Chemical Kinetics Modeling

New Mechanisms, Surrogate Fuels, Reaction Path Analysis, and other Topics

Charles Westbrook

July, 2008

Reaction Design

This is a very exciting and busy time for kinetic modeling -- Outline of Subjects

- New mechanisms for n-alkanes, biodiesel, oxygenates, hepta-methyl nonane, soot precursors

- Implications for new, more realistic fuel surrogates for transportation fuels

- New kinetic modeling tools, including Reaction Path Analysis

New fuel mechanisms

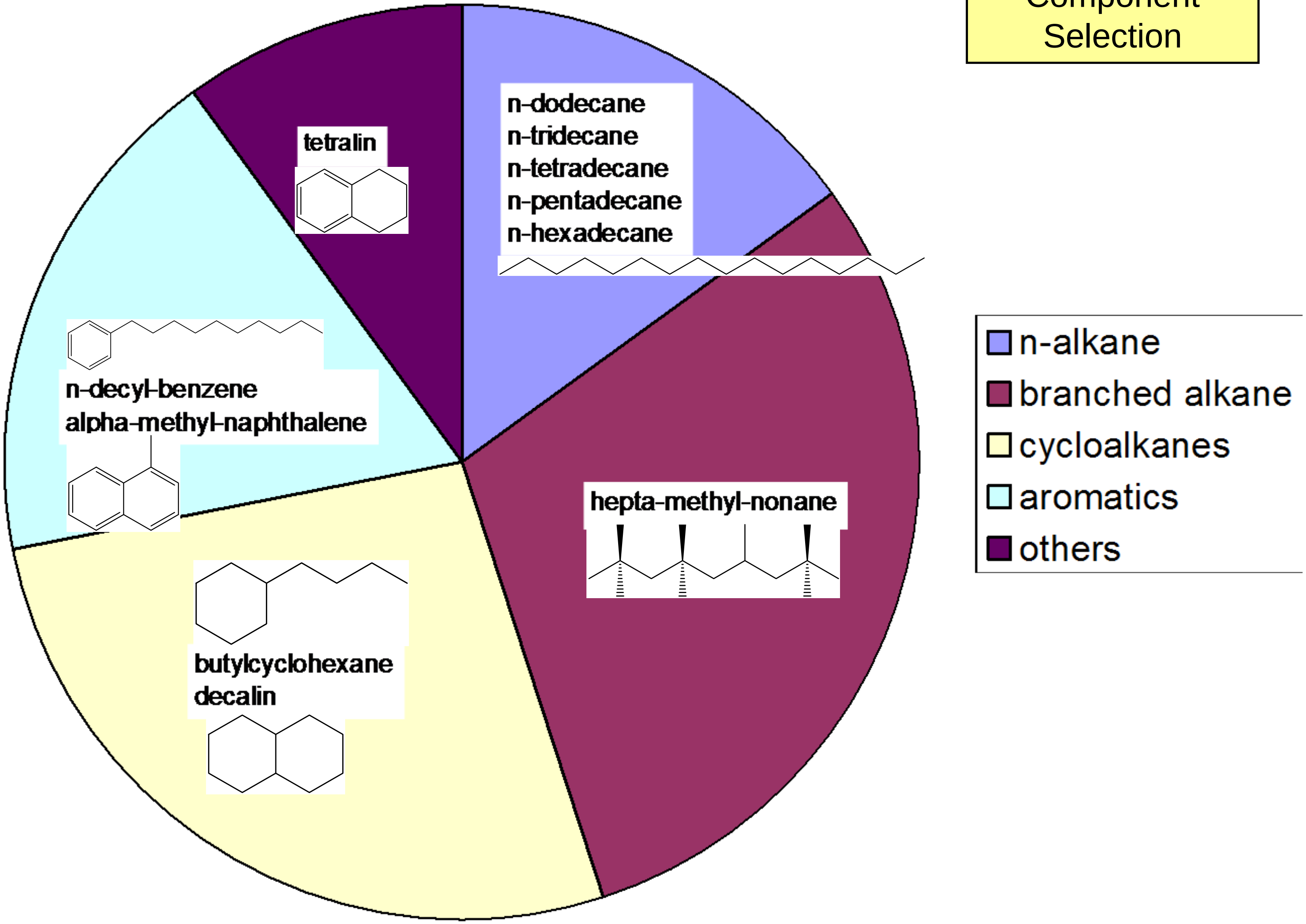
- n-alkanes from n-C_8H_{18} to n-$C_{16}H_{34}$
- 2,2,4,4,6,8,8-heptamethyl nonane
- methyl decanoate $CH_3O(CO)C_9H_{19}$
- family of small alkyl esters
- benzene formation reactions
- Illustrate with reaction path analysis tool in new Chemkin

Chemical Kinetics Modeling of Large n-Alkanes Up to n-Hexadecane

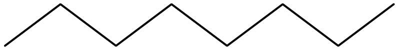
Charles Westbrook, Olivier Herbinet, William Pitz, Henry Curran, Emma Silke

Fuel Surrogate Palette for Diesel

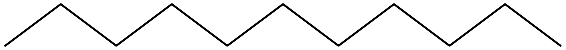
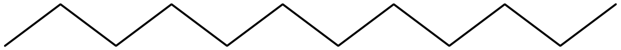
Surrogate Fuel Component Selection



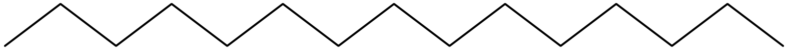
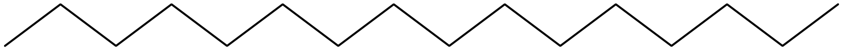
We have greatly extended the components in the palette that can be modeled in the high molecular weight range:

- n-octane (n-C8H18)

- n-nonane (n-C9H20)

- n-decane (n-C10H22)

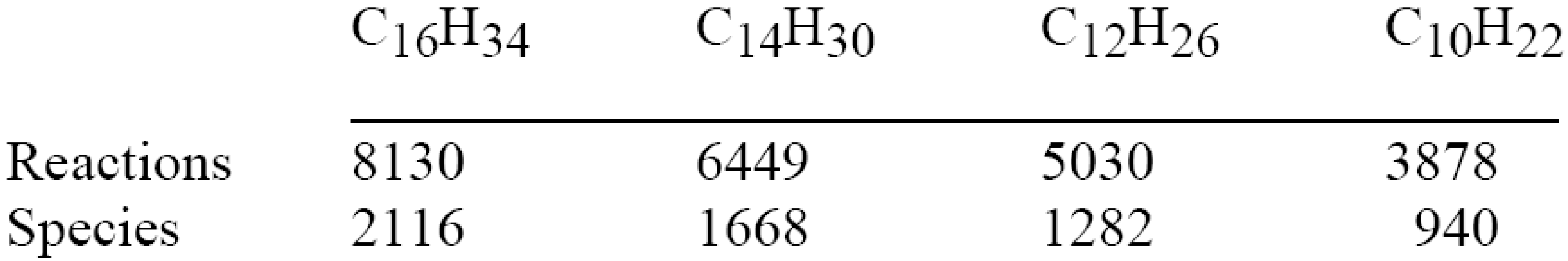
- n-undecane (n-C11H24)

- n-dodecane (n-C12H26)

- n-tridecane (n-C13H28)

- n-tetradecane (n-C14H30)

- n-pentadecane (n-C15H32)

- n-hexadecane (n-C16H34)


Chemical kinetic mechanism for nC8-nC16 surrogate components:

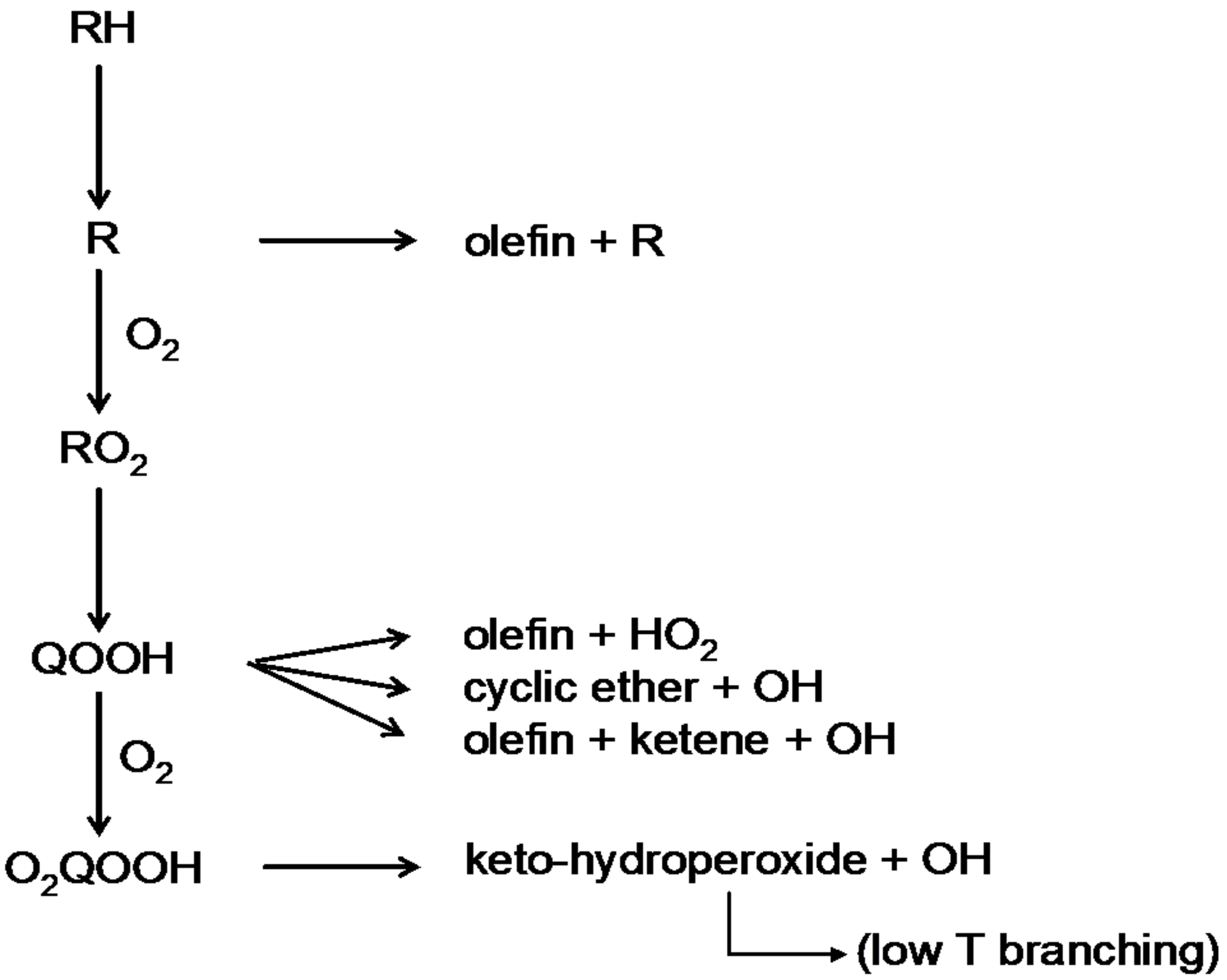
- 2116 species
- 8130 reactions
- Low and high temperature chemistry => can use to investigate low temperature combustion strategies
- Same reaction rate rules as highly validated n-heptane mechanism
- Tailor the mechanism to fit specific fuels for computational efficiency



	$C_{16}H_{34}$	$C_{14}H_{30}$	$C_{12}H_{26}$	$C_{10}H_{22}$
Reactions	8130	6449	5030	3878
Species	2116	1668	1282	940

Includes high and low temperature ignition chemistry: Important for predicting low temperature combustion regimes

Detailed Chemical Kinetics for Components



High Temperature Mechanism

Reaction Class 1: Unimolecular fuel decomposition

Reaction Class 2: H-atom abstractions

Reaction Class 3: Alkyl radical decomposition

Reaction Class 4: Alkyl radical + O2 = olefin + HO2

Reaction Class 5: Alkyl radical isomerization

Reaction Class 6: H atom abstraction from olefins

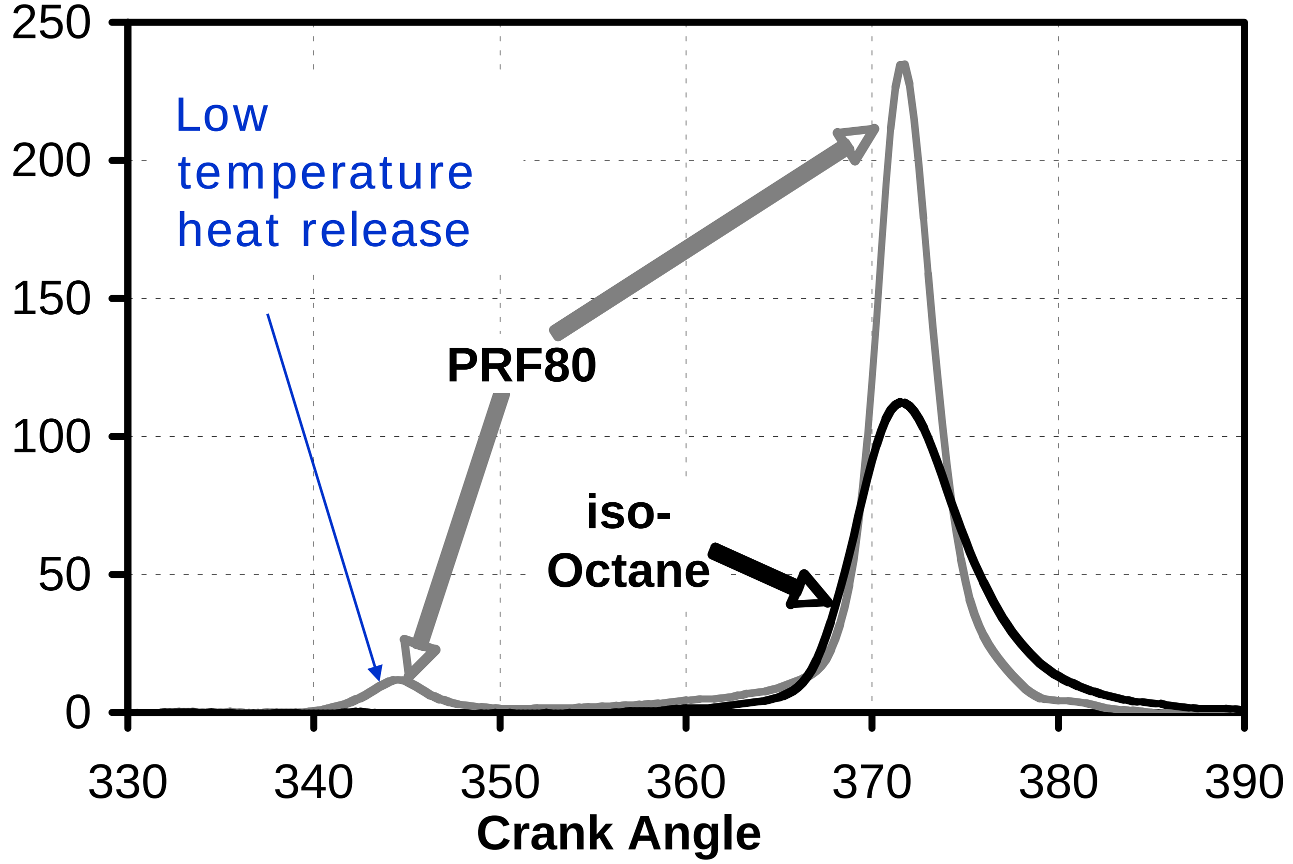
Reaction Class 7: Addition of radical species to olefins

Reaction Class 8: Alkenyl radical decomposition

Reaction Class 9: Olefin decomposition

Alkylperoxy radical isomerization controls the behavior In an HCCI engine

- Heat release rates in HCCI combustion of two fuels, iso-octane with no low T heat release, and PRF-90 with two stage heat release



Results from experiments of Sjöberg and Dec, SNL 2006

Low Temperature (High Pressure) Mechanism

Reaction Class 10: Alkyl radical addition to O2

Reaction Class 11: R + R’O2 = RO + R’O

Reaction Class 12: Alkylperoxy radical isomerization

Reaction Class 13: RO2 + HO2 = ROOH + O2

Reaction Class 14: RO2 + H2O2 = ROOH + HO2

Reaction Class 15: RO2 + CH3O2 = RO + CH3O + O2

Reaction Class 16: RO2 + R’O2 = RO + R’O + O2

Reaction Class 17: RO2H = RO + OH

Reaction Class 18: Alkoxy radical decomposition

Reaction Class 19: QOOH decomposition and production of cyclic ethers

Reaction Class 20: QOOH beta decomposition to produce olefin + HO2

Reaction Class 21: QOOH decomposition to small olefin, aldehyde and OH

Reaction Class 22: Addition of QOOH to molecular oxygen O2

Reaction Class 23: O2QOOH isomerization to carbonylhydroperoxide + OH

Reaction Class 24: Carbonylhydroperoxide decomposition

Reaction Class 25: Reactions of cyclic ethers with OH and HO2

Mechanism validation included a wide range of experimental results

- Relatively few experiments, but they cover all of the important parameters ranges
- Shock tubes

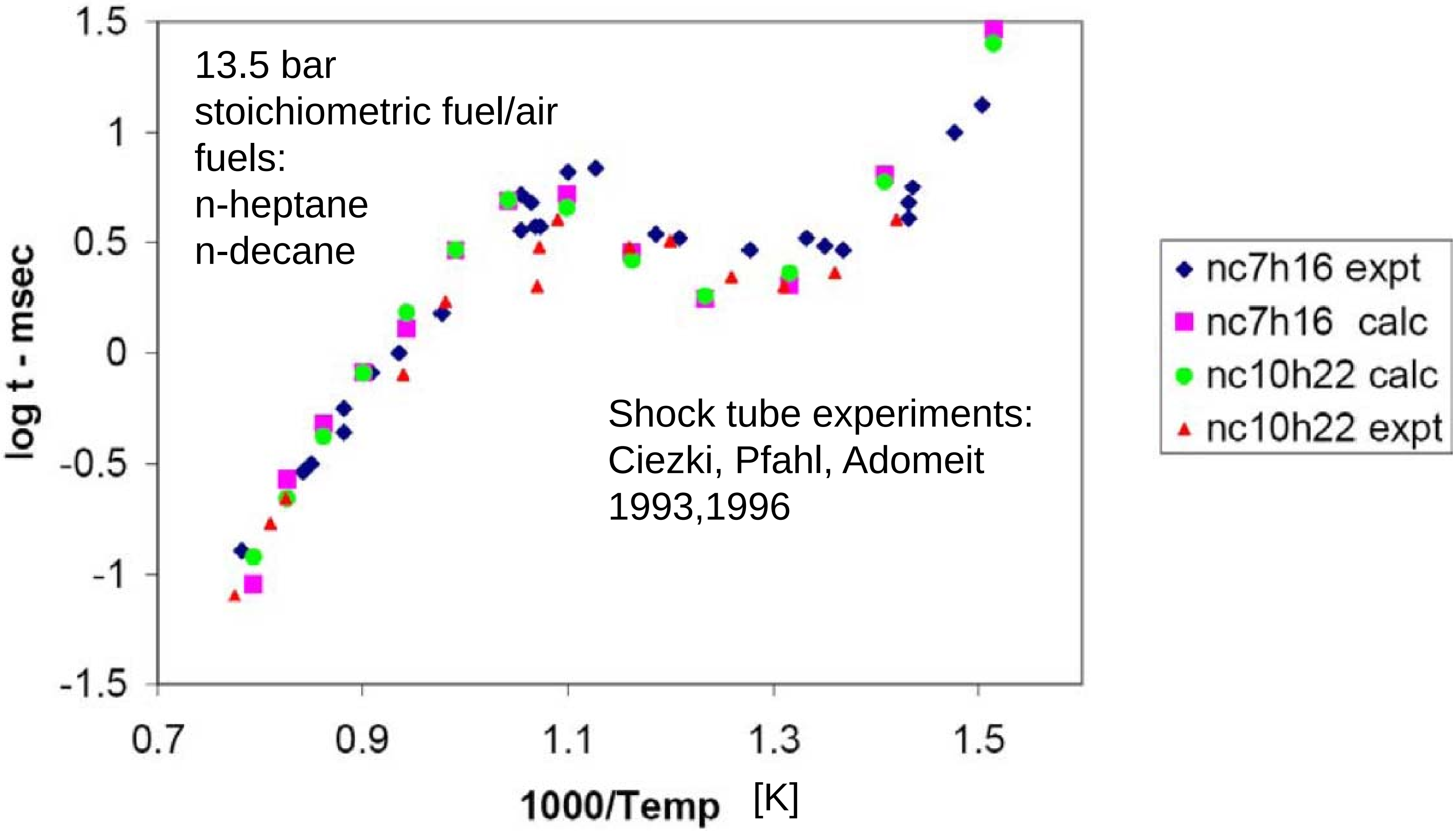
Burcat and Olchanski	C10
Davidson, Hanson	C10
Zhukov et al.	C10
Pfahl, Adomeit et al.	C10
Horning et al.	C10

Mechanism validation II

- Rapid compression machine
  - Kumar et al., C10
- Jet-stirred reactor
  - Dagaut et al. C10, C16
- Turbulent flow reactor
  - Dryer et al. C10
  - Agosta, Cernansky et al. C12
- Alkane pyrolysis
  - Zhou et al. C9, C11, C12, C13, C16
  - Herbinet et al. C12

Good agreement with ignition delay times at “engine-like” conditions over the low to high temperature regime in the shock tube

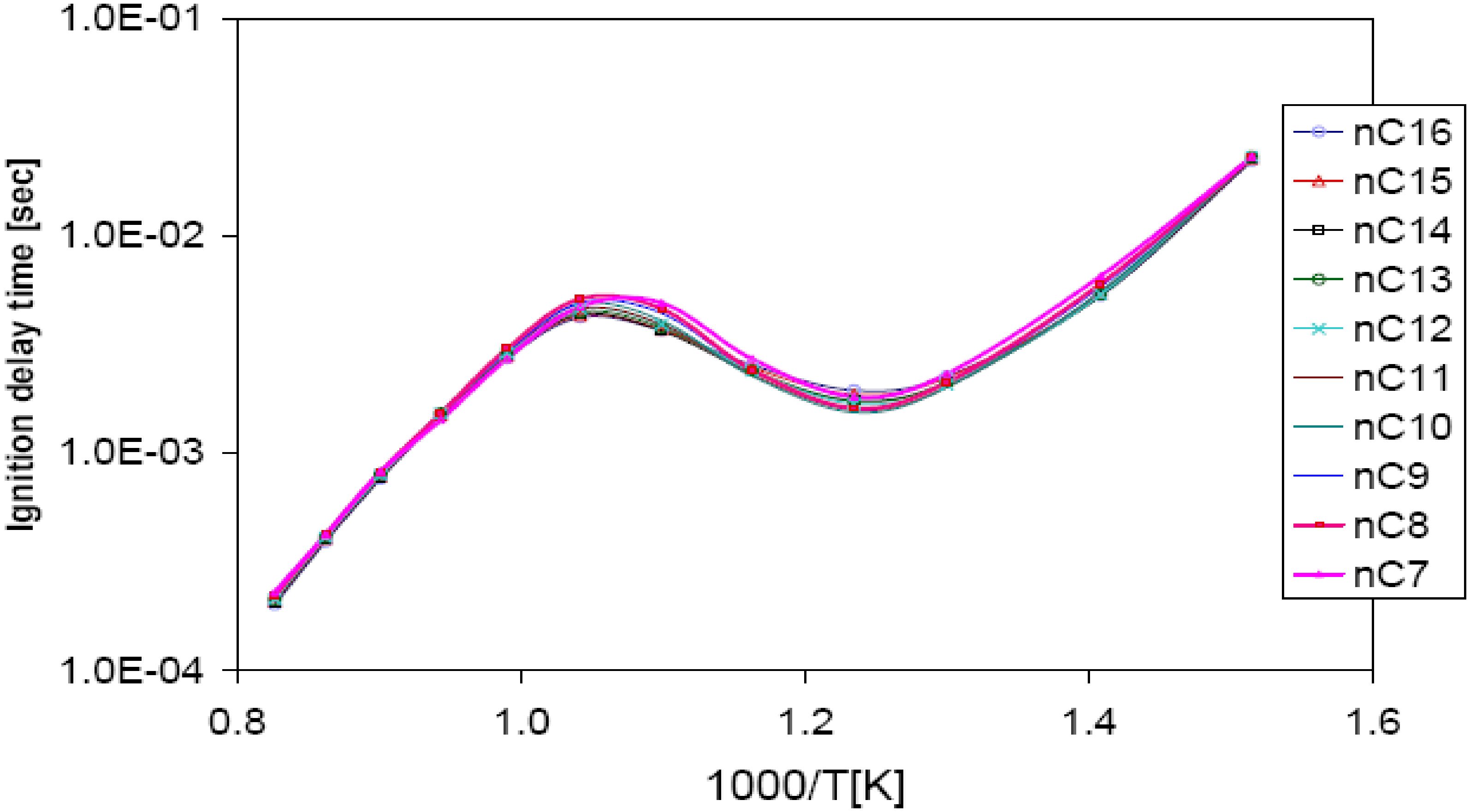
Experimental
Validation
Data



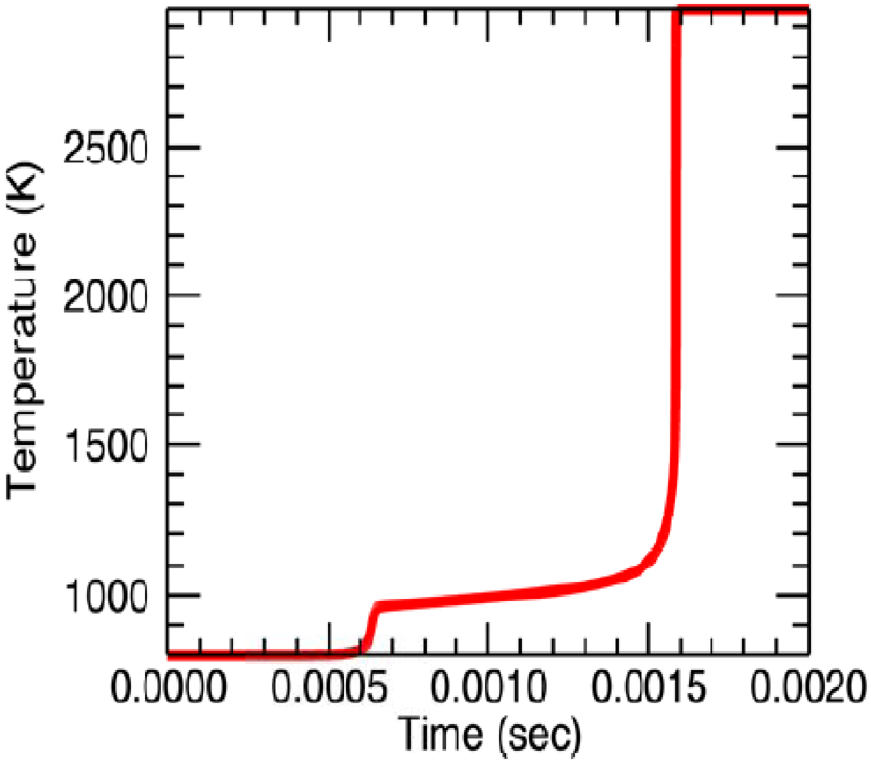
13.5 bar
stoichiometric fuel/air
fuels:
n-heptane
n-decane

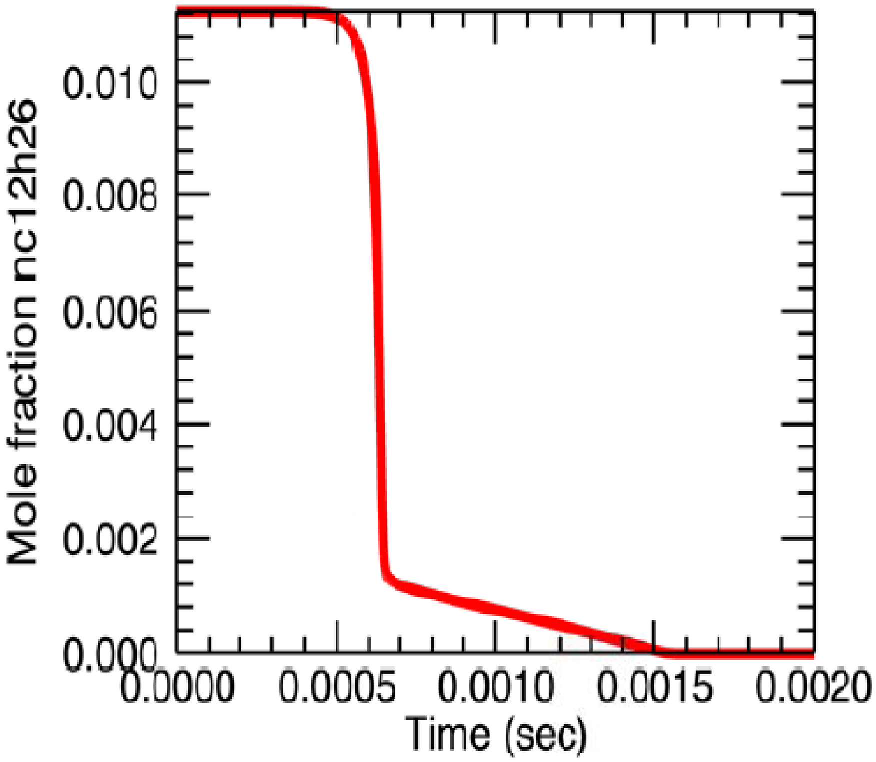
Shock tube experiments:
Ciezki, Pfahl, Adomeit
1993,1996

All large n-alkanes have very similar ignition properties



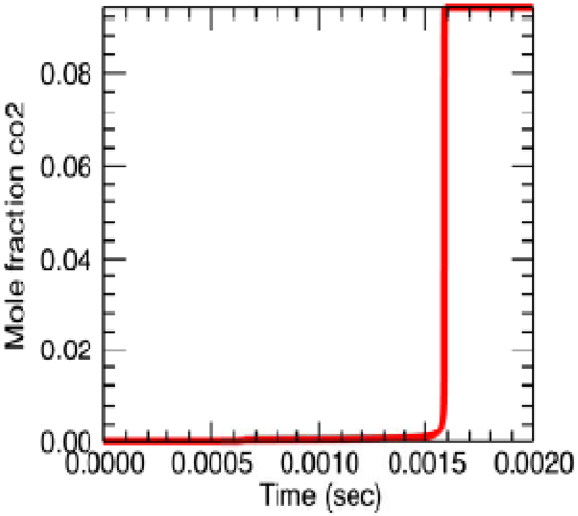
Ignition of n-dodecane at 800K, 13 bar pressure is a familiar 2-stage ignition

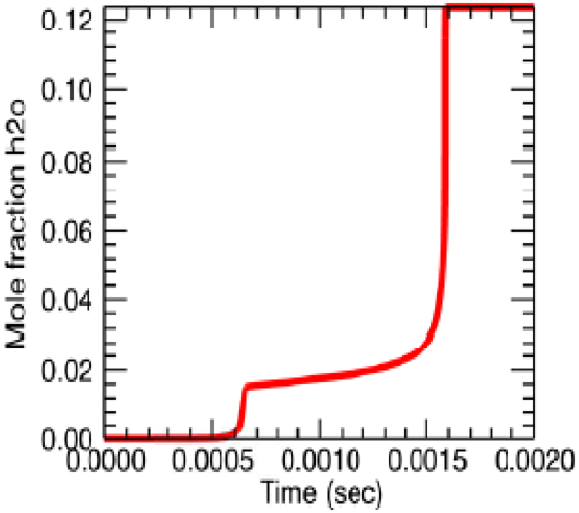


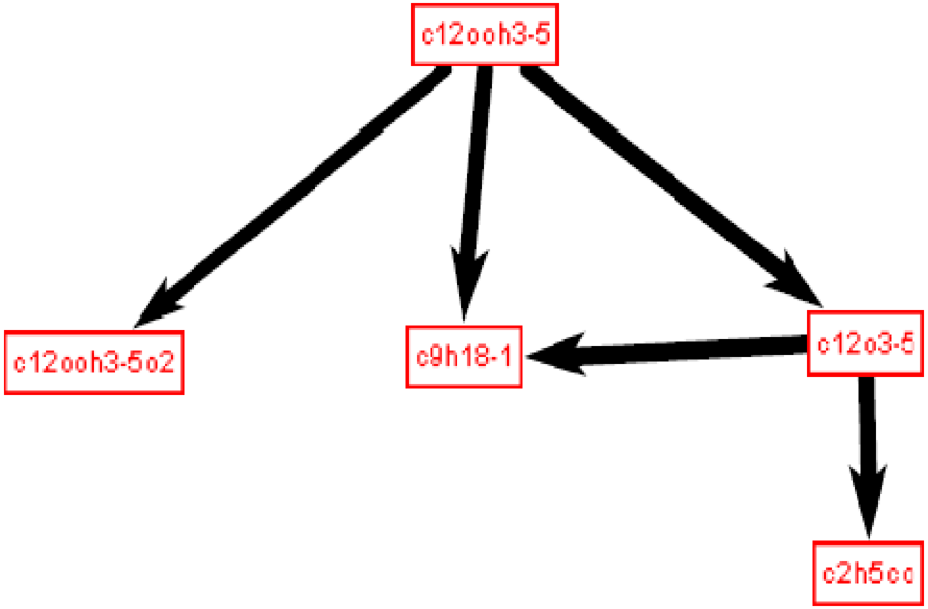


Note that 80% of the fuel is consumed in the first stage ignition

First stage produces H2O but very little CO2





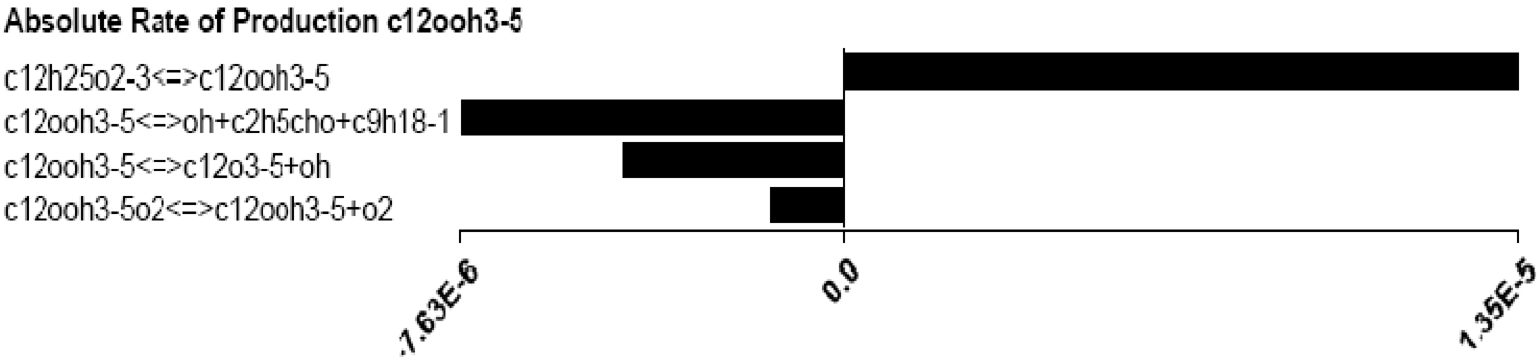


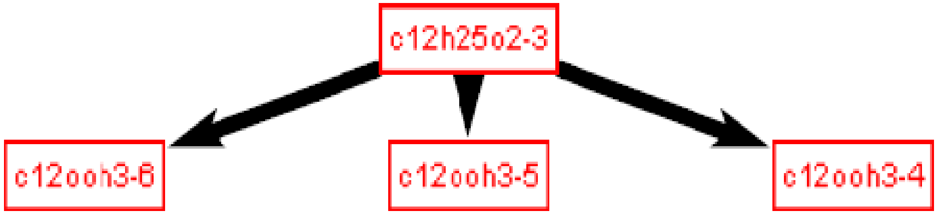
QOOH species can react by 3 pathways

QOOH + O2 → O2QOOH

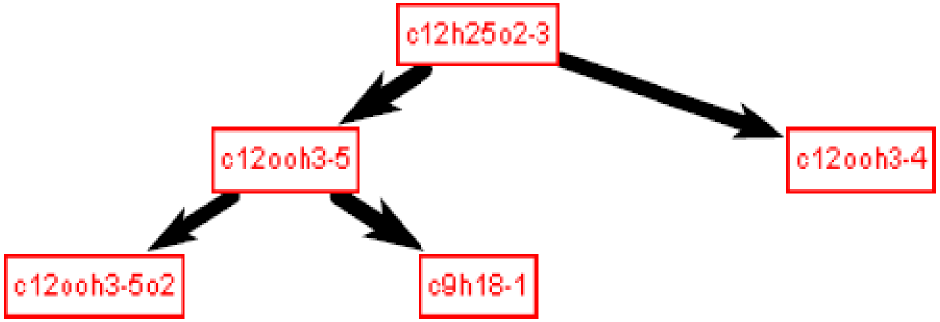
QOOH → β-scission

QOOH → cyclic ether





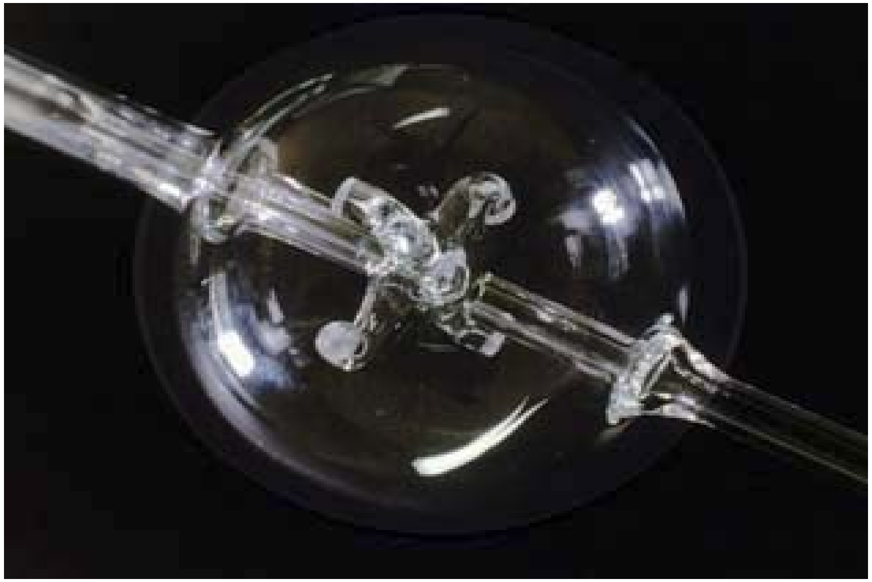
Each QOOH species has multiple possible reaction pathways available



The rates of those possible reaction pathways depends on the exact structure of the QOOH species

Experimental
Validation
Data

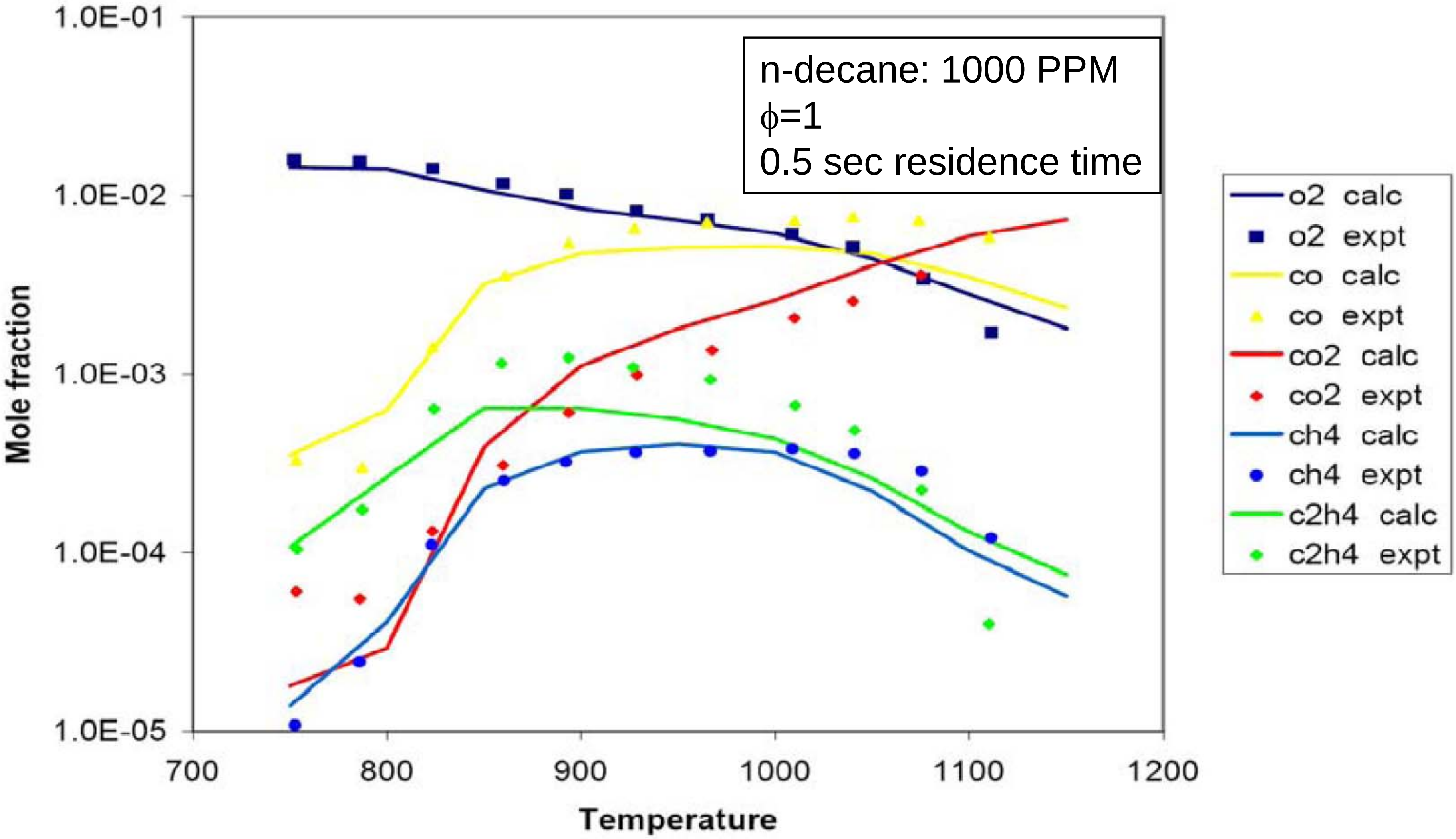
Jet-stirred reactor comparisons



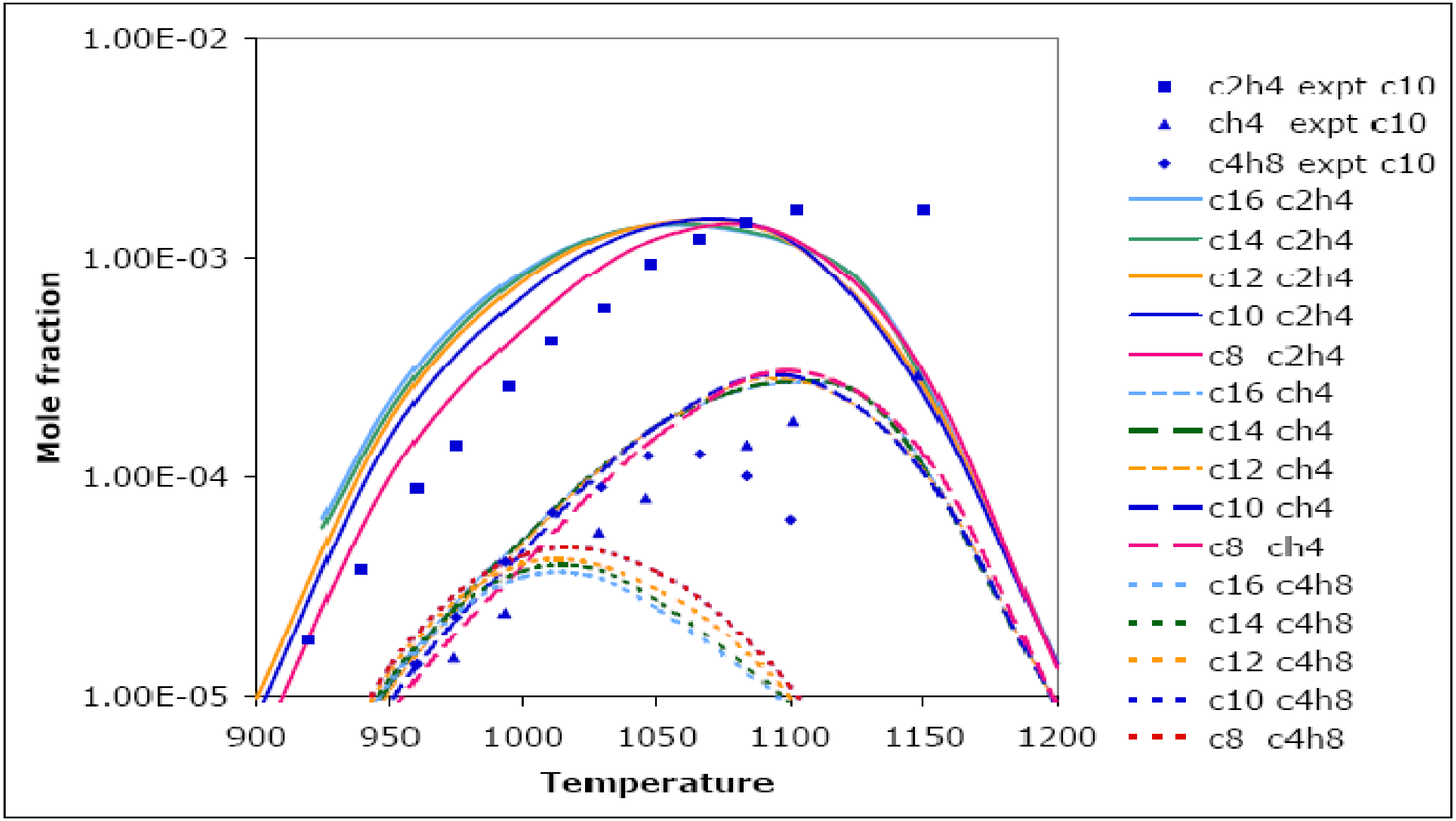
- Experimental data: Dagaut et al. 1994
- Pressure: 10 atm
- Equivalence ratio: 1.0
- Residence time: 0.5 s
- 1000 PPM of n-decane in O2/N2

Model agrees well with jet-stirred reactor measurements for n-decane at 10 atm

Experimental Validation Data



Different n-alkanes produce very similar intermediate levels, with important implications for surrogate fuels



Fuel levels adjusted to equal amounts of Carbon at 700ppm in n-decane

Surrogate fuels

- past use of n-heptane surrogate for diesel
- many similarities between all large n-alkanes
- n-decane surrogate for kerosene (Dagaut)
- n-hexadecane surrogate for biodiesel
- n-decane and methyl decanoate similarities
- role of methyl ester group
- potential of n-cetane + methyl decanoate or smaller methyl ester for biodiesel surrogate

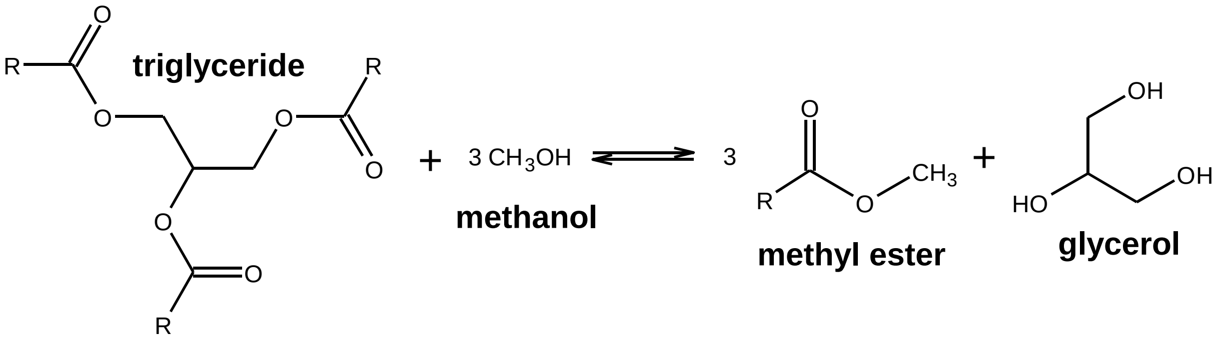
Detailed Chemical Kinetic Mechanism for a Biodiesel Surrogate

Olivier Herbinet, William J. Pitz
and Charles K. Westbrook

Biodiesel fuels

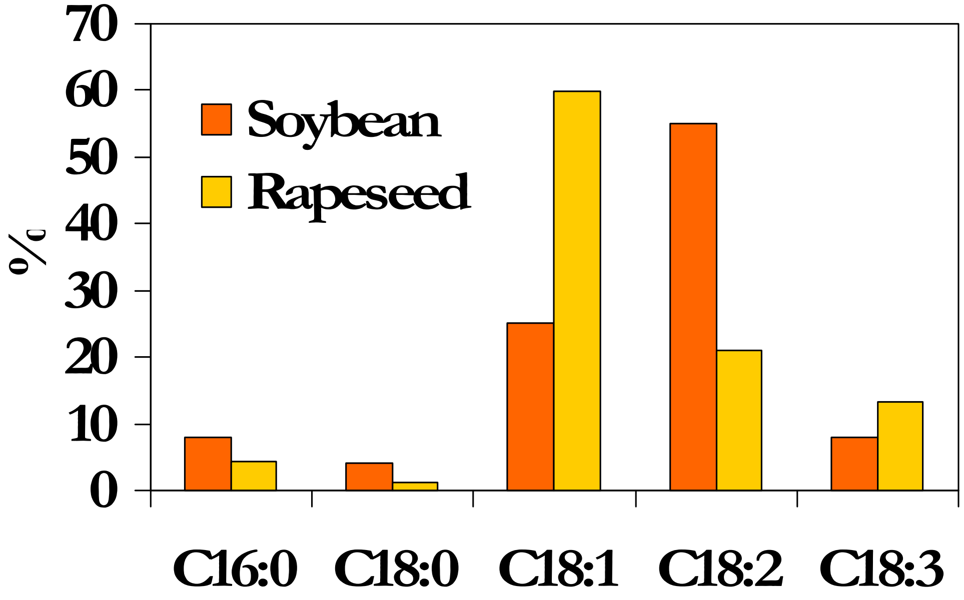
Biodiesel fuels produced from various oleaginous plants

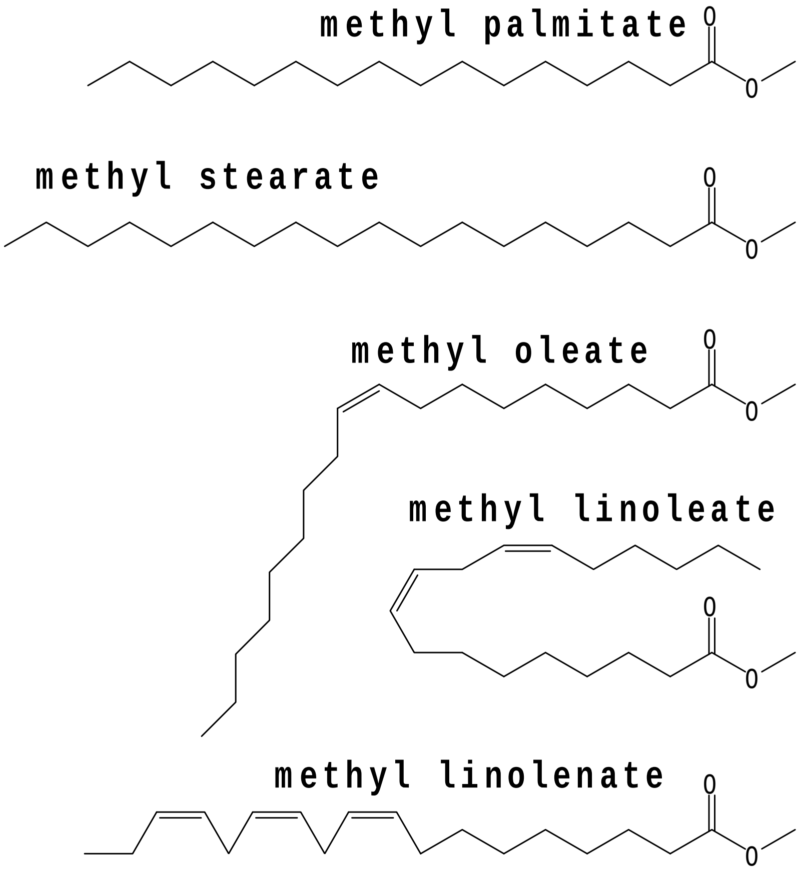
US: soybean / Europe: rapeseed



(R = hydrocarbon chain)

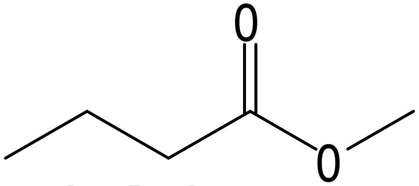
Composition of Biodiesels



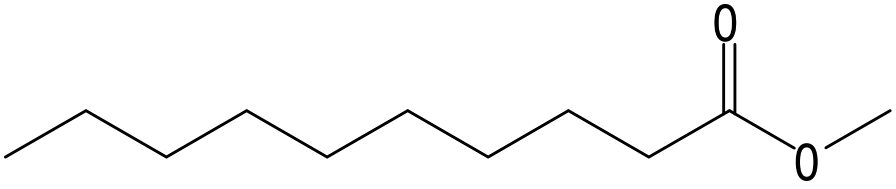


Choice of Surrogates

- Methyl butanoate :
  - ☐ Modeling in 2000
  - ☐ Understanding of the chemistry

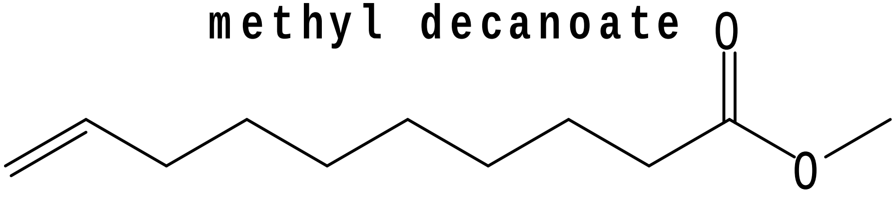

methyl butanoate

Molecular size too small compared to biodiesel


methyl decanoate

Good compromise:

→ methyl decanoate

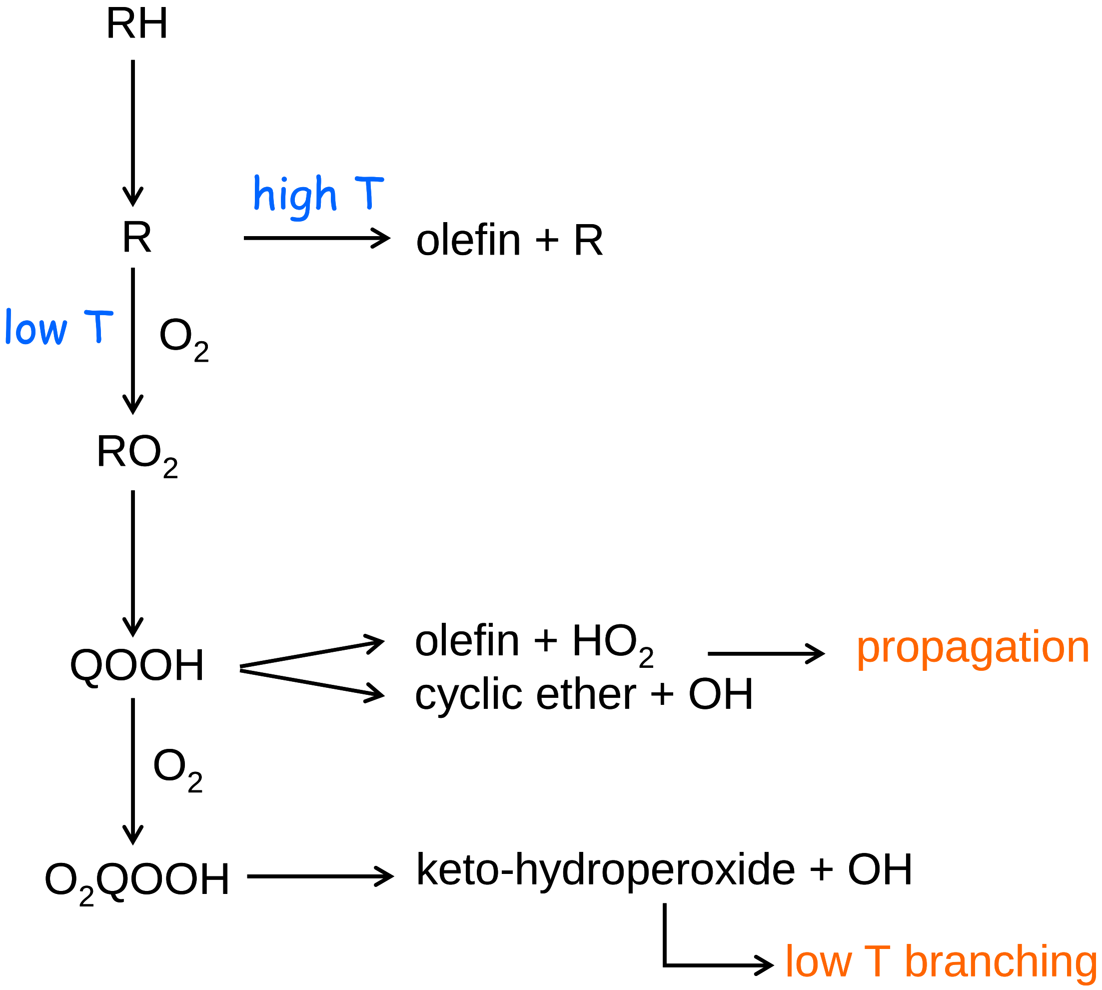

methyl decenoate

Mechanism Structure

- Written in a systematic way (reaction rate rules)
- High and low T chemistry

→ 8580 reactions

→ 3034 species



RH

R

high T

olefin + R

low T

O_2

RO_2

QOOH

olefin + HO_2

cyclic ether + OH

propagation

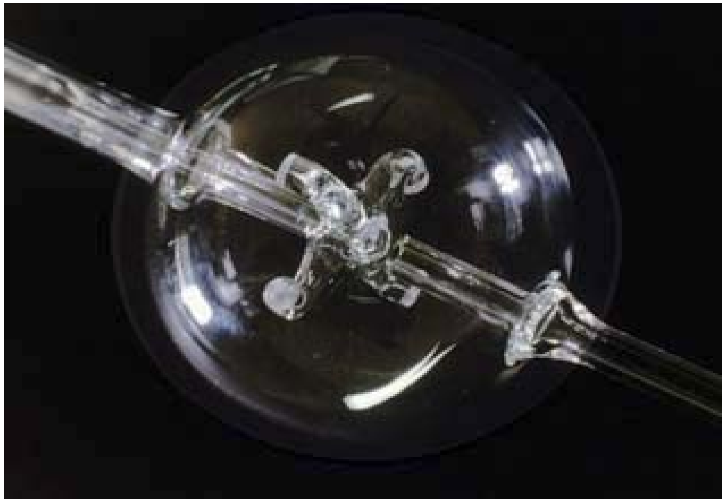
O_2

O_2QOOH

keto-hydroperoxide + OH

low T branching

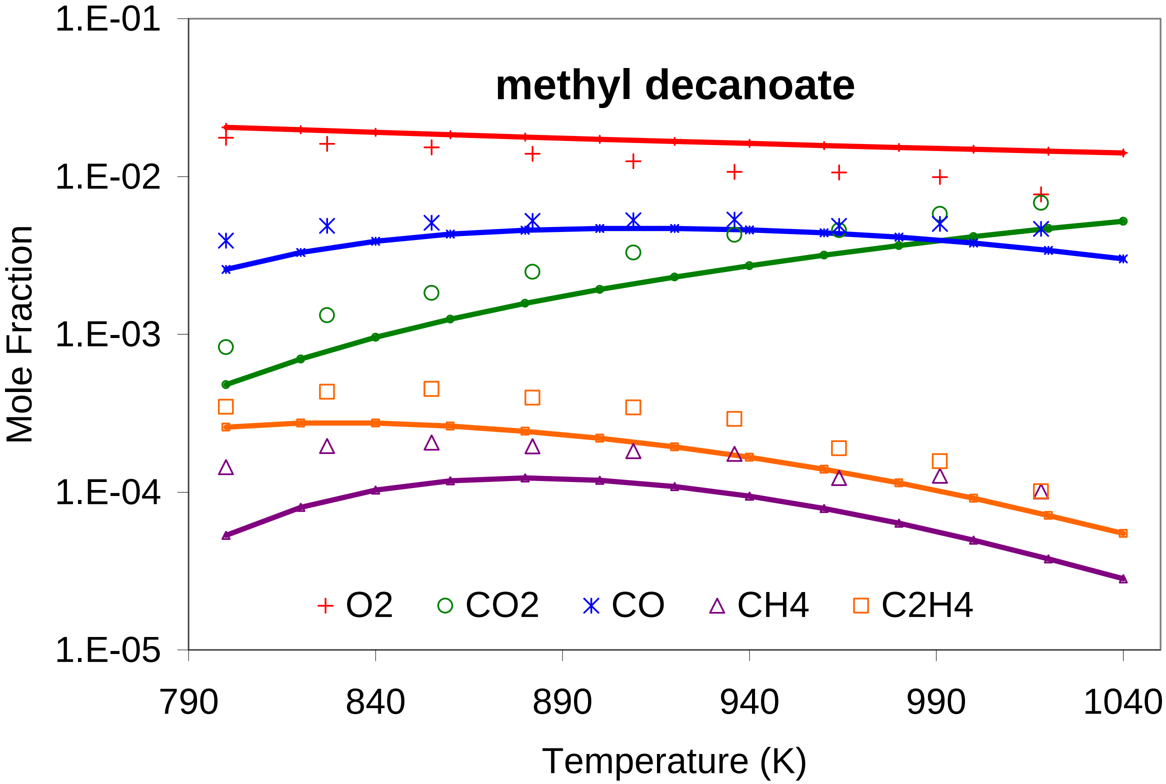
Rapeseed Oil Methyl Esters in a Jet Stirred Reactor (Dagaut et al.)



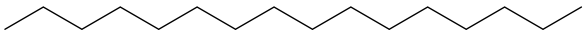
- Pressure: 10 atm
- Equivalence ratio: 0.5, in air
- Residence time: 1s

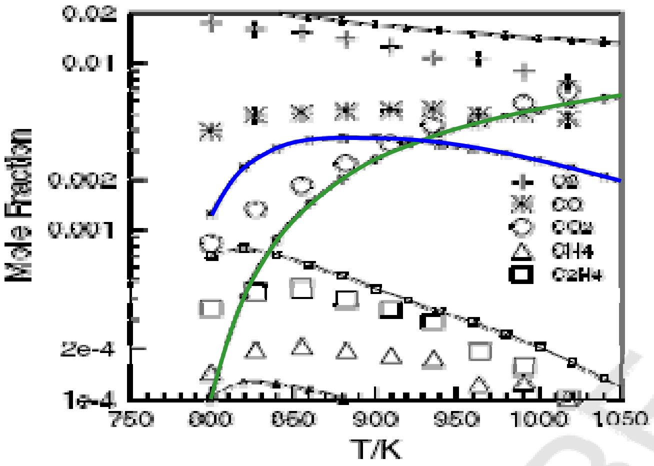
- RME: $C_{18}H_{33}O_2$ (from Dagaut et al.)
- Methyl Decanoate: $C_{11}H_{22}O_2$
- Initial mole fraction: 500 ppm → 818 ppm

Rapeseed Oil Methyl Esters in a JSR



n-hexadecane (Dagaut et al.)





The early formation of CO_2 is better reproduced by the MD mechanism

Early CO_2 formation reduces effectiveness of oxygenated fuels for reducing soot formation

Photoionization Mass Spectrometry and Modeling Studies of the Flame Chemistry of Ethyl and Methyl Esters

Terrill A. Cool, Juan Wang, Bin Yang

School of Applied and Engineering Physics, Cornell University

Nils Hansen, Tina Kasper

Combustion Research Facility, Sandia National Laboratories

Charles K. Westbrook

Lawrence Livermore National Laboratory

Katharina Kohse-Höinghaus, Patrick Osswald

Physikalische Chemie I, Universität Bielefeld

Frederick L. Dryer

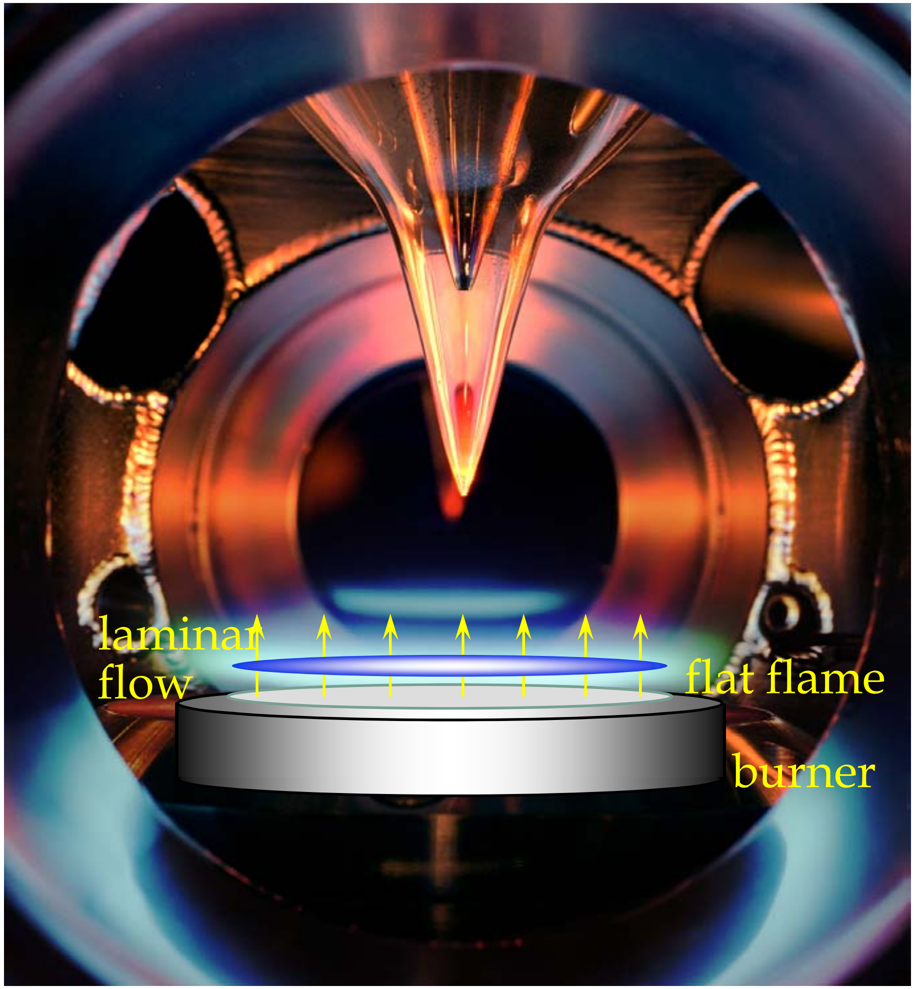
Department of Mechanical and Aerospace Engineering, Princeton University

Phillip R. Westmoreland

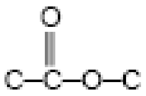
Department of Chemical Engineering, University of Massachusetts Amherst

1-D Laminar Low-Pressure Premixed Flames for the Development and Testing of Kinetic Mechanisms

- **Molecular-beam sampling “freezes“ chemistry.**
- **Photoionization TOF mass spectrometry offers the appeal of a universal detector with rapid data collection.**
- **Identification of species**
  - ✓ **by mass**
  - ✓ **by ionization energy**
- **Axially resolved mole fraction profiles of combustion intermediates are directly compared with flame modeling predictions.**

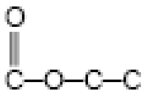


Study Fuel Isomers



$\mathrm{C-\overset{O}{\overset{\|}{C}}-O-C}$

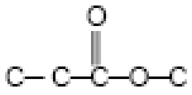
Methyl Acetate



$\mathrm{\overset{O}{\overset{\|}{C}}-O-C-C}$

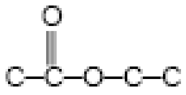
Ethyl Formate

Isomers of $C_3H_6O_2$ (*m*/*z*=74)



$\mathrm{C-C-\overset{O}{\overset{\|}{C}}-O-C}$

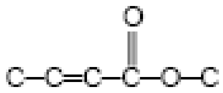
Methyl Propanoate



$\mathrm{C-\overset{O}{\overset{\|}{C}}-O-C-C}$

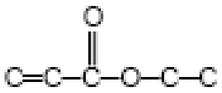
Ethyl Acetate

Isomers of $C_4H_8O_2$ (*m*/*z*=88)



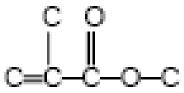
$\mathrm{C-C{=}C-\overset{O}{\overset{\|}{C}}-O-C}$

Methyl Crotonate



$\mathrm{C{=}C-\overset{O}{\overset{\|}{C}}-O-C-C}$

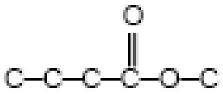
Ethyl Propenoate



$\mathrm{C{=}\overset{C}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-O-C}$

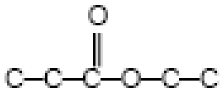
Methyl 2-Methylpropenoate

Isomers of $C_5H_8O_2$ (*m*/*z*=100)



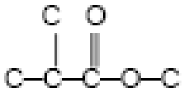
$\mathrm{C-C-C-\overset{O}{\overset{\|}{C}}-O-C}$

Methyl Butanoate



$\mathrm{C-C-\overset{O}{\overset{\|}{C}}-O-C-C}$

Ethyl Propanoate

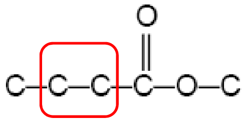


$\mathrm{C-\overset{C}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-O-C}$

Methyl Isobutanoate

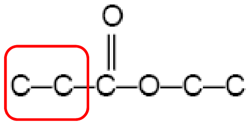
Isomers of $C_5H_{10}O_2$ (*m*/*z*=102)

Study Influences of Fuel Structure



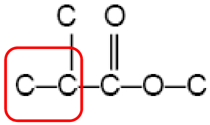
$\mathrm{C-\boxed{C-C}-\overset{\overset{O}{\|}}{C}-O-C}$

Methyl Butanoate



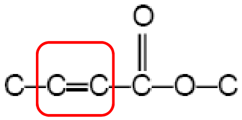
$\mathrm{\boxed{C-C}-\overset{\overset{O}{\|}}{C}-O-C-C}$

Ethyl Propanoate



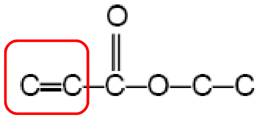
$\mathrm{\boxed{C-\overset{\overset{C}{|}}{C}}-\overset{\overset{O}{\|}}{C}-O-C}$

Methyl Isobutanoate



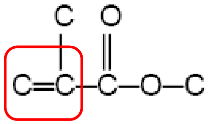
$\mathrm{C-\boxed{C=C}-\overset{\overset{O}{\|}}{C}-O-C}$

Methyl Crotonate



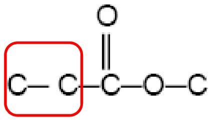
$\mathrm{\boxed{C=C}-\overset{\overset{O}{\|}}{C}-O-C-C}$

Ethyl Propenoate



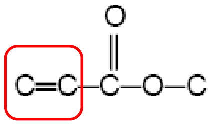
$\mathrm{\boxed{C=\overset{\overset{C}{|}}{C}}-\overset{\overset{O}{\|}}{C}-O-C}$

Methyl 2-Methylpropenoate



$\mathrm{\boxed{C-C}-\overset{\overset{O}{\|}}{C}-O-C}$

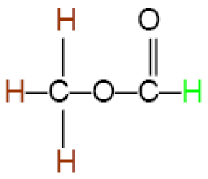
Methyl Propanoate



$\mathrm{\boxed{C=C}-\overset{\overset{O}{\|}}{C}-O-C}$

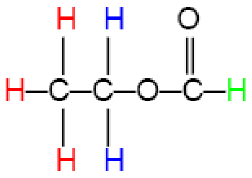
Methyl Propenoate

Using Fuel Structures to Guide Mechanism Development



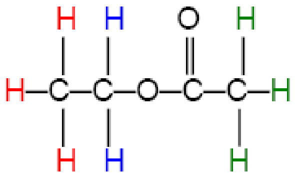
Methyl Formate

H-atom abstractions from similar sites use the same rates

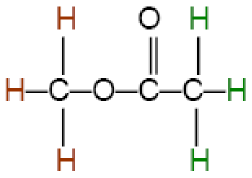


Ethyl Formate

Model species for H-atom abstractions included propane and DME for terminal methyl radicals, propane for secondary H-atoms, and other hydrocarbons with similar C-H bond energies

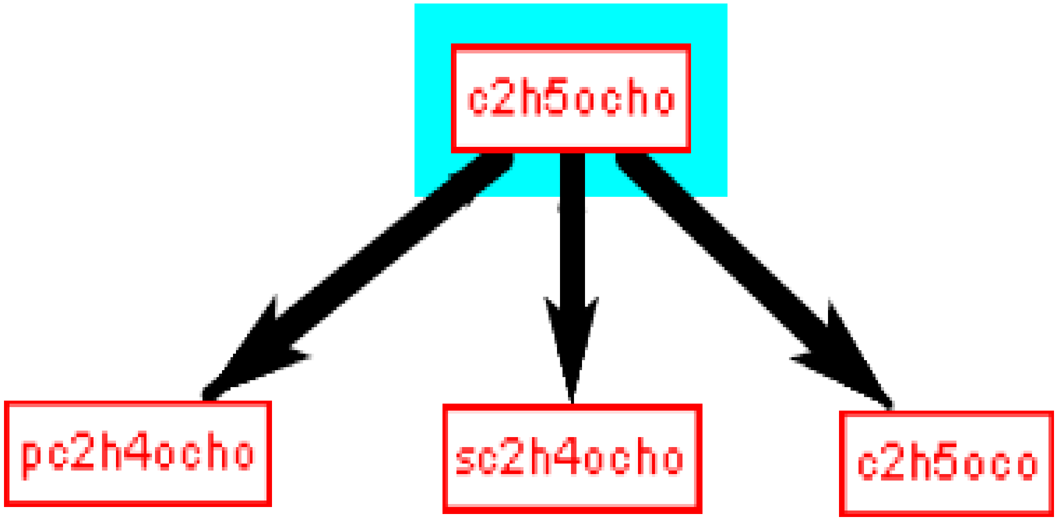


Ethyl Acetate

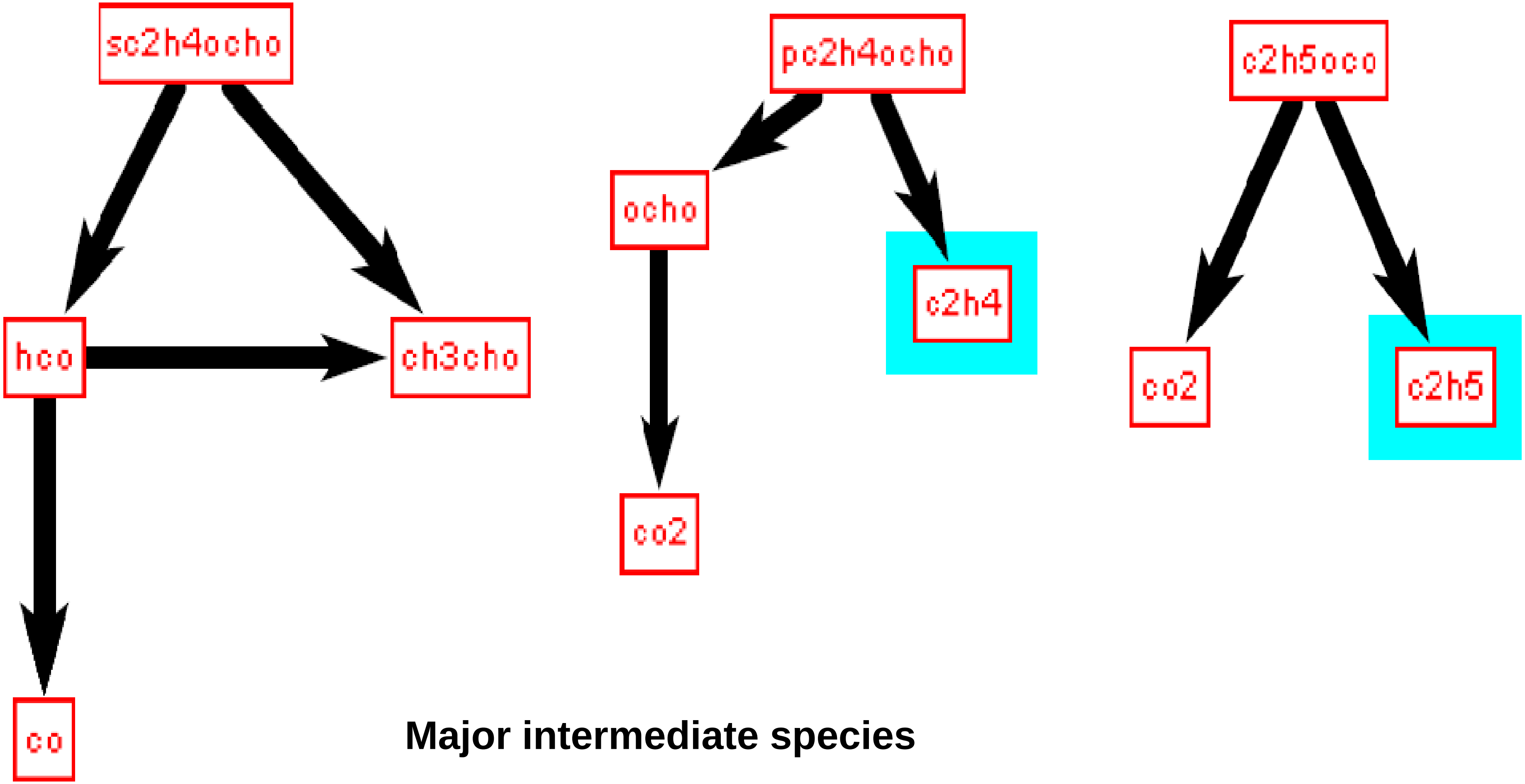


Methyl Acetate

Ethyl formate produces three principal radicals



Ethyl formate produces two distinct families of products

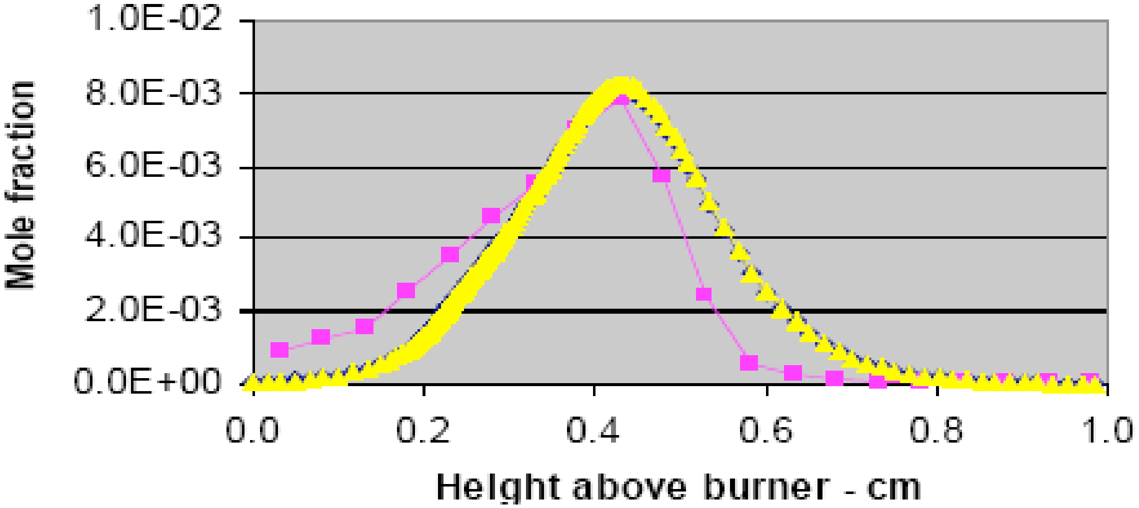


Major intermediate species

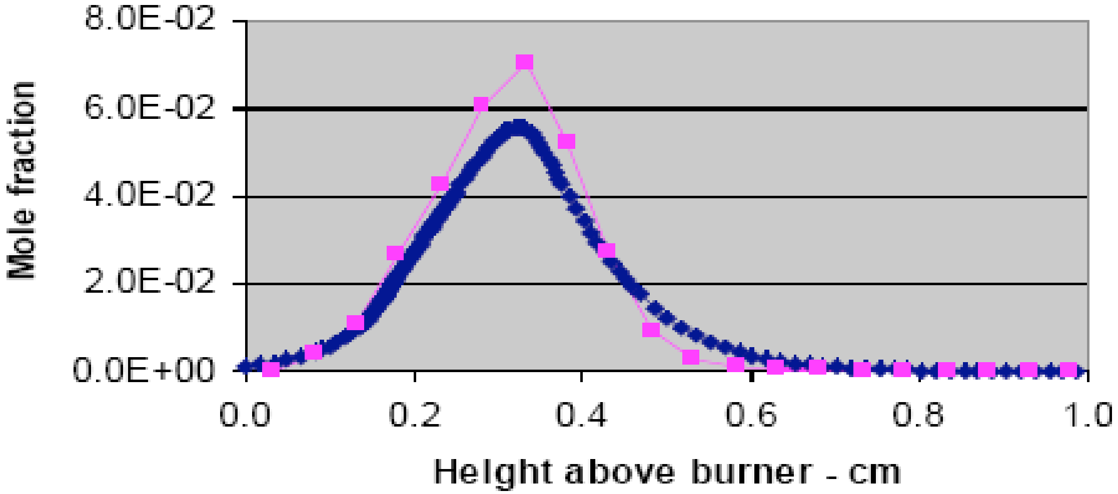
Acetaldehyde, formaldehyde, CO and methane

Ethene, acetylene, ketene and CO_2

Mole Fraction Profiles for Ethylene

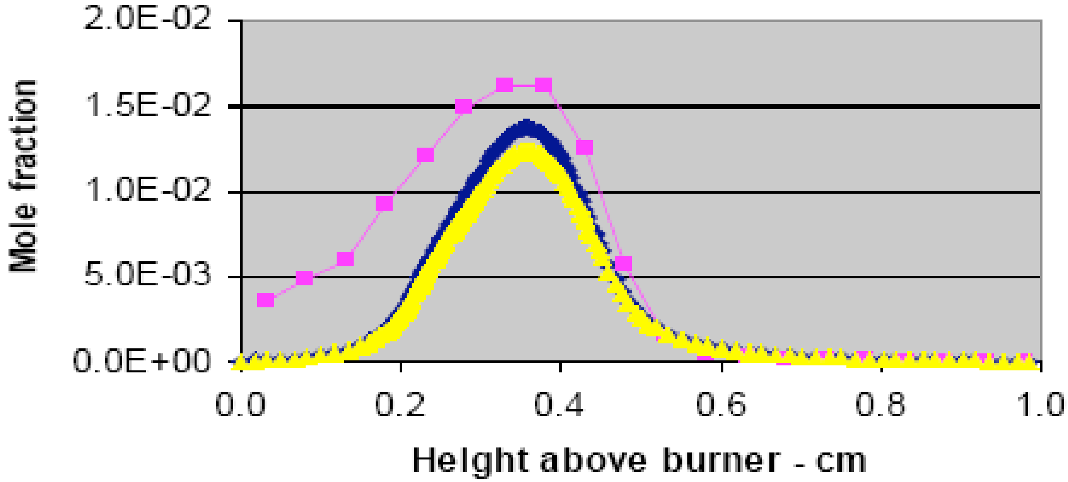


Methyl Acetate

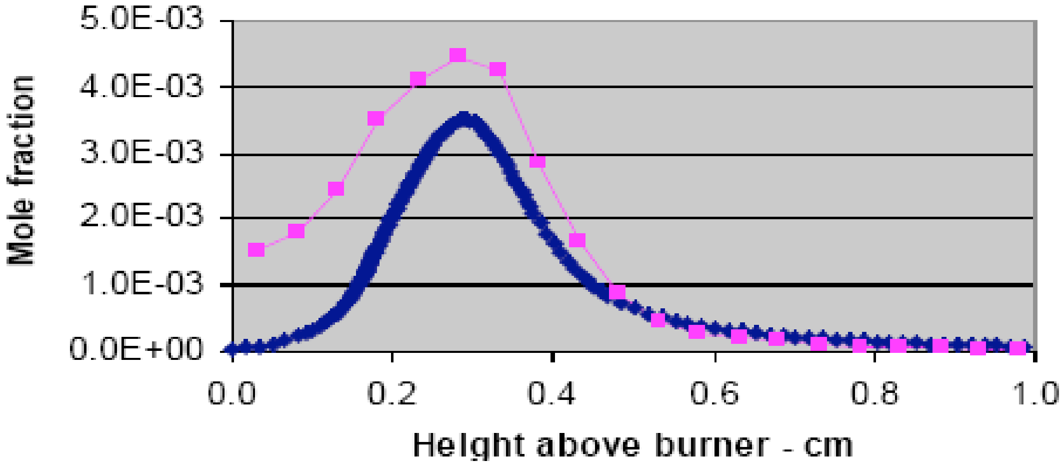


Ethyl Formate

Mole Fraction Profiles for Formaldehyde



Methyl Acetate



Ethyl Formate

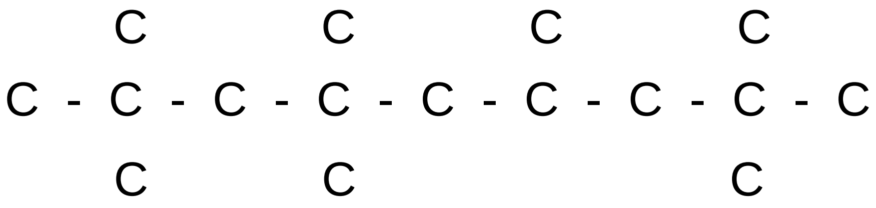
A Detailed Chemical Kinetic Mechanism for 2,2,4,4,6,8,8-heptamethyl nonane

Charles Westbrook

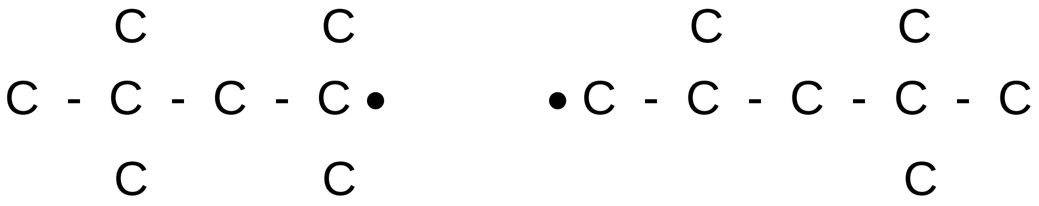
July, 2008

Reaction Design

2,2,4,4,6,8,8-heptamethyl nonane is 2 iso-octyl radicals

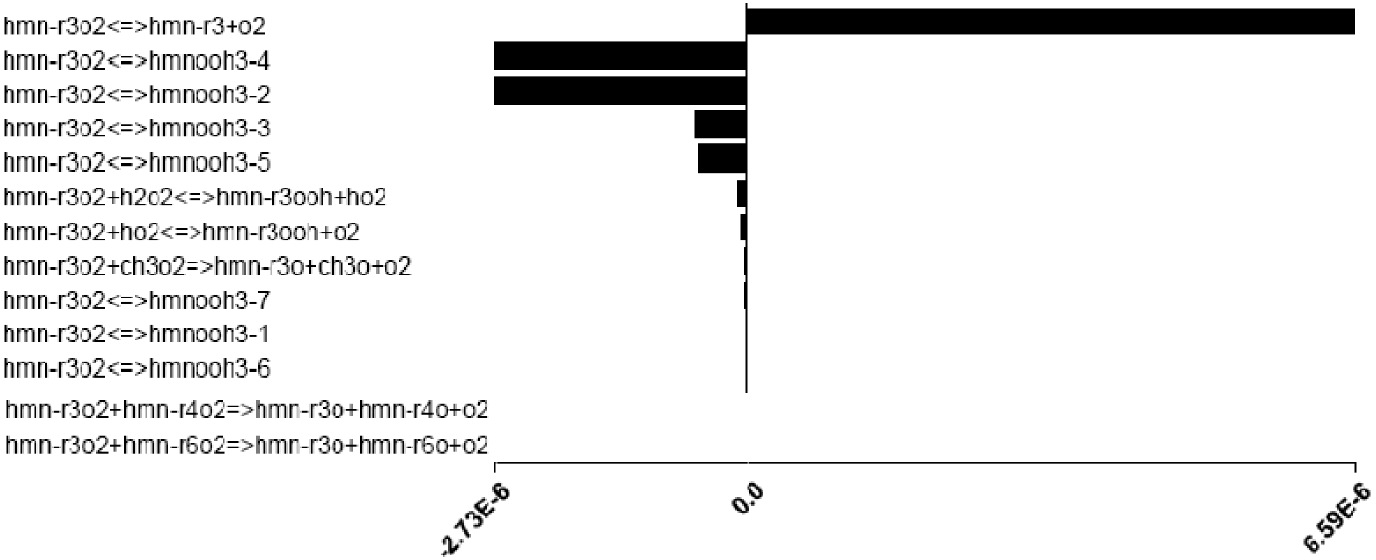


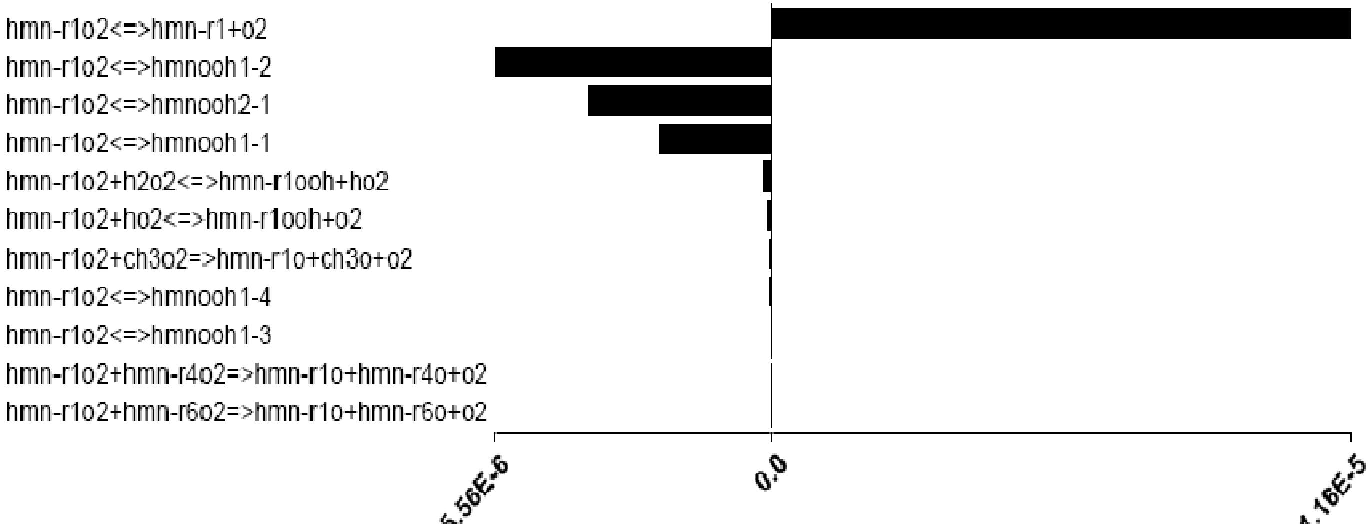
$$C - \underset{C}{\overset{C}{C}} - C - \underset{C}{\overset{C}{C}} - C - \overset{C}{C} - C - \underset{C}{\overset{C}{C}} - C$$



$$C - \underset{C}{\overset{C}{C}} - C - \underset{C}{\overset{C}{C}}\bullet \qquad \bullet C - \overset{C}{C} - C - \underset{C}{\overset{C}{C}} - C$$

$$C - \underset{C}{\overset{C}{C}} - C - \underset{\bullet}{\overset{C}{C}} - C \qquad C - \underset{C}{\overset{C}{C}} - C - \overset{C}{C} - C\bullet$$

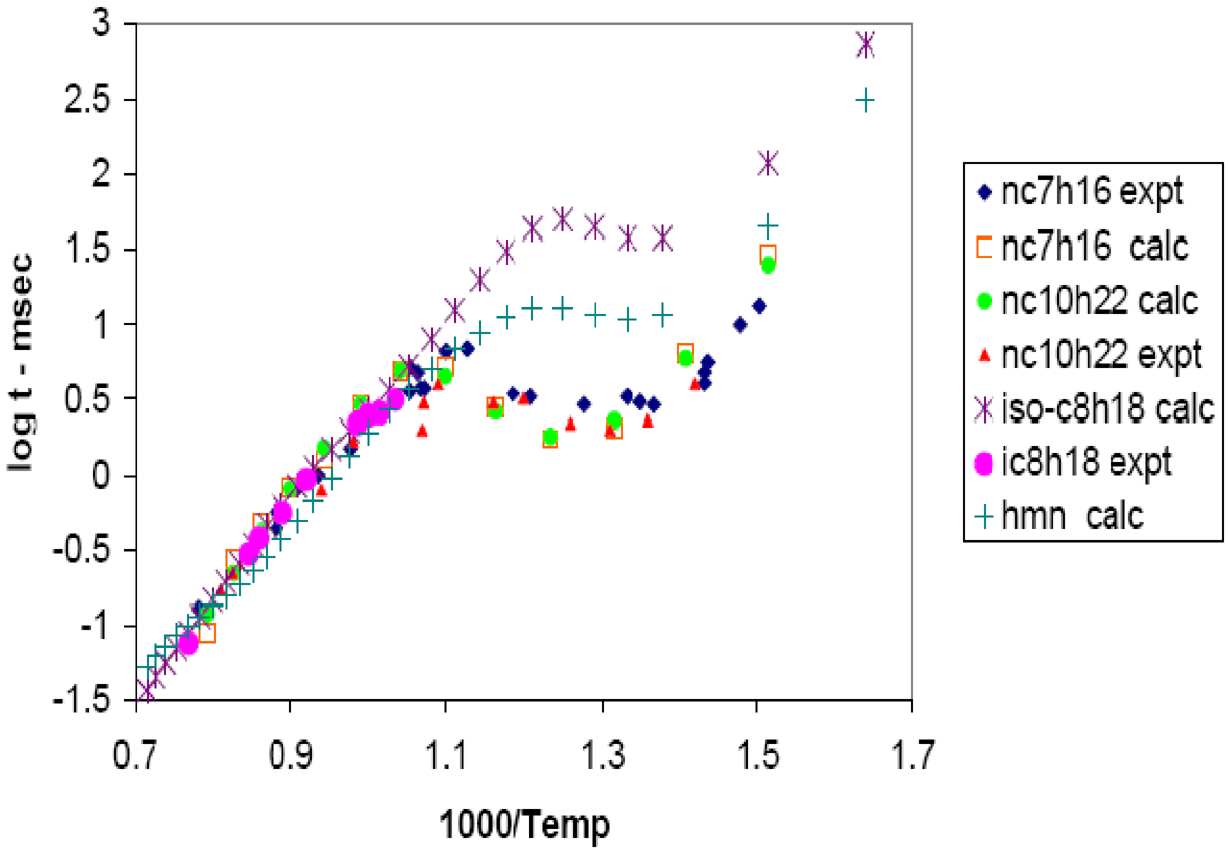

Absolute Rate of Production hmn-r3o2


Absolute Rate of Production hmn-r1o2

Example of use of reaction path analysis tools to find mechanism errors

HMN and iso-octane ignition is slower than n-alkanes only in the Low Temperature regime

13.5 bar pressure



Major Benzene Formation Pathways Revisited

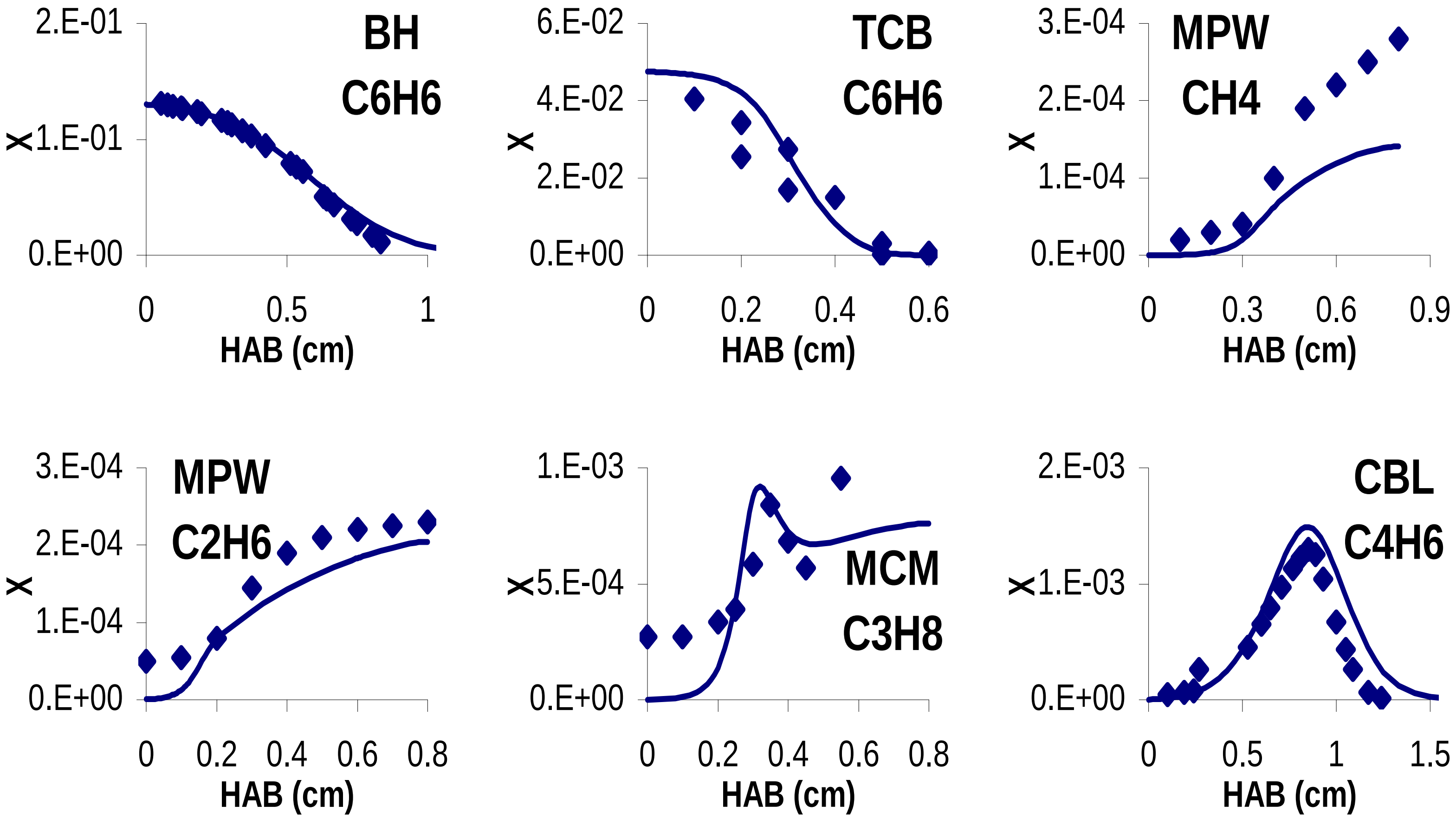
- **Class 1: Acetylene addition (Westmoreland et al., 1989; Frenklach et al., 1985)**
  - **R1:** $C_2H_2 + CH_2CHCHCH = C_6H_6 + H$
  - **R2:** $C_2H_2 + HCCHCCH = C_6H_5$
- **Class 2: C_3 combination (Hopf, 1971; Miller-Melius, 1992)**
  - **R3:** $H_2CCCH + H_2CCCH = C_6H_6$
  - **R4:** $H_2CCCH + CH_2CCH_2 = C_6H_6 + H$
  - **R5:** $H_2CCCH + H_2CCCH = C_6H_5 + H$
  - **R6:** $H_2CCCH + CH_2CHCH_2 =$ FULVENE + 2H

Natural Gas, Synfuel, Indicator Fuels, Biofuels

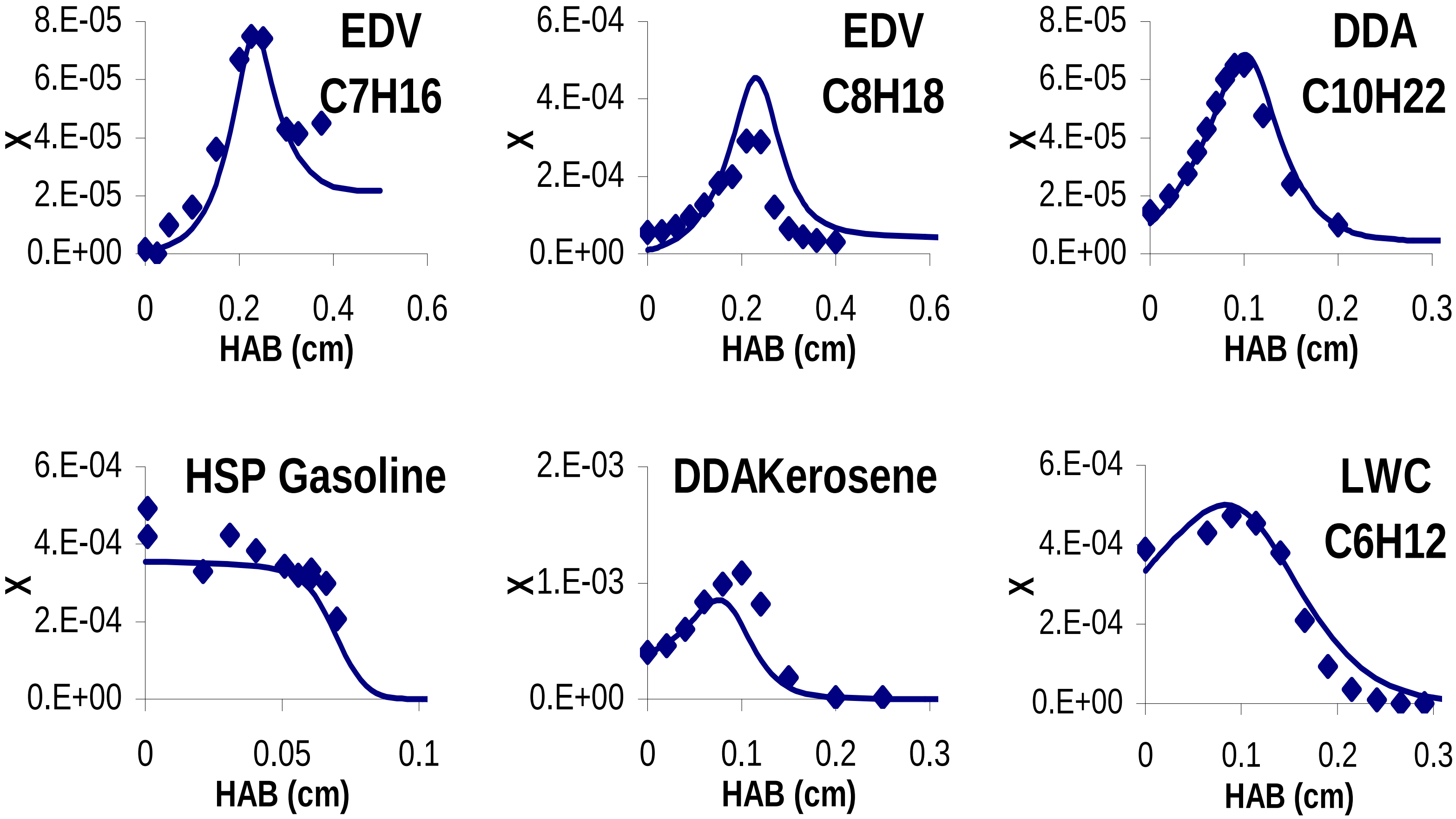
- **Class 3: Combination of CH_3 and C_5H_5**
  - **R7:** $C_5H_5 + CH_3 = C\text{-}C_6H_8 = C_6H_6 + 2H$
- **Class 4: Cascading dehydrogenation (Zhang et al., 2007)**
  - **R8:** $\text{cycloC}_6\text{-R} \leftrightarrow C\text{-}C_6H_{10}(-R) \leftrightarrow C\text{-}C_6H_8(-R) \leftrightarrow C_6H_6(-R)$
- **Class 5: De-alkylation**
  - **R9:** $C_6H_5\text{-}R + H = C_6H_6 + R$

Liquid Fuels from Oil and Coal

Modeled Benzene Concentrations



Modeled Benzene Concentrations



Overall conclusions

- Many new detailed mechanisms are being developed
- Use of automatic mechanism generation is growing rapidly
- The “richness” of the palette of mechanisms is increasing rapidly
- Kinetic modeling tools are improving rapidly
  - Reaction path analysis
  - Critical compression ratio
  - HCCI multizone models