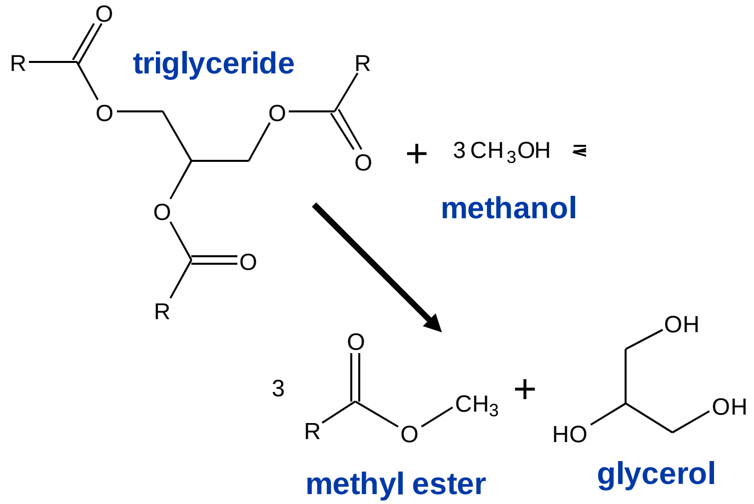
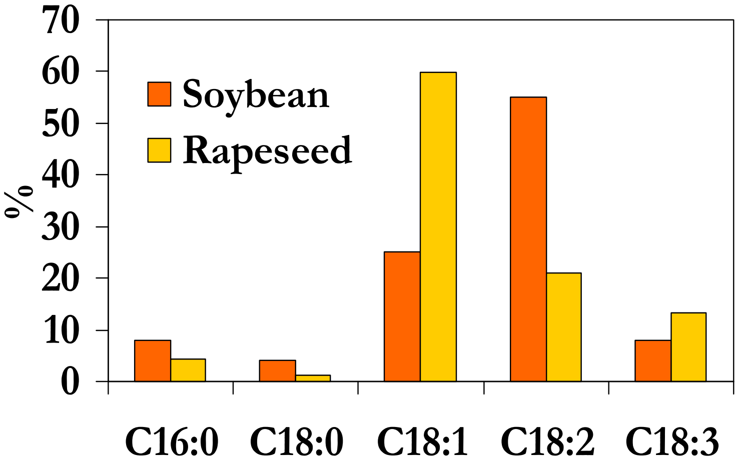
Biodiesel Fuel Kinetic Mechanisms

Charles Westbrook

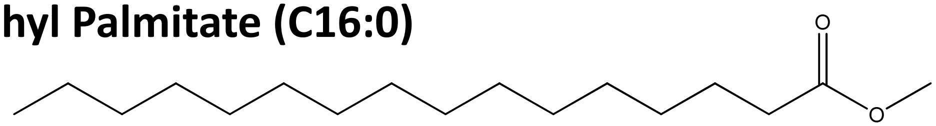
Tsinghua-Princeton
2014 Summer School on Combustion
July 20-25, 2014

Composition of Biodiesels

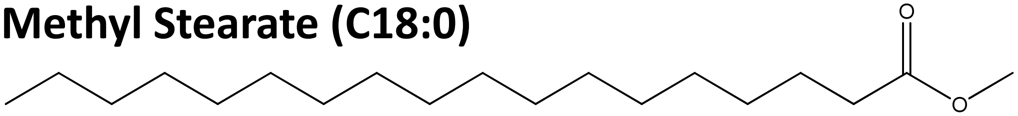




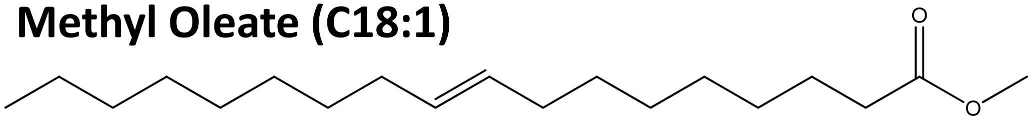
Methyl Palmitate (C16:0)



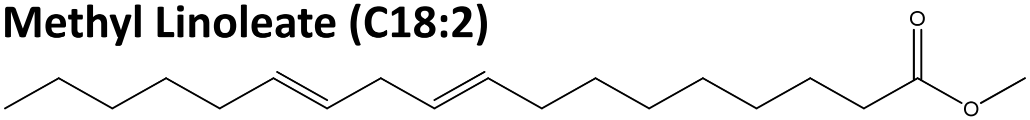
Methyl Stearate (C18:0)



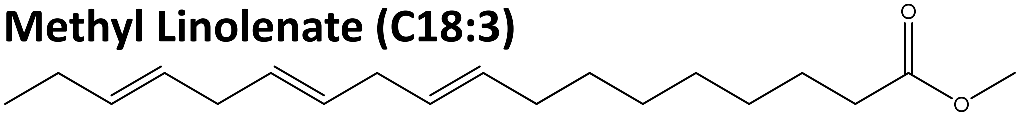
Methyl Oleate (C18:1)



Methyl Linoleate (C18:2)



Methyl Linolenate (C18:3)



Cetane numbers of biodiesel components

- Methyl stearate C18:0 CN = 101
- Methyl oleate C18:1 CN = 59
- Methyl linoleate C18:2 CN = 38
- Methyl linolenate C18:3 CN = 23
- Methyl palmitate C16:0 CN = 86

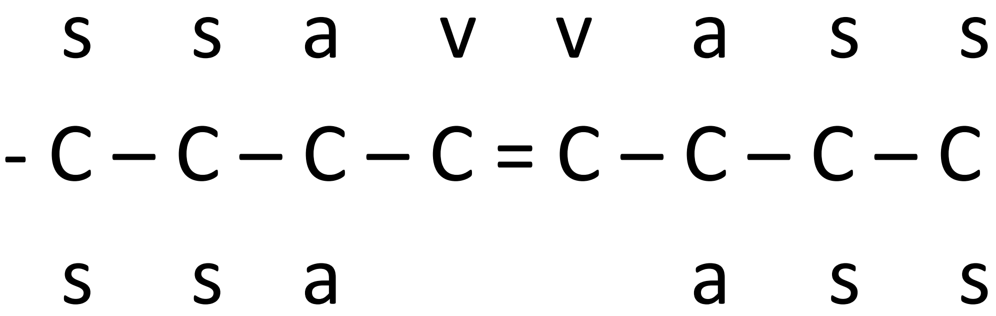
Number of C = C double bonds strongly affects CN
Chain length strongly affects CN

Effects of C = C double bonds in long chain molecules

$$\begin{array}{cccccccccccccccc}
 & s & & s & & s & & s & & s & & s & & s & & s \\
- & C & - & C & - & C & - & C & - & C & - & C & - & C & - & C\ - \\
 & s & & s & & s & & s & & s & & s & & s & & s
\end{array}$$

With no C = C double bonds, all CH2 groups in the chain have the same C – H (and C – O O) bonds

C = C double bonds reduce low T reactivity



$$\begin{array}{cccccccc} s & s & a & v & v & a & s & s \\ -C & -C & -C & -C & =C & -C & -C & -C \\ s & s & a & & & a & s & s \end{array}$$

- Inserting one C=C double bond changes the C-H bond strength for 6 H atoms in the C chain
- Allylic C – H bond sites are weaker than most others
- Therefore they are preferentially abstracted by radicals
- O_2 is also very weakly bound at allylic sites and falls off rapidly, inhibiting low T reactivity

Two double bonds make a huge difference

s s a v v a s s s

\- C - C - C - C = C - C - C - C - C -

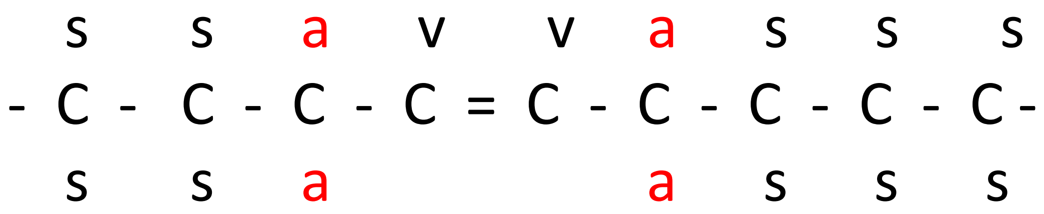
s s a a s s s

Two double bonds make a huge difference

$$\begin{array}{ccccccccccccccccccc}
 & s & & s & & a & & v & & v & & a & & s & & s & & s & \\
- & C & - & C & - & C & - & C & = & C & - & C & - & C & - & C & - & C & - \\
 & s & & s & & a & & & & & & a & & s & & s & & s &
\end{array}$$

$$\begin{array}{ccccccccccccccccccc}
 & s & & s & & a & & v & & v & & a' & & v & & v & & a & \\
- & C & - & C & - & C & - & C & = & C & - & C & - & C & = & C & - & C & - \\
 & s & & s & & a & & & & & & a' & & & & & & a &
\end{array}$$

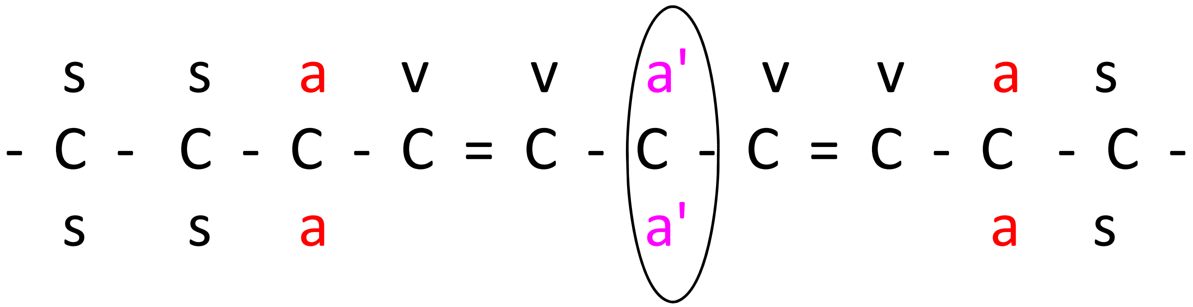
Two double bonds make a huge difference



s s a v v a s s s

- C - C - C - C = C - C - C - C - C -

s s a a s s s



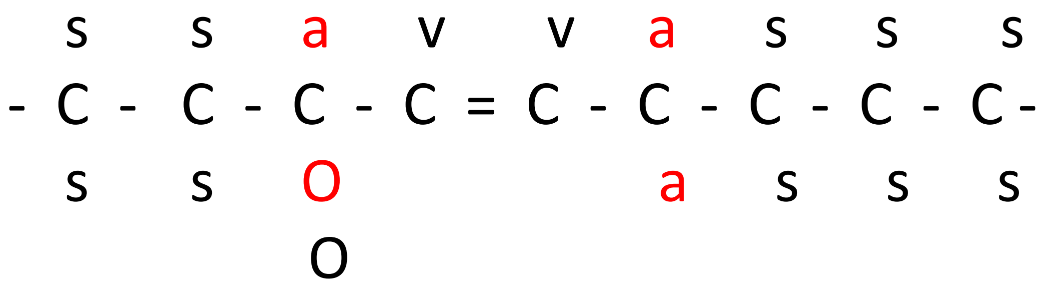
s s a v v a' v v a s

- C - C - C - C = C - C - C = C - C - C -

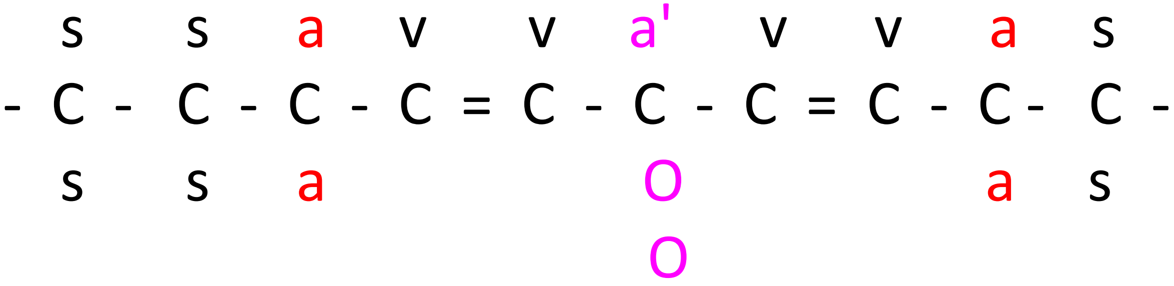
s s a a' a s

C – H s site > C – H a site > C – H a’ site

The same trend occurs when O2 is added to these sites



$$\begin{array}{ccccccccccccccccccc} & s & & s & & a & & v & & v & & a & & s & & s & & s & \\ - & C & - & C & - & C & - & C & = & C & - & C & - & C & - & C & - & C & - \\ & s & & s & & O & & & & & & a & & s & & s & & s & \\ & & & & & O & & & & & & & & & & & & & \end{array}$$



$$\begin{array}{ccccccccccccccccccccc} & s & & s & & a & & v & & v & & a' & & v & & v & & a & & s & \\ - & C & - & C & - & C & - & C & = & C & - & C & - & C & = & C & - & C & - & C & - \\ & s & & s & & a & & & & & & O & & & & & & a & & s & \\ & & & & & & & & & & & O & & & & & & & & & \end{array}$$

C – O2 s site > C – O2 a site > C – O2 a’ site

37.6 27 16

All of the “secondary” C-H bonds are the same in methyl stearate (saturated biodiesel component)

14-Jun	modj	modo2xj	DeltaH
m	-129.9	-170.94	-41.04
2	-134.69	-165.78	-31.09
3	-130.4	-168	-37.6
4	-130.4	-168	-37.6
5	-130.4	-168	-37.6
6	-130.4	-168	-37.6
7	-130.4	-168	-37.6
8	-130.4	-168	-37.6
9	-130.4	-168	-37.6
10	-130.4	-168	-37.6
11	-130.4	-168	-37.6
12	-130.4	-168	-37.6
13	-130.4	-168	-37.6
14	-130.4	-168	-37.6
15	-130.4	-168	-37.6
16	-130.4	-168	-37.6
17	-130.4	-168	-37.6
18	-127.75	-164.54	-36.79

Methyl oleate has one C=C double bond, so there is one pair of allylic, weak C-H bonds

14-Jun	mod9dj	mod9do2	DeltaH	
m	-102.52	-143.56	-41.04	
2	-107.31	-138.4	-31.09	
3	-103.02	-140.62	-37.6	
4	-103.02	-140.62	-37.6	
5	-103.02	-140.62	-37.6	
6	-103.02	-140.62	-37.6	
7	-103.02	-140.62	-37.6	
8	-113.77	-140.71	-26.94	●
9	-92.47	-137.42	-44.95	
10	-92.47	-137.42	-44.95	
11	-113.77	-140.71	-26.94	●
12	-103.02	-140.62	-37.6	
13	-103.02	-140.62	-37.6	
14	-103.02	-140.62	-37.6	
15	-103.02	-140.62	-37.6	
16	-103.02	-140.62	-37.6	
17	-103.02	-140.62	-37.6	
18	-100.37	-137.16	-36.79	

Methyl linolenate has three C=C double bonds, one pair of allylic, weak C-H bonds and two very weak, *bis*-allylic CH$_2$ locations

14-Jun	mod9d12d15d	ro2	DeltaH	
m	-47.15	-88.2	-41.05	
2	-51.94	-83.04	-31.1	
3	-47.65	-85.26	-37.61	
4	-47.65	-85.26	-37.61	
5	-47.65	-85.26	-37.61	
6	-47.65	-85.26	-37.61	
7	-47.65	-85.26	-37.61	
8	-58.4	-85.35	-26.95	
9	-37.1	-82.06	-44.96	
10	-37.1	-82.06	-44.96	
11	-70.11	-86.49	-16.38	●
12	-37.1	-82.06	-44.96	
13	-37.1	-82.06	-44.96	
14	-70.11	-86.49	-16.38	●
15	-37.1	-82.06	-44.96	
16	-37.1	-82.06	-44.96	
17	-58.4	-85.35	-26.95	
18	-45	-81.8	-36.8	

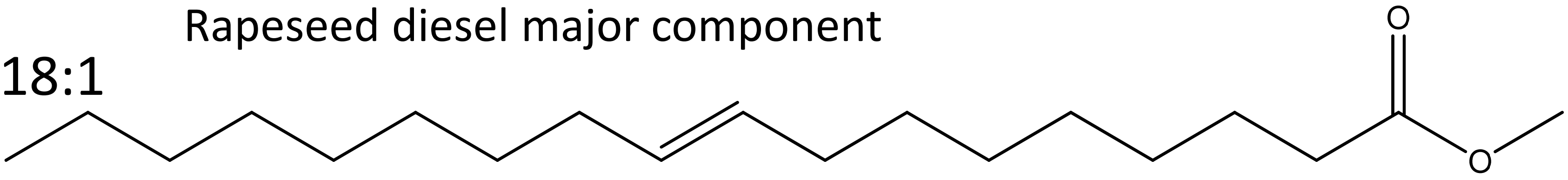
Effects of C=C double bonds

- Allylic and bis-allylic C – O_2 bonds are much weaker than C – O_2 bonds at ordinary secondary sites
- Differences are dramatic at *bis*-allylic sites
- Lifetime of RO_2 adduct is significantly reduced due to these weaker C – O_2 bonds
- Rapid dissociation of these RO_2 adducts sharply reduces rates of low T isomerization and heat release
- All the same effects should occur in unsaturated hydrocarbons

Differences between soy and rapeseed fuels

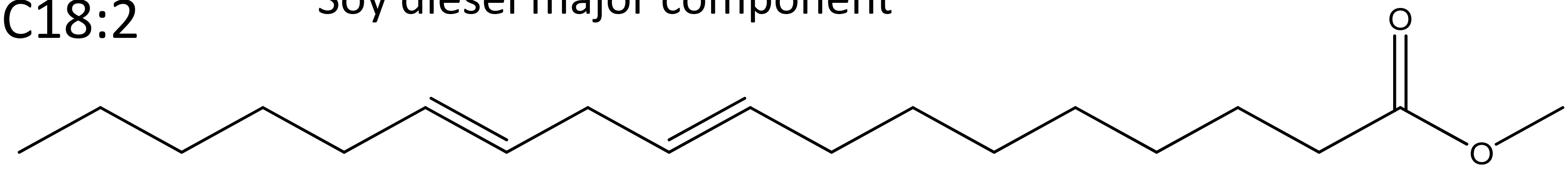
Rapeseed diesel major component

C18:1



C18:2

Soy diesel major component



Rapeseed CN = 54   Soy CN = 47

Double bonds in the carbon chain inhibit low T chemistry

Plant and animal fat oils have different fatty acid profiles that affect reactivity in a diesel engine

	Sunflower	Safflower	Linseed	Jatropha	Cottonseed	Corn	Olive	beef tallow	Palm	Peanut	Soy	rapeseed
palmitate	7	7	7	4	23	10	13	28	46	11	8	4
stearate	5	2	1	8	3	4	4	21	4	8	4	1
oleate	19	13	19	49	20	38	72	47	40	49	25	60
linoleate	68	78	19	38	53	48	10	3	10	32	55	21
linolenate	1	0	54	1	1	0	1	1	0	0	8	14
CN	49	50	39	58	51	49	55	58	62	54	47	54

With models for all 5 major components, we can now model all these types of biodiesel:

- Not a surrogate model, but a real biodiesel (B100) model !

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	Sunflower	Safflower	Linseed	Jatropha	Cottonseed	Corn	Olive	beef tallow	Palm	Peanut	Soy	rapeseed
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stearate	5	2	1	8	3	4	4	21	4	8	4	1
oleate	19	13	19	49	20	38	72	47	40	49	25	60
linoleate	68	78	19	38	53	48	10	3	10	32	55	21
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oleate	19	13	19	49	20	38	72	47	40	49	25	60
linoleate	68	78	19	38	53	48	10	3	10	32	55	21
linolenate	1	0	54	1	1	0	1	1	0	0	8	14
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stearate	5	2	1	8	3	4	4	21	4	8	4	1
oleate	19	13	19	49	20	38	72	47	40	49	25	60
linoleate	68	78	19	38	53	48	10	3	10	32	55	21
linolenate	1	0	54	1	1	0	1	1	0	0	8	14
CN	49	50	39	58	51	49	55	58	62	54	47	54

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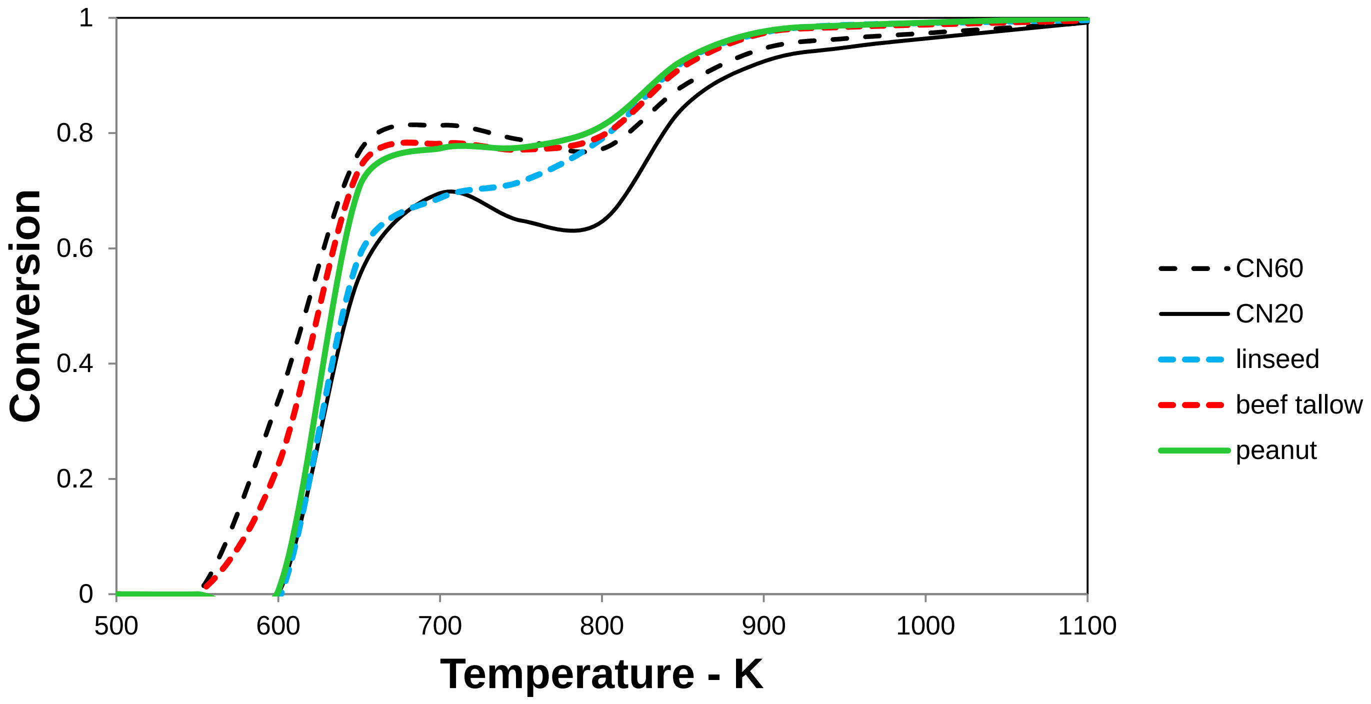
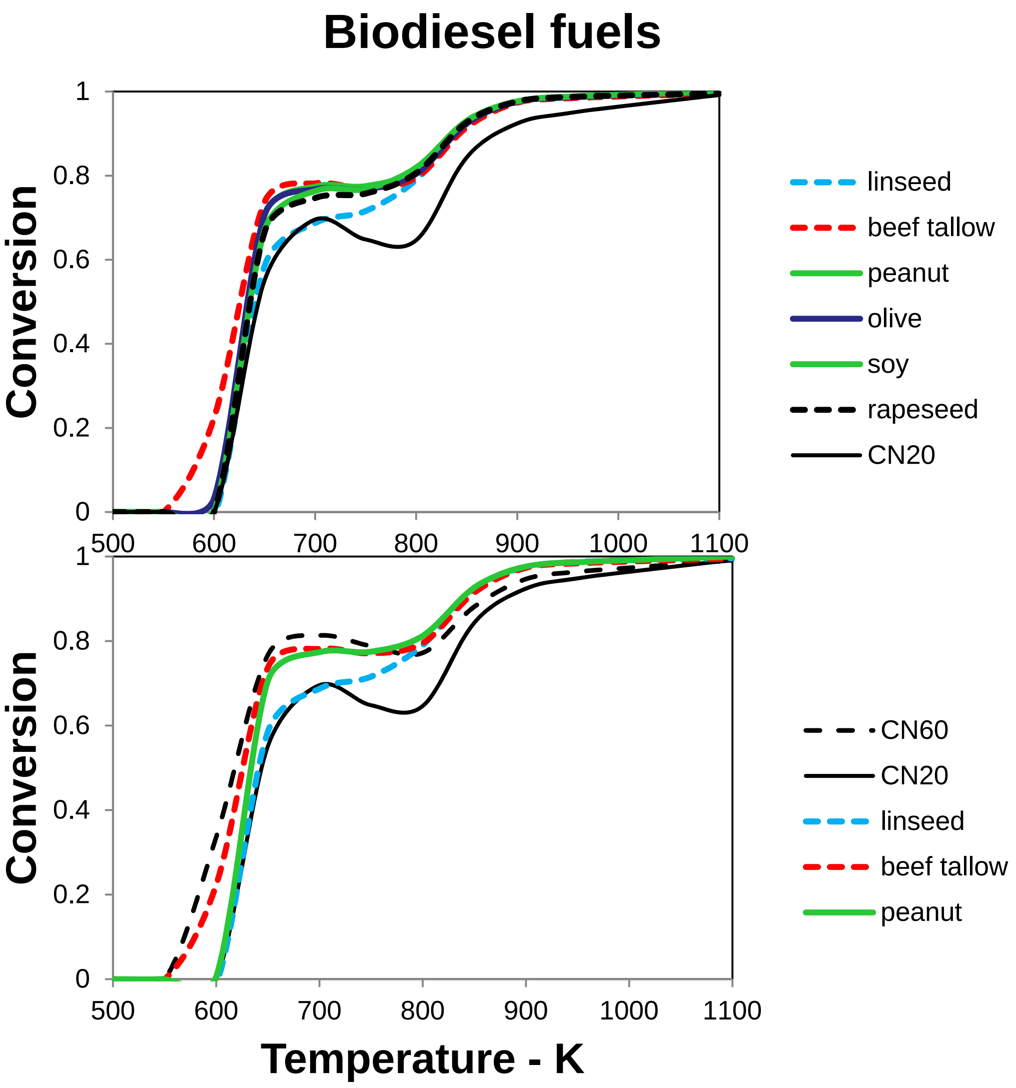
Comparisons between biodiesel and PRF CN



Most plant/fat biodiesel fuels fall into a range of

40 ≤ CN ≤ 60

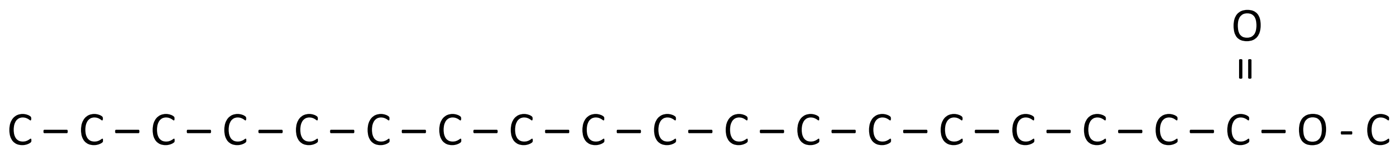
CN range for biodiesel fuels is consistent with PRF range



Use of THERM code to apply Benson’s bond additivity rules to compute thermochemical data

- Ritter and Bozzelli code
- Uses tables of bond energies and other data
- Examples of how to use THERM
- Other code families exist to do the same tasks
- Product is a set of JANAF coefficients

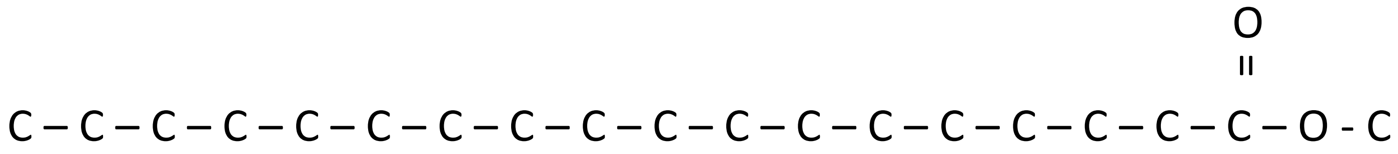
```
 SPECIES
 MOD
Thermo estimation for molecule
 MOD
C19H38O2
 UNITS:KCAL
 GROUPS   6
   Gr # -  GROUP ID  - Quantity  Gr # -  GROUP ID  - Quantity
      1 - C/C/H3         -  1 |     4 - CO/C/O         -  1
      2 - C/C2/H2        - 15 |     5 - O/C/CO         -  1
      3 - C/C/CO/H2      -  1 |     6 - C/H3/O         -  1
  Hf    S   Cp 300    400    500    600    800   1000   1500
-176.74 225.79 111.09 138.64 163.25 184.19 217.39 242.00
.00
          CPINF =  328.85
  NROTORS:19
 SYMMETRY           9
  CREATION DATE:  5/19/11
  ENDSPECIES
```



$$C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-\overset{\overset{O}{\parallel}}{C}-O-C$$

Radicals in this fuel

p	primary	c/c/h3,1
s	secondary	c/c2/h2,15
rcoocj	end methoxy group	c/h3/o,1
ccjcoor	adjacent to C=O	c/c/co/h2,1



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

```
 SPECIES
 MDO2H11
Thermo estimation for molecule
 MDO2H11                                                     C19H32O4
 UNITS:KCAL
 GROUPS  12
   Gr # -  GROUP ID  - Quantity  Gr # -  GROUP ID  - Quantity
      1 - C/C/H3         -  1 |     7 - C/C2/H2        -  5
      2 - C/C/CD/H2      -  2 |     8 - C/C/CO/H2      -  1
      3 - C/CD2/H2       -  1 |     9 - CO/C/O         -  1
      4 - C/CD2/H/O      -  1 |    10 - O/C/CO         -  1
      5 - OO/C/H         -  1 |    11 - C/H3/O         -  1
      6 - CD/C/H         -  6 |    12 - OI             -  1
  Hf    S   Cp 300    400    500    600    800   1000   1500
-119.88 234.93 109.82 137.00 160.31 179.71 209.69 231.74    .00
          CPINF =  306.00
  NROTORS:18
 SYMMETRY          9
  CREATION DATE:  5/21/11
  ENDSPECIES
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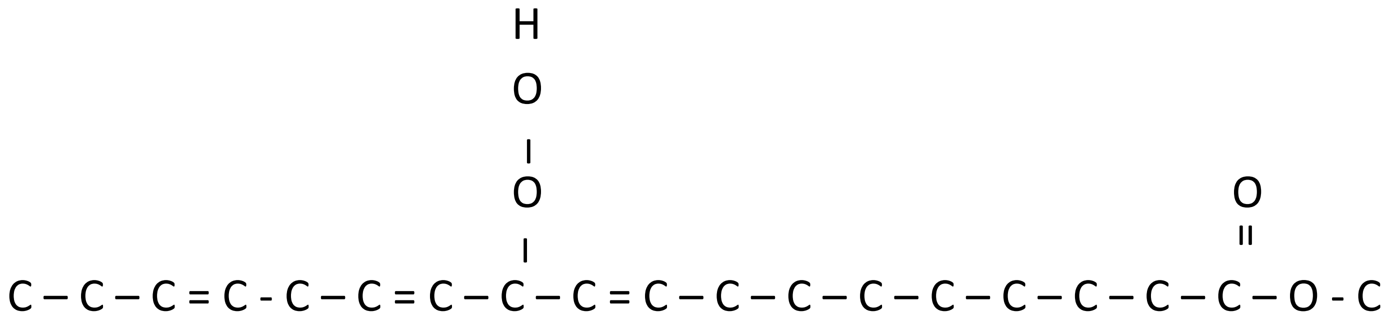
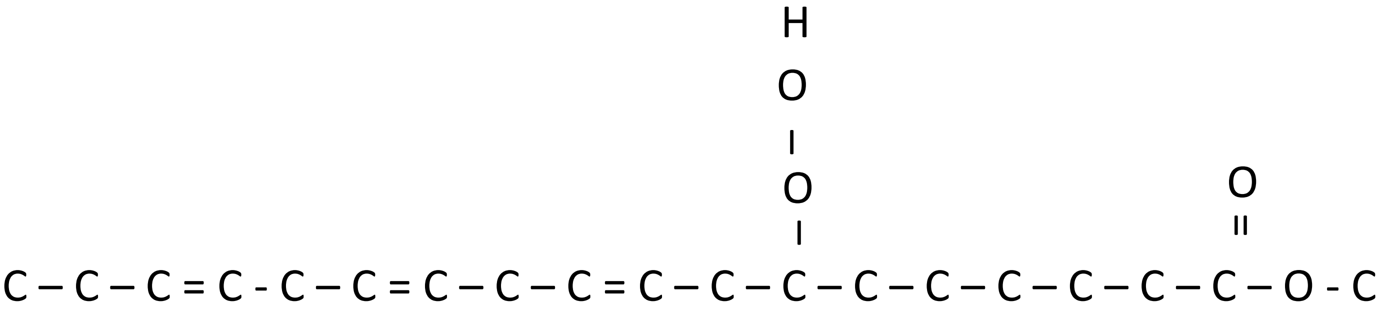


$$\mathrm{C-C-C=C-C-C=C-\overset{\overset{\overset{H}{|}}{O}\,\text{-}\,O\,|}{C}-C=C-C-C-C-C-C-C-C-\overset{O}{\overset{\|}{C}}-O-C}$$

Radicals in this fuel

p	primary	c/c/h3,1
s	secondary	c/c2/h2,5
alperox		oo/c/h,1
vins	vinyl	cd/c/h,6
allyls	allyl	c/c/cd/h2,2
bis-allyl		c*ccjc*c
rcoocj	end methoxy group	c/h3/o,1
ccjcoor	adjacent to C=O	c/c/co/h2,1



$$C-C-C=C-C-C=C-C-C=C-C-\overset{\substack{H\\O\\|\\O\\|}}{C}-C-C-C-C-C-\overset{\substack{O\\\|}}{C}-O-C$$

An “ideal” biodiesel fuel

- Methyl stearate is a solid at room temperature
- Methyl linoleate and linolenate degrade thermally due to slow reactions involving the multiple C=C double bonds
- Efforts are in progress to use genetic engineering to modify soy DNA to accelerate conversion of stearate to oleate and eliminate conversion of oleate to linoleate and linolenate
- Wallis et al., 2002, Trends Biochem. Sci. 27,467-473

Current biodiesel mechanism is incomplete

- Needs upgrade like all other large molecule mechanisms
- For multiply-unsaturated components, fate of small multiply-unsaturated small molecules is poorly known
- Not all C and H is accounted for

Kinetic Modeling of Autoignition: Engine Knock, HCCI and fuel economy

Charles Westbrook

Tsinghua-Princeton
2014 Summer School on Combustion
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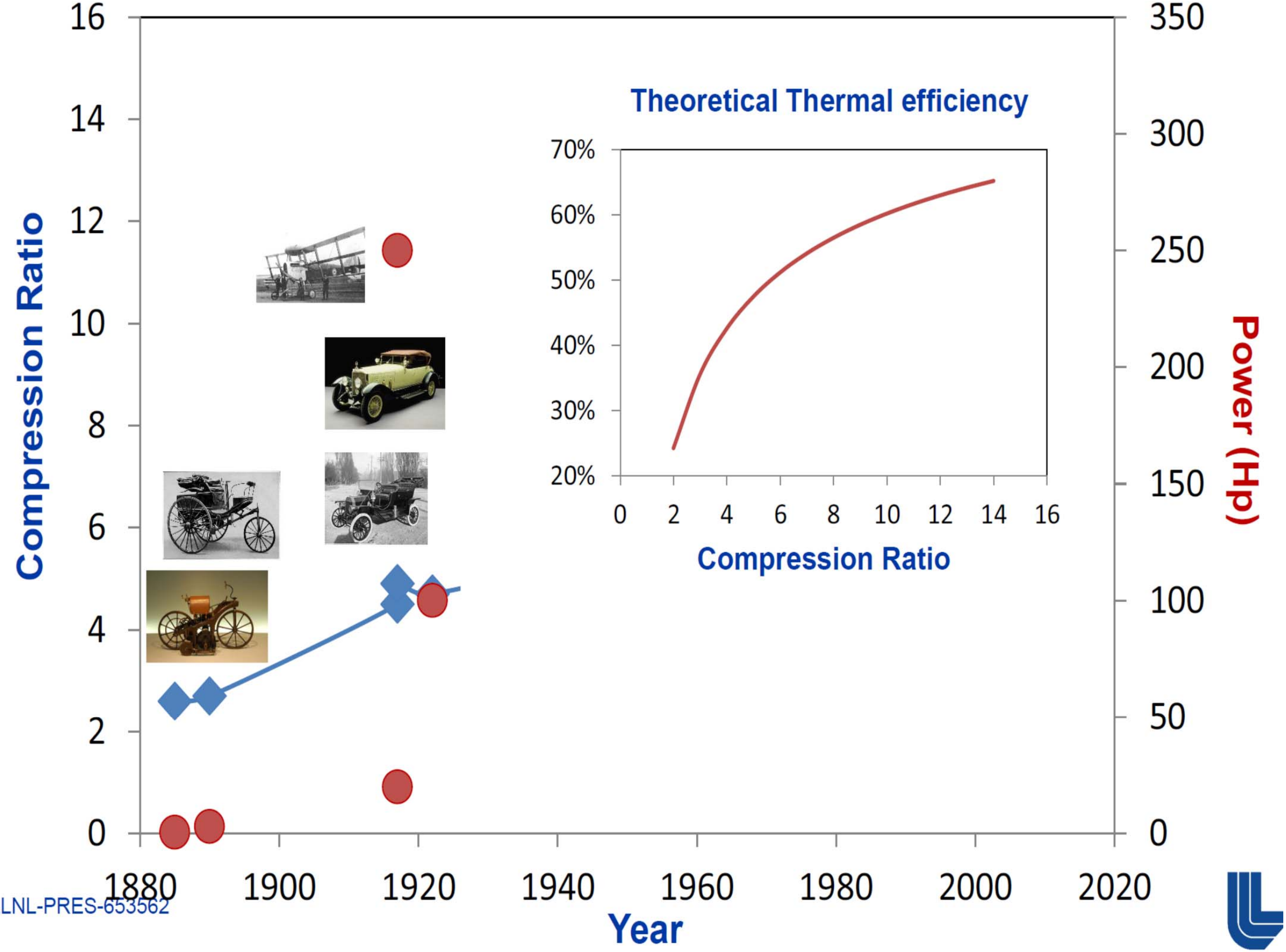
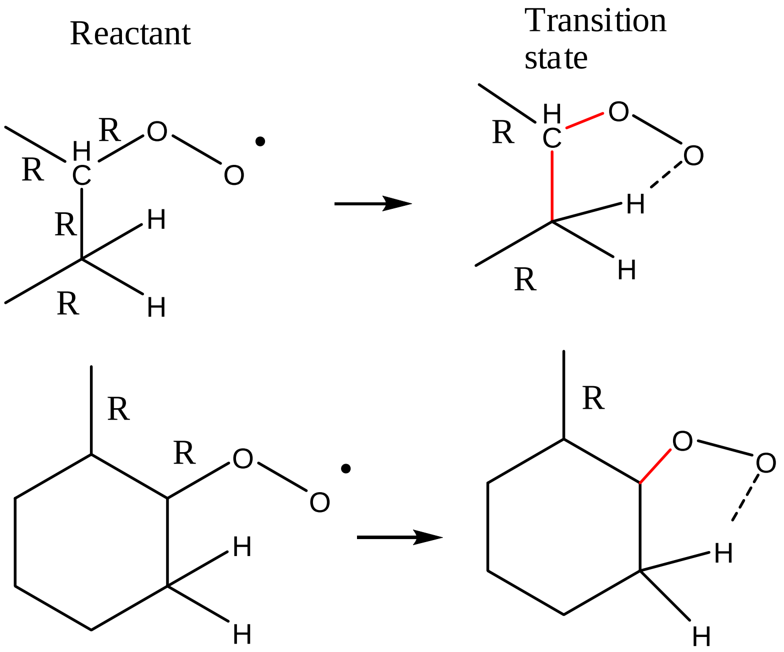

16
14
12
10
8
6
4
2
0
Compression Ratio
350
300
250
200
150
100
50
0
Power (Hp)
1880
1900
1920
1940
1960
1980
2000
2020
Year
Theoretical Thermal efficiency
70%
60%
50%
40%
30%
20%
0
2
4
6
8
10
12
14
16
Compression Ratio

The fuel situation in 1922 looks pretty familiar

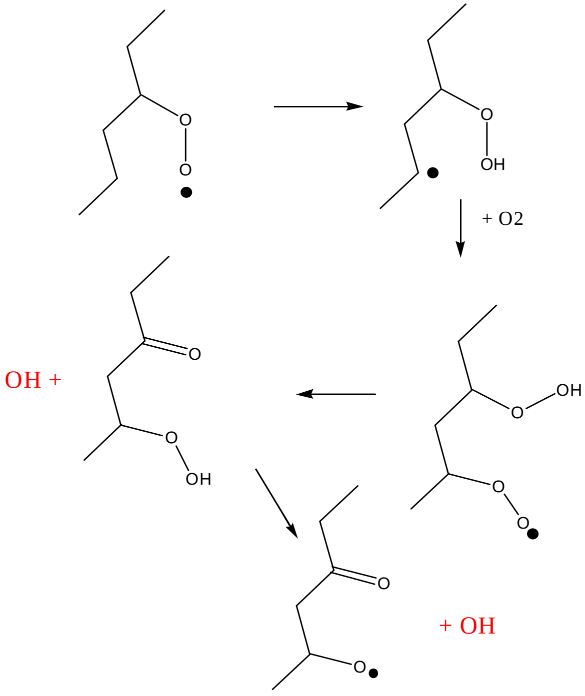
- Thomas Midgley, Chief of Fuels Section for General Motors, 1922
  - US Geological Survey -- 20 years left of petroleum reserves
  - Production of 5 billion gallons of fuel in 1921

- Potential new sources of petroleum
  - Oil shale
  - Oils from coal
  - Alcohol fuels from biomass
- Higher efficiency a high priority for conservation reasons
  - People will not buy a car “lacking in acceleration and hill climbing”
  - Solution is higher compression ratio, then at about 4.25 : 1
  - Obstacle is engine knock, whose origin is unknown
  - Result was development of TEL as antiknock
  - Phenomenological picture with no fundamental understanding

Explanation of engine knock, ON, antiknocks, diesel ignition, and HCCI ignition came in the 1990's from DOE/BES theoretical chemistry and supercomputing and EERE knock working group



Alkylperoxy radical isomerization rates are different in paraffin and cyclic paraffin hydrocarbons



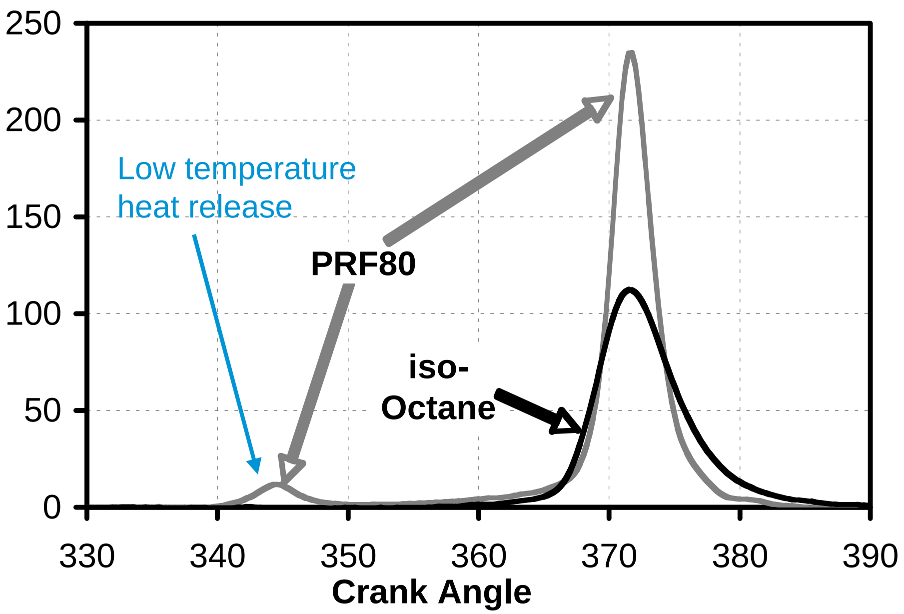
Low temperature chain branching paths

Most work has been done for alkane fuels, and many questions remain for aromatics, cyclic paraffins, large olefins

Chemistry of alkylperoxy radical isomerization has reached street-level awareness

- Heat release rates in HCCI combustion of two fuels, iso-octane with no low T heat release, and PRF-80 with two stage heat release

- We are seeing researchers debating which makes the better HCCI fuel. Both debaters have completely accepted the existence and source of the low T reactivity.



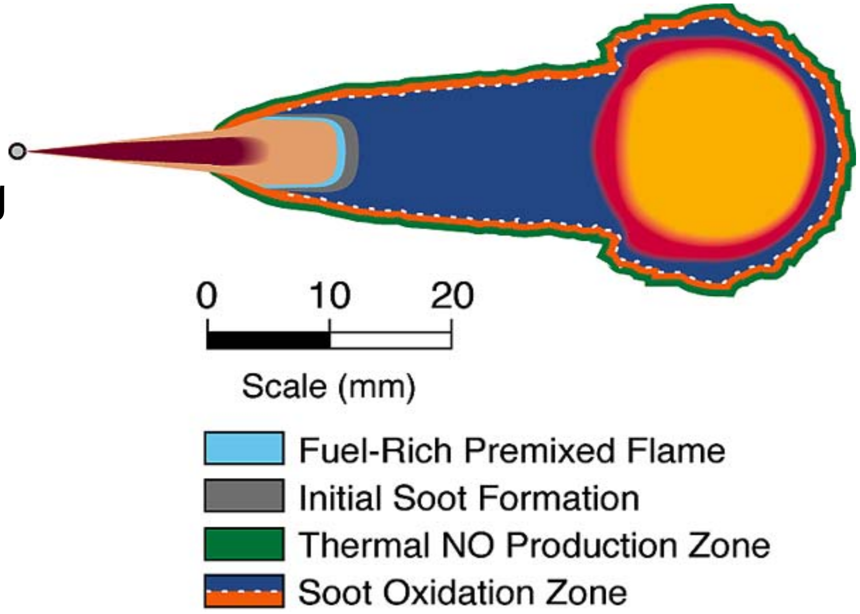
This is serious, black-belt fuel chemistry and computational chemistry

Results from experiments of Sjöberg and Dec, SNL 2006

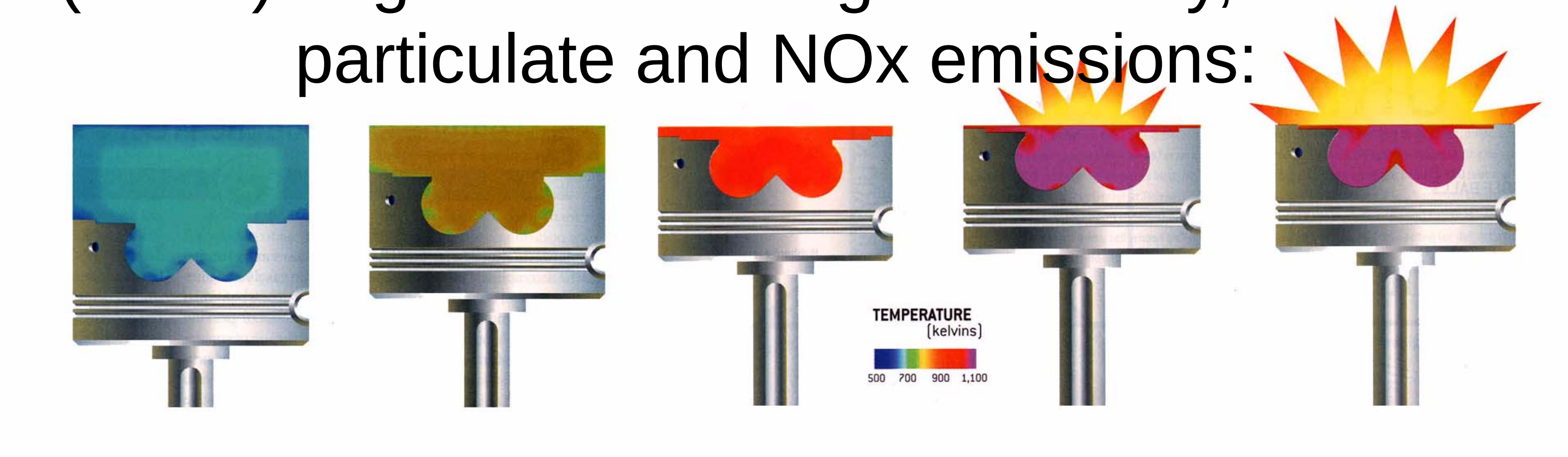
New conceptual picture developed 1990 - 1997

- Extended role of multiple advanced laser diagnostic techniques
- Team led by John Dec, SNL
- Explains
  - 2 stages in diesel burning
  - ignition and cetane
  - sooting logic
- This is serious, black-belt optical physics science

Lots still unknown,
soot chemistry, spray dynamics
fuel effects, etc.



Homogeneous Charge Compression Ignition (HCCI) engine delivers high efficiency, and low particulate and NOx emissions:



Advantages:

- low NO_x
- low particulate matter
- high efficiency

Technical challenges:

- engine control
- multi-cylinder balancing
- startability
- low power output
- high HC and CO emissions

Have we have come a long way since 1922?

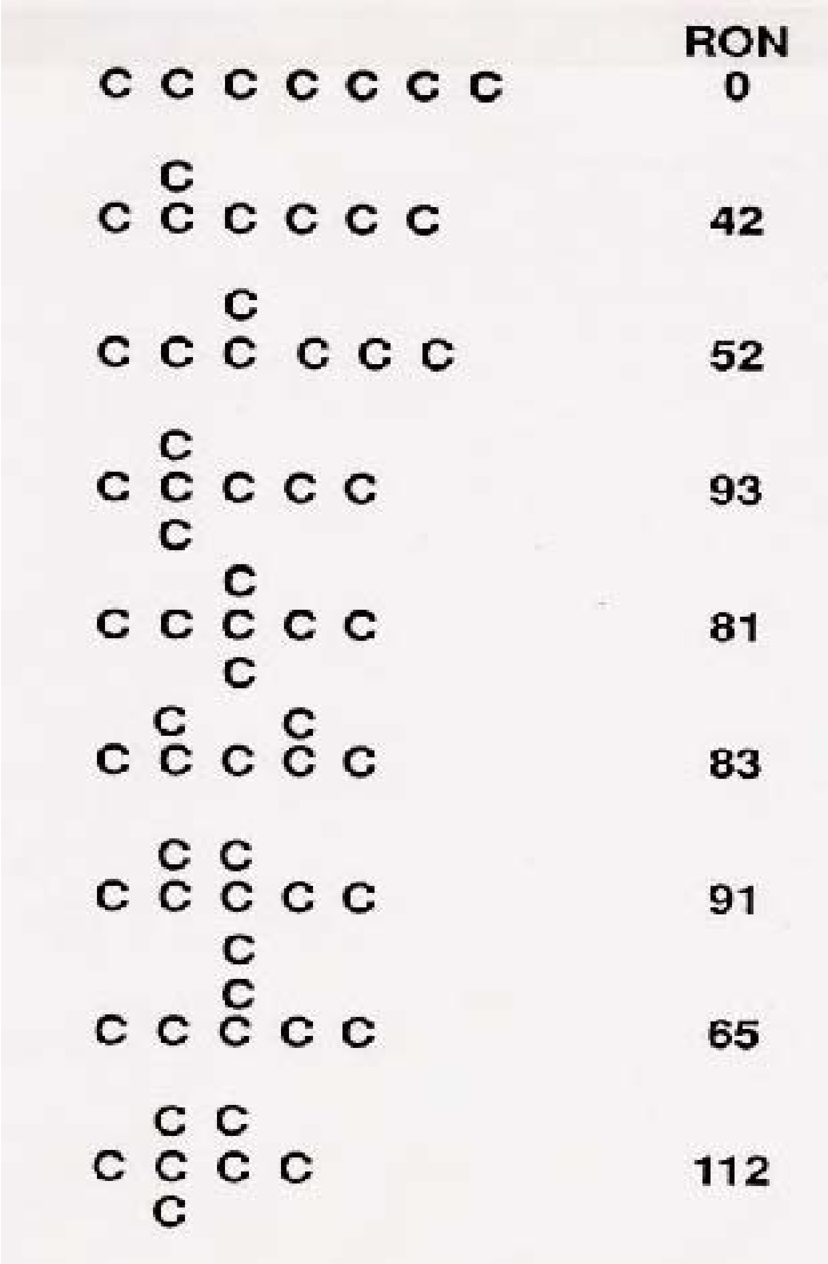
- We still are looking to oil shale, oil sands and biomass for the future
- However, our understanding of knocking, antiknocks and low T chemistry has grown enormously
  - e.g., Current engine designers debate how much low T heat release is best, and take its sources for granted
- Conceptual model for diesel combustion has led to breakthroughs
  - e.g., Understanding of anti-sooting action of oxygenates
- Entirely new concept engine (HCCI) is being developed

Great majority of this progress is due to basic science understanding, e.g., optical diagnostics, quantum chemistry and electronic structure theory, high performance computing, etc.

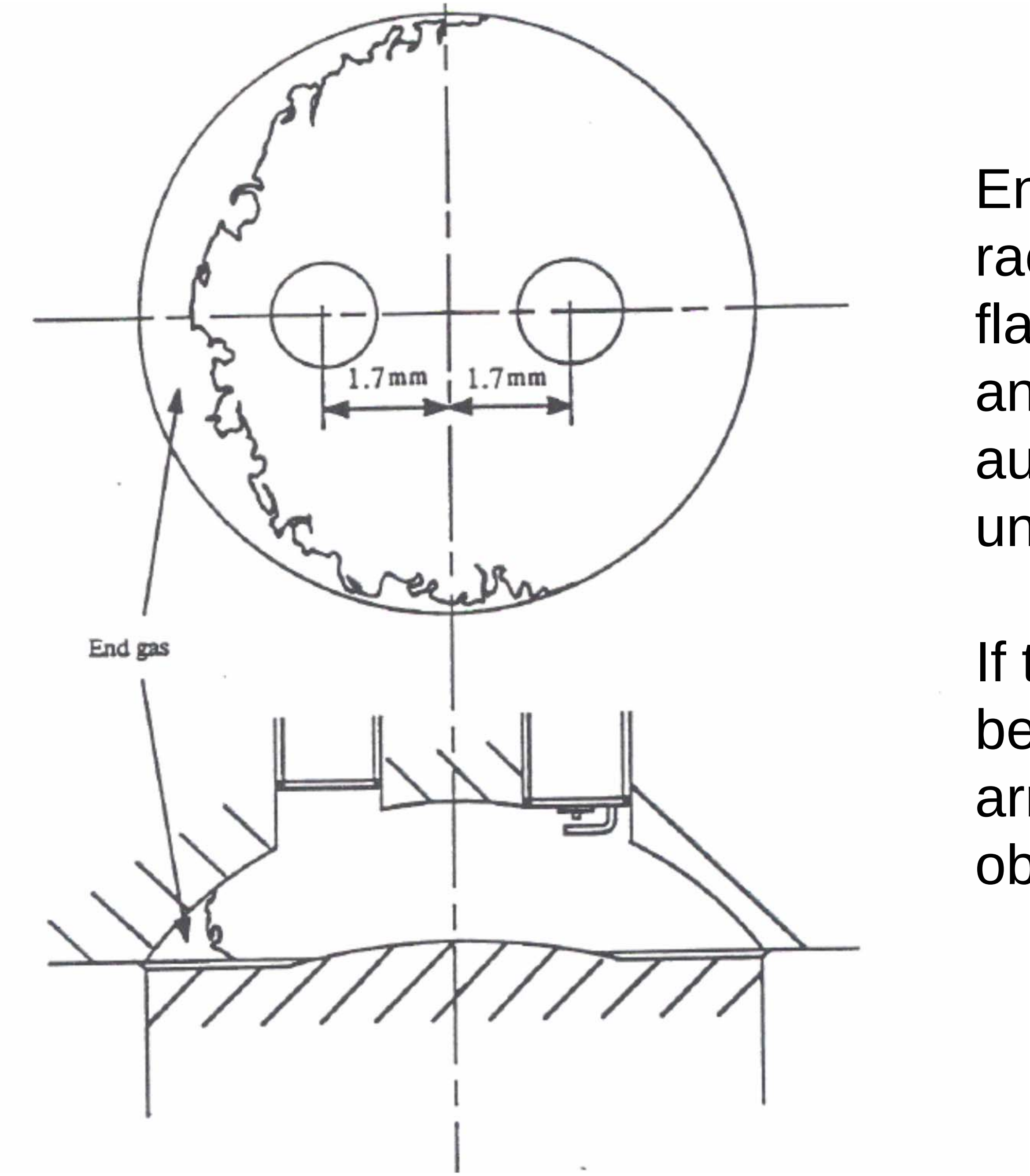
We have used basic science advances to make big jumps in understanding, but we are back to trial and error in many cases

Octane numbers of heptanes are due exclusively to their different molecular structures

This was recognized in 1920’s but no explanation in fundamental terms had been provided prior to our work



Engine knock is an undesirable thermal ignition



Engine knock is a race between the flame in the engine and thermal autoignition of the unburned “end gas”

If the end gas ignites before the flame arrives, knock is observed

We focus on three distinct chain branching pathways

1) $H + O_2 \rightarrow O + OH$ High T

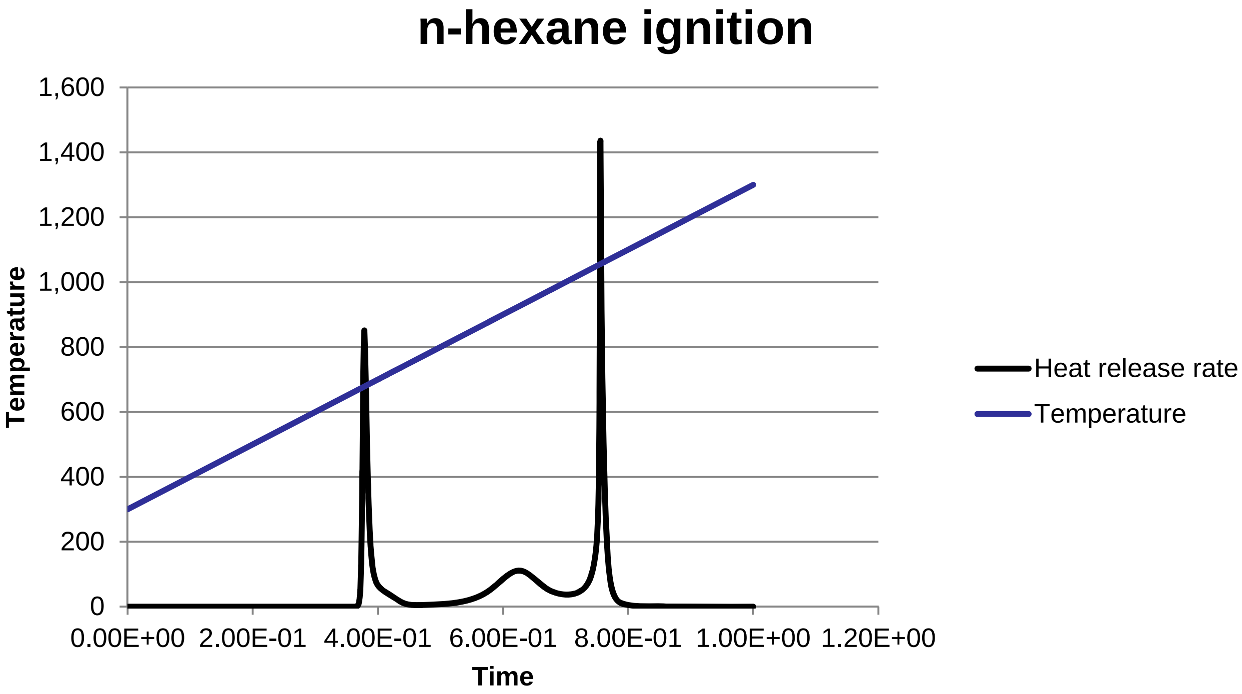
2) $H + O_2 + M \rightarrow HO_2 + M$ Medium T

$RH + HO_2 \rightarrow R + H_2O_2$

$H_2O_2 + M \rightarrow OH + OH + M$

3) $R + O_2 \rightarrow RO_2$ Low T

$RO_2 \rightarrow QOOH \rightarrow O_2QOOH \rightarrow$ 3+ radicals


n-hexane ignition
Temperature
1,600
1,400
1,200
1,000
800
600
400
200
0
0.00E+00
2.00E-01
4.00E-01
6.00E-01
8.00E-01
1.00E+00
1.20E+00
Time
Heat release rate
Temperature

Chain branching at high temperatures

$$H + O_2 \rightarrow O + OH$$

- Activation energy is relatively high (16.8 kcal/mol)
- H atoms produced by thermal decomposition of radicals
  e.g. C_2H_5 , C_2H_3 , HCO, iC_3H_7 , etc.
  Activation energies relatively high (~ 30 kcal/mol)
- Therefore this sequence requires high temperatures
- Illustrated best by shock tube experiments

Chain branching often occurs over a series of reactions

$$H + O_2 + M \rightarrow HO_2 + M$$

$$RH + HO_2 \rightarrow R + H_2O_2$$

$$H_2O_2 + M \rightarrow OH + OH + M$$

- At temperatures below about 900K, H_2O_2 decomposition is inhibited, leading to degenerate chain branching
- At higher temperatures, H_2O_2 decomposes as quickly as it is formed, leading to conventional chain branching
- Other low temperature chain branching paths can be much longer than this sequence (see below)

H_2O_2 decomposes at a fairly distinct temperature

- Reaction consuming H_2O_2 is:

$$H_2O_2 + M \rightarrow OH + OH + M$$

$$k_+ = 1.2 \times 10^{17} \times \exp(-45500/RT)$$

- Resulting differential equation is:

$$\frac{d\,[H_2O_2]}{d\,t} = -[H_2O_2]\,[M]\,k_+$$

Characteristic time for H_2O_2 decomposition

$$\frac{d\,[\,H_2O_2\,]}{d\,t} = -[\,H_2O_2\,]\;[\,M\,]\;k_+$$

define $\tau = [\,H_2O_2\,] \,/\, (d\,[\,H_2O_2\,]/dt)$

$\tau = 1 \,/\, (\,k_+\,[M])$

$\tau = 8.3 \times 10^{-18} \times \exp(22750/T) \times [M]^{-1}$

At RCM conditions, with [M] ~ 1×10^{-4} mol-cm^{-3}, values of τ are approximately:

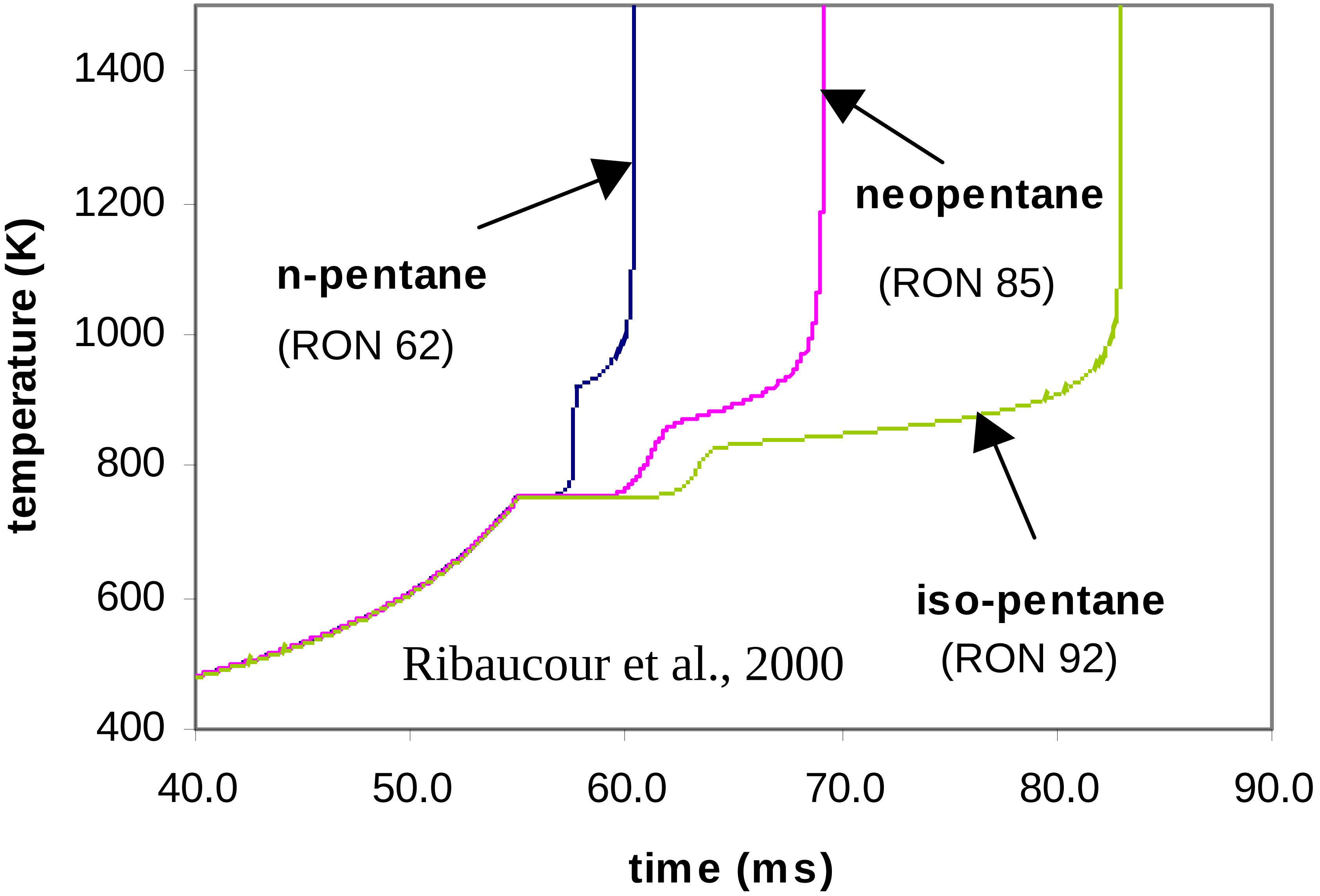
7.8 ms at 900K	640 μs at 1000K	80 μs at 1100K

At higher compressions (pressures), values of τ are smaller at comparable temperatures

Rapid compression machine and some turbulent flow reactor experiments are controlled by H_2O_2 decomposition

- Rapid compression machine (RCM) usually operates in a degenerate branching mode
  - H_2O_2 produced at temperatures lower than 900K
  - When system reaches H_2O_2 decomposition temperature, ignition is observed
- Many turbulent flow reactor experiments operate at temperatures between 900 - 1100K where H_2O_2 decomposes as quickly as it is produced

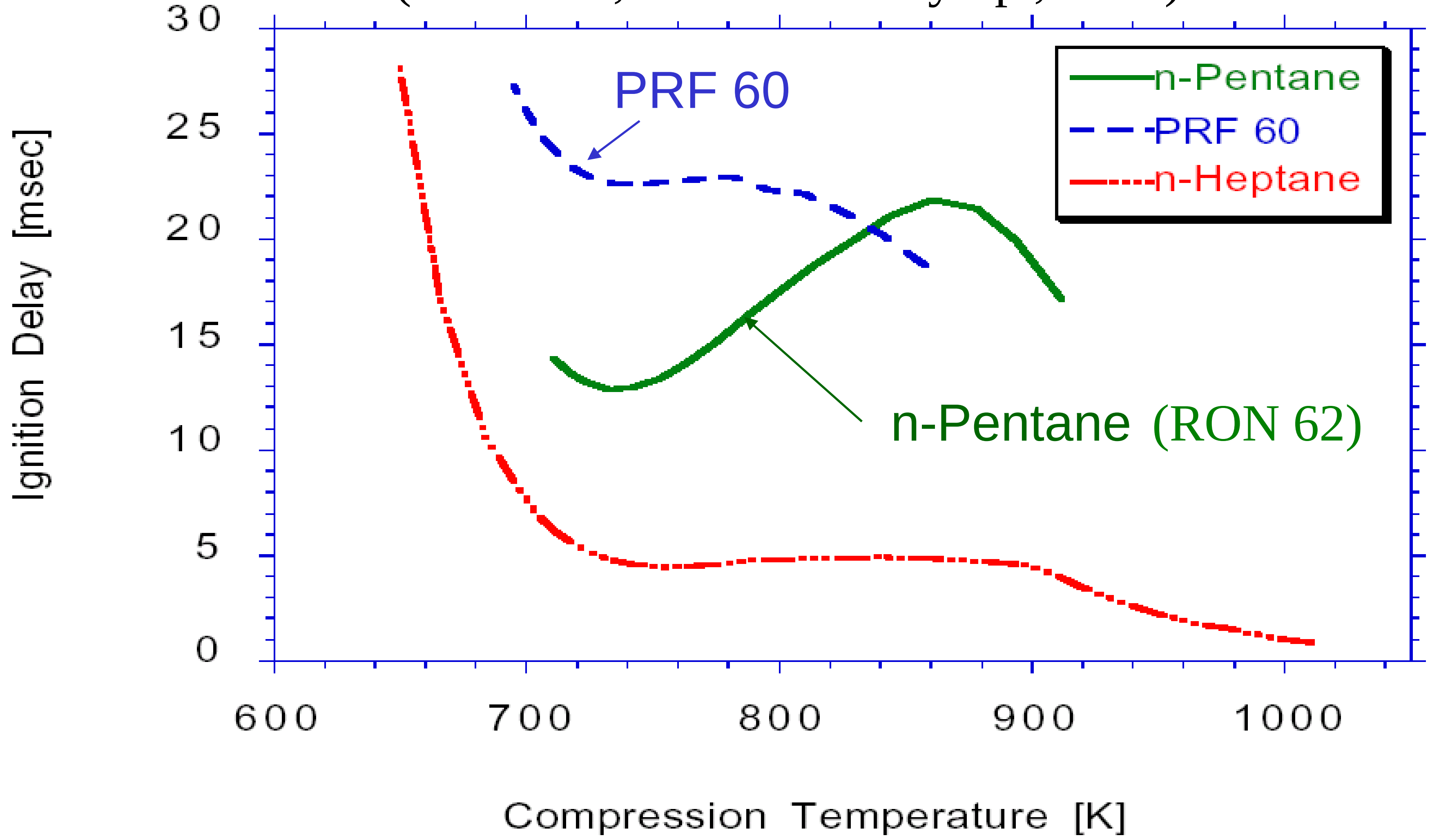
Pentane isomers ignite in order of their octane numbers



Ribaucour et al., 2000

n-Pentane (RON 62) and PRF 60 show different behavior in rapid compression machine

(Cox et al., 26th Comb. Symp., 1996)



Role of H_2O_2 decomposition is very general

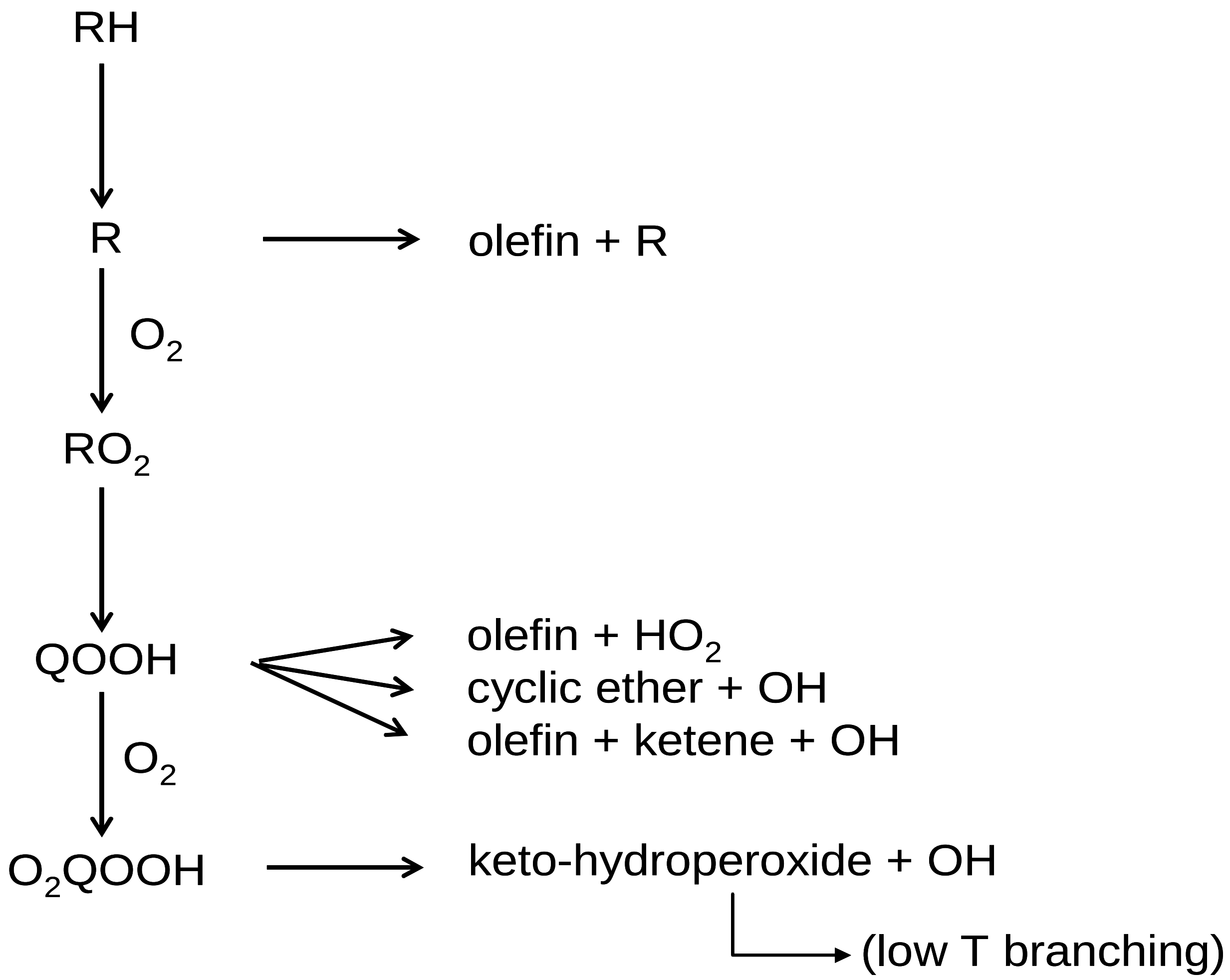
- RCM ignition
- Engine knock
- HCCI ignition
- Diesel ignition
- Each system follows a unique pathway in the relevant phase space to arrive at this ignition temperature where H_2O_2 decomposes

Kinetic features of engine knock

- History of octane numbers and empirical observations
- End gas self-ignition prior to flame arrival
- Actual ignition driven by H_2O_2 decomposition at ~ 900K
- Kinetic influence of molecular size and structure
- Effects of additives, both promoters and inhibitors
- Reduced models must retain H_2O_2 decomposition reaction to describe ignition
- Issue of real SI engine fuel being complex mixture of components
- Lots of kinetics research still needed (aromatics, cyclics, etc.)

Detailed Chemical Kinetics for Components

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



RH

R

olefin + R

O_2

RO_2

QOOH

olefin + HO_2

cyclic ether + OH

olefin + ketene + OH

O_2

O_2QOOH

keto-hydroperoxide + OH

(low T branching)

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 + O_2 = olefin + HO_2

Reaction Class 5: Alkyl radical isomerization

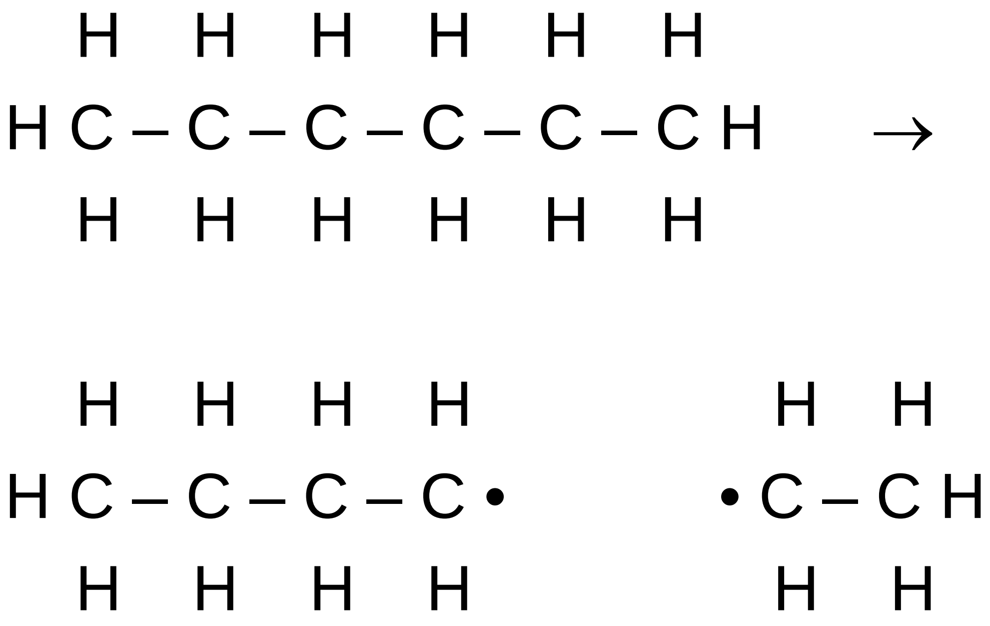
Reaction Class 6: H atom abstraction from olefins

Reaction Class 7: Addition of radical species to olefins

Reaction Class 8: Alkenyl radical decomposition

Reaction Class 9: Olefin decomposition

Class 1 – Unimolecular fuel decomposition

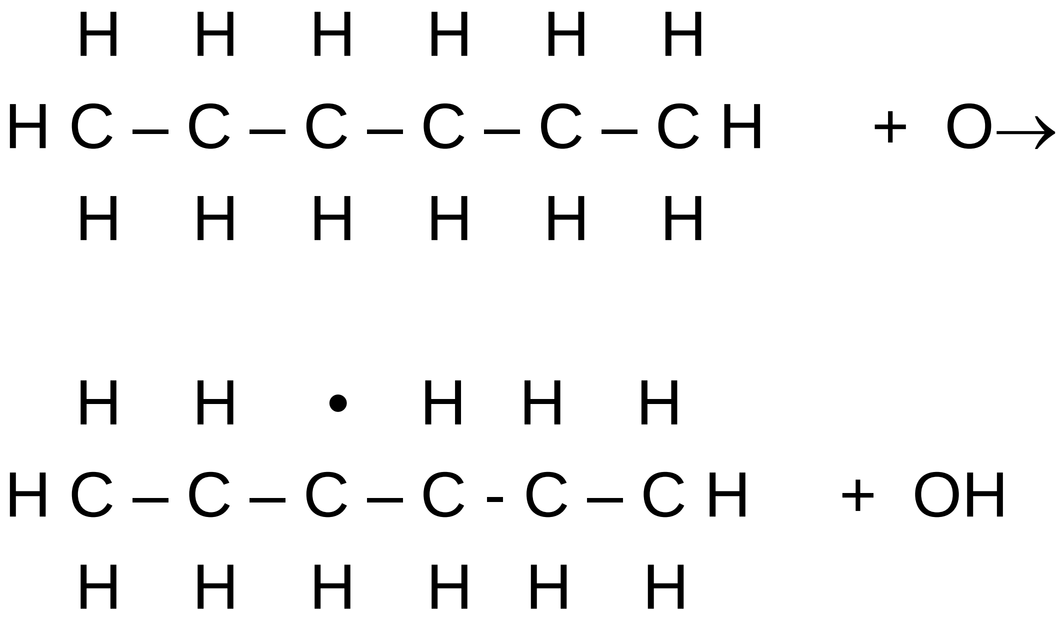


$$H\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}H \quad \rightarrow$$

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

Products are two alkyl radicals pC_4H_9 and C_2H_5

Class 2 – H atom abstractions

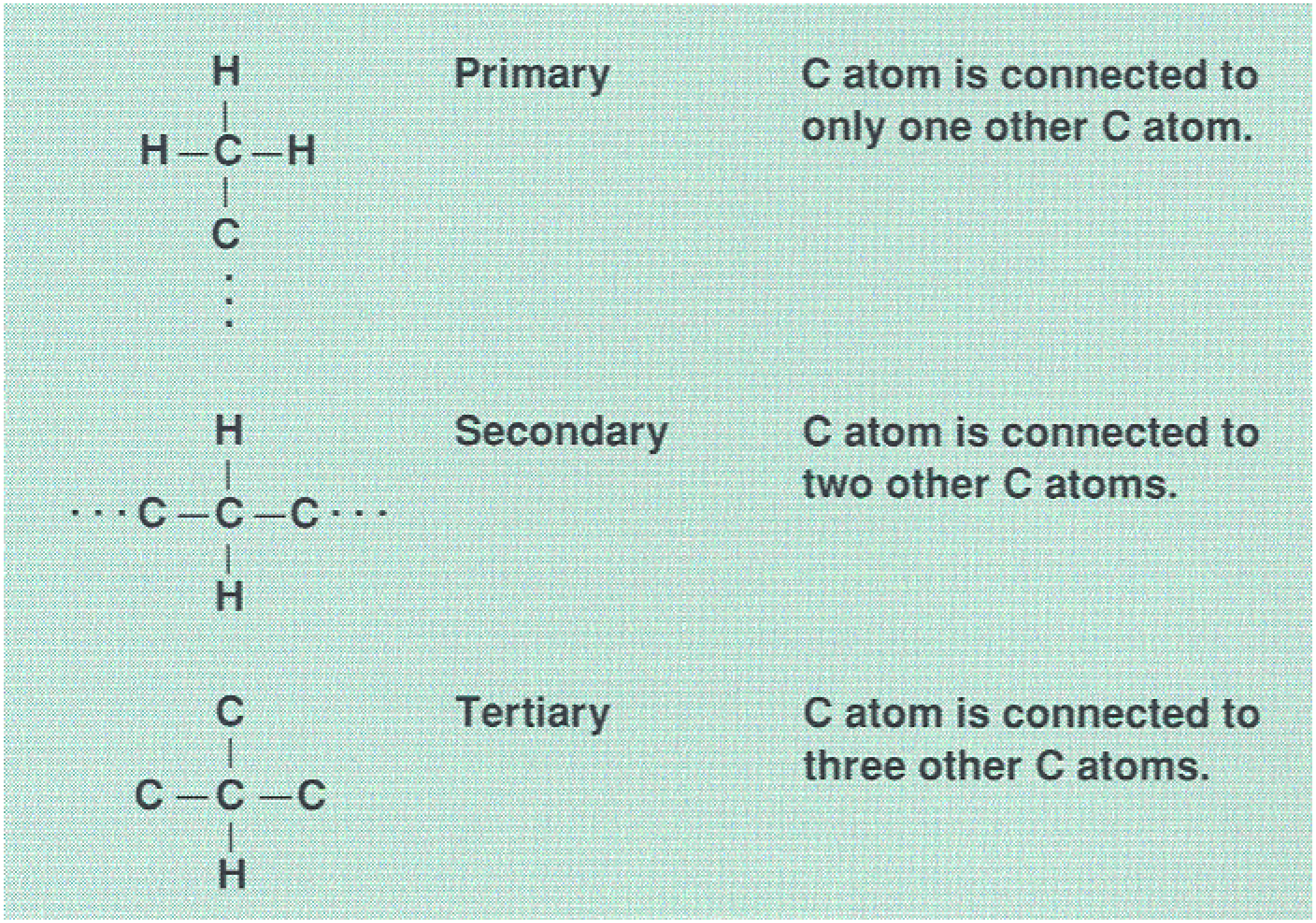


$$\begin{array}{ccccccccccccc} & H & & H & & H & & H & & H & & H & \\ H & C & - & C & - & C & - & C & - & C & - & C & H \\ & H & & H & & H & & H & & H & & H & \end{array} \quad + \; O \rightarrow$$

$$\begin{array}{ccccccccccccc} & H & & H & & \bullet & & H & & H & & H & \\ H & C & - & C & - & C & - & C & - & C & - & C & H \\ & H & & H & & H & & H & & H & & H & \end{array} \quad + \; OH$$

Rate depends on the abstracting radical and on the site where the H is located (more later)

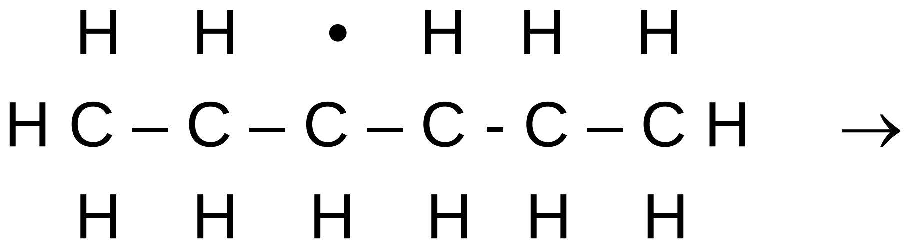
Two major keys to low temperature reactions



	Primary	C atom is connected to only one other C atom.
	Secondary	C atom is connected to two other C atoms.
	Tertiary	C atom is connected to three other C atoms.

BE (primary) > BE (secondary) > BE (tertiary)

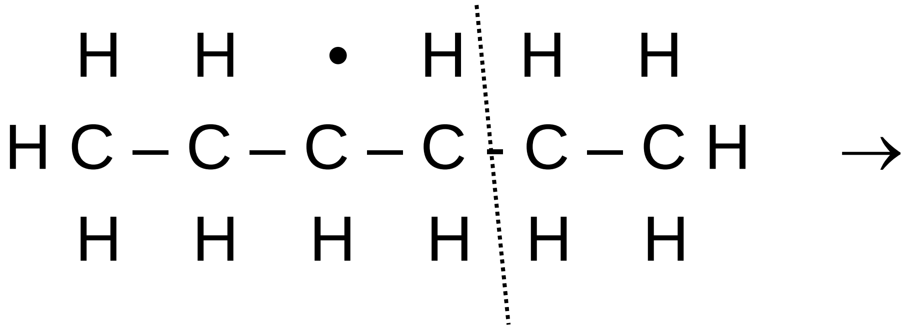
Class 3 – radical decomposition



$$\begin{array}{cccccccccccccc} & H & & H & & \bullet & & H & & H & & H & & \\ H & C & – & C & – & C & – & C & - & C & – & C & H & \rightarrow \\ & H & & H & & H & & H & & H & & H & & \end{array}$$

Decomposition reaction based on beta-scission or “one bond away”

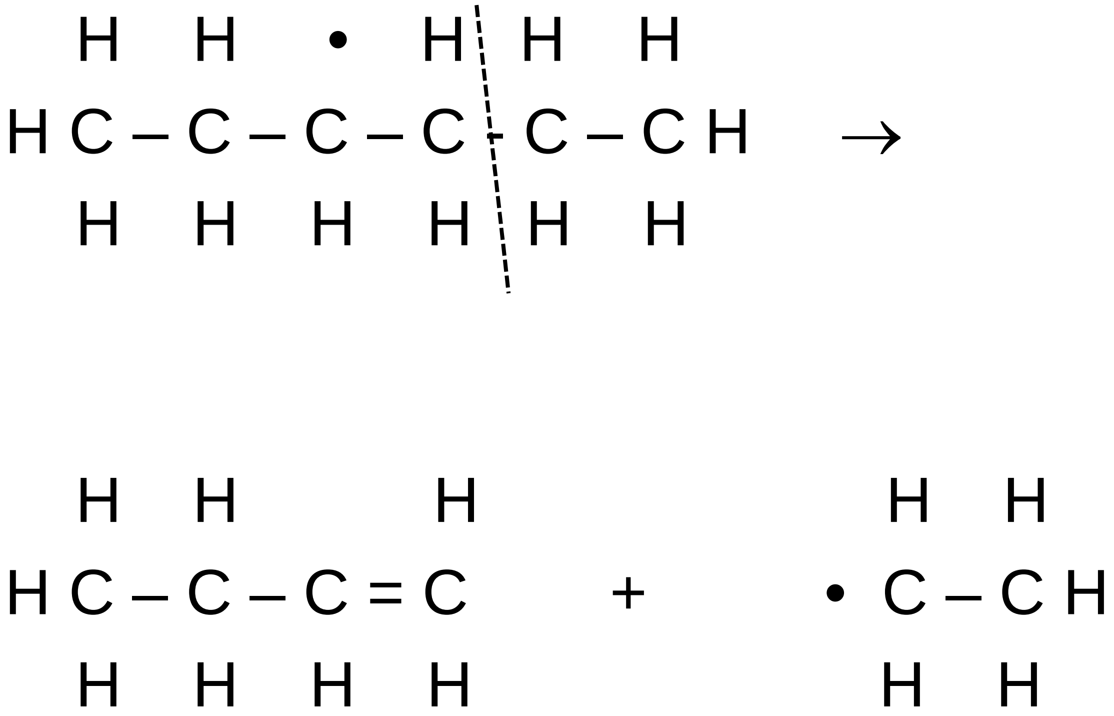
Class 3 – radical decomposition



$$\begin{array}{ccccccccccccc} & \mathrm{H} & & \mathrm{H} & & \bullet & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & \\ \mathrm{H} & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & \mathrm{H} \quad \rightarrow \\ & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & \end{array}$$

Decomposition reaction based on beta-scission or “one bond away”

Class 3 – radical decomposition

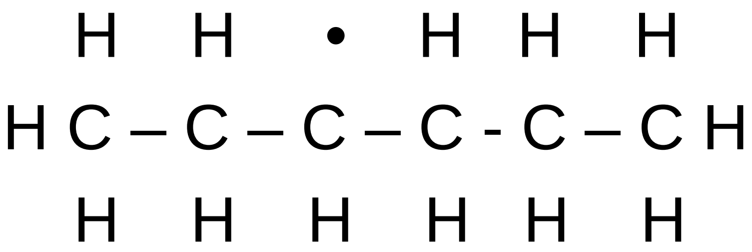


$$\mathrm{H}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\bullet}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{H} \rightarrow$$

$$\mathrm{H}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\mathrm{C}}=\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}} \quad + \quad \bullet\,\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{H}$$

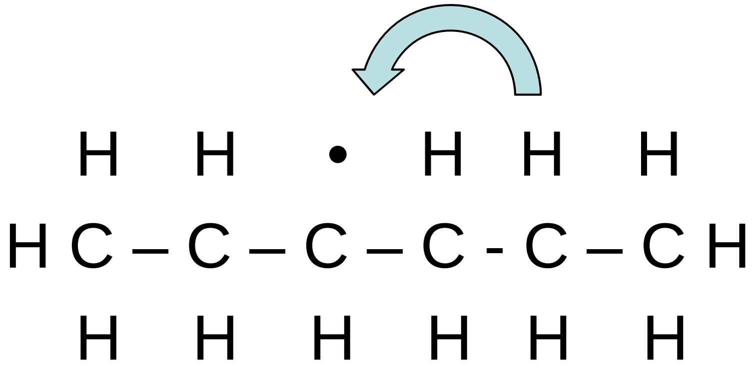
${}_1C_4H_8$ + C_2H_5 one stable olefin and one radical

Class 5: Alkyl radical isomerization



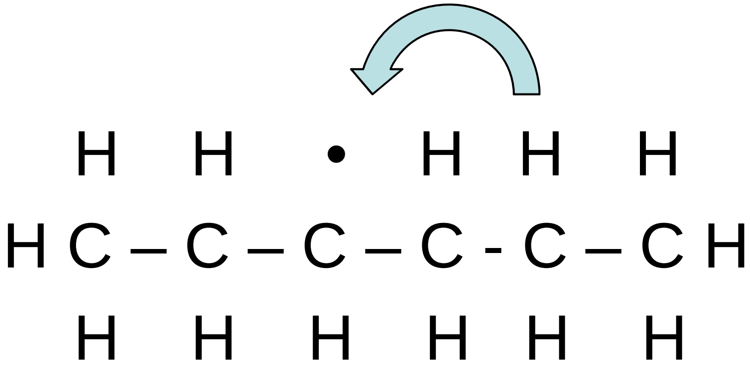
$$\begin{array}{ccccccccccccc} & H & & H & & \bullet & & H & & H & & H & \\ H & C & – & C & – & C & – & C & - & C & – & C & H \\ & H & & H & & H & & H & & H & & H & \end{array}$$

Class 5: Alkyl radical isomerization



$$\begin{array}{ccccccccccccc} & H & & H & & \bullet & & H & & H & & H & \\ H & C & - & C & - & C & - & C & - & C & - & C & H \\ & H & & H & & H & & H & & H & & H & \end{array}$$

Class 5: Alkyl radical isomerization



H H • H H H

H C – C – C – C - C – C H

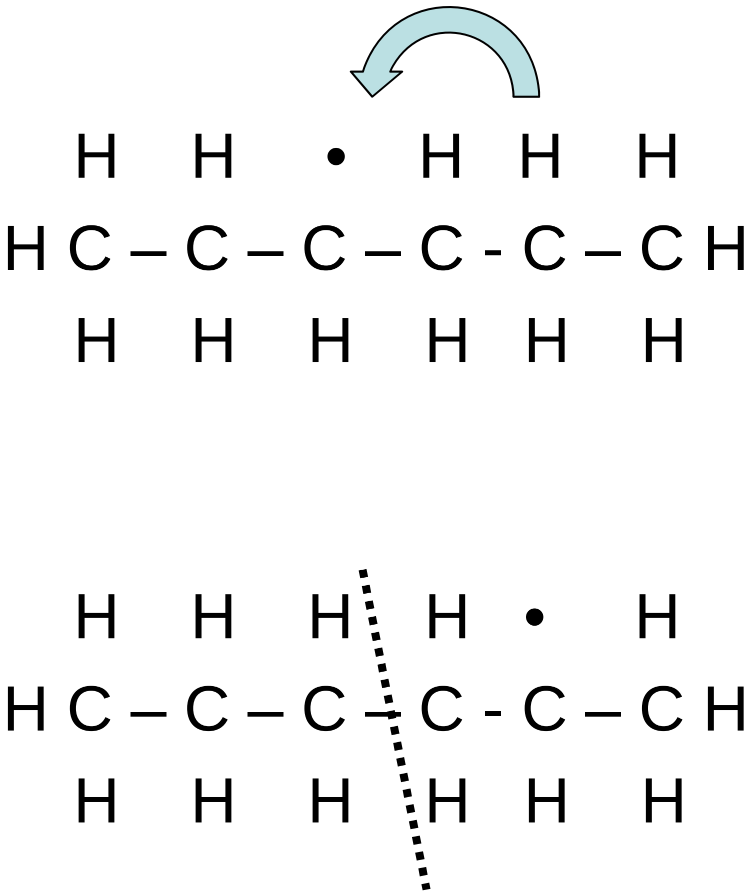
H H H H H H

H H H H • H

H C – C – C – C - C – C H

H H H H H H

Class 5: Alkyl radical isomerization



H H • H H H

H C – C – C – C - C – C H

H H H H H H

H H H H • H

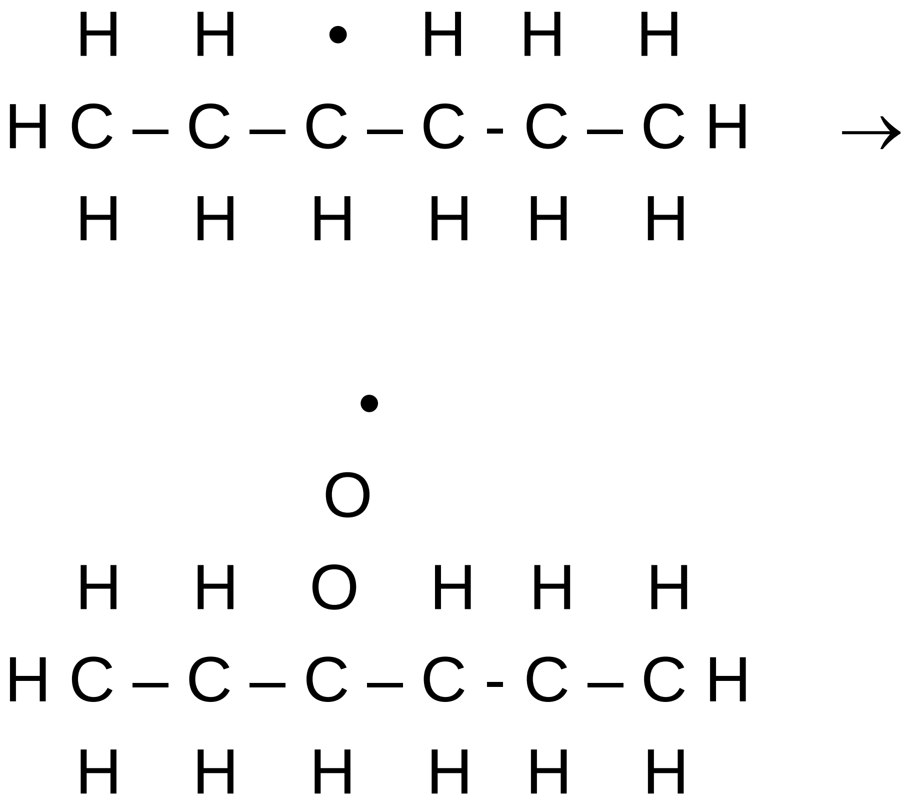
H C – C – C – C - C – C H → nC3H7 + C3H6

H H H H H H

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

Class 10 – addition of O_2 to alkyl radical

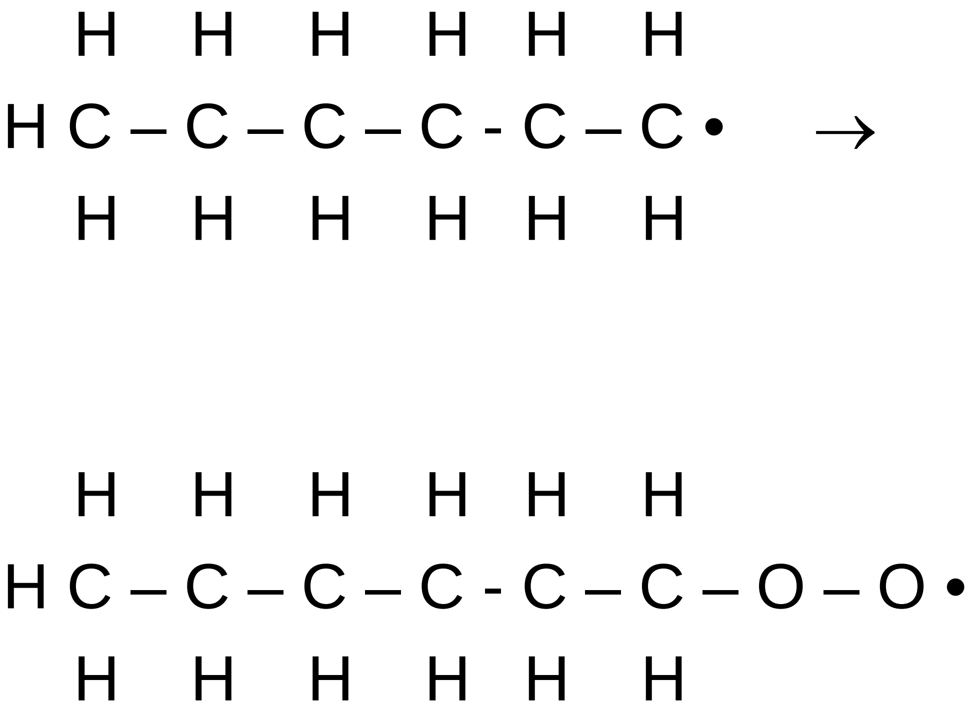


$$\begin{array}{ccccccccccc} & H & & H & & \bullet & & H & & H & & H & \\ H & C & – & C & – & C & – & C & - & C & – & C & H & \rightarrow \\ & H & & H & & H & & H & & H & & H & \end{array}$$

$$\begin{array}{ccccccccccc} & & & & & \bullet & & & & & & & \\ & & & & & O & & & & & & & \\ & H & & H & & O & & H & & H & & H & \\ H & C & – & C & – & C & – & C & - & C & – & C & H \\ & H & & H & & H & & H & & H & & H & \end{array}$$

Rate depends on the type of site where the O_2 attaches

Class 10 – addition of O_2 to alkyl radical

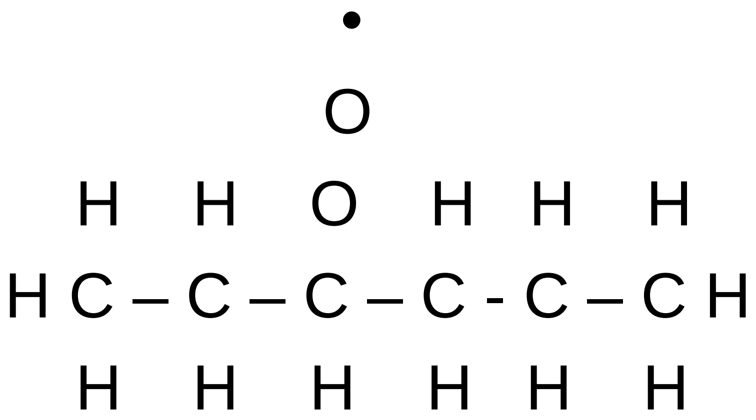


$$\begin{array}{ccccccccccccc} & H & & H & & H & & H & & H & & H & \\ H & C & - & C & - & C & - & C & - & C & - & C & \bullet \quad \rightarrow \\ & H & & H & & H & & H & & H & & H & \end{array}$$

$$\begin{array}{ccccccccccccccccc} & H & & H & & H & & H & & H & & H & & & & & \\ H & C & - & C & - & C & - & C & - & C & - & C & - & O & - & O & \bullet \\ & H & & H & & H & & H & & H & & H & & & & & \end{array}$$

Rate depends on the type of site where the O_2 attaches

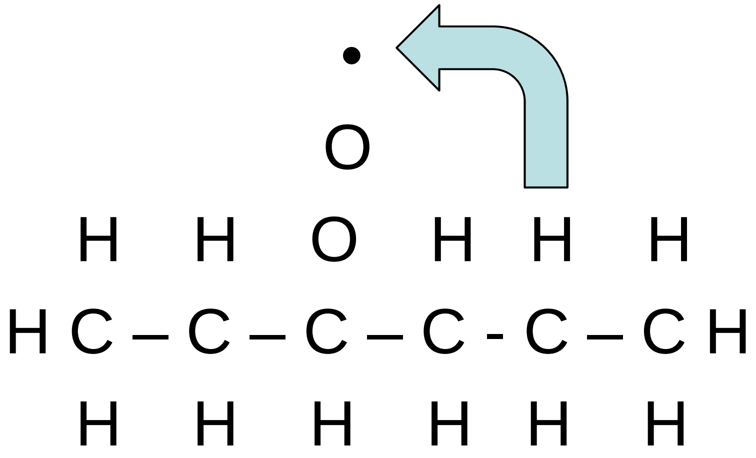
Class 12 – RO_2 isomerization



$$\begin{array}{ccccccccccccc} & & & & & \bullet & & & & & & & \\ & & & & & O & & & & & & & \\ & H & & H & & O & & H & & H & & H & \\ H & C & - & C & - & C & - & C & - & C & - & C & H \\ & H & & H & & H & & H & & H & & H & \end{array}$$

Transfer H atom within the molecule

Class 12 – RO_2 isomerization



•

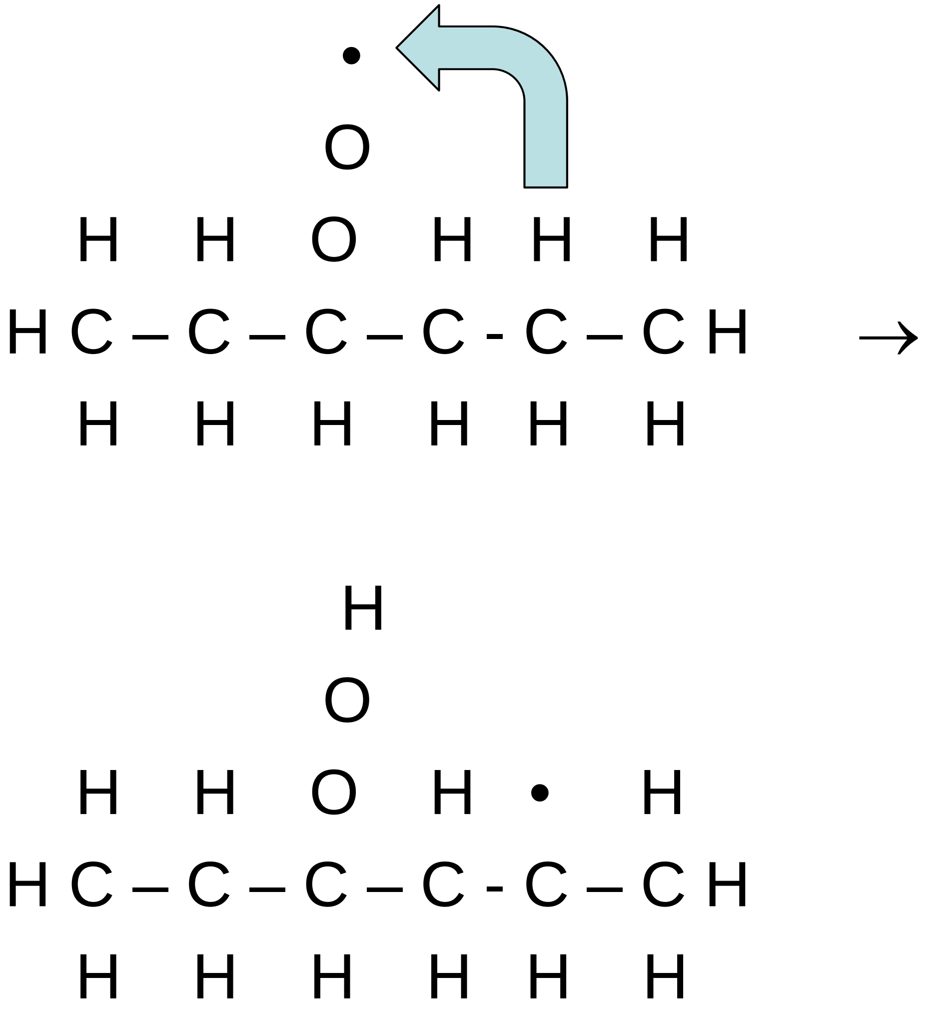
O

H H O H H H

H C – C – C – C - C – C H

H H H H H H

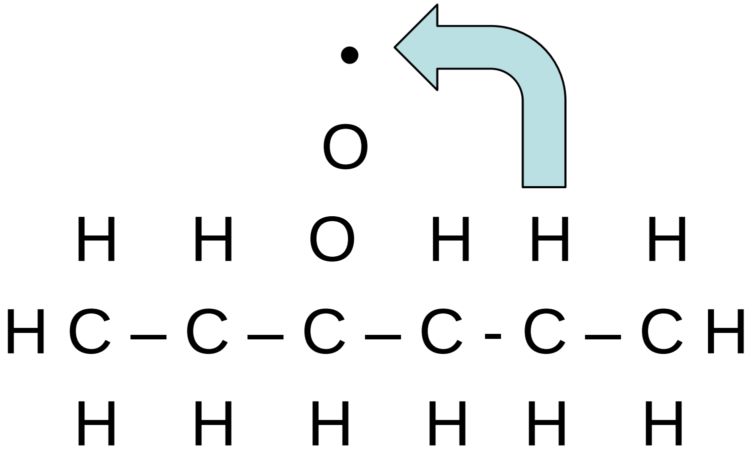
Class 12 – RO_2 isomerization



•
O
H H O H H H
H C – C – C – C - C – C H →
H H H H H H

H
O
H H O H • H
H C – C – C – C - C – C H
H H H H H H

Class 12 – RO$_2$ isomerization

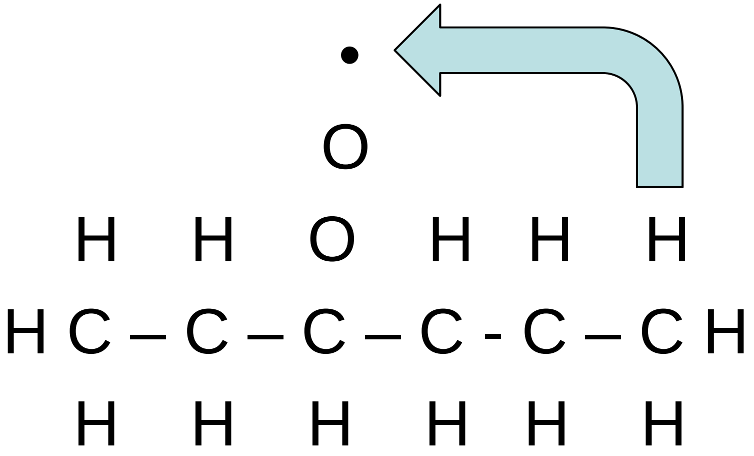


•
O
H H O H H H
H C – C – C – C - C – C H
H H H H H H

6-membered transition
state ring, secondary
→ C – H bonds
2 H atoms available

H
O
H H O H • H
H C – C – C – C - C – C H
H H H H H H

Class 12 – RO_2 isomerization



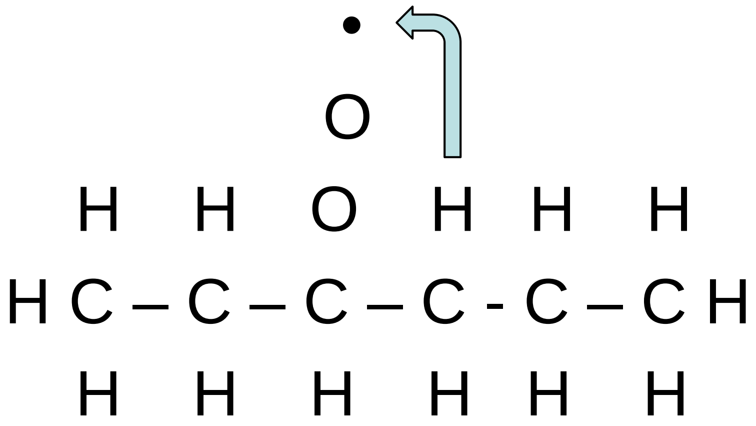
•
O
H H O H H H
H C – C – C – C - C – C H
H H H H H H

→

7-membered transition
state ring, tertiary
C – H bonds
3 H atoms available

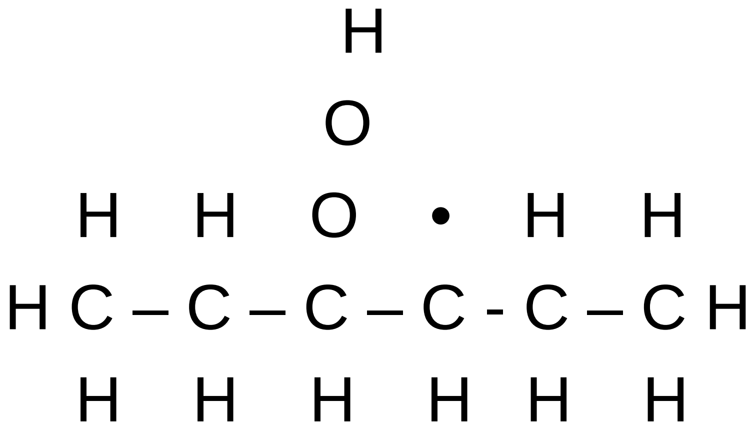
H
O
H H O H H •
H C – C – C – C - C – C H
H H H H H H

Class 12 – RO_2 isomerization



$$\begin{array}{ccccccccccccc}
 & & & & & \bullet & & & & & & & \\
 & & & & & O & & & & & & & \\
 & H & & H & & O & & H & & H & & H & \\
H & C & – & C & – & C & – & C & - & C & – & C & H \\
 & H & & H & & H & & H & & H & & H &
\end{array}$$

5-membered transition
state ring, secondary
→ C – H bonds
2 atoms available



$$\begin{array}{ccccccccccccc}
 & & & & & H & & & & & & & \\
 & & & & & O & & & & & & & \\
 & H & & H & & O & & \bullet & & H & & H & \\
H & C & – & C & – & C & – & C & - & C & – & C & H \\
 & H & & H & & H & & H & & H & & H &
\end{array}$$

Rates of Class 12 reactions

- Size of the transition state ring, “transition state ring strain energy barrier”
  - 5 membered ring has highest energy barrier
  - 7 membered ring has lowest energy barrier

- Type of C – H bond that is broken to remove the H atom
  - Primary bond strongest, tertiary bond is weakest

- Number of equivalent H atoms

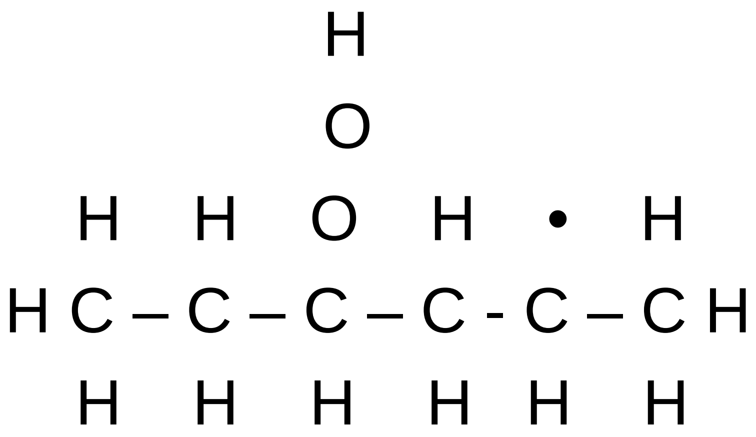
We have rules for each class of reactions: Reaction rates for RO_2 isomerization rate constants

$$k = A\,T^n \exp(-E_a/RT)$$

Rate constant expressions for $R\dot{O}_2$ isomerization reactions (cm^3–mol–sec–cal units)

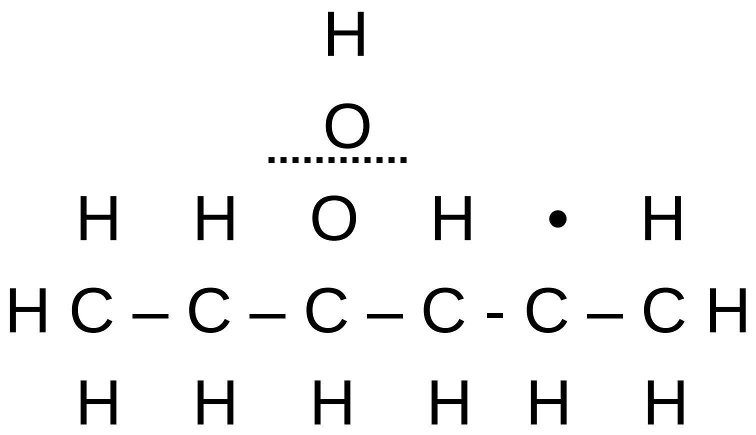
Ring size	Site	Rate expression (per H atom)		
		A	n	ϵ_a
5	Primary	1.00×10^{11}	0.0	29400.
	Secondary	1.00×10^{11}	0.0	26850.
	tertiary	1.00×10^{11}	0.0	24100.
6	Primary	1.25×10^{10}	0.0	24400.
	Secondary	1.25×10^{10}	0.0	20850.
	tertiary	1.25×10^{10}	0.0	19100.
7	Primary	1.56×10^{9}	0.0	22350.
	Secondary	1.56×10^{9}	0.0	19050.
	tertiary	1.56×10^{9}	0.0	17050.
8	Primary	1.95×10^{8}	0.0	25550.
	Secondary	1.95×10^{8}	0.0	22050.
	tertiary	1.95×10^{8}	0.0	20050.

Class 19 – QOOH decomposition into cyclic ether



$$\begin{array}{ccccccccccccc}
 & & & & & \mathrm{H} & & & & & & & \\
 & & & & & \mathrm{O} & & & & & & & \\
 & \mathrm{H} & & \mathrm{H} & & \mathrm{O} & & \mathrm{H} & & \bullet & & \mathrm{H} & \\
\mathrm{H} & \mathrm{C} & – & \mathrm{C} & – & \mathrm{C} & – & \mathrm{C} & - & \mathrm{C} & – & \mathrm{C} & \mathrm{H} \\
 & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} &
\end{array}$$

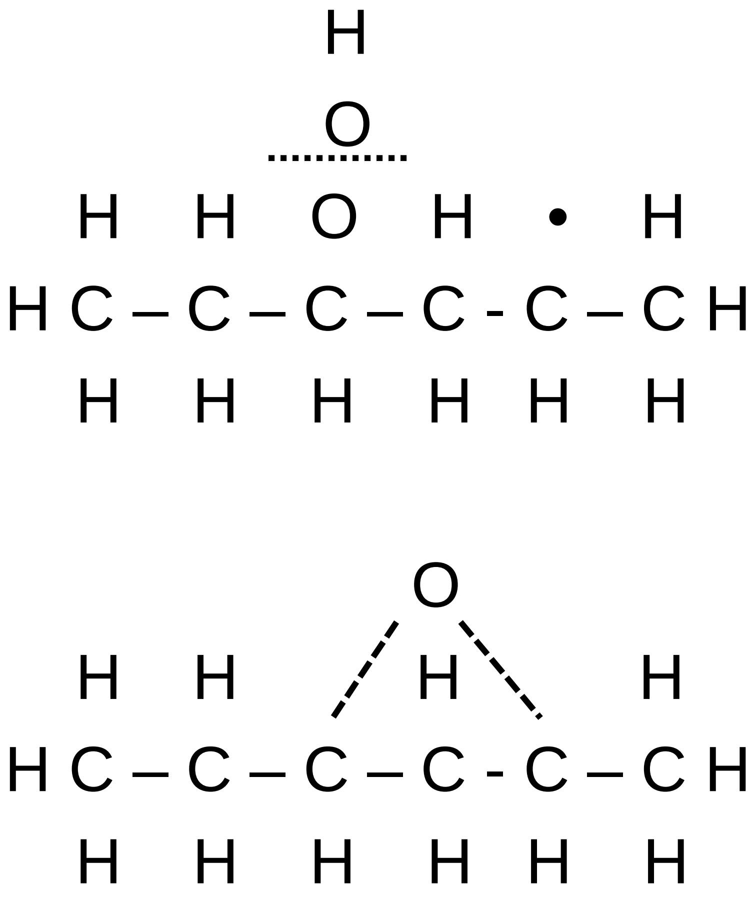
Class 19 – QOOH decomposition into cyclic ether



$$\begin{array}{ccccccccccccc}
 & & & & & \mathrm{H} & & & & & & & \\
 & & & & & \mathrm{O} & & & & & & & \\
 & & & & & \cdots\cdots & & & & & & & \\
 & \mathrm{H} & & \mathrm{H} & & \mathrm{O} & & \mathrm{H} & & \bullet & & \mathrm{H} & \\
\mathrm{H} & \mathrm{C} & – & \mathrm{C} & – & \mathrm{C} & – & \mathrm{C} & - & \mathrm{C} & – & \mathrm{C} & \mathrm{H} \\
 & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} &
\end{array}$$

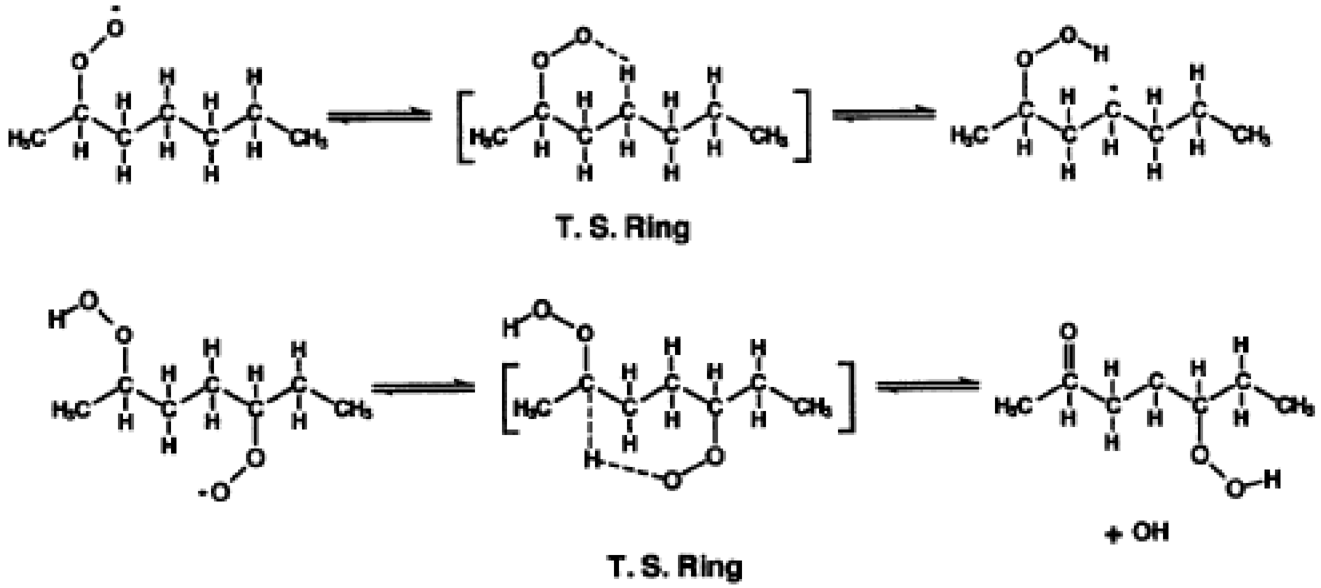
Reaction begins by breaking O – O bond,
which produces OH radical

Class 19 – QOOH decomposition into cyclic ether



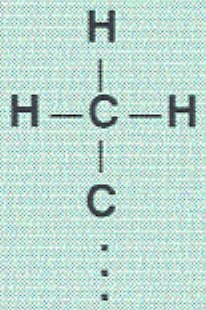
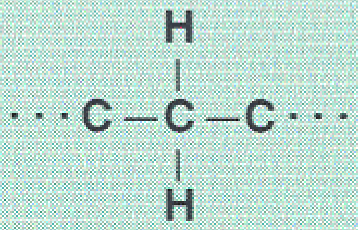
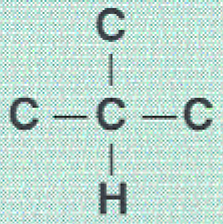
4-membered ring
cyclic ether

Low temperature kinetics involve intra-molecular H atom transfers

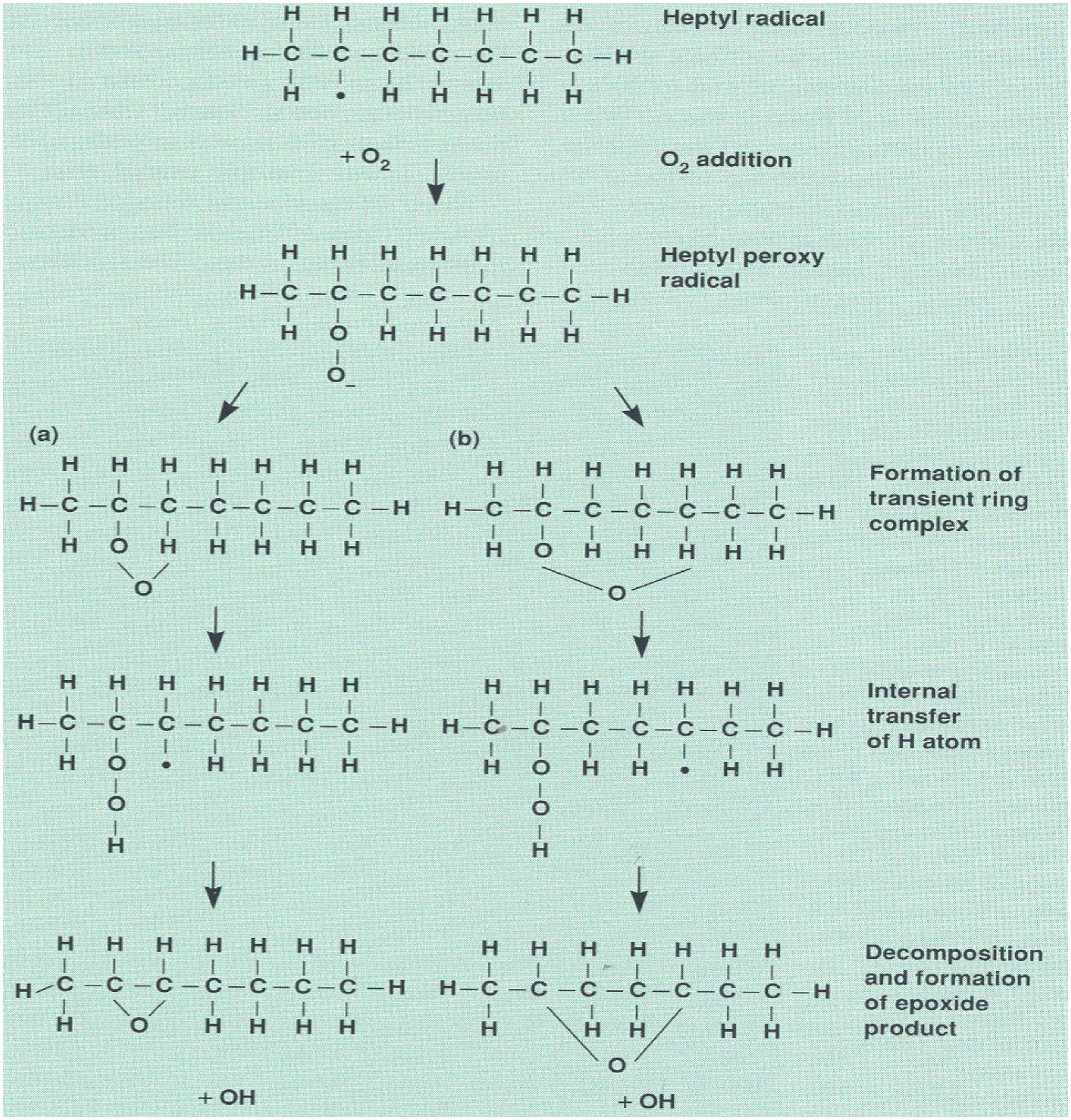


These reactions lead to OH radical production at low temperatures, which then produce water and heat This heating reduces the time delay for the fuel to reach the H_2O_2 decomposition temperature

Two major keys to low temperature reactions

	**Primary**	C atom is connected to only one other C atom.
	**Secondary**	C atom is connected to two other C atoms.
	**Tertiary**	C atom is connected to three other C atoms.

BE (primary) > BE (secondary) > BE (tertiary)



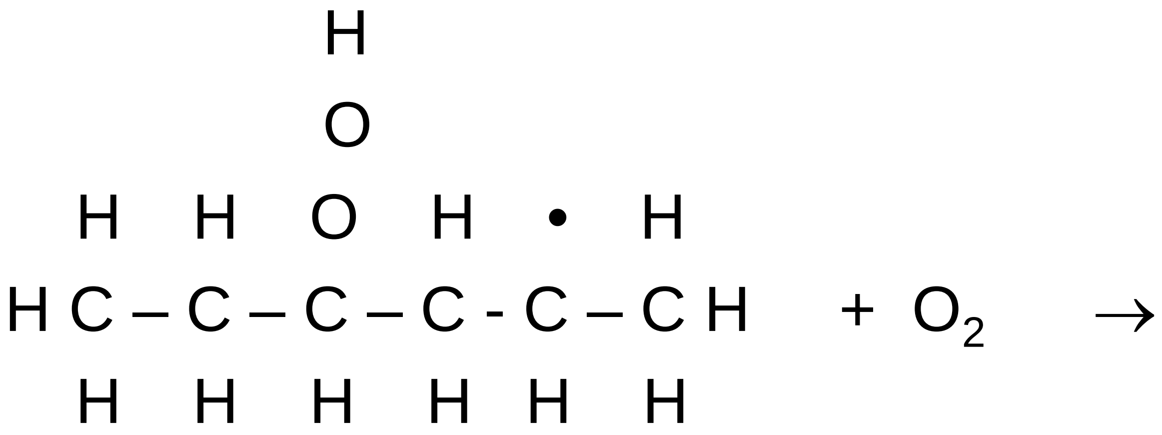
RSE (5-ring) >

RSE (6-ring) >

RSE (7-ring) <

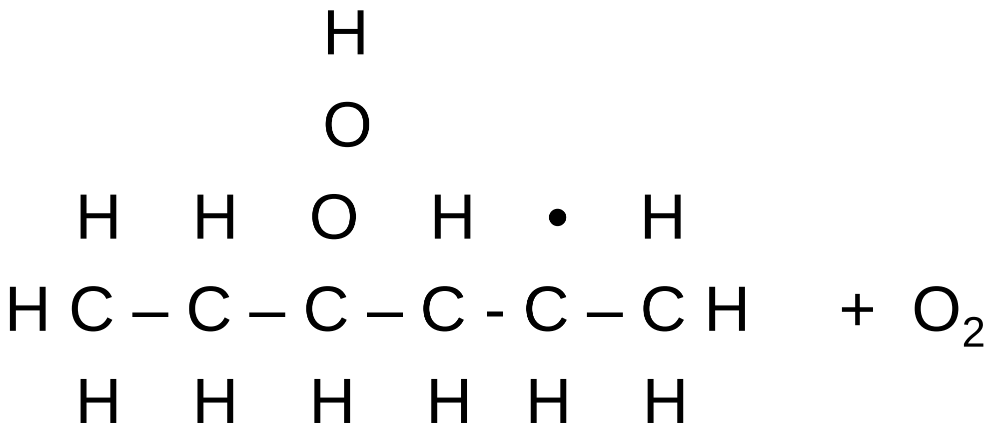
RSE (8-ring)

Class 22 – addition of O_2 to QOOH

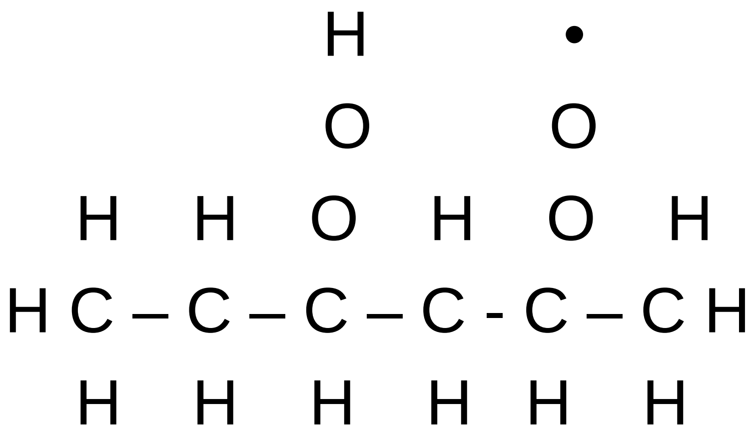


$$\mathrm{H}\,\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\overset{\overset{\mathrm{H}}{\mathrm{O}}}{\mathrm{O}}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\bullet}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}\,\mathrm{H} \quad + \; O_2 \quad \rightarrow$$

Class 22 – addition of O_2 to QOOH

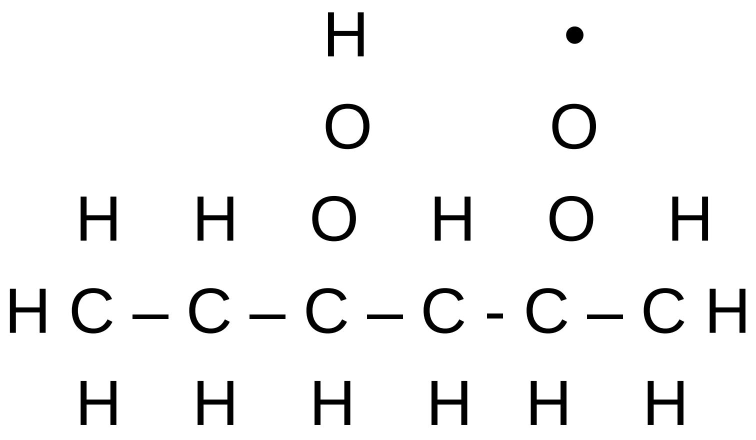


$$\begin{array}{ccccccccccccccc}
 & & & & & \mathrm{H} & & & & & & & & & \\
 & & & & & \mathrm{O} & & & & & & & & & \\
 & \mathrm{H} & & \mathrm{H} & & \mathrm{O} & & \mathrm{H} & & \bullet & & \mathrm{H} & & & \\
\mathrm{H} & \mathrm{C} & – & \mathrm{C} & – & \mathrm{C} & – & \mathrm{C} & - & \mathrm{C} & – & \mathrm{C} & \mathrm{H} & + & O_2 \\
 & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & &
\end{array}$$



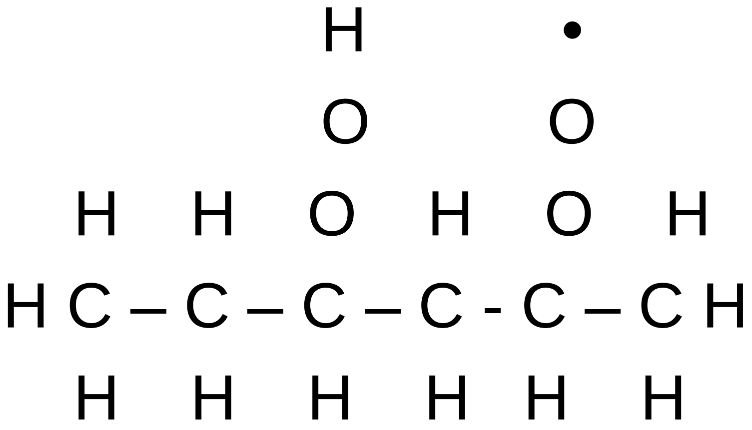
$$\begin{array}{ccccccccccccc}
 & & & & & \mathrm{H} & & & & \bullet & & & \\
 & & & & & \mathrm{O} & & & & \mathrm{O} & & & \\
 & \mathrm{H} & & \mathrm{H} & & \mathrm{O} & & \mathrm{H} & & \mathrm{O} & & \mathrm{H} & \\
\mathrm{H} & \mathrm{C} & – & \mathrm{C} & – & \mathrm{C} & – & \mathrm{C} & - & \mathrm{C} & – & \mathrm{C} & \mathrm{H} \\
 & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} &
\end{array}$$

Class 23 – isomerization of O_2QOOH

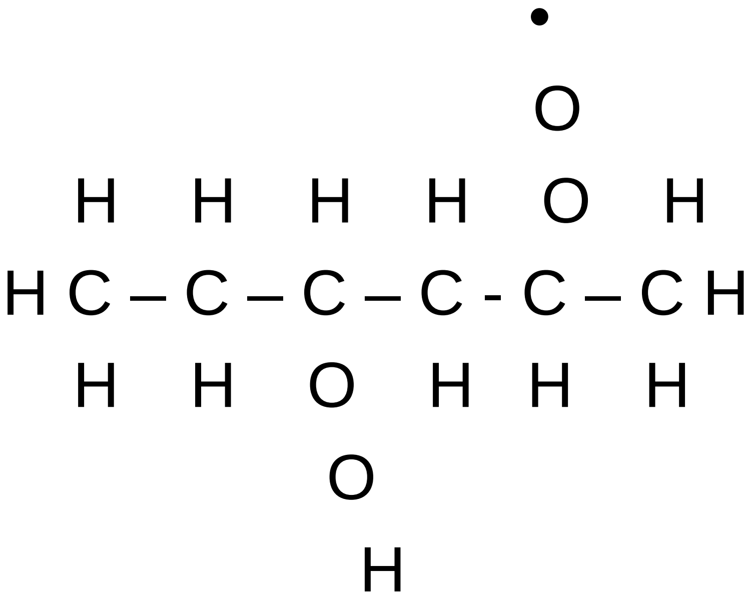


$$\begin{array}{ccccccccccccc}
 & & & & & H & & & & \bullet & & & \\
 & & & & & O & & & & O & & & \\
 & H & & H & & O & & H & & O & & H & \\
H & C & - & C & - & C & - & C & - & C & - & C & H \\
 & H & & H & & H & & H & & H & & H &
\end{array}$$

Class 23 – isomerization of O_2QOOH

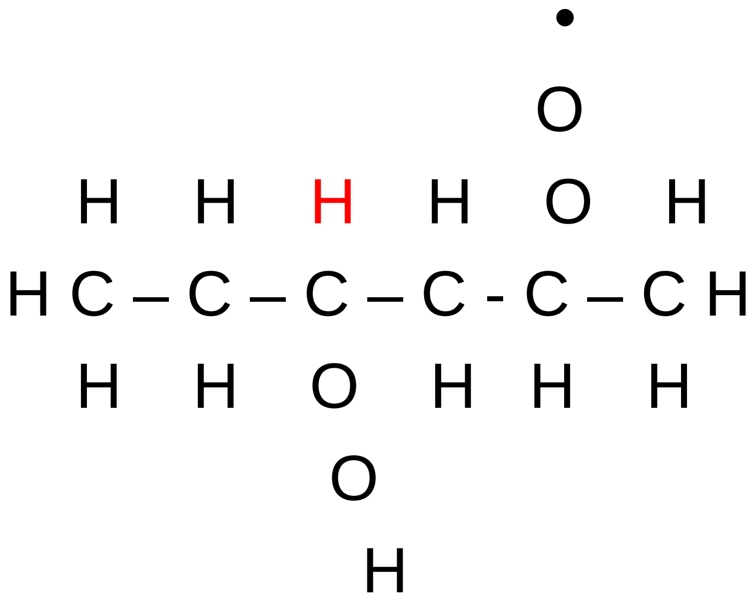


$$\begin{array}{ccccccccccccc} & & & & & \mathrm{H} & & & & \bullet & & & \\ & & & & & \mathrm{O} & & & & \mathrm{O} & & & \\ & \mathrm{H} & & \mathrm{H} & & \mathrm{O} & & \mathrm{H} & & \mathrm{O} & & \mathrm{H} & \\ \mathrm{H} & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & \mathrm{H} \\ & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & \end{array}$$



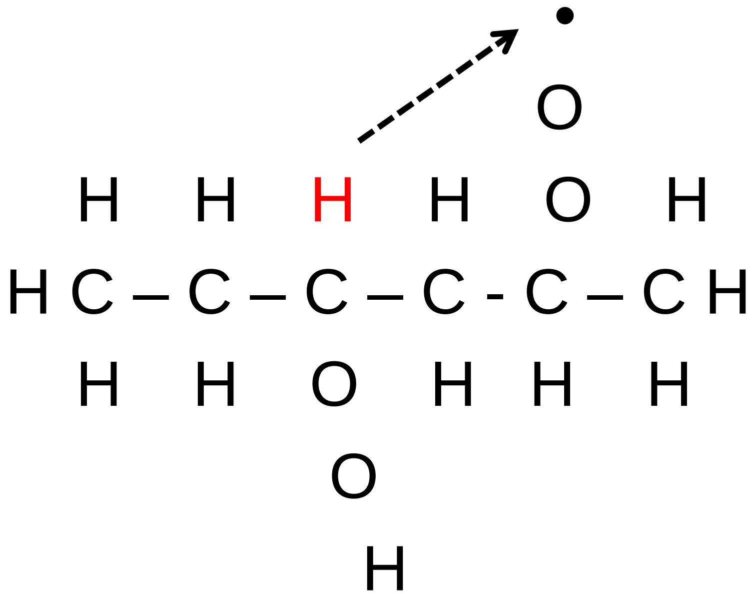
$$\begin{array}{ccccccccccccc} & & & & & & & & & \bullet & & & \\ & & & & & & & & & \mathrm{O} & & & \\ & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{O} & & \mathrm{H} & \\ \mathrm{H} & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & \mathrm{H} \\ & \mathrm{H} & & \mathrm{H} & & \mathrm{O} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & \\ & & & & & \mathrm{O} & & & & & & & \\ & & & & & \mathrm{H} & & & & & & & \end{array}$$

Class 23 – isomerization of O_2QOOH



$$\begin{array}{ccccccccccccc}
 & & & & & & & & & \bullet & & & \\
 & & & & & & & & & O & & & \\
 & H & & H & & \color{red}{H} & & H & & O & & H & \\
H & C & – & C & – & C & – & C & - & C & – & C & H \\
 & H & & H & & O & & H & & H & & H & \\
 & & & & & O & & & & & & & \\
 & & & & & H & & & & & & &
\end{array}$$

Class 23 – isomerization of O_2QOOH



•

O

H H H H O H

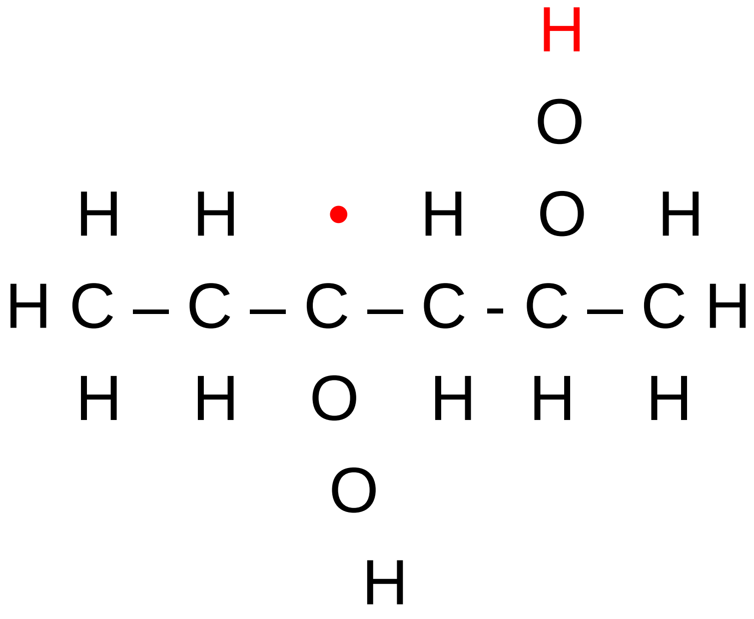
H C – C – C – C - C – C H

H H O H H H

O

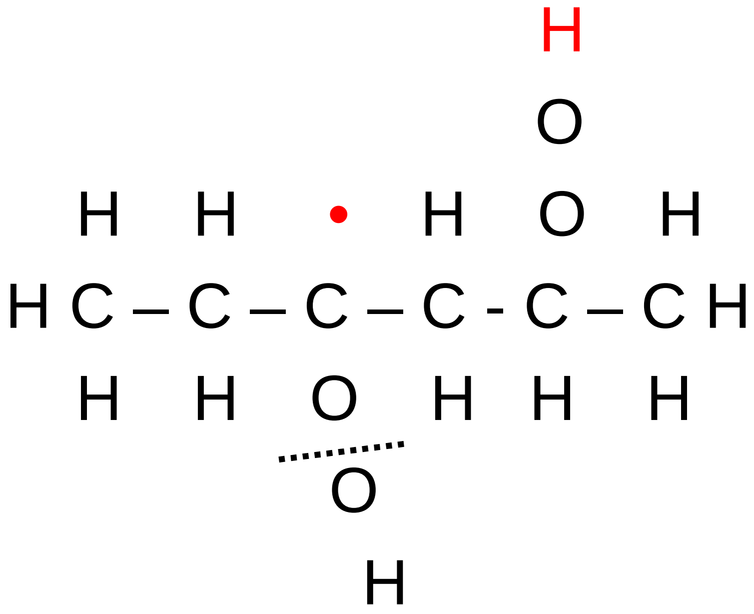
H

Class 23 – isomerization of O_2QOOH

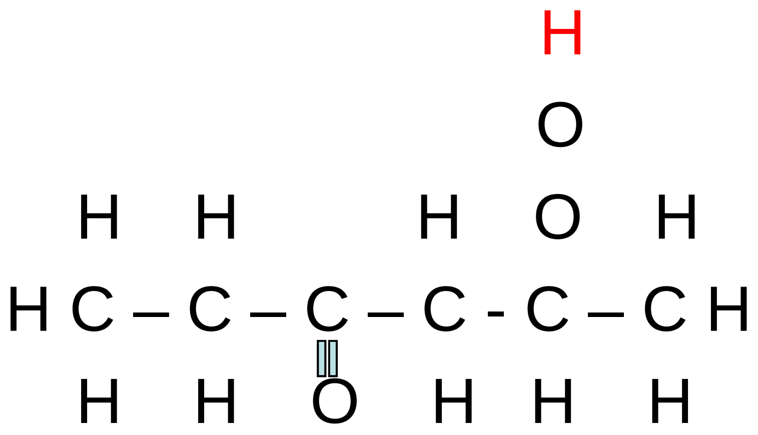


$$\begin{array}{ccccccccccccc}
 & & & & & & & & & H & & & \\
 & & & & & & & & & O & & & \\
 & H & & H & & \bullet & & H & & O & & H & \\
H & C & – & C & – & C & – & C & - & C & – & C & H \\
 & H & & H & & O & & H & & H & & H & \\
 & & & & & O & & & & & & & \\
 & & & & & H & & & & & & &
\end{array}$$

Class 23 – isomerization of O_2QOOH



Class 23 – isomerization of O_2QOOH

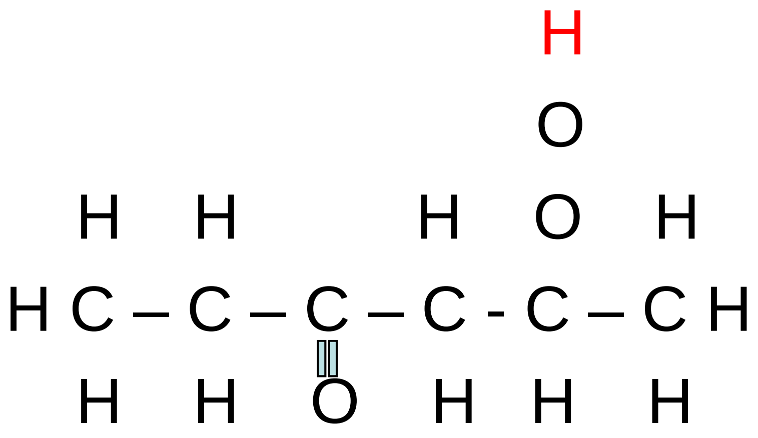


$$\begin{array}{ccccccccccccc}
 & & & & & & & & & H & & & \\
 & & & & & & & & & O & & & \\
 & H & & H & & & & H & & O & & H & \\
H & C & - & C & - & C & - & C & - & C & - & C & H \\
 & & & & & \| & & & & & & & \\
 & H & & H & & O & & H & & H & & H &
\end{array}$$

to produce a ketohydroperoxide species

+ OH   (#1)

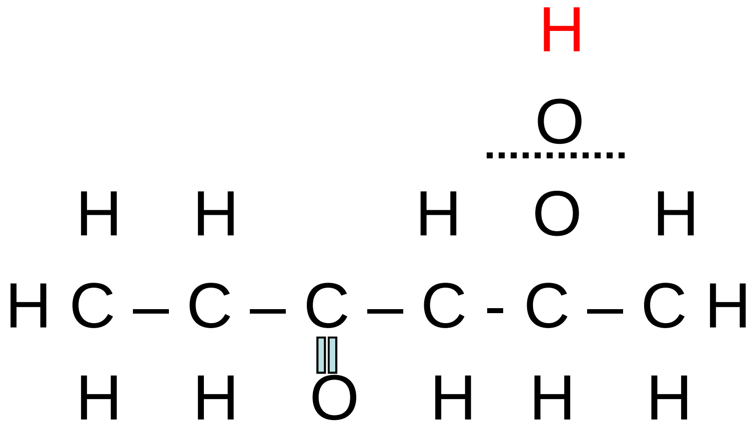
Class 24 – decomposition of ketohydroperoxide



$$\begin{array}{ccccccccccccc}
 & & & & & & & & & \color{red}{H} & & & \\
 & & & & & & & & & O & & & \\
 & H & & H & & & & H & & O & & H & \\
H & C & - & C & - & C & - & C & - & C & - & C & H \\
 & & & & & \| & & & & & & & \\
 & H & & H & & O & & H & & H & & H &
\end{array}$$

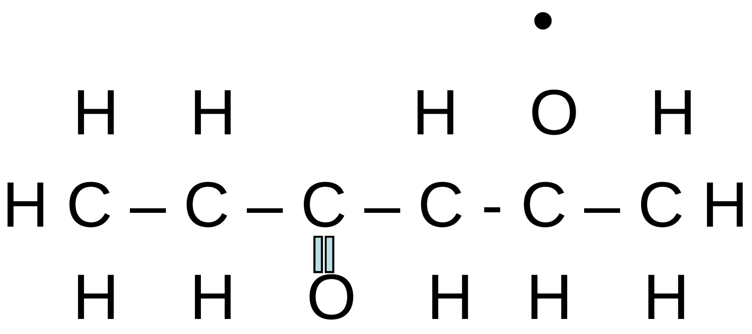
Because this is a stable species, it requires a temperature increase to break the O – O bond

Class 24 – decomposition of ketohydroperoxide



$$\begin{array}{ccccccccccc}
 & & & & & & & & \mathrm{H} & & \\
 & & & & & & & & \mathrm{O} & & \\
 & & & & & & & & \cdots\cdots & & \\
\mathrm{H} & & \mathrm{H} & & & & \mathrm{H} & & \mathrm{O} & & \mathrm{H} \\
\mathrm{HC} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{CH} \\
 & & & & \| & & & & & & \\
\mathrm{H} & & \mathrm{H} & & \mathrm{O} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H}
\end{array}$$

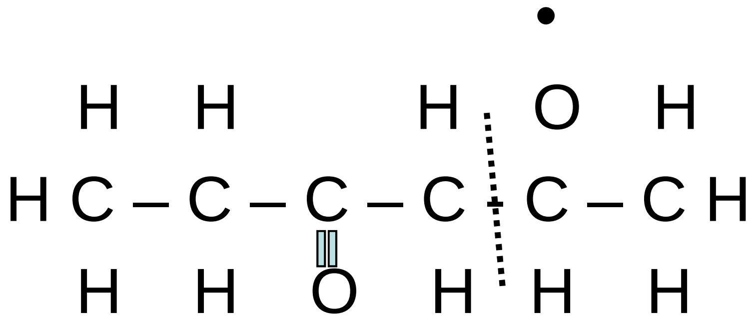
Class 24 – decomposition of ketohydroperoxide



$$\begin{array}{ccccccccccccc} & & & & & & & & & \bullet & & & \\ & H & & H & & & & H & & O & & H & \\ H & C & – & C & – & C & – & C & - & C & – & C & H \\ & & & & & \| & & & & & & & \\ & H & & H & & O & & H & & H & & H & \end{array}$$

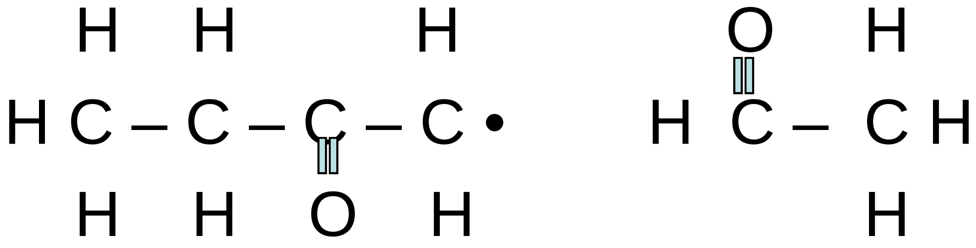
\+ OH (#2)

Class 24 – decomposition of ketohydroperoxide



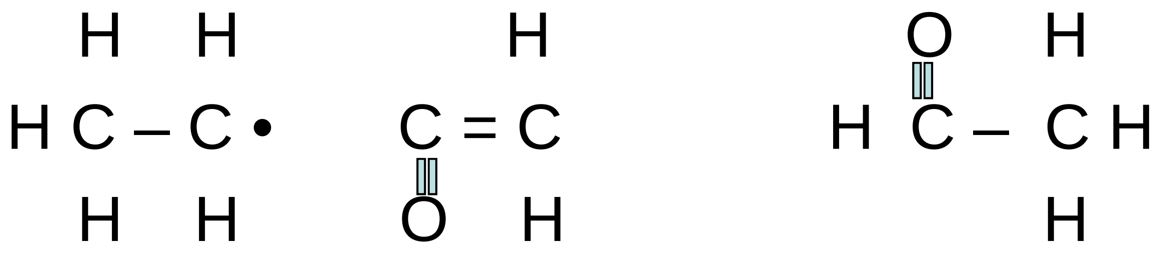
$$\begin{array}{ccccccccccccc} & & & & & & & & & & \bullet & & \\ & H & & H & & & & H & & & O & & H \\ H & C & - & C & - & C & - & C & - & C & - & C & H \\ & & & & & \| & & & & & & & \\ & H & & H & & O & & H & & H & & H & \end{array}$$

Class 24 – decomposition of ketohydroperoxide



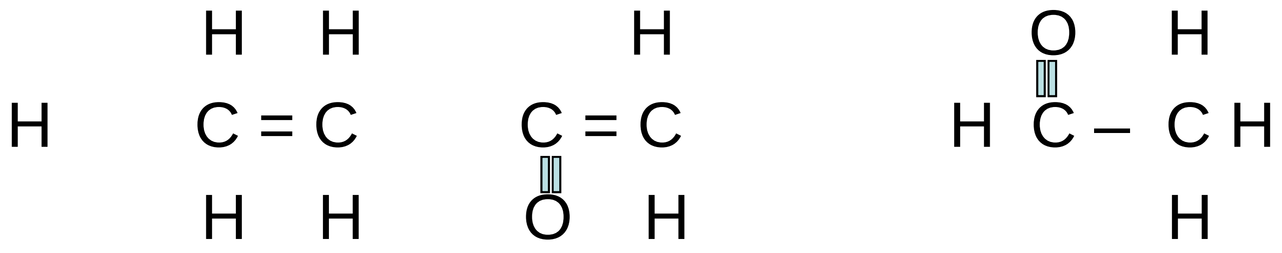
$$\mathrm{CH_3{-}CH_2{-}C({=}O){-}CH_2\bullet} \qquad \mathrm{HC({=}O){-}CH_3}$$

Class 24 – decomposition of ketohydroperoxide



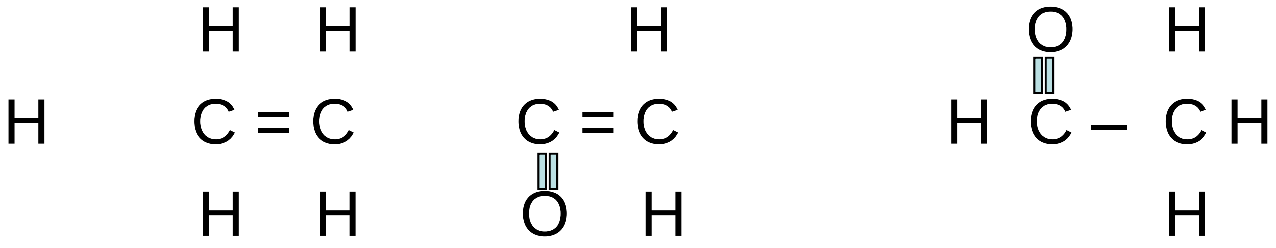
$$\begin{array}{cccc} & \mathrm{H} & & \mathrm{H} \\ \mathrm{H} & \mathrm{C} & – & \mathrm{C}\,\bullet \\ & \mathrm{H} & & \mathrm{H} \end{array} \qquad \begin{array}{ccc} & & \mathrm{H} \\ \mathrm{C} & = & \mathrm{C} \\ \Vert & & \\ \mathrm{O} & & \mathrm{H} \end{array} \qquad \begin{array}{cccccc} & \mathrm{O} & & \mathrm{H} & \\ & \Vert & & & \\ \mathrm{H} & \mathrm{C} & – & \mathrm{C} & \mathrm{H} \\ & & & \mathrm{H} & \end{array}$$

Class 24 – decomposition of ketohydroperoxide



$$\mathrm{H}\qquad \begin{array}{c}\mathrm{H}\\ \mathrm{C}\\ \mathrm{H}\end{array} = \begin{array}{c}\mathrm{H}\\ \mathrm{C}\\ \mathrm{H}\end{array} \qquad\qquad \begin{array}{c}\\ \mathrm{C}\\ \|\\ \mathrm{O}\end{array} = \begin{array}{c}\mathrm{H}\\ \mathrm{C}\\ \mathrm{H}\end{array} \qquad\qquad \mathrm{H}\ \begin{array}{c}\mathrm{O}\\ \|\\ \mathrm{C}\\ \\ \end{array} - \begin{array}{c}\mathrm{H}\\ \mathrm{C}\\ \mathrm{H}\end{array}\mathrm{H}$$

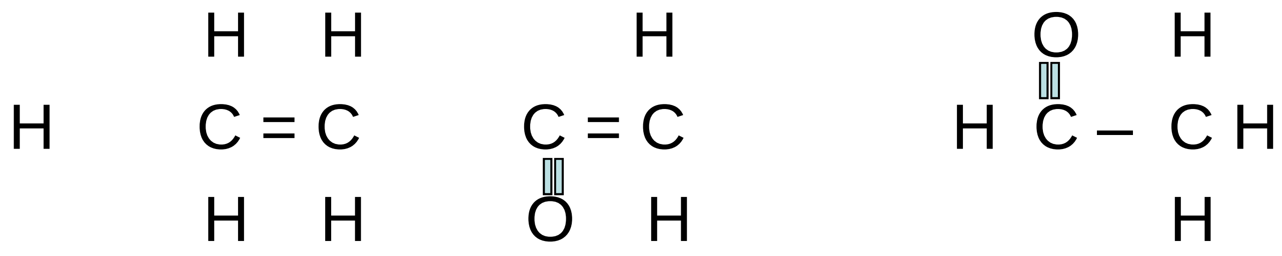
Class 24 – decomposition of ketohydroperoxide



$$H \qquad H_2C=CH_2 \qquad O=C=CH_2 \qquad HC(=O)-CH_3$$

H (radical) + ethene + ketene + acetaldehyde

Class 24 – decomposition of ketohydroperoxide



$$\mathrm{H} \qquad \begin{array}{ccc} \mathrm{H} & & \mathrm{H} \\ \mathrm{C} & = & \mathrm{C} \\ \mathrm{H} & & \mathrm{H} \end{array} \qquad \begin{array}{ccc} & & \mathrm{H} \\ \mathrm{C} & = & \mathrm{C} \\ \Vert & & \\ \mathrm{O} & & \mathrm{H} \end{array} \qquad \begin{array}{ccccc} & \mathrm{O} & & \mathrm{H} & \\ & \Vert & & & \\ \mathrm{H} & \mathrm{C} & - & \mathrm{C} & \mathrm{H} \\ & & & \mathrm{H} & \end{array}$$

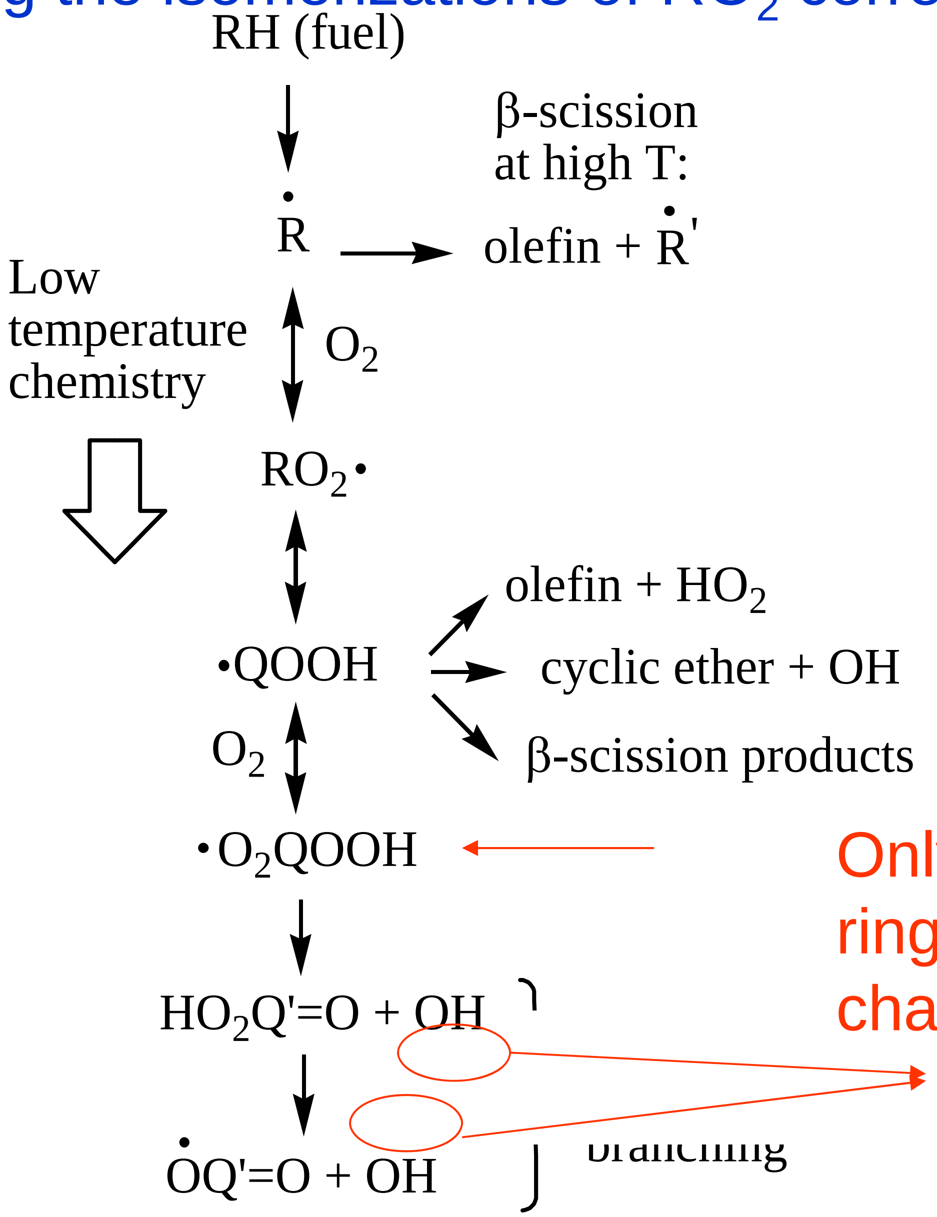
H (radical) + ethene + ketene + acetaldehyde

and don’t forget OH (#1) and OH (#2)

Alkylperoxy radical isomerization, followed by the dihydroperoxide pathway

- At least 3 small radical species
  - OH + OH + H (or another OH or HO_2)
- Several small stable species, many of them highly reactive aldehydes and olefins
- These reaction pathways provide intense chain branching
- This pathway quits when increasing temperature shuts down the R + O_2 and O_2 + QOOH equilibria

Key to understanding the low temperature chemistry of MCH was getting the isomerizations of RO_2 correct:



RH (fuel)

$\dot{R}$ → olefin + $\dot{R}'$

β-scission at high T:

Low temperature chemistry

O_2

$RO_2\bullet$

$\bullet QOOH$ → olefin + HO_2

$\bullet QOOH$ → cyclic ether + OH

$\bullet QOOH$ → β-scission products

O_2

$\bullet O_2QOOH$

$HO_2Q'=O + OH$

$\dot{O}Q'=O + OH$

branching

Only 6-membered rings lead to significant chain branching

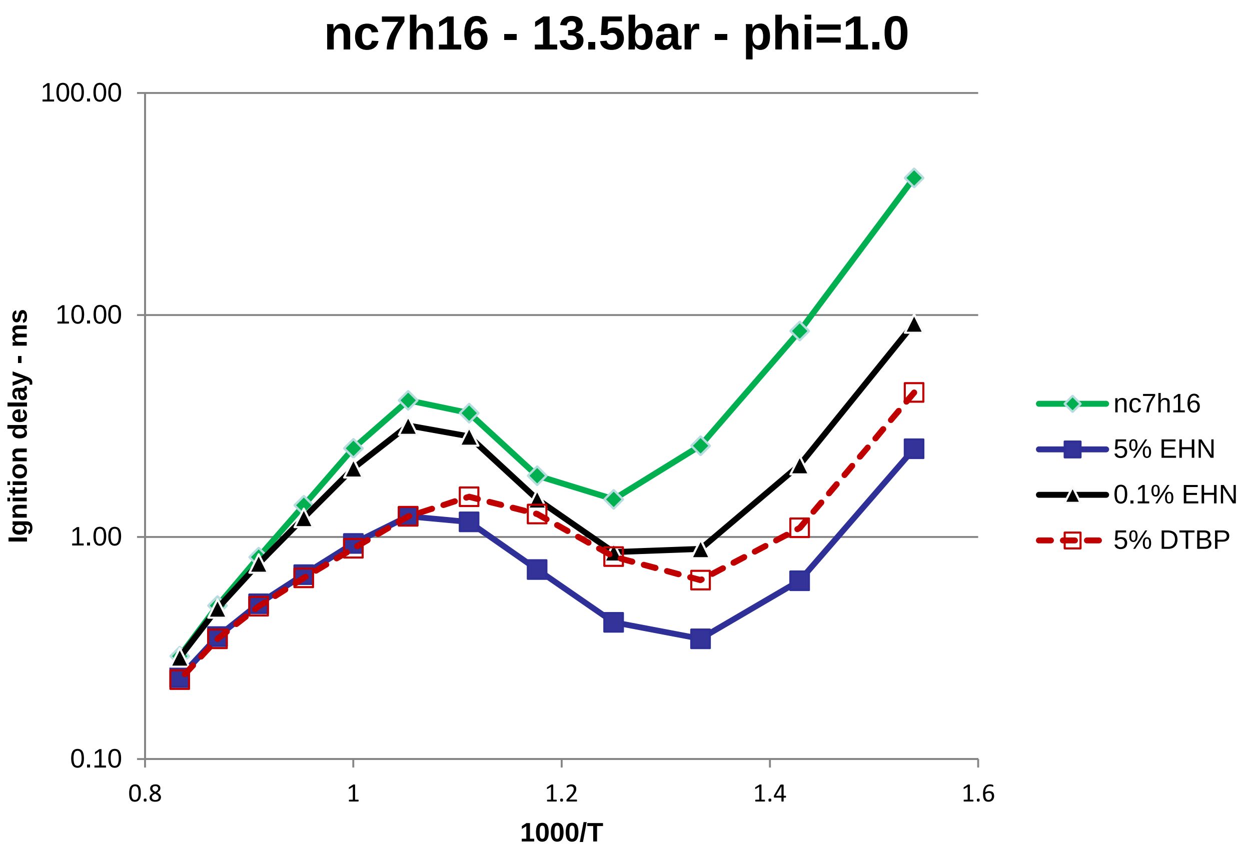
2 OH's produced

Alkyl radical isomerization possible for most fuels

- Remember the key kinetic factors
- Primary, secondary and tertiary C – H bonds
- Ring strain energy variations with ring size, especially for nearest-neighbor abstractions
- Other molecular structure effects
- If you understand these arguments, you also understand all the kinetic factors that determine cetane numbers (CN) in Diesel engines

Review knocking factors

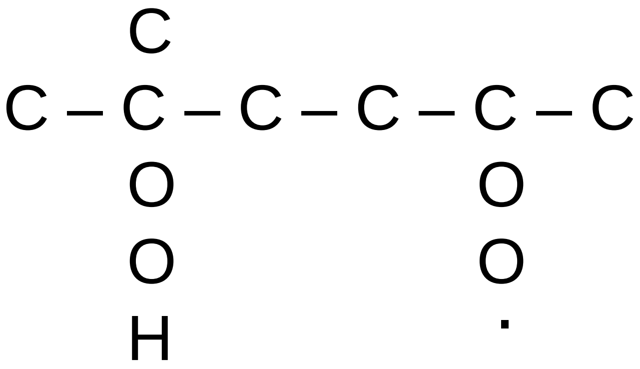
- Primary C-H bonds inhibit ignition
  - Initial H abstraction from fuel
  - RO2 internal abstraction/isomerization
  - O2QOOH internal abstraction/isomerization
- Larger rings have lower ring strain barriers
- Results in ignition advantages for n-alkanes
- Disadvantages for heavily branched alkanes
- Additional obstacles to ignition due to allylic and *bis*-allylic sites in biodiesel and similar fuels
- Anti-knock additives remove radical species, cetane ignition enhancers provide additional radicals



nc7h16 - 13.5bar - phi=1.0
Ignition delay - ms
100.00
10.00
1.00
0.10
0.8
1
1.2
1.4
1.6
1000/T
nc7h16
5% EHN
0.1% EHN
5% DTBP

Additional factors at low T

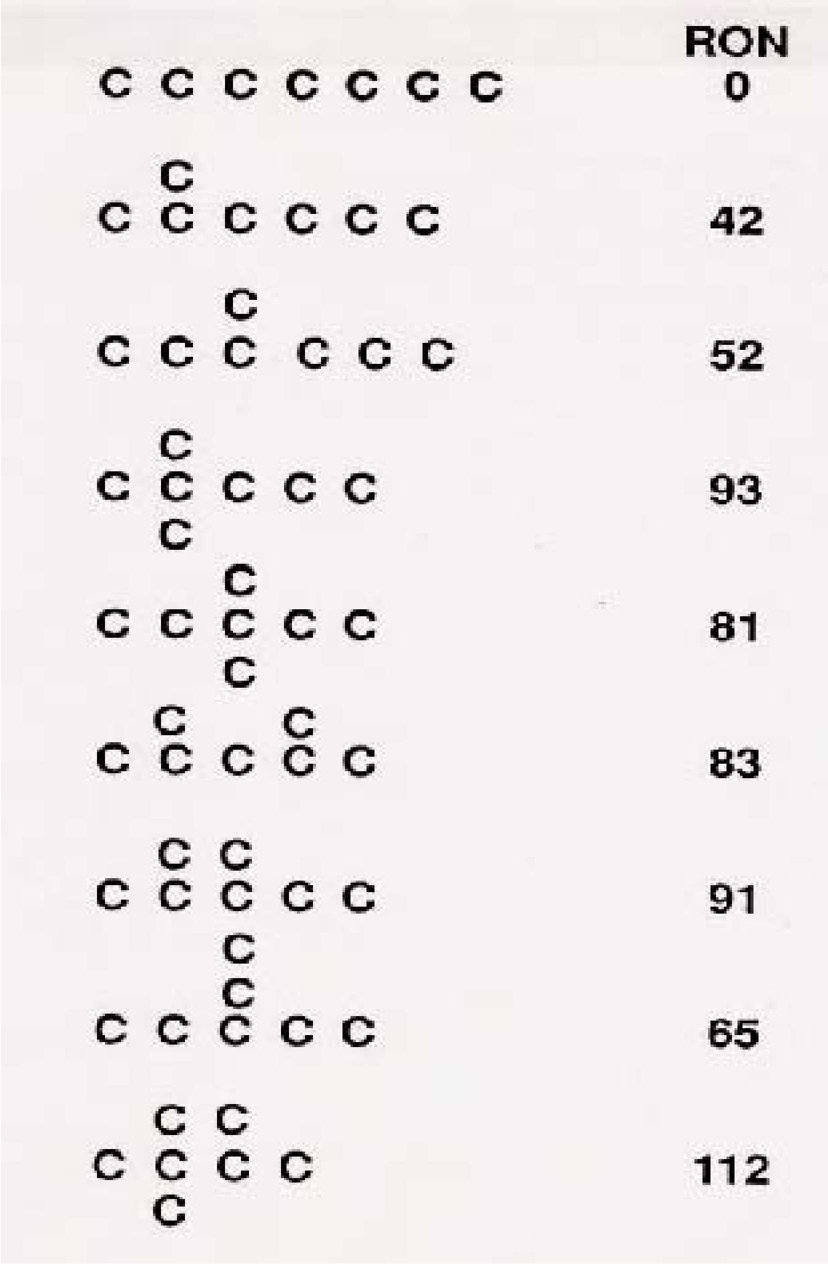
- Tertiary C-H sites create problems, need to improve models



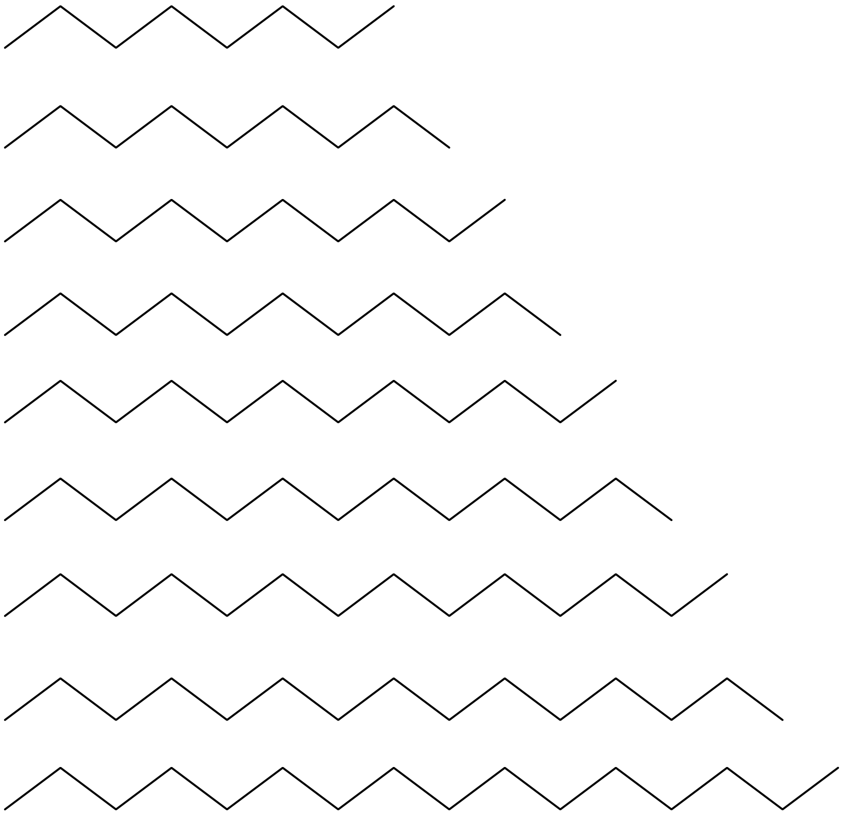
$$\begin{array}{ccccccccccc} & & C & & & & & & & & \\ C & - & C & - & C & - & C & - & C & - & C \\ & & O & & & & & & O & & \\ & & O & & & & & & O & & \\ & & H & & & & & & \cdot & & \end{array}$$

Octane numbers of heptanes are due exclusively to their different molecular structures

Low octane fuels have lots of secondary C-H bonds and high octane fuels have lots of primary C-H bonds and lots of tight, 5-membered TS rings



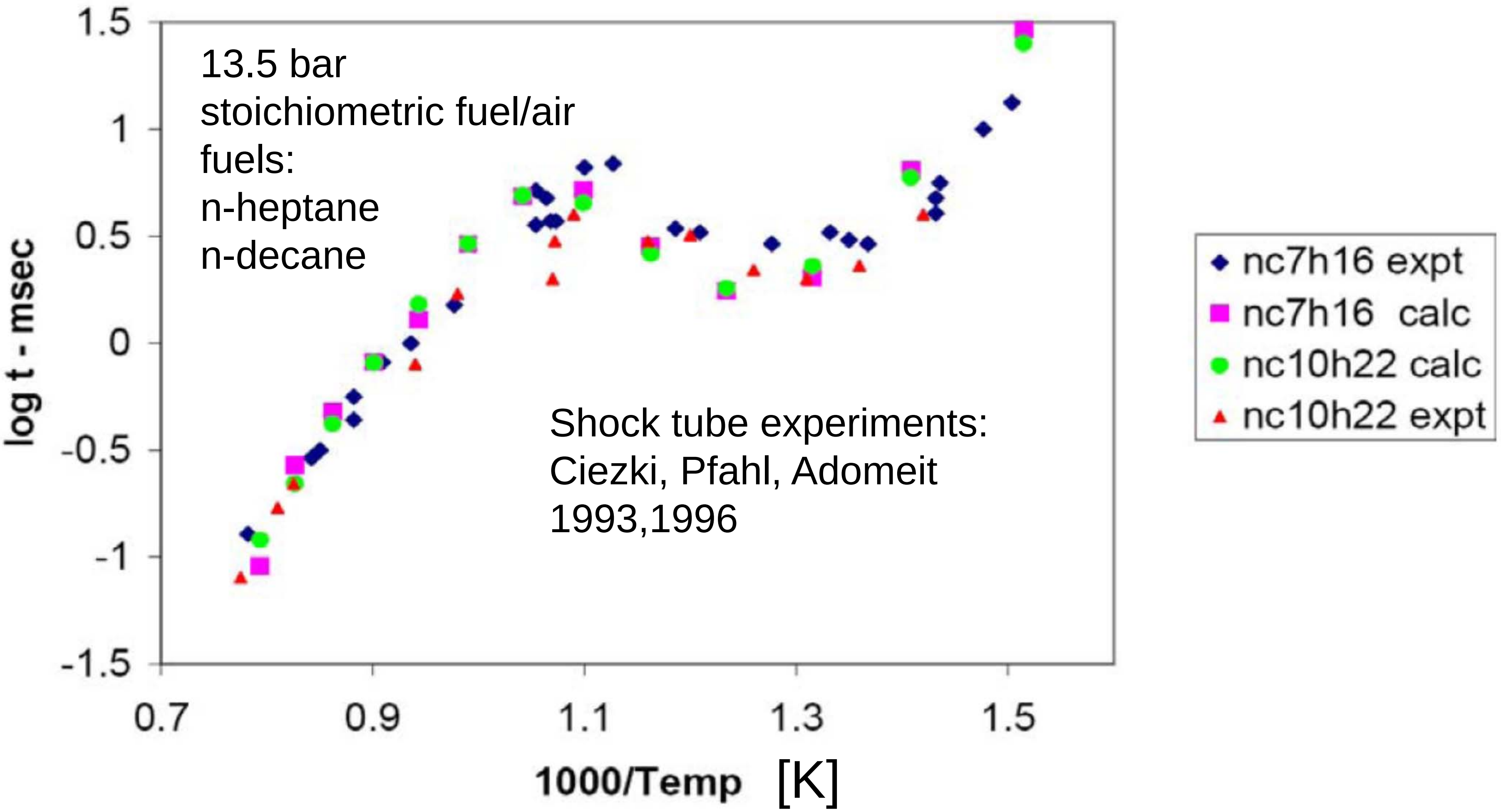
N-alkanes all have straight C chains with lots of secondary C – H bonds and low ring strain energy barriers



- 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)

Experimental Validation Data

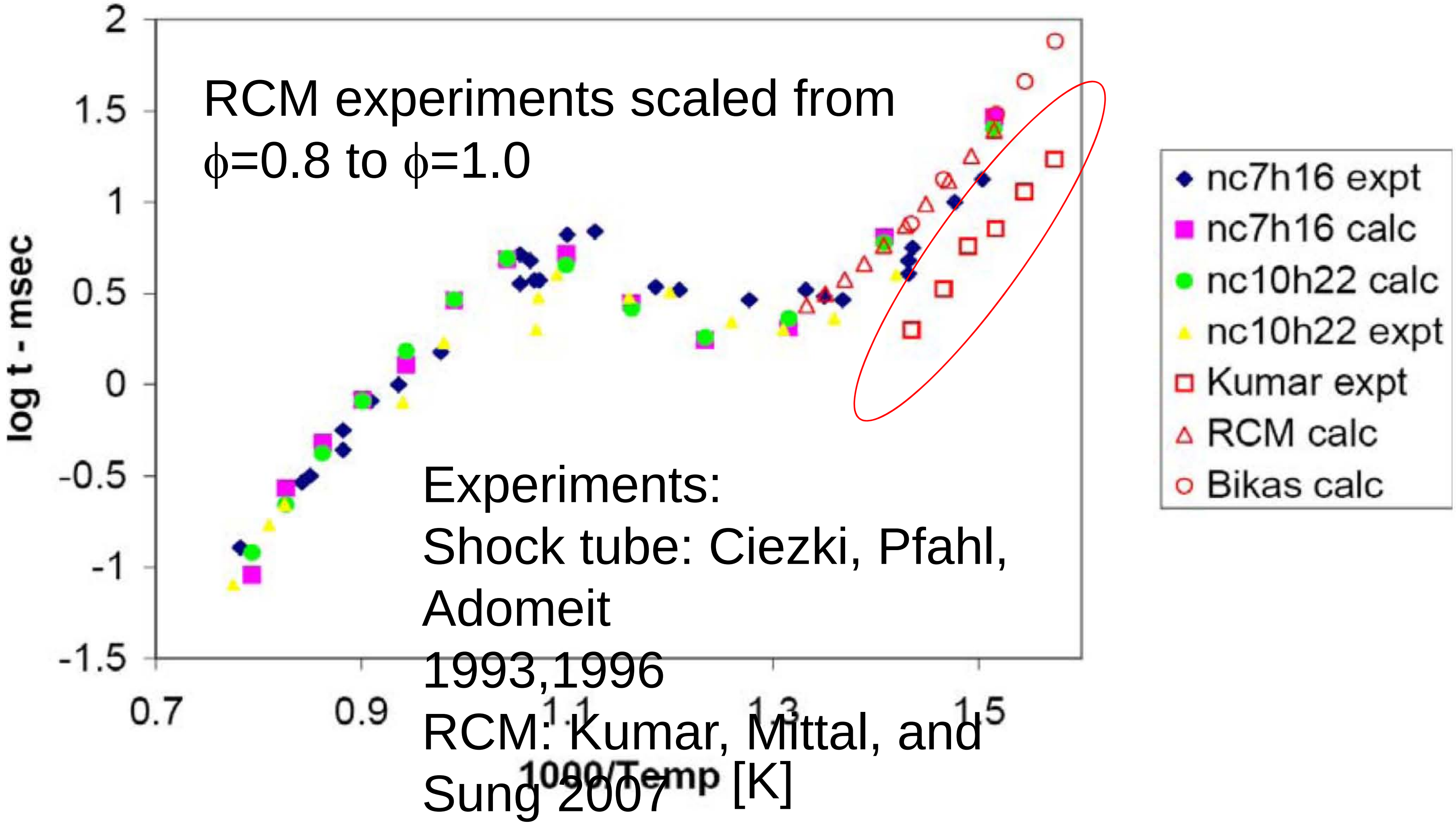
Good agreement with ignition delay times at "engine-like" conditions over the low to high temperature regime in the shock tube


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

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

Comparison to rapid compression machine data which is at “engine-like” conditions (14.3 bar, n-decane)

Experimental Validation Data

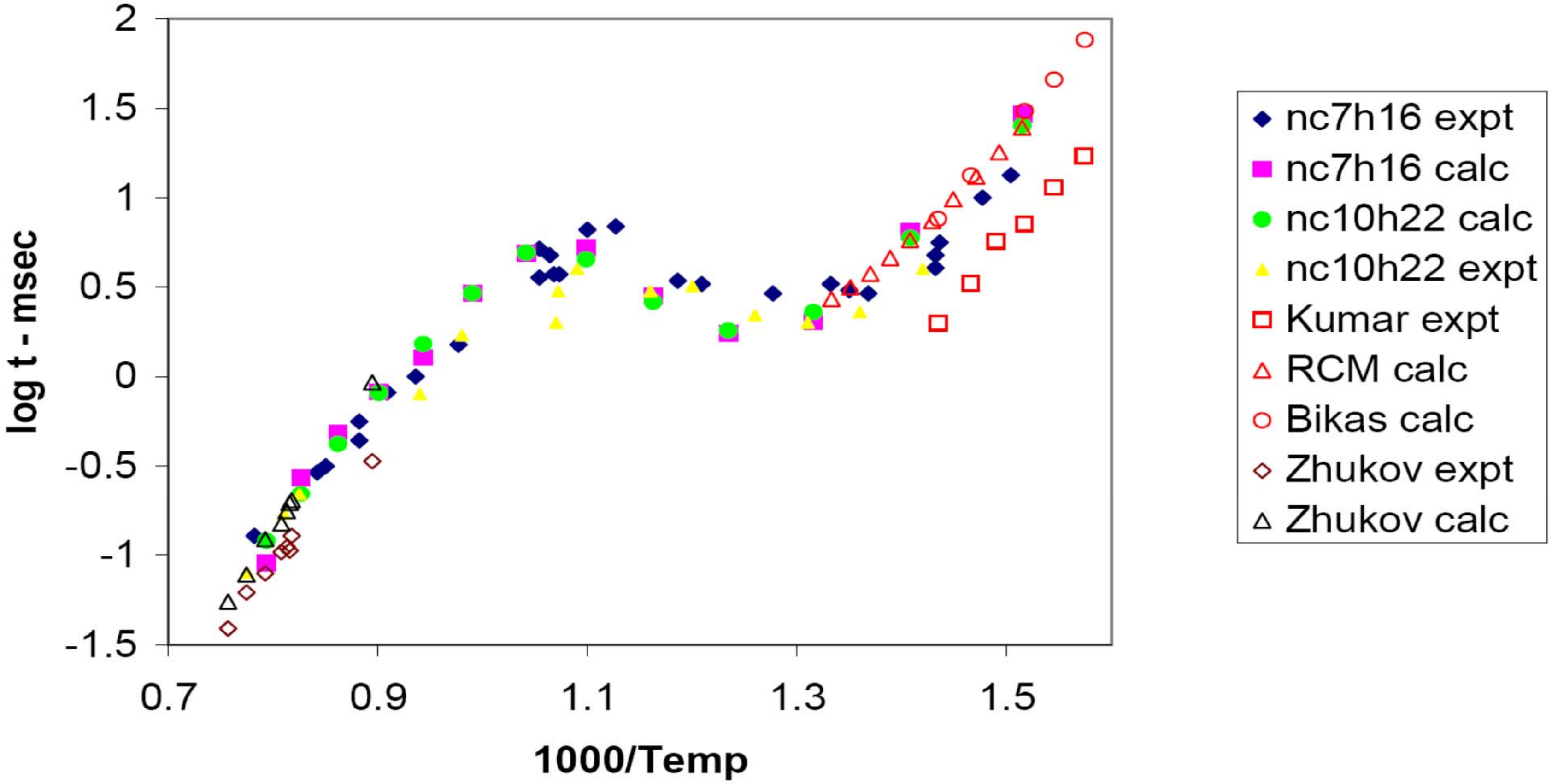


RCM experiments scaled from ϕ=0.8 to ϕ=1.0

Experiments:
Shock tube: Ciezki, Pfahl, Adomeit 1993,1996
RCM: Kumar, Mittal, and Sung 2007

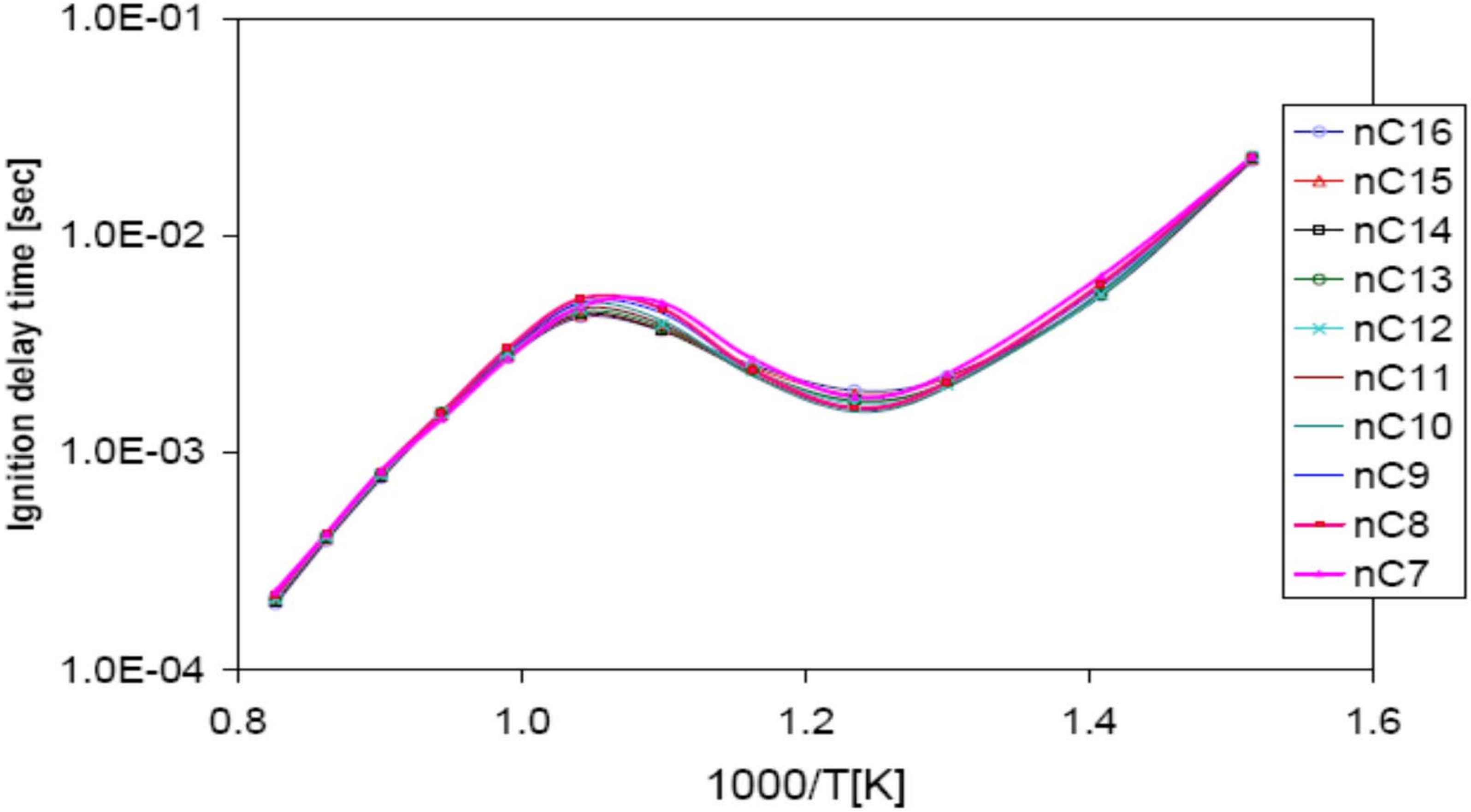
Family of ignition simulations – a valuable analysis tool

n-decane, ϕ = 1.0, 13 bar pressure

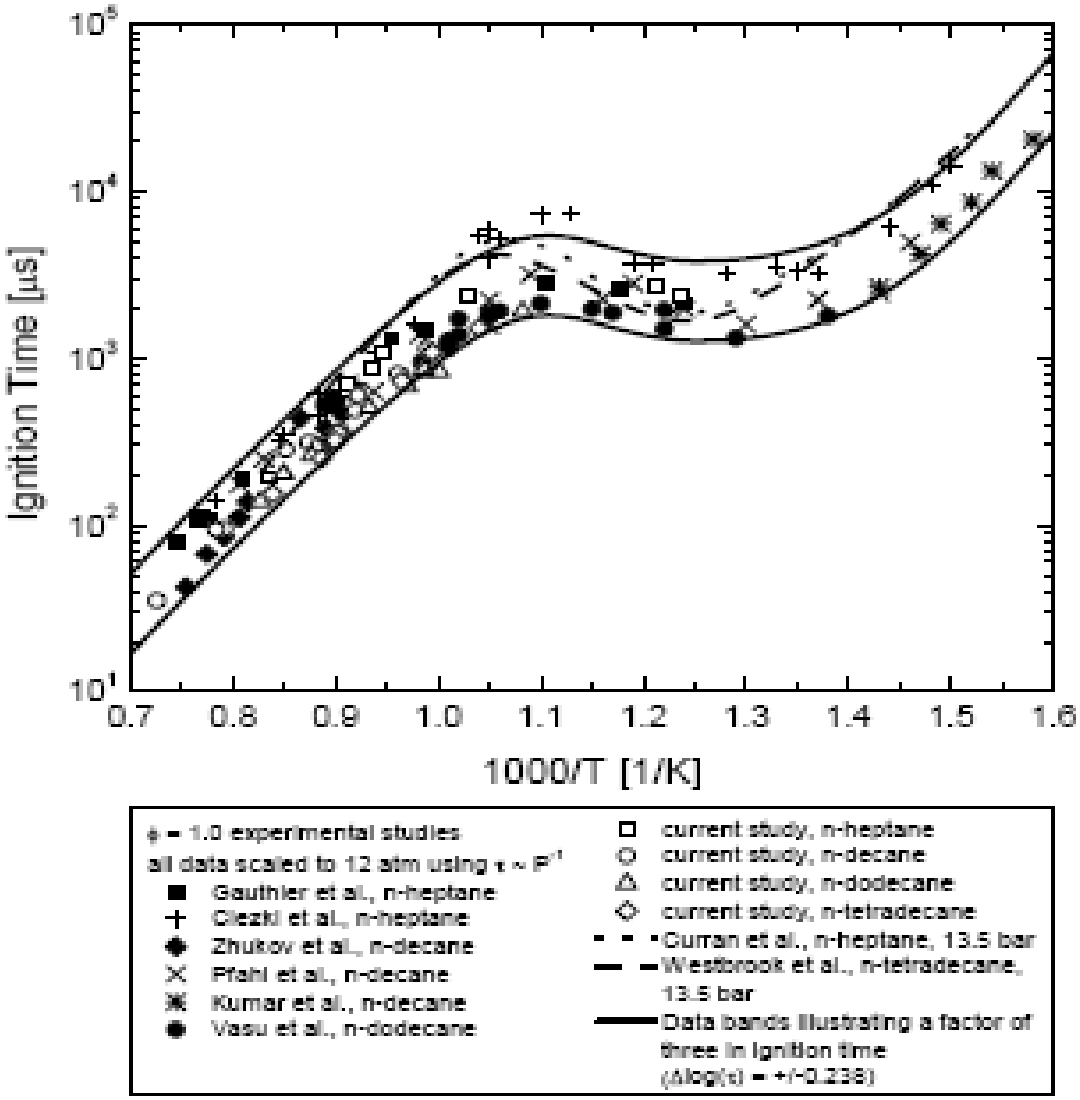


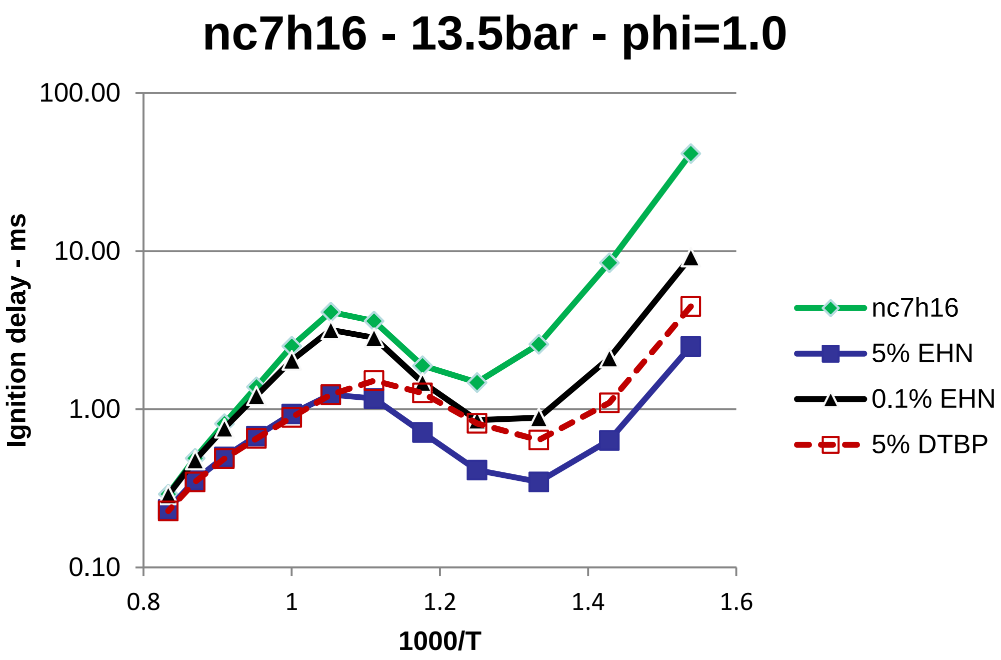
Same approach used by Petersen et al. for propane ignition analyses

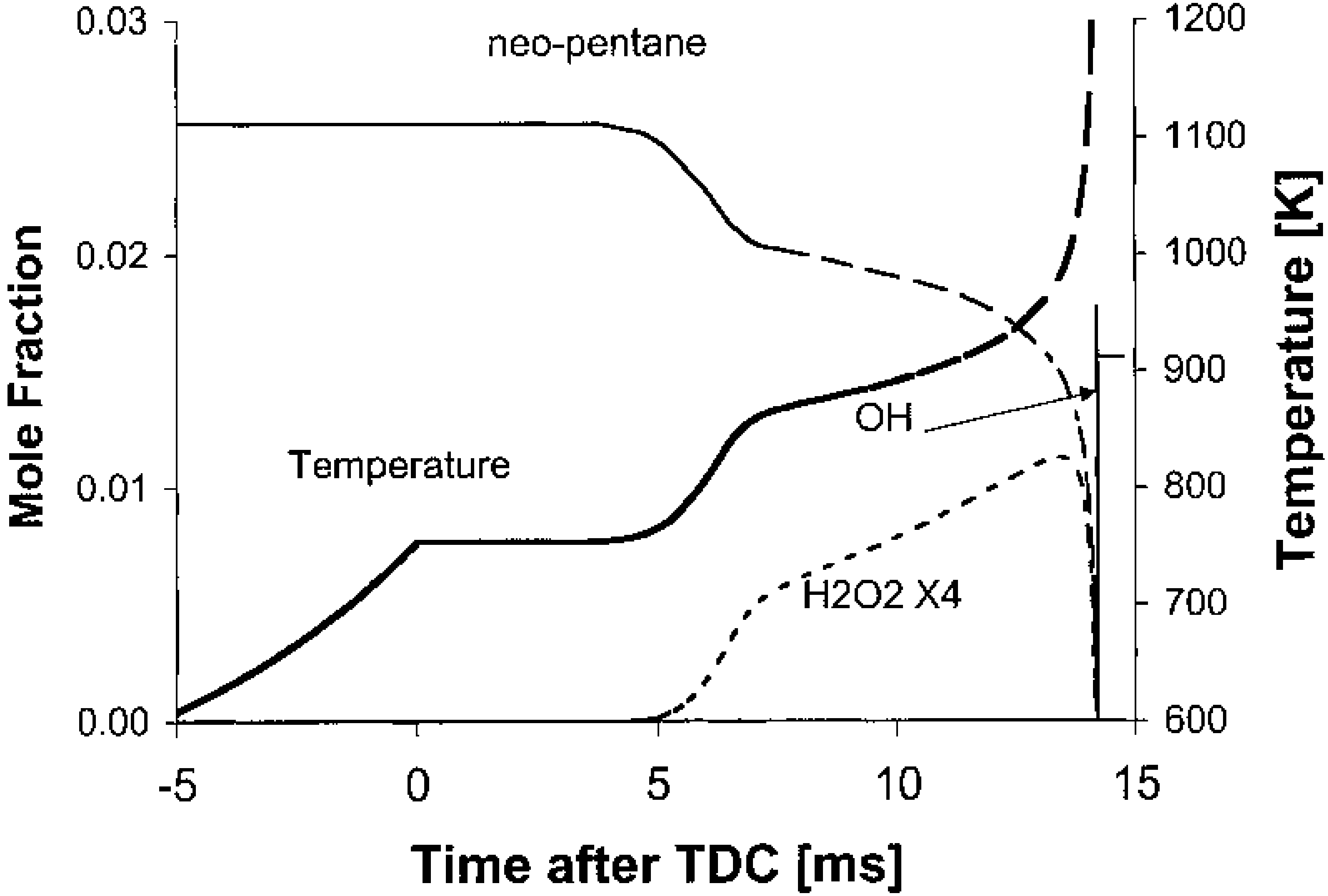
All large n-alkanes have very similar ignition properties



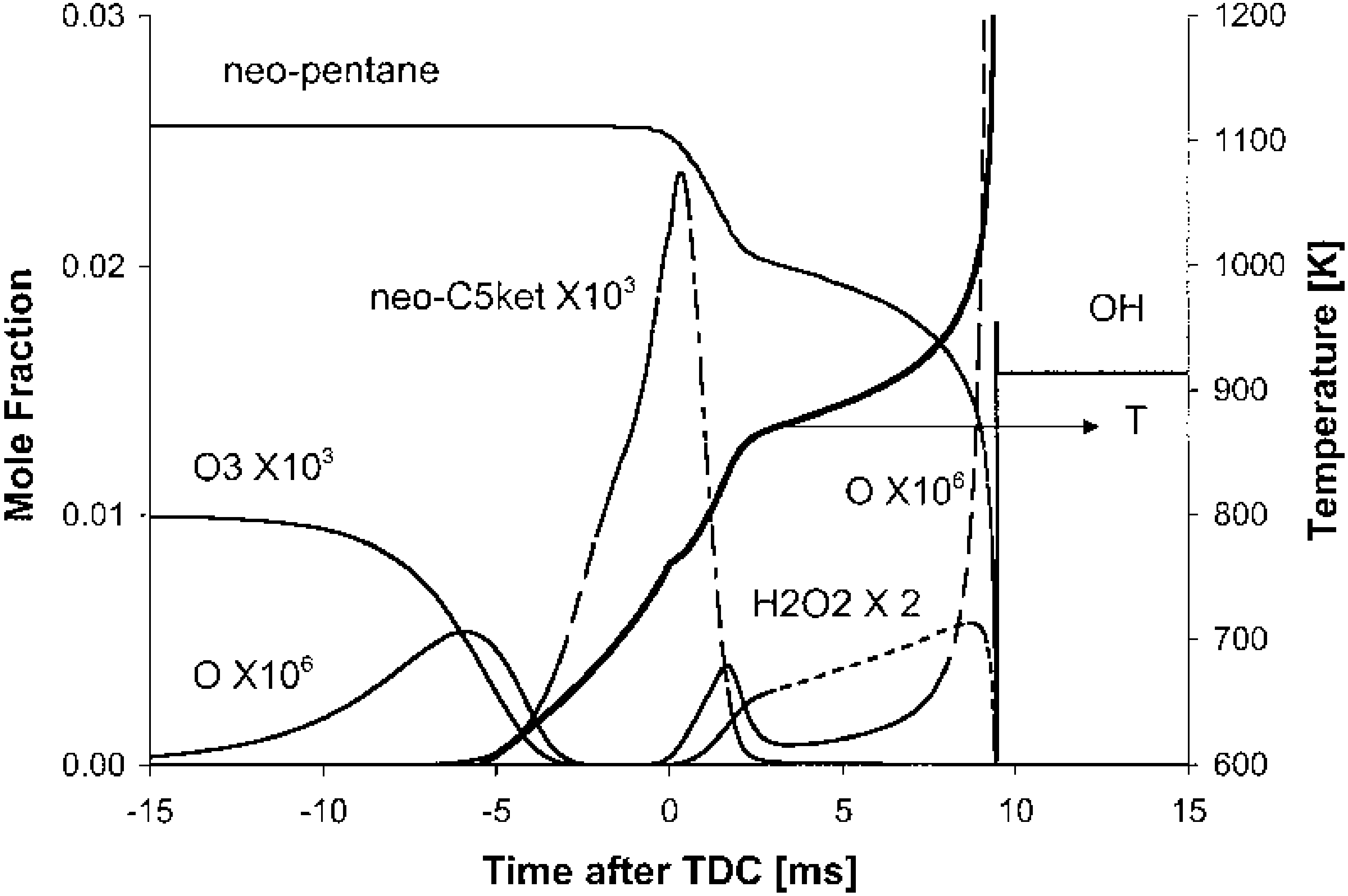
New experiments agree with our computer predictions




nc7h16 - 13.5bar - phi=1.0
100.00
10.00
1.00
0.10
Ignition delay - ms
0.8
1
1.2
1.4
1.6
1000/T
nc7h16
5% EHN
0.1% EHN
5% DTBP

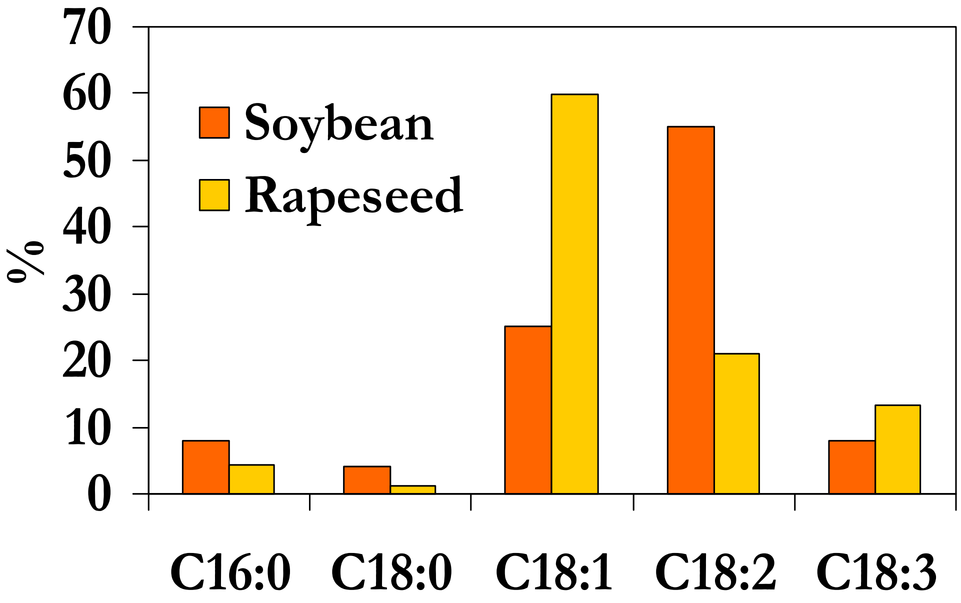


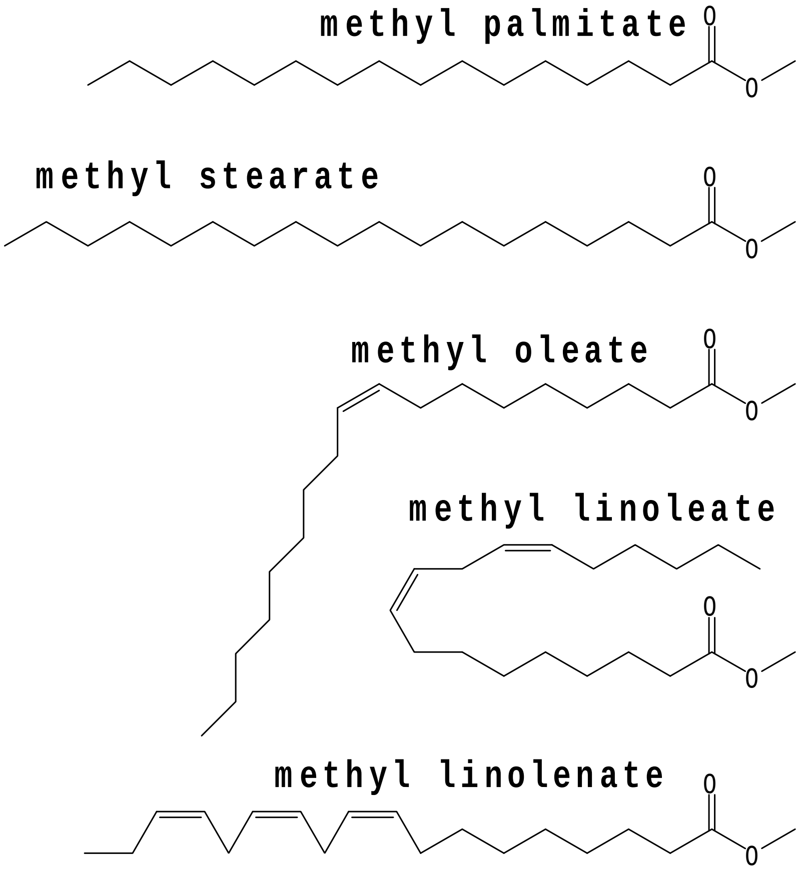
neo-pentane
Temperature
OH
H2O2 X4
Mole Fraction
0.03
0.02
0.01
0.00
Temperature [K]
1200
1100
1000
900
800
700
600
-5
0
5
10
15
Time after TDC [ms]



neo-pentane
neo-C5ket X10^3
OH
T
O3 X10^3
O X10^6
H2O2 X 2
O X10^6
Mole Fraction
0.03
0.02
0.01
0.00
Temperature [K]
1200
1100
1000
900
800
700
600
-15
-10
-5
0
5
10
15
Time after TDC [ms]

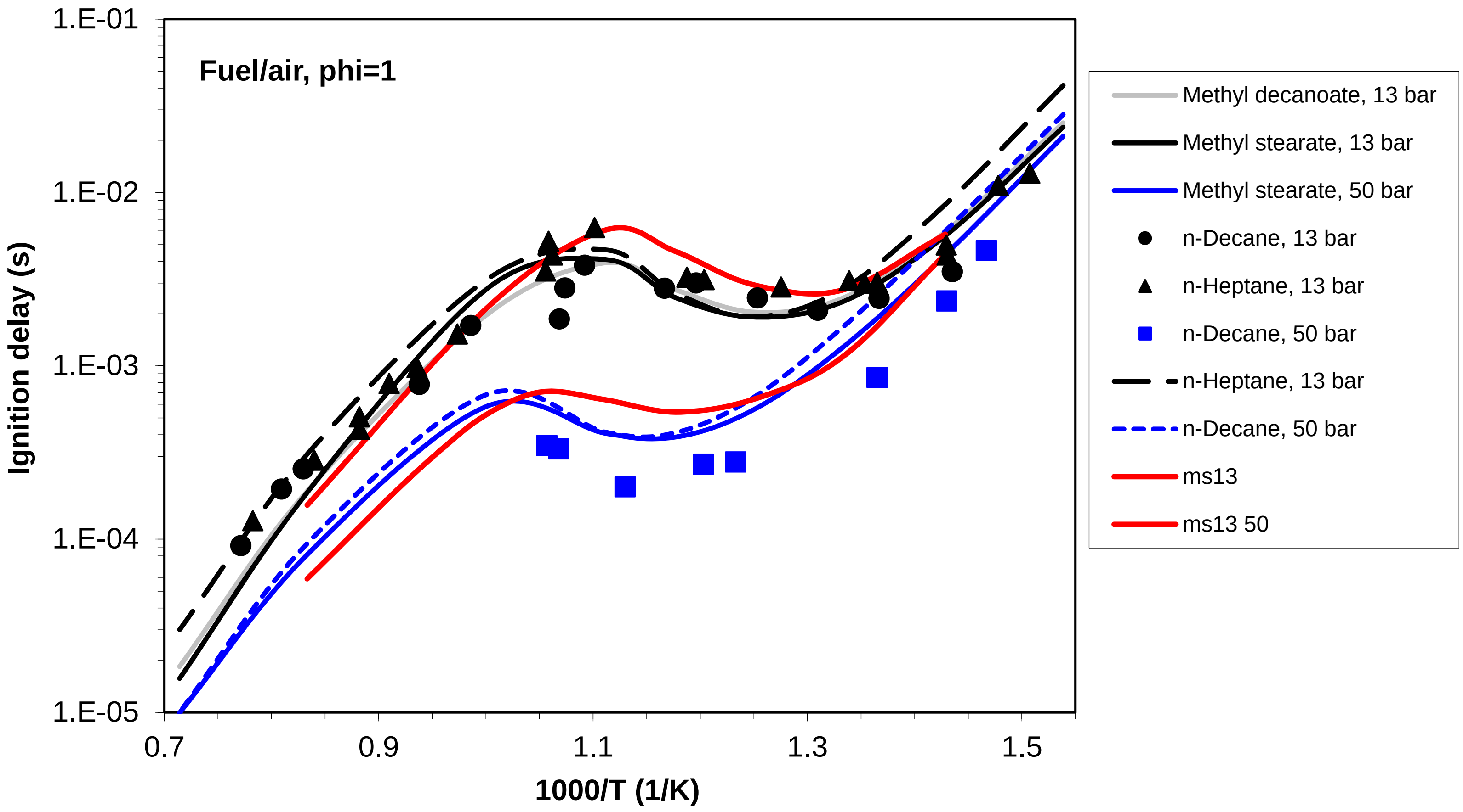
Composition of Biodiesels



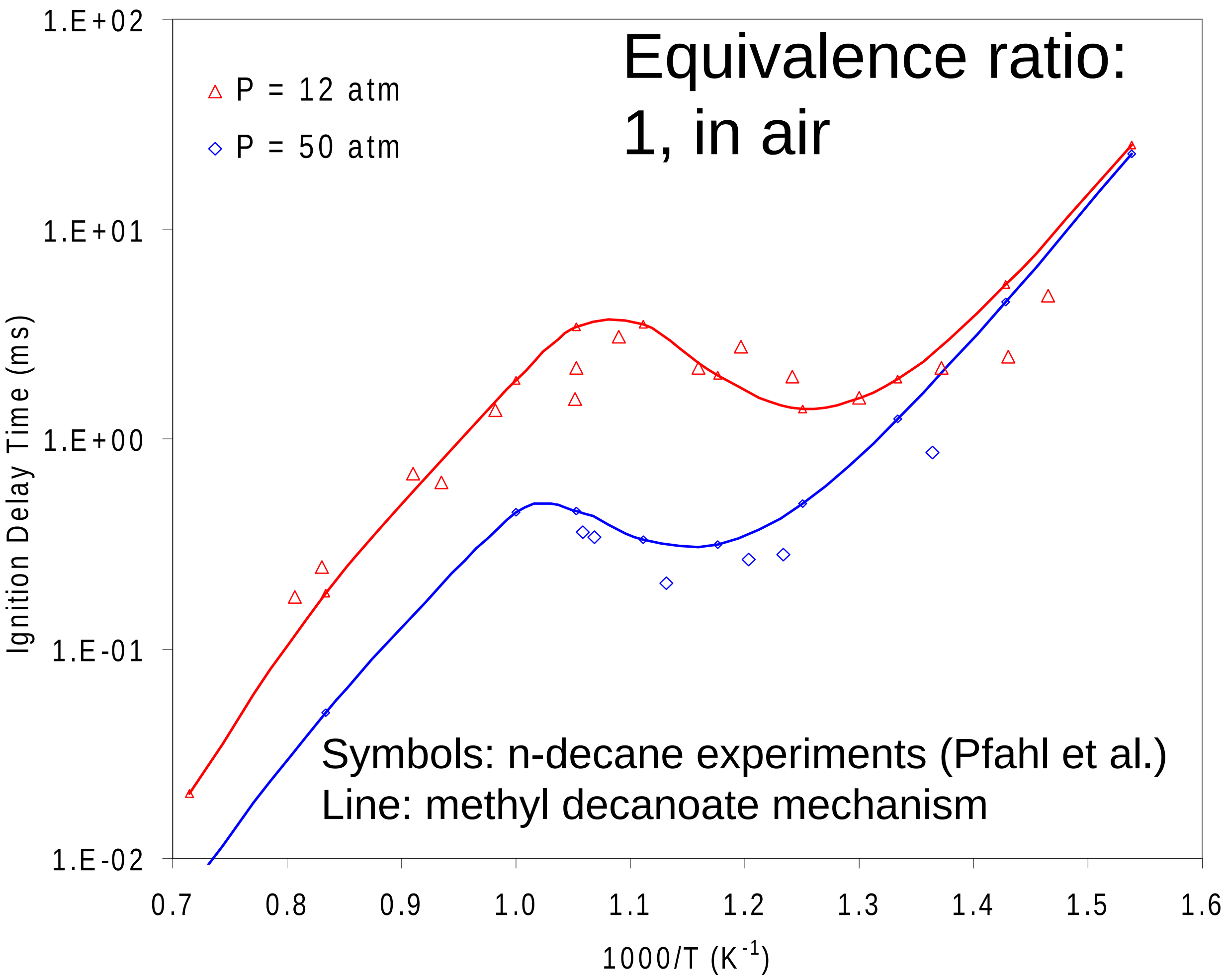


Biodiesel fuels can be made from vegetable oils such as soy, palm, flaxseed, canola, and olive oil and animal fats

Methyl stearate (n-C_{18} methyl ester) has the same ignition properties as large alkanes



Comparison with n-Decane Ignition Delay Times



Equivalence ratio: 1, in air

Symbols: n-decane experiments (Pfahl et al.)
Line: methyl decanoate mechanism

Ignition delay times very close

n-Alkanes:

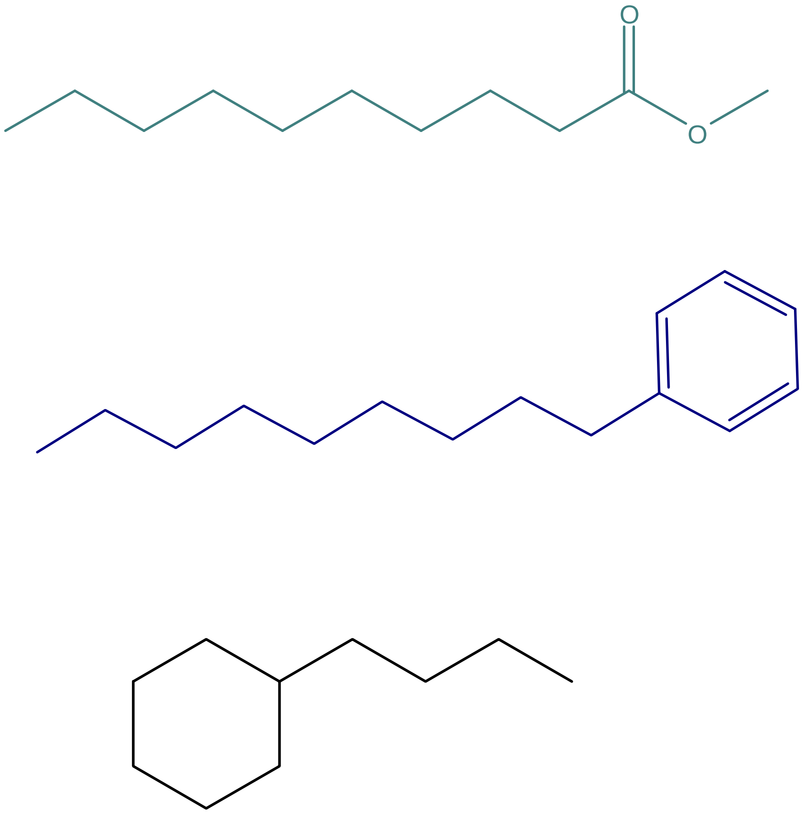
cannot reproduce the early formation of CO_2

but

reproduce the reactivity of methyl esters very well

Interesting note

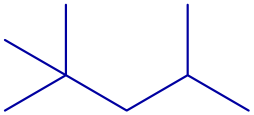
Experience with biodiesel and methyl esters suggests strategies for kinetic modeling of n-alkyl benzenes and n-alkyl cyclohexanes



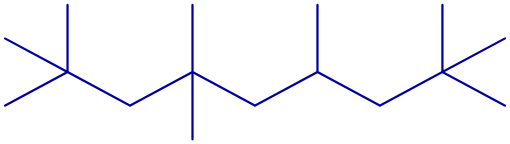
Branched hydrocarbons are different

- Both octane and cetane rating systems have a straight-chain reference fuel that is easy to ignite and a branched reference fuel that is hard to ignite
- iso-octane and 2,2,4,4,6,8,8-heptamethyl nonane
- n-heptane and n-hexadecane
- Are all branched hydrocarbons as similar to each other as the straight-chain hydrocarbons?
- Very few laboratory experiments available for mechanism validation of HMN
- Base a reaction mechanism on previous sets of reaction classes

- Iso-octane

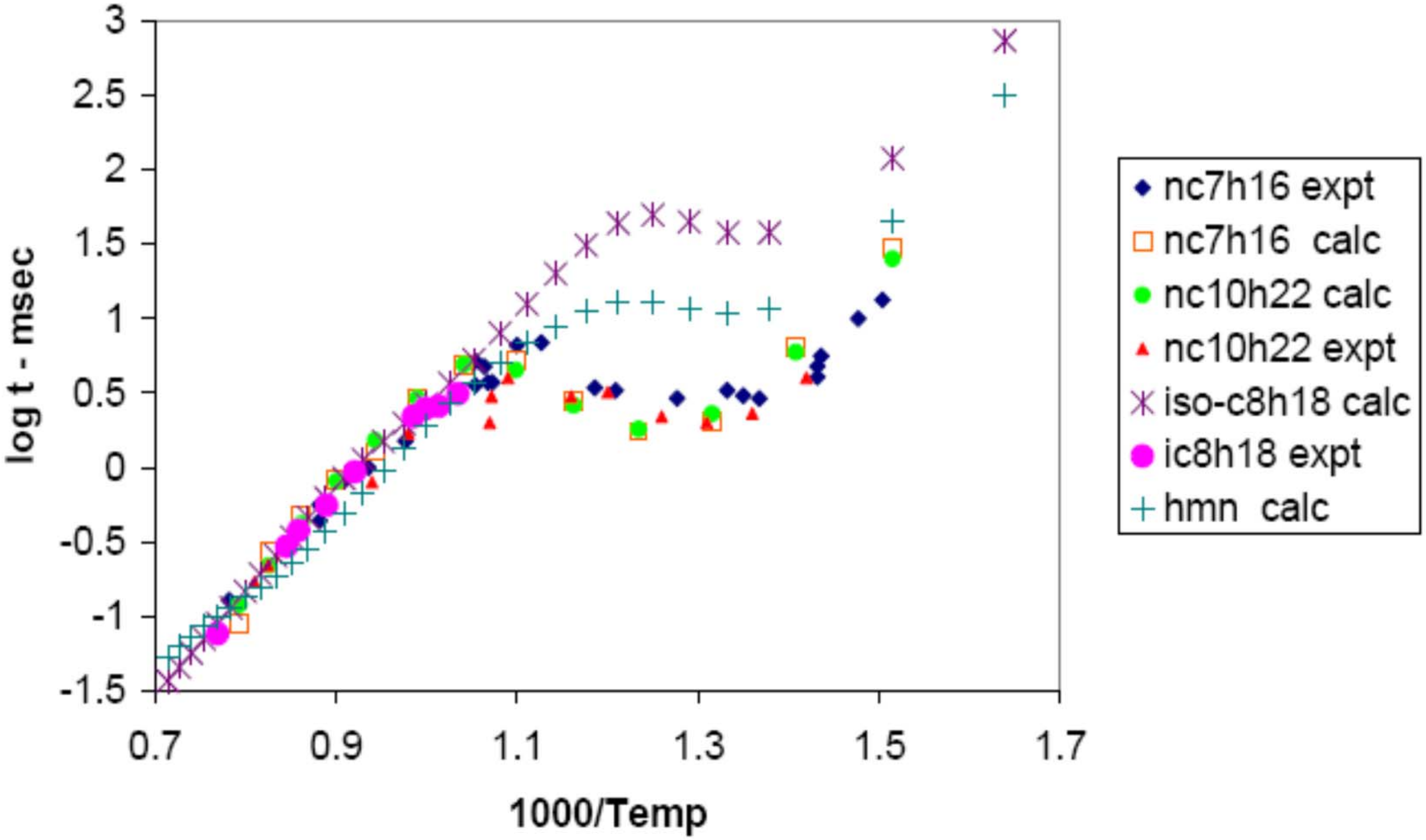


- 2,2,4,4,6,8,8 heptamethylnonane (iso

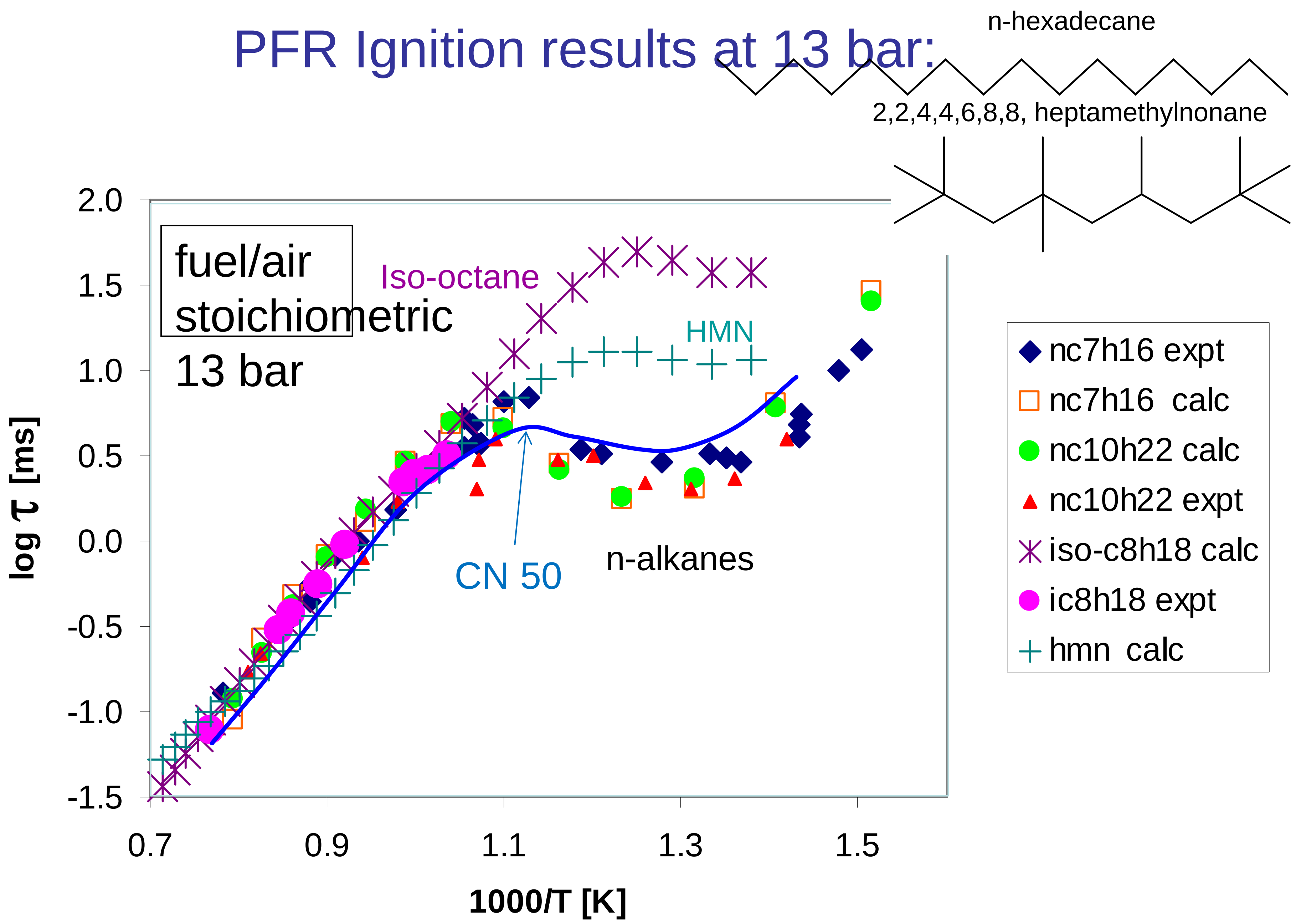


HMN and iso-octane ignite slower than n-alkanes only in the Low Temperature regime

13.5 bar pressure



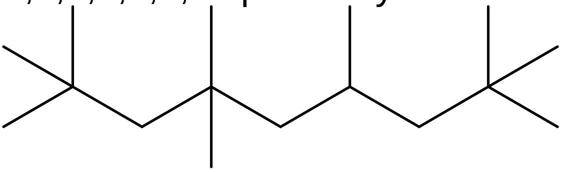
PFR Ignition results at 13 bar:

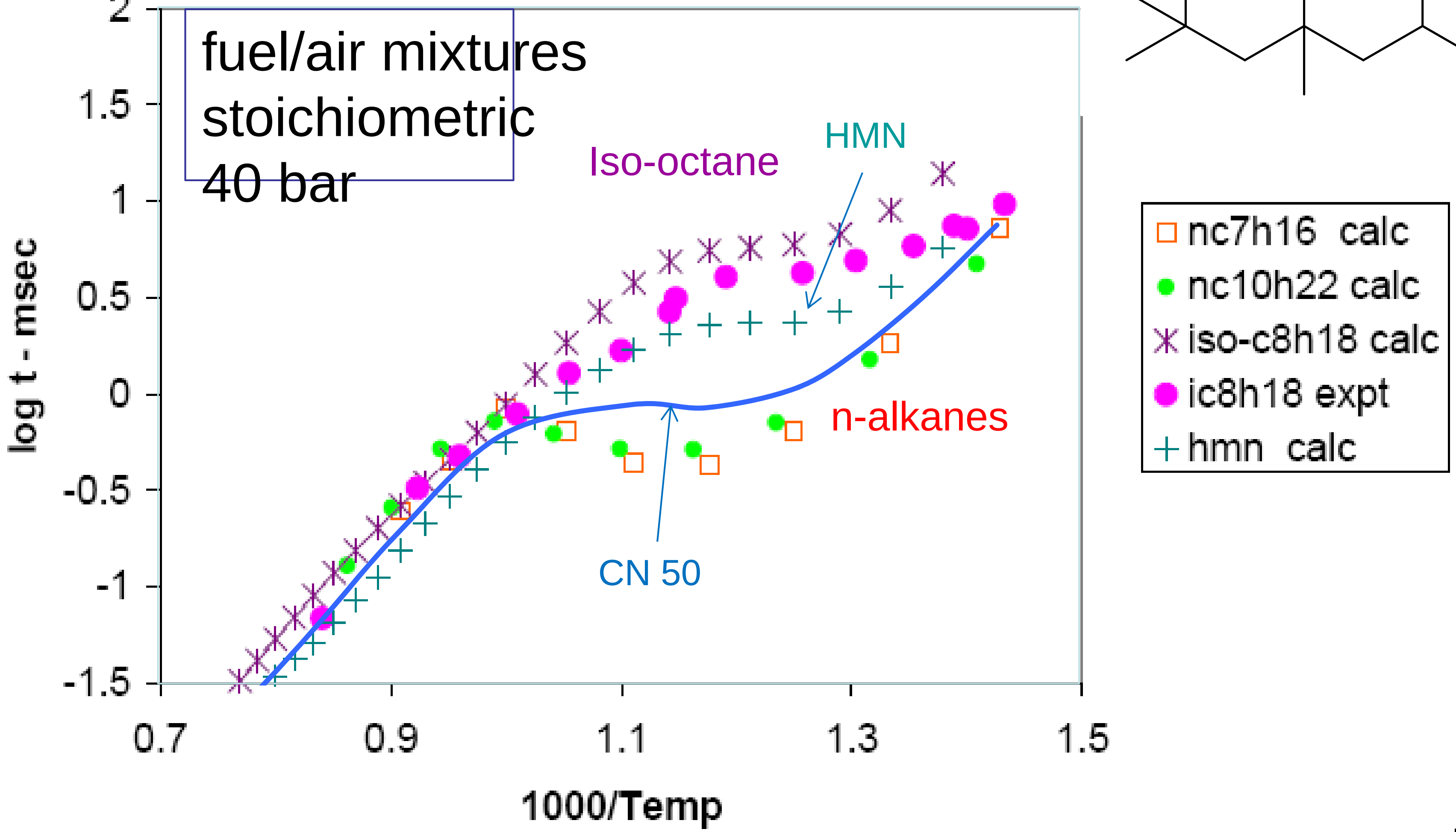


PFR Ignition results at 40 bar:

n-hexadecane

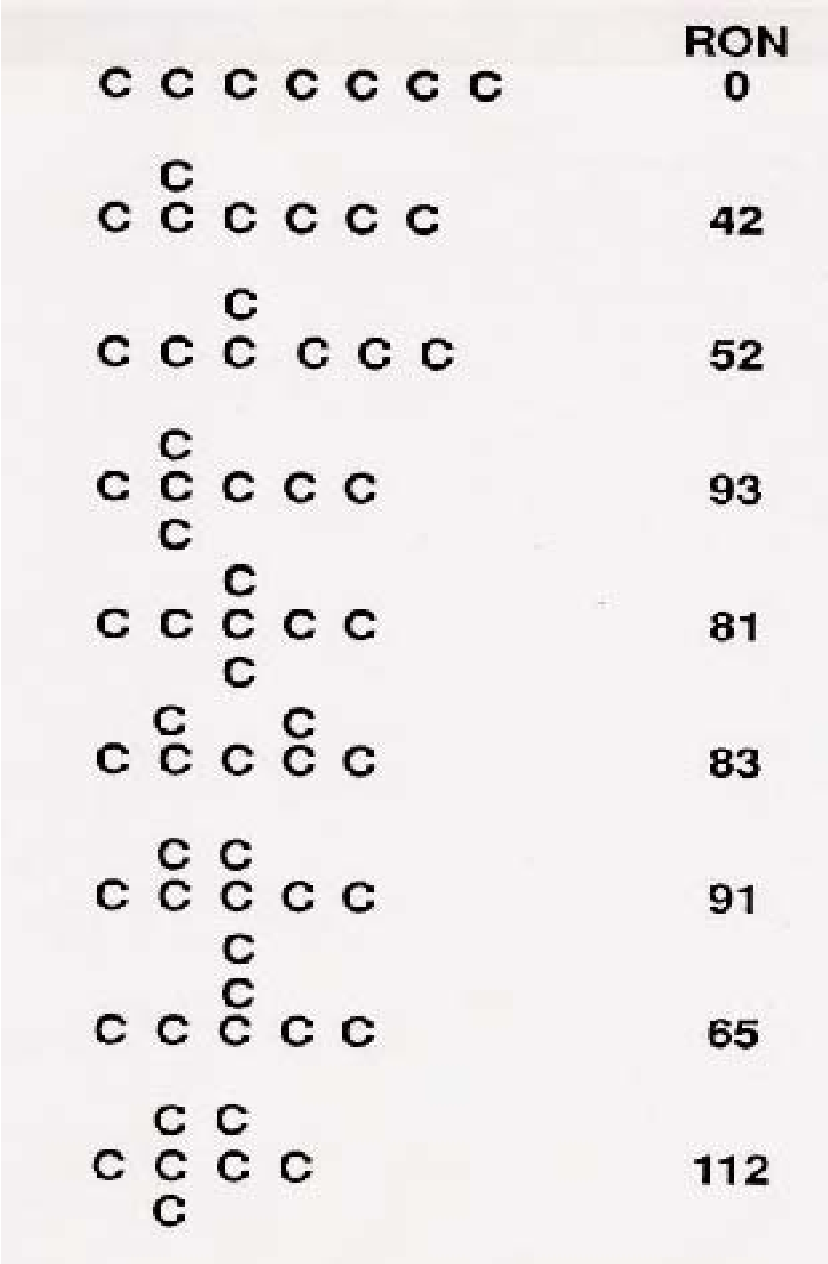
2,2,4,4,6,8,8, heptamethylnonane



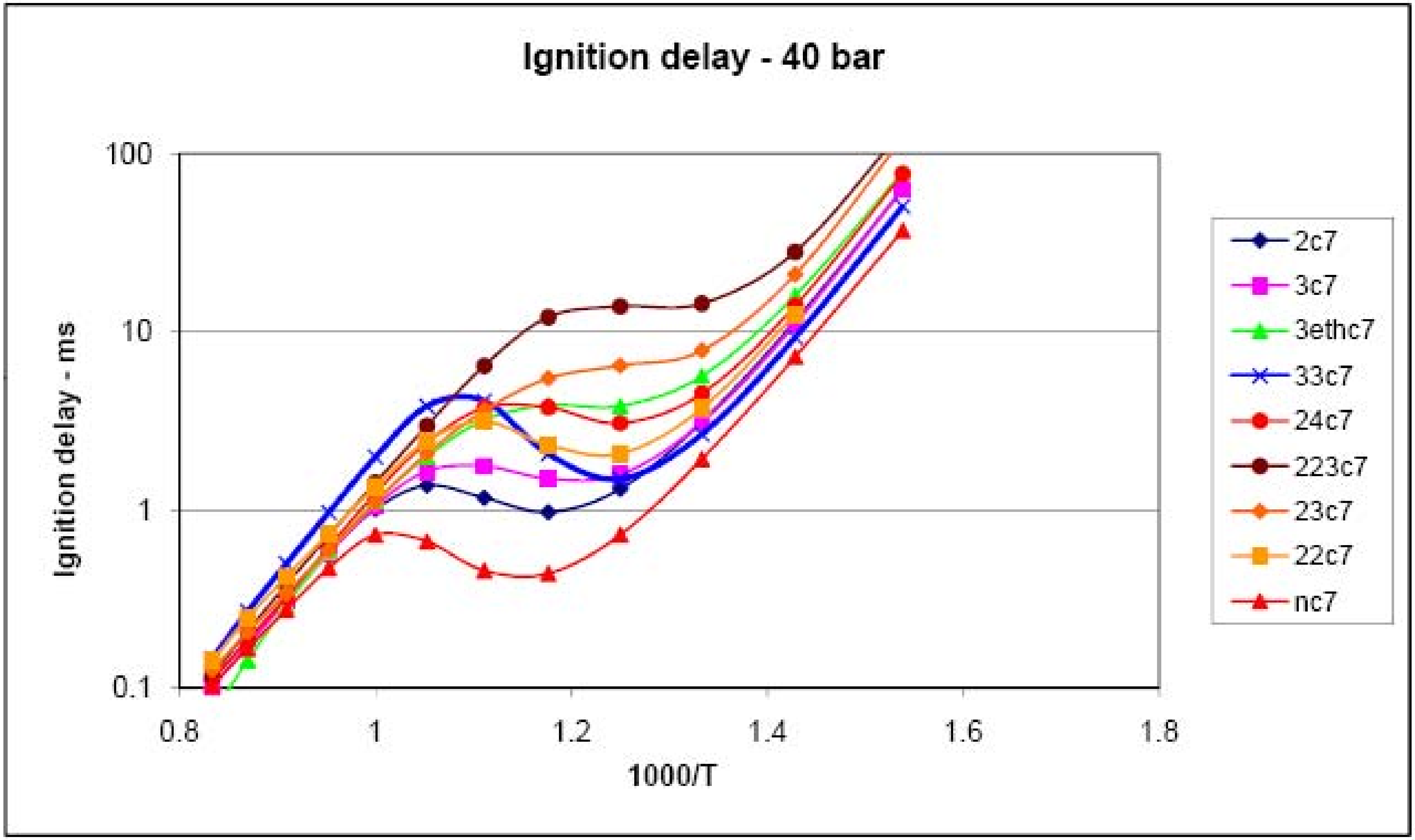


Octane numbers of heptanes are due exclusively to their different molecular structures

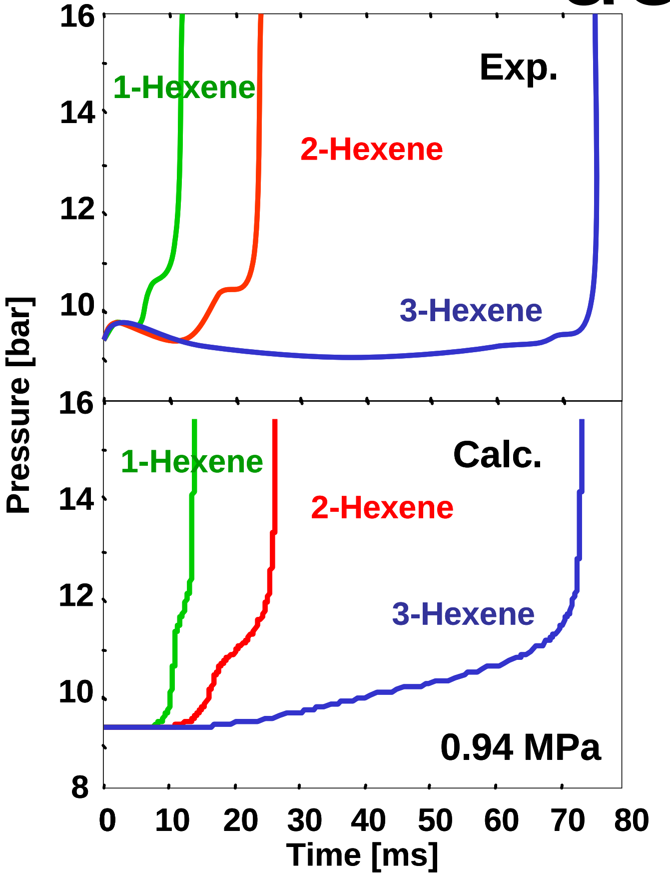
Low octane fuels have lots of secondary C-H bonds and high octane fuels have lots of primary C-H bonds and lots of tight, 5-membered TS rings

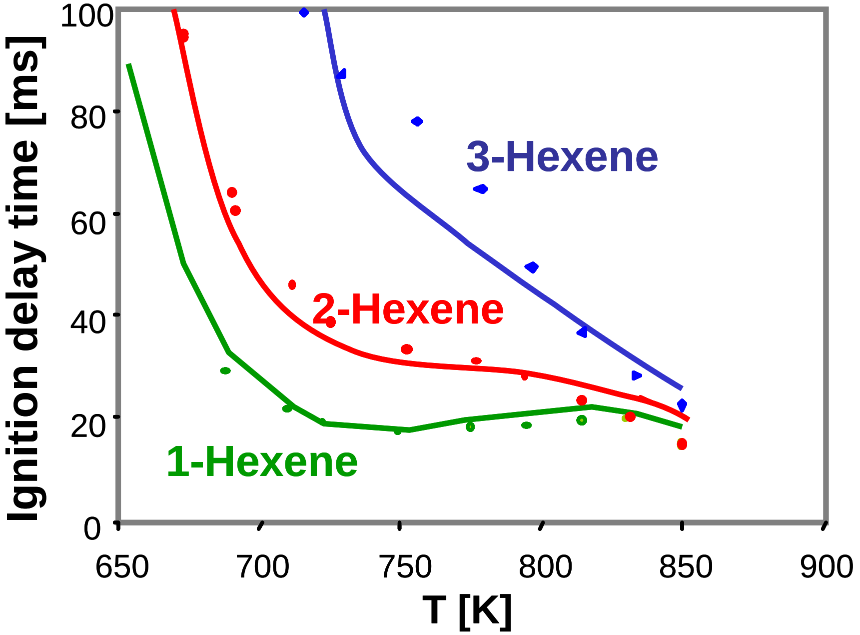


Heptane isomers provide an interesting family of fuels
RON varies from 0 to 112



Effect of the position of the double bond



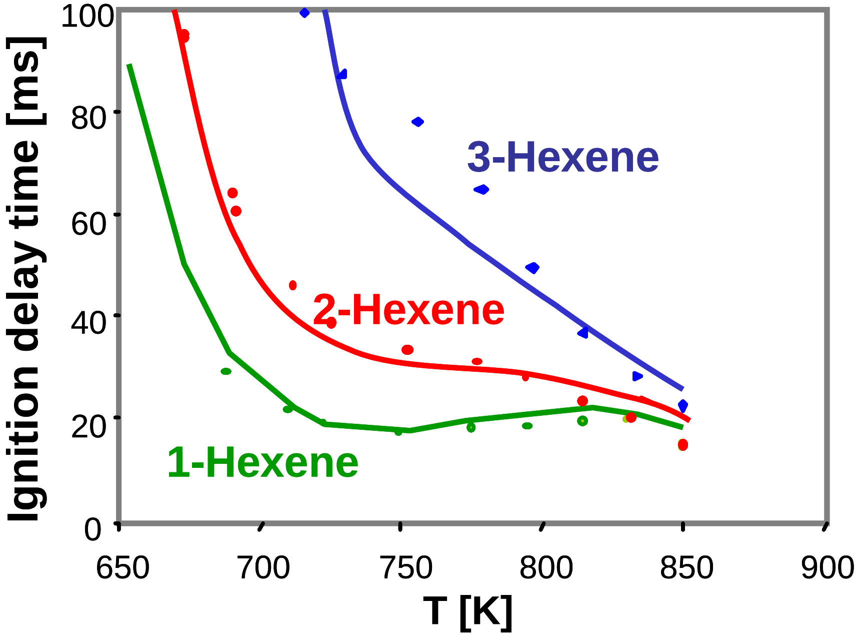


The length of the free saturated carbon chain determines the reactivity

C = C - C - C - C - C 1-hexene

C - C = C - C - C - C 2 – hexene

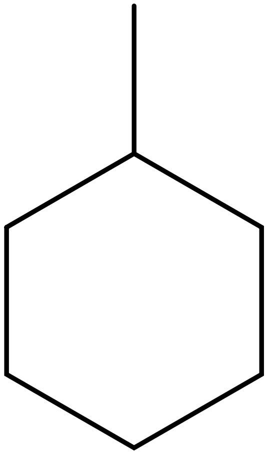
C - C - C = C - C - C 3 – hexene



RCM Ignition delay times of hexene isomers (0.86-1.09 MPa, Φ=1):

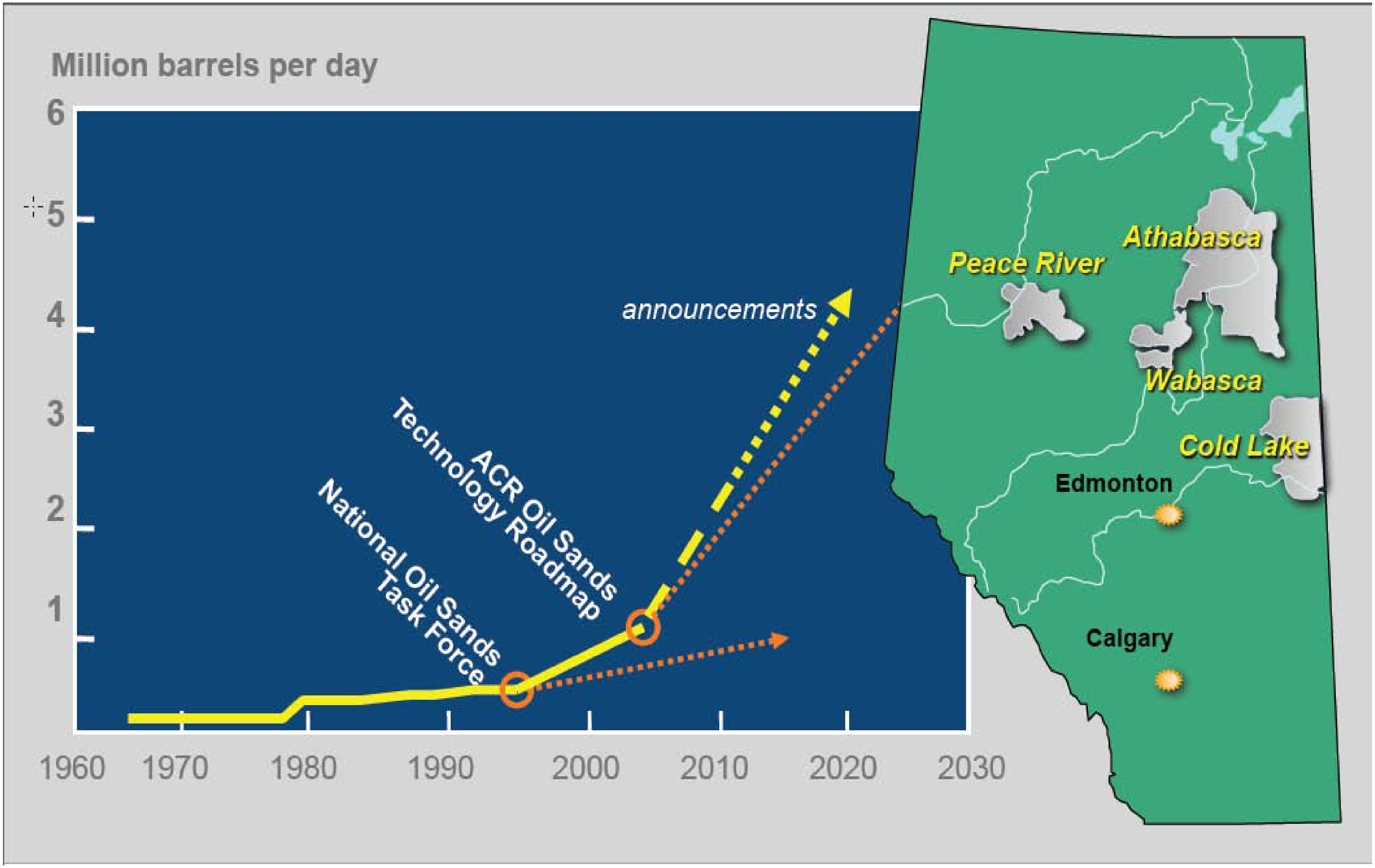
Cycloalkanes: methyl cyclohexane

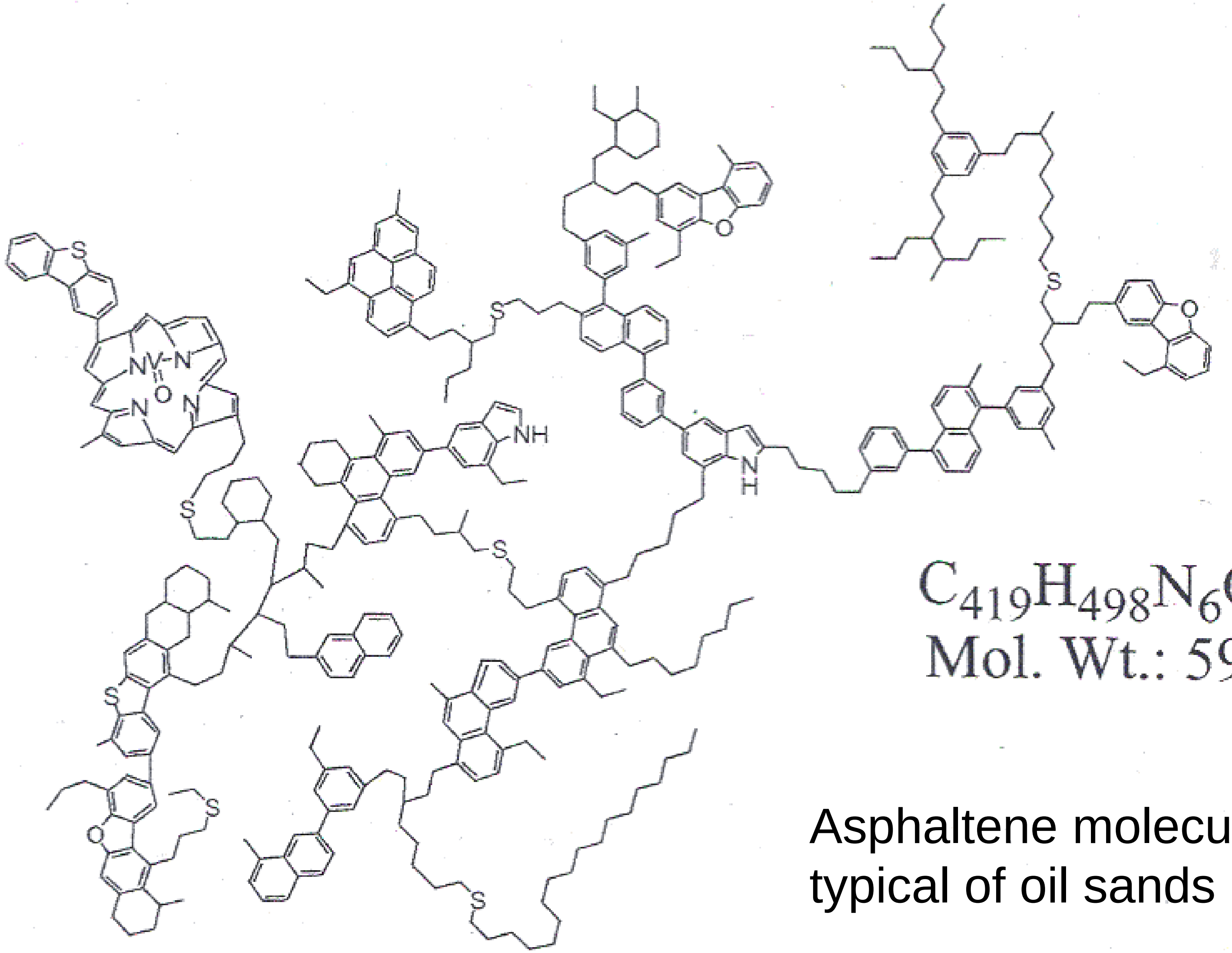
- Cycloalkanes are interesting due to oil sands
- Cycloalkanes are present in most practical fuels and surrogate fuels



methylcyclohexane

Oil-sand derived fuels have focused attention on cyclo-alkanes

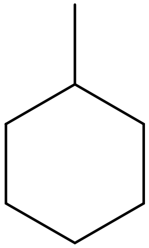




$C_{419}H_{498}N_6O_4S_8V$
Mol. Wt.: 5989.94

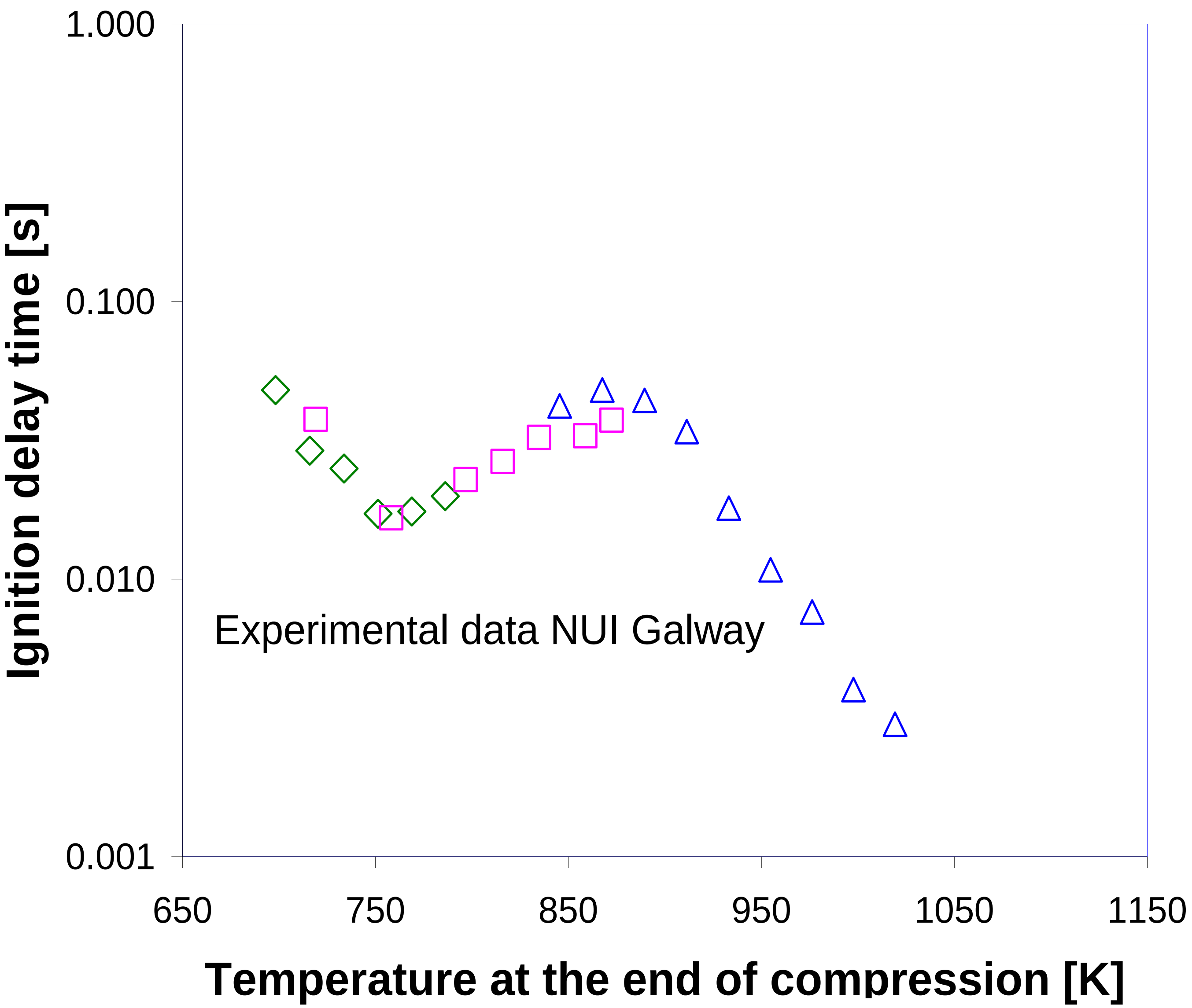
Asphaltene molecule
typical of oil sands

Experiments: Rapid compression machine (RCM) at NUI Galway

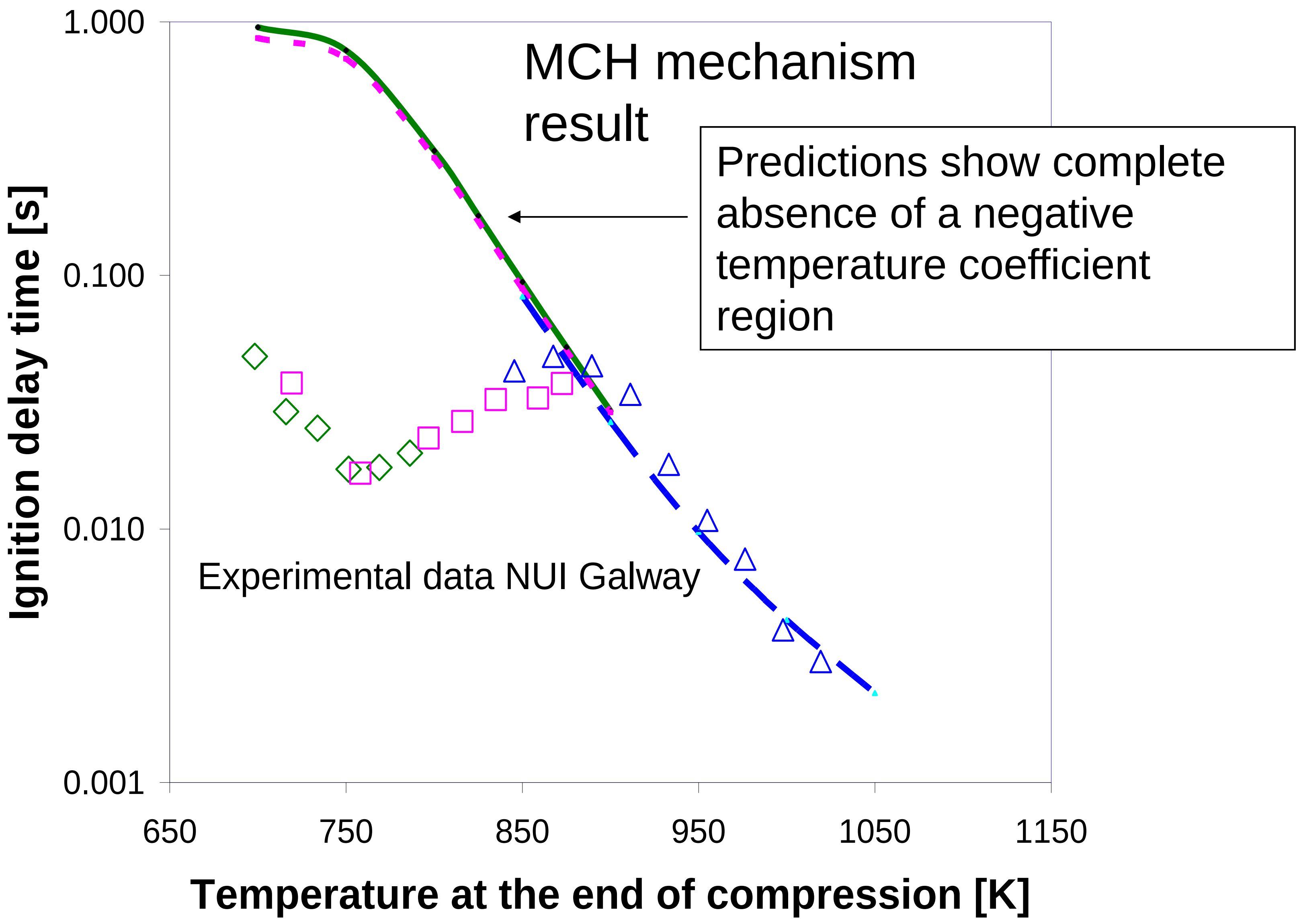


- Opposed piston RCM originally used by Shell
  - => fast compression times of about 16 ms
- Large crevice on perimeter of piston to contain wall boundary layer
  - =>uniform temperatures across combustion chamber
- Use N_2 and Ar as diluents to attain range of compressed gas temperatures
- Stoichiometric mixtures of $MCH/O_2/Ar/N_2$
- 10,15 and 20 atm pressure at the end of compression.

Experimental data at 10 atm shows distinct NTC region:



N-alkane based RO2 isomerization rates gave too slow ignition delay times in rapid compression machine at low temperatures:



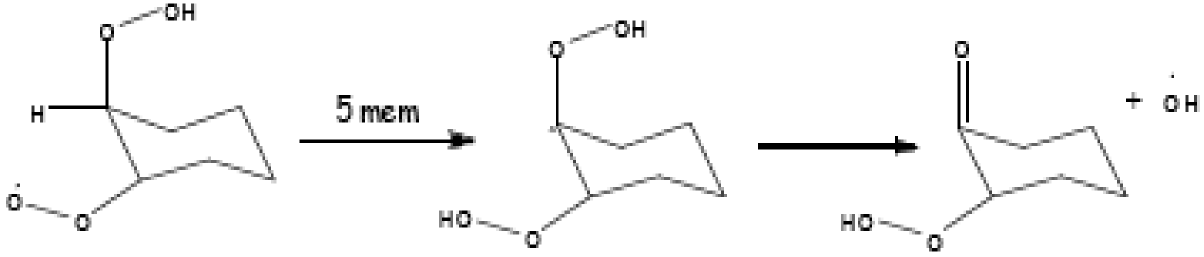
MCH mechanism result

Predictions show complete absence of a negative temperature coefficient region

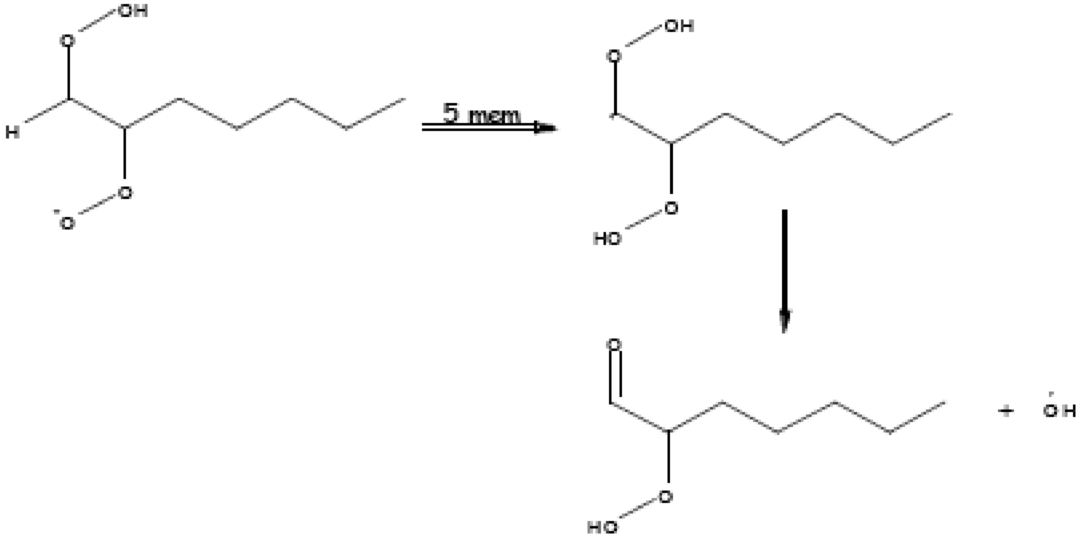
Experimental data NUI Galway

Rates of important isomerization reactions were estimated by comparison with known reactions for alkanes

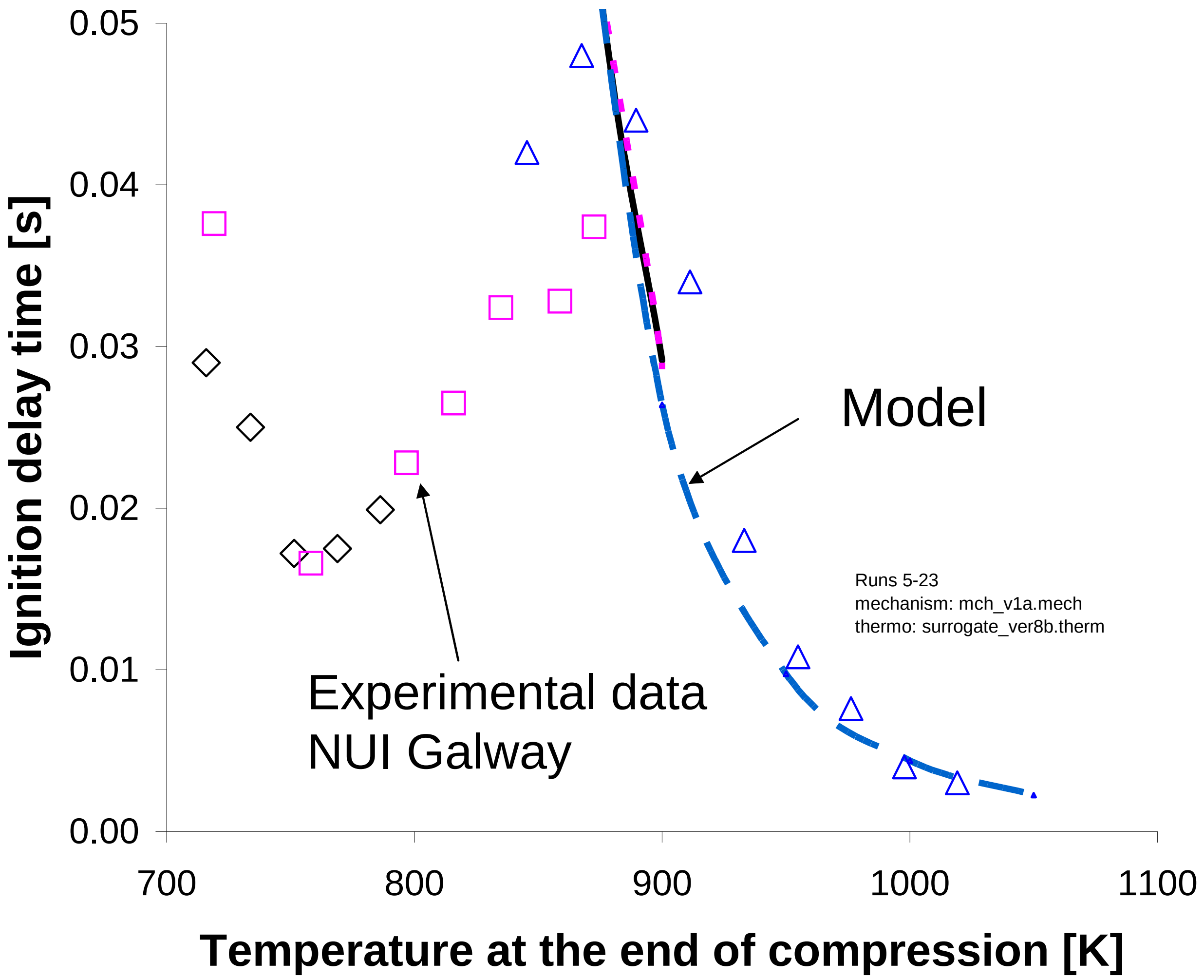
CHX



nH



Comparisons with rapid compression machine results shows predicted low temperature chemistry for MCH is too slow

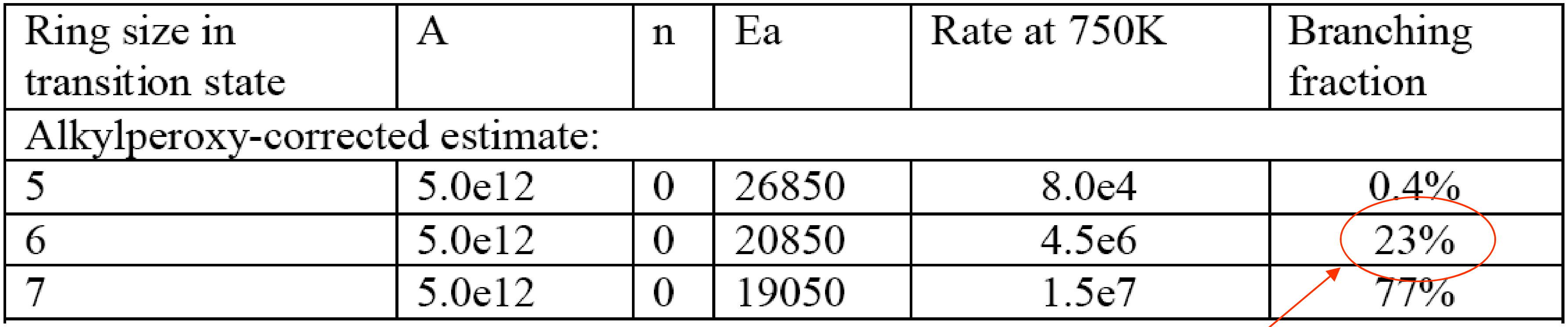


Model

Experimental data
NUI Galway

Runs 5-23
mechanism: mch_v1a.mech
thermo: surrogate_ver8b.therm

Examine RO2 isomerization rate constants based on n-alkane rates:



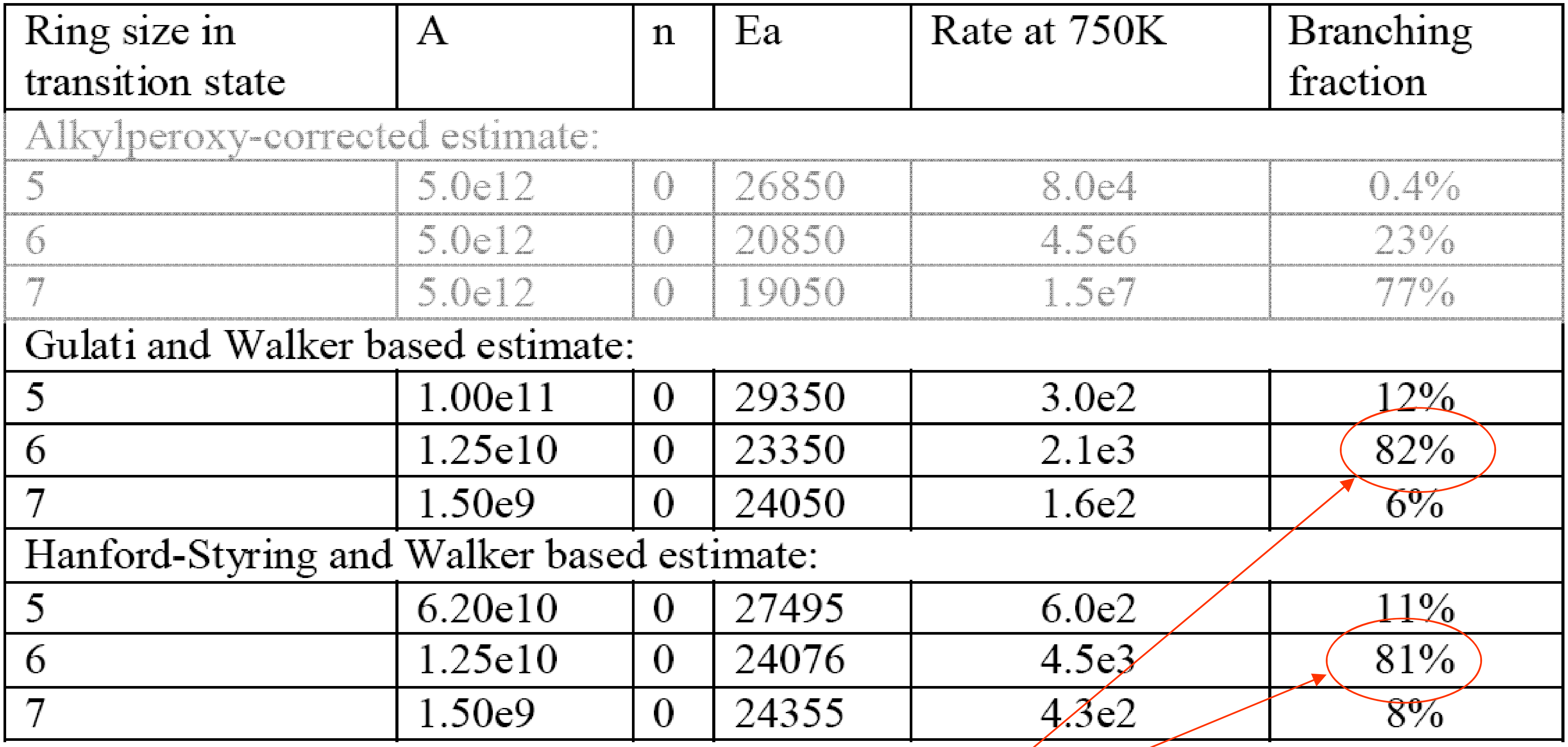
Ring size in transition state	A	n	Ea	Rate at 750K	Branching fraction
Alkylperoxy-corrected estimate:					
5	5.0e12	0	26850	8.0e4	0.4%
6	5.0e12	0	20850	4.5e6	23%
7	5.0e12	0	19050	1.5e7	77%

Small fraction going to six membered ring that leads to chain branching

Walker et al. had carried out low temperature kinetic experiments on simple cycloalkanes.

- Small amounts of cyclohexane added to H2/O2
- Derived cyclohexylperoxy (RO2) isomerization rates from initial products observed

Experimentally-based RO2 isomerization rate constants give lots of 6 membered rings and chain branching:



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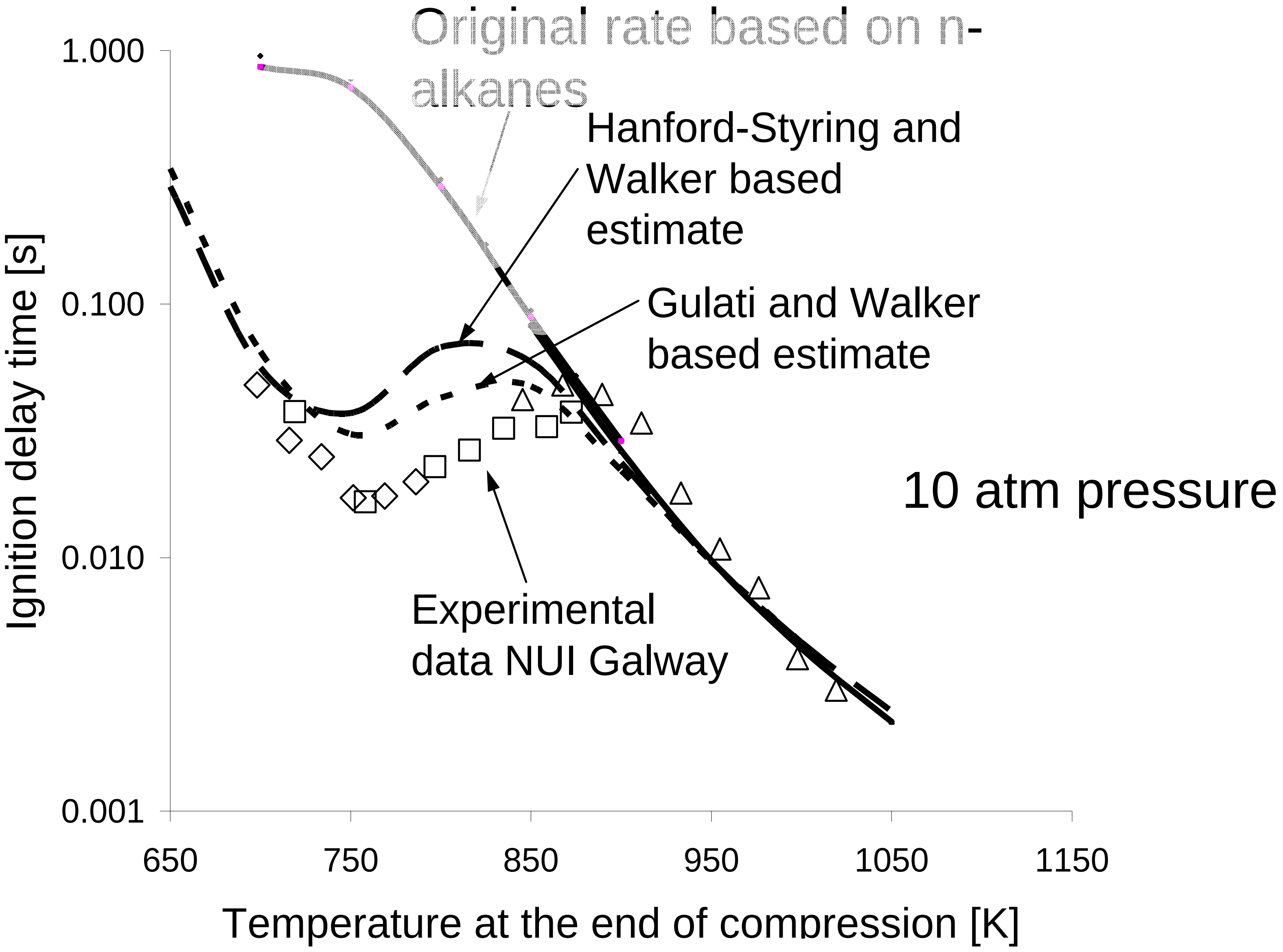
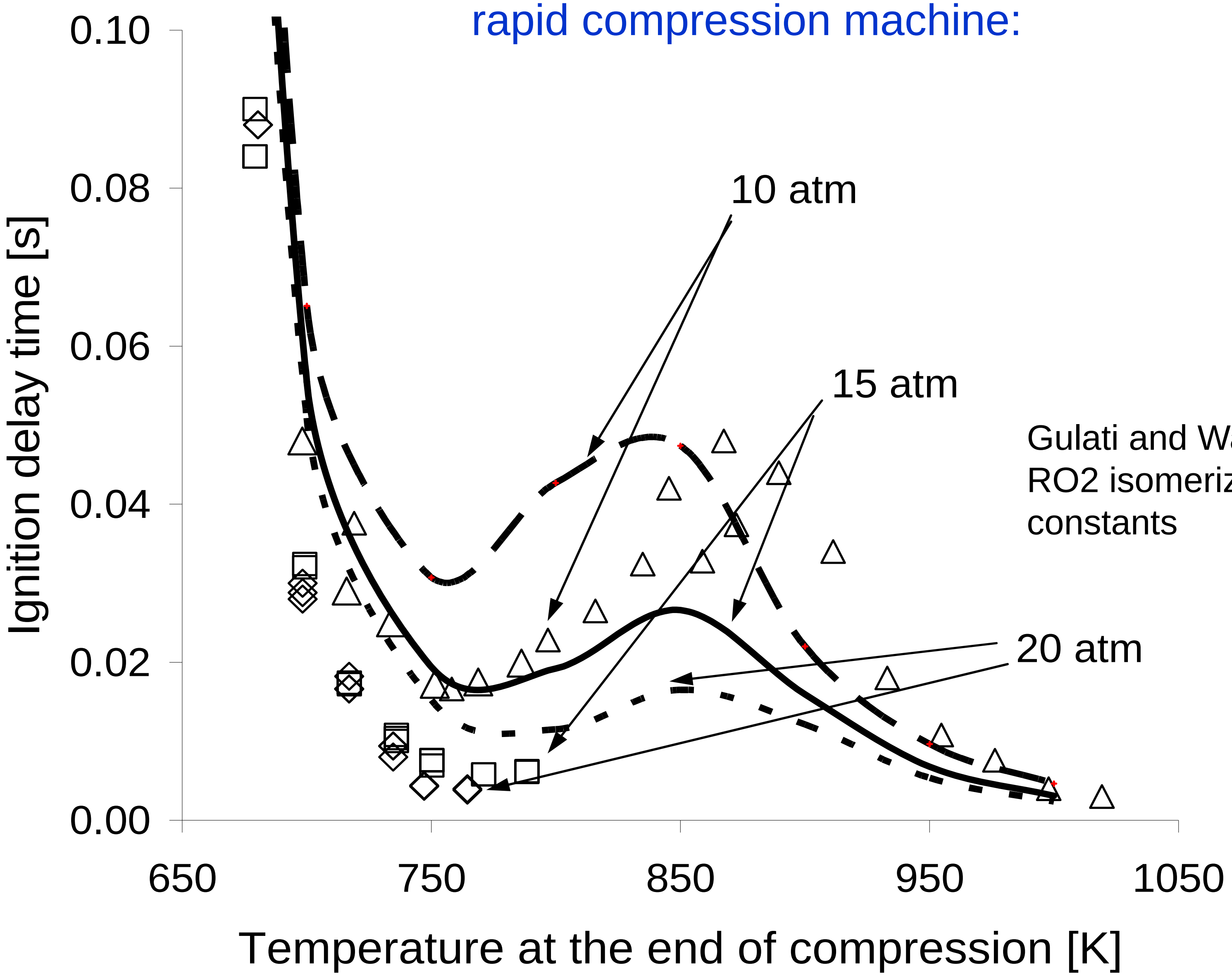
5	5.0e12	0	26850	8.0e4	0.4%
6	5.0e12	0	20850	4.5e6	23%
7	5.0e12	0	19050	1.5e7	77%
Gulati and Walker based estimate:					
5	1.00e11	0	29350	3.0e2	12%
6	1.25e10	0	23350	2.1e3	82%
7	1.50e9	0	24050	1.6e2	6%
Hanford-Styring and Walker based estimate:					
5	6.20e10	0	27495	6.0e2	11%
6	1.25e10	0	24076	4.5e3	81%
7	1.50e9	0	24355	4.3e2	8%

Rate constants emphasize 6-membered rings

New MCH isomerization rates give good behavior for low temperature chemistry in rapid compression machine:

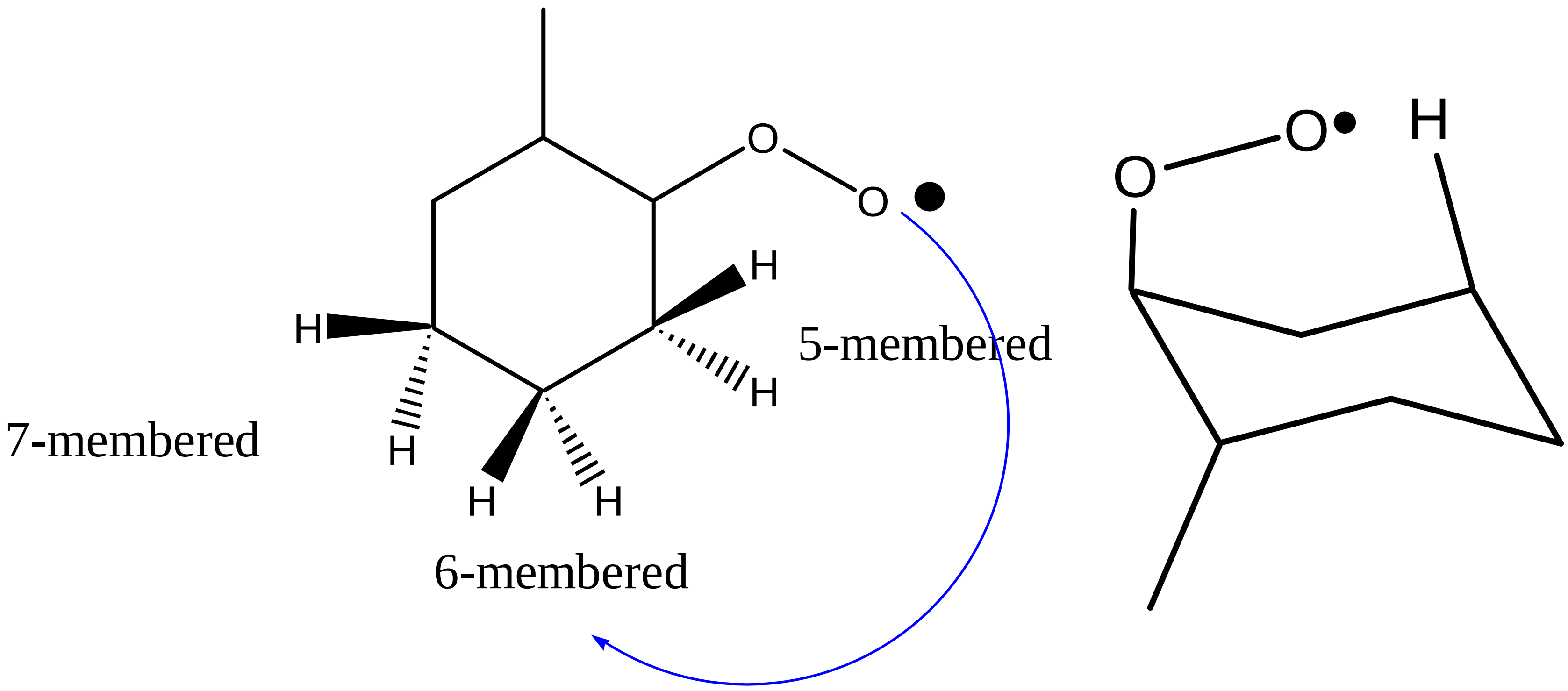


Behavior at other pressures also follows trends in rapid compression machine:



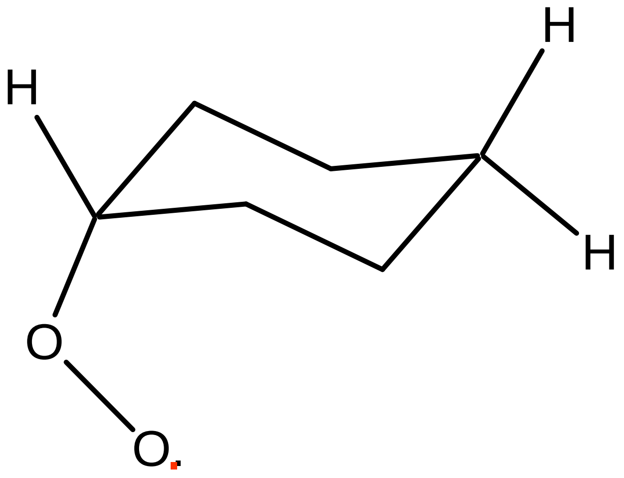
Gulati and Walker based
RO2 isomerization rate
constants

6-member ring RO_2 isomerization:

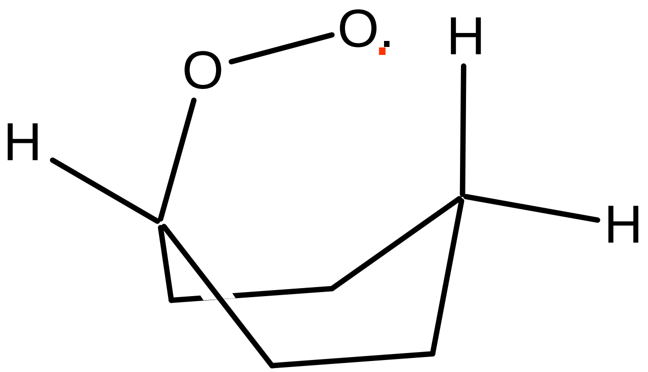


Low temperature RO_2 isomerizations are a key

Trans (chair) ring form of cyclohexylperoxy does not readily isomerize



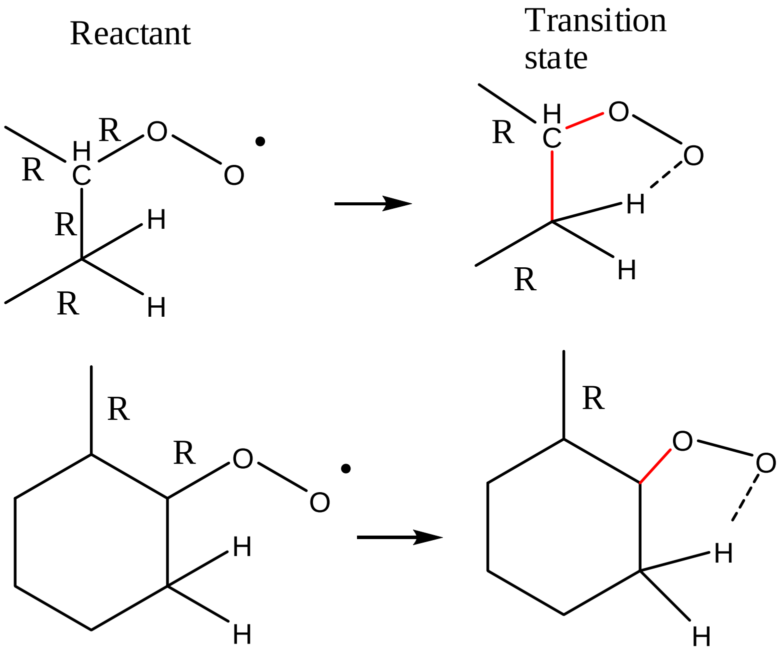
Cis (boat) ring form of cyclohexylperoxy does isomerize



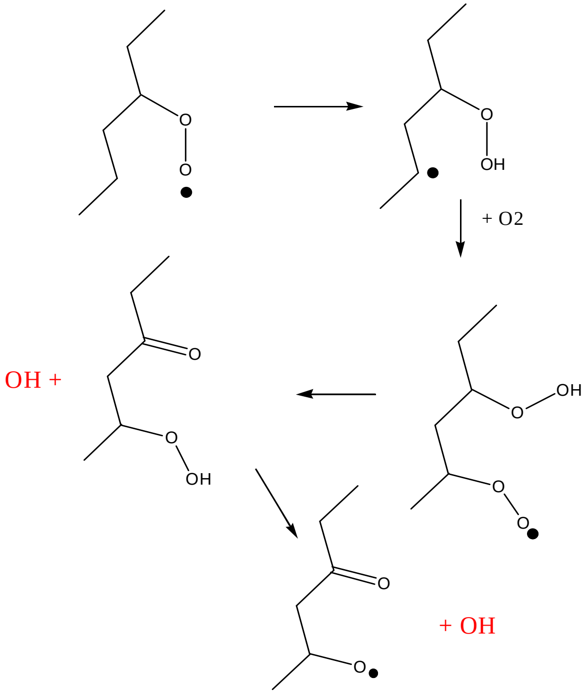
Compare Handford-Styring rates to n/iso-alkane rates and see diff in A-factor and Ea

Ring size in transition state	A	n	Ea [cal]	Rate at 750K	Branching fraction
Hanford-Styring and Walker based estimate:					
5	6.20e10	0	27495	6.0e2	11%
6	4.63e10	0	24076	4.5e3	81%
7	5.50e9	0	24355	4.3e2	8%
Non-cyclic alkylperoxy rates [7]					
5	1.00e11	0	26850	1.5e3	9%
6	1.25e10	0	20850	1.0e4	64%
7	1.50e9	0	19050	4.4e3	27%

Explanation of engine knock, ON, antiknocks, diesel ignition, and HCCI ignition came in the 1990's from DOE/BES theoretical chemistry and supercomputing and EERE knock working group



Alkylperoxy radical isomerization rates are different in paraffin and cyclic paraffin hydrocarbons



Low temperature chain branching paths

Most work has been done for alkane fuels, and many questions remain for aromatics, cyclic paraffins, large olefins

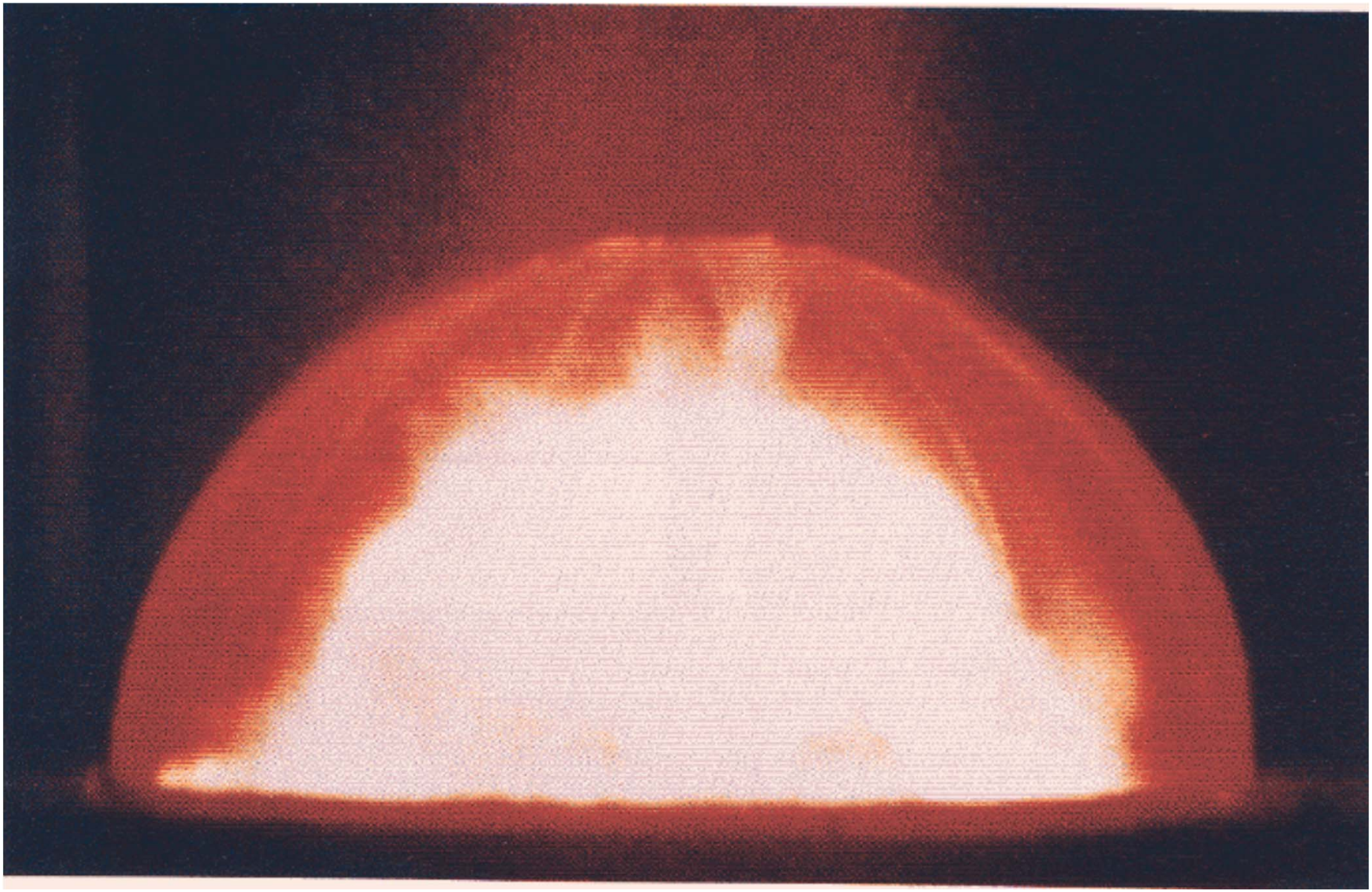
There are many poorly understood phenomena

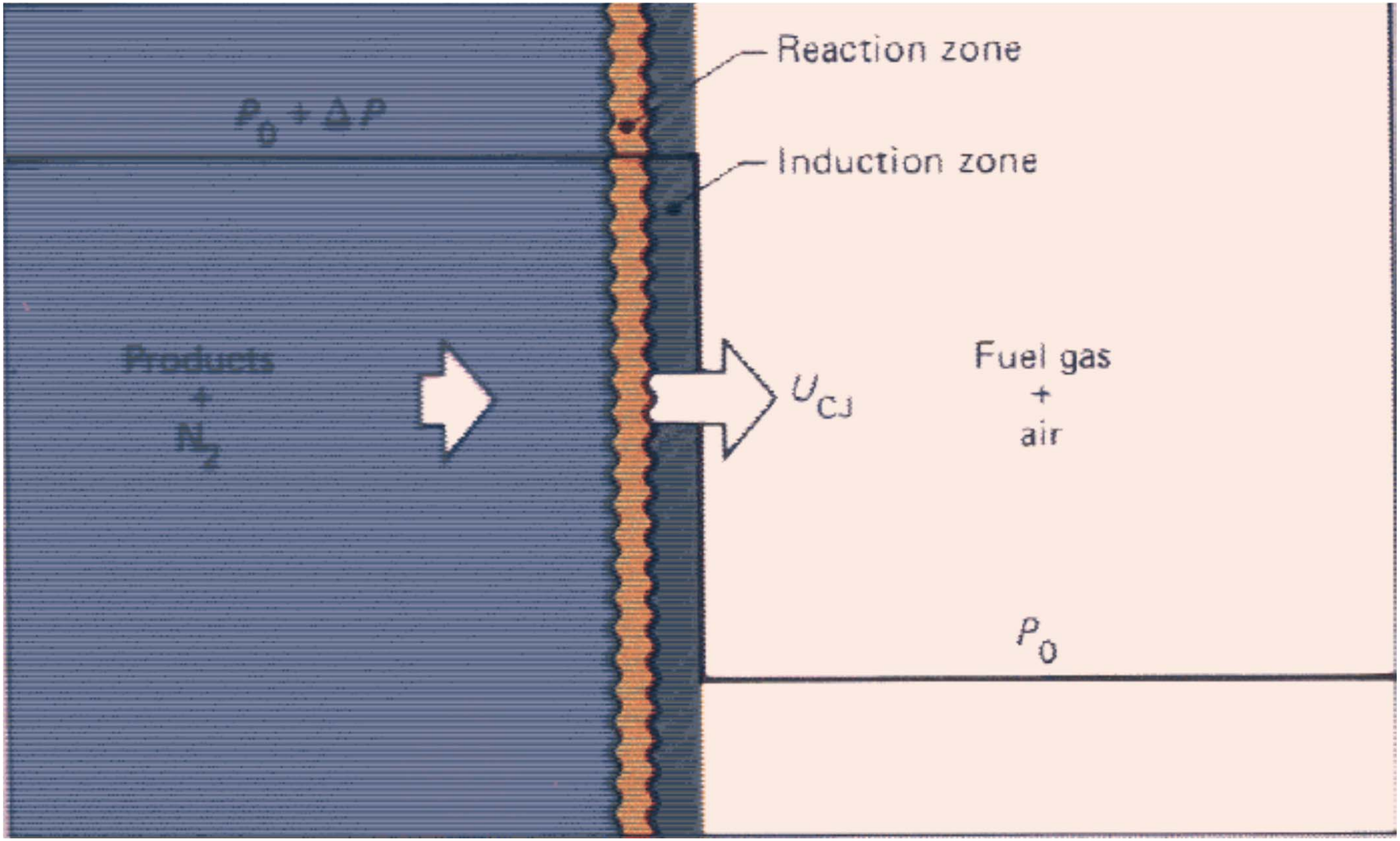
- All of our intuition, experience and theory of flame properties is based on flames at atmospheric and lower pressures
- In engines, at high pressures due to compression, unburned gas temperatures are also quite high
- Characteristic times to autoignition can be much shorter than characteristic times for flame propagation
- Assumptions built into our picture of flame propagation break down at high pressures, and it is not clear how to define limiting conditions
- Extrapolation of flame data to 100 bar not appropriate; great need for high pressure “flame” data of all kinds
- We don’t know very much about combustion at high pressures
- We simply extrapolate phenomena from atmospheric pressure to high pressure, but they probably are no longer valid
- We don’t even know if “flames” still exist

Chemical Kinetics Modeling of Detonation Parameters

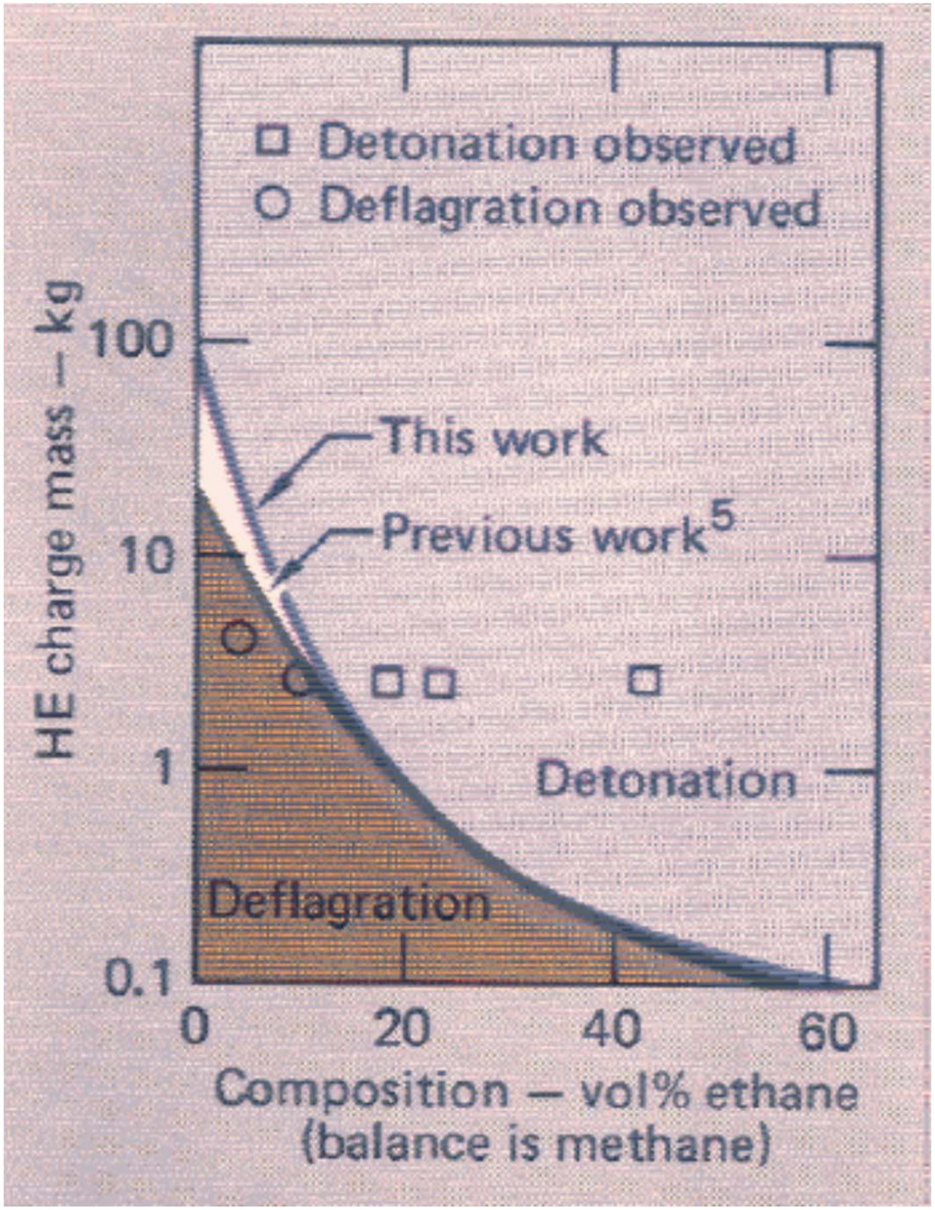
Charles Westbrook

Tsinghua-Princeton
2014 Summer School on Combustion
July 20-25, 2014





Chematic of ZND formulation of detonation structure (Zeldovich, von Neumann, Doring)



Compute homogeneous, constant volume ignition delay time.

Initial conditions determined using the Chapman-Jouguet conditions of the stable detonation, which can be calculated a priori from basic thermochemical properties

This ignition delay is then converted to an ignition length and then to an equivalent energy scale.

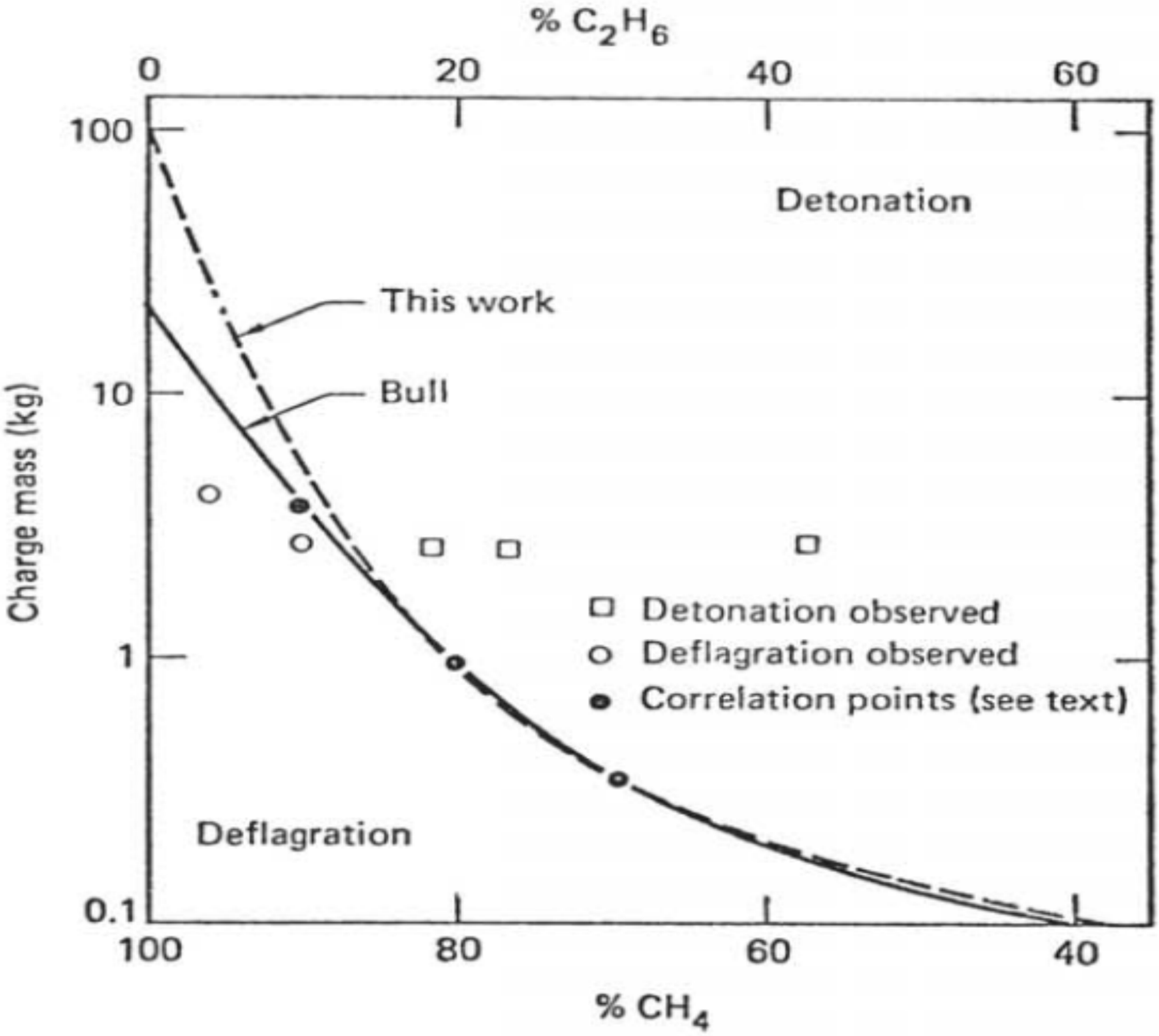


Fig. 5 Detonation thresholds as functions of composition.

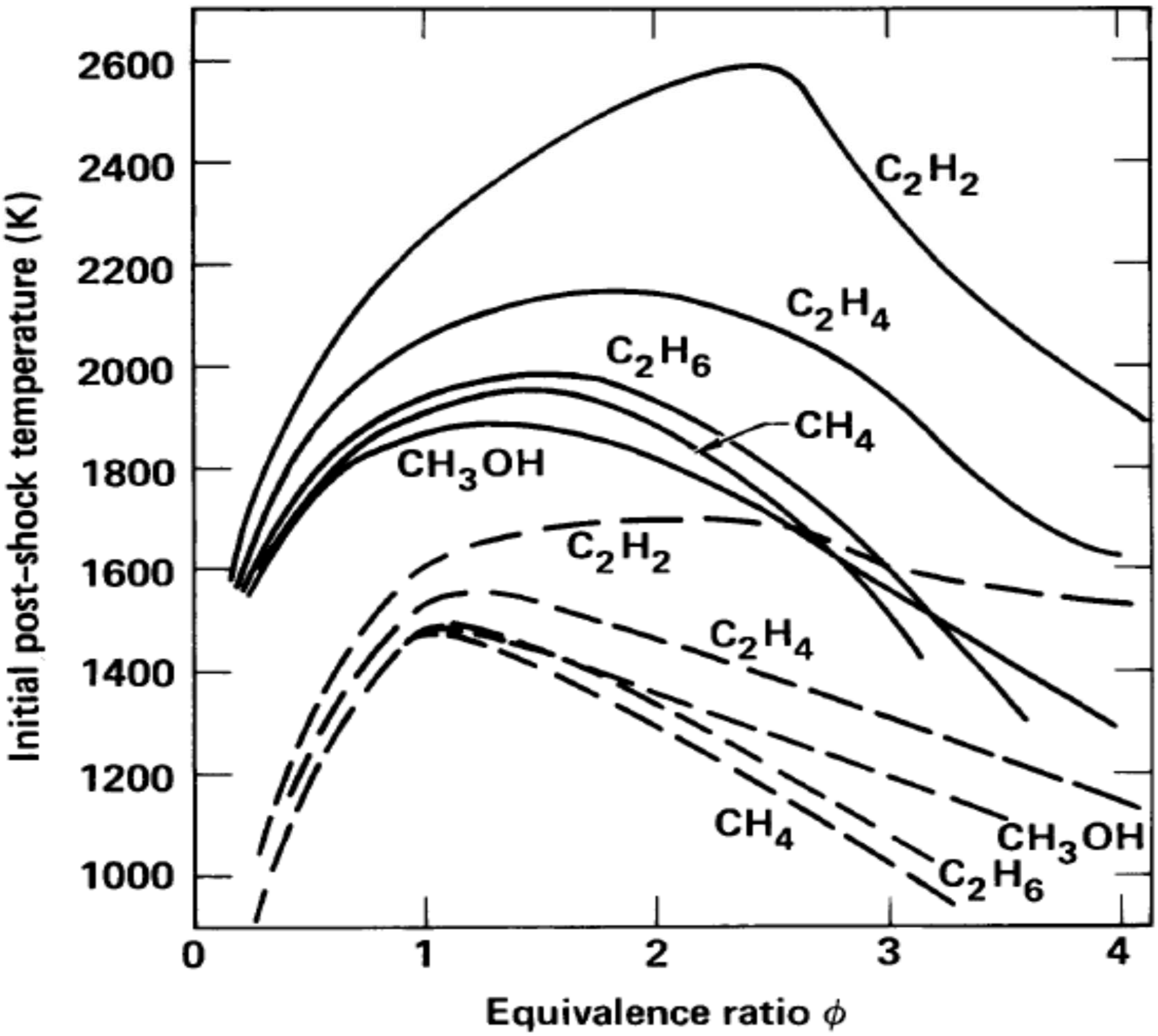


Fig. 1. Postshock unreacted temperatures for fuel–oxygen (solid curves) and fuel–air (dashed curves) mixtures.

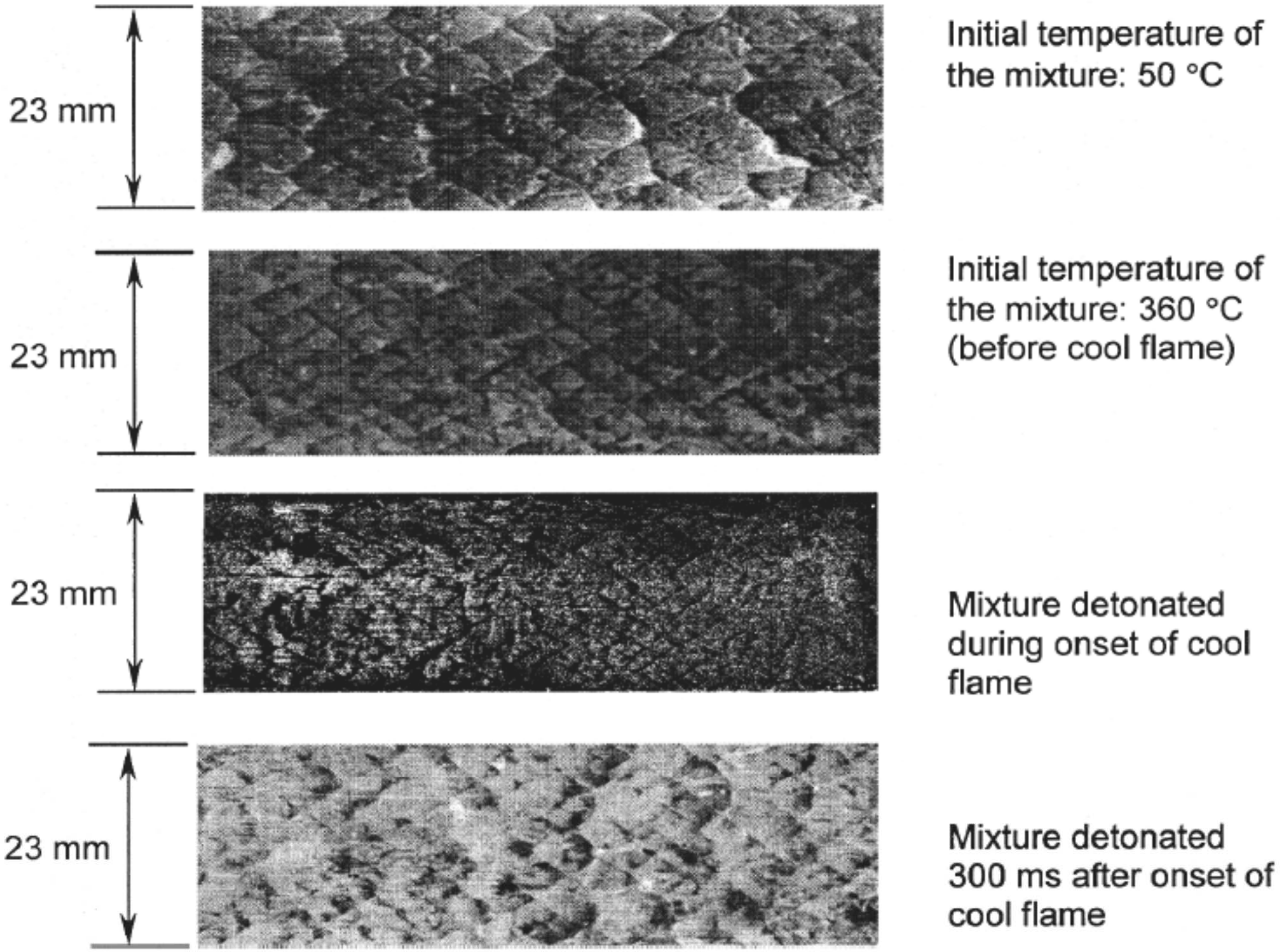
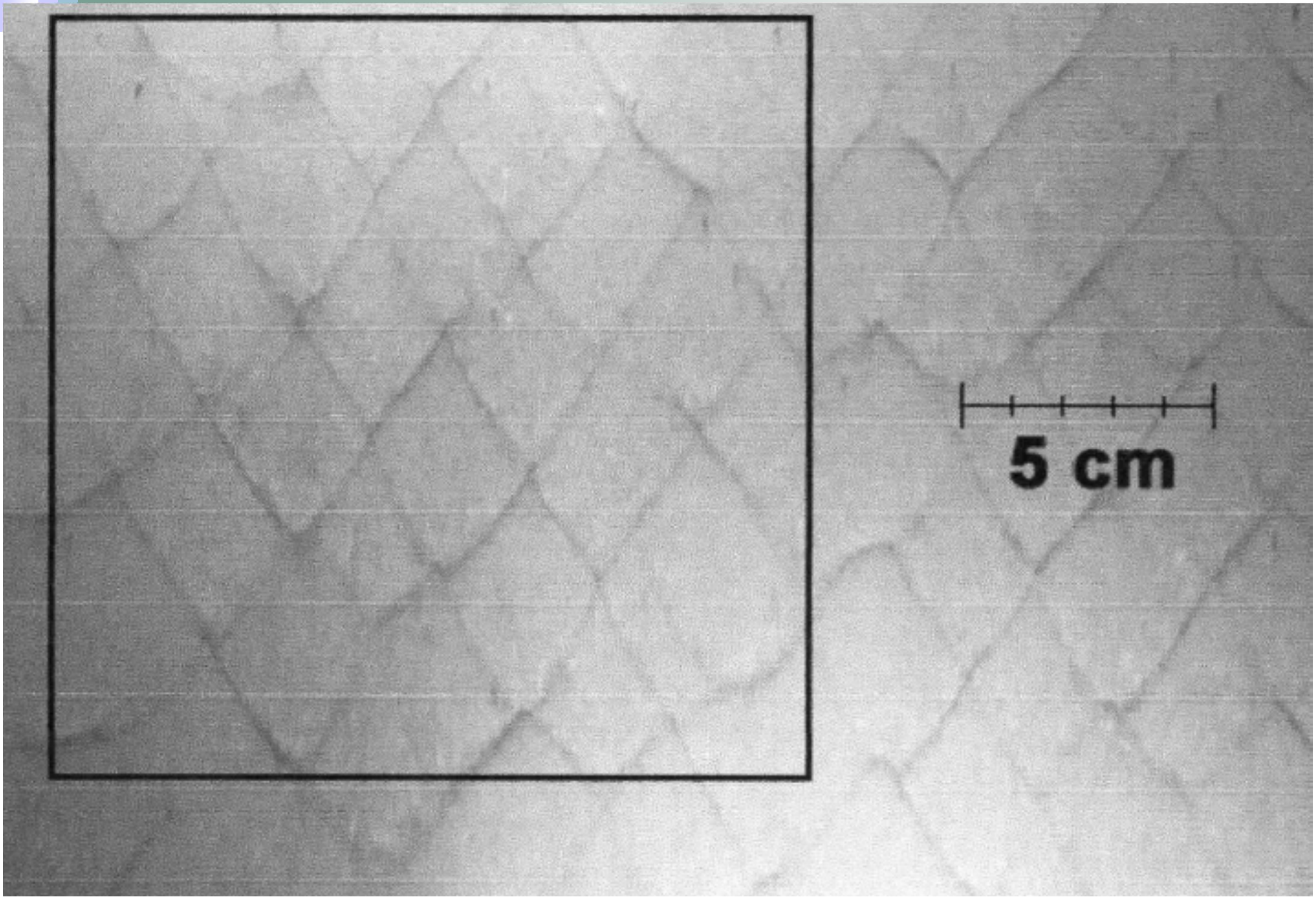
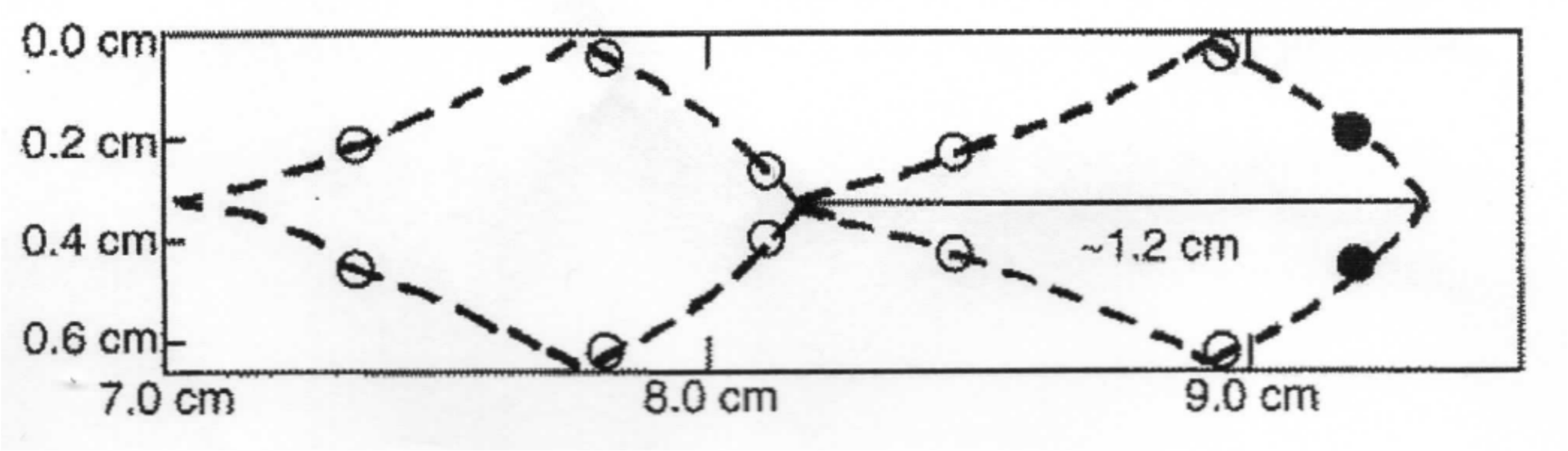


FIG. 2. Samples of smoked foils.


5 cm



Detonation cells, showing typical quantities used for geometric parameters to correlate with other detonation parameters

Most commonly, the computed ignition delay time is multiplied by a velocity to produce a computed ignition delay length scale, which is then assumed proportional to cell size. The computed ignition delay length ** 3 i.e., cubed, is assumed proportional to critical detonation initiation energy.

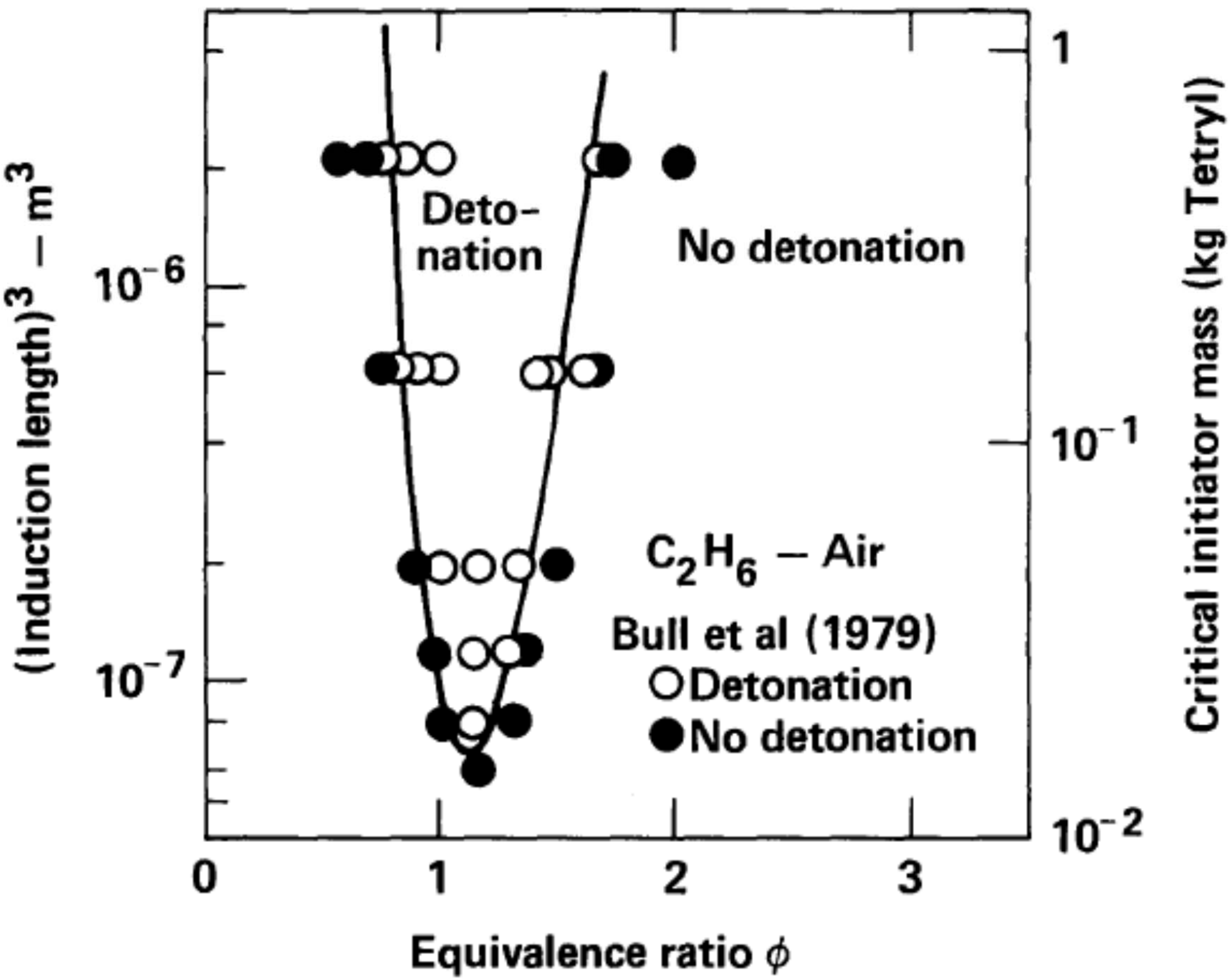


Fig. 3. Cube of induction length for C_2H_6-air mixtures, with data from Bull et al. [8] on critical initiation energy.

Methane vs. Natural Gas

- Initial goal of program was to assess safety of LNG to resist detonations
- Scientific question was to determine the detonability of methane
- Kinetic modeling study showed that methane ignition is vastly different from that of natural gas
- Real issue is detonability of natural gas

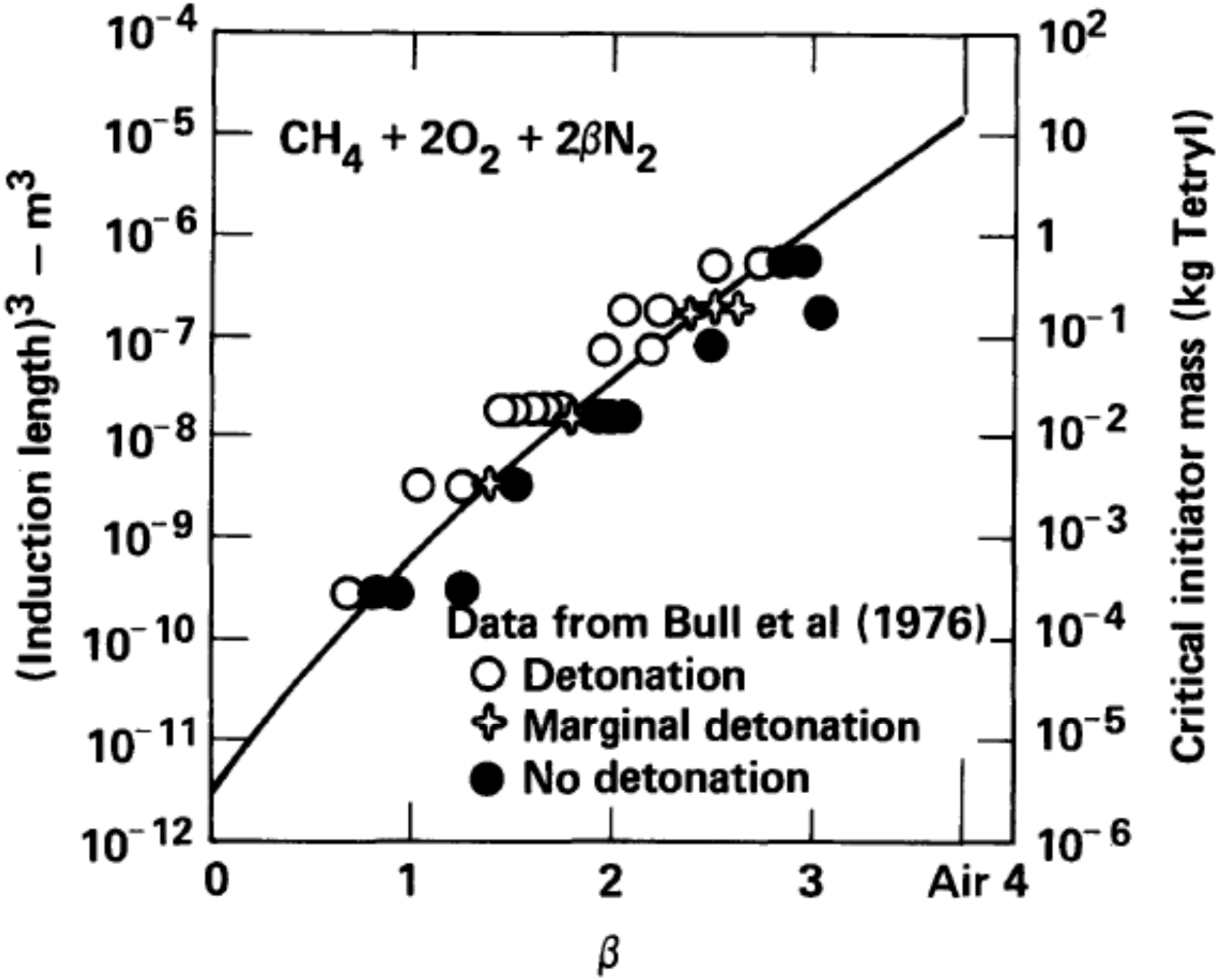
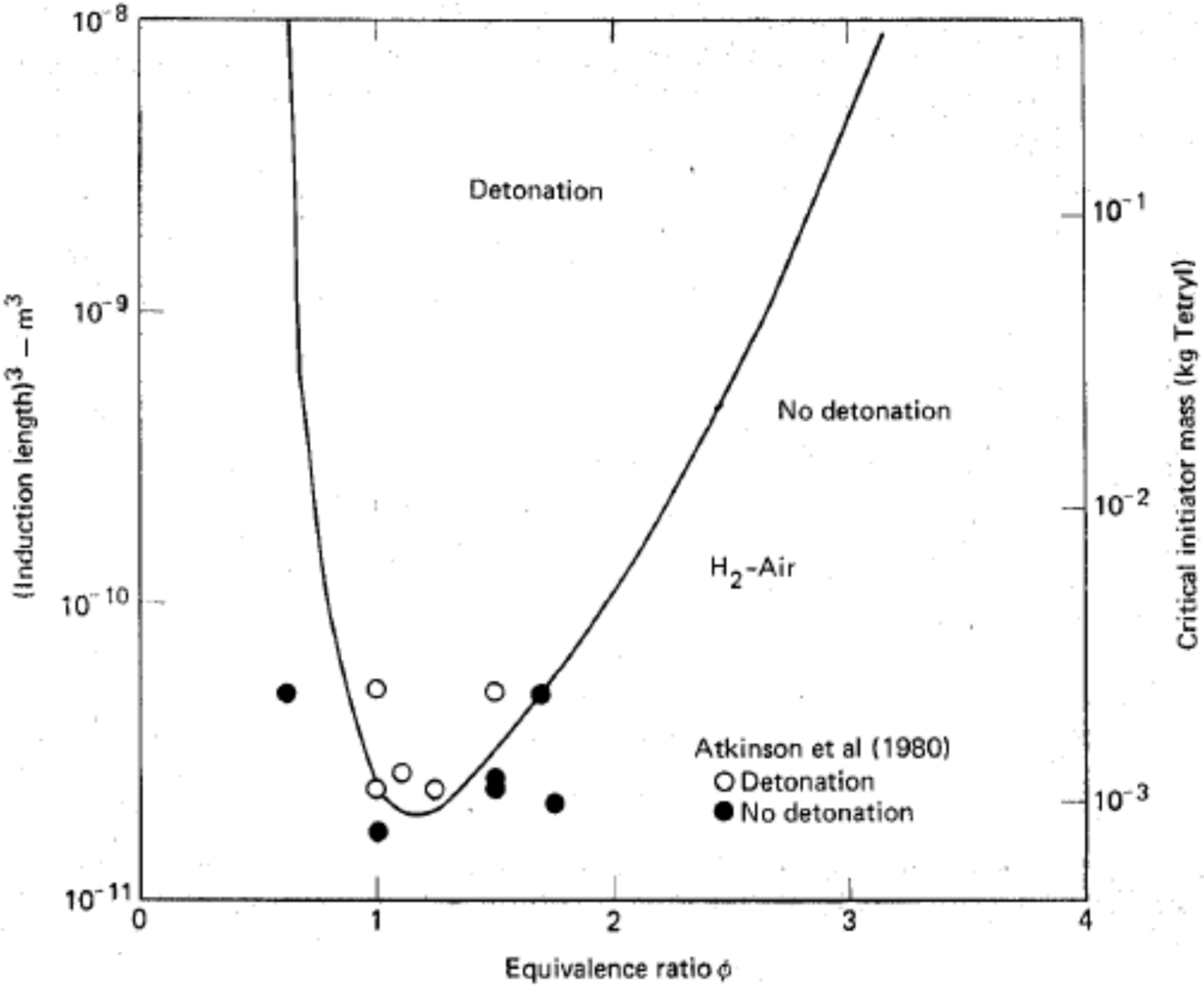


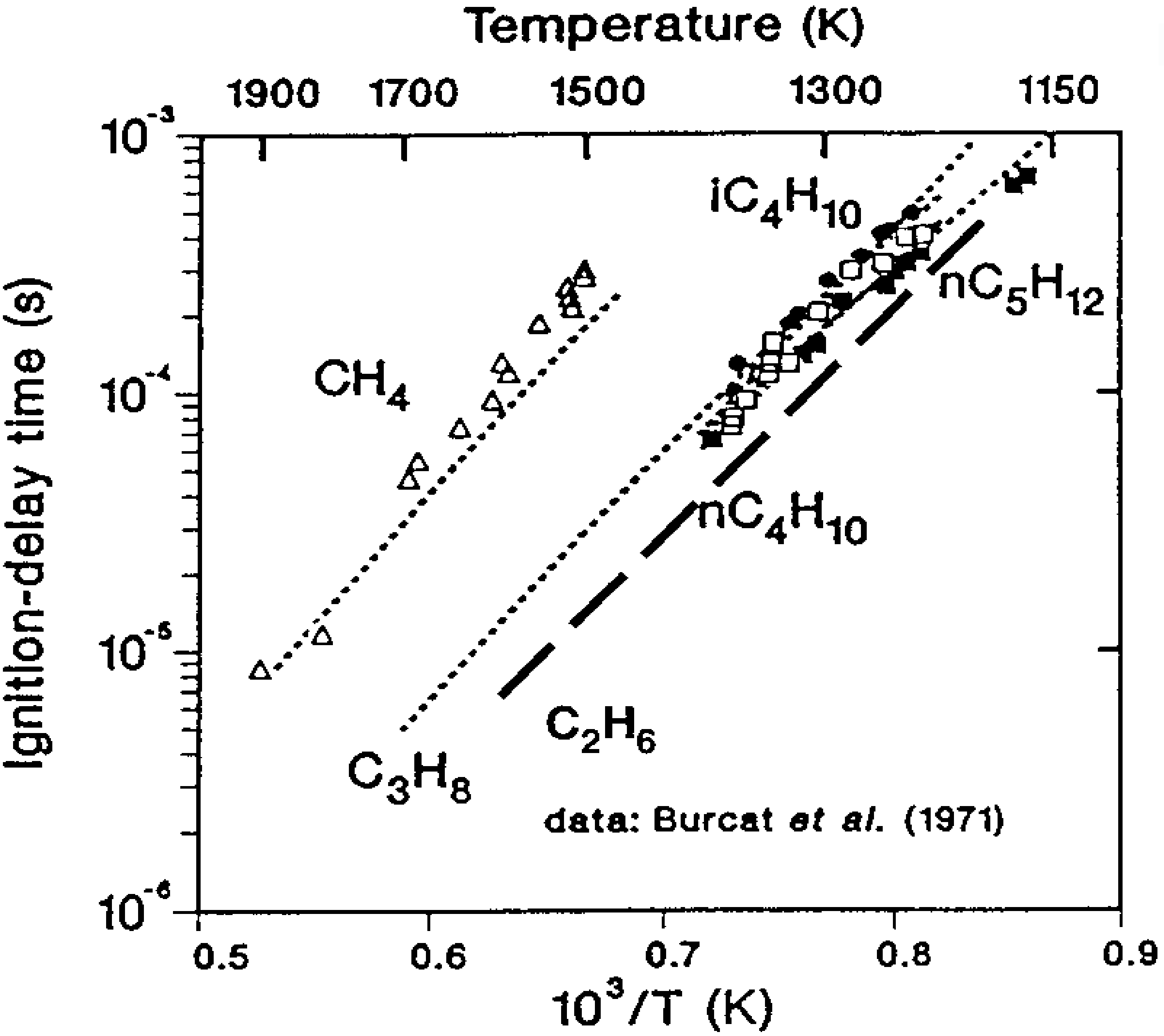
Fig. 8. Cube of induction length for CH_4-$2O_2$-$2\beta N_2$ mixtures. Also shown are data from Bull et al. [42] for critical initiation energy.



10^{-8}
10^{-9}
10^{-10}
10^{-11}
(Induction length)^3 — m^3
10^{-1}
10^{-2}
10^{-3}
Critical initiator mass (kg Tetryl)
0
1
2
3
4
Equivalence ratio ϕ
Detonation
No detonation
H_2-Air
Atkinson et al (1980)
○ Detonation
● No detonation

Later developments

- J. Shepherd (Caltech) improved this simplified analysis to get better correlations
- Anything that affects kinetic ignition will also affect detonation cell sizes
    - inhibitors, promoters, cool flames
- Chemical kinetic models are being included in CFD detonation models


Temperature (K)
1900
1700
1500
1300
1150
10^{-3}
10^{-4}
10^{-5}
10^{-6}
Ignition-delay time (s)
iC_4H_{10}
nC_5H_{12}
CH_4
nC_4H_{10}
C_2H_6
C_3H_8
data: Burcat *et al.* (1971)
0.5
0.6
0.7
0.8
0.9
$10^3/T$ (K)

Examples of results of faulty thermochemical data

- High temperature ignition of natural gas
- Natural gas is a mixture of methane (~90%), ethane (5-10%), and higher hydrocarbons
- Methane is often used as a surrogate for natural gas
- Ignition and detonations are particular concerns

Alkane ignitions

- Methane ignites very slowly
  - Influence of methyl radical

- Ethane is unusually ignitable
  - Unusual in production of ethyl radicals and H atoms

- Larger n-alkanes ignite at intermediate rates

- Natural gas ignition is a good example of ignition sensitizing

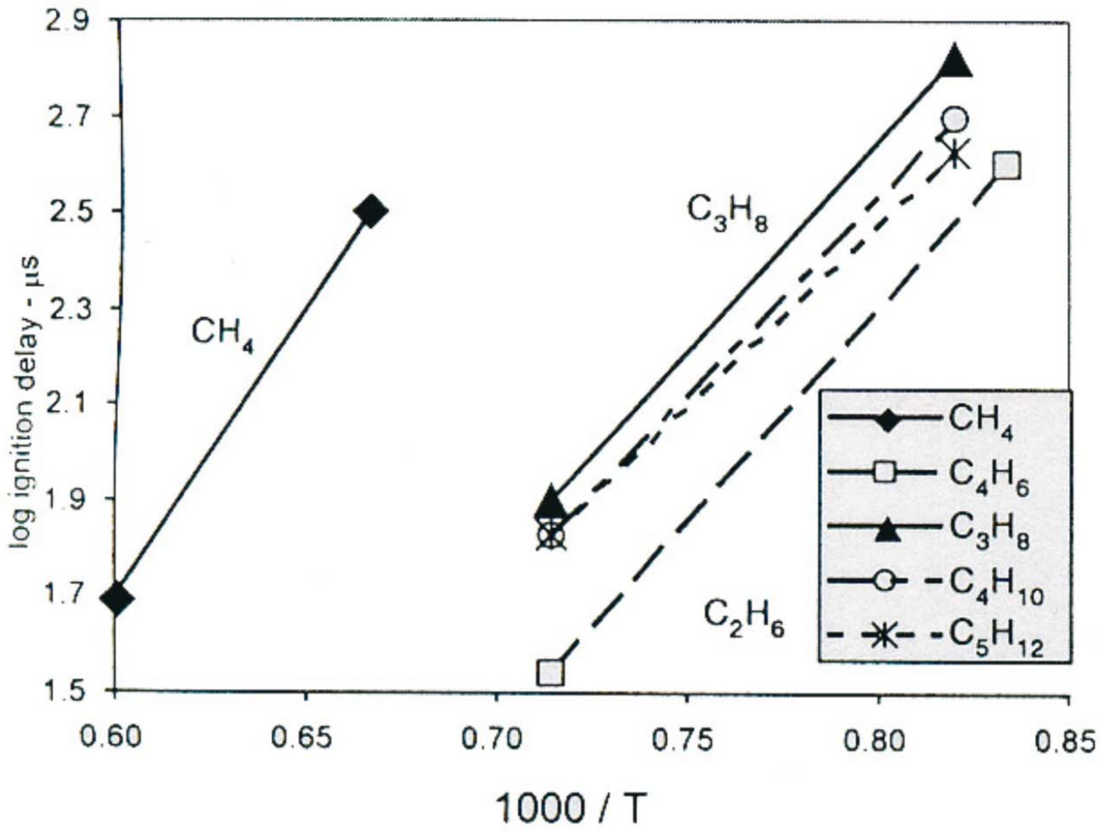
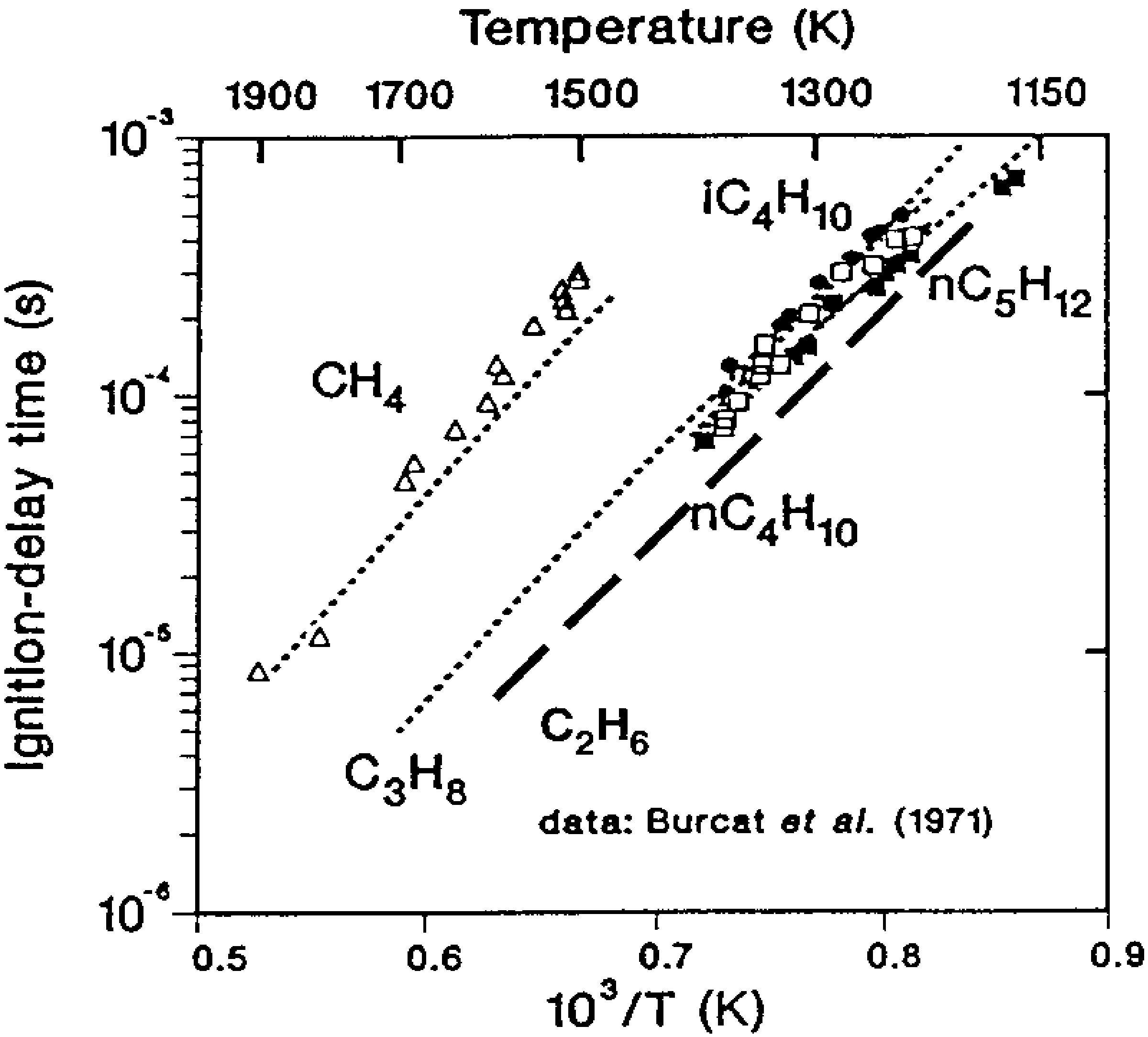


Figure 2 Shock tube ignition delay measurements from the study of Burcat et al. [29].

1971 paper in Combustion and Flame



Comparisons between experimental and kinetic modeling ignition

Ignition of natural gas

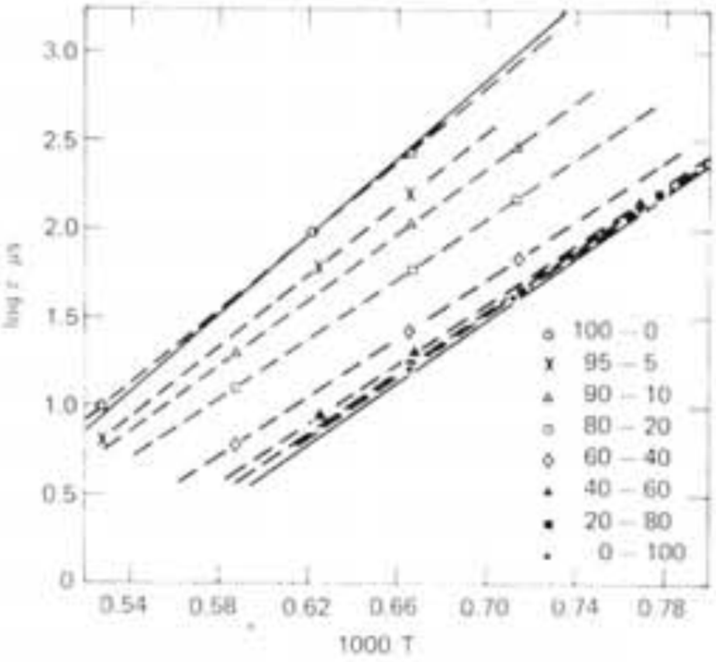
Studied as a mixture of 90% methane (CH_4) and 10% ethane (C_2H_6)

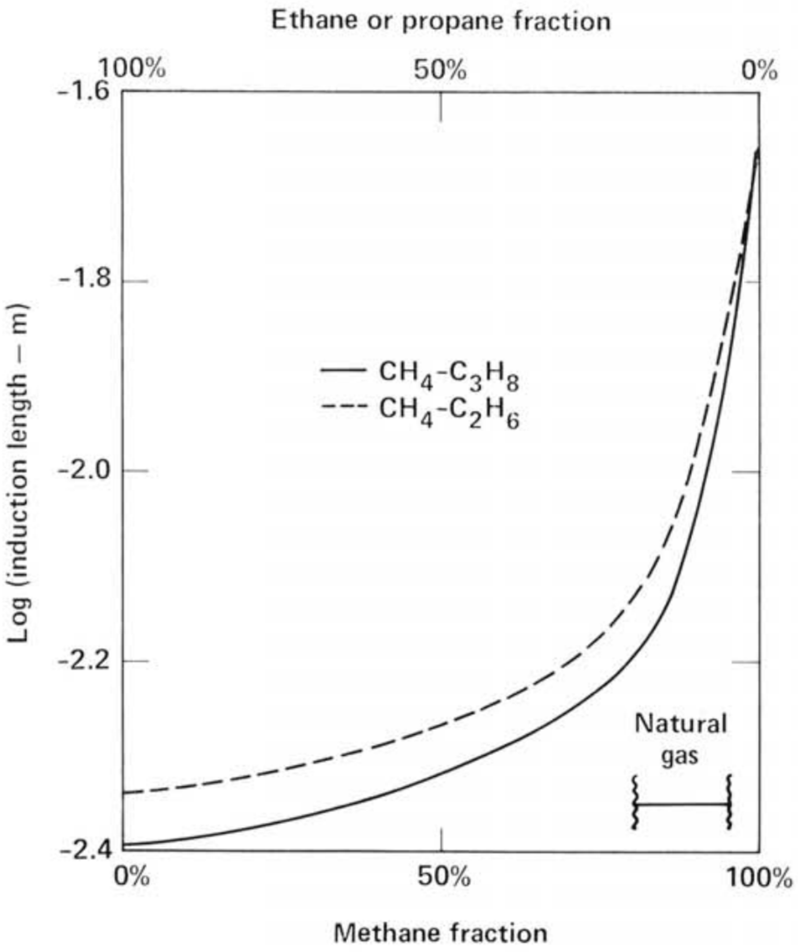
$$C_2H_6 + R = H_2 + C_2H_5$$

$$C_2H_5 = C_2H_4 + H$$

$$CH_4 + R = RH + CH_3$$

$$CH_3 + CH_3 = C_2H_6$$


log τ, μs
3.0
2.5
2.0
1.5
1.0
0.5
0
0.54
0.58
0.62
0.66
0.70
0.74
0.78
1000/T
○ 100 – 0
x 95 – 5
▲ 90 – 10
□ 80 – 20
◇ 60 – 40
▴ 40 – 60
■ 20 – 80
• 0 – 100


Ethane or propane fraction
100%
50%
0%
Log (induction length – m)
-1.6
-1.8
-2.0
-2.2
-2.4
— CH_4-C_3H_8
--- CH_4-C_2H_6
Natural gas
0%
50%
100%
Methane fraction

Kinetic modeling of natural gas ignition

$$C_2H_6 + H = H_2 + C_2H_5$$

Poor knowledge of thermochemistry of C2H5 radical

Result: rate computed for H2 + C2H5 unexpectedly very high

Eventually better C2H5 thermochemistry corrected this error

Detailed Chemical Kinetic Models for Surrogate Practical Fuels

Charles Westbrook

Tsinghua-Princeton
2014 Summer School on Combustion
July 20-25, 2014

Practical hydrocarbon fuels present new challenges for kinetic modeling

- For many years, methane and propane were “large” fuel molecules, and they still can be challenging
- Most common transportation fuels produced from petroleum or other common sources contain molecules much larger than C1 to C4
- Hydrogen and C1 – C4 species will continue to be an essential part of fuel models and still need lots of work
- Large fuel species modeling requires significant computing resources
- Mechanism reduction will be necessary for applications with realistic geometry

All petroleum-derived fuels contain a complex mixture of HC molecules

- Refining produces a still-complex mixture that is "targeted" towards its application type
- Gasoline $6 < C < 10$
- Jet fuel $9 < C < 13$
- Diesel $13 < C < 22$

- HCCI $1 < C < 22$

Variability of real transportation fuels

- Composition of gasolines at different gas stations on a single day is often quite different
- Composition of same gas station will vary every day
- Same is true of diesel and other fuels
- Quantity used to test fuels is often not very demanding or specific (e.g., ON, CN)

There are two important pathways for practical fuel mixture mechanisms

- Reference fuels
  - Gasoline - n-heptane and iso-octane
  - Diesel - heptamethyl nonane and n-hexadecane
  - Jet fuel – n-dodecane (?) and iso-dodecane (?)

- For the first time, we now have detailed kinetic mechanisms for both diesel and gasoline primary reference fuels

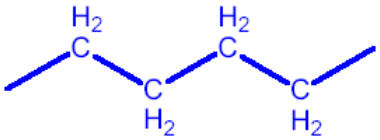
- Surrogate fuels

Use of surrogate fuels is an important current theme in combustion chemistry

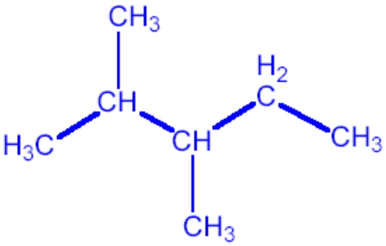
- First surrogate for diesel fuel was n-heptane
- Early surrogates included one representative from each fuel molecule class

Classes of compounds in practical fuels

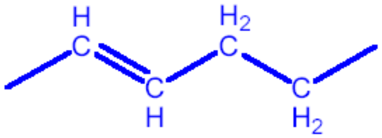
n-paraffin



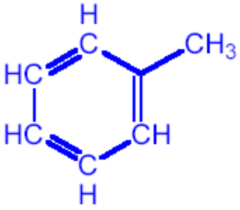
iso-paraffin



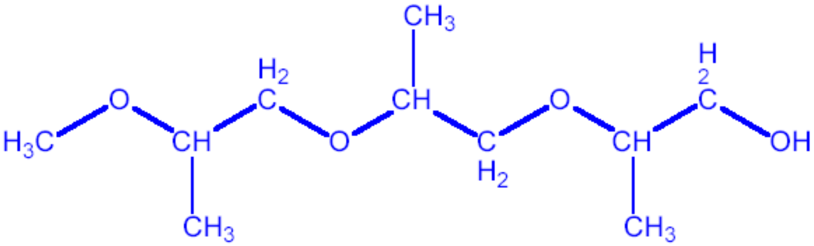
olefin



cyclo-alkane

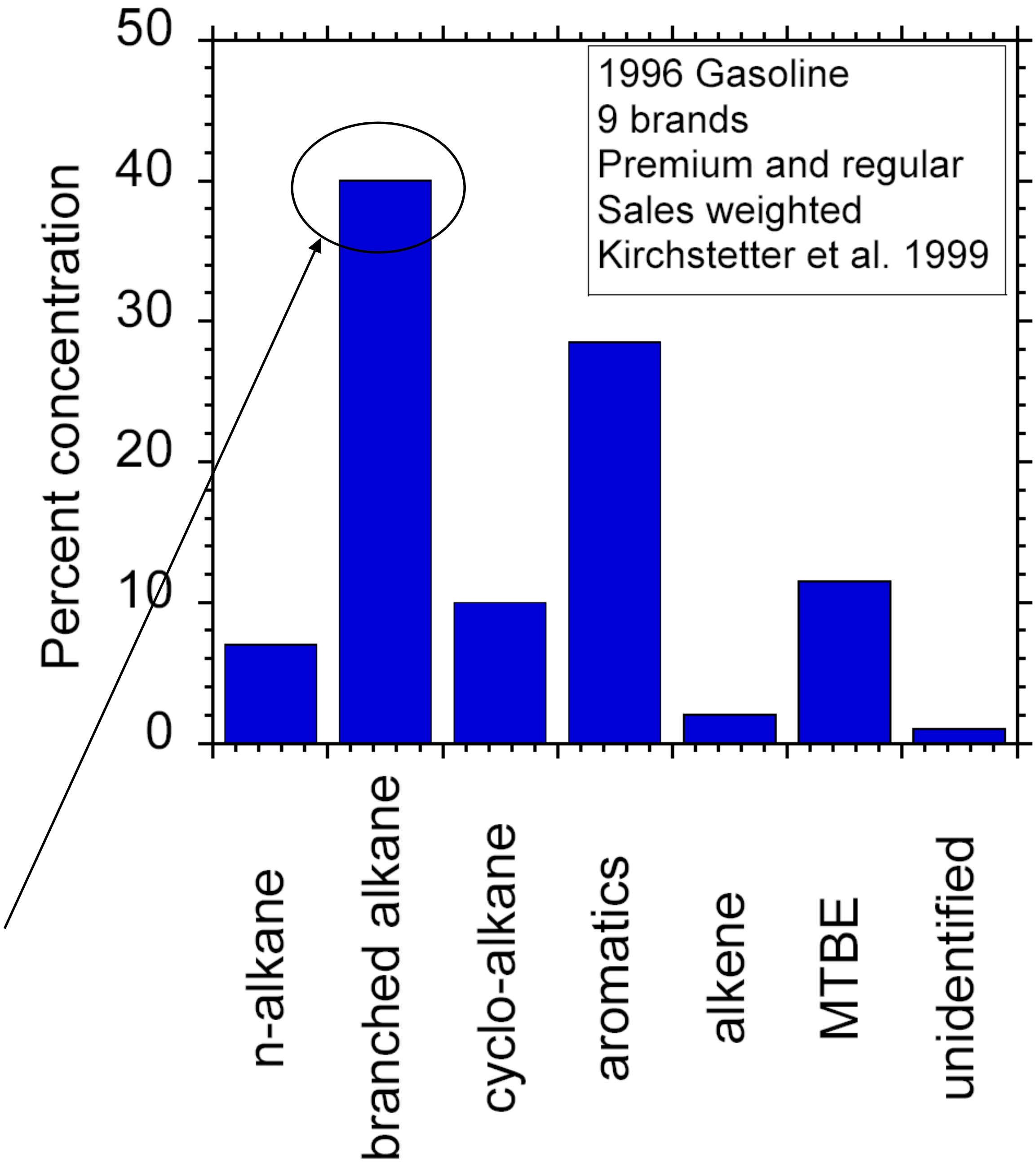


aromatic



oxygenate

Gasoline composition

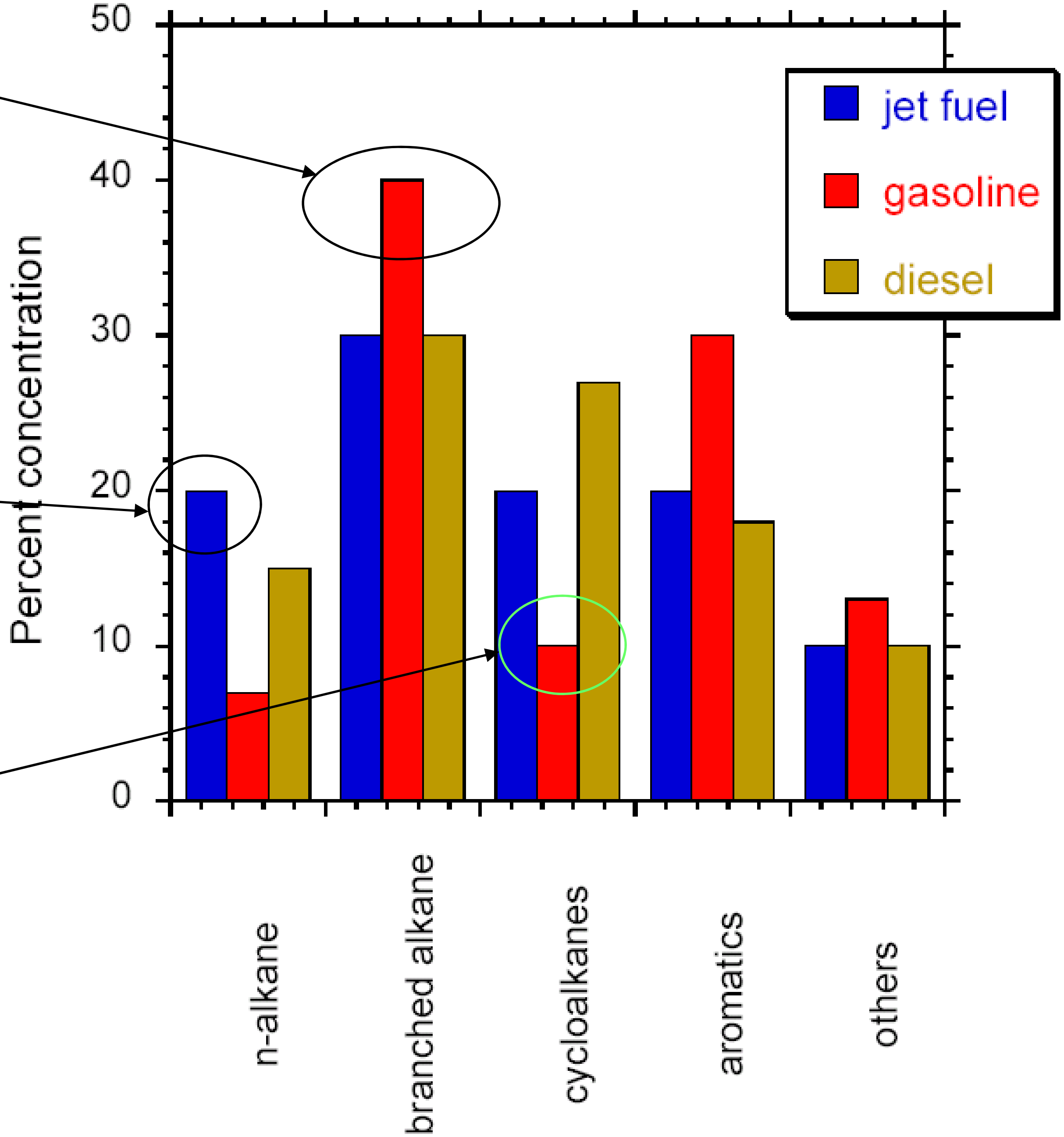


Many branched paraffins

Gasoline has many branched alkanes

Jet fuel has the highest n-alkane

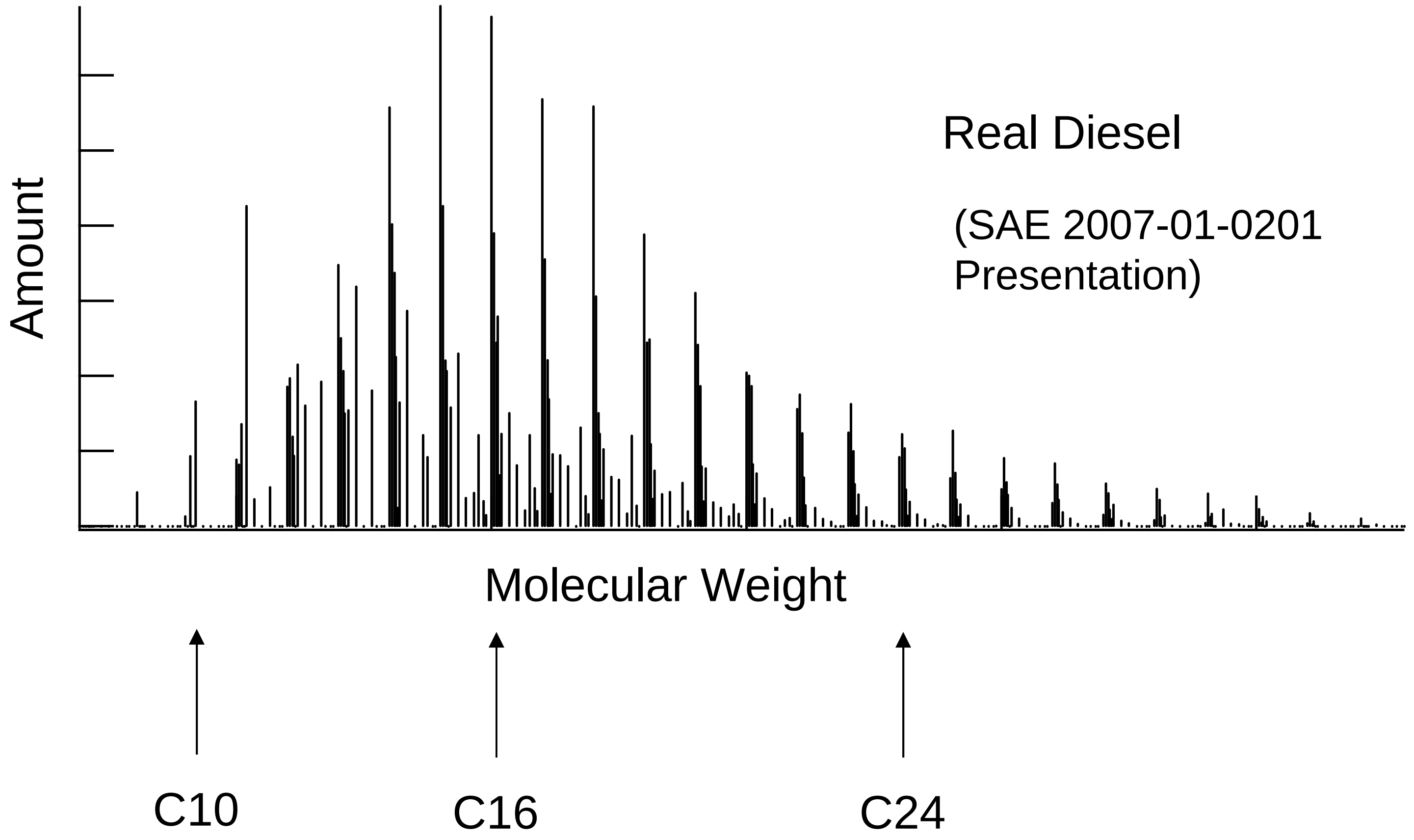
Gasoline is lower in cycloalkanes



Fuel components that have higher molecular weights are needed

Surrogate Fuel Component Selection

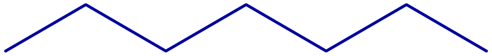
- Diesel fuel has mostly C14 to C24 components centered around C16



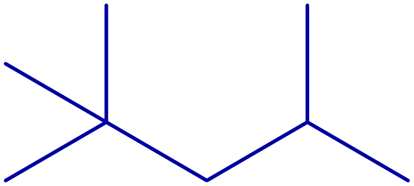
(SAE 2007-01-0201 Presentation)

Recommended components by the surrogate fuel working group, gasoline team

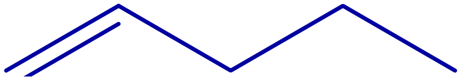
- n-heptane



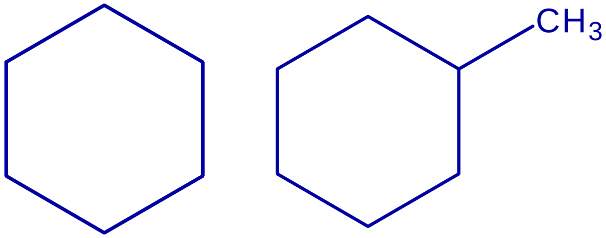
- iso-octane



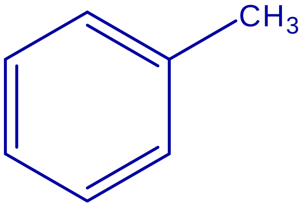
- pentene



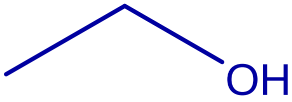
- cyclohexane, methylcyclohexane



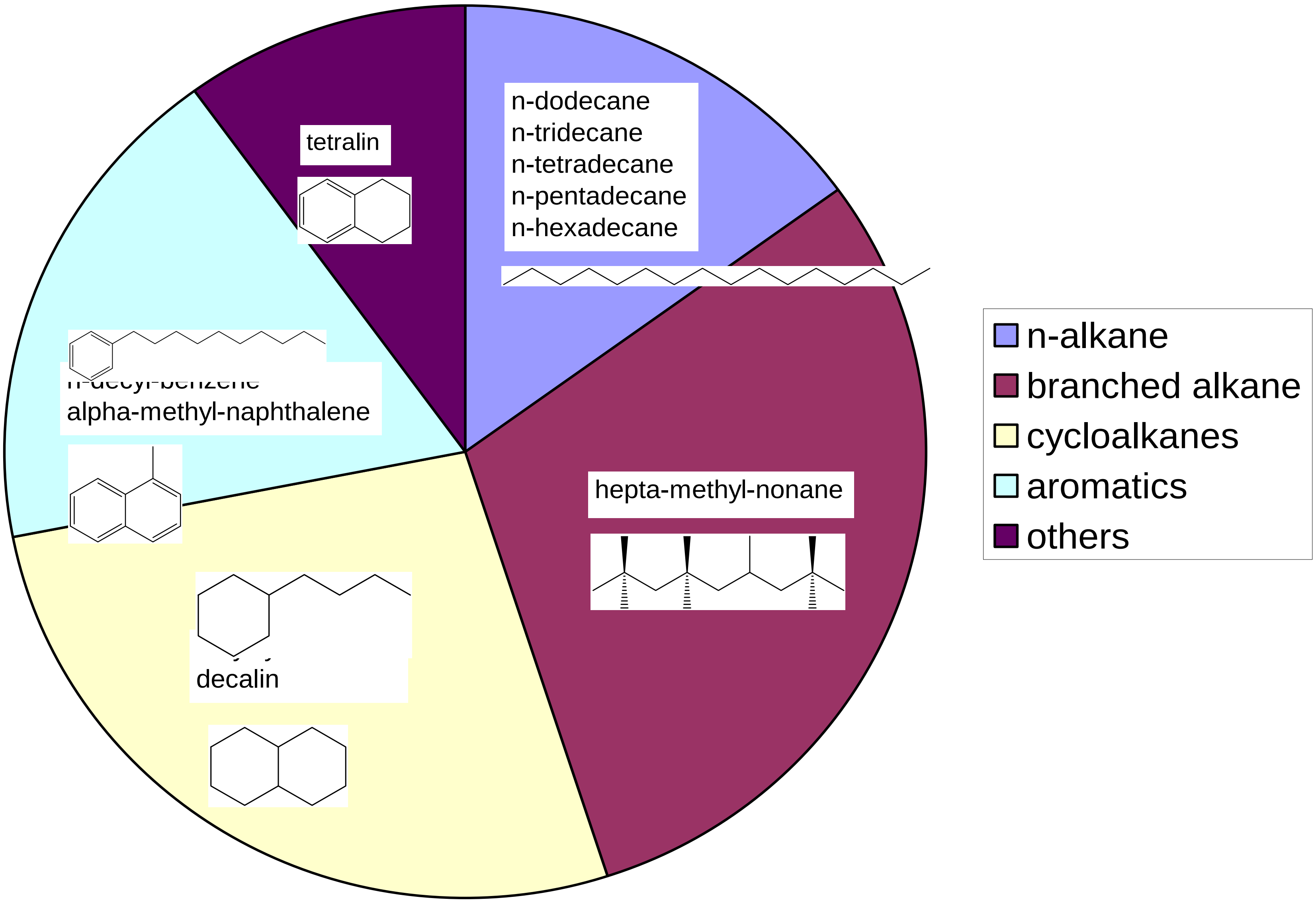
- toluene



- ethanol



Fuel Surrogate Palette for Diesel



Use of surrogate fuels is an important current theme in combustion chemistry

- Advantages of having multiple samples from each class of molecules

- Our research has been focused on developing kinetic models for many examples in each class

- Mechanism reduction can then be applied to those fuel components to be used

In some classes, we have many examples of fuels with reaction mechanisms

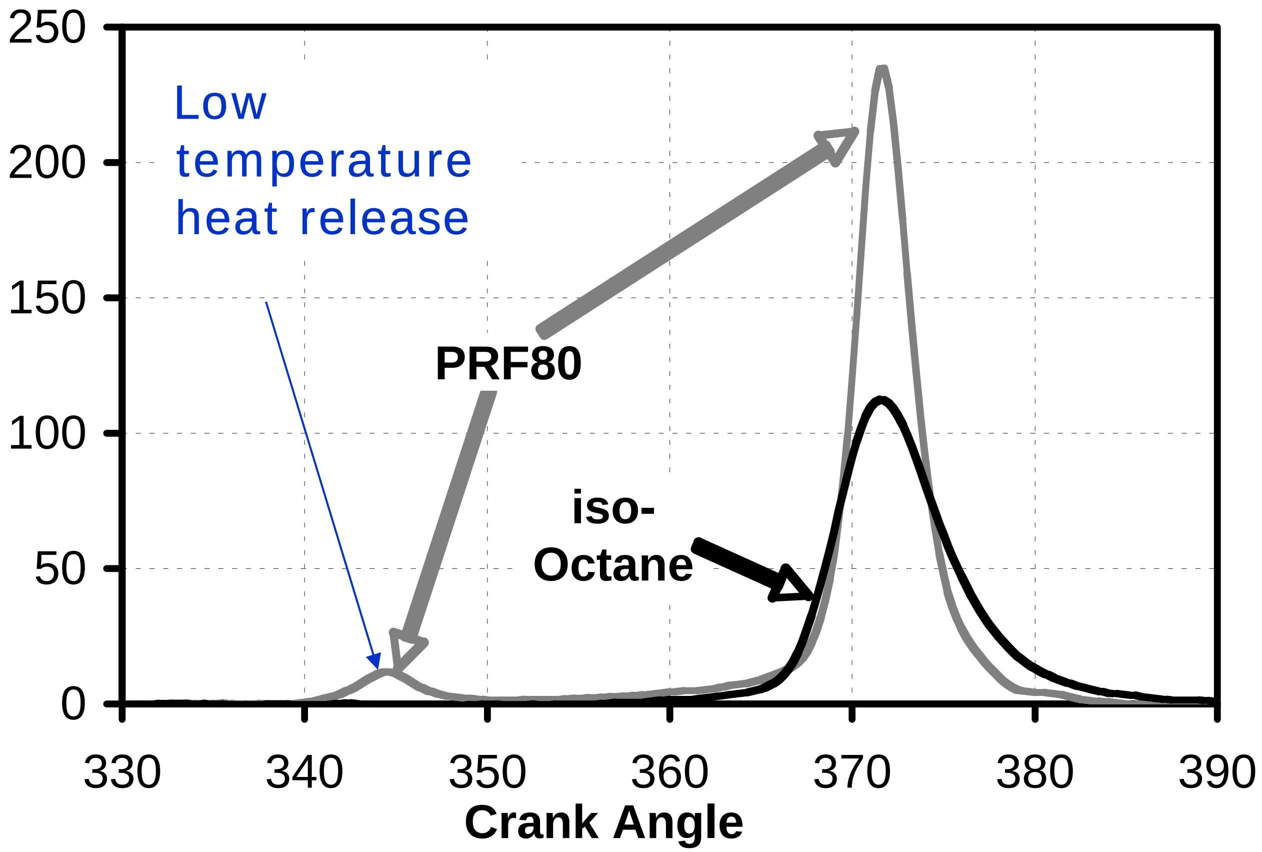
- n-paraffins
  - CH_4 (methane) through $nC_{16}H_{34}$ (n-hexadecane)

- iso-paraffins
  - all isomers through octanes, selected larger iso-paraffins

- Large variety of olefins through C8 and selected larger species

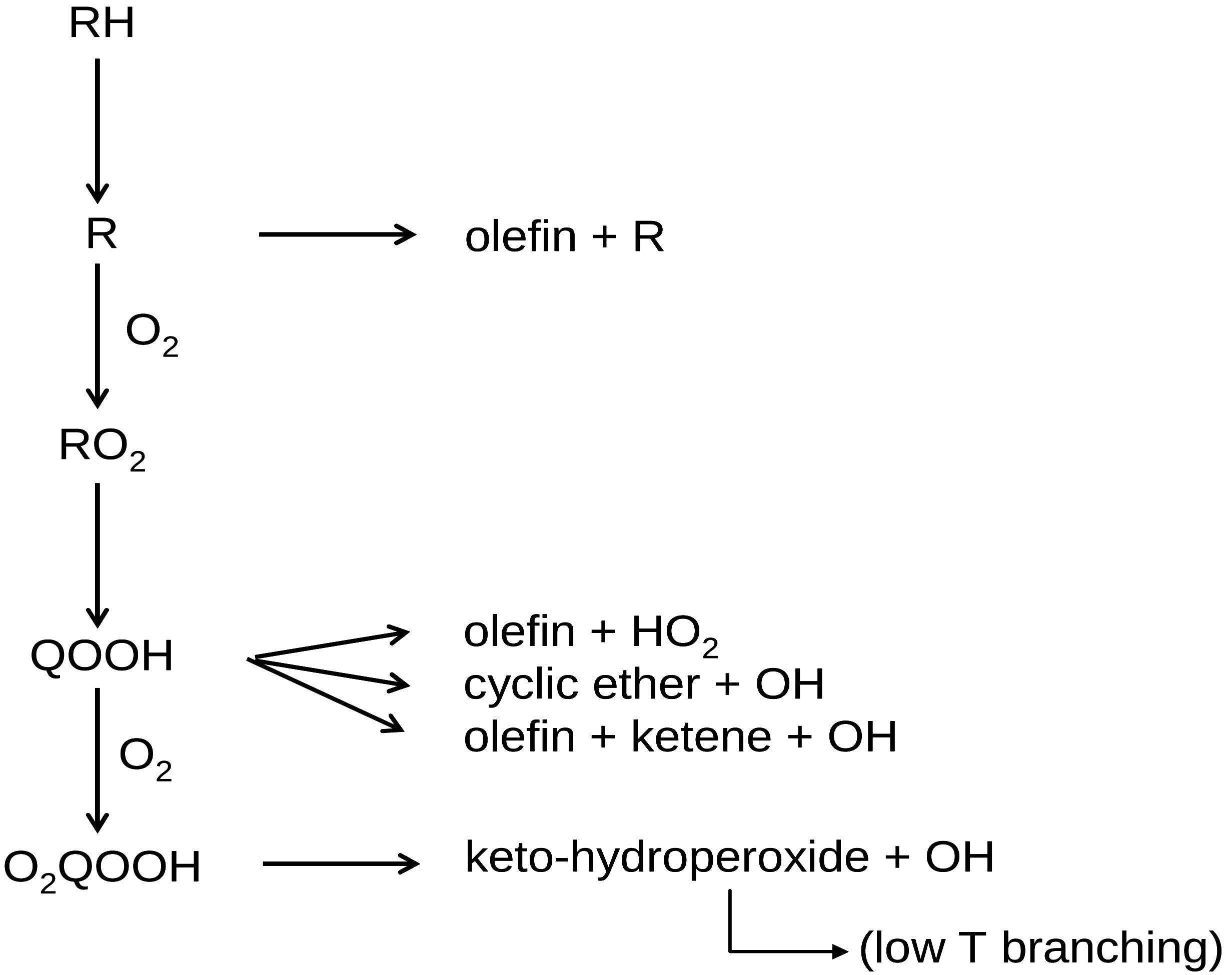
Alkylperoxy radical isomerization and low temperature are important in all types of engines

- 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

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



RH

R → olefin + R

O_2

RO_2

QOOH → olefin + HO_2

cyclic ether + OH

olefin + ketene + OH

O_2

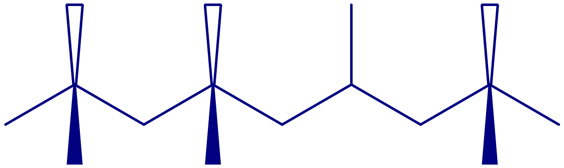
O_2QOOH → keto-hydroperoxide + OH

(low T branching)

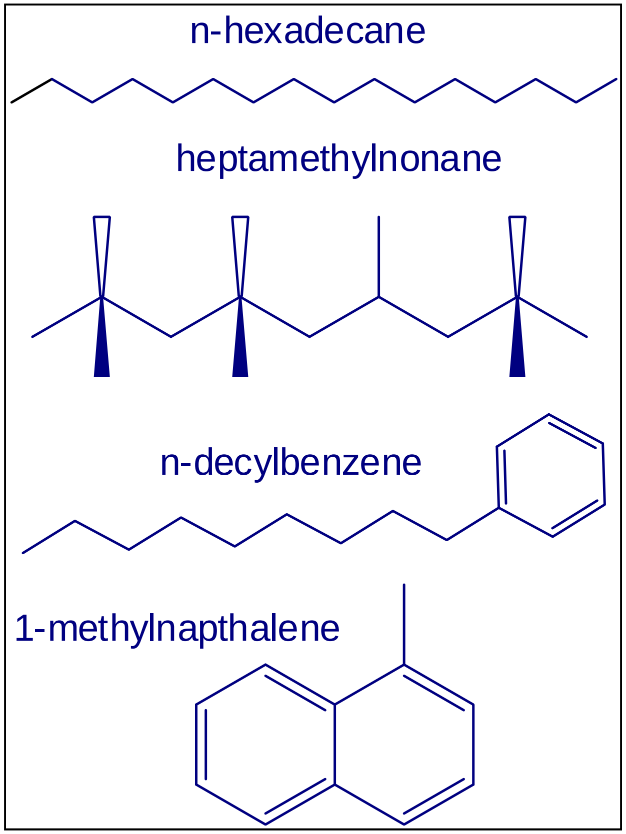
n-Hexadecane and heptamethyl nonane are primary reference fuels for diesel and recommended diesel surrogate components

- The two primary reference fuels for diesel ignition properties (cetane number)
  - n-hexadecane

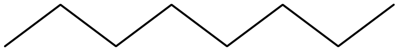
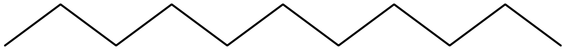
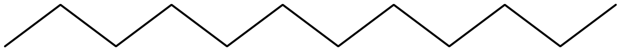
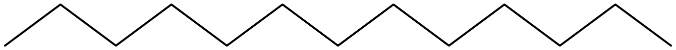
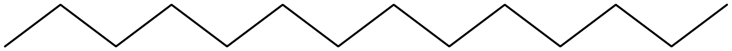
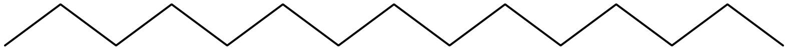
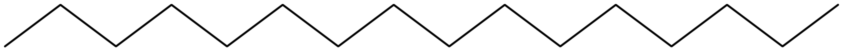
  - 2,2,4,4,6,8,8 heptamethylnonane



Recommended surrogate for diesel fuel (Farrell et al., 2007):

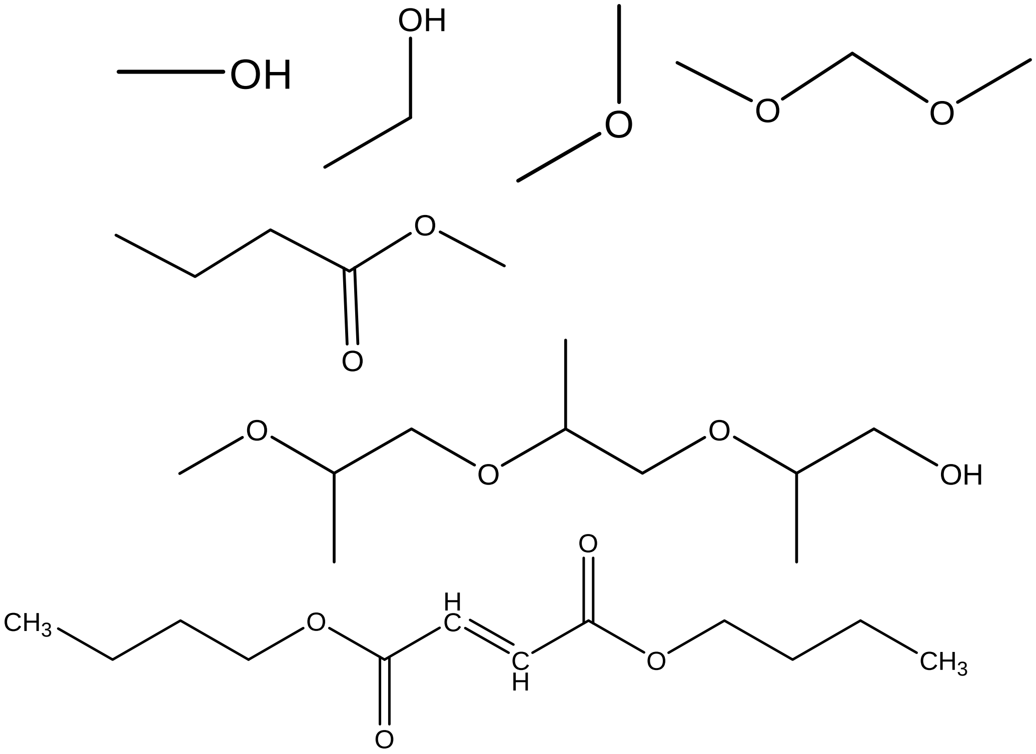


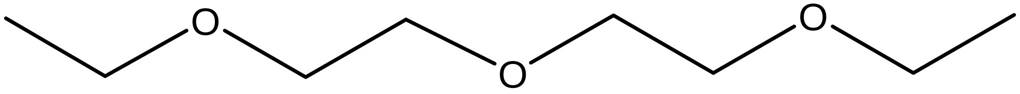
We have greatly extended the components in the palette that can be modeled into the high molecular weight range:

- n-octane (n-C_8H_{18}) 
- n-nonane (n-C_9H_{20}) 
- n-decane (n-$C_{10}H_{22}$) 
- n-undecane (n-$C_{11}H_{24}$) 
- n-dodecane (n-$C_{12}H_{26}$) 
- n-tridecane (n-$C_{13}H_{28}$) 
- n-tetradecane (n-$C_{14}H_{30}$) 
- n-pentadecane (n-$C_{15}H_{32}$) 
- n-hexadecane (n-$C_{16}H_{34}$) 

We have mechanisms for many oxygenated components

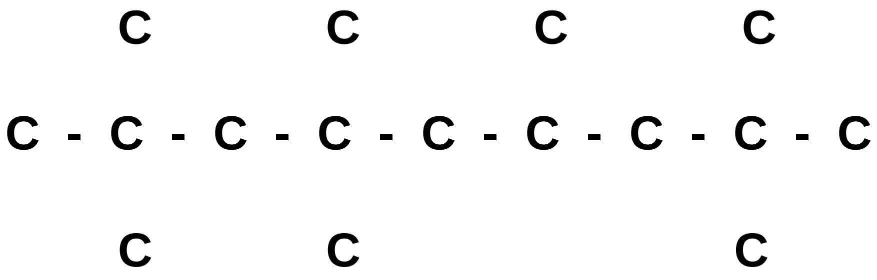
- Methanol, ethanol
- dimethyl ether, dimethoxymethane
- Methyl butanoate (surrogate for biodiesel)
- TPGME (tripropylene glycol monomethyl ether)
- DBM (di-butyl maleate)
- DGE (diethylene glycol diethyl ether)



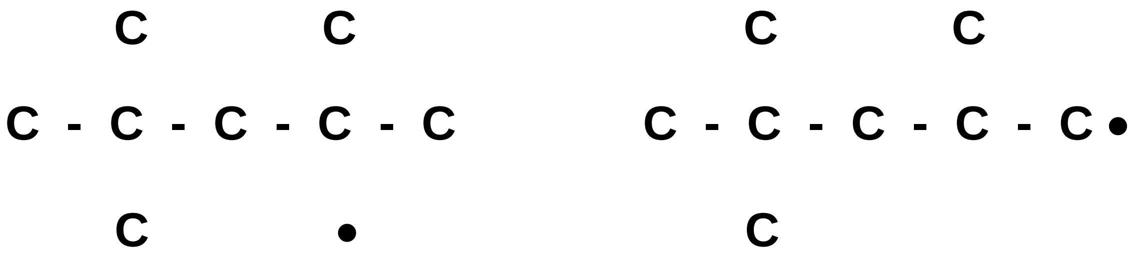


We have developed a detailed kinetic reaction mechanism for the other diesel PRF, heptamethyl nonane

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



$$\begin{array}{ccccccccccccccccc}
 & & C & & & & C & & & & C & & & & C & & \\
C & - & C & - & C & - & C & - & C & - & C & - & C & - & C & - & C \\
 & & C & & & & C & & & & & & & & C & &
\end{array}$$



$$\begin{array}{ccccccccc}
 & & C & & & & C & & \\
C & - & C & - & C & - & C & - & C \\
 & & C & & & & \bullet & &
\end{array}
\qquad
\begin{array}{ccccccccc}
 & & C & & & & C & & \\
C & - & C & - & C & - & C & - & C\bullet \\
 & & C & & & & & &
\end{array}$$

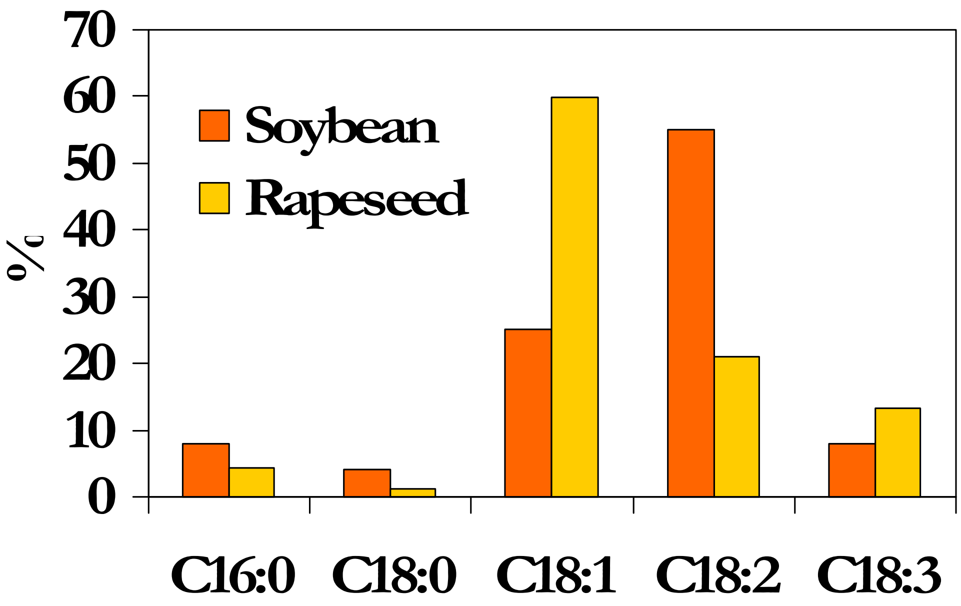
We should expect HMN kinetics to be quite similar to iso-octane

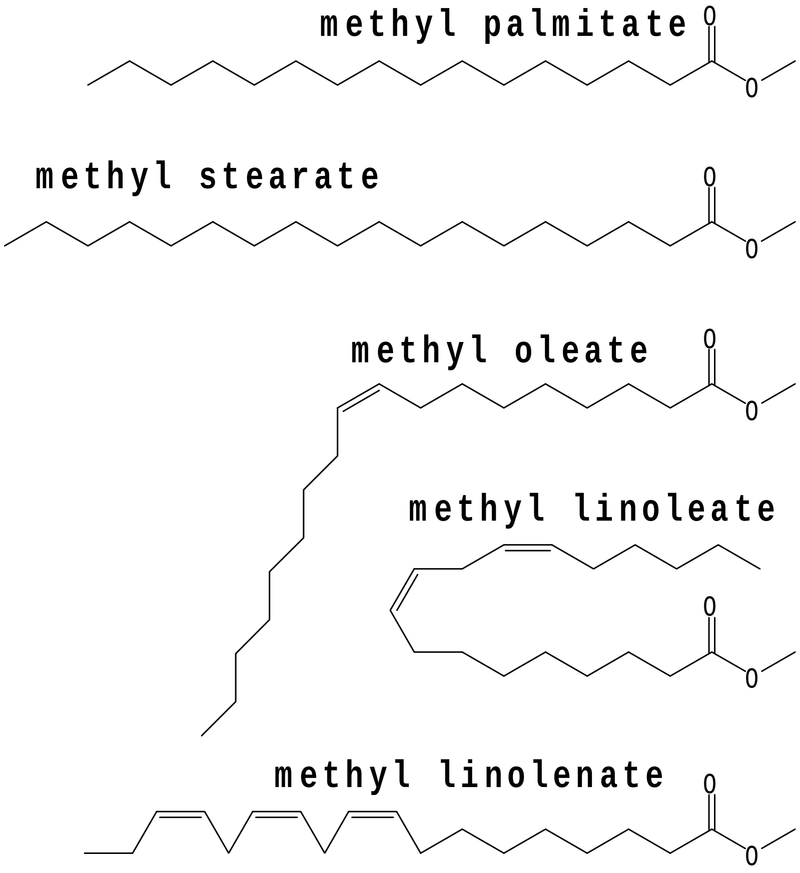
We have been modeling the effect of the position of the double bond

on ignition of olefins

		Amount of low T reactivity
C = C - C - C - C - C	1-hexene	high
C - C = C - C - C - C	2 – hexene	medium
C - C - C = C - C - C	3 – hexene	low

Composition of Biodiesels



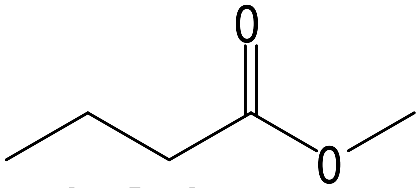


see paper Tuesday afternoon by Naik for more complete description of biodiesel fuel kinetics

Choice of Surrogates

- Methyl butanoate :

Molecular size too small compared to biodiesel

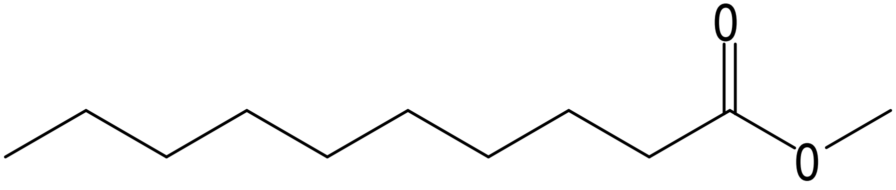


methyl butanoate

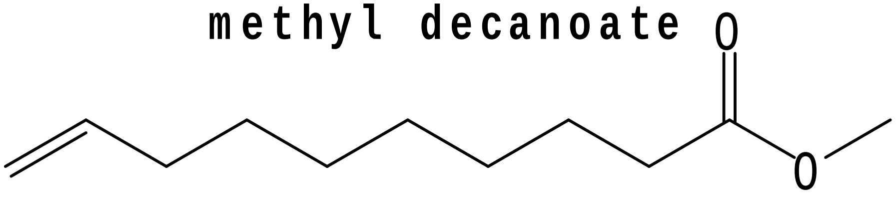
More realistic:

→ methyl decanoate

→ methyl decenoate

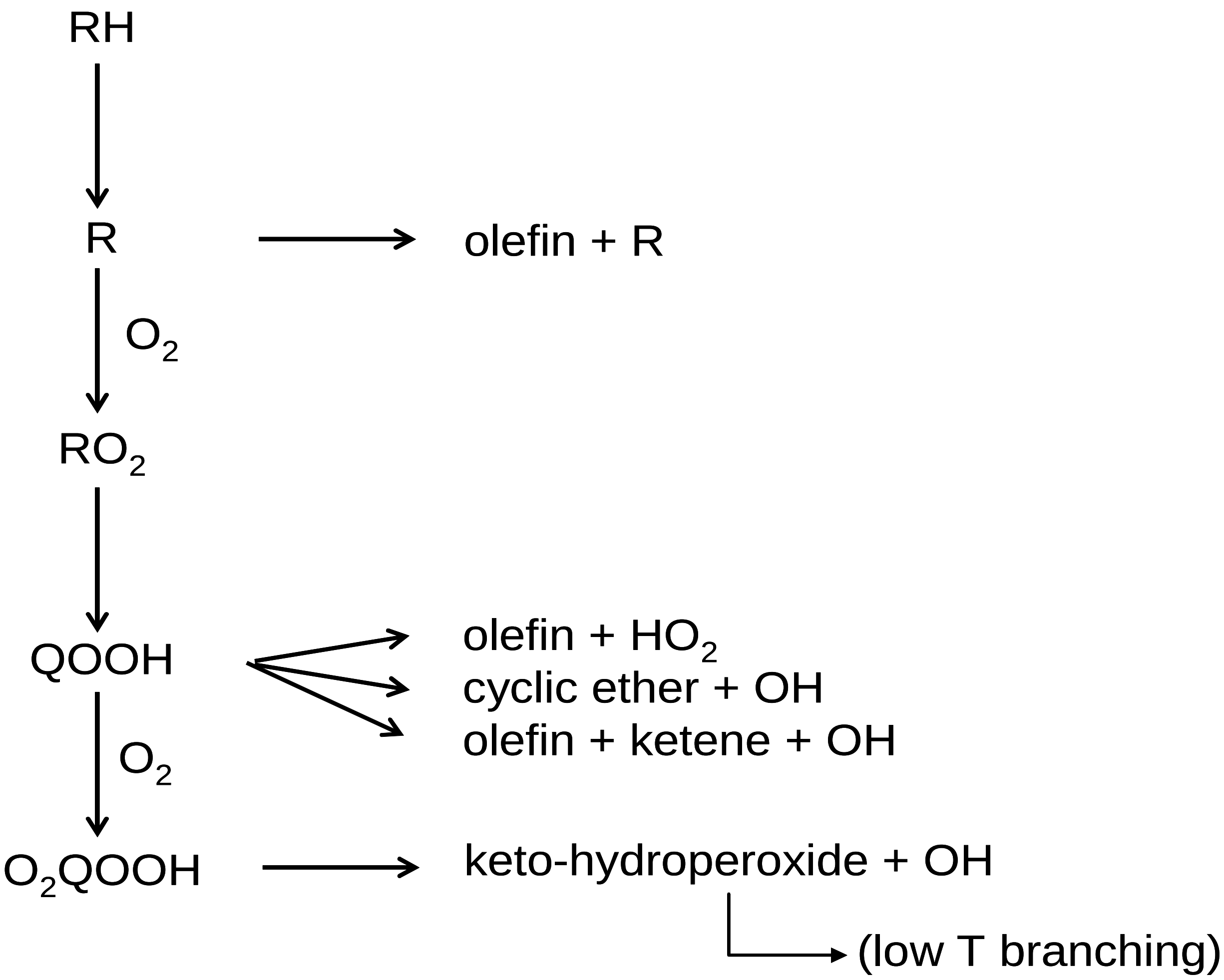


methyl decanoate



methyl decenoate

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



RH

R → olefin + R

O_2

RO_2

QOOH → olefin + HO_2, cyclic ether + OH, olefin + ketene + OH

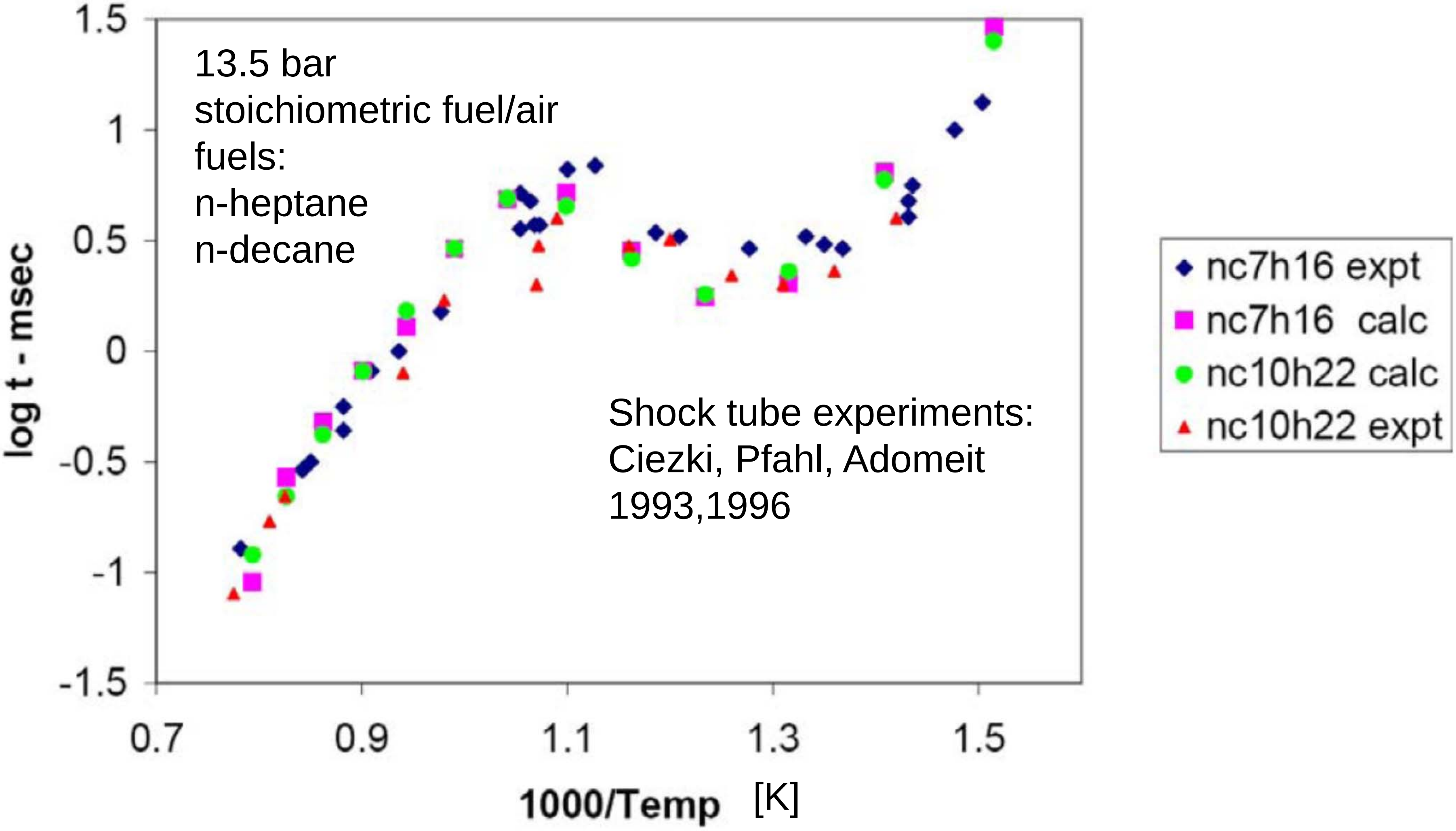
O_2

O_2QOOH → keto-hydroperoxide + OH

(low T branching)

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

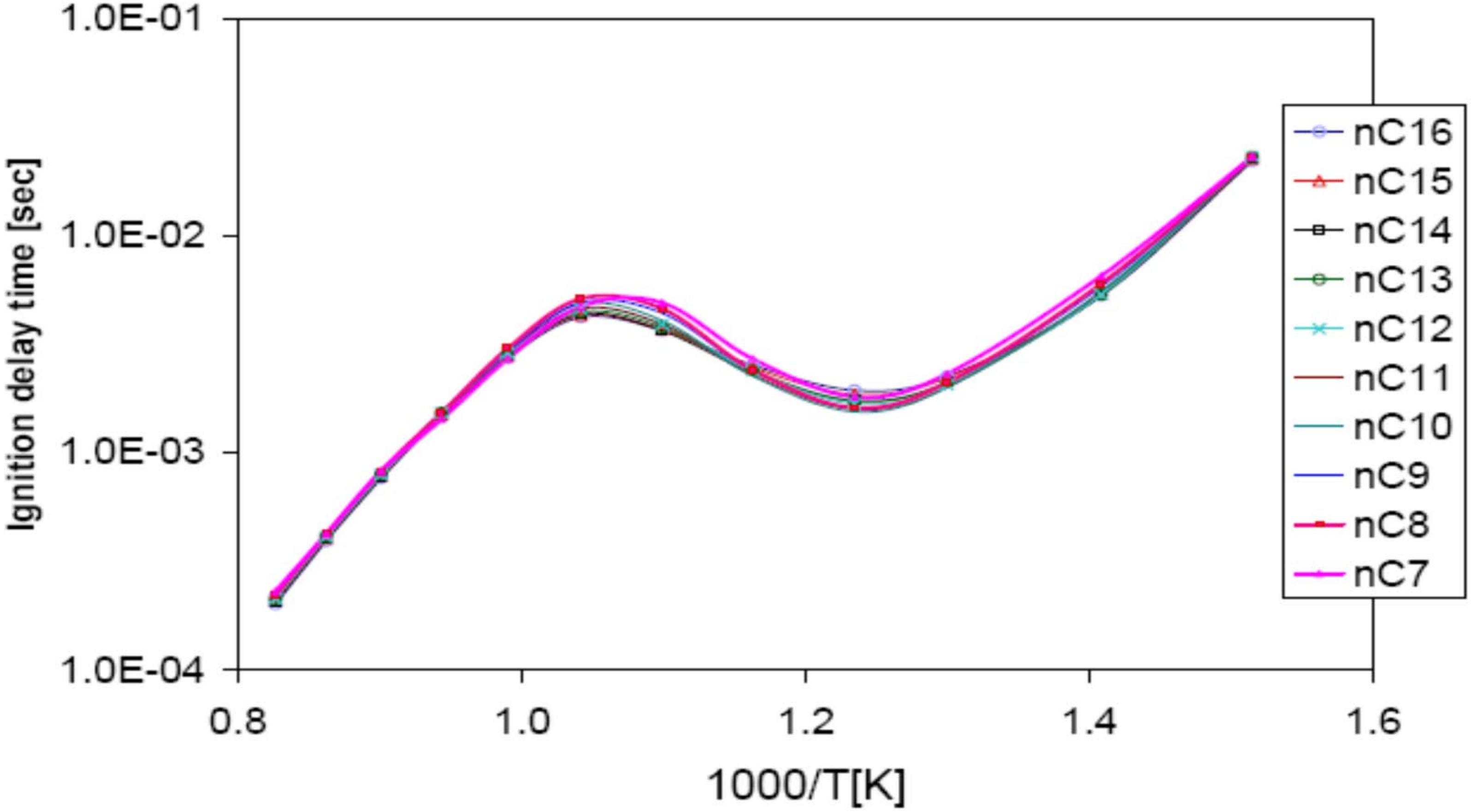
Experimental
Validation
Data

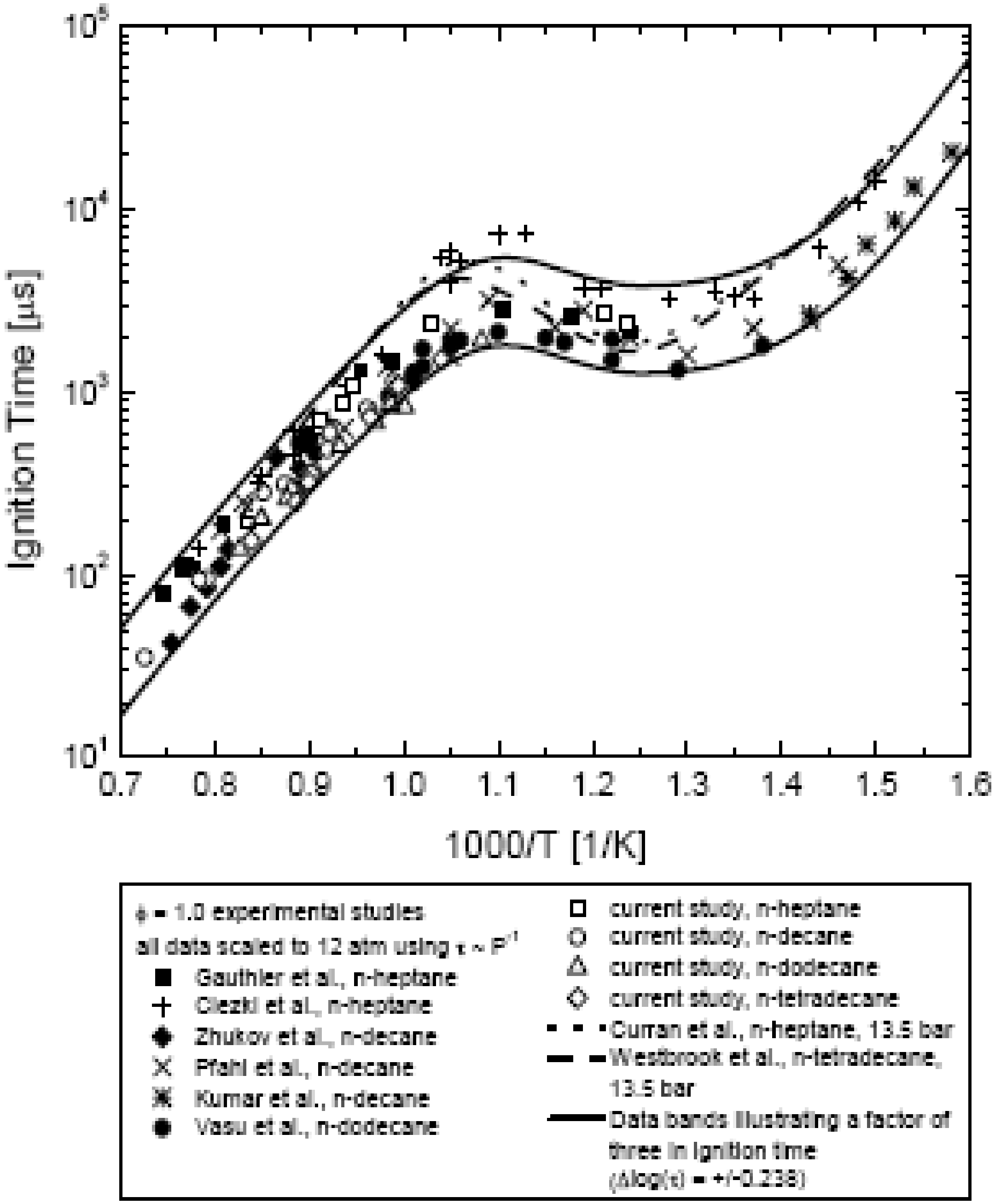


13.5 bar
stoichiometric fuel/air
fuels:
n-heptane
n-decane

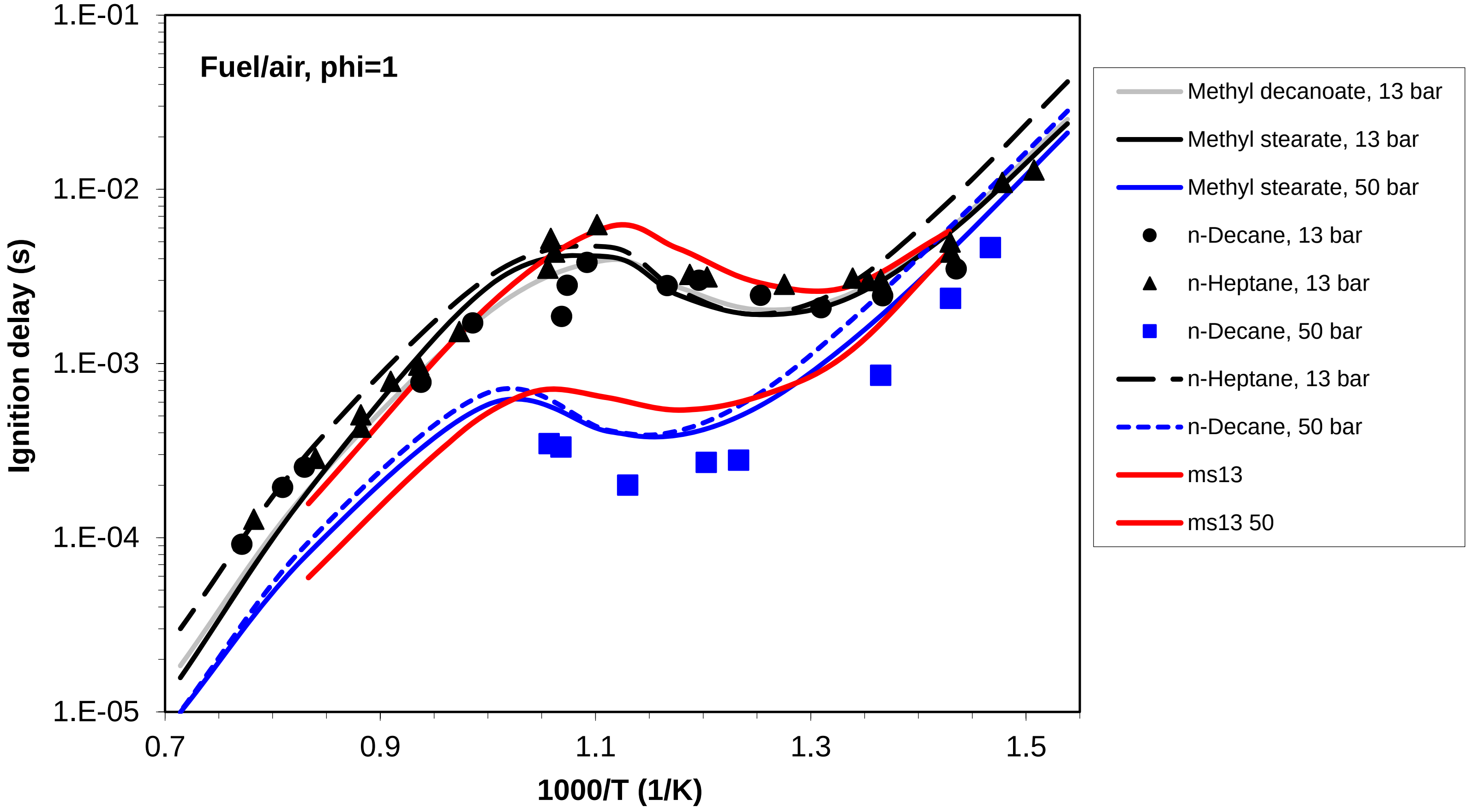
Shock tube experiments:
Ciezki, Pfahl, Adomeit
1993,1996

All large n-alkanes have very similar ignition properties

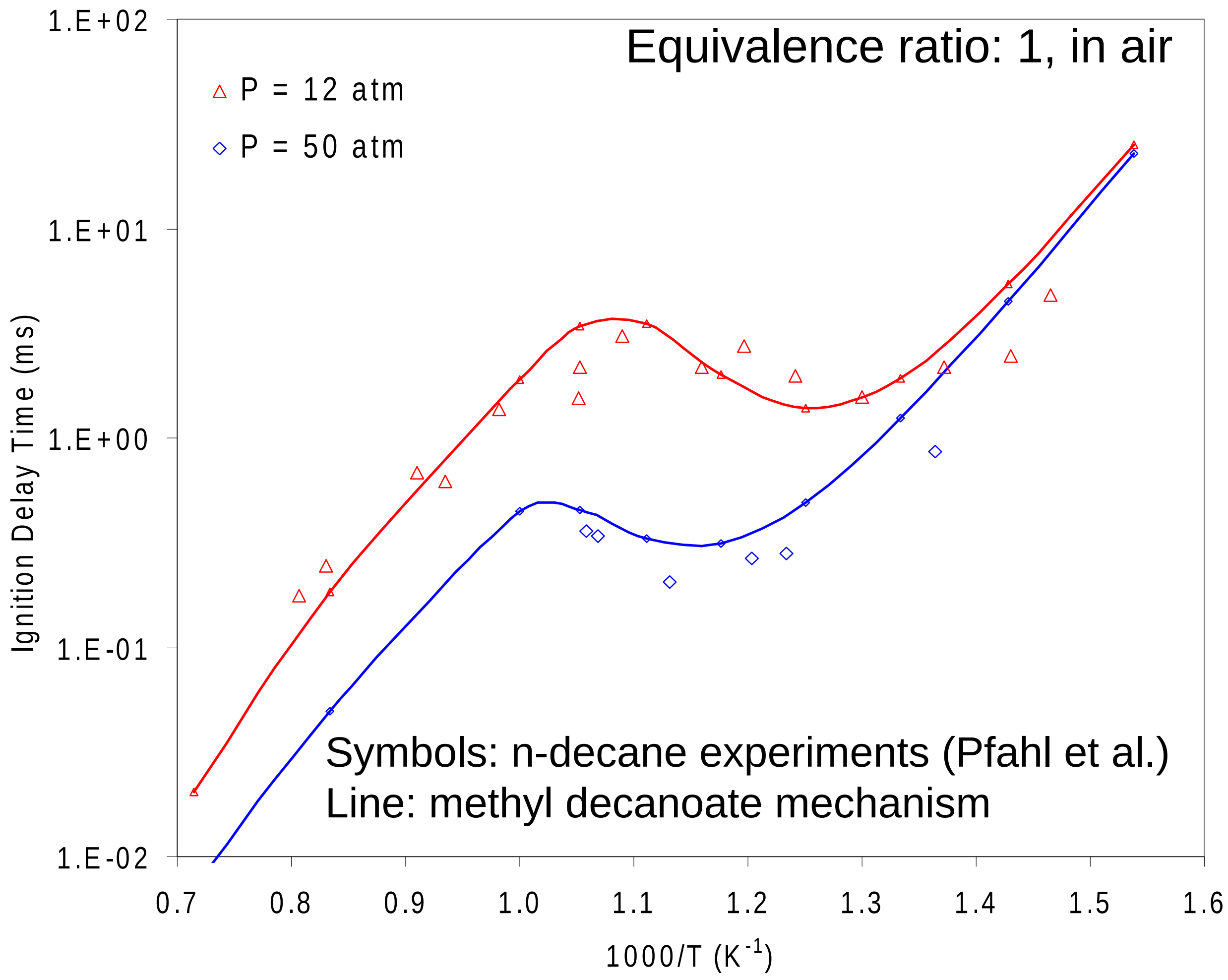



Ignition Time [µs]
10^5
10^4
10^3
10^2
10^1
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1000/T [1/K]
ϕ = 1.0 experimental studies
all data scaled to 12 atm using τ ~ P^{-1}
■ Gauthier et al., n-heptane
+ Ciezki et al., n-heptane
◆ Zhukov et al., n-decane
× Pfahl et al., n-decane
✳ Kumar et al., n-decane
● Vasu et al., n-dodecane
□ current study, n-heptane
○ current study, n-decane
△ current study, n-dodecane
◇ current study, n-tetradecane
Curran et al., n-heptane, 13.5 bar
Westbrook et al., n-tetradecane, 13.5 bar
Data bands illustrating a factor of three in ignition time
(Δlog(τ) = +/-0.238)

Methyl stearate (n-C_{18} methyl ester) has the same ignition properties as large alkanes



Comparison with n-Decane Ignition Delay Times



Ignition delay times very close

n-Alkanes:

cannot reproduce the early formation of CO_2

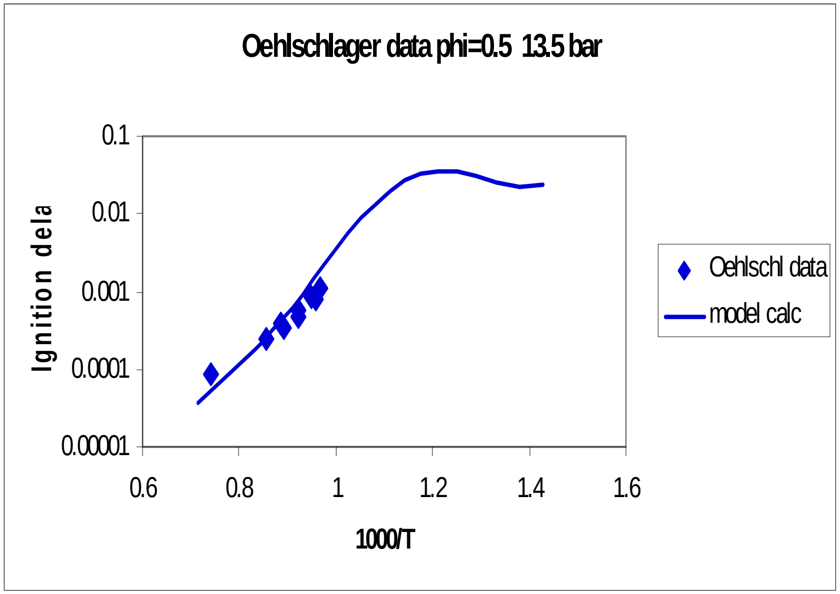
but

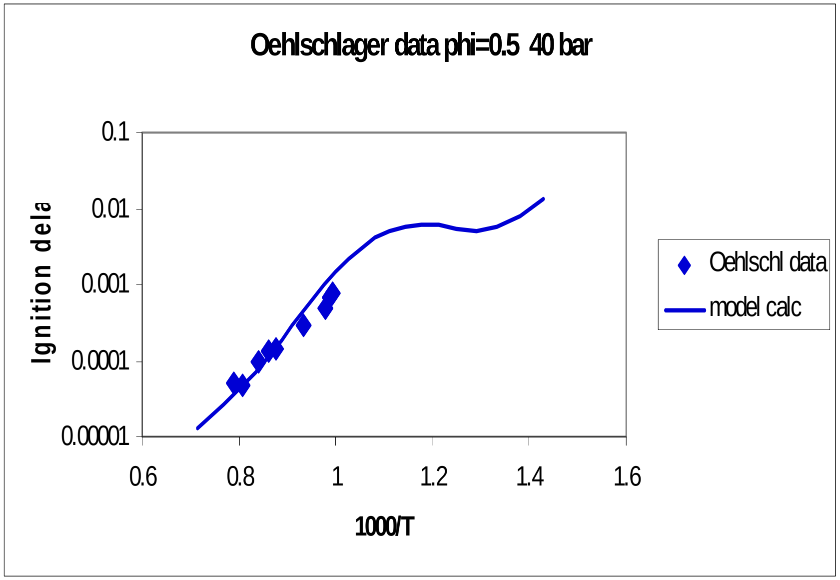
reproduce the reactivity of methyl esters very well

Branched hydrocarbons are different

- Both octane and cetane rating systems have a straight-chain reference fuel that is easy to ignite and a branched reference fuel that is hard to ignite
- iso-octane and 2,2,4,4,6,8,8-heptamethyl nonane
- n-heptane and n-hexadecane
- Are all branched hydrocarbons as similar to each other as the straight-chain hydrocarbons?
- Very few laboratory experiments available for mechanism validation of HMN
- Base a reaction mechanism on previous sets of reaction classes

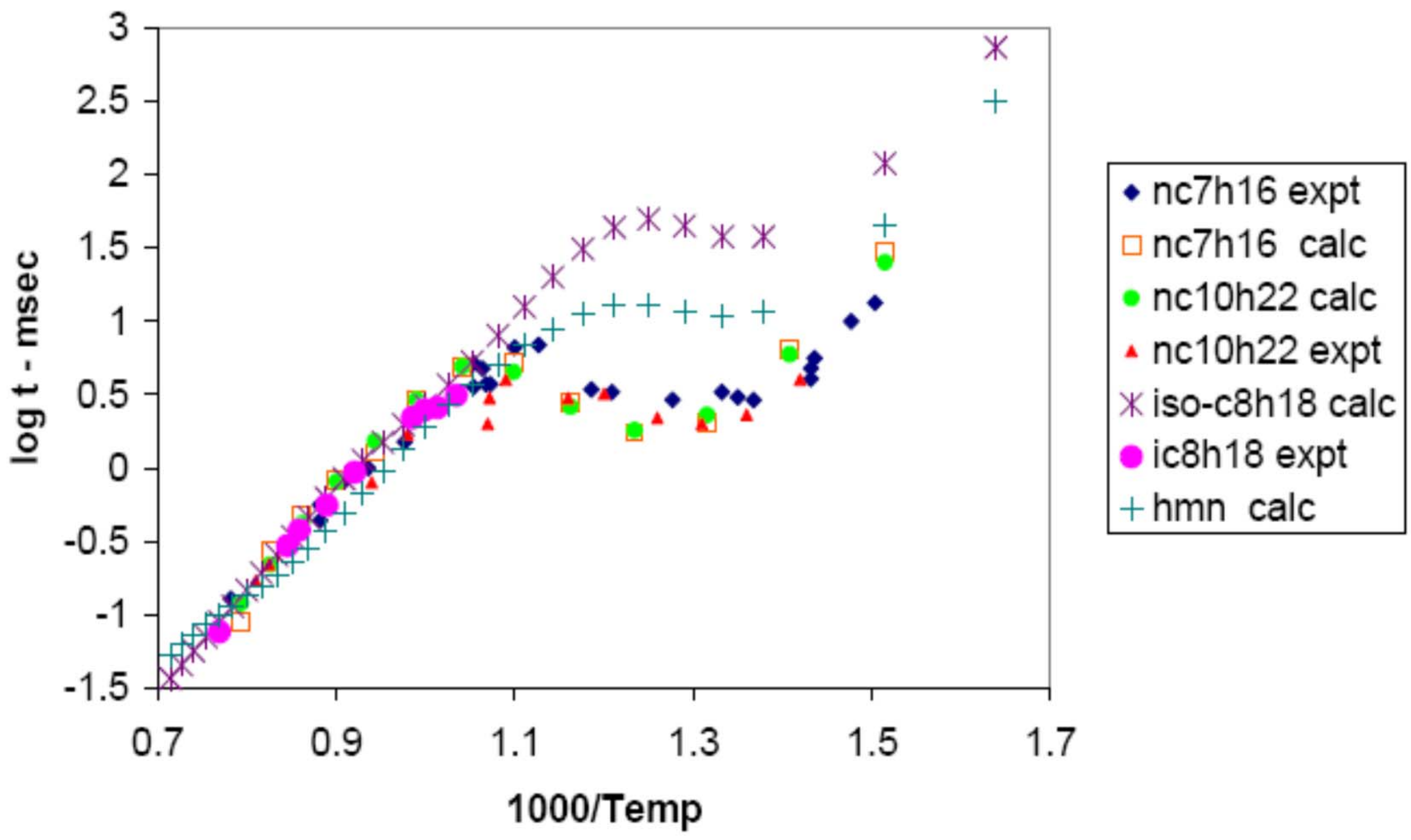
Recent experimental results show excellent agreement with modeling





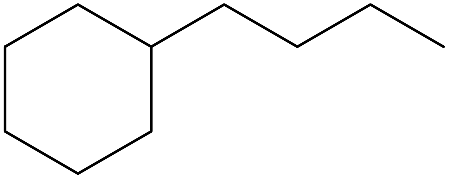
HMN and iso-octane ignition is slower than n-alkanes only in the Low Temperature regime

13.5 bar pressure

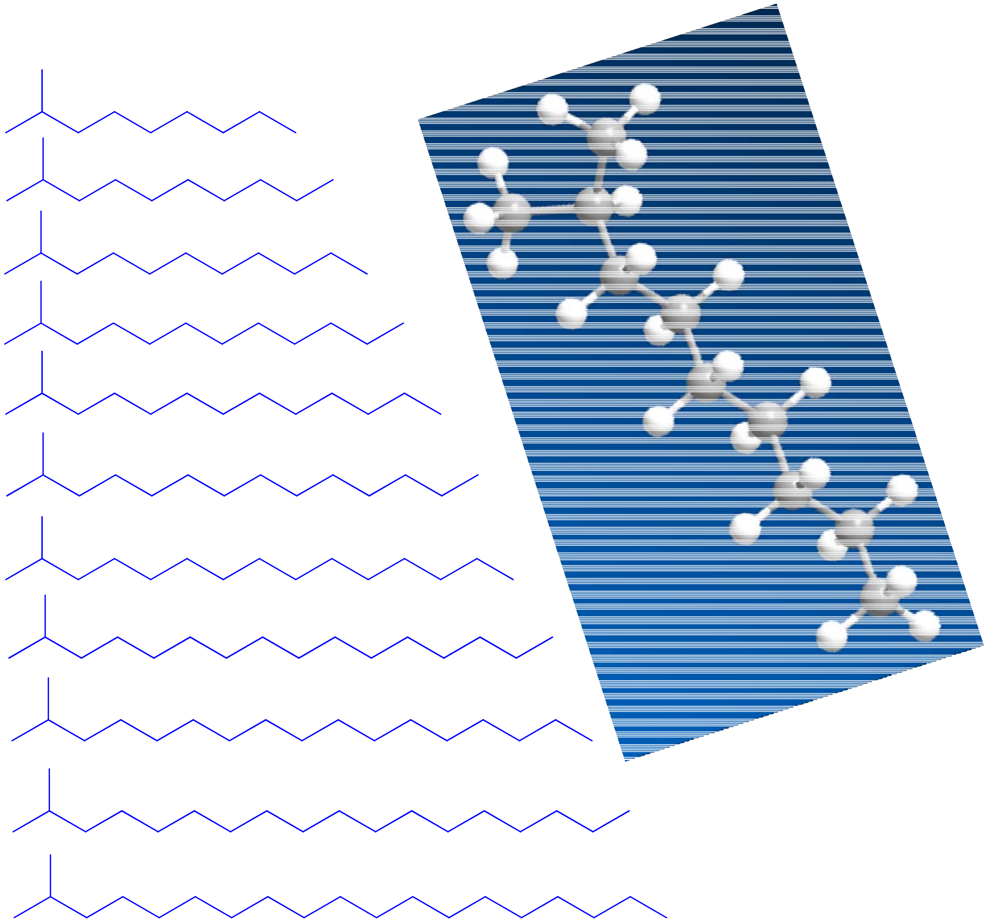


Interesting note

Experience with straight chain, biodiesel and methyl esters suggests strategies for kinetic modeling of n-alkyl benzenes and n-alkyl cyclohexanes



Assembled chemical kinetic model for a whole series of iso-alkanes to represent this chemical class in gasoline and diesel fuels

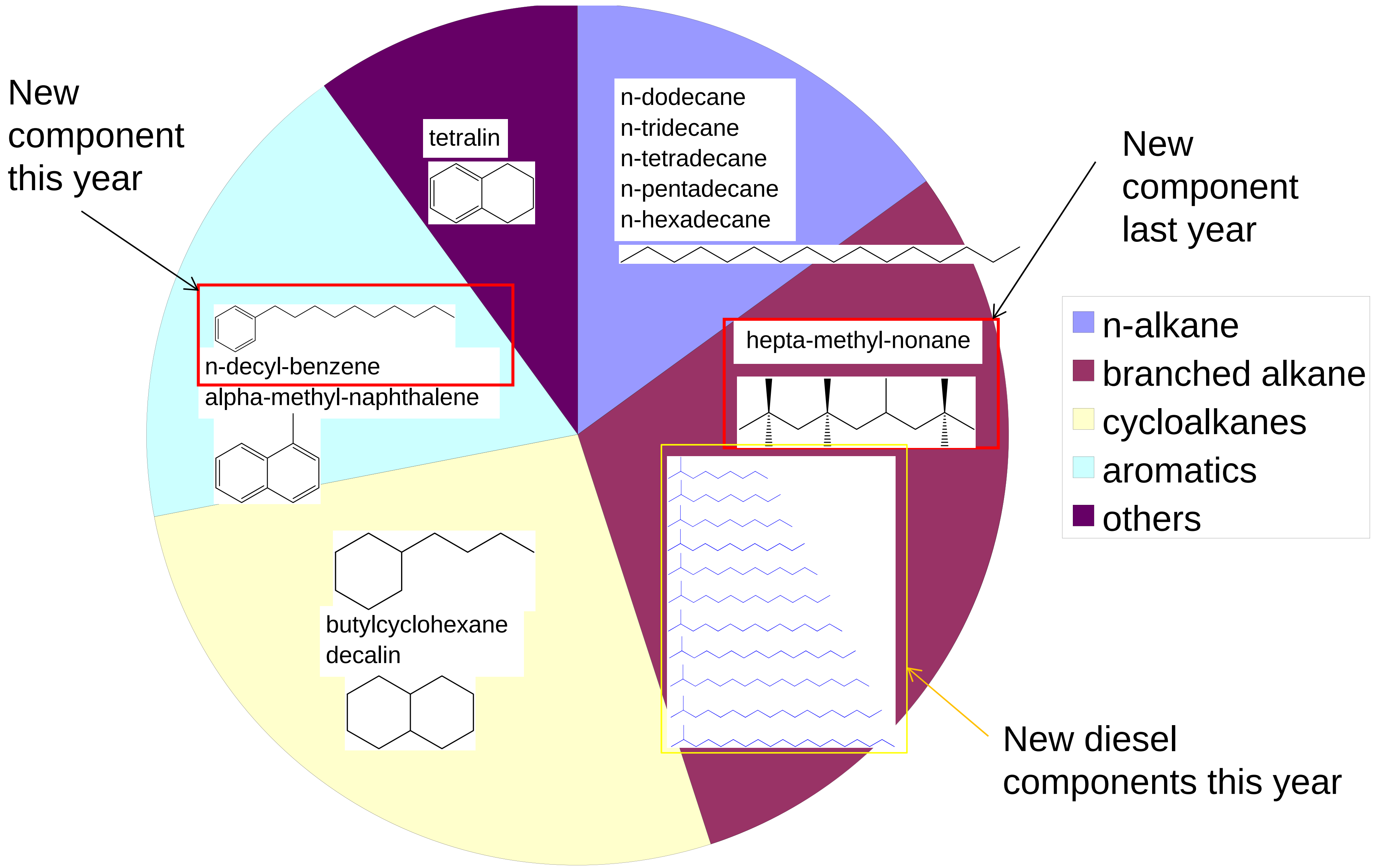


Includes all 2-methyl alkanes up to C20 which covers the entire distillation range for gasoline and diesel fuels

Built with the same reaction rate rules as our successful iso-octane and iso-cetane mechanisms.

7,900 species
27,000 reactions

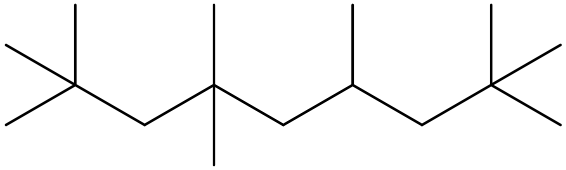
Diesel Fuel Surrogate palette:



Have assembled primary reference fuel mechanism for diesel fuel

- Diesel PRF:
  - n-cetane
  - iso-cetane

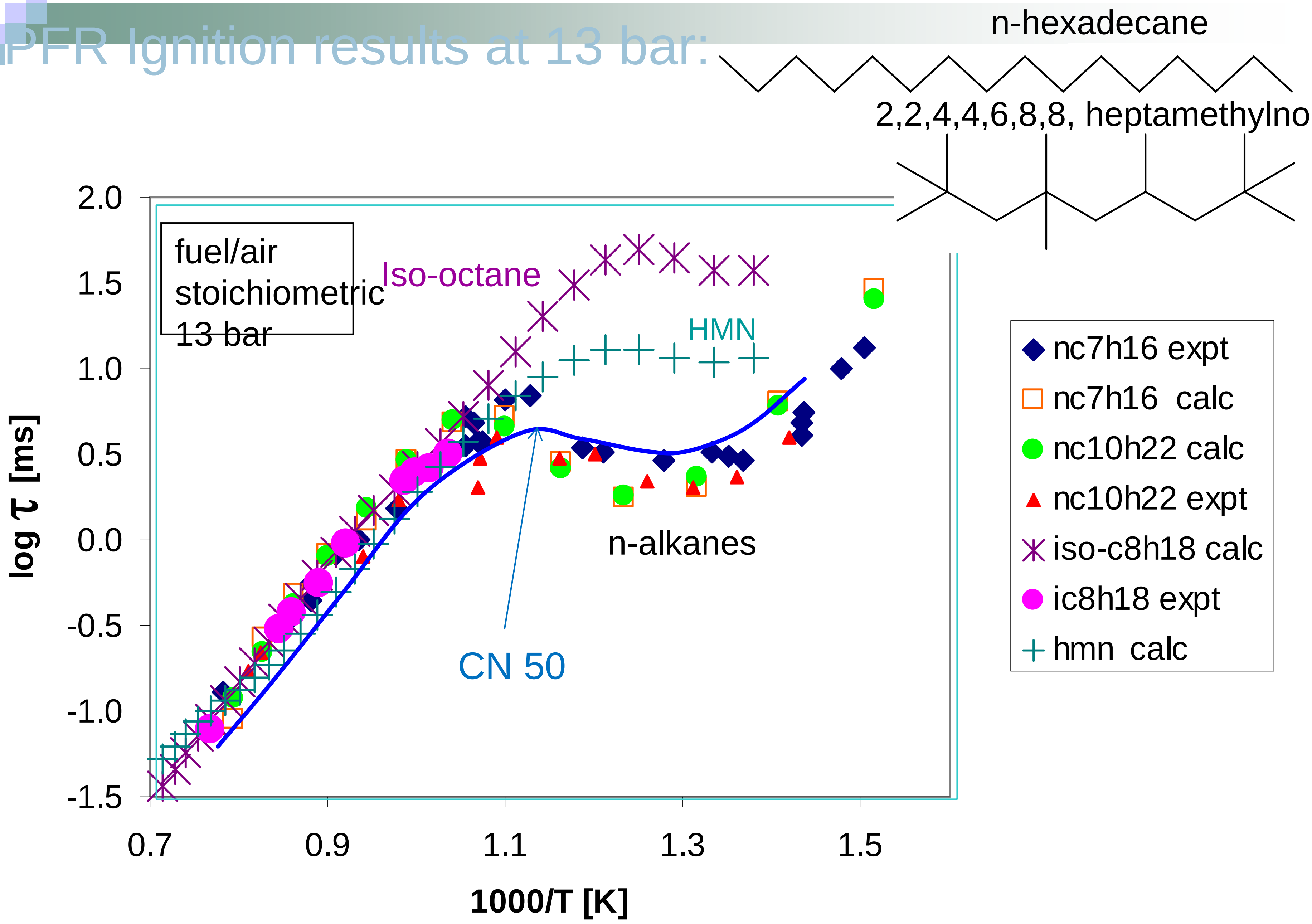
(n-hexadecane)



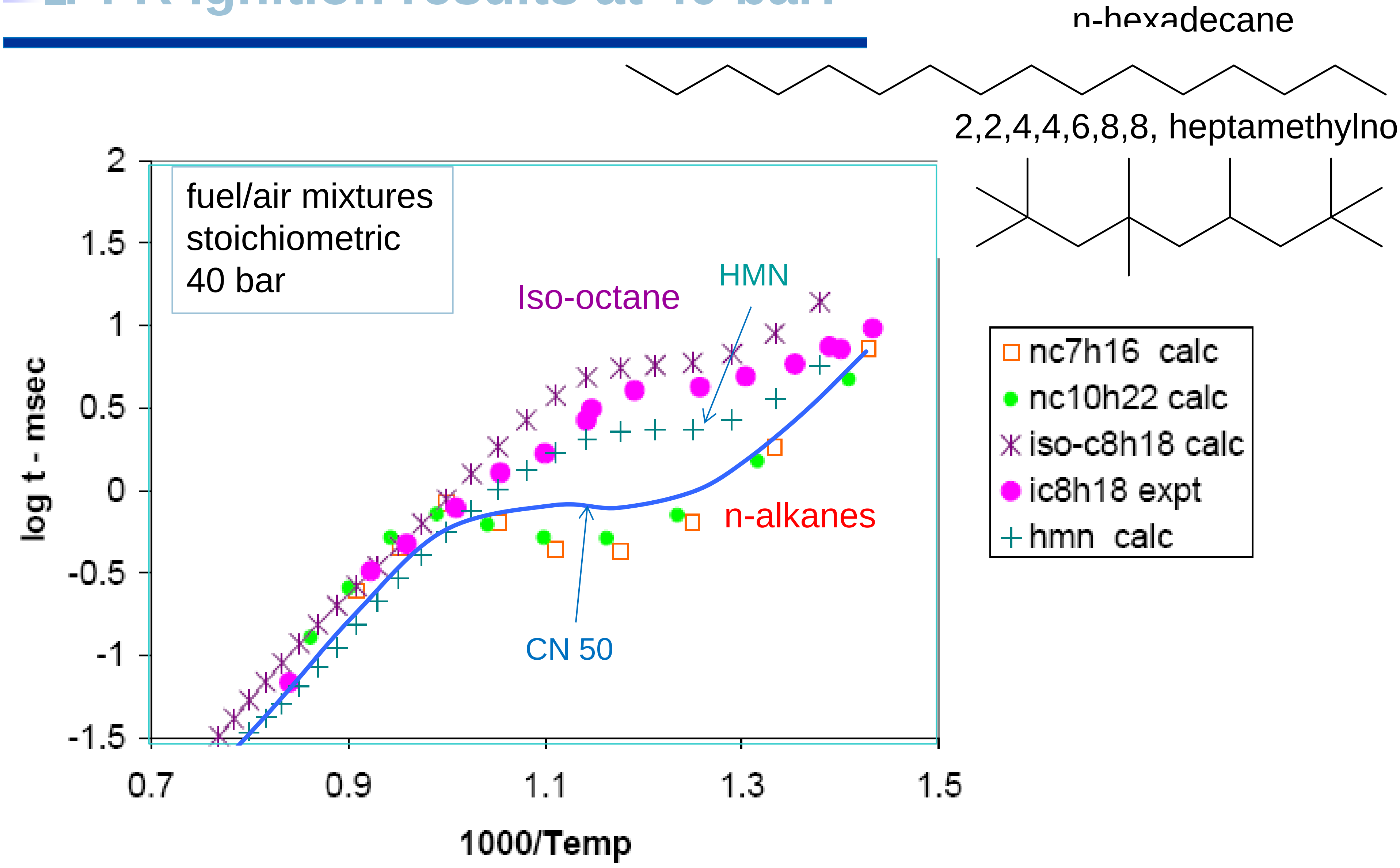
(2,2,4,4,6,8,8-heptamethylnonane

- PRF for Diesel mechanism:
  - 2,837 species
  - 10,719 reactions

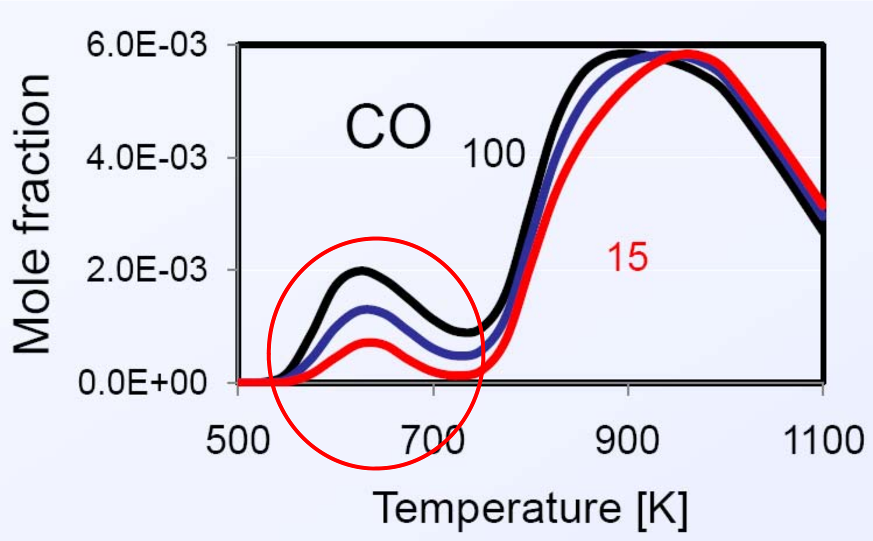
PFR Ignition results at 13 bar:



PFR Ignition results at 40 bar:

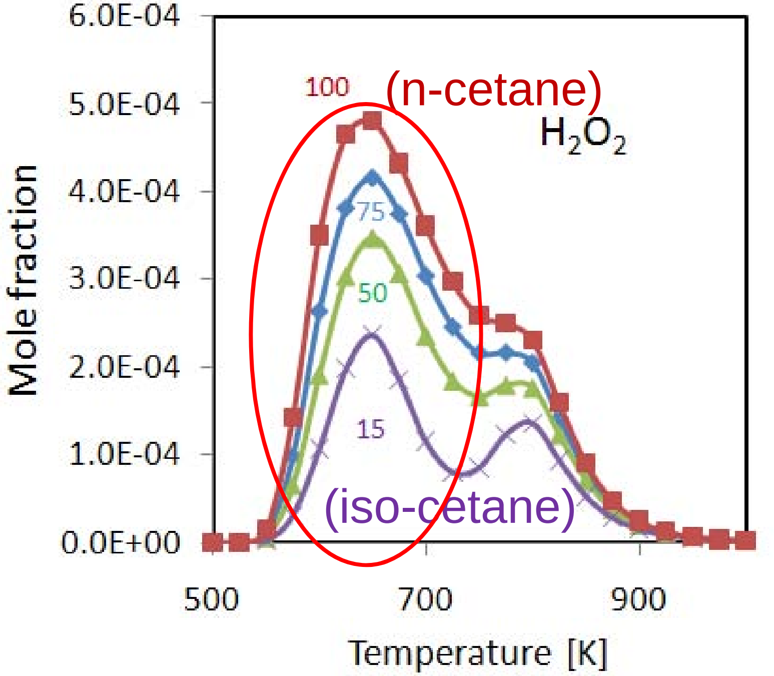


Diesel PRFs: Cetane number has a big effect at low temperatures

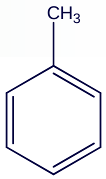


Perfectly stirred reactor
stoichiometric mixtures
10 atm

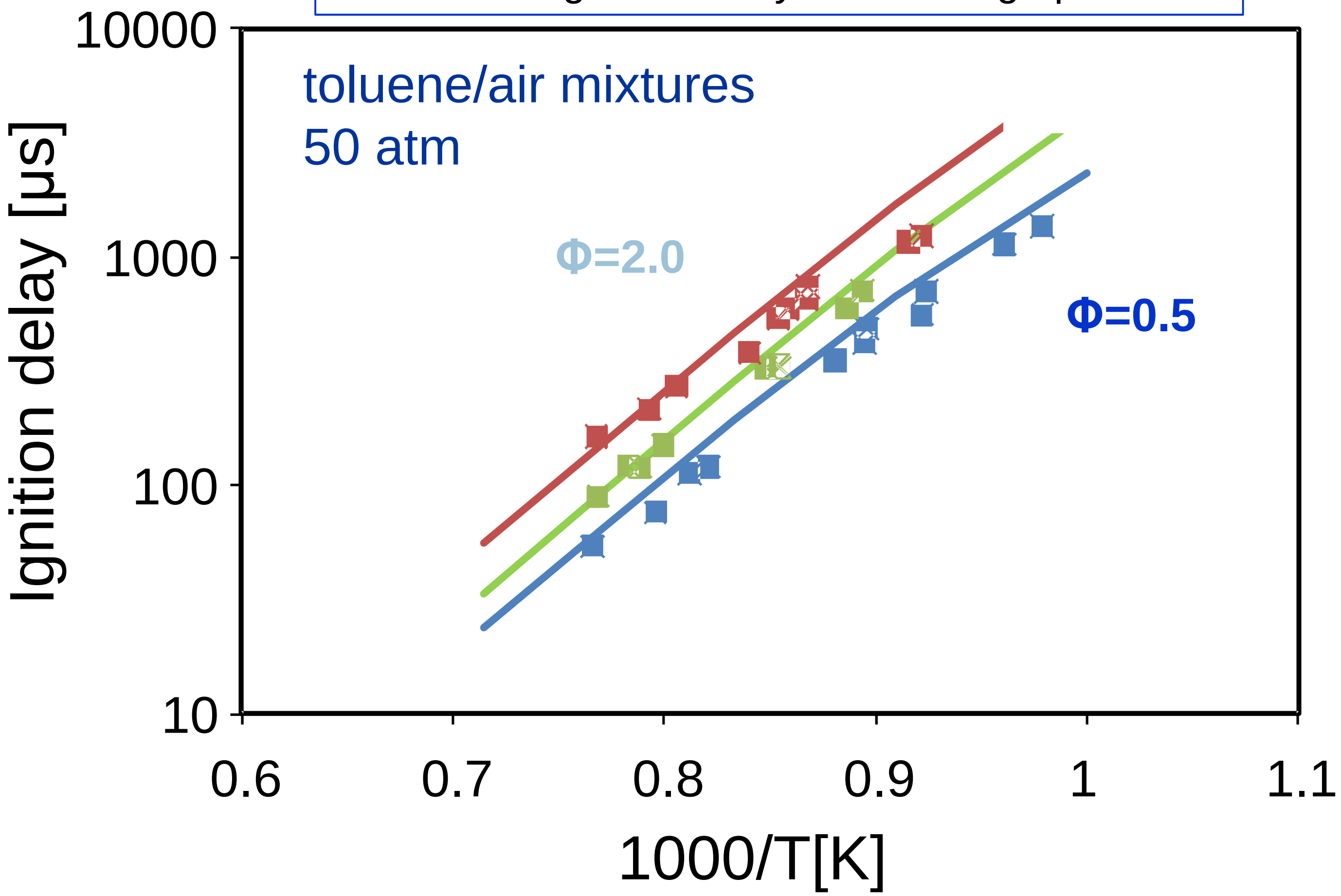
High cetane PRFs lead to more H2O2 which decomposes to reactive OH radicals



Improved toluene model well predicts ignition at high pressure

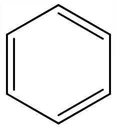


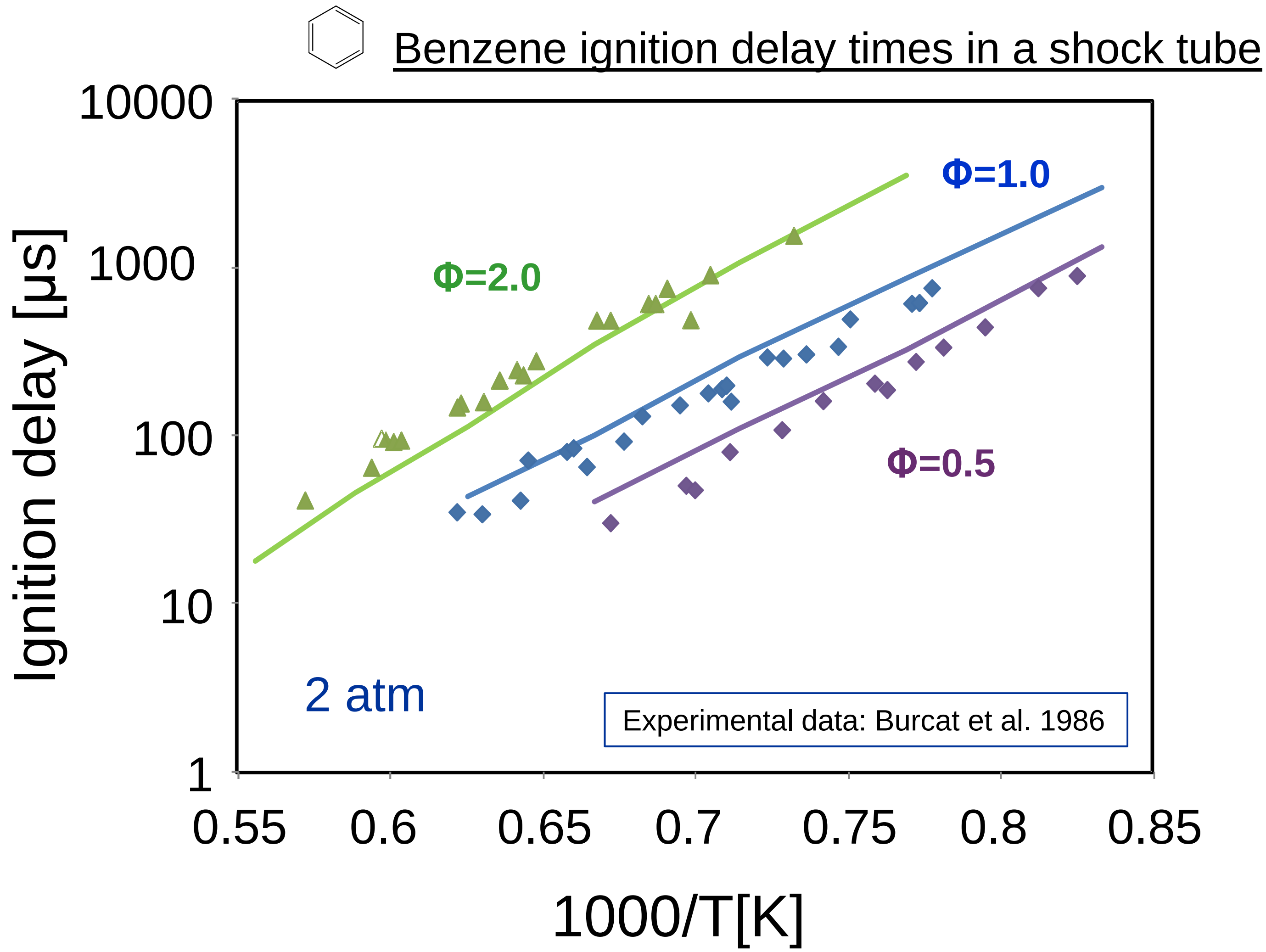
Shock tube ignition delay times at high pressure



Experimental data: Shen, Vanderover and Oehlschlaeger (2009)

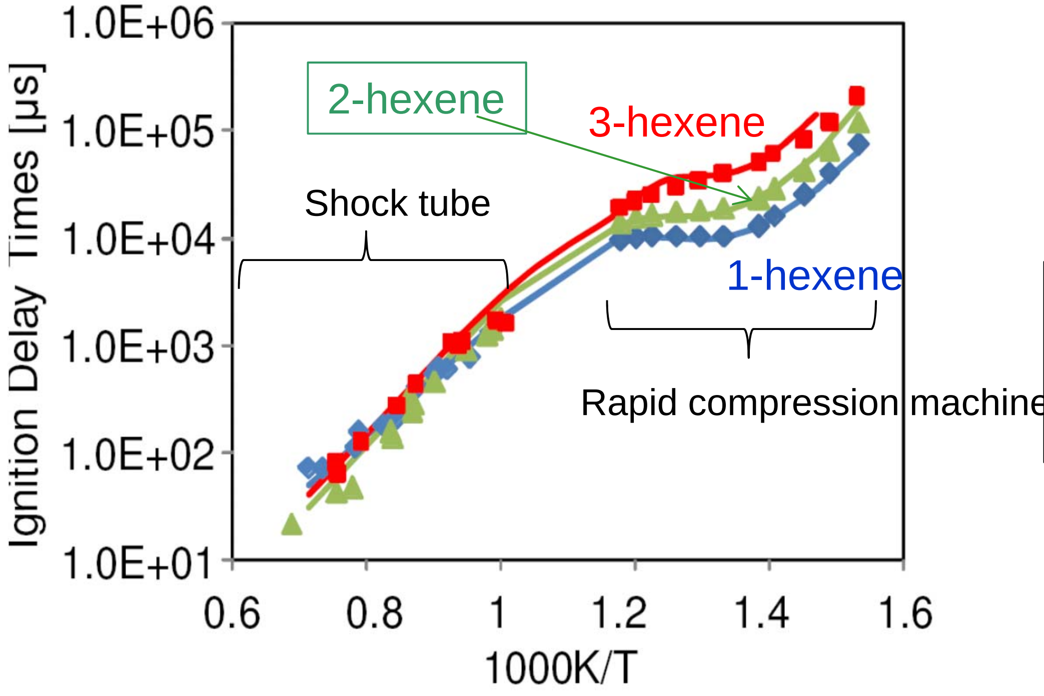
Improving building blocks for toluene: benzene





Benzene ignition delay times in a shock tube

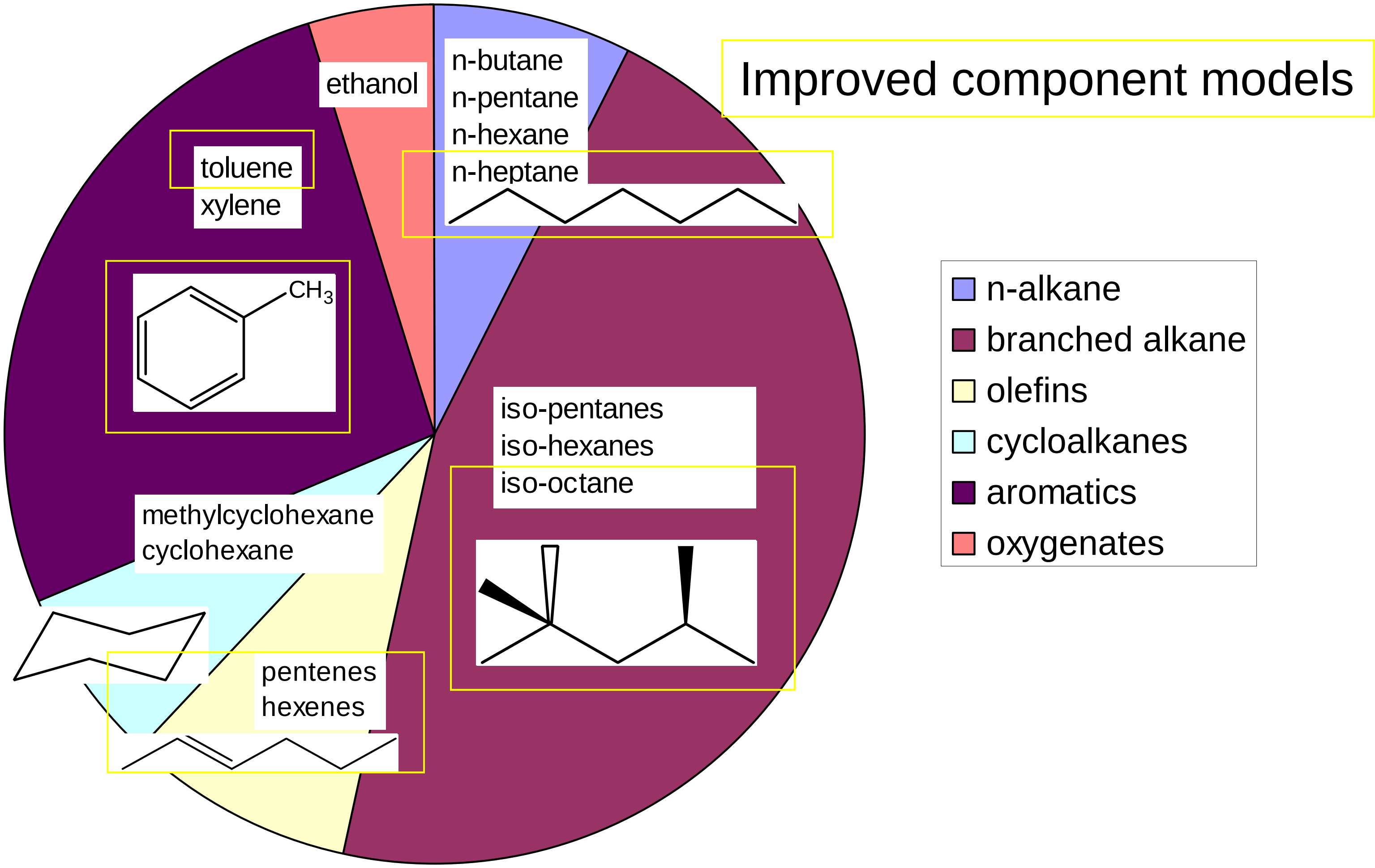
Improved the predictive behavior of hexenes and pentenes mechanisms over the entire temperature range



Mehl, Pitz, Westbrook, Yasunaga and Curran, The 33rd International Symposium on Combustion, 2010.

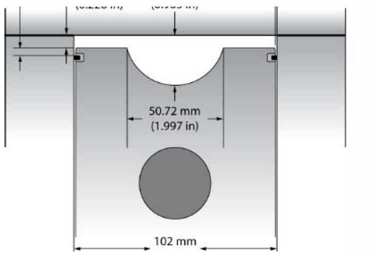
RCM experiments: Vanhove et al. 2007
Shock tube experiments: Yasunaga and Curran, 2010

Recent improvements to fuel surrogate models: Gasoline

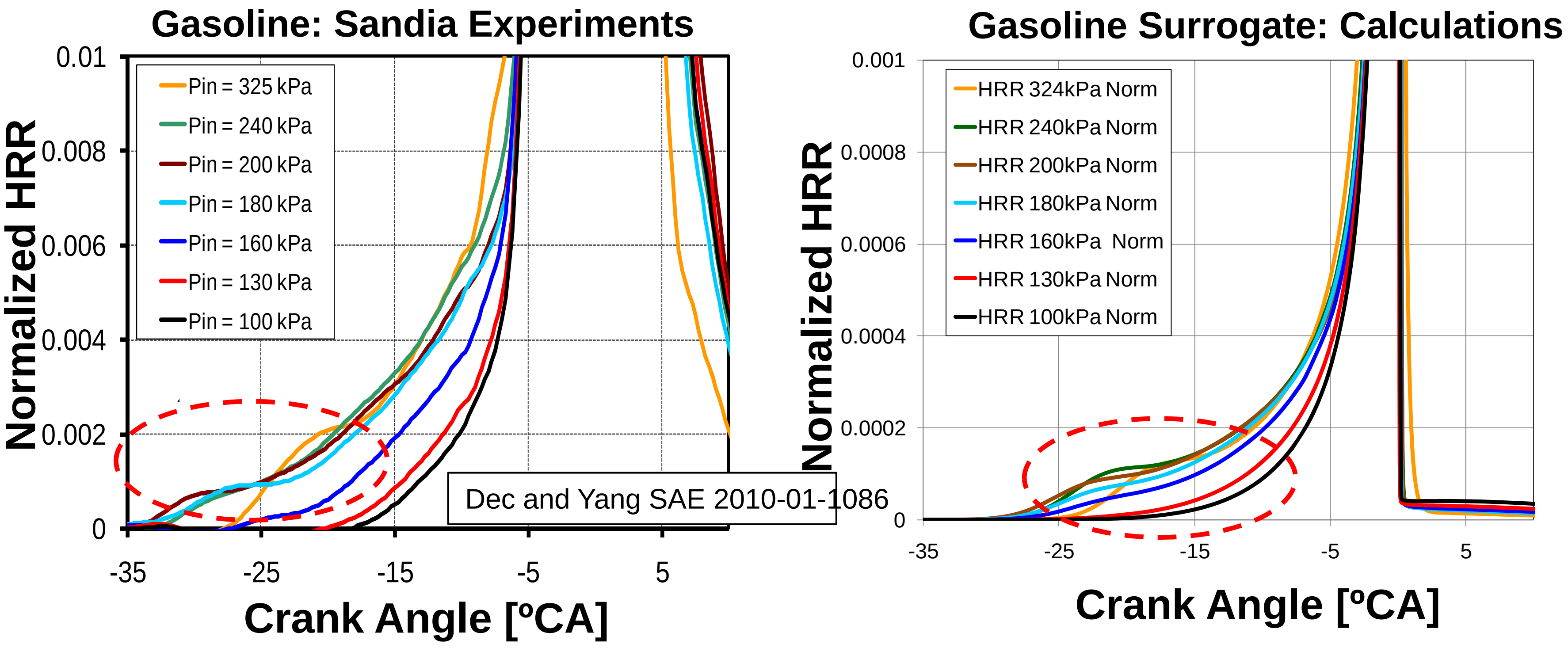


Improved component models

Successful simulation of intermediate heat release in HCCI engine using gasoline surrogate blends



Dec and Yang, 2010: Intermediate heat release allows highly retarded combustion phasing and high load operation with gasoline

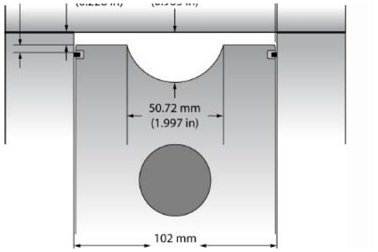

Gasoline: Sandia Experiments

Gasoline Surrogate: Calculations

Dec and Yang SAE 2010-01-1086

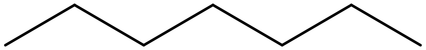
(Curves are aligned by time of peak heat release and normalized by total heat release)

4-component gasoline surrogate:
Matched gasoline composition targets and reactivity

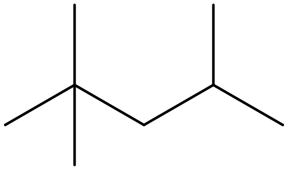


Gasoline surrogate:

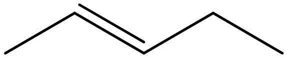
n-heptane (n-alkanes)



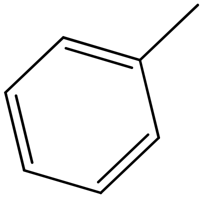
iso-octane (iso-alkanes)



2-hexene (olefins)



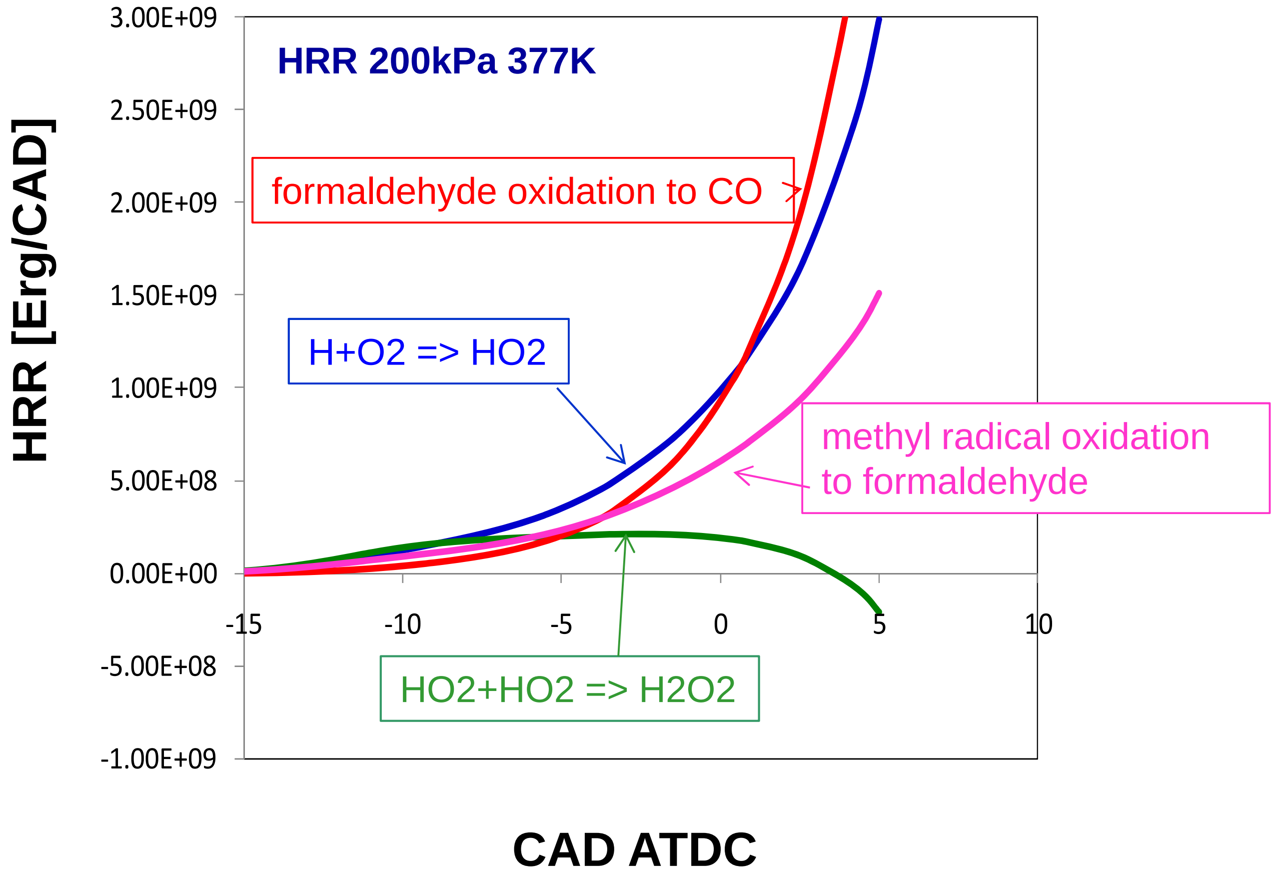
toluene (aromatics)



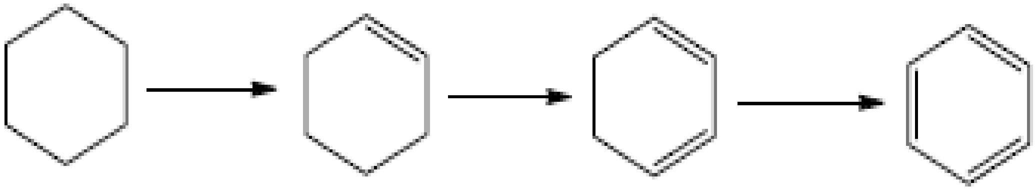
	Surrogate (%Vol)	Gasoline (%Vol)
n-alkanes	0.16	0.731
iso- alkanes	0.57	
olefins	0.04	0.04
aromatics	0.23	0.23
A/F Ratio	14.60	14.79
H/C	1.92	1.95

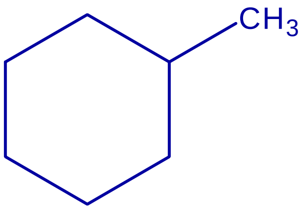
Matched the reactivity of a mixture having the same RON and MON as the gasoline

Reaction contributions to intermediate heat release rate



Cyclic paraffins are a fuel type that is poorly represented



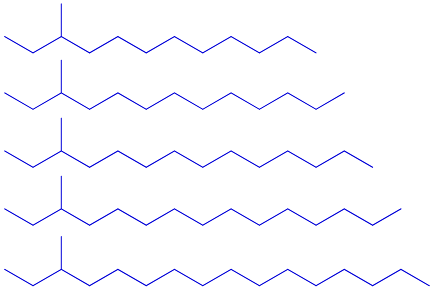


Next steps

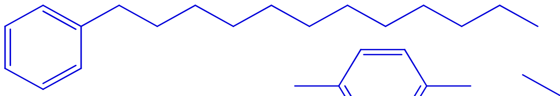
- We are continuing to add new species to each fuel class in the surrogate palette
- We have added 2-methyl and are adding 3-methyl alkanes to simulate F-T fuels
- We are adding component models for biodiesel species with double bonds

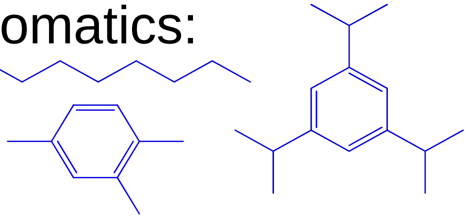
Next Activities

- Develop detailed chemical kinetic models for another series iso-alkanes: 3-methyl alkanes



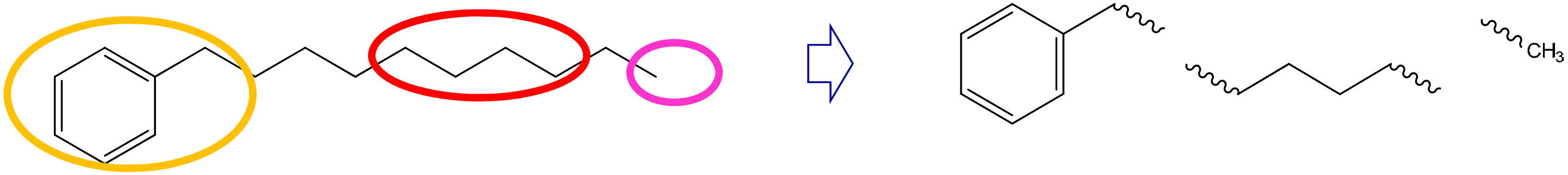
- Validation of 2-methyl alkanes mechanism with new data from shock tubes, jet-stirred reactors, and counterflow flames
- Develop detailed chemical kinetic models for alkyl aromatics:





- More accurate surrogates for gasoline and diesel
- Further develop mechanism reduction using functional group method

n-decylbenzene - Diesel Fuels



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