Lawrence Livermore National Laboratory

Needs for Development of Chemical Kinetic Models for High Pressure Applications

Workshop on Techniques for High-Pressure Combustion

Argonne National Laboratory

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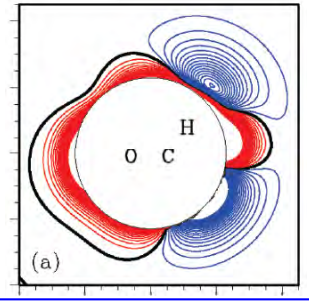
LLNL-PRES-496616

Development of chemical kinetic models for fuels

Fundamental experimental measurements



Ab initio calculations

```
oh         7/13/ 0 rucich   1o   1    0    0g   300.000  5000.000 1710.000    01
 2.85376040e+00 1.02994334e-03-2.32666477e-07 1.93750704e-11-3.15759847e-16    2
 3.69949720e+03 5.78756825e+00 3.41896226e+00 3.19255801e-04-3.08292717e-07    3
 3.64407494e-10-1.00195479e-13 3.45264448e+03 2.54433372e+00                   4
```

c3h8+oh<=>nc3h7+h2o 1.054e+10 0.970 1.586e+03

C1C2 base chemistry

Thermodynamic database

Reaction rate constants

Experimental validation

Detailed chemical kinetic model for practical fuels

Reaction rate rules

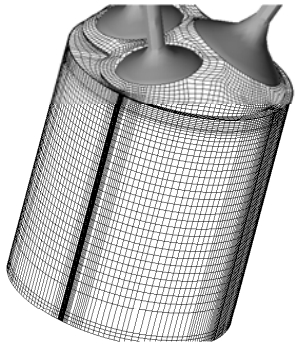
Chemical kinetic model reduction

High temperature mechanism
Reaction class 1: Unimolecular fuel decomposition
Reaction class 2: H atom abstractions from fuel
Reaction class 3: Alkyl radical decomposition
Reaction class 4: Alkyl radical + O_2 = olefin + HO_2
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

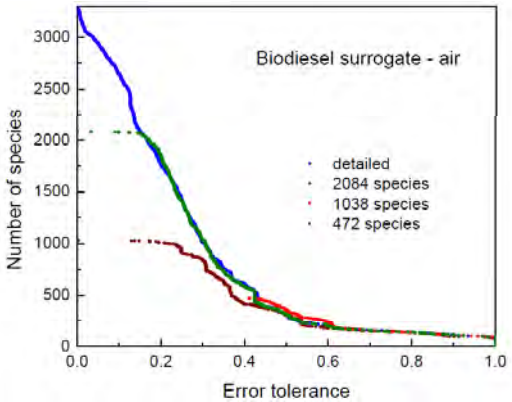
CFD code

Who are our "Customers"?

Engine developers



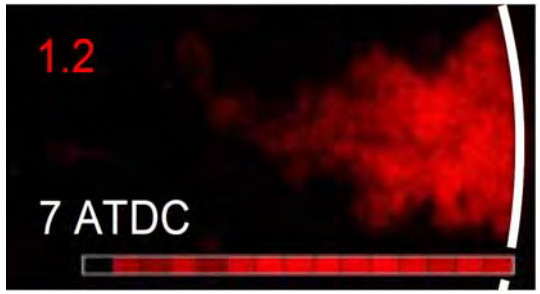
CFD engine modelers



Mechanism reduction specialists

Other customers:

- Model in situ measurements in engines:
  - Example: Formaldehyde measurements in diesel engine. Use chemical kinetic model to find source of formaldehyde.
- HCCI engine experimentalists
  - Can use detailed chemistry without highly reduced model



Genzale, Reitz and Musculus 2008

Who are our “suppliers”?

Experimentalists who supply of experimental data for mechanism validation

Jet Stirred Reactors

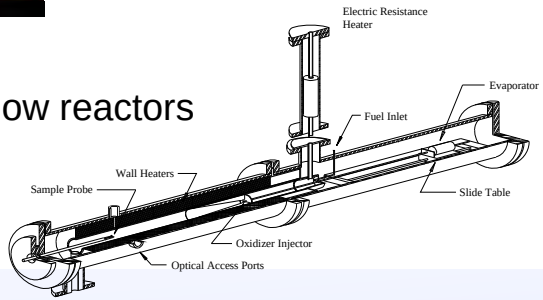
Premixed Laminar Flames

Shock tube

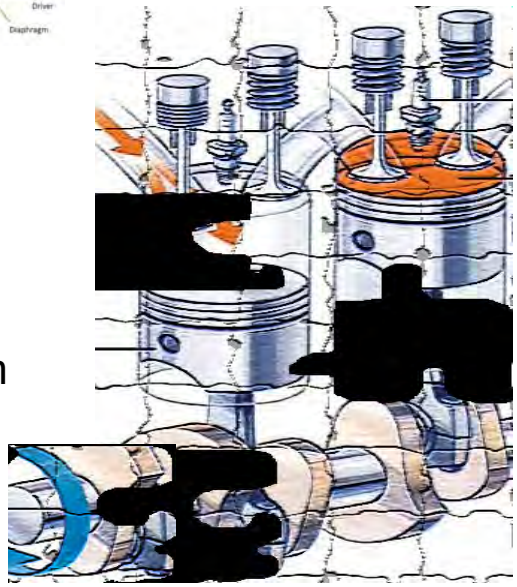
Rapid Compression Machines

Non Premixed Flames

High pressure flow reactors



Engine Combustion



Combustion Parameters

Temperature

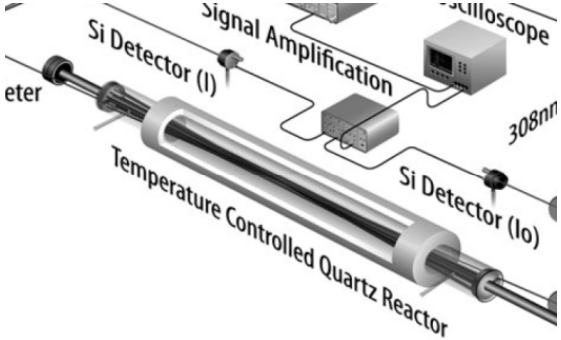
Pressure

Mixture fraction (air-fuel ratio)

Mixing of fuel and air

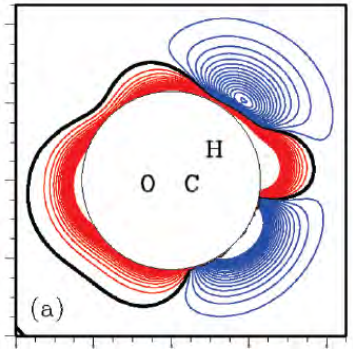
“Suppliers” (continued):

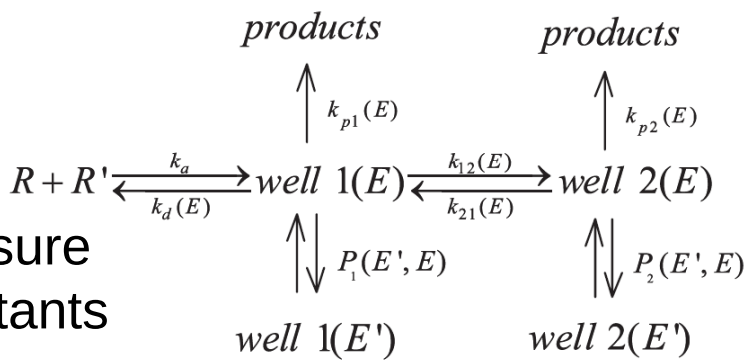
- Experimentalists who provide:
  - fundamental reaction rate constants
  - product channels
  - effects of pressure and temperature on rate constants
  - transport properties
  - thermodynamic properties



Who are our “Suppliers”? (continued)

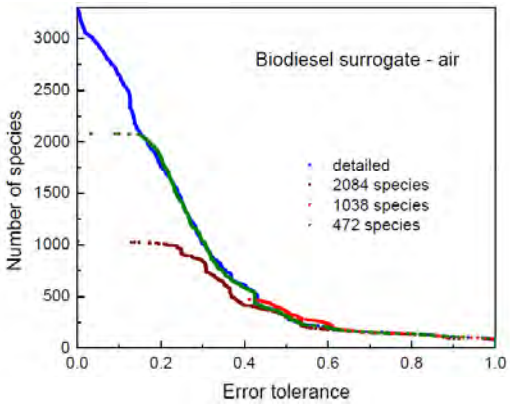
- Theoreticians and modelers who provide reaction path, rate constant, thermodynamic properties and transport properties
  - Ab initio calculations
    - Thermodynamic properties (heat of formation, heat capacity)
    - Reaction rate constants
    - Product channels
  - Master equation analysis for pressure dependence of reaction rate constants
  - Molecular dynamics to obtain transport coefficients
  - Equation of State modelers who provide vaporization characteristics (needed to know what surrogate fuel will work)



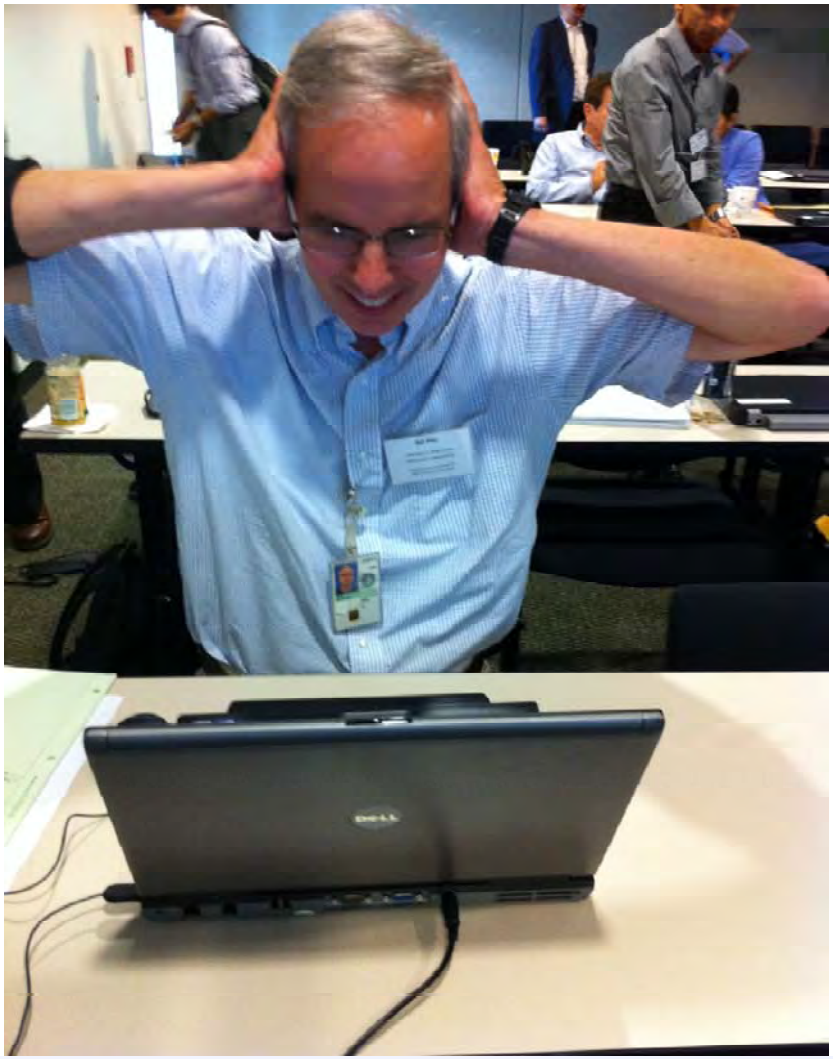


Who are our “Suppliers”? (continued)

- Those who enable the use of chemical kinetic models in codes
  - Mechanism reduction specialists
  - Numerical methods specialists
    - Develop faster chemistry solvers

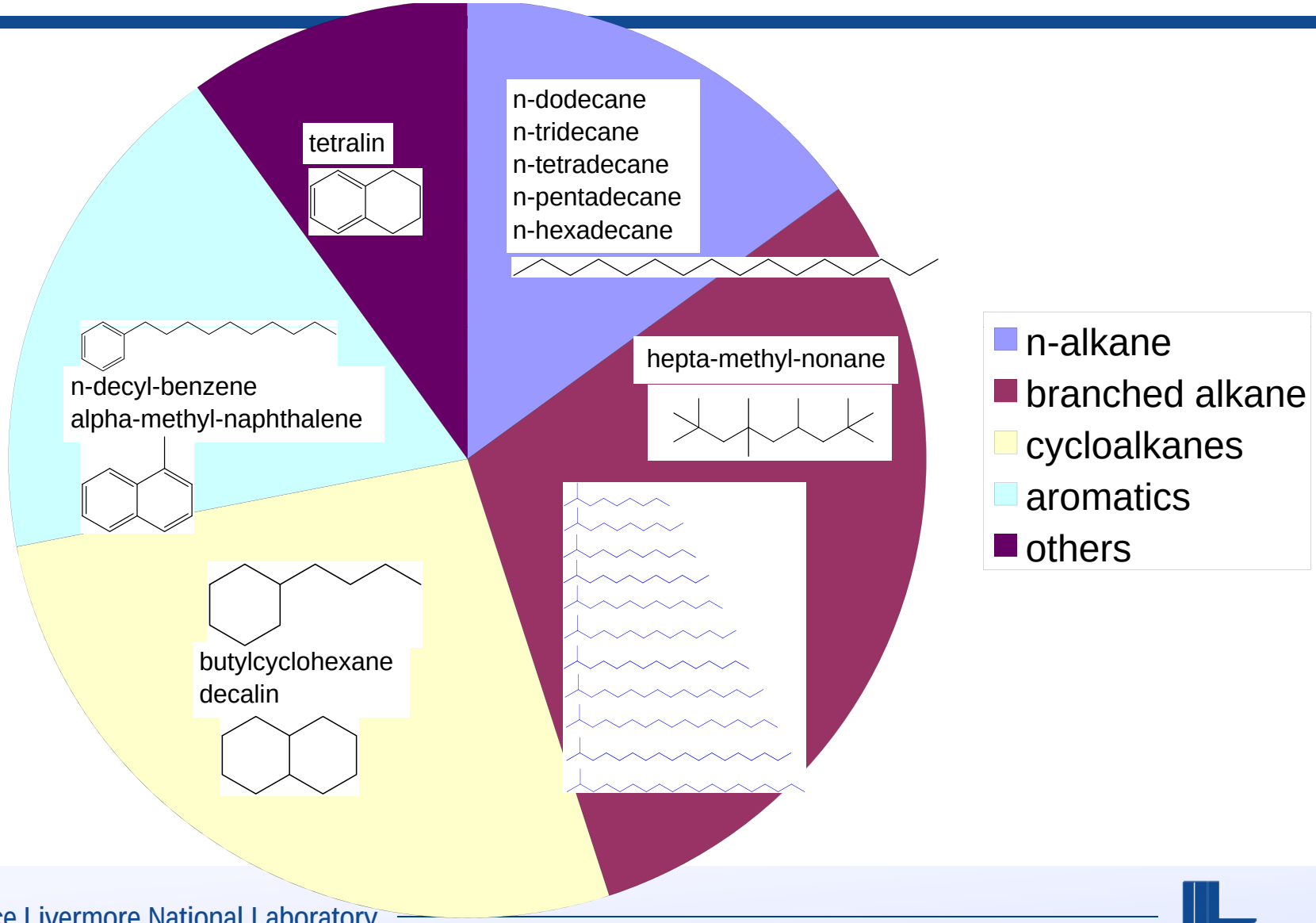


What are some specific needs of chemical kinetic modelers?



Typical chemical kinetic modeler

Experimental data needed for many different fuel components: Diesel fuel surrogate palette



Specific examples of needs:
Needs for different reaction classes

We assign reaction rate rules by reaction classes:

High temperature mechanism

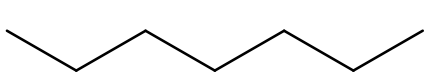
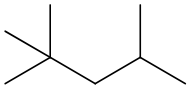
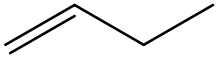
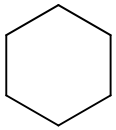
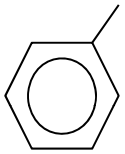
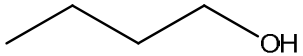
Reaction class 1: Unimolecular fuel decomposition
Reaction class 2: H atom abstractions from fuel
Reaction class 3: Alkyl radical decomposition
Reaction class 4: Alkyl radical + O_2 = olefin + HO_2
Reaction class 5: Alkyl radical isomerization
Reaction class 6: H atom abstraction from olefins
Reaction class 7: Addition of radical species to olefins
Reaction class 8: Alkenyl radical decomposition
Reaction class 9: Olefin decomposition

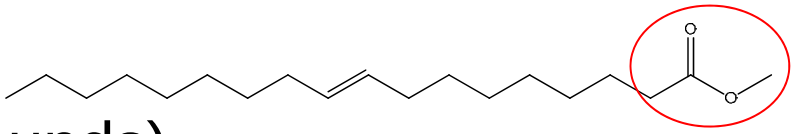
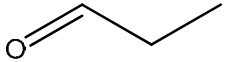
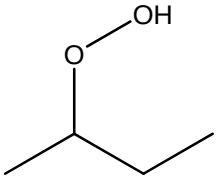
Specific needs:
Reaction classes for low temperature reactions

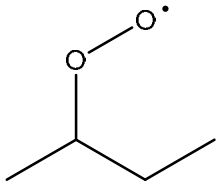
Low temperature mechanism

Reaction class 10: Alkyl radical addition to O_2 ($R + O_2$)
Reaction class 11: $R + R'O_2 = RO + R'O$
Reaction class 12: Alkylperoxy radical isomerization
Reaction class 13: $RO_2 + HO_2 = ROOH + O_2$
Reaction class 14: $RO_2 + H_2O_2 = ROOH + HO_2$
Reaction class 15: $RO_2 + CH_3O_2 = RO + CH_3O + O_2$
Reaction class 16: $RO_2 + R'O_2 = RO + R'O + O_2$
Reaction class 17: ROOH = RO + OH
Reaction class 18: RO Decomposition
Reaction class 19: QOOH = Cyclic Ether + OH
Reaction class 20: QOOH = Olefin + HO_2
Reaction class 21: QOOH = Olefin + Aldehyde or Carbonyl + OH
Reaction class 22: Addition of QOOH to molecular oxygen O_2
Reaction class 23: O_2QOOH isomerization to carbonylhydroperoxide + OH
Reaction class 24: Carbonylhydroperoxide decomposition
Reaction class 25: Reactions of cyclic ethers with OH and HO_2

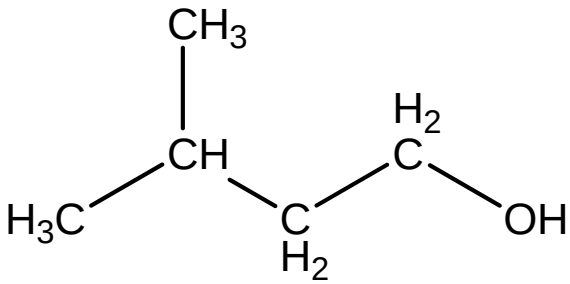
Need reaction rate rules for many chemical classes of fuels

- Alkanes  
- Alkenes 
- Cycloalkanes 
- Aromatics 
- Alcohols 

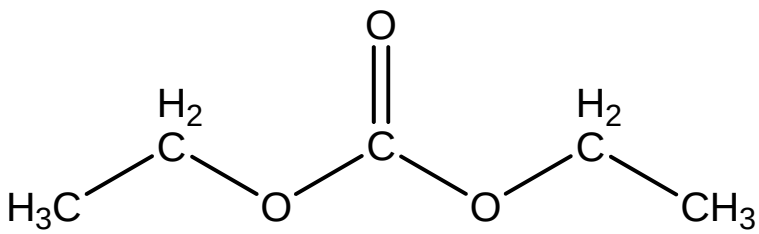
- Methyl esters (biodiesel compounds) 
- Carbenes (aldehydes, ketenes) 
- Special structures in intermediate species:
  - Alkylhydroperoxides 

  - Alkylperoxy 

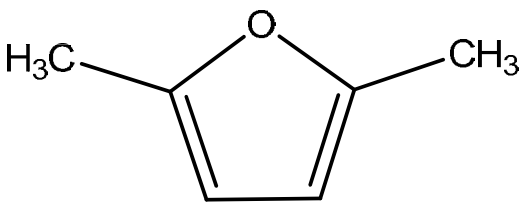
Many reaction rate rules are not known for biofuels



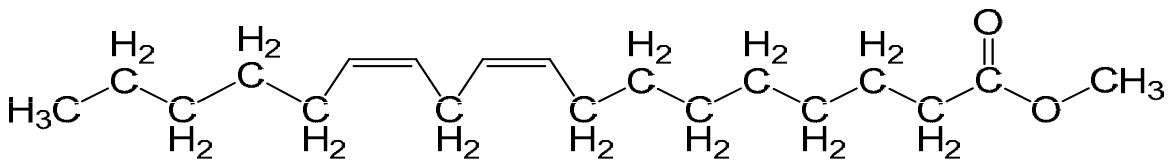
iso-pentanol (JBEI biofuel)



diethylcarbonate
(biofuel for diesel vehicles in Columbia, made from sugar cane)

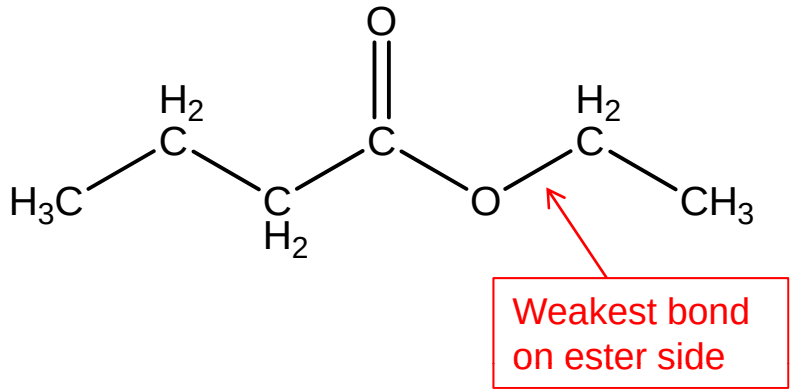


2,5-dimethyl furan
(biomass surrogate)



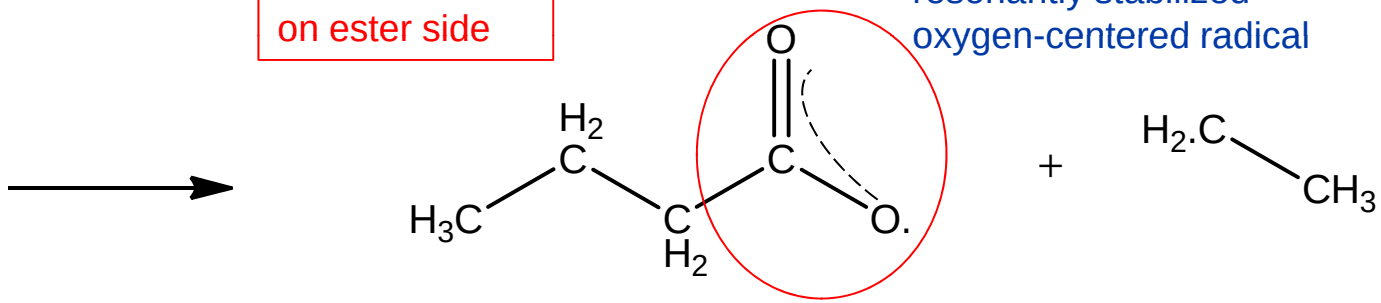
methyl esters
(biodiesel components)

Reaction class 1: Unimolecular fuel decomposition:
Usually specify initiation reactions by reverse rate: this sometimes involves little-studied radicals



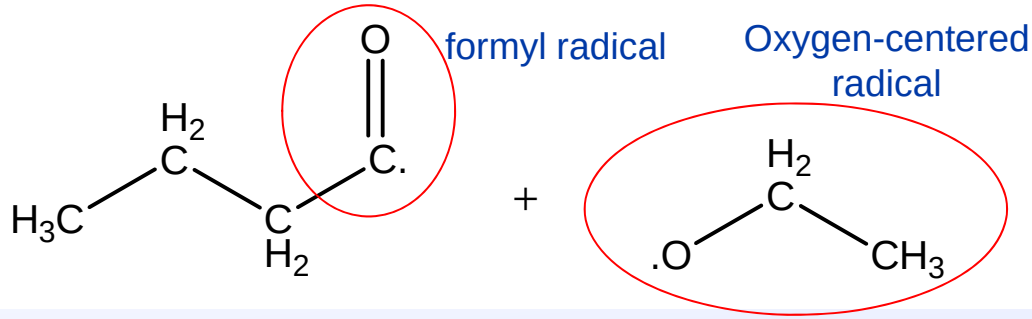
Biodiesel molecule (ethyl ester)

resonantly stabilized
oxygen-centered radical



formyl radical

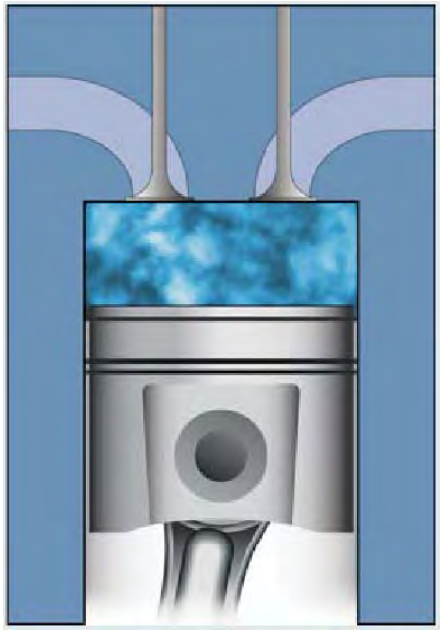
Oxygen-centered
radical



Fuel + OH reaction is the most important fuel consumption reaction under diesel and HCCI engine conditions

Reaction Class 2: H atom abstractions from fuel:
fuel + OH => fuel radical + H2O

Diesel engine



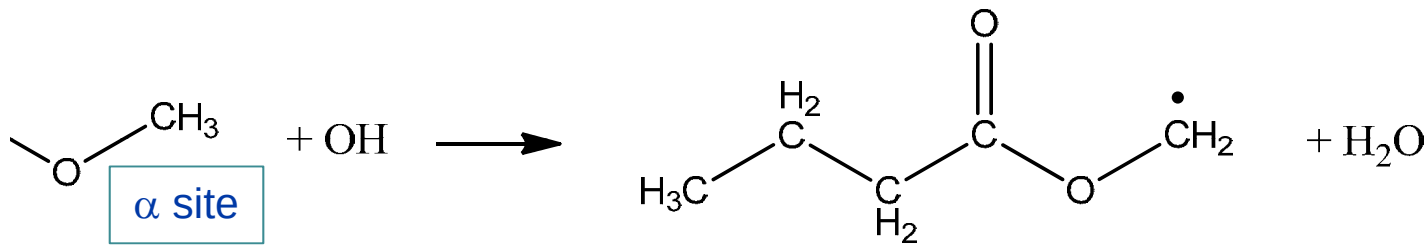
HCCI engine

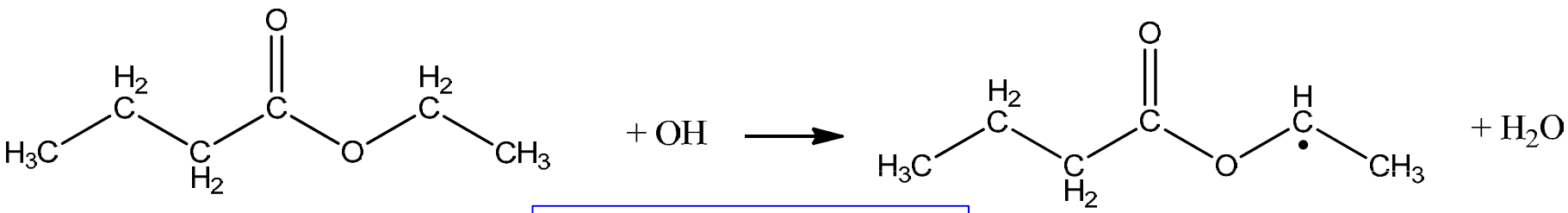
High pressure and low temperature processes produce a lot of OH radicals

The rate constants of biofuels + OH reaction are particularly uncertain

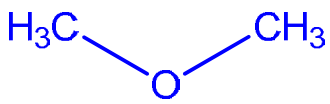
Class 2

Rate of abstraction of H atoms on ester structure in biodiesel?





How does the α site behave? Does it behave like an ether? (It has a C-H bond strength ~4 kcal greater than an ether)



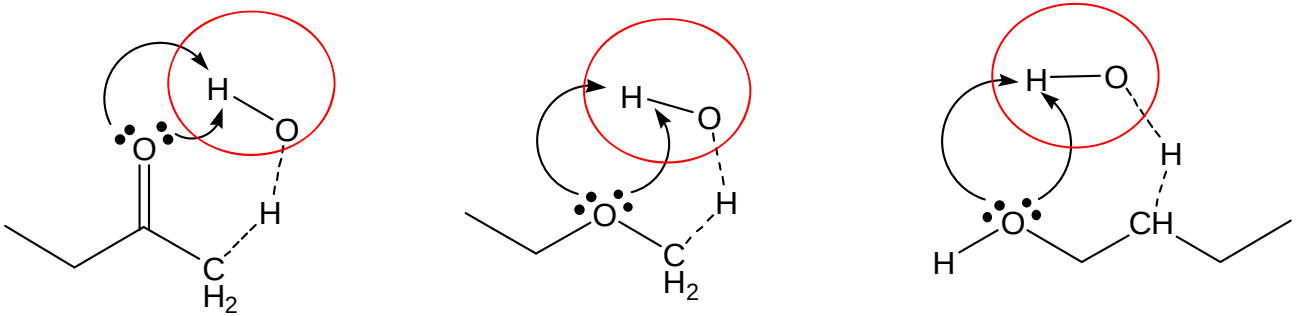
dimethyl ether

OH abstraction reactions often behave differently in biofuels than hydrocarbons

Class 2

Oxygen atoms in fuel allow formation of ring-like transition states:

OH radicals



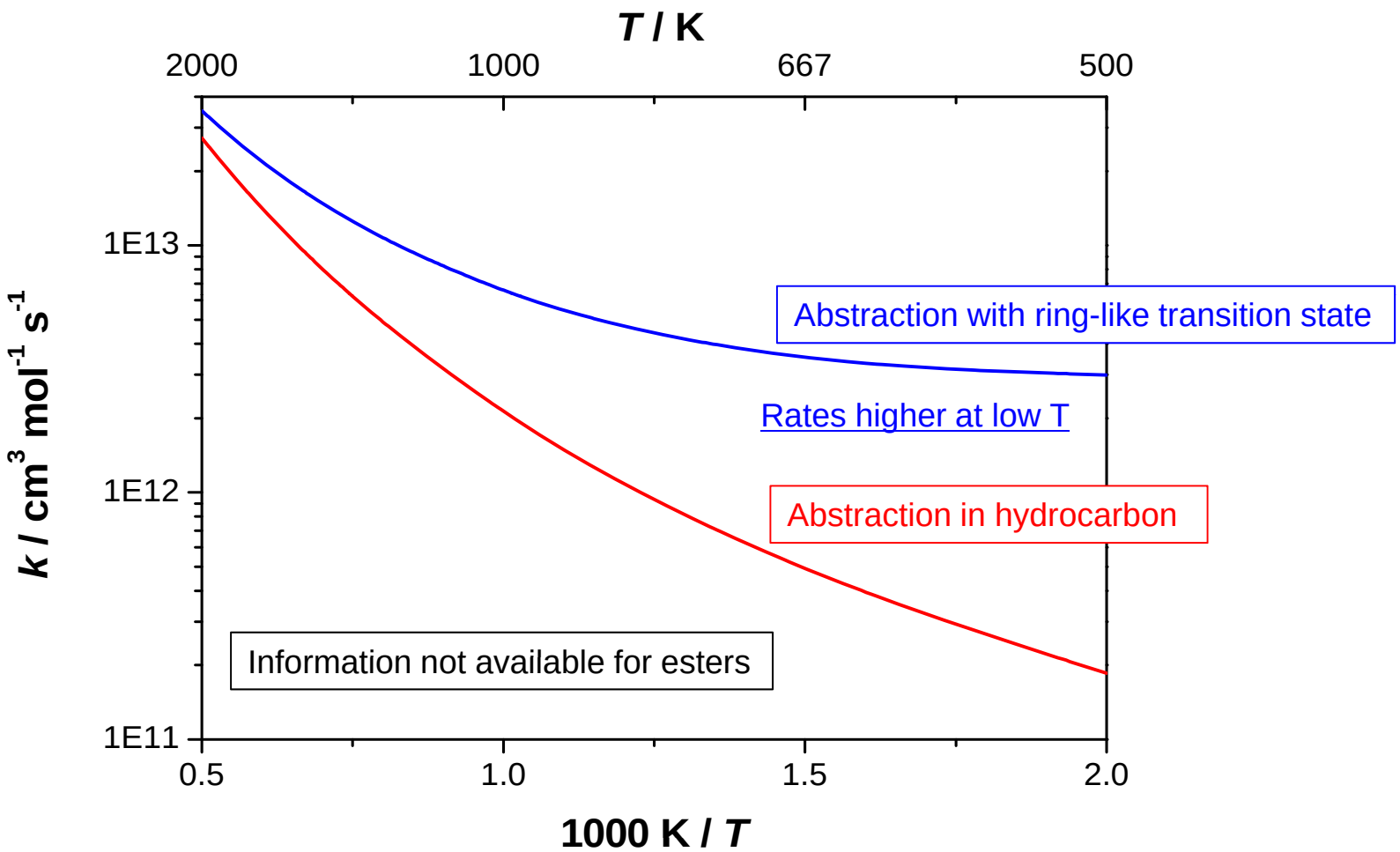
Ketones + OH **Ethers + OH** **Alcohols + OH**

Esters + OH?

(From Curran et al. ICCK 2011)

Ring-like transition states can lead to faster reaction rates

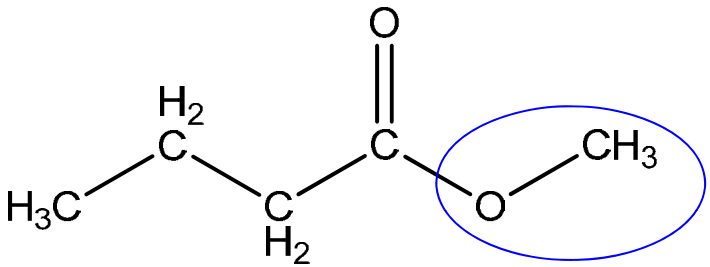
Class 2



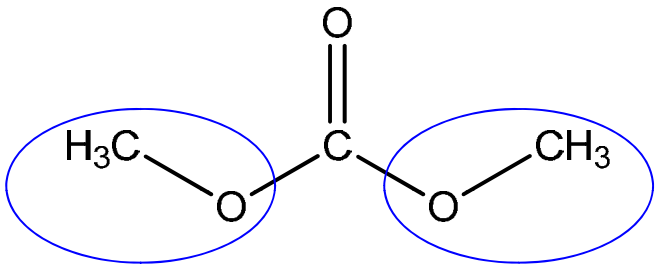
Need: OH + biodiesel rate constants: Use model compounds to get experimental OH abstraction rates

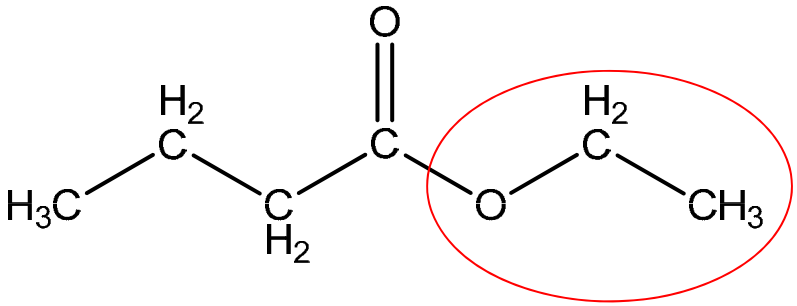
Class 2

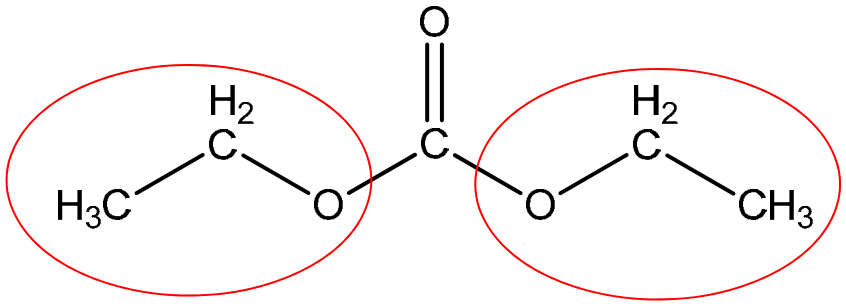
Methyl and ethyl ester biofuels



Model compound to react with OH

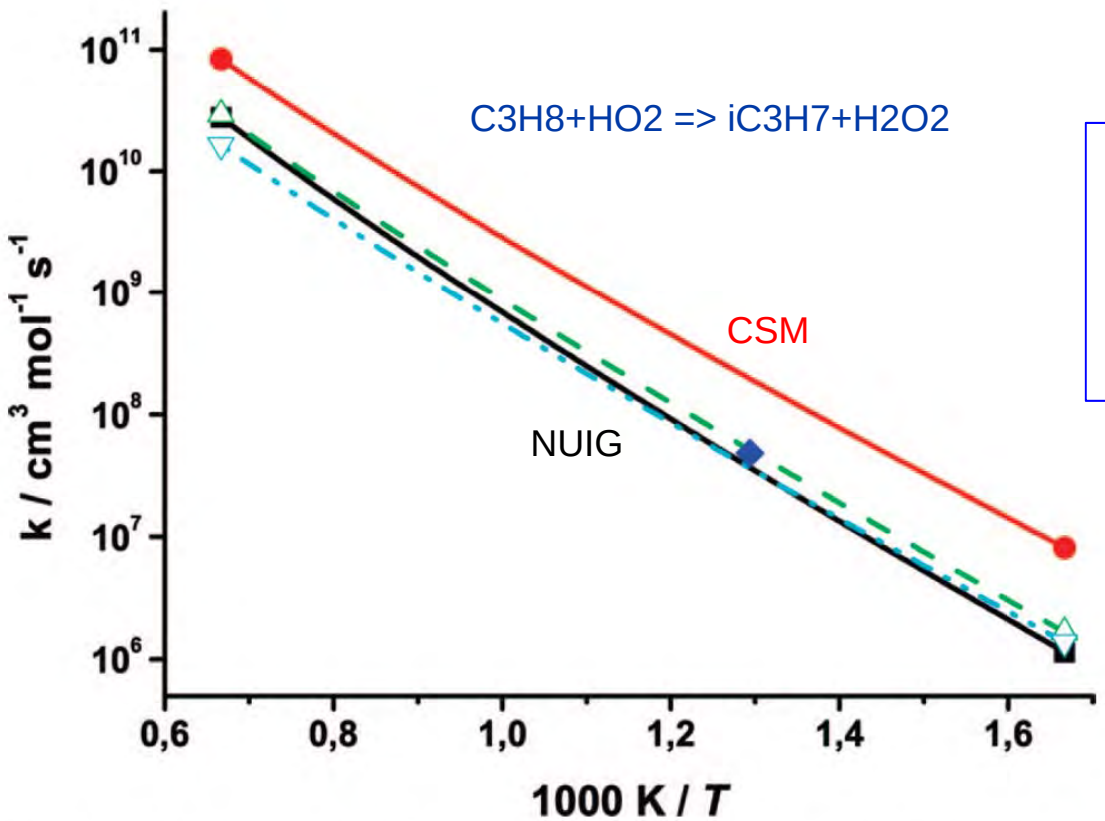






Need more accurate rates constants for: HO2 + alkanes
Uncertainty in rate of a factor of 3 - 6

Reaction Class 2



Ignition very sensitive to this rate constant under RCM conditions

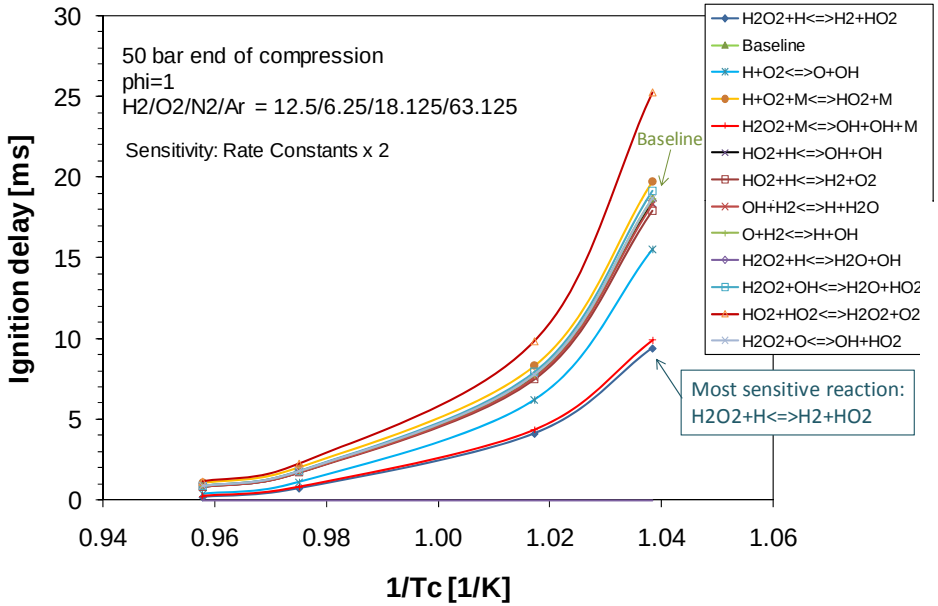
Figure 6. $k(C_3H_8 + HO_2^{\bullet} \rightarrow i\text{-}C_3H_7^{\bullet} + H_2O_2)$. This work (—■—), Carstensen[18] (—●—), Scott[8] (--Δ--), Orme[14] (-··▽-··), Baldwin[11] (◆).

Fuel + HO2 shows high sensitivity when the fuel is hydrogen

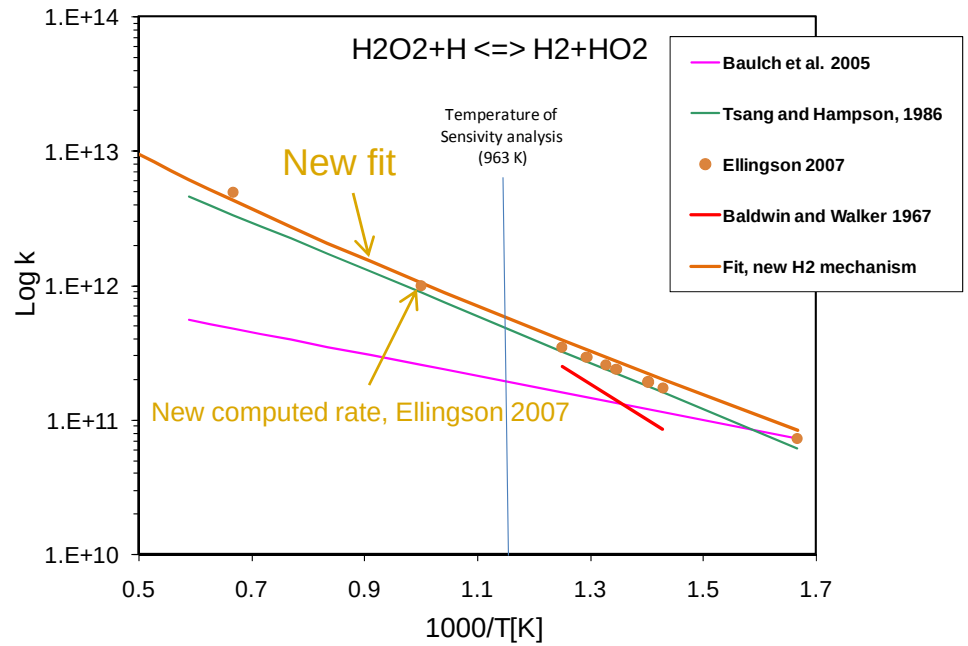
Class 2

Sensitivity results under conditions in rapid compression machine:

$H_2O_2 + H \Leftrightarrow H_2 + HO_2$



New rate constant fit:



Important branching sequence at high pressure:

$H_2 + HO_2 \Rightarrow H + H_2O_2$

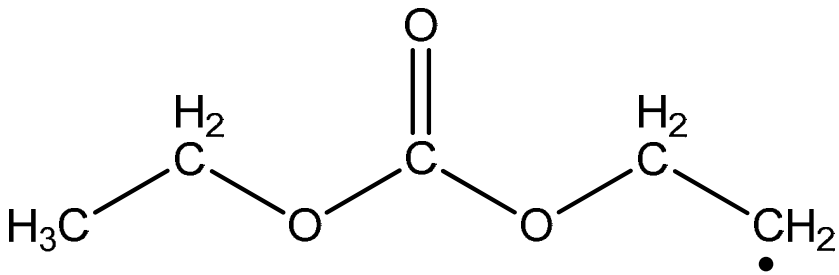
$H_2O_2 \Rightarrow OH + OH$

Retarding reaction:

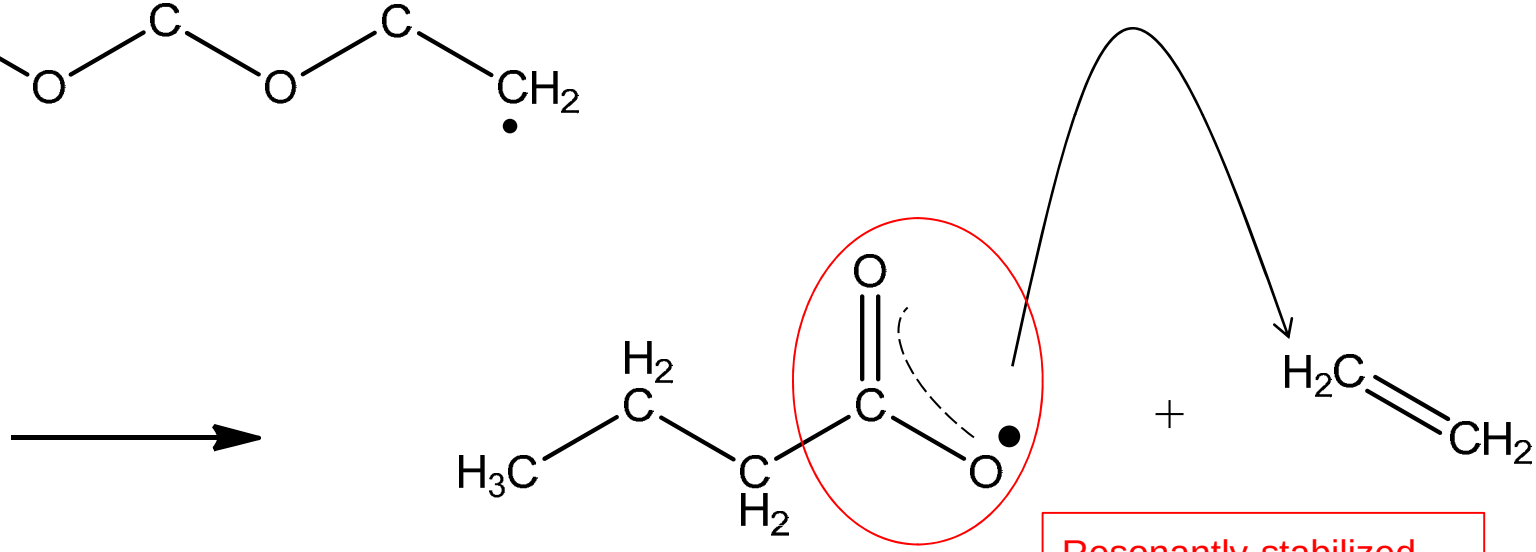
$HO_2 + HO_2 \Rightarrow H_2O_2 + O_2$

New types of molecular structures in biofuels: Reaction class 3: Alkyl radical decomposition

Biofuel molecule (diethylcarbonate)



resonantly stabilized radical adds to double bond

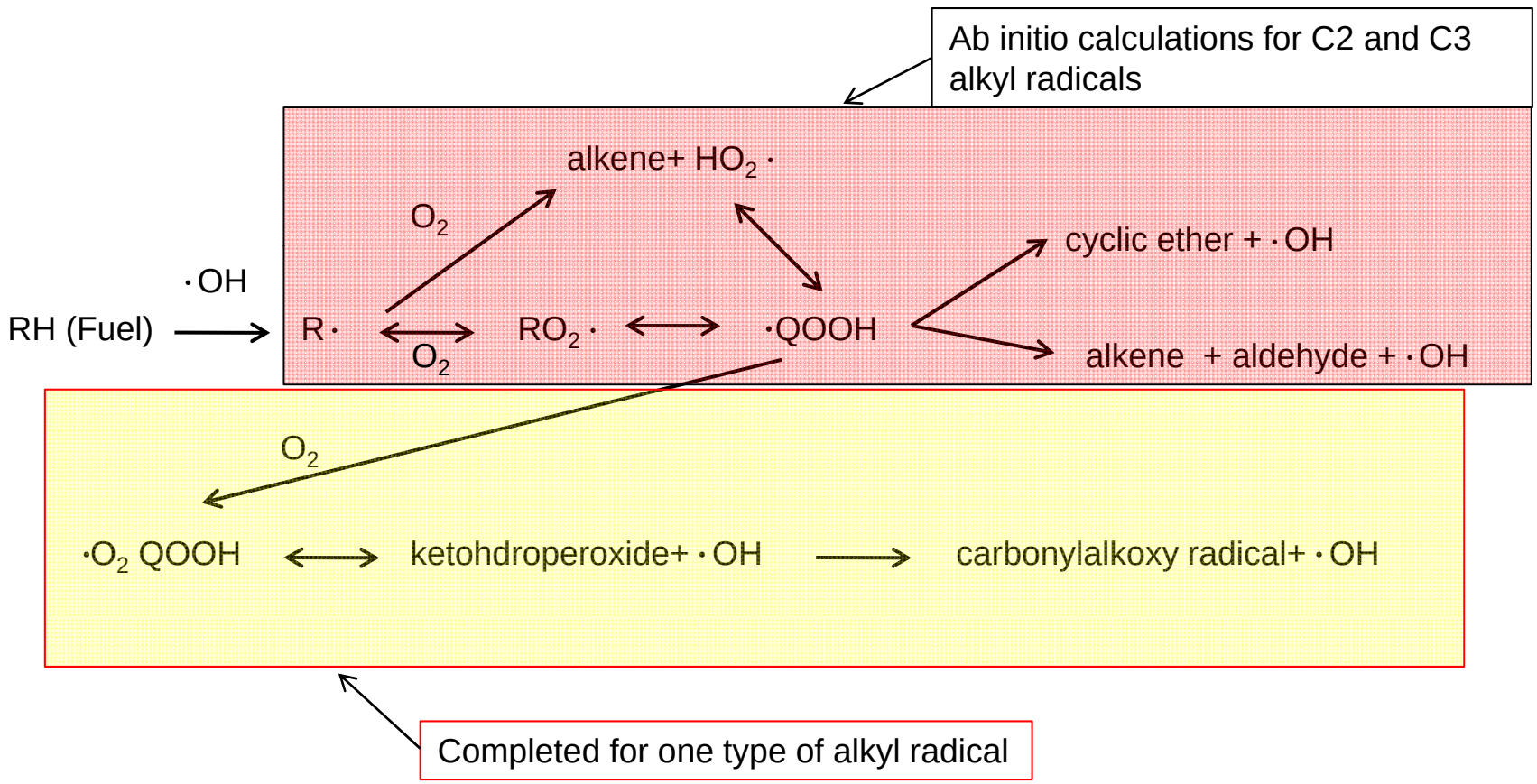


Resonantly-stabilized, oxygen-centered radical

We specify this rate constant by the reverse rate

No analogous reactions available to estimate rate constant

Need complete low temperature chemistry scheme with rate constants from computational chemistry validated by experiments



Need reaction rate rules that can be used for all n- and iso-alkanes

RO2 isomerization reaction rate constant rules

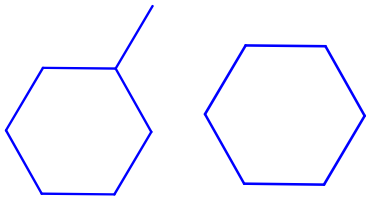
Class 12

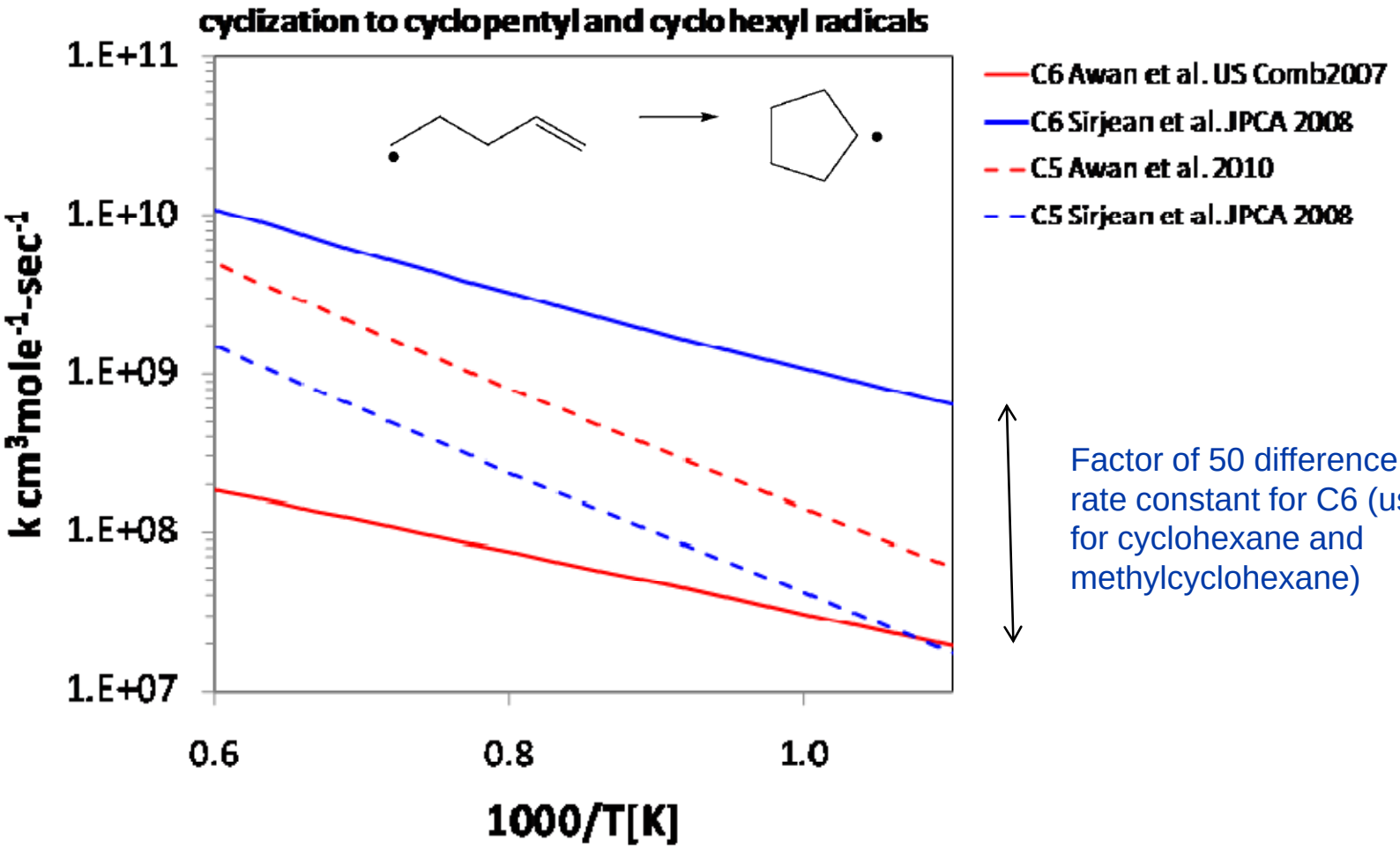
Rize Size	Site	A	n	E_A
5	1°	1.00E+11	0.0	29,000
	2°	1.00E+11	0.0	26,450
	3°	1.00E+11	0.0	23,700
6	1°	1.25E+10	0.0	24,000
	2°	1.25E+10	0.0	20,450
	3°	1.25E+10	0.0	18,700
7	1°	1.56E+09	0.0	21,950
	2°	1.56E+09	0.0	18,650
	3°	1.56E+09	0.0	16,650
8	1°	1.95E+08	0.0	25,150
	2°	1.95E+08	0.0	21,650
	3°	1.95E+08	0.0	19,650

Full R+O2 rate constants available from ab. inito calculations

Some rate constants available, but a complete set of ab initio rate constants are needed for each ring size.

Other needs: Need better cyclization rate constants for cycloalkanes





Factor of 50 difference in rate constant for C6 (used for cyclohexane and methylcyclohexane)

Summary: Needs for high pressure applications that are not being met: Chemical kinetics

- Rate constants for R+O2 and QOOH+O2 reaction systems:
  - For all the possible combinations of primary, secondary and tertiary sites; and 4-7 ring-size transition states in ROO isomerization
  - HO2 elimination path that consider primary, secondary, tertiary types of C-H and R-OO bonds
  - Provide rate constants valid over a wide range of temperature and pressure
  - Validated against low temperature chemistry experiments

Needs for high pressure applications that are not being met: Experiments

- High pressures up to 100 atm at temperatures down to 700K (Current RCM data is available up to about 45 atm; Shock tube data is available down to 800K for reactive fuels or fuel mixtures, like those containing n-decane)
- Species information for internal combustion engine conditions (700-1200 K, 10-60 atm).
- Effect of exhaust gas recirculation on ignition under internal combustion engine conditions
- Flame speeds at higher pressure (10-30 atm in engines)

Other things that need to be measured that aren't being measured:

- High molecular weight compounds
  - Alkylated-benzenes
  - Alkylated-cyclohexanes
  - Methyl esters
- Rate constants
  - for new molecular structures introduced by biofuels at high pressure (up to 100 atm)

Summary

- Need experimental data from many different experimental devices for “new” fuel components
- Need rate constant information for new types of fuel molecular structures
- Need complete R+O2 chemistry from ab initio calculations for different chemical classes (n-alkanes, iso-alkanes, cycloalkanes, alkenes, aromatics, etc.)