UNIVERSITEIT GENT

FACULTY OF ENGINEERING AND ARCHITECTURE

Experimental and kinetic modeling study of the pyrolysis and oxidation of 1,5-hexadiene: The reactivity of allylic radicals and their role in the formation of aromatics

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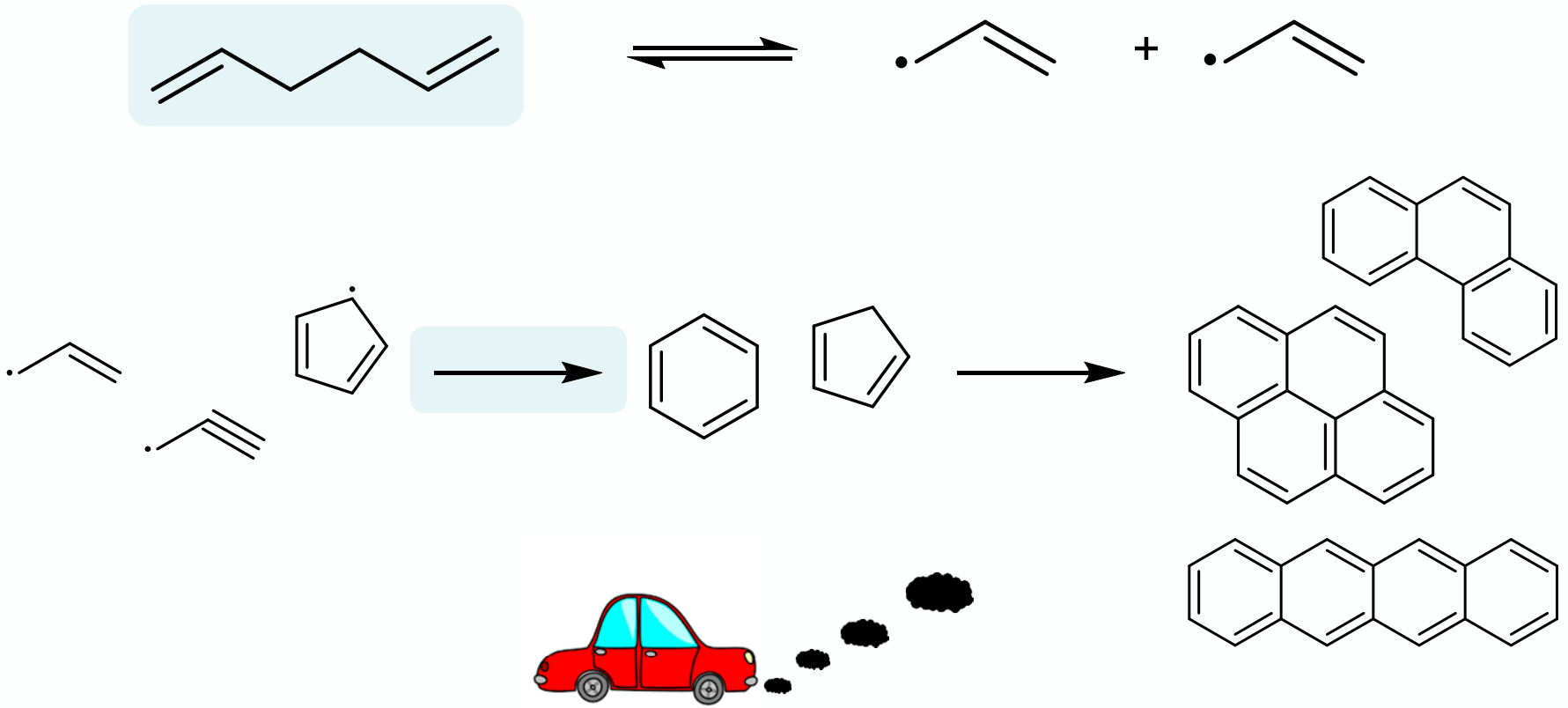
http://icck2017.engr.uic.edu/

Chicago, USA 21st – 25th May 2017

Local host: Ken Brezinsky (UIC)
Program chair: Rob Tranter (ANL)
Contact: icck2017@uic.edu

Soot formation

Model compound **hexadiene** for the role of allyl radicals in formation of aromatics



Outline of talk

Experimental procedure - JSR

Kinetic model development – Genesys

Model performance

ROP/sensitivity analysis

Aromatics formation

Experimental procedure

Jet-stirred reactor

Process conditions

ϕ = 1.0, 2.0, ∞

$F_V = 4.06\ 10^{-5}\ m^3\ s^{-1}$

t = 2.0 s

P = 1.07 bar

T = 500 K – 1100 K

Analysis

3 GC's for online quantification:

→ Carbosphere column and TCD detector

→ PLOT-Q column and FID detector (proc. by methanizer)

→ HP-5ms column and FID detector

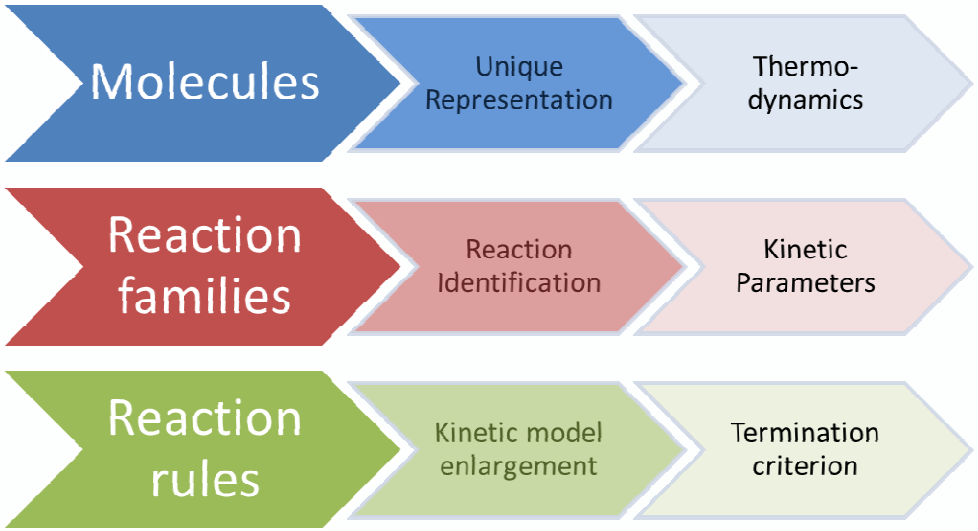
1 GC for on- or offline identification:

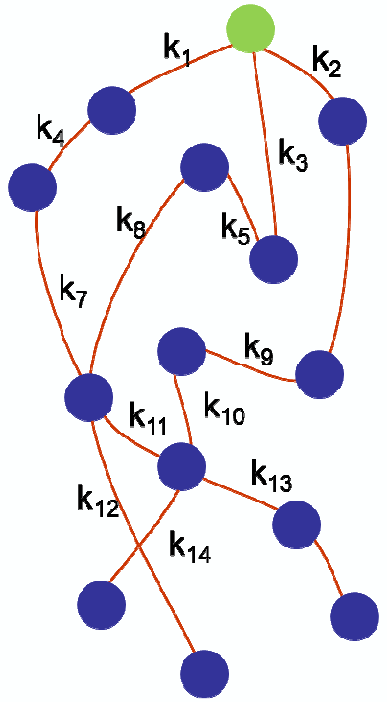
→ PLOT-Q or HP-5ms column and quadrupole MS

Kinetic model development

Genesys

Generation of reacting systems





Kinetic and thermodynamic data

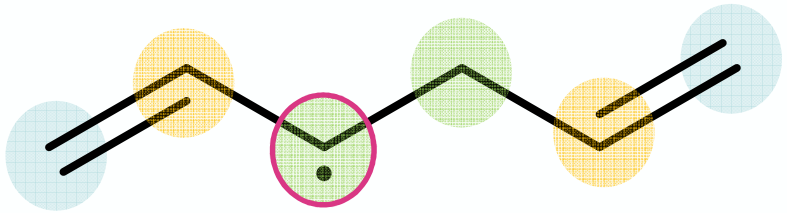
- Genesys species and group additive value databases for HCs[1,2]
- Literature data or analogies for allylic HCs and oxygenates
- Literature QM data for key reactions[3]
- Propene oxidation mechanism[4] and aromatics chemistry[5,6]

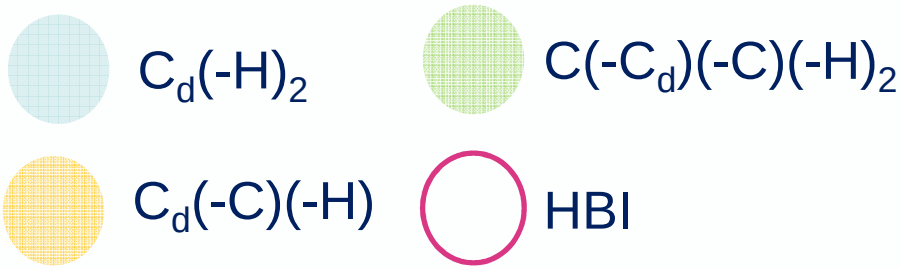
[1] M.K. Sabbe, M.F. Reyniers, M. Waroquier, G.B. Marin, Chemphyschem, 11 (2010) 195-210.
[2] M.K. Sabbe, F. De Vleeschouwer, M.F. Reyniers, M. Waroquier, G.B. Marin, Journal of Physical Chemistry A, 112 (2008) 12235-12251.
[3] A. Fridlyand, P.T. Lynch, R.S. Tranter, K. Brezinsky, Journal of Physical Chemistry A, 117 (2013) 4762-4776.
[4] S.M. Burke, W. Metcalfe, O. Herbinet, F. Battin-Leclerc, F.M. Haas, J. Santner, F.L. Dryer, H.J. Curran, Combustion and Flame, 161 (2014) 2765-2784
[5] O. Herbinet, B. Husson, M. Ferrari, P.A. Glaude, F. Battin-Leclerc, Proc. Combust. Inst., 34 (2013) 297-305.
[6] S. Sharma, M.R. Harper, W.H. Green, Combustion and Flame, 157 (2010) 1331-1345.

GAV for thermodynamic data

Benson's group additivity method

& Hydrogen bond increment method





GAV database:

Cp at different temperatures

$\Delta H_f°(298\ K)$

$S°\ (298\ K)$

NASA polynomials

(CHEMKIN format)

ΔGAVs for Arrhenius parameters

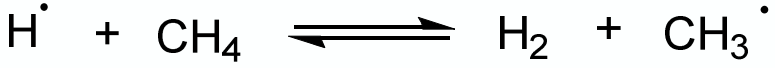
ΔGAV databases implemented in Genesys

→ H abstraction reactions

→ addition/β-scission reactions

$$k(T) = \kappa n_e \tilde{A} \exp\left(-\frac{E_a}{RT}\right)$$

ΔGAV reference reaction

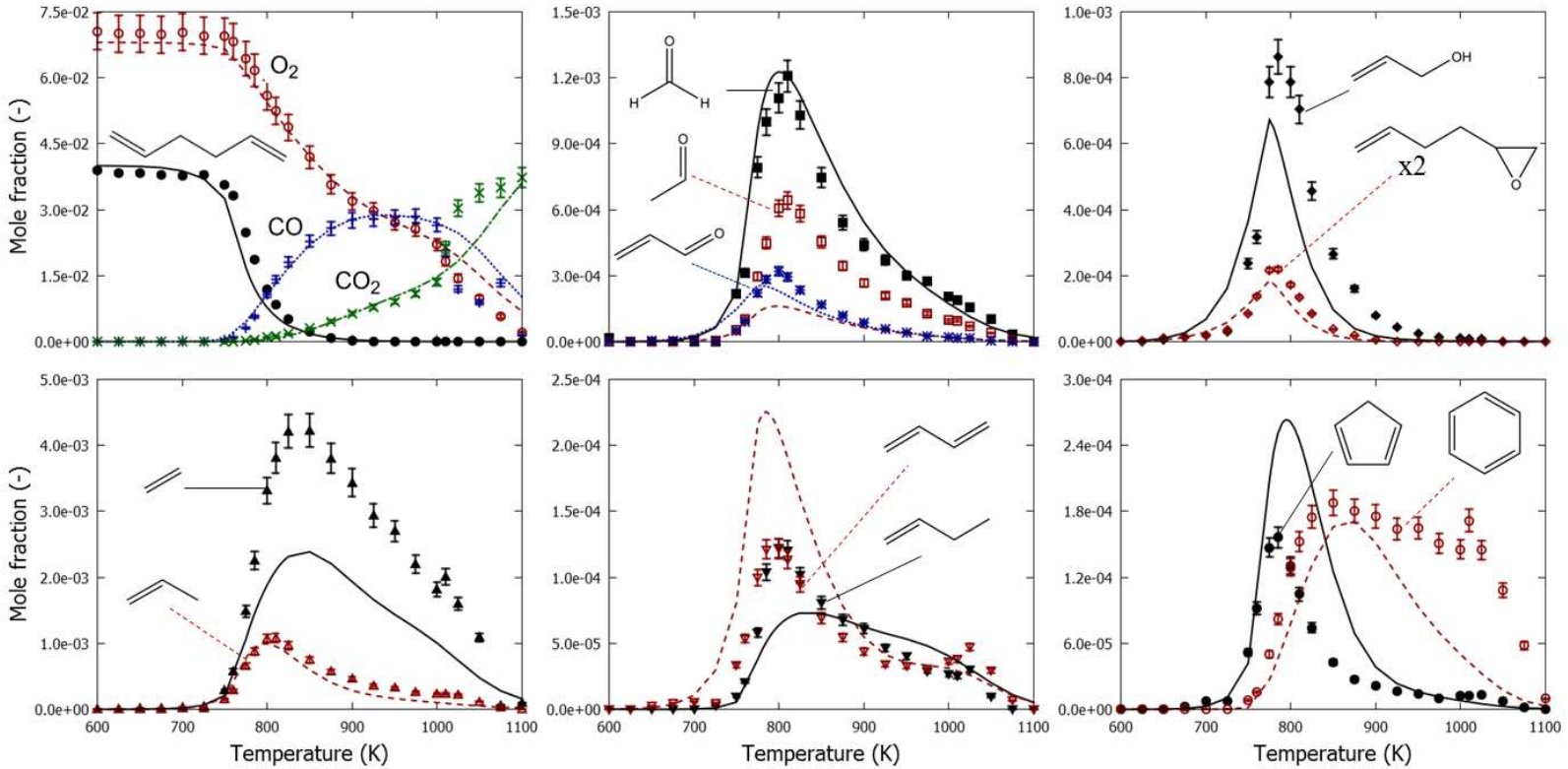


$$E_a = E_{a,ref} + \sum_{i=1}^{n} \Delta GAV_{E_a}^{0}(X_i)$$

$$log\tilde{A} = log\tilde{A}_{ref} + \sum_{i=1}^{n} \Delta GAV_{log\tilde{A}}^{0}(X_i)$$

Model performance

ϕ=2.0



No low temperature reactivity

Acrolein, prop-2-en-1-ol and but-3-enyl-oxiran main oxygenated species

Qualitative agreement between model simulations and experiments

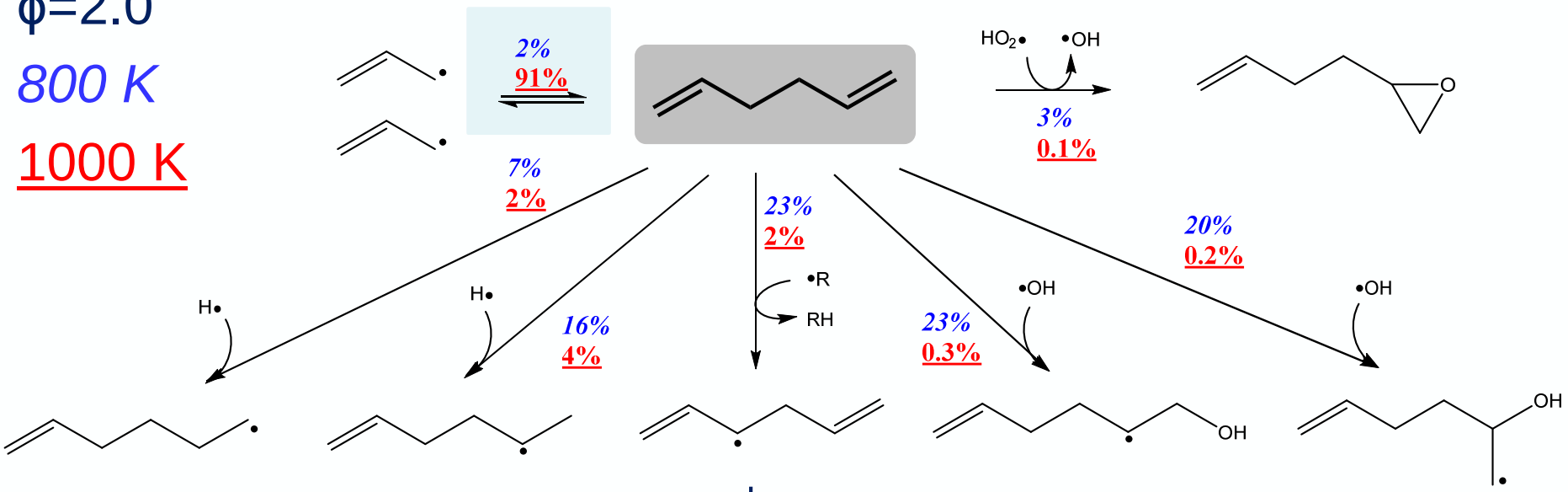
Main discrepancies for ethene and acetaldehyde for oxidation

Rate of production analysis HXD

ϕ=2.0

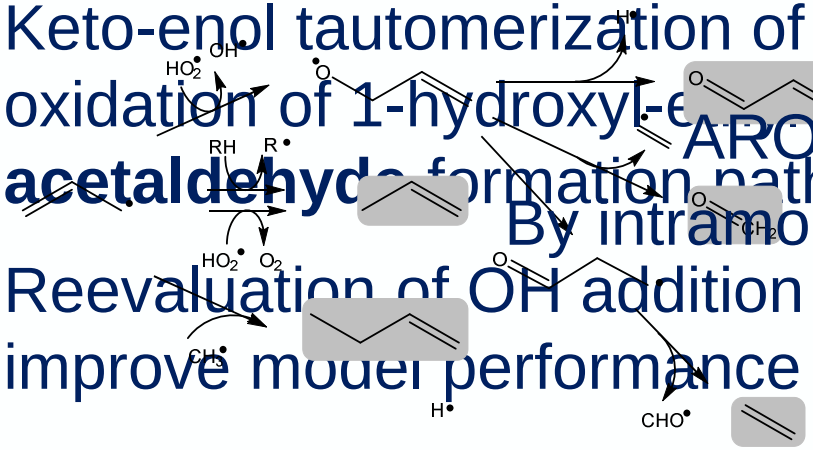
800 K

1000 K



Keto-enol tautomerization of ethenol and oxidation of 1-hydroxyl-ethyl radical main **acetaldehyde** formation pathway

Reevaluation of OH addition to HXD to improve model performance



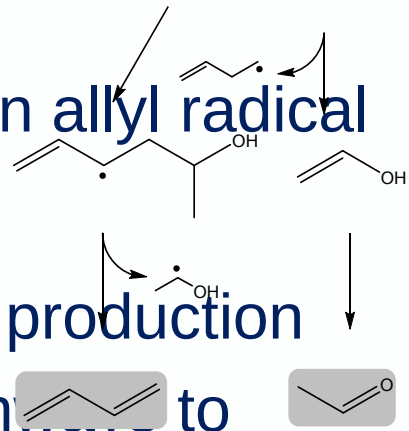
HO_2• important in allyl radical consumption

AROMAdocs

By intramolecular addition

30 % of **ethene** production

Revise allyl pathways to improve model performance



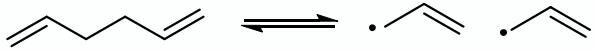
Sensitivity analysis

Normalized sensitivity coefficients for 1,5-hexadiene mole fraction at ϕ=2.0

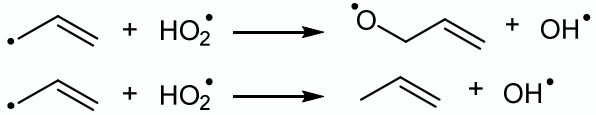
Lowest T: Primary 1,5-HXD decomposition

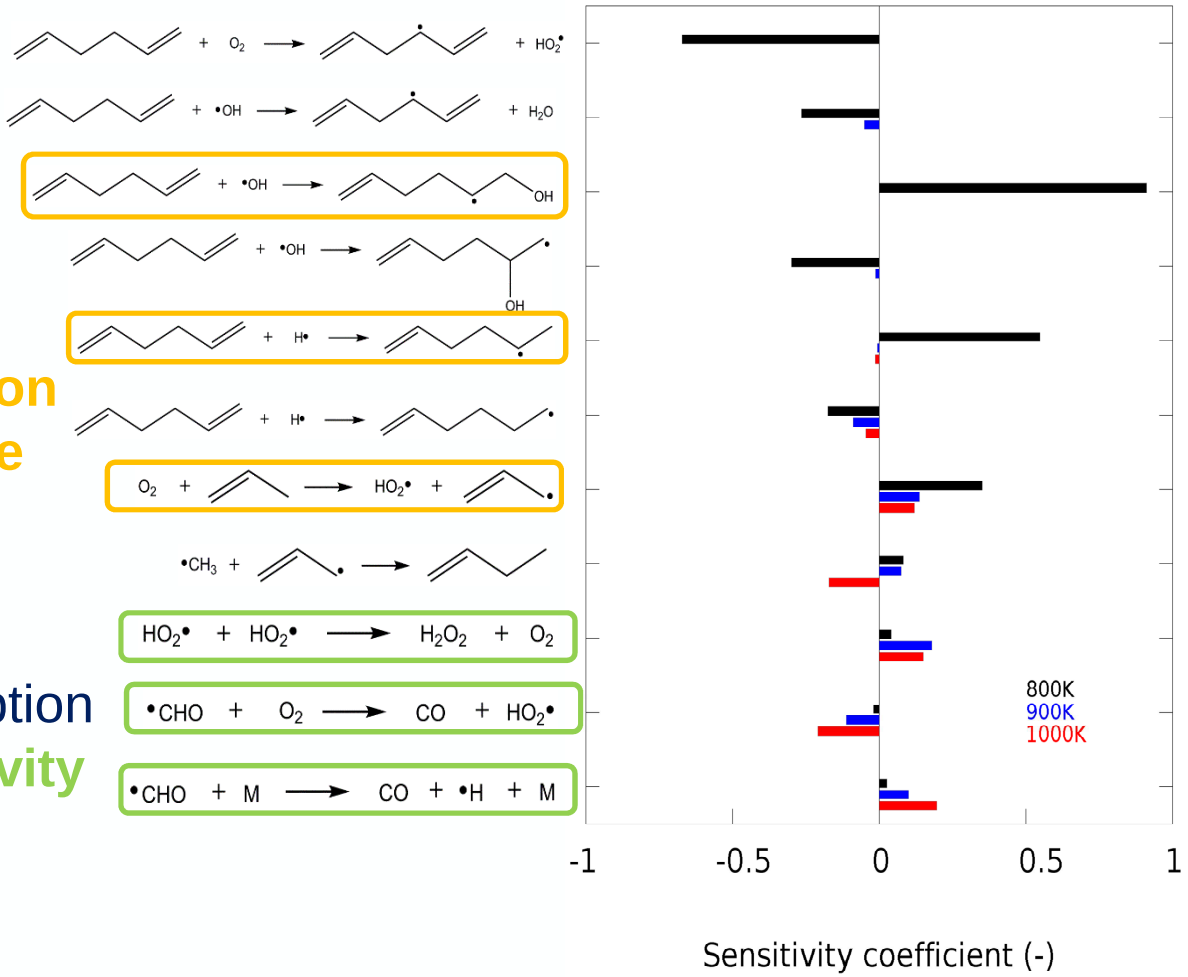
Higher T: Secondary combustion chemistry

Reactions that imply **formation** of **allyl** radicals have **positive** coefficients



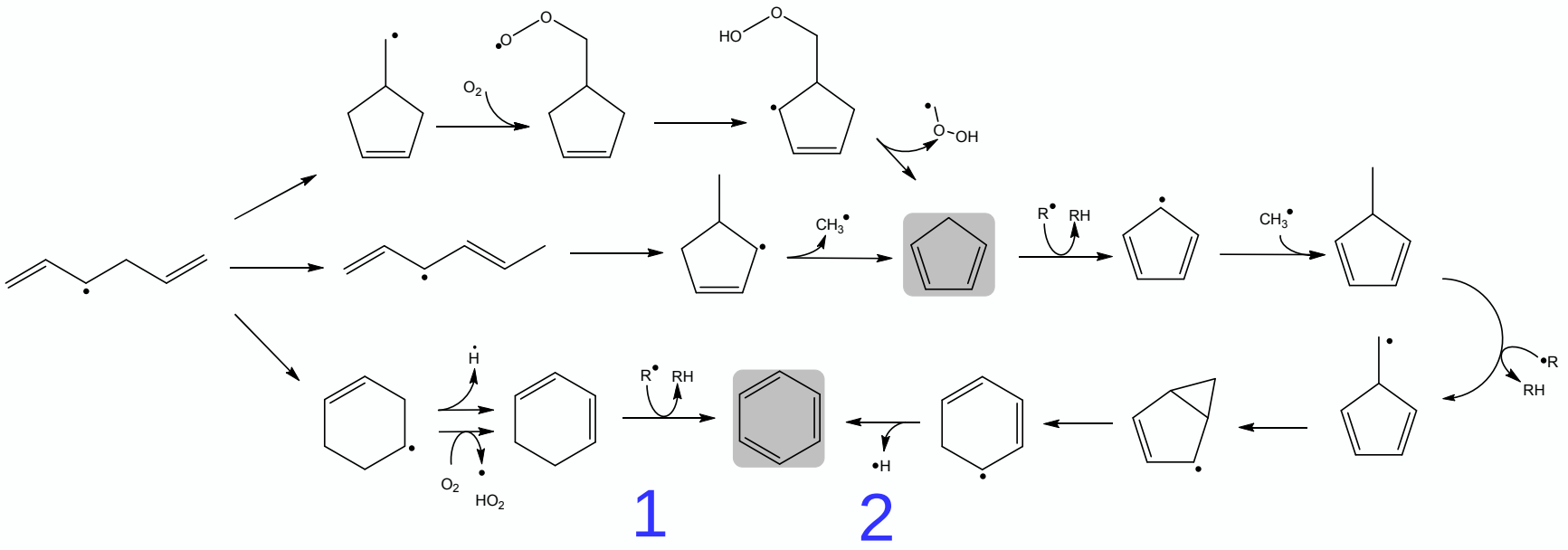
$HO_2^{\bullet}$ radicals main consumption of allyl radicals, **high sensitivity** for 1,5-HXD mole fraction





Aromatics formation

1,3-cyclopentadiene and **benzene** starting from 1,5-hexadienyl radical



2 main pathways for benzene formation

Similar pathways for formation of styrene and toluene

Conclusions

Oxidation and pyrolysis **experiments** in jet-stirred reactor

New developed **kinetic model** with automatic kinetic model generation and literature reported QM calculations

Qualitative good model performance

1,5-hexadiene mole fraction **sensitive to allyl** radicals

Main **aromatic formation** pathways unraveled

Acknowledgements

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Thank you