2.5A Combustion Technology Reducing Environmental Impact

Chemistry-Oriented Fuel Design for Internal Combustion Engines

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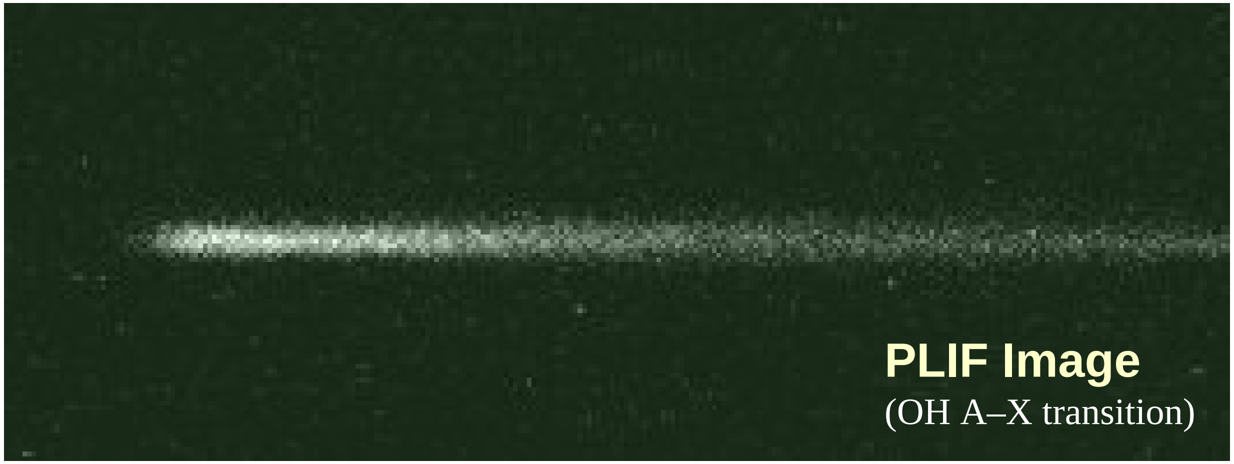
Chemical Kinetics

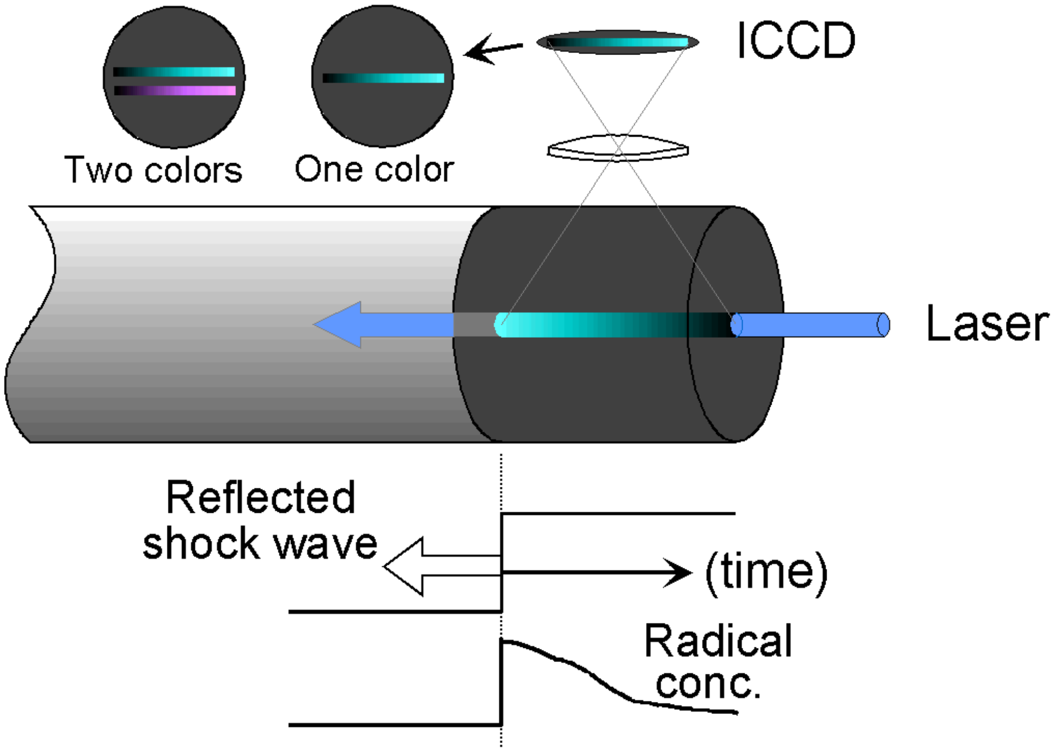
of Combustion

Background Knowledge in Physical Chemistry



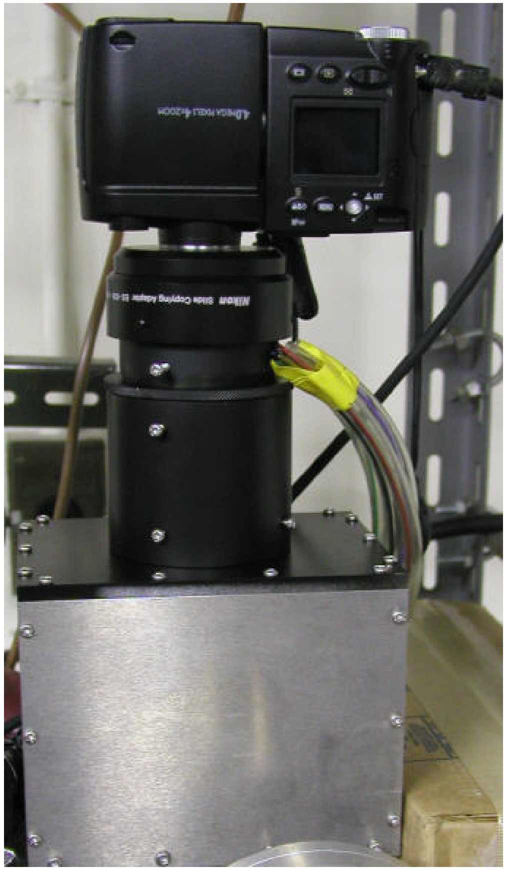
Experimental (ST-PLIFI)

T. Seta *et al.*, *Rev. Sci. Instr.*, **76**, 064103 (2005).

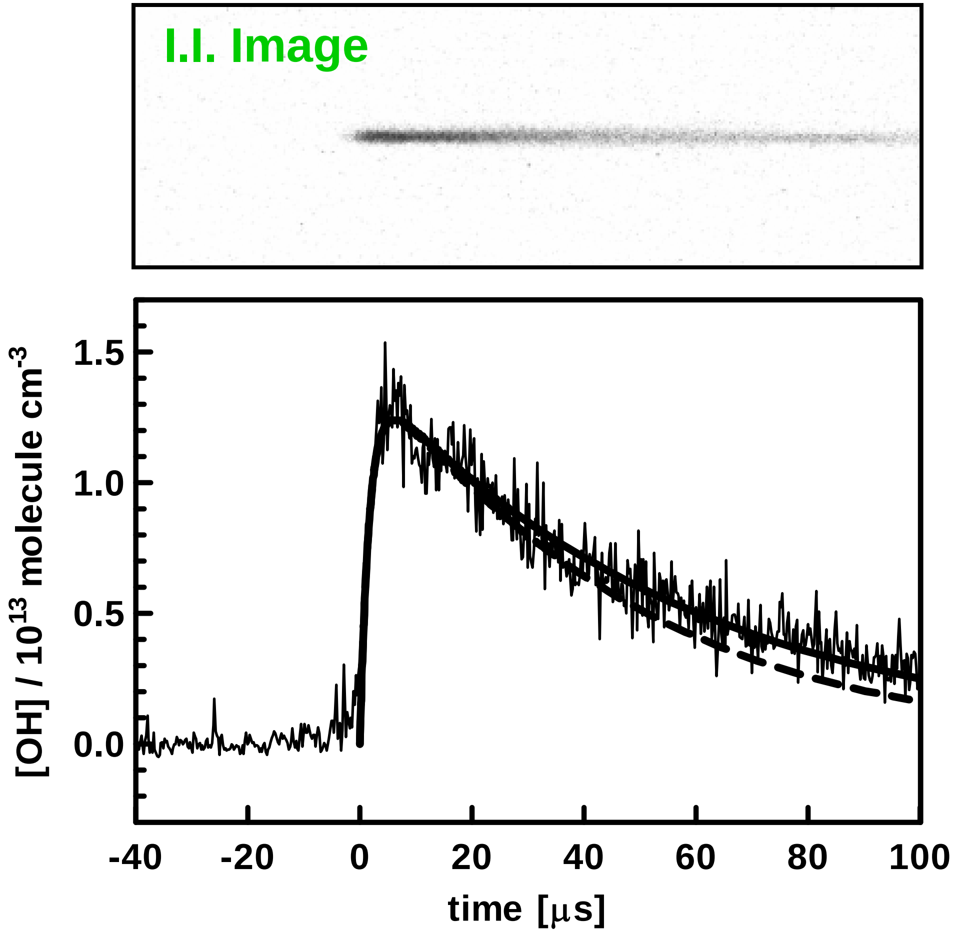


Principle of PLIFI (Pulsed LIF Imaging)
detection of radicals in a shock tube

LIF Detection Manifold



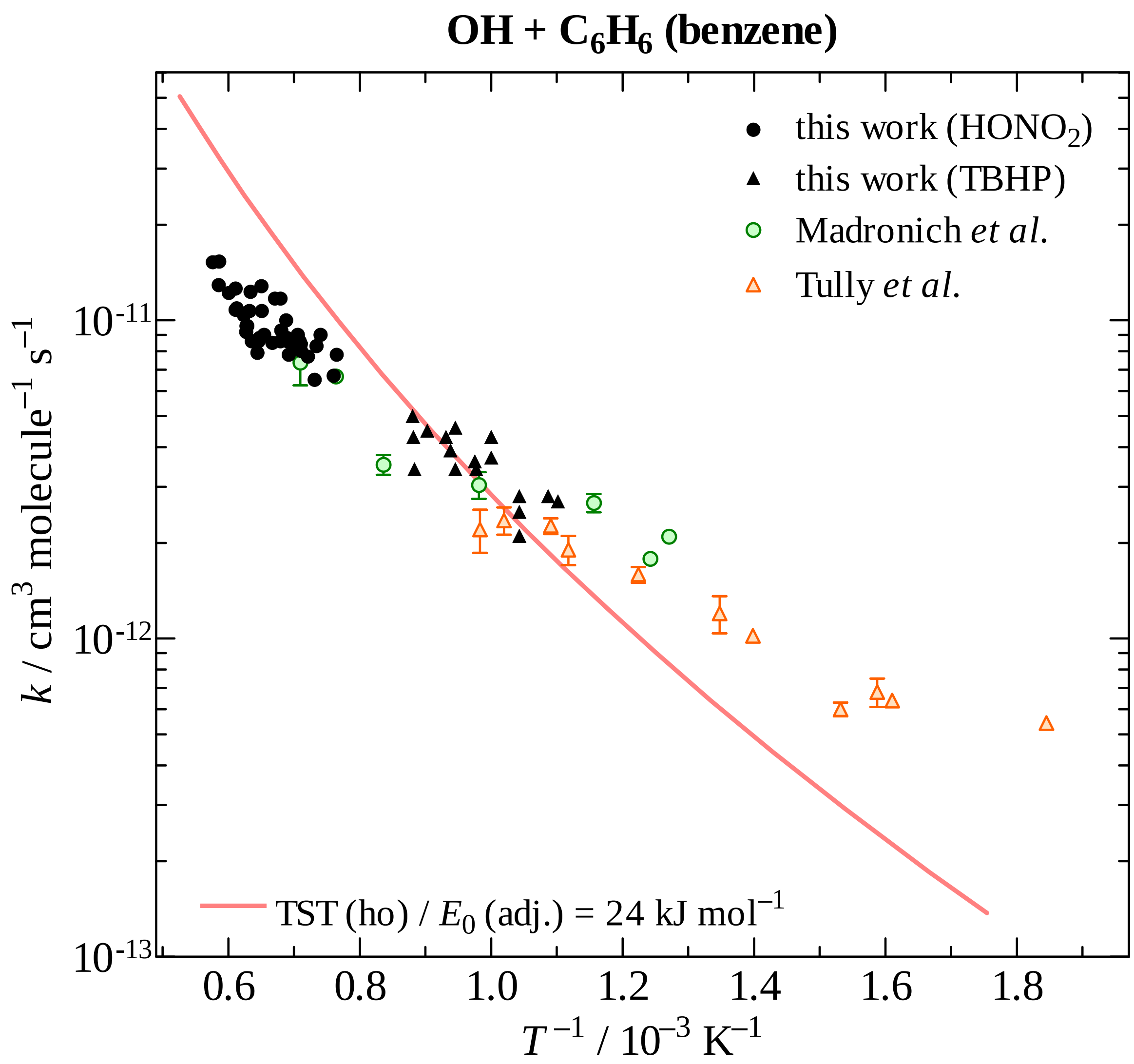
Kinetic Measurement for OH + Benzene



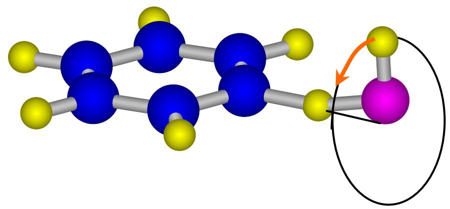
T = 1451 K, P = 1.80 atm, $[HNO_3]_0 = 1.38 \times 10^{13}$ cm^{-3}, $[C_6H_6]_0 = 1.87 \times 10^{15}$ cm^{-3}

Measured Rate Constant

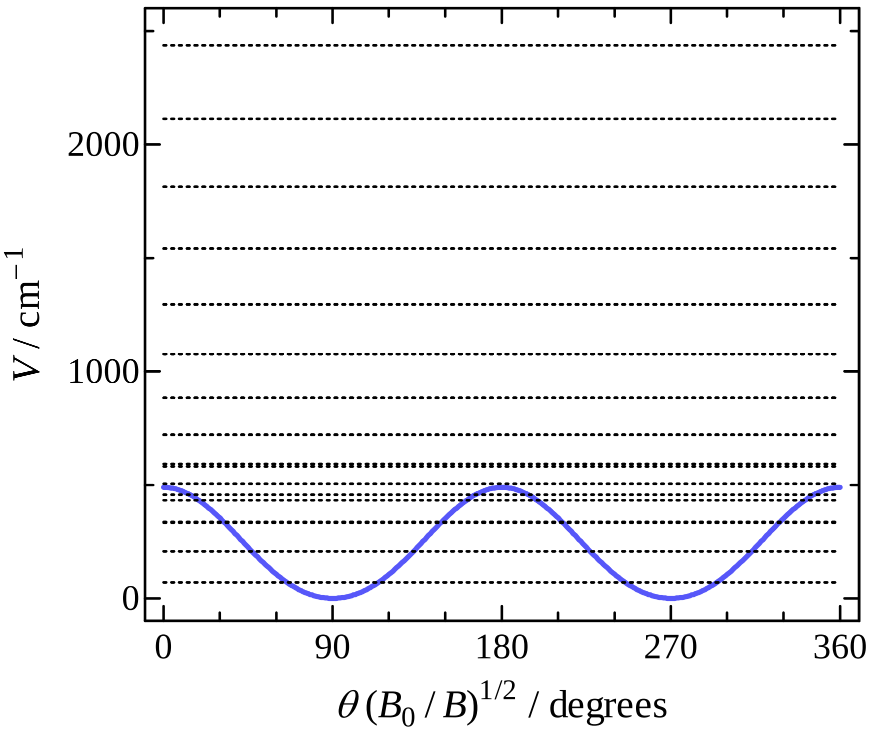
TST [based on B3LYP/6-31G(d)] does NOT Reproduce the experiments

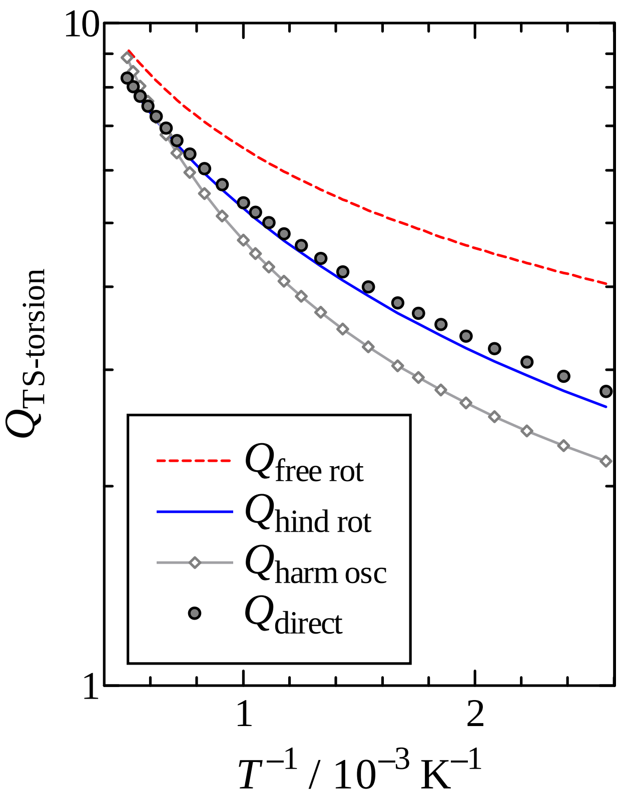


Hindered **Intramolecular Rotation** of TS

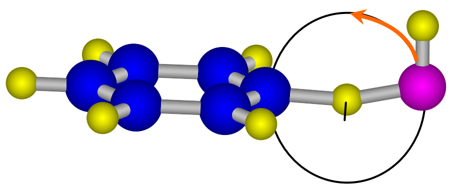


Q (Intramolecular rotation)
≠ *Q* (harmonic oscillator)
≠ *Q* (free rotor)
~ *Q* (Pitzer-Gwinn approx. for H.R.)

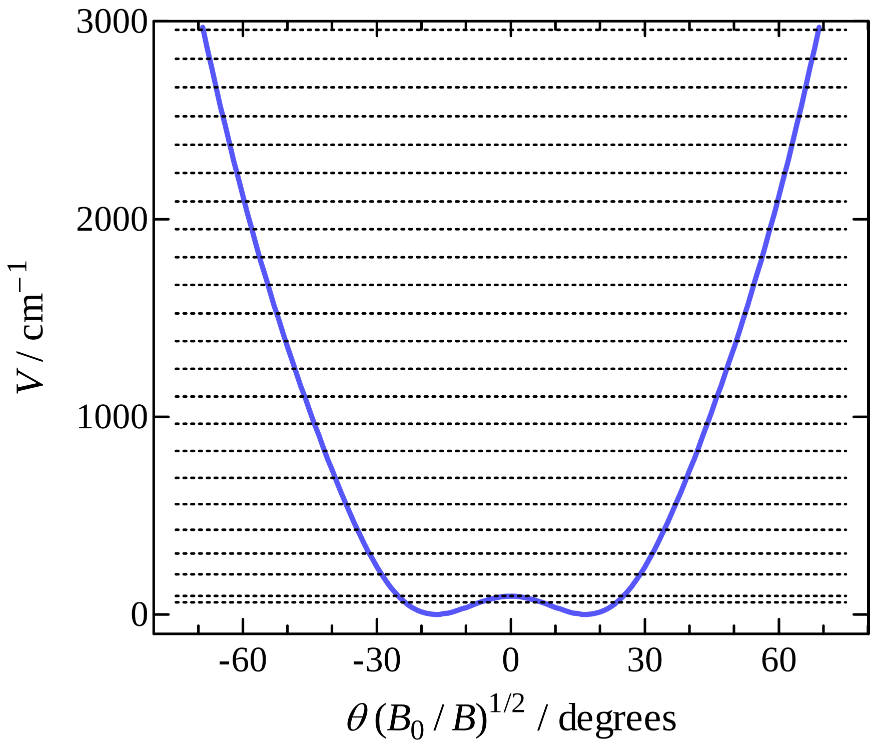


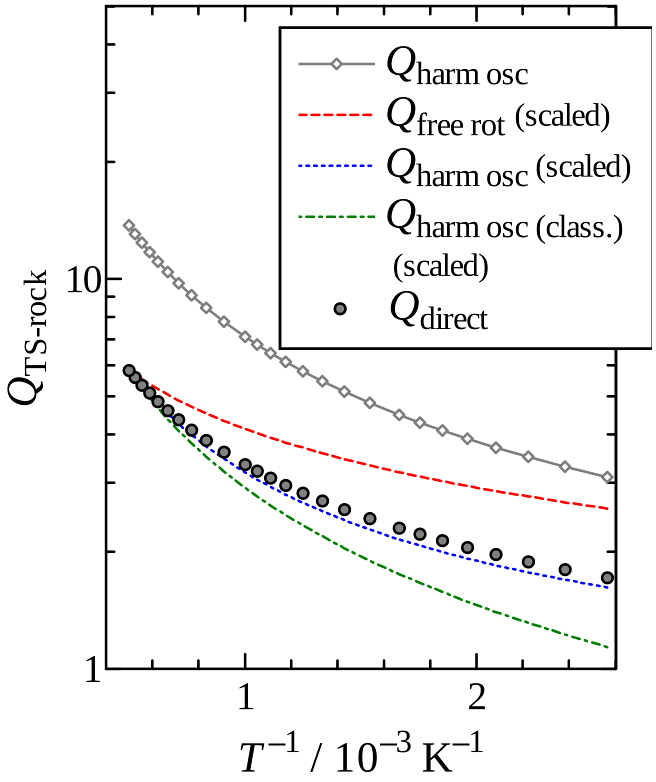


Unharmonic **C–HOH Rocking** Vibration of TS

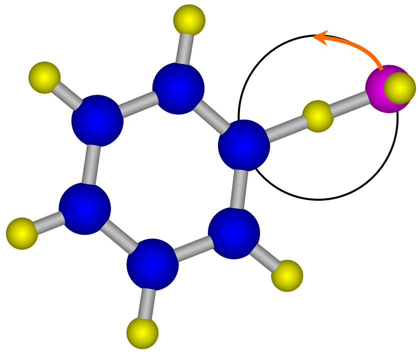


Q (C–HOH Rock)
$\neq Q$ (harmonic oscillator)
$\neq Q$ (free rotor)
$\sim Q$ (scaled harmonic oscillator)

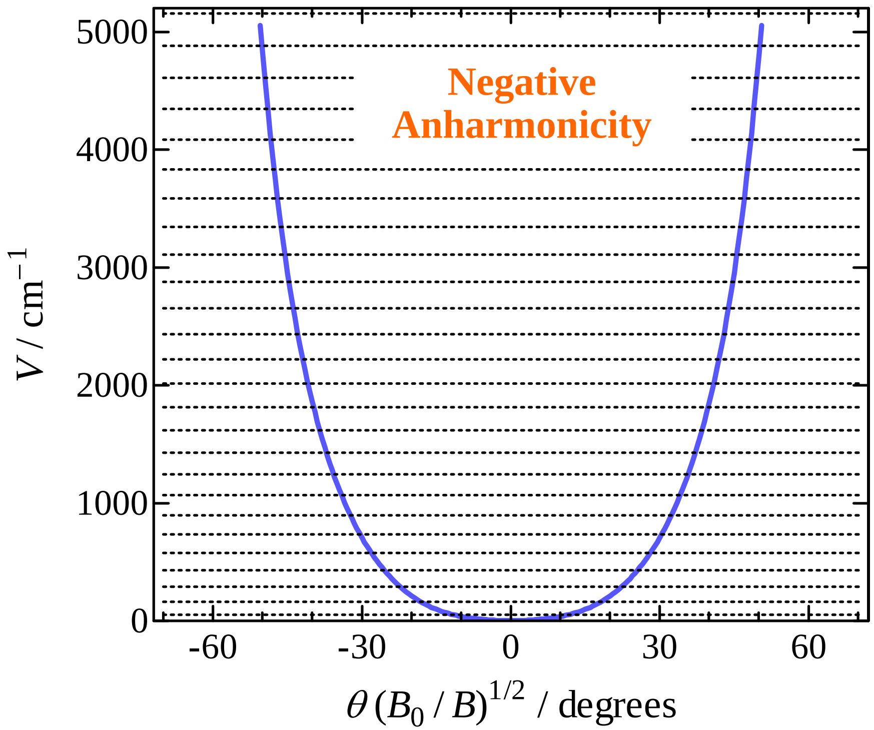


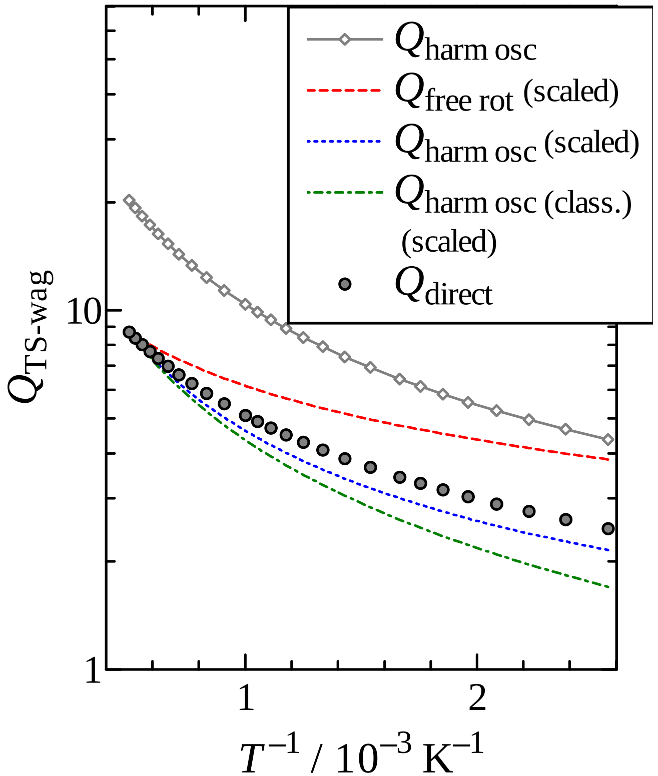


Unharmonic **C–HOH Wagging** Vibration of TS



Q (C–HOH Wag)
≠ *Q* (harmonic oscillator)
≠ *Q* (free rotor)
≠ *Q* (scaled harmonic oscillator)



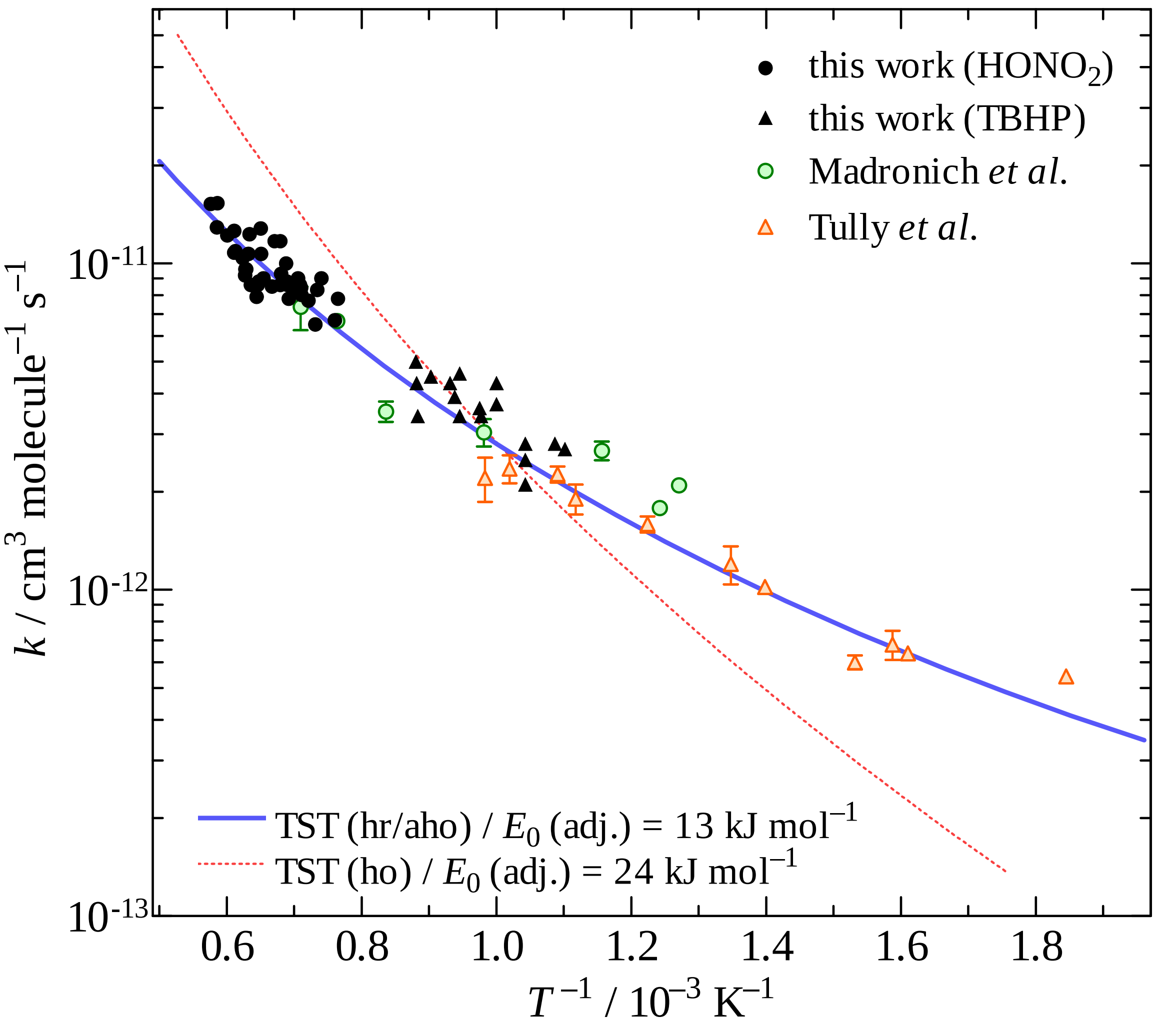


TST with Unharmonicity of TS vibrations

T. Seta *et al.*, *J. Phys. Chem. A*, **110**, 5081 (2006).

TST with anhamonic oscillator
DID REPRODUCED the experiments.

OH + C_6H_6 (benzene)



Kinetic Mechanism

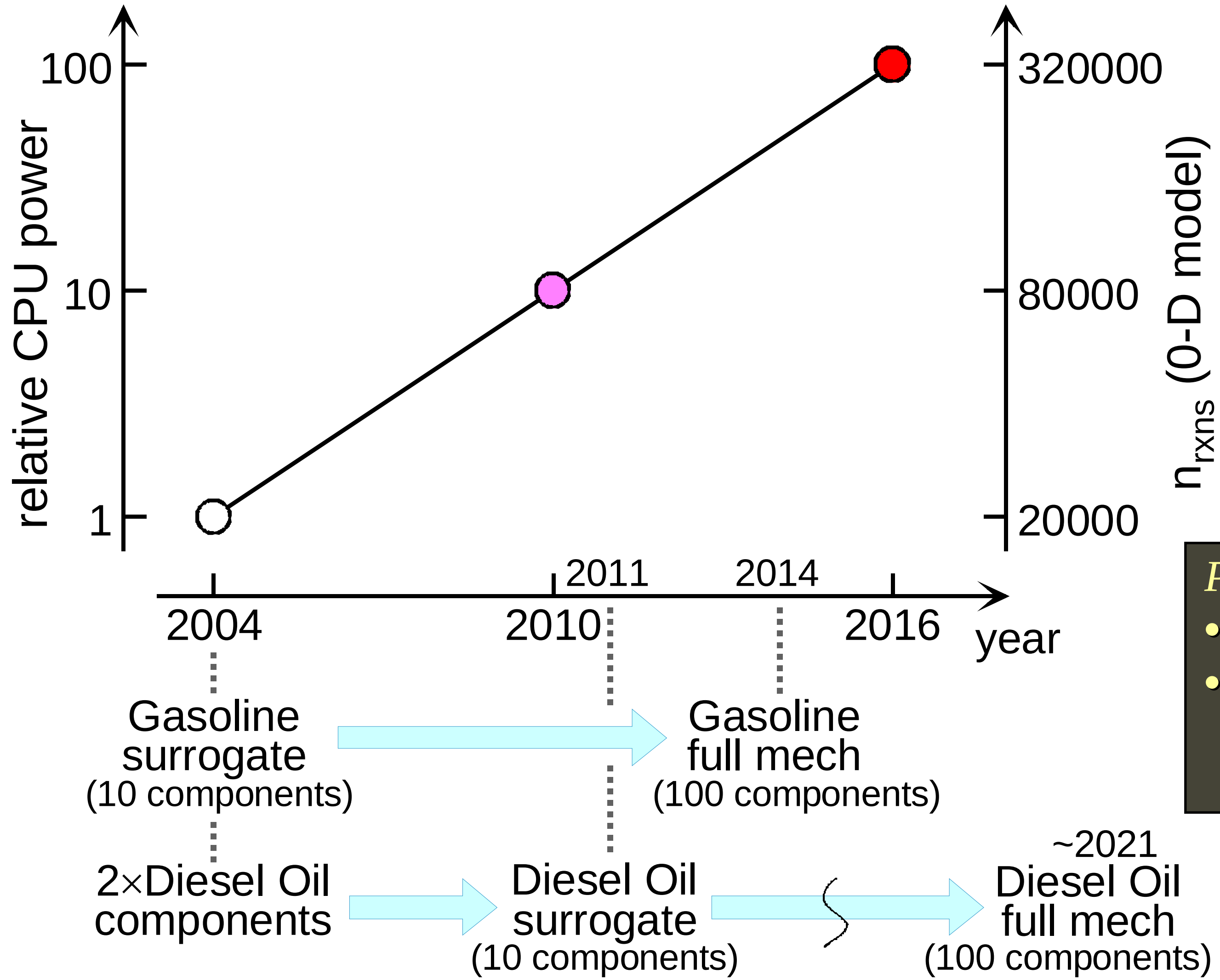
of Combustion

Structured Knowledge in Chemical Kinetics

```
species
 h h2 o o2 oh h2o n2 co hco co2 ch3 ch4 ho2 h2o2 ch2o ch3o c2h6
 c2h4 c2h5 ch2 ch c2h c2h2 c2h3 ch3oh ch2oh ch2co hcco c2h5oh
 pc2h4oh sc2h4oh ch3co ch2cho ch3cho c3h4-a c3h4-p c3h6 c4h6 nc3h7
 ic3h7 c3h8 ic4h7 ic4h8 c4h7 c4h8-2 c4h8-1 sc4h9 pc4h9 tc4h9 ic4h9
 ic4h10 c4h10 ch3coch3 ch3coch2 c2h5cho c2h5co c5h9 c5h10-1 c5h10-2
 ic5h12 ac5h11 bc5h11 cc5h11 dc5h11 ac5h10 bc5h10 cc5h10 ic5h9
 nc5h12 c5h11-1 c5h11-2 c5h11-3 neoc5h12 neoc5h11 c2h5o ch3o2
 c2h5o2 ch3o2h c2h5o2h c2h3o1-2 ch3co2 c2h4o1-2 c2h4o2h o2c2h4oh
 ch3co3 ch3co3h c2h3co c2h3cho c3h5o c3h6ooh1-2 c3h6ooh1-3 c3h6ooh2-1
 c3h6ooh1-2o2 c3h6ooh1-3o2 c3h6ooh2-1o2 nc3h7o ic3h7o nc3h7o2h
 ic3h7o2h nc3h7o2 ic3h7o2 c3h6o1-3 ic4h8o ic4h8oh io2c4h8oh ic4h7o
 c4h7o c4h8oh-1 c4h8oh-2 o2c4h8oh-1 o2c4h8oh-2 c4h8ooh1-2o2 c4h8ooh1-3o2
 c4h8ooh1-4o2 c4h8ooh2-1o2 c4h8ooh2-3o2 c4h8ooh2-4o2 tc4h8ooh-io2
 ic4h8ooh-io2 ic4h8ooh-to2 c4h8ooh1-2 c4h8ooh1-3 c4h8ooh1-4 c4h8ooh2-1
 c4h8ooh2-3 c4h8ooh2-4 ic4h8o2h-i ic4h8o2h-t tc4h8o2h-i c4h8o1-2
…………………….
```

```
reactions
 ch3+h(+m)=ch4(+m)            2.138e+15  -0.400      0.0
 ch4+h=ch3+h2                 1.727e+04   3.000   8224.0
 ch4+oh=ch3+h2o               1.930e+05   2.400   2106.0
 ch4+o=ch3+oh                 2.130e+06   2.210   6480.0
 c2h6+ch3=c2h5+ch4            5.500e-01   4.000   8280.0
 hco+oh=co+h2o                3.020e+13   0.000      0.0
 co+oh=co2+h                  9.430e+03   2.250  -2351.0
 h+o2=o+oh                    1.920e+14   0.000  16440.0
 o+h2=h+oh                    5.080e+04   2.670   6292.0
 o+h2o=oh+oh                  1.213e+05   2.620  15370.0
 oh+h2=h+h2o                  2.160e+08   1.510   3430.0
 hco+m=h+co+m                 1.860e+17  -1.000  17000.0
 h2o2+oh=h2o+ho2              2.400e+00   4.040  -2162.0
 c2h4+o=ch3+hco               1.320e+08   1.550    427.0
 c2h4+h(+m)=c2h5(+m)          1.081e+12   0.450   1822.0
 ch3+oh(+m)=ch3oh(+m)         5.649e+13   0.100      0.0
 c2h6+h=c2h5+h2               5.370e+02   3.500   5200.0
 ch3oh+ho2=ch2oh+h2o2         3.980e+13   0.000  19400.0
 c2h5+o2=c2h4+ho2             1.220e+30  -5.760  10100.0
 c2h6+oh=c2h5+h2o             5.125e+06   2.060    855.0
 c2h6+o=c2h5+oh               1.130e+14   0.000   7850.0
 ch3+ho2=ch3o+oh              1.990e+13   0.000      0.0
 ............
```

Increasing Computational Power



Problems are :

- **How to construct**
- **How to lump or simplify the mechanism**

Strategies: KUCRS system

http://www.frad.t.u-tokyo.ac.jp/~miyoshi/KUCRS/

KUCRS:

Knowledge-basing Utilities for Complex Reaction Systems

— Built on:

- Core Library Classes
  - Reusable and General-Purpose
  - Platform Independent (ANSI C++/STL)

— Enables Implementation of:

- Systematic Knowledge on
  - Chemical Change of Molecules
  - Rate Parameters

— Knowledge-Base from:

- Experimental and Theoretical Investigations

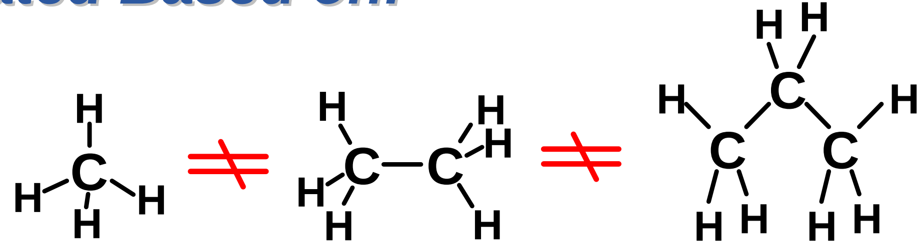
Kinetic Mechanism of combustion

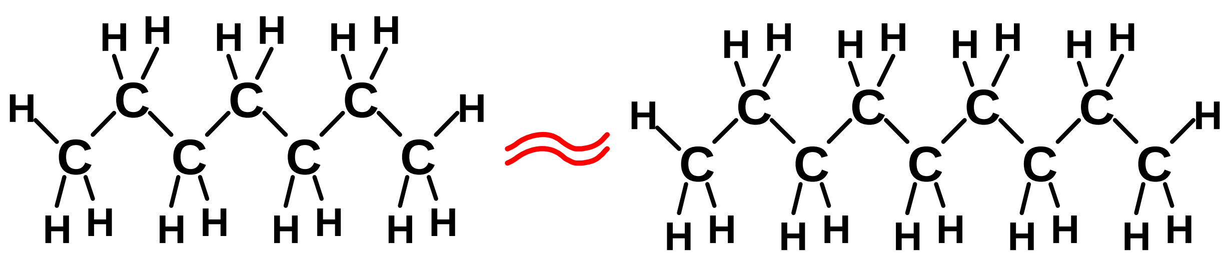
— *Neither Possible nor Necessary to Measure:*

- the RATE PARAMETERS for all reactions
- the THERMOCHEMICAL Properties of all species

— *But Can Be Estimated Based on:*

- **the ANALOGY**

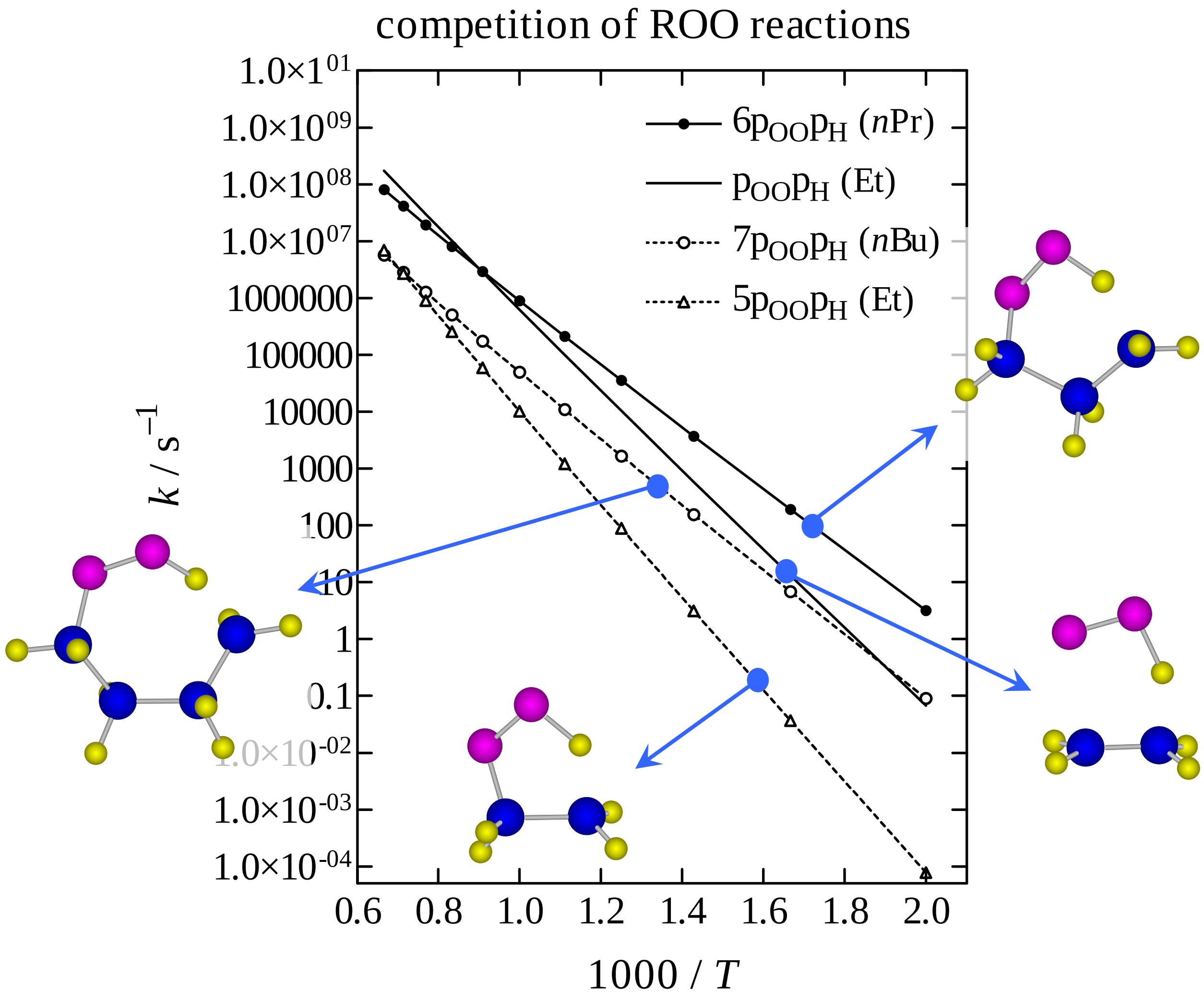




- **the EMPIRICAL Rules**

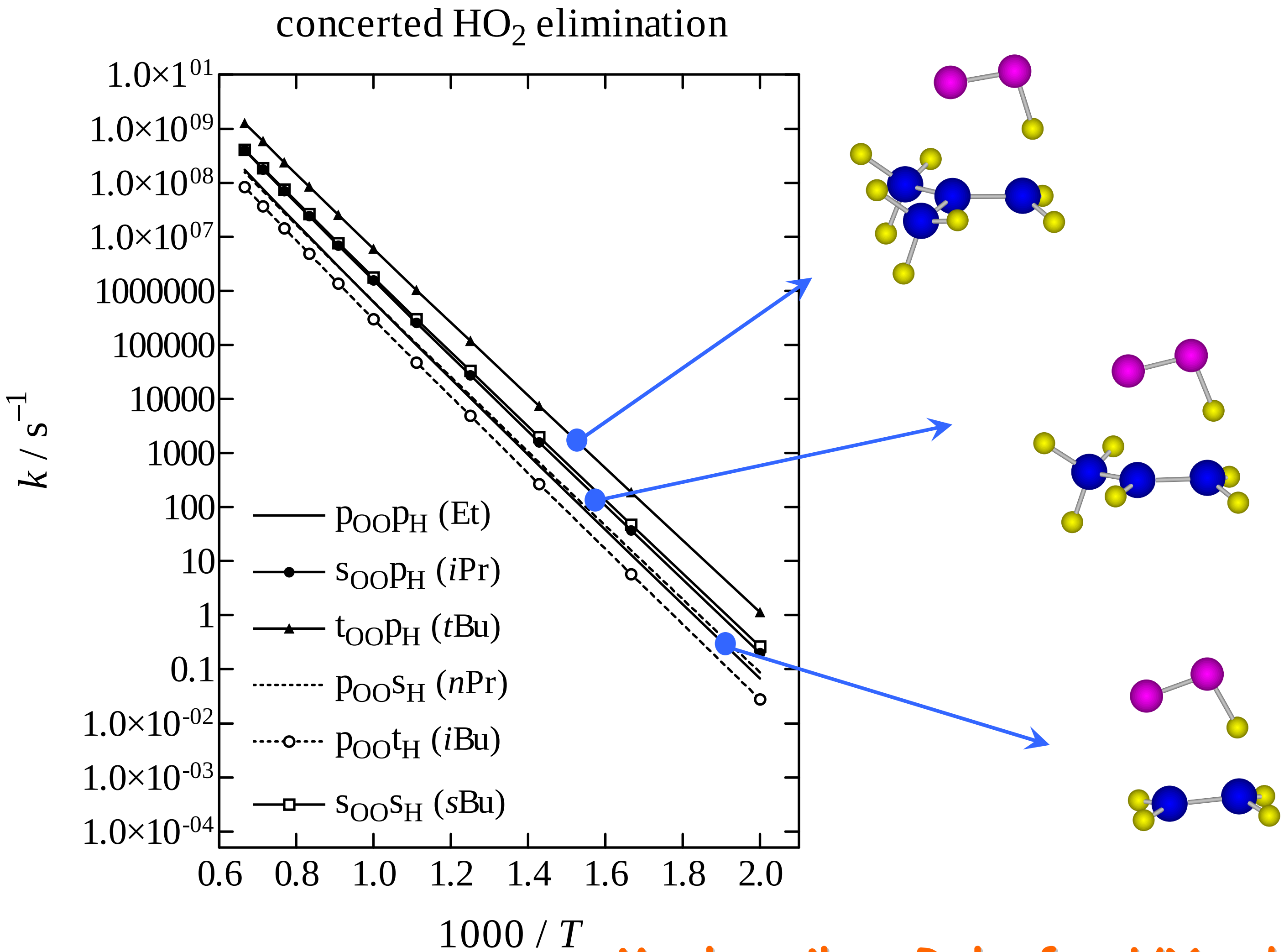
Key Reactions – fate of RO_2

Competing Processes (HPL rate constants)



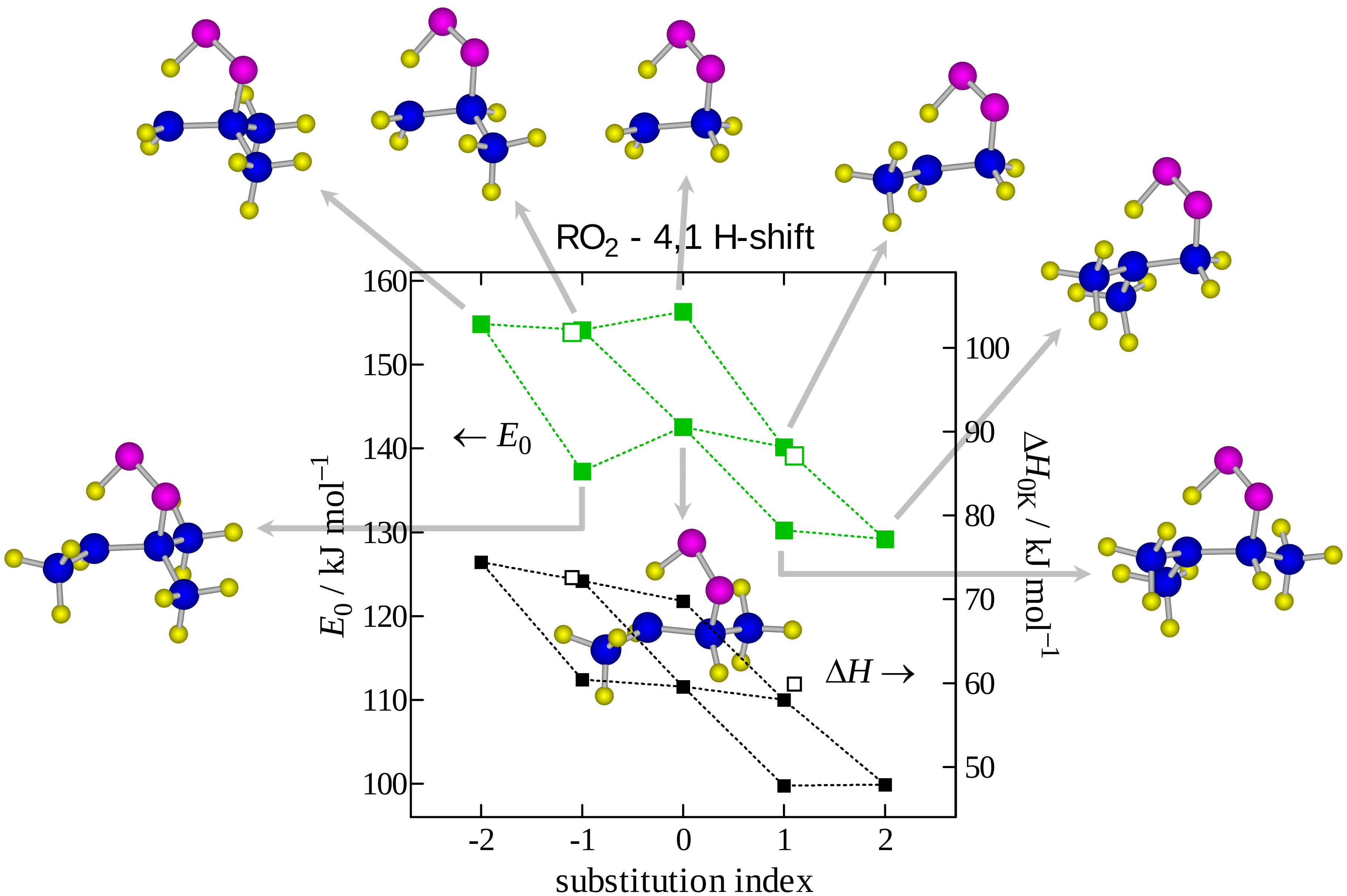
Key Reactions – HO_2 Elimination from RO_2

General Trends in Substituent Effect

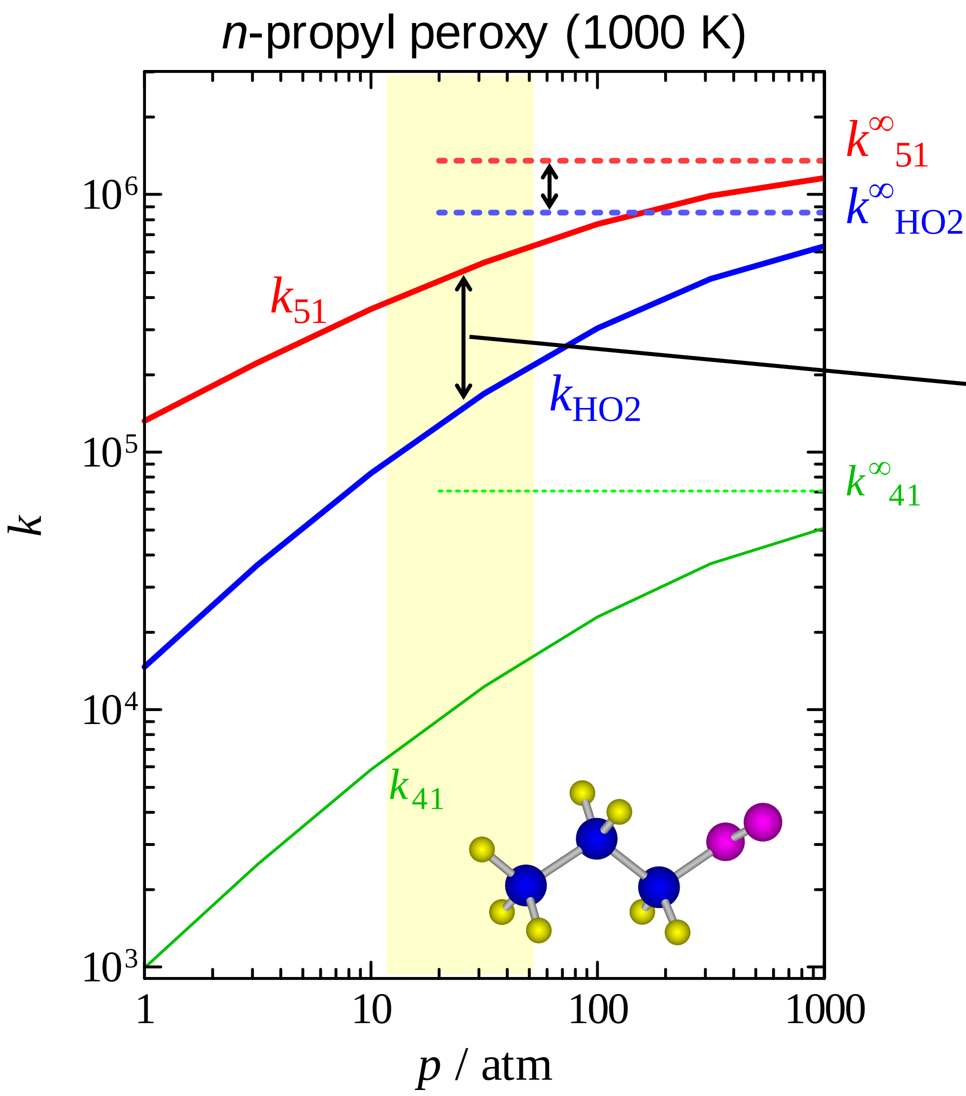


Markovnikov Rule for HX addition !

Rate Parameters: **4,1-H Shift Isomerization**



Unimolecular Effect (population dissipation)



Key Competing Reactions

Larger Difference than H.P.L. !

Complex rate parameters
- **Channel**-dependent
- **P,T**-dependent
- **Molecular Size**-dependent

Designing Fuel
for Internal Combustion Engines

Characterization of a Complex Chemical System

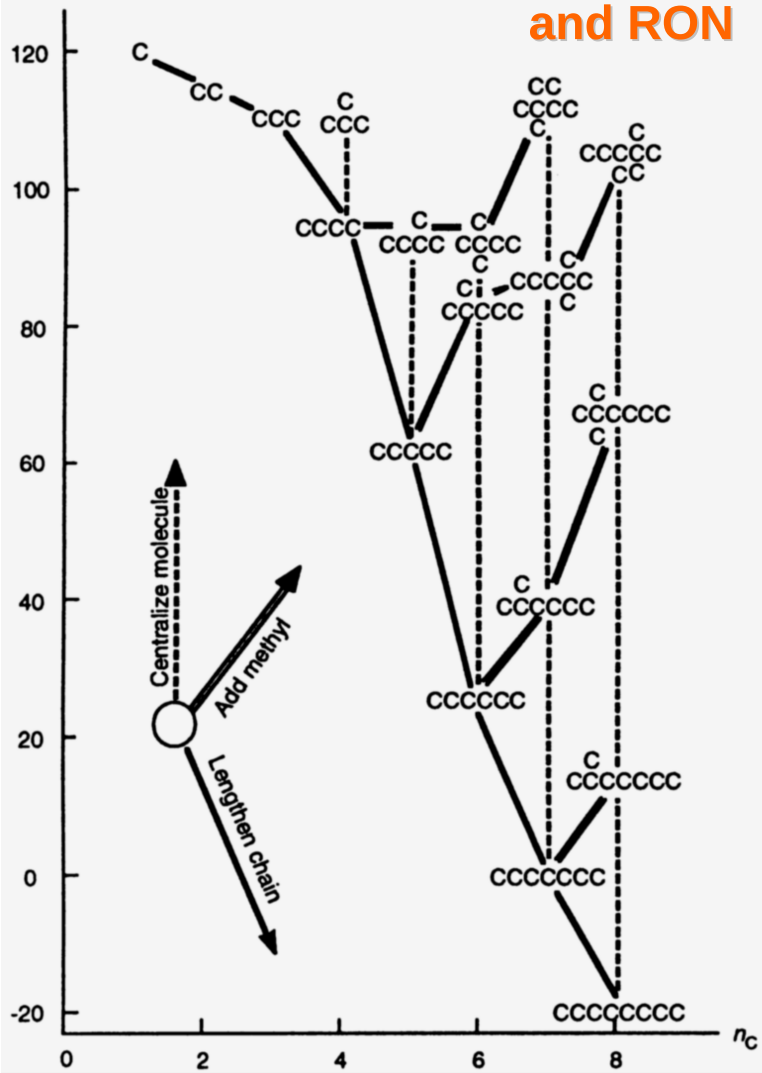
$$\begin{pmatrix} x_1' \\ x_2' \\ \vdots \\ x_n' \end{pmatrix} = \begin{pmatrix} r_{11} & r_{12} & \cdots & r_{1n} \\ r_{21} & r_{22} & \cdots & r_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ r_{n1} & r_{n2} & \cdots & r_{nn} \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{pmatrix}$$

Eigenvalue Analysis
of locally linearized system

Automotive Fuels

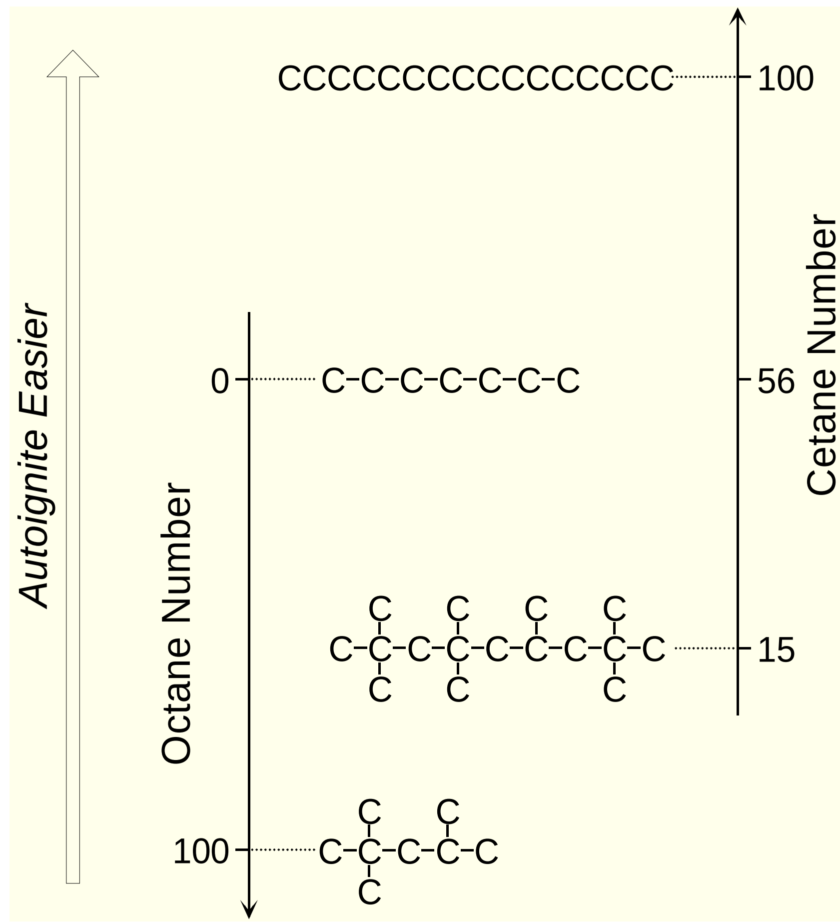
Gasoline

Chemical Structure and RON

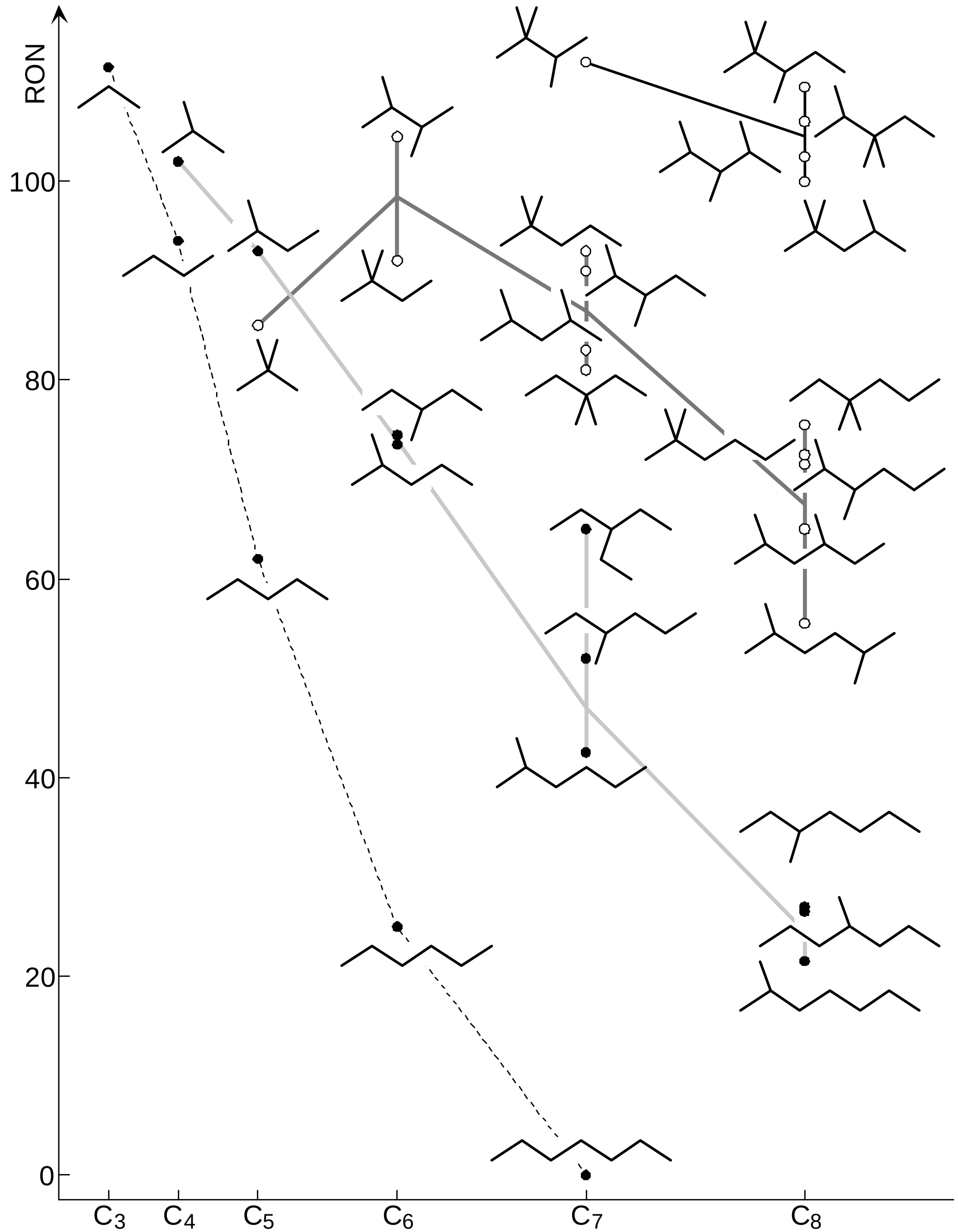


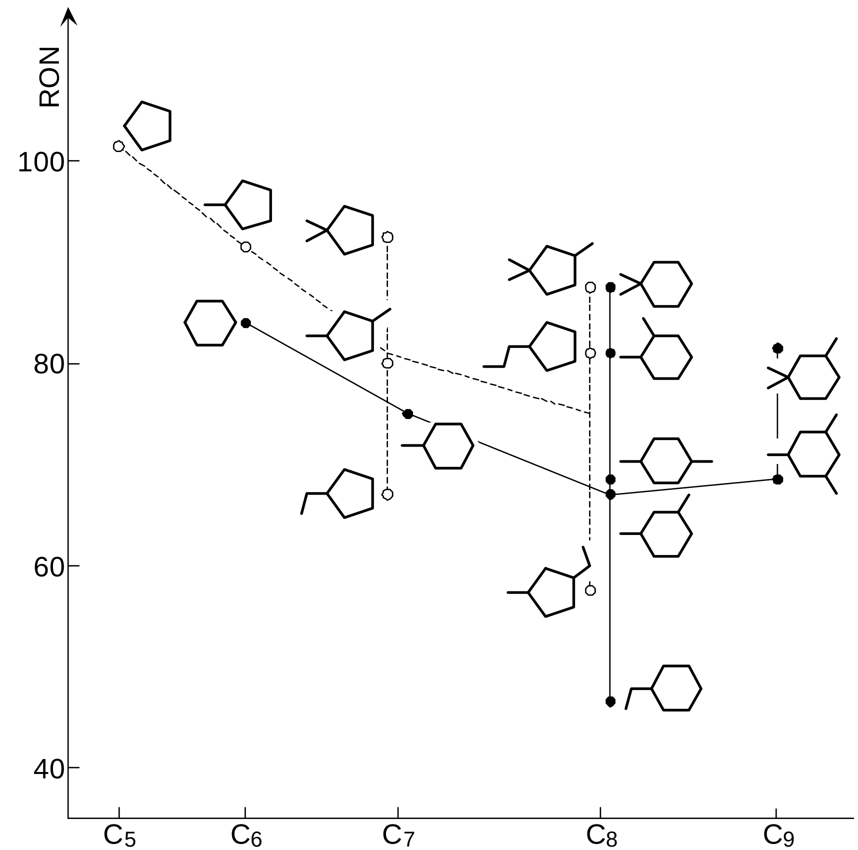
Diesel Fuel

Chemical Structure and CN or RON



Models: **Test-Set Fuel Molecules**



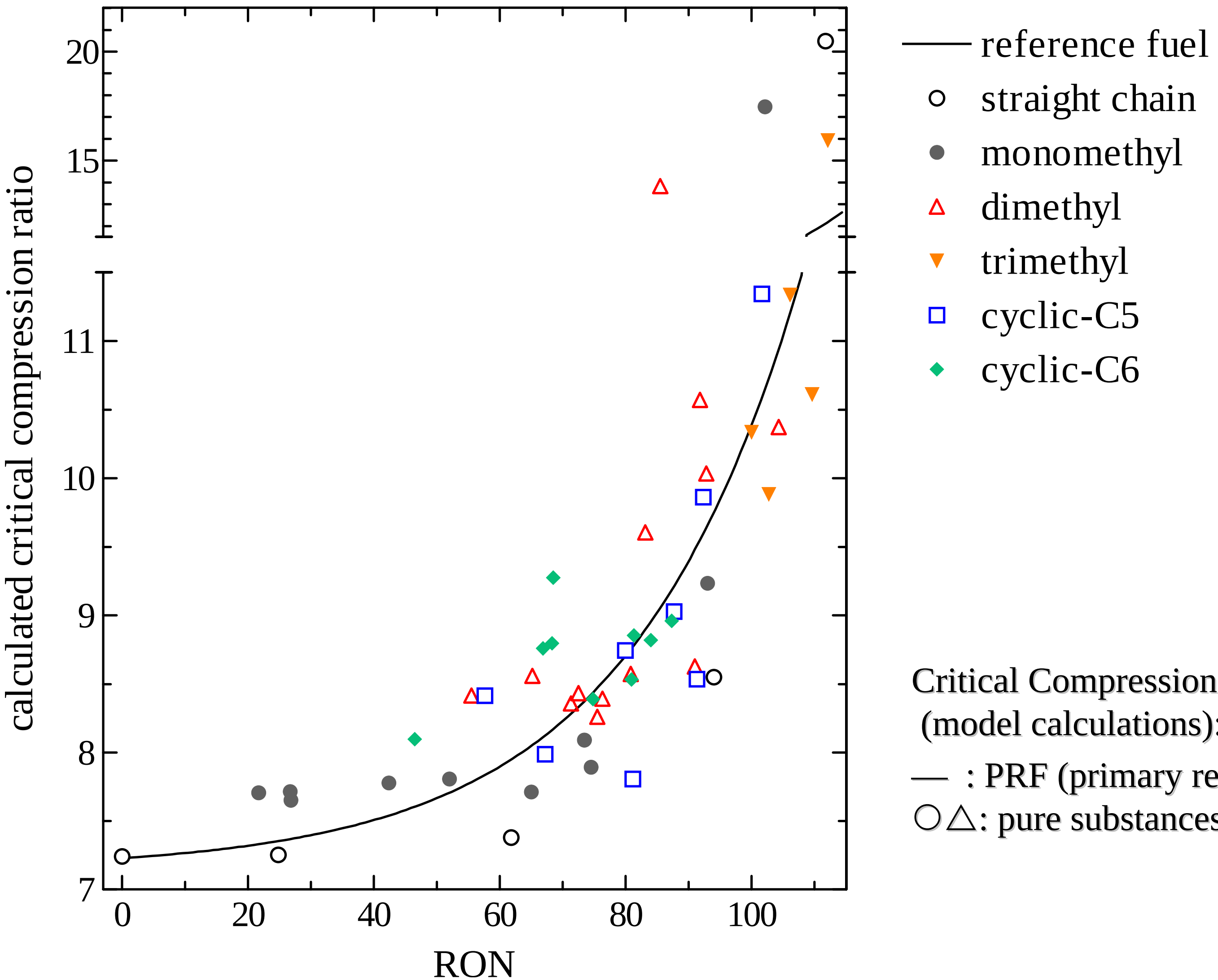


33 non-cyclic **alkanes** and
17 cyclic alkanes

Up to ~8000 rxns / fuel

Models: Ignition Behavior vs. RON

Critical Compression Ratio vs. RON for Alkanes

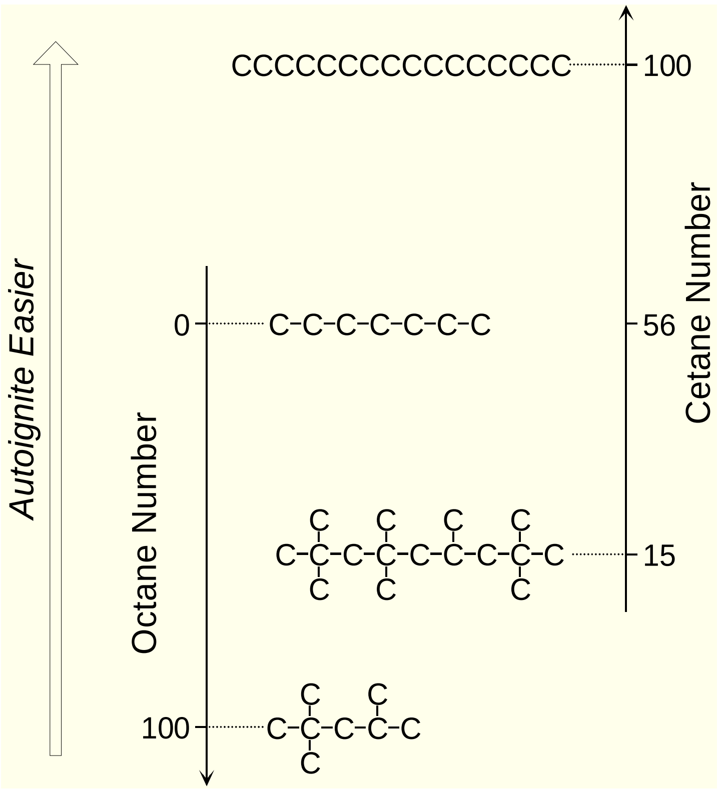


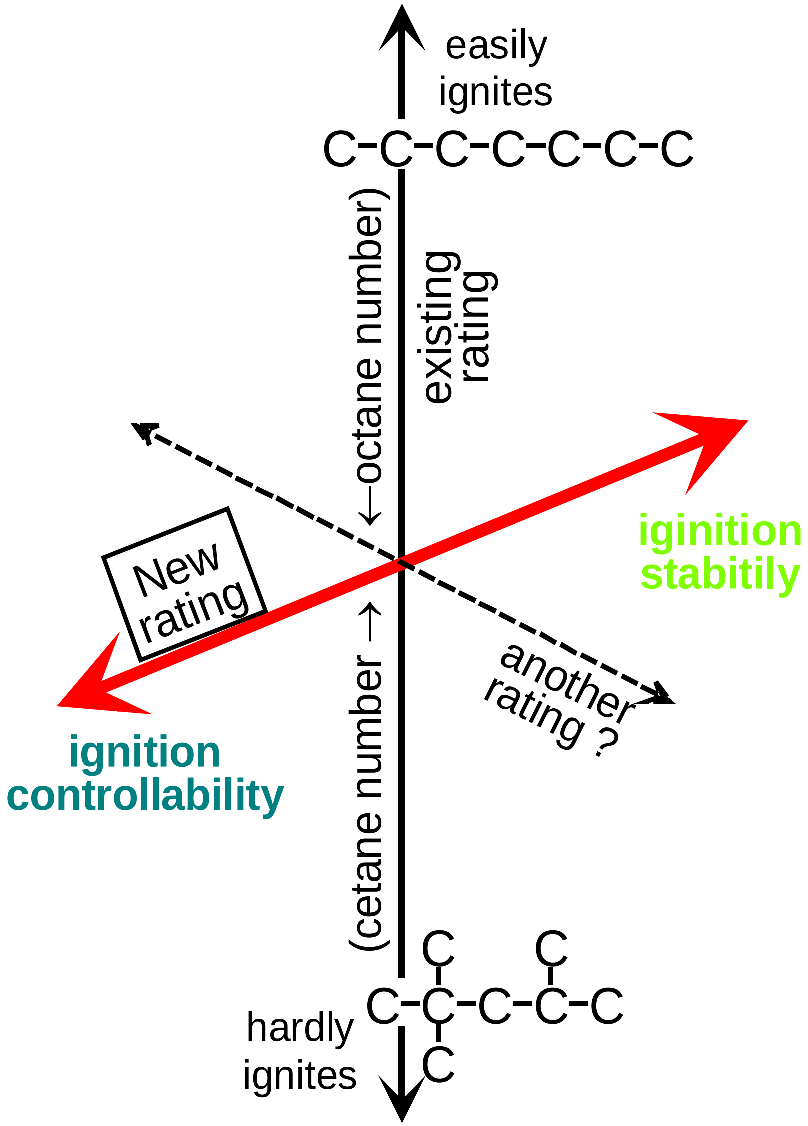
Critical Compression Ratio vs. RON (model calculations):

— : PRF (primary reference fuel)

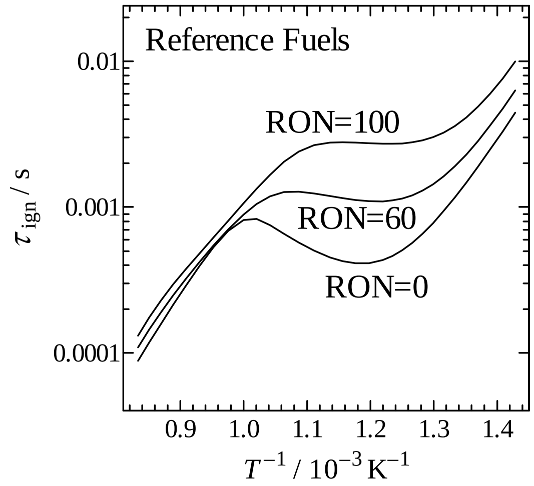
○△: pure substances

Fuel Rating

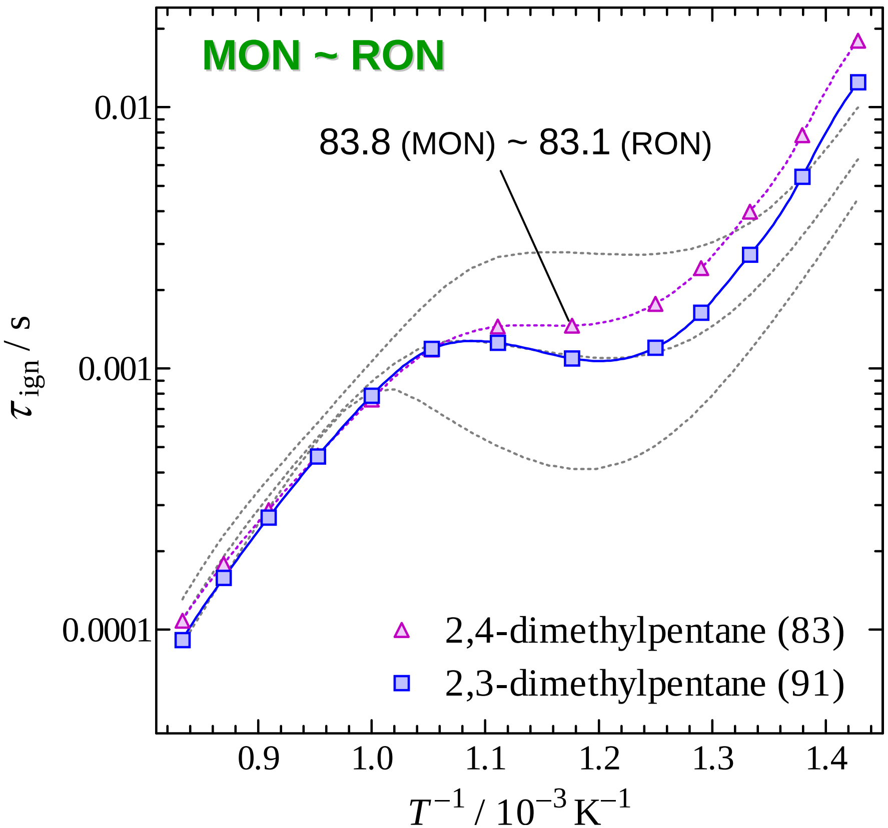

Autoignite Easier
CCCCCCCCCCCCCCCC
100
Cetane Number
56
15
0
C-C-C-C-C-C-C
Octane Number
100

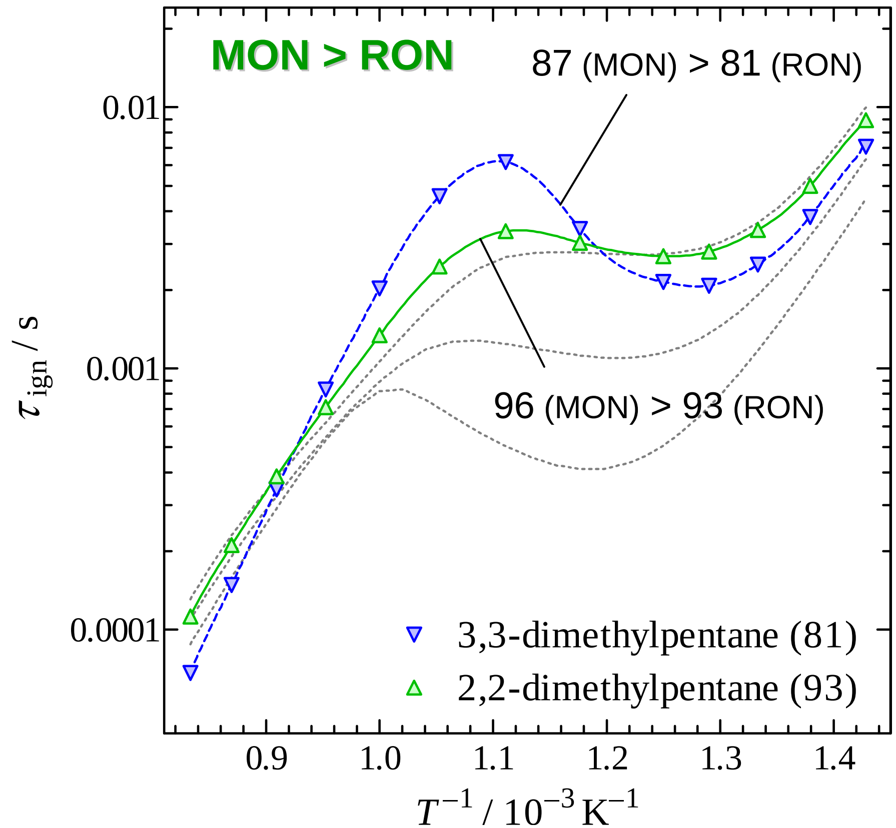

easily
ignites
C-C-C-C-C-C-C
(cetane number → ←octane number)
existing
rating
New
rating
iginition
stabitily
ignition
controllability
another
rating ?
hardly
ignites

Ignition Property of Fuels

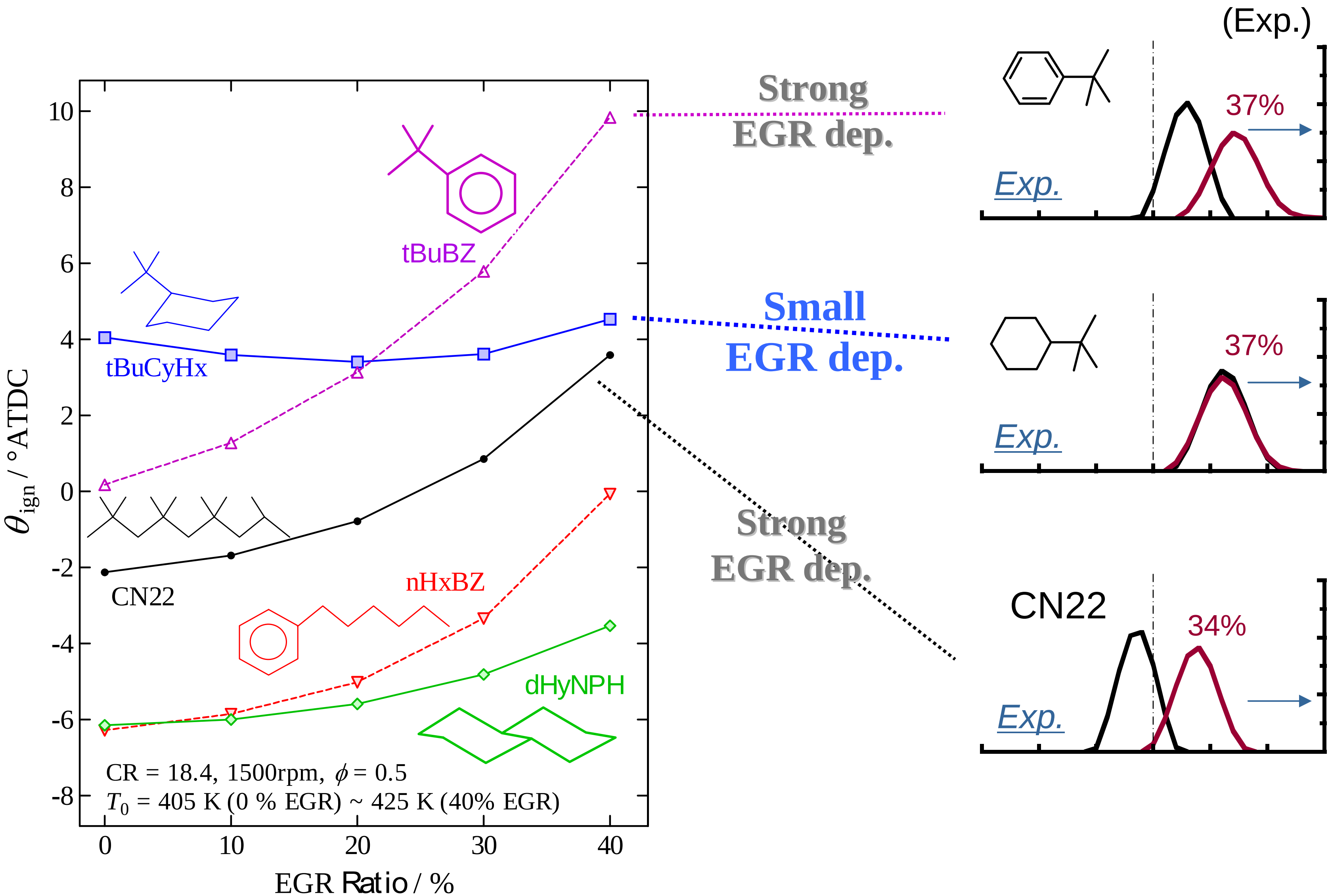


! Different Temperature Dependence for Fuels with Similar RON





an example of Unexpected Behaviors



H_2O / CO_2 Recycle

T_{inkake} [K] = 405 K + EGR [%] / 2

Published Papers and Information on Web:

KUCRS system

(detailed kinetic model generation software):

http://www.frad.t.u-tokyo.ac.jp/~miyoshi/KUCRS/

OH + benzene/toluene:

T. Seta, M. Nakajima, and A. Miyoshi,

J. Phys. Chem. A, **110**, 5081-5090 (2006).

ST-PLIFI Apparatus:

T. Seta, M. Nakajima, and A. Miyoshi,

Rev. Sci. Instr., **76**, 064103 (2005).