Special Session on Chemical Kinetics
International Energy Agency - Annual Task Leaders Meeting 2010

Detailed chemical kinetic models for cleaner internal combustion engines

Nancy in Europe

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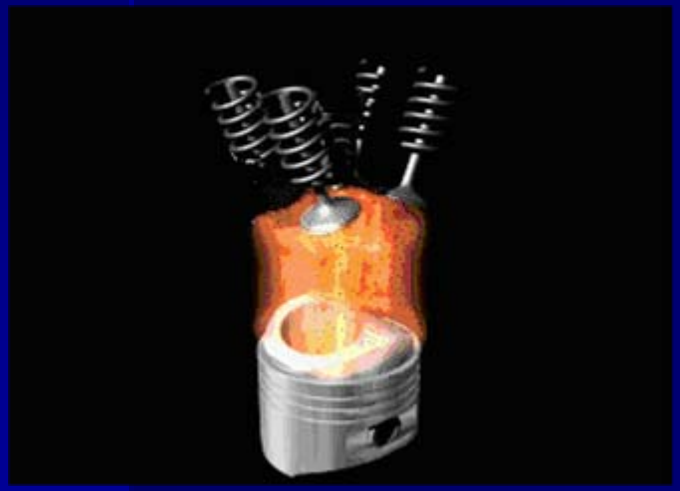
BACKGROUND
Global warming mitigation

Need of more efficient and cleaner gas turbines and engines



High working efficiency
but low particulate and NOx emissions
(lower temperature combustion)

Homogeneous Charge Compression Ignition (HCCI) engine

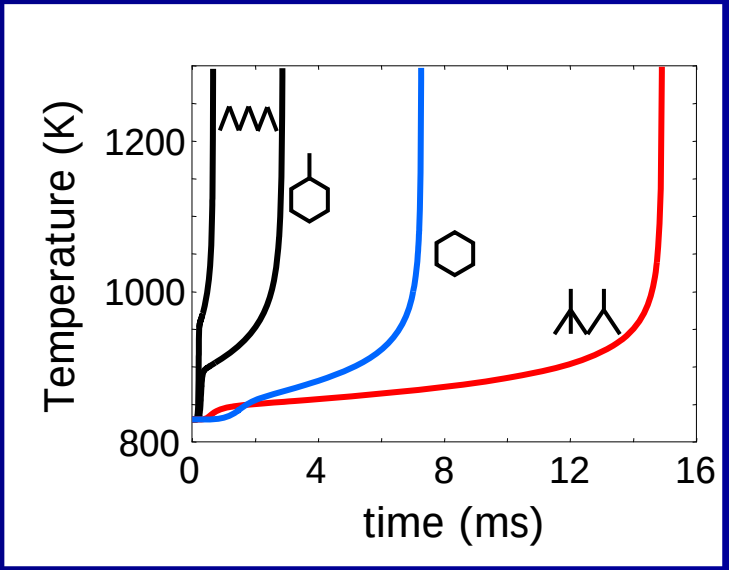
A better understanding of combustion chemistry

BACKGROUND

To better understand combustion chemistry by using detailed chemical kinetic models

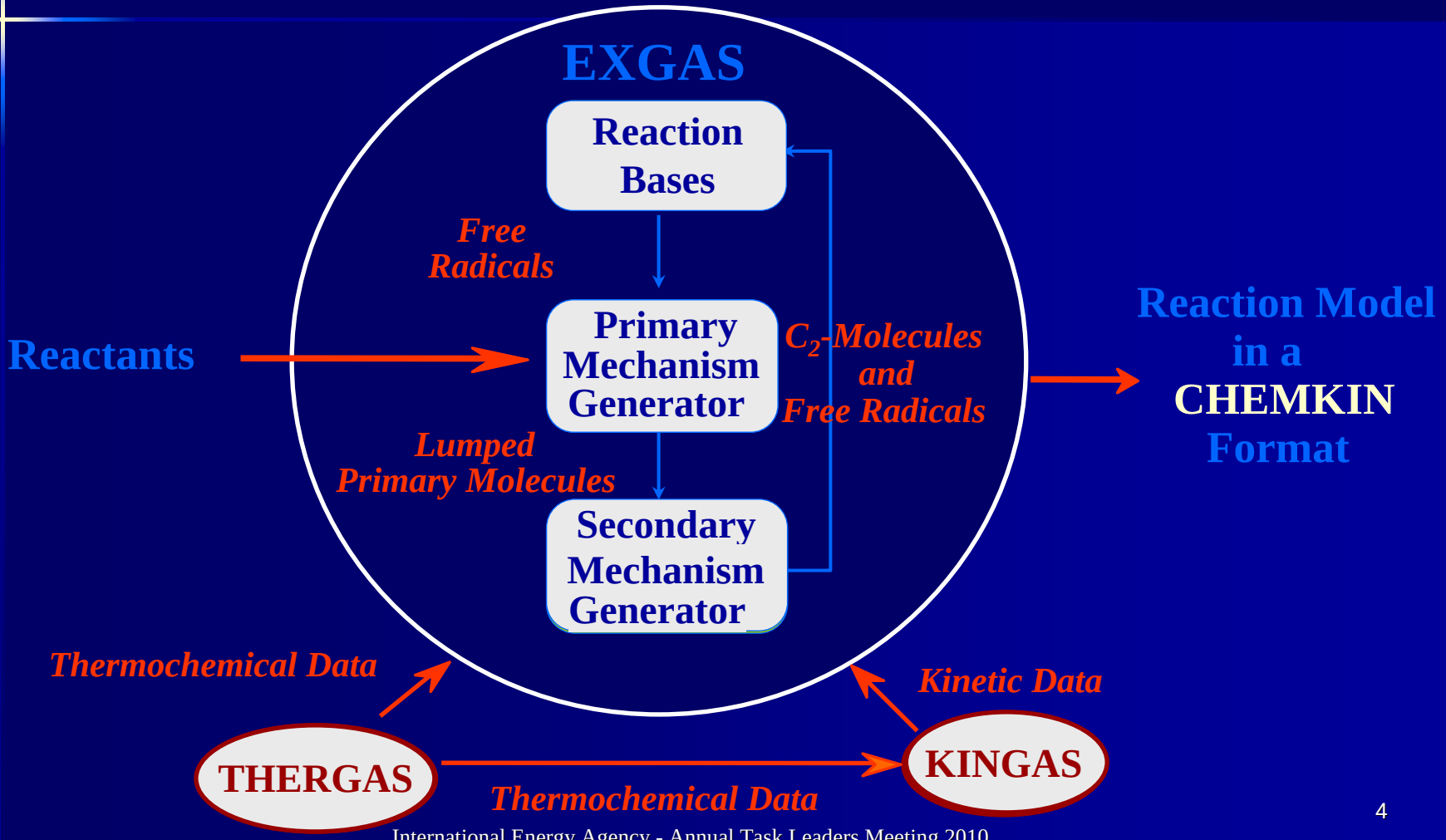
Definition of proper surrogates

Development of chemical mechanisms (elementary reactions)

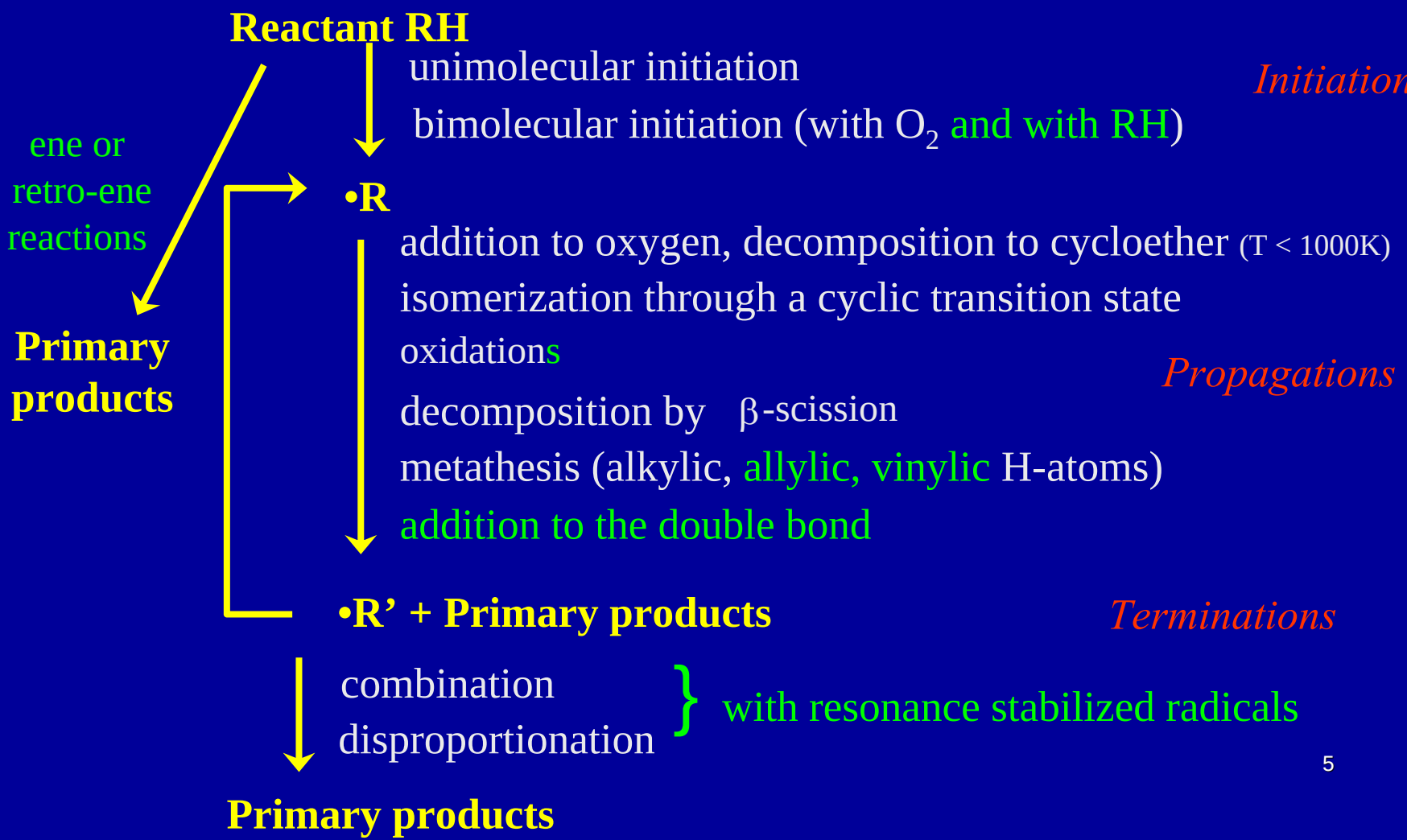


Simulation for validation purpose

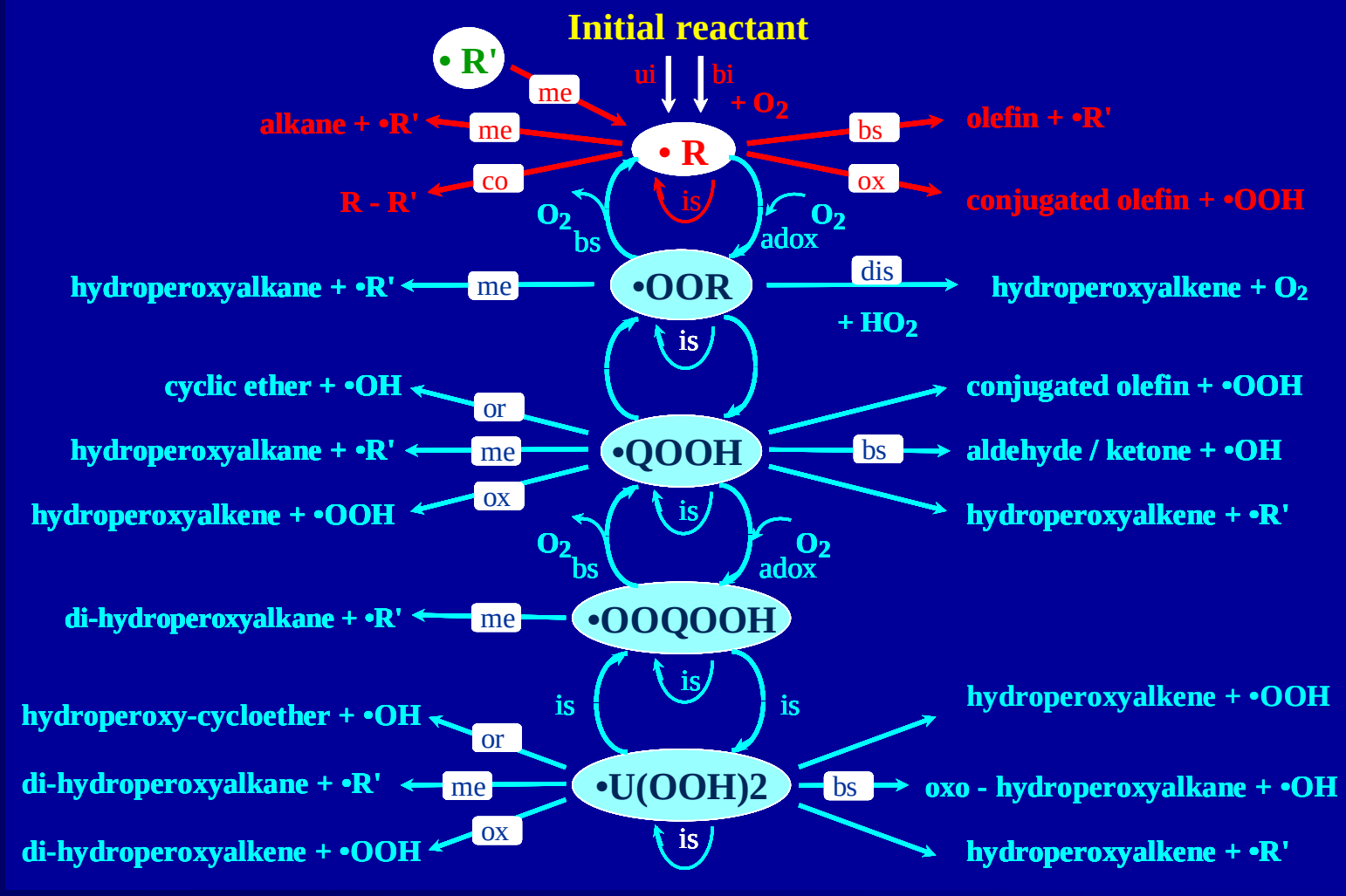
AUTOMATIC GENERATION OF DETAILED MECHANISMS FOR OXIDATION REACTIONS



ALGORITHM OF GENERATION OF THE PRIMARY MECHANISM FOR ALKANES, CYCLIC ALKANES, METHYL ESTERS AND ALKENES



STRUCTURE OF THE PRIMARY MECHANISM FOR ALKANES



REACTION BASES

1 - C_0-C_2 reaction base (781 reactions)

• All the elementary reactions involving radicals or molecules containing from 0 to 2 atoms of carbon)

2 - C_3-C_5 reaction base for unsaturated compounds (450 reactions)

• Including the reactions of allene, propyne, 1,3-butadiene, 1-butyne, 2-butyne, cyclopentene and derived species with rate constants of the literature

3 - reaction base for small aromatic species (328 reactions)

• Including the reactions of benzene, toluene, phenol, ethylbenzene, styrene, benzaldehyde and derived species with rate constants of the literature

Validated in an extended range of temperatures and for various types of reactors

MAIN KINETIC DATA OF THE PRIMARY MECHANISM OF LINEAR ALKANES

Combust. Flame, (*1998*, 2005) ; Ph. D. Thesis of P.A. Glaude (1999) and F. Buda (2006)

($k = A \times T^b \times \exp(-E/RT)$, Units : cm3, mol, s, cal)

H-abstraction (per H atom)		Primary H (i.e. R-CH_3)			Secondary H (i.e. R1-CH_2-R2)		
		lg A	b	E	lg A	b	E
Initiation with O_2		12.84	0	ΔHr	12.84	0	ΔHr
Oxidation	n>4	11.43	0	5000	11.99	0	5000
	n≤4	11.60	0	5000	12.16	0	5000
H-atom abstraction by							
	•O•	13.23	0	7850	13.11	0	5200
	•H	6.98	2	7700	6.65	2	5000
	•OH	5.95	2	450	6.11	2	-770
	•CH_3	-1	4	8200	11.0	0	9600
	•OOH	11.30	0	17000	11.30	0	15500

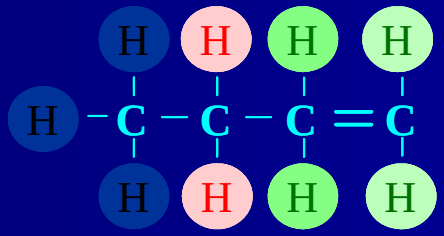
Other reactions		lg A	b	E
Addition of a free radical to O_2		Calculated by additivity method		
Beta-scission of a free radical	to •CH_3 + molecule	13.30	0	31000
	to •R + molecule	13.30	0	28700
	to •OOH + molecule	12.92	0	26000
	to •OH + molecule	9.00	0	7500
Cyclic ether formation	3 members ring	11.78	0	17950
	4 members ring	10.96	0	16600
	5 members ring	9.56	0	7000
	6 members ring	8.23	0	1950
Disproportionation of •OOR and •OOH		11.30	0	-1300
Isomerizations and unimolecular initiations		Calculated according to the methods proposed by S.W. Benson		

MAIN KINETIC DATA OF THE PRIMARY MECHANISM OF ALKENES

Combust. Flame, (2001) **Ph. D. Thesis of B. Heyberger (2002)**

The presence of the double bond induces an important increase of the number of kinetic parameters

H Abstractions:



Radical	Allylic H									Vinylic H					
	Primary			Secondary			Tertiary			Secondary			Tertiary		
	lgA	b	E	lgA	b	E	lgA	b	E	lgA	b	E	lgA	b	E
•O•	10.8	0.7	25	10.6	0.7	13	10.5	0.7	5	10.7	0.7	36	10.8	0.7	32
•H	4.8	2.5	10	4.4	2.5	-7	4.4	2.5	-12	5.6	2.5	51	5.6	2.5	41
•OH	6.0	2	-1	6.2	2	-6	6.1	2	-11	6.0	2	12	6.0	2	6
$•CH_3$	-1.3	3.5	24	11.9	0	29	11.9	0	22	-1.7	3.5	54	-1.7	3.5	50
$•HO_2$	3.5	2.6	58	3.5	2.6	52	4.2	2.6	45						

MORE ACCURATE KINETIC DATA USING QUANTUM MECHANICS CALCULATIONS

15.3 kcalmol

21.1 kcalmol

36.7 kcalmol

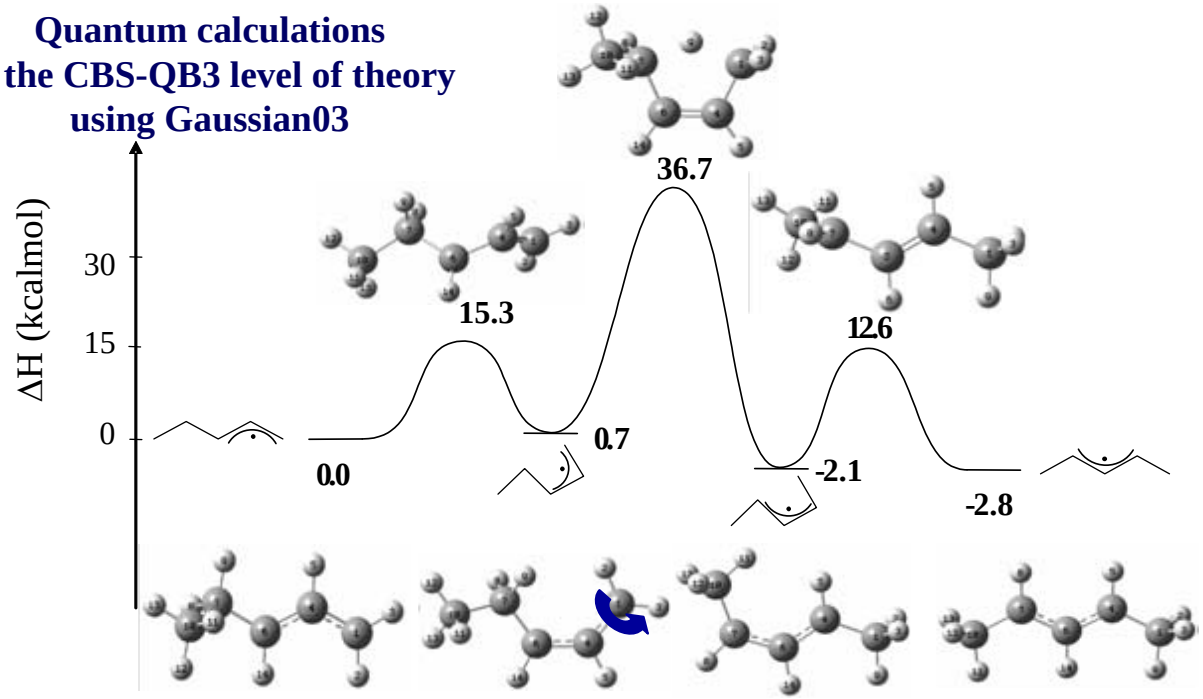
Isomerisation :

Cis-trans conversion

Isomerisation

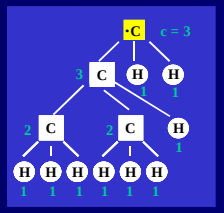
Unsaturated 5 members ring

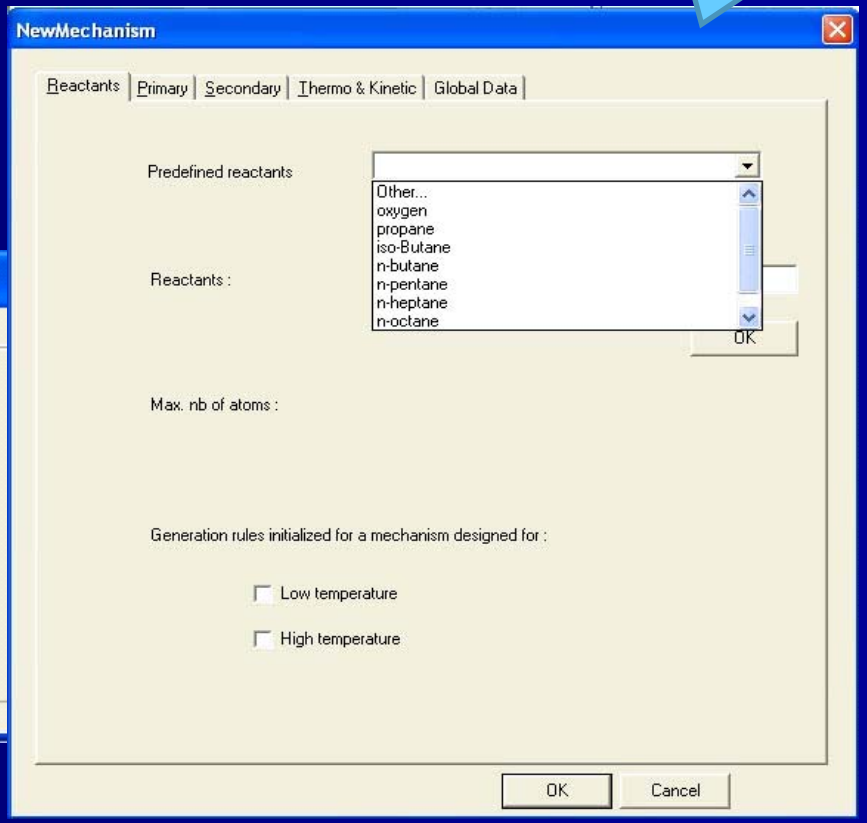
Quantum calculations
at the CBS-QB3 level of theory
using Gaussian03



EXGAS-ALKANES

Coming soon EXGAS-ALKANES-ESTERS



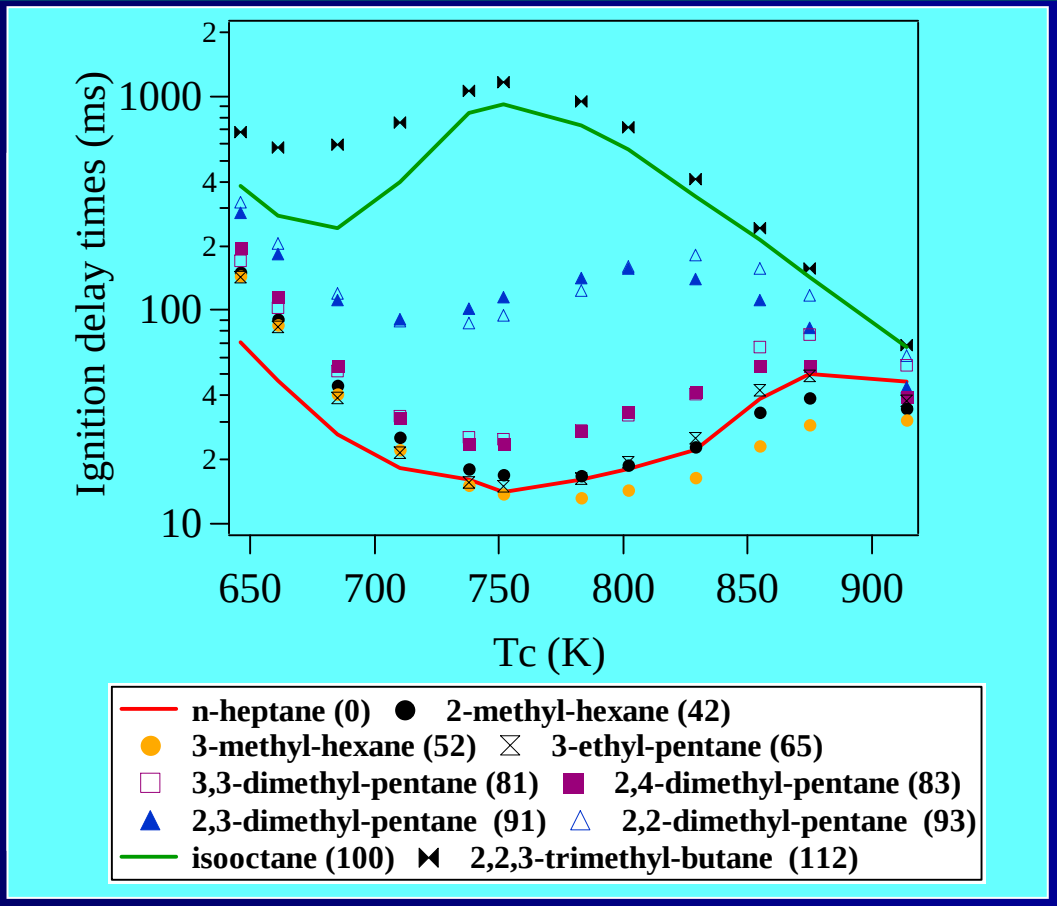


F. BUDA, R. BOUNACEUR, V. WARTH, P.A. GLAUDE, R. FOURNET et F. BATTIN-LECLERC, "Progress towards an unified detailed kinetic model for the autoignition of alkanes from C4 to C10 between 600 and 1200 K", "Combustion and Flame" 142, 170-186 (2005)

J. BIET, M.H. HAKKA, V. WARTH, P.A. GLAUDE, F. BATTIN-LECLERC
"Experimental and modeling study of the low-temperature oxidation of large alkanes", "Energy & Fuels" 22, 2258-2269 (2008),

EXAMPLE OF MODELLING: *isomers of heptane*

Mechanism for n-heptane containing 1817 reactions



Correct correlation with RON at 650K

Slight inversions at higher temperatures

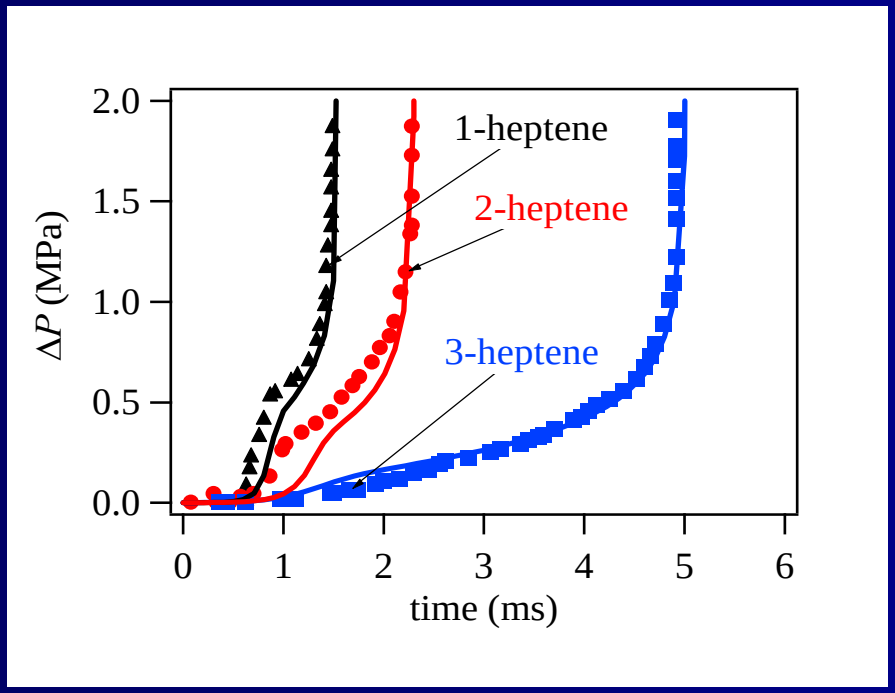
F. BUDA, R. BOUNACEUR, V. WARTH, P.A. GLAUDE, R. FOURNET, F. BATTIN-LECLERC
"**Progress towards an unified detailed kinetic model for the autoignition of alkanes from C4 to C10 between 600 and 1200 K** ", "Combustion&Flame", 142, 170 (2005).

EXAMPLE OF MODELLING: *3 linear isomers of heptene*

Pressure changes of heptenes/«air» mixtures
measured in a rapid compression machine (Cambridge - USA)

(Tc = 627 K, Pc = 41.6 bar, at Φ = 0.4, Tanaka et al., 2003)

Symbols are experiments, lines are simulations



1-heptene: 7178 reactions
2-heptene: 8515 reactions
3-heptene: 3032 reactions

Still problems in modelling the formation of products

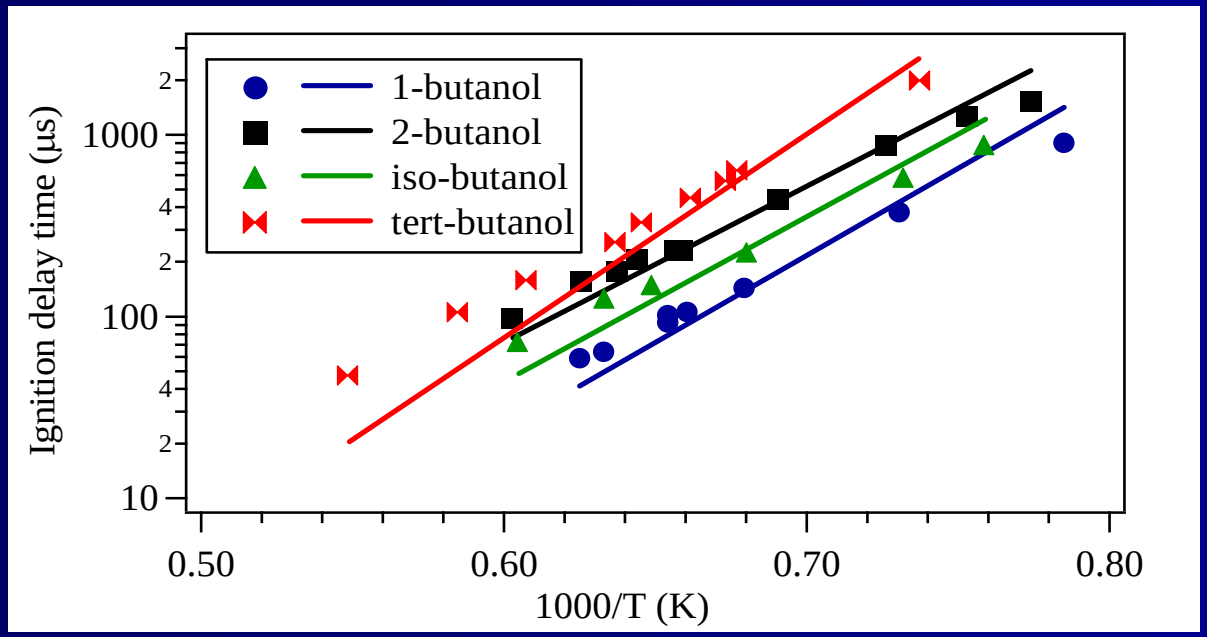
R. BOUNACEUR, V. WARTH, B. SIRJEAN, P.A. GLAUDE, R. FOURNET, F. BATTIN-LECLERC
"Influence of the position of the double bond on the autoignition of linear alkenes at low temperature", "Proceedings of the Combustion Institute", 32, 387 (2009).

EXAMPLE OF MODELLING: *4 isomers of butanol*

Ignition delay times of butanol/O_2/Ar mixtures measured in a shock tube (Troy - USA)

($P_{reflected\ shock} \approx 1$ bar, at $\Phi = 1$, with 1% butanol)

Symbols are experiments, lines are simulations



Not yet validated for modelling the formation of products

J.T. MOSS, A.M. BERKOWITZ, M.A. OEHLSCHLAEGER, J. BIET, V. WARTH, P.A. GLAUDE, F. BATTIN-LECLERC
"An experimental and kinetic modelling study of the oxidation of the four isomers of butanol", "The Journal of physical chemistry A" 112, 10843-10855 (2008)

Obtain validation experimental results under a widest range of operating conditions

Reactors for which the physical model is the simplest possible

Shock tube
for auto-ignition
delay times
measurements

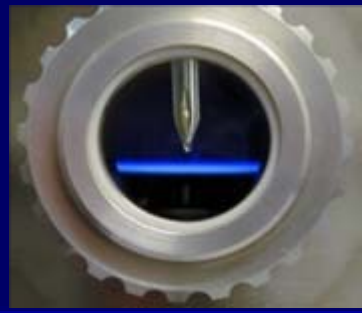
Atmospheric
premixed laminar flame
for laminar flame
speed measurements

Jet-stirred reactor

Low pressure (6.7 kPa)
premixed laminar flame

Products analysis

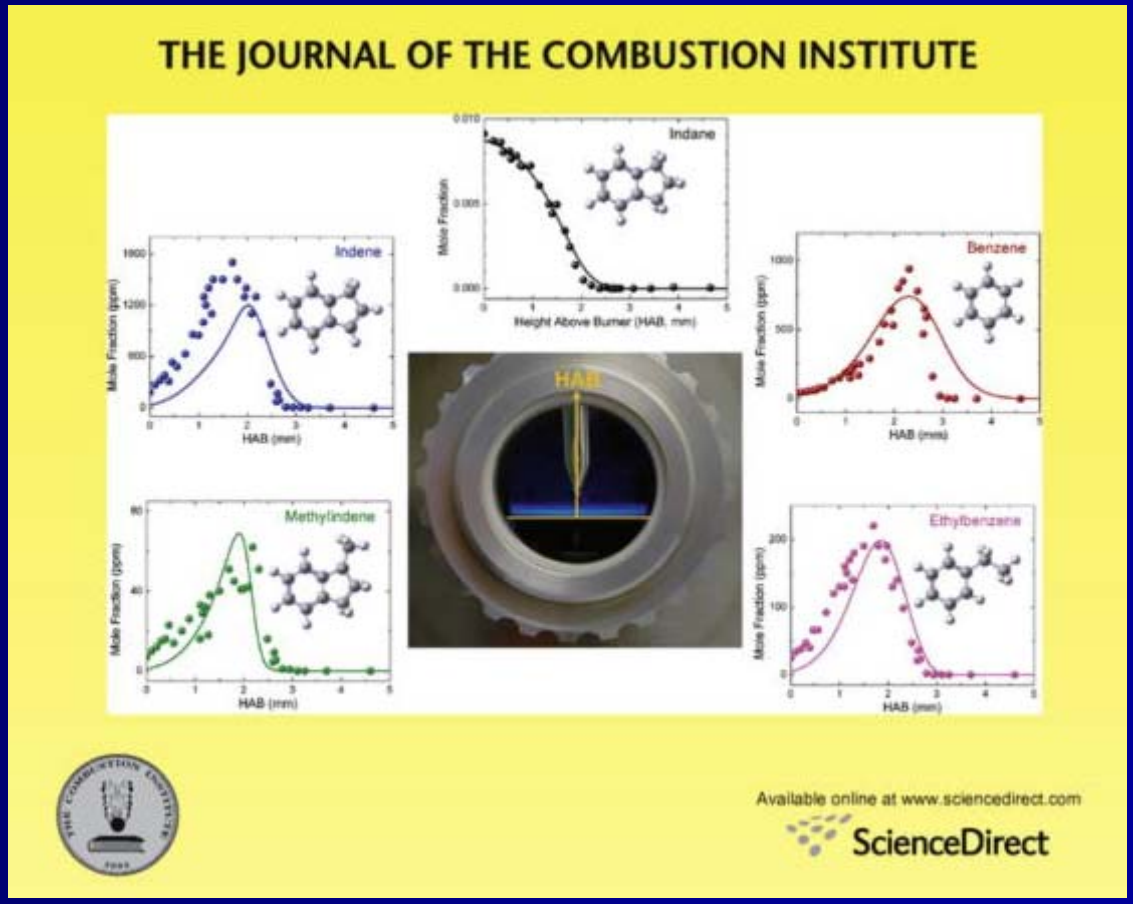
Low pressure premixed laminar flame



Study of a lean premixed
methane flame
doped with indane

(P = 6.7 kPa, at Φ = 0.67,
$C_{10}H_{10}/CH_4$ = 12.8%, with Ar as dilutant)

Model including 1658 reactions



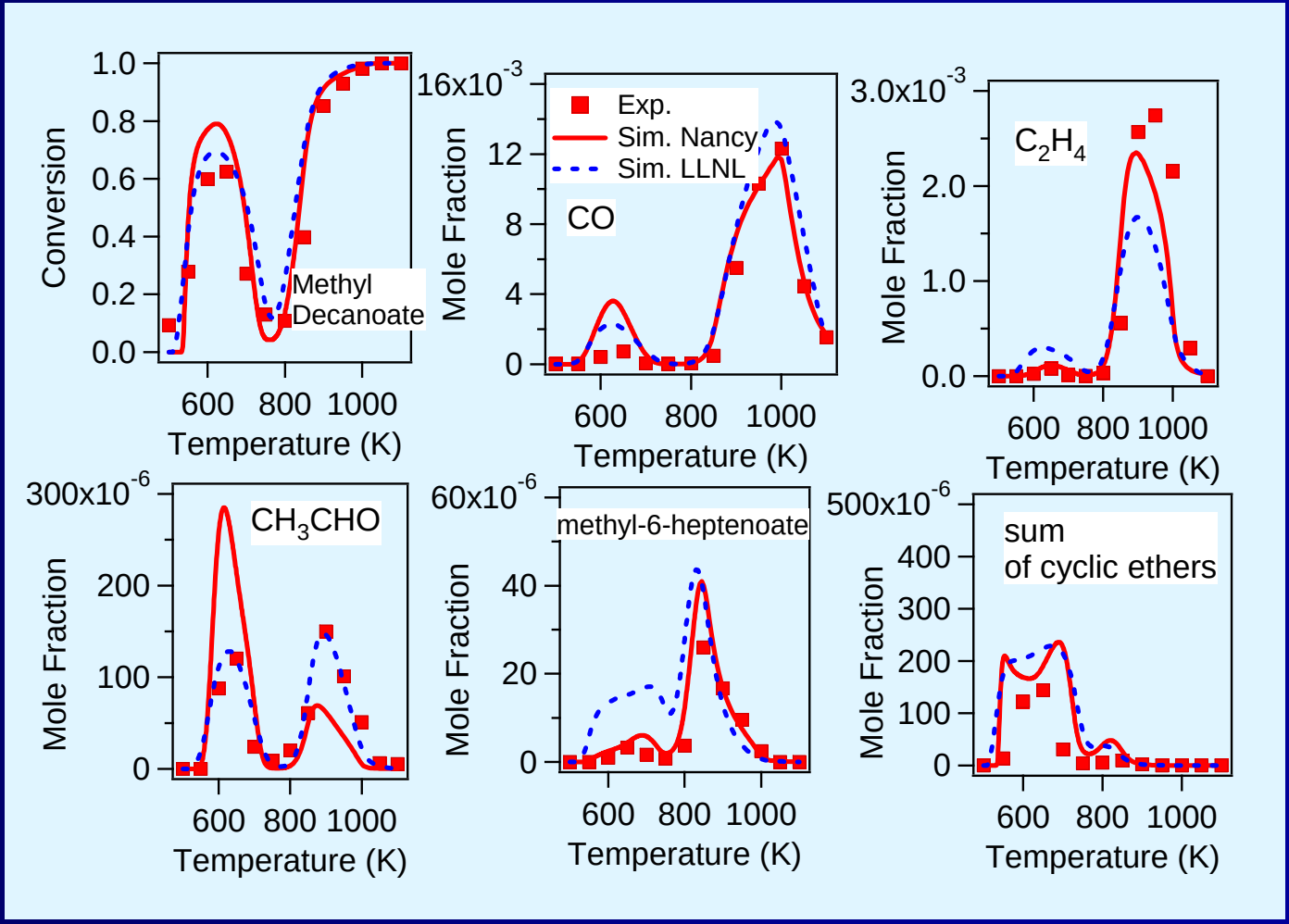
E. POUSSE, Z. TIAN, P.A. GLAUDE, R. FOURNET, F. BATTIN-LECLERC
"**A lean methane premixed flame doped with components of diesel fuel -part III: indane and comparison between n-butylbenzene, n-propylcyclohexane and indane**", "Combustion&Flame", 157, 1236 (2010).

Jet-stirred reactor

Study of the oxidation of methyl decanoate
(P = 1 bar, at Φ = 1, with He as dilutant)

Model of Nancy :
Glaude et al., Combust Flame, 2010, in press

Model of LLNL:
Herbinet et al., Combust Flame, 2008, 154, 507.



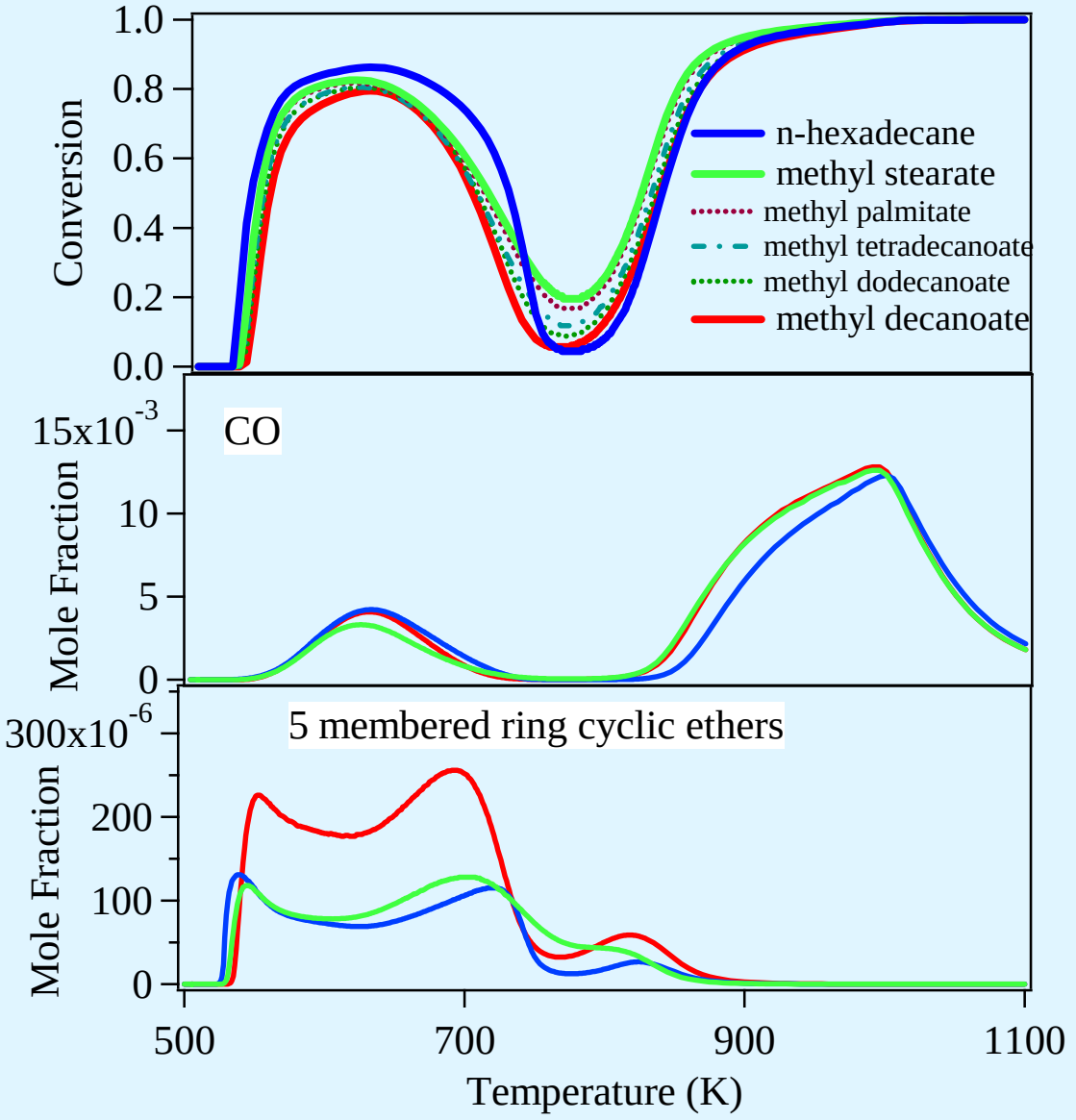
Reactivity of large methyl esters

Modeling of the oxidation of C_{11}-C_{19} methyl esters and n-hexadecane in a jet-stirred reactor *(P = 1 bar, at Φ = 1, concentration of C atoms kept constant)*

Model for methyl decanoate including 43 444 reactions

Model for methyl stearate including 7171 reactions

Herbinet et al., Proc. Combust. Inst., 2010, in press.



Future work

Develop better defined and more accurate detailed chemical models

1-Write models
for an enlarged range of initial reactants
with more accurate parameters based on theoretical calculations

2-Obtain validation experimental results
under a widest range of operating conditions
with careful measurements of minor combustion products

Other DCPR permanent researchers involved in the project

Pierre-Alexandre GLAUDE

Valérie WARTH

René FOURNET

Olivier HERBINET

Roda BOUNACEUR