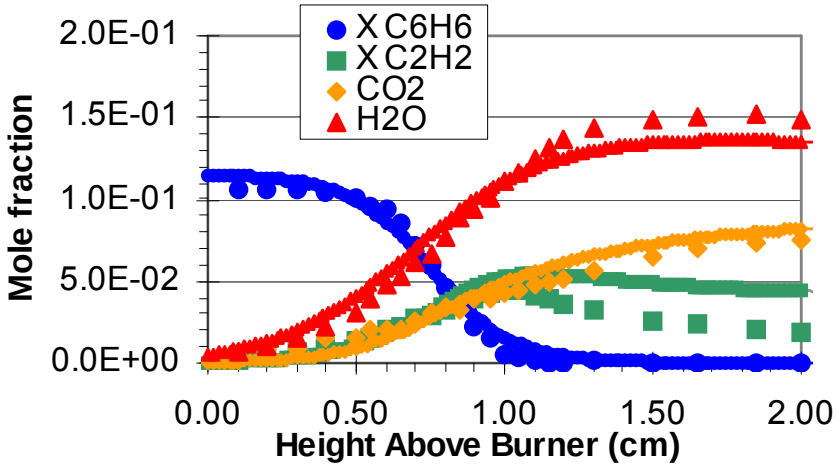
Temperature: Measured by Pt/PtRh10% thermocouple

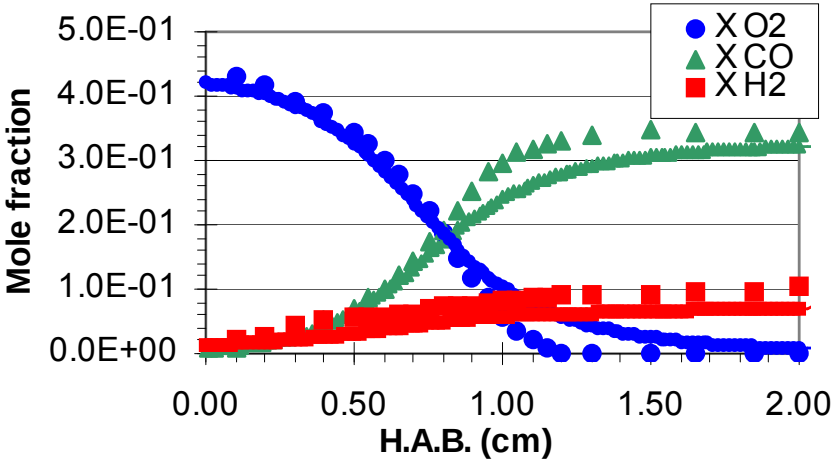


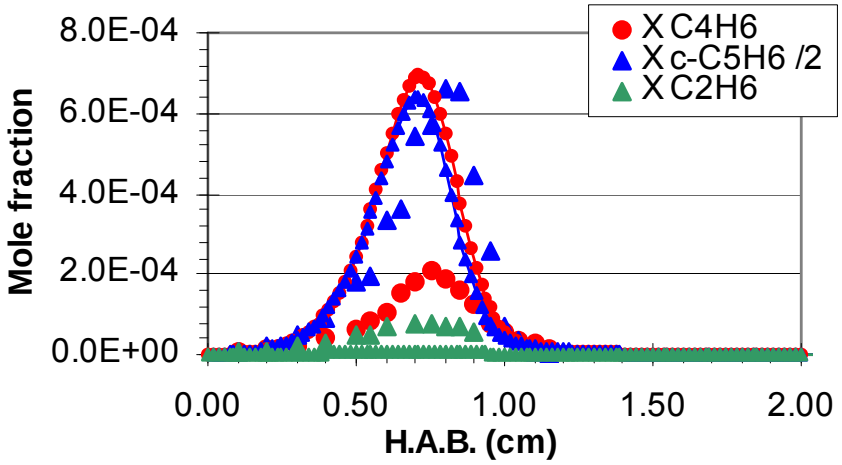
Flames studied in the present work

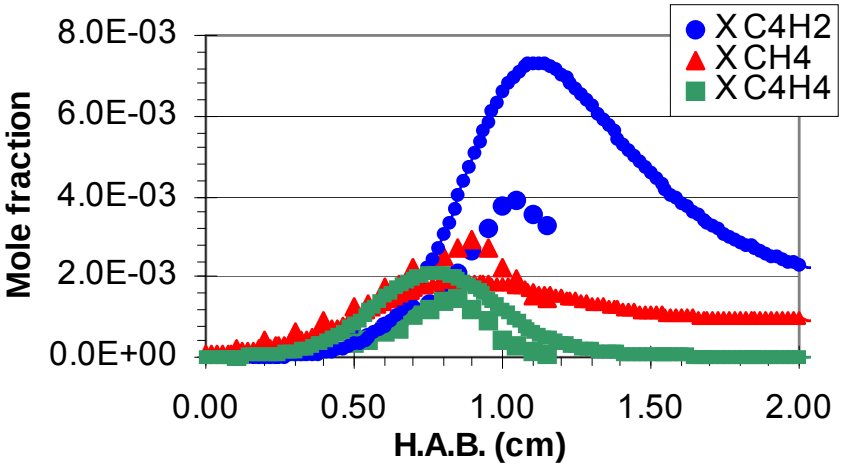
Flame Code	Fuel	Flame parameters			Mole fractions		
		Equivalence ratio	C/O	Total flow rate (l/min)	X Fuel	X O_2	X Ar
FB20	Benzene	2.00	0.80	5.50	0.116	0.436	0.448
FB18	Benzene	1.80	0.72	5.50	0.116	0.484	0.400
FB10	Benzene	1.00	0.40	5.50	0.027	0.204	0.768
FB07	Benzene	0.70	0.28	5.50	0.027	0.292	0.681
FBC20	Benzene / Cyclopentene	2.00	0.77	5.5	0.088 / 0.031	0.447	0.434
FC20	Cyclopentene	2.00	0.80	5.5	0.133	0.414	0.453
FT20	Toluene	2.00	0.78	5.50	0.099	0.445	0.456
FT18	Toluene	1.80	0.70	5.50	0.099	0.494	0.407
FT10	Toluene	1.00	0.39	5.5	0.026	0.203	0.774
FT07	Toluene	0.70	0.27	5.5	0.026	0.290	0.687
FTP21	Toluene / Propyne	2.10	0.82	5.5	0.099 / 0.011	0.448	0.445
FTP22	Toluene / Propyne	2.20	0.85	5.5	0.099 / 0.022	0.448	0.434

Benzene flame with an equivalence ratio of 2

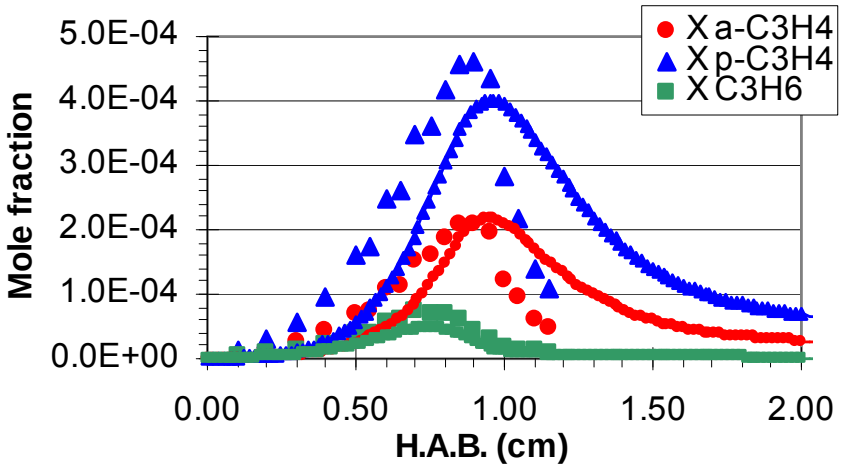


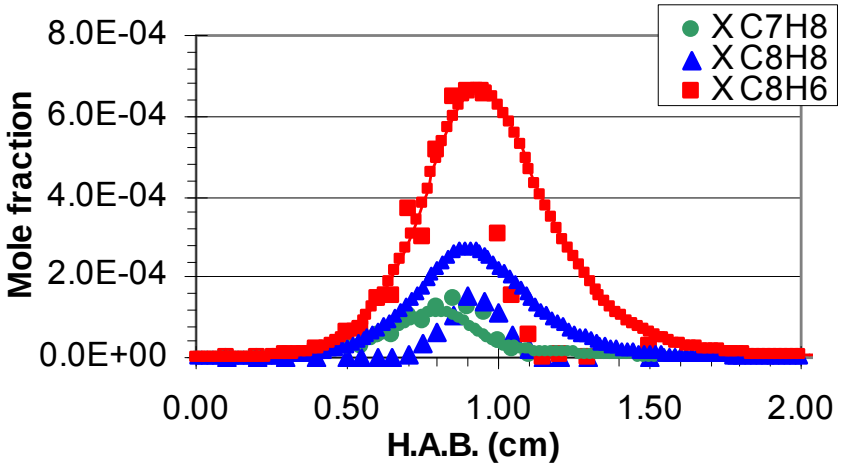


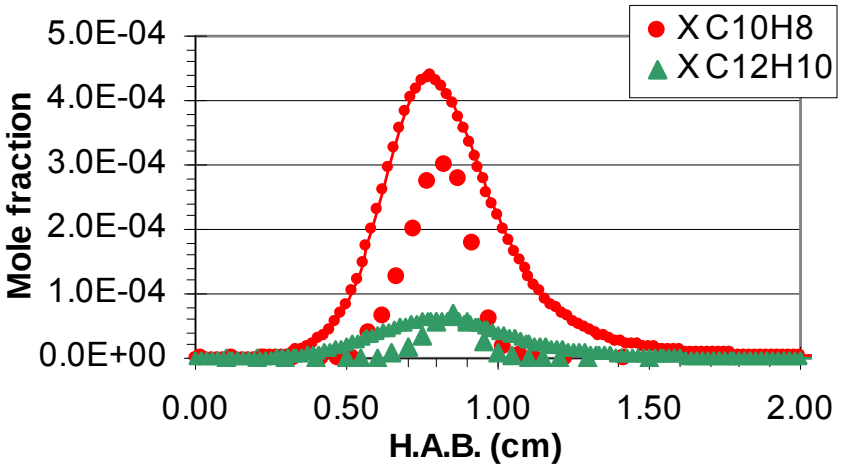


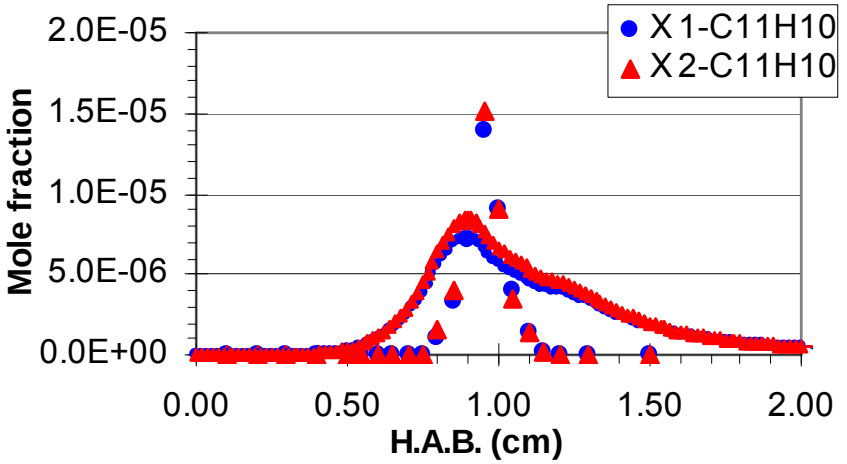


Benzene flame with an equivalence ratio of 2

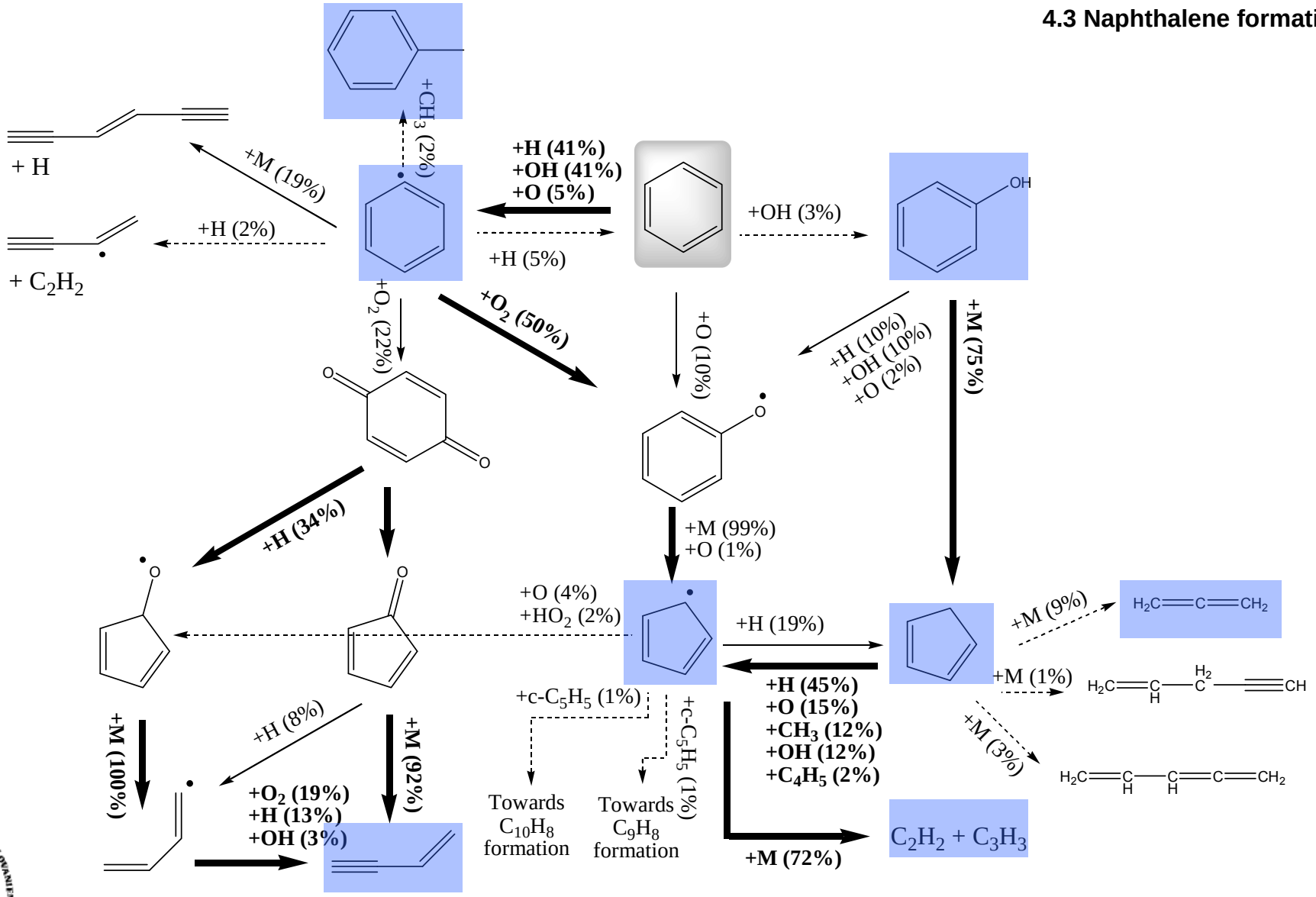




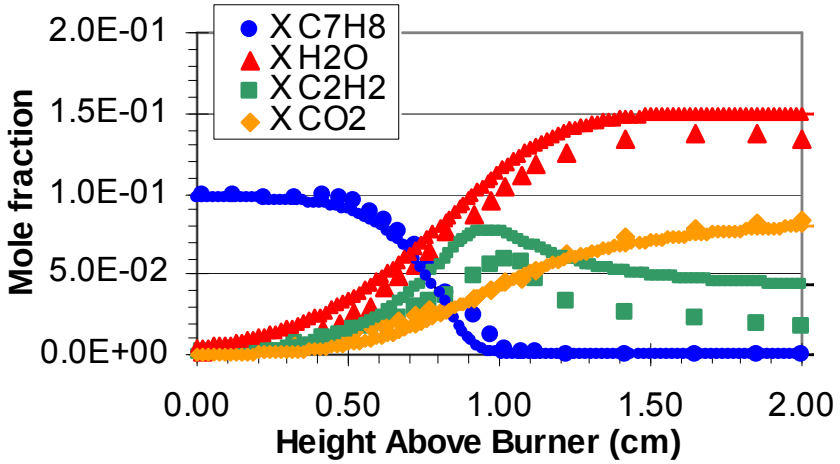


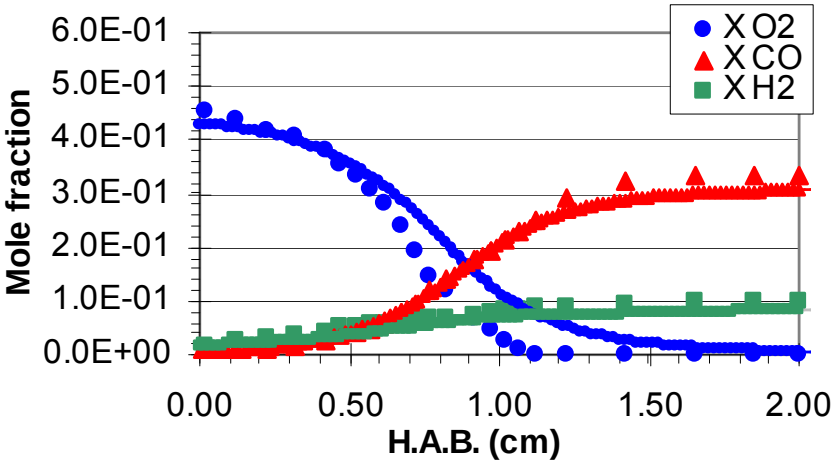


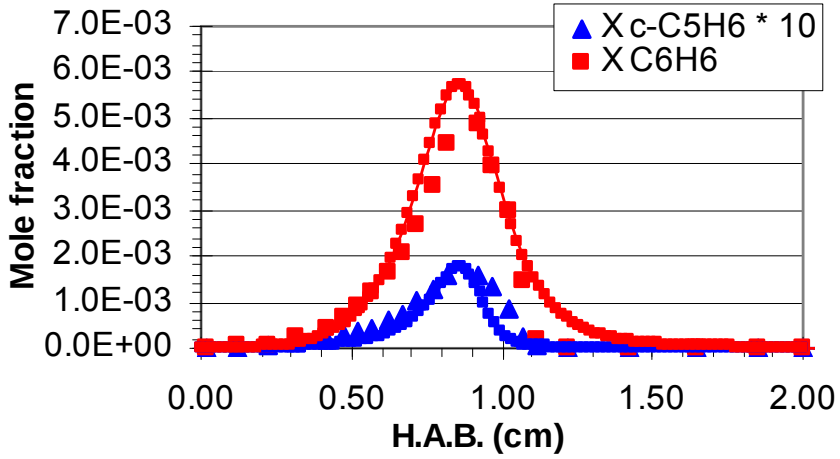
Benzene flame with an equivalence ratio of 2: Kinetic scheme

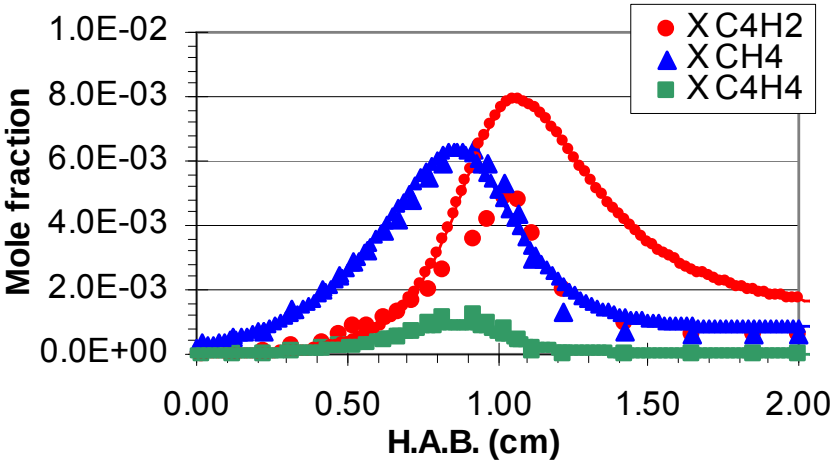


Toluene flame with an equivalence ratio of 2

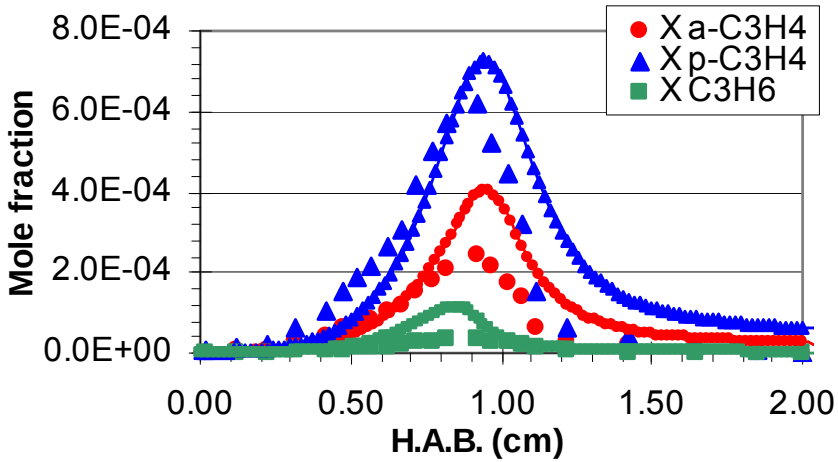


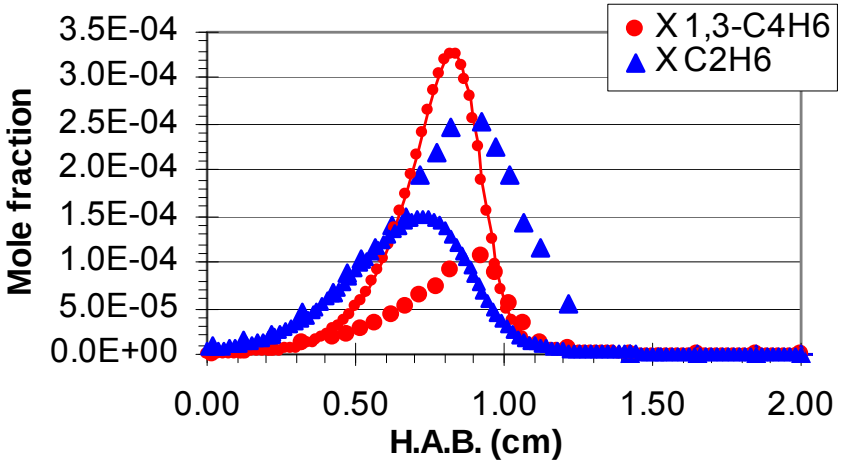


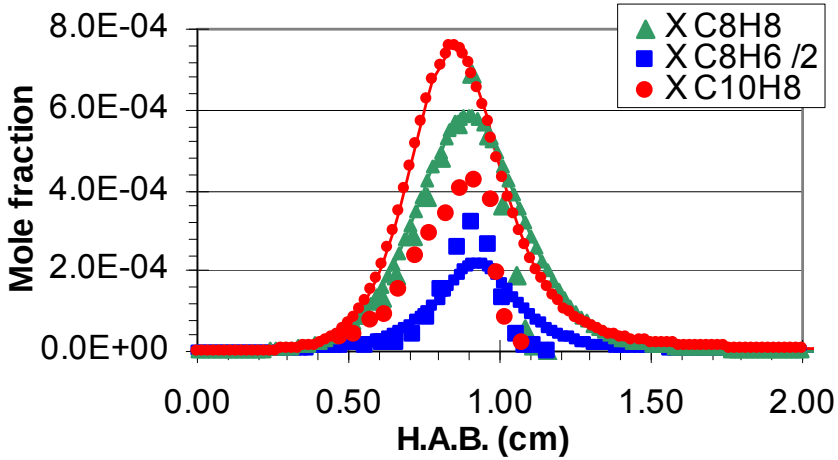


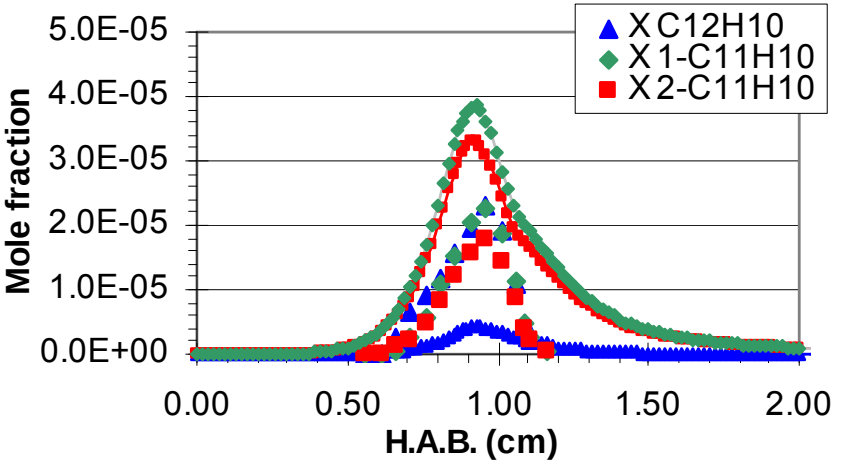


Toluene flame with an equivalence ratio of 2



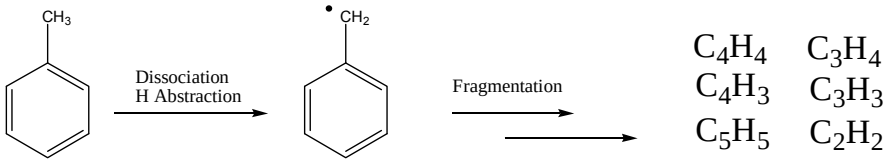






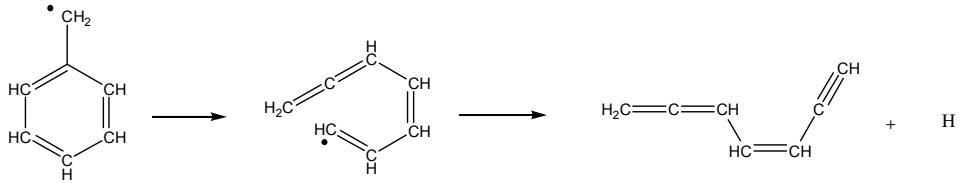
First steps of toluene combustion

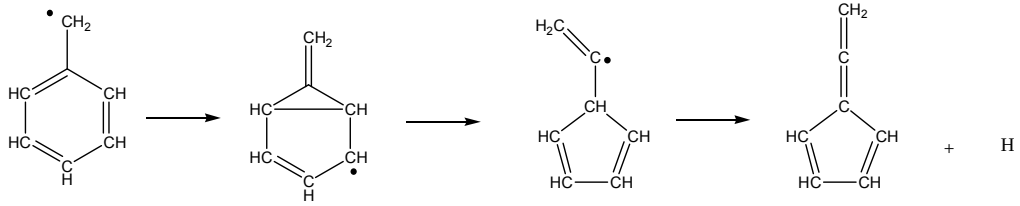
First steps of toluene combustion ?

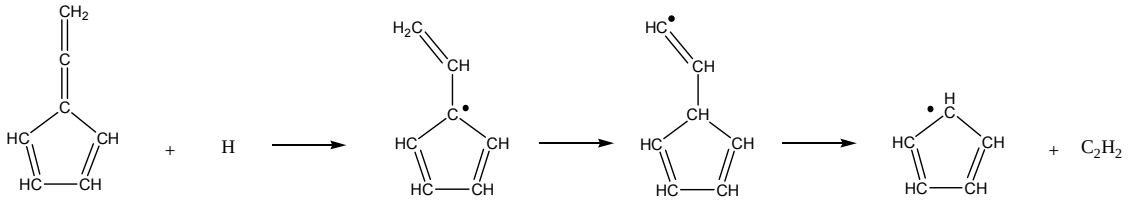


Jones et al. (1997) J. Phys Chem. A, 101, 7105

Decomposition of benzyl radical ?







Cavallotti et al. (2009) Proc. Comb. Inst., 32, 115

According to theoretical studies, benzyl decomposition mainly produces C_7H_6 + H.

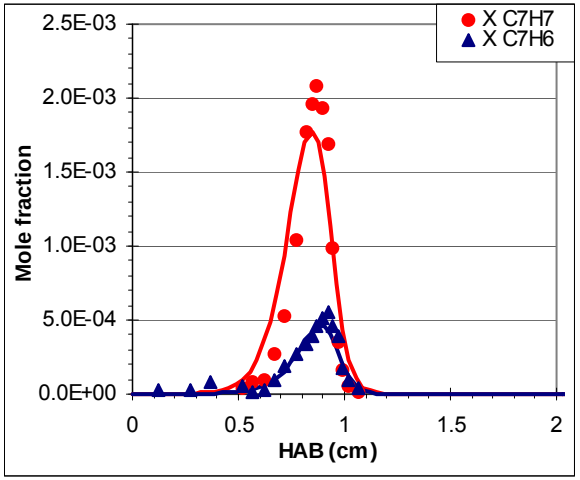
C_7H_6 may be either :

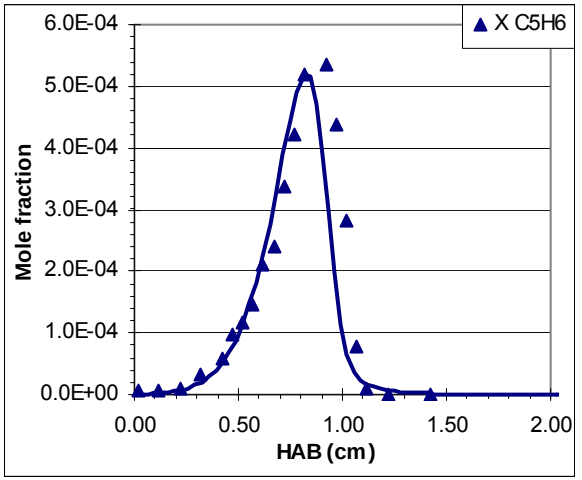
a linear C_7H_6, precursor of C_4, C_3, C_2 and C_5 chemical species
fulvenallene and dissociates into C_5H_5 + C_2H_2 after an H addition.

To reproduce the measured C_5H_6 mole fraction we have to consider the fulvenallene pathway

Experimental evidences on a C_7H_6 pathway

In order to verify this assumption we have measured C_7H_7 and C_7H_6 mole fraction profiles along the rich toluene flame by Molecular Beam Mass Spectrometry (MBMS)



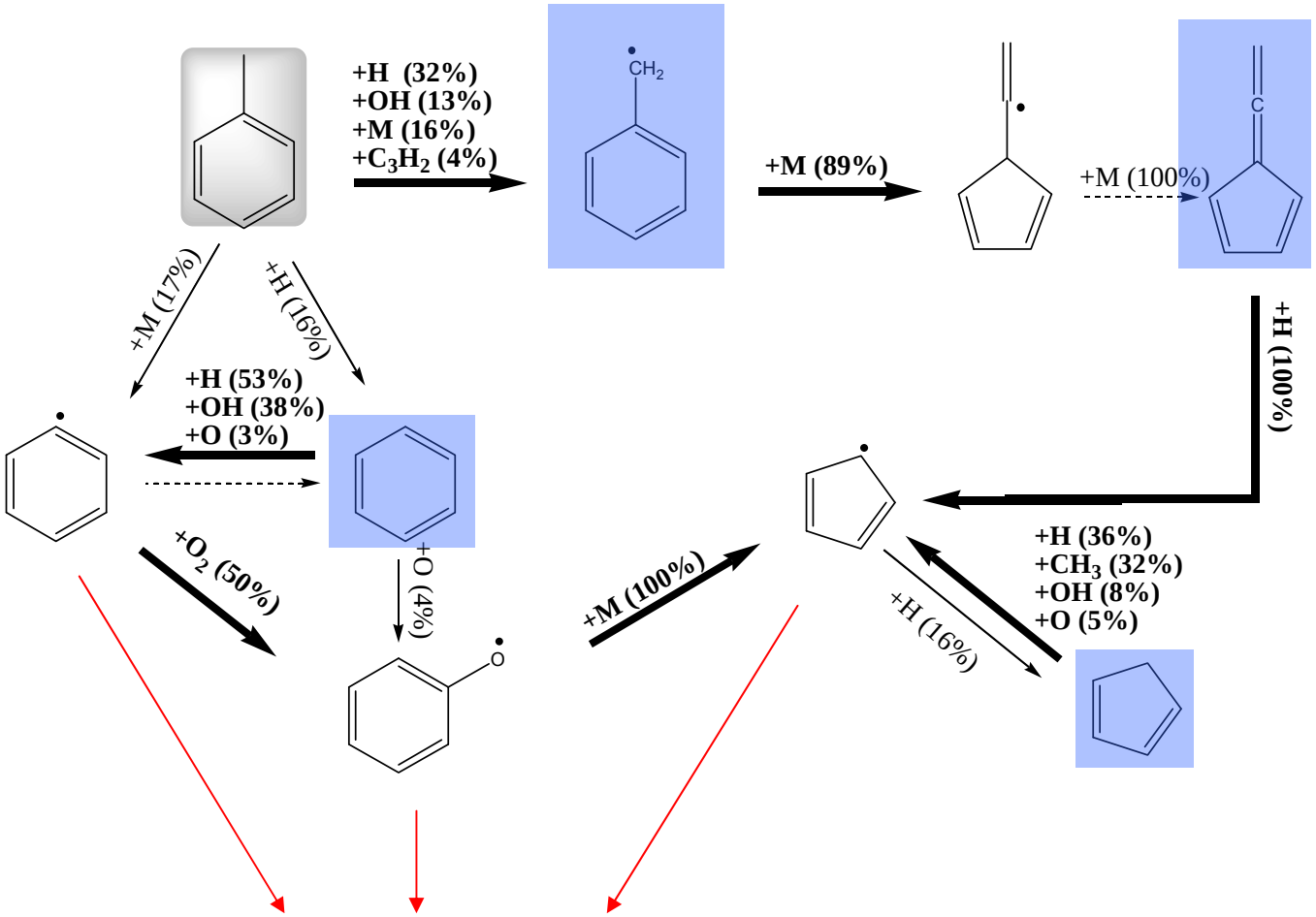


We obtain a close agreement between experiment and kinetic modeling

We can validate a $C_7H_8 \xrightarrow{-H} C_7H_7 \rightarrow C_7H_6 + H \rightarrow C_5H_5 + C_2H_2$ route

It might be the fulvenallene pathway but we are unable to demonstrate it since we do not have structural information on the C_7H_6 measured.

Toluene flame with an equivalence ratio of 2: Kinetic scheme



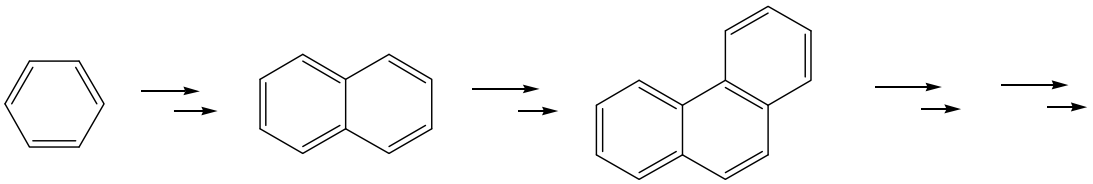
Towards benzene kinetic scheme

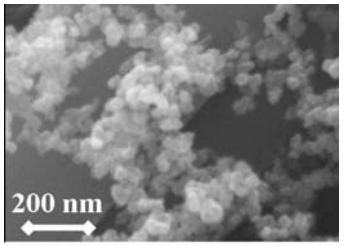
C_5H_5 formation

65 % from fulvenallenne
20 % from phenoxy radical

From reactants to PAH and soot

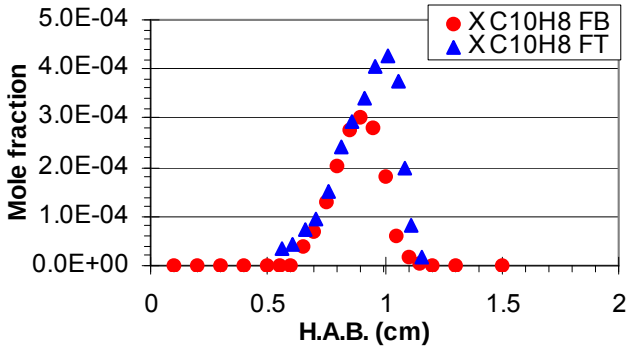
General pathway …





A good kinetic modeling of first PAH is necessary to predict larger PAH and soot formation

Naphthalene production in benzene and toluene flames

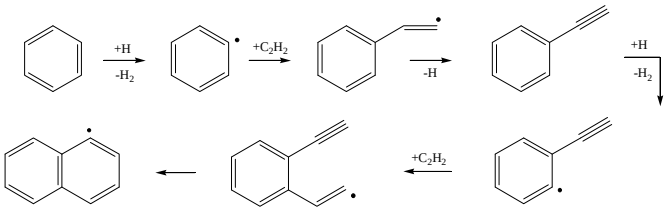


At same equivalence ratio, the toluene flame produces more $C_{10}H_8$ than benzene flame

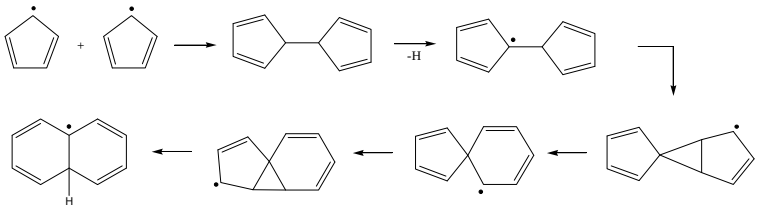
Naphthalene formation

Which pathway for naphthalene production ?

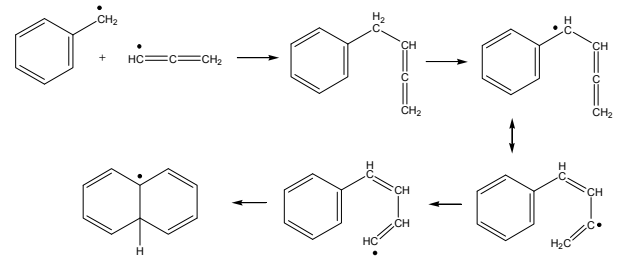
Hydrogen Abstraction C_2H_2 Addition (Frenklach, 2002)



Cyclopentadienyl pathway (Marinov, 1996)



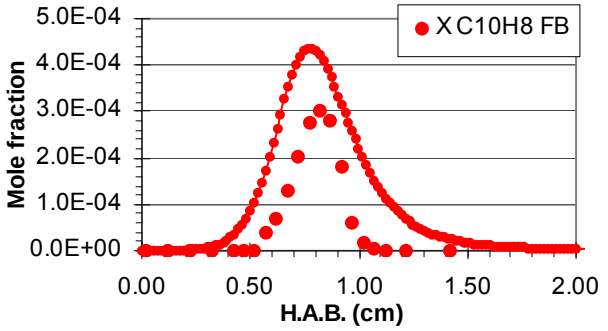
C_7 + C_3 Pathway (Colcket, 1994)

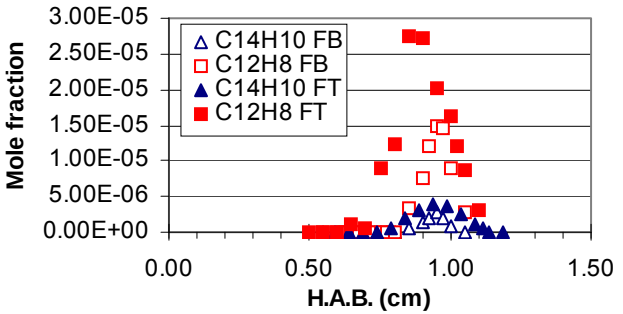


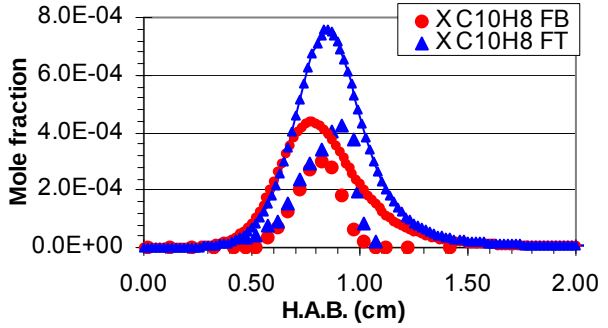
100 %

70 %

30 %







Conclusions and perspectives

1. Several **structures of benzene and toluene flames have been measured** over a **wide range of equivalence ratios**.

2. A **kinetic model** with a good predictive capability **has been developed** for rich benzene and toluene combustion.

3. Consumption of benzyl radical **into a C_7H_6 intermediate giving cyclopentadienyl** has been validated.

4. Toluene flames have higher concentration in PAH than benzene flames. The modeling study shows that **naphthalene production** routes **highly depend on reactant**: naphthalene is mainly produced by the **C_5 pathway in the benzene flame and also by the C_7+C_3 route in the toluene flame**.

The kinetic mechanism developed in this work will help further works on PAH formation and could be useful for future modeling of soot formation.

Aknowledgements

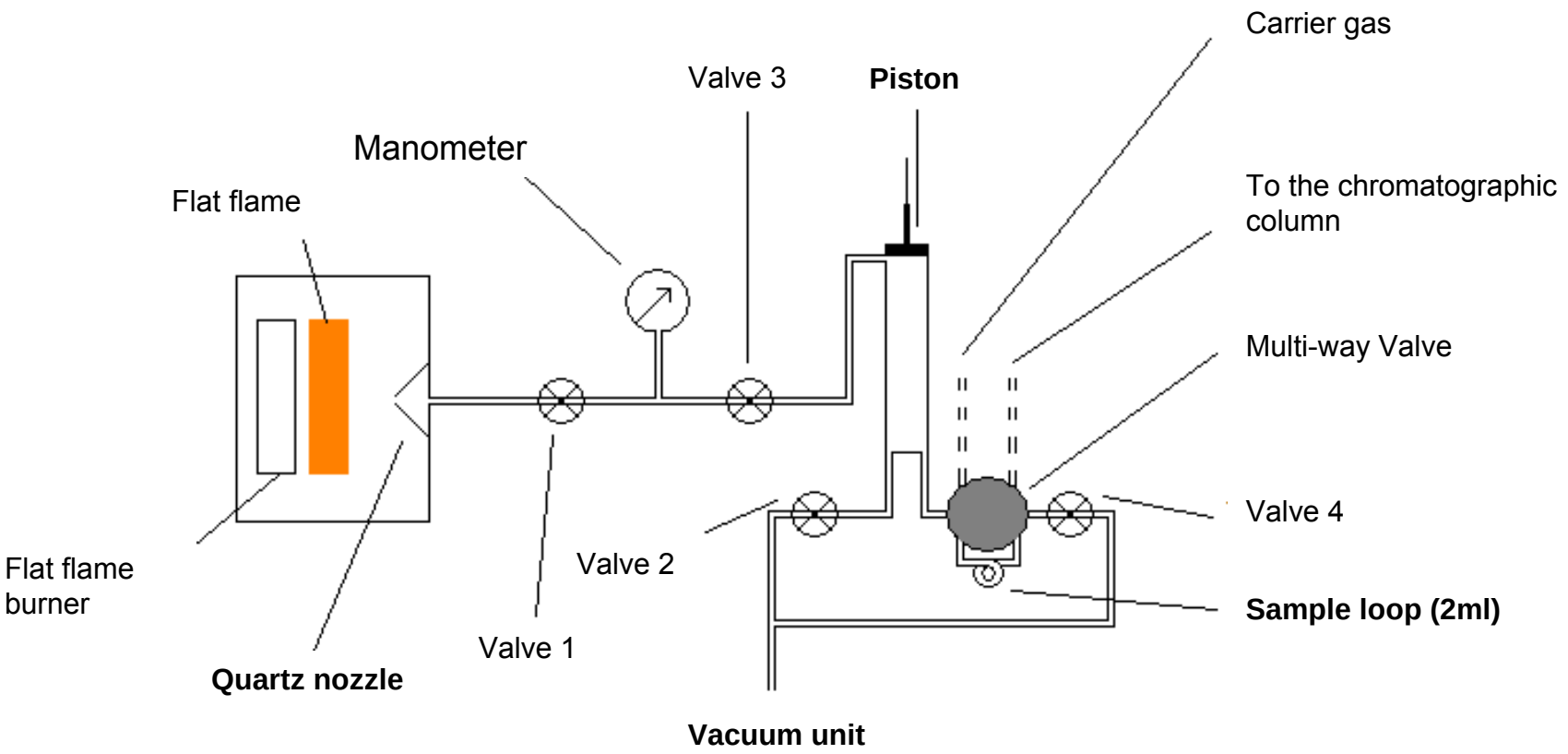
- **Ministère de la Région Wallonne (Belgium) for the financial support**

- **Members of the lab:**
  - **Prof. Jacques Vandooren**
  - **Valéry Detilleux**
  - **Catherine Duynslaegher**
  - **Nicolas Leplat**
  - **Xavier Lories**
  - **Christiane Smets**
  - **Pierre Van Tiggelen**

- **You for your kind attention**

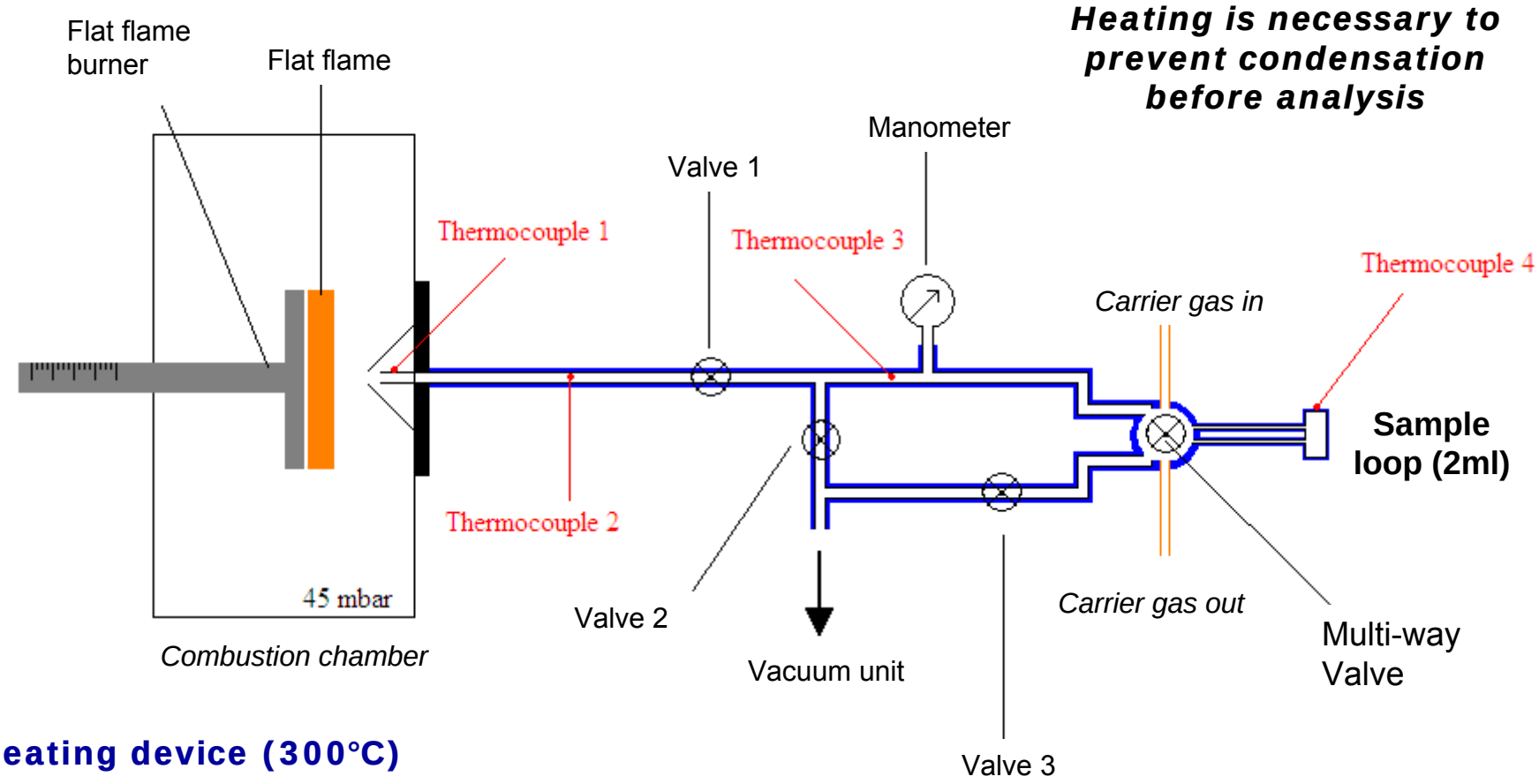
Chromatographic injection setup 1/2

For permanent gases of combustion and hydrocarbons from C_1 to C_6



Chromatographic injection setup 2/2

For hydrocarbons from C_7 to C_{14}



Phenoxy radical overestimation

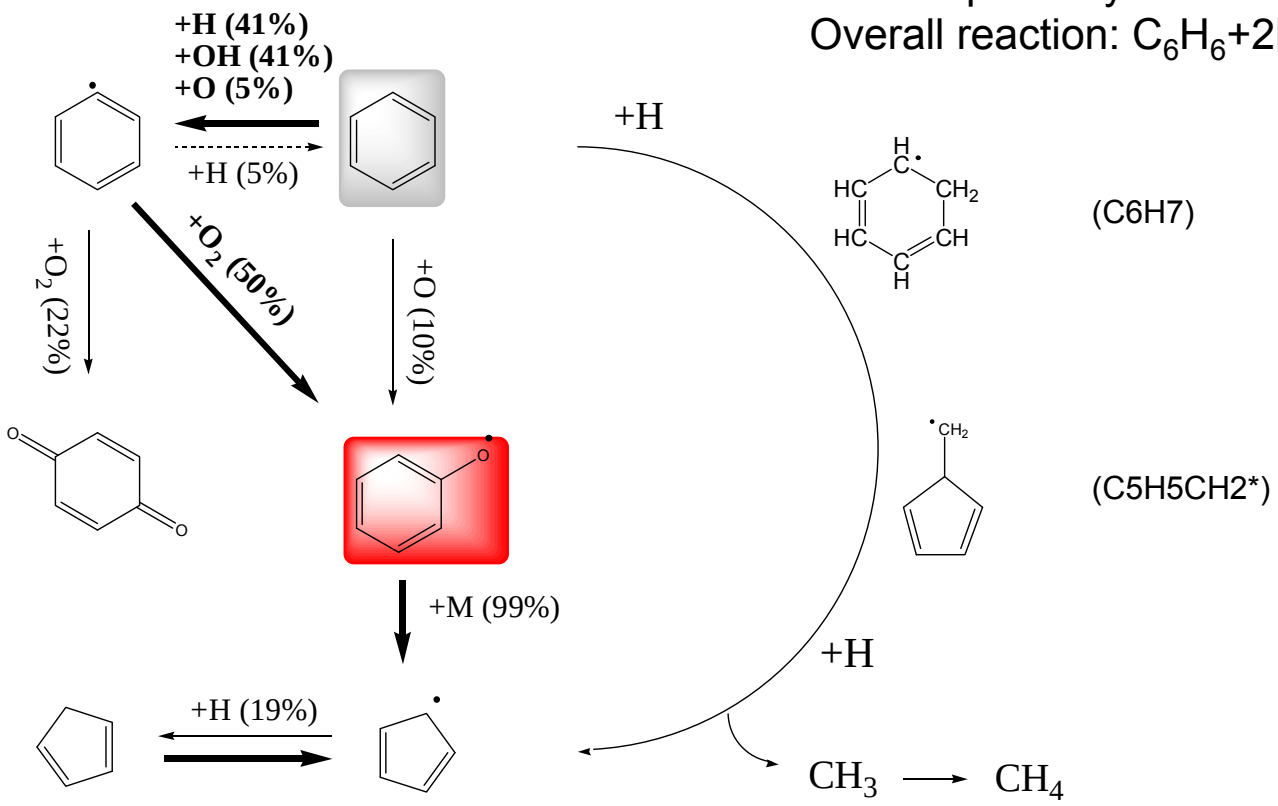
Maximum mole fractions of :

C_6H_5O	is overestimated ≈ 100 times by the kinetic model
CH_3	is underestimated
C_5H_5 / C_5H_6	is well predicted

Assumption :

A direct pathway between C_6H_6 and C_5H_5 ?

Overall reaction: $C_6H_6+2H \Rightarrow C_5H_5+CH_3$



Toluene flame with an equivalence ratio of 2: Kinetic scheme