KUCRS – automatic reaction scheme generation tool

Department of Chemical Systems Engineering, University of Tokyo

Akira Miyoshi

KUCRS System

KUCRS: *Knowledge-basing Utilities for Complex Reaction Systems*

— *Tools for rule-based construction of kinetic model*

- built on compilation of class libraries:
  - *molecule* class (species identification, properties [including σ etc.], manipulation, *etc.*)
  - *specAdmin* class (species administration)
  - *reaction* class (reaction description with detection of duplication and dead-end species, *etc.*)

— *User customizable*

- reaction "macro" definition in external text files
- user customizable external "name" library
- open source software distributed under GPL

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

KUCRS — features

— *SMILES support*   ***after version 2010.03.31**

- fuel input
  'CCC' $\rightarrow$ propane, 'CC(C)C' $\rightarrow$ isobutane
- species output
  '[O]OC(C)(C)COO', 'C=C=C', '[O]CC(C)=C', etc.
- species library maintenance

— *Concurrent processing of multiple fuel input*

- no complex merging process required
- generates "cross" reactions including:
  $R + R'O_2 \rightarrow RO + R'O$
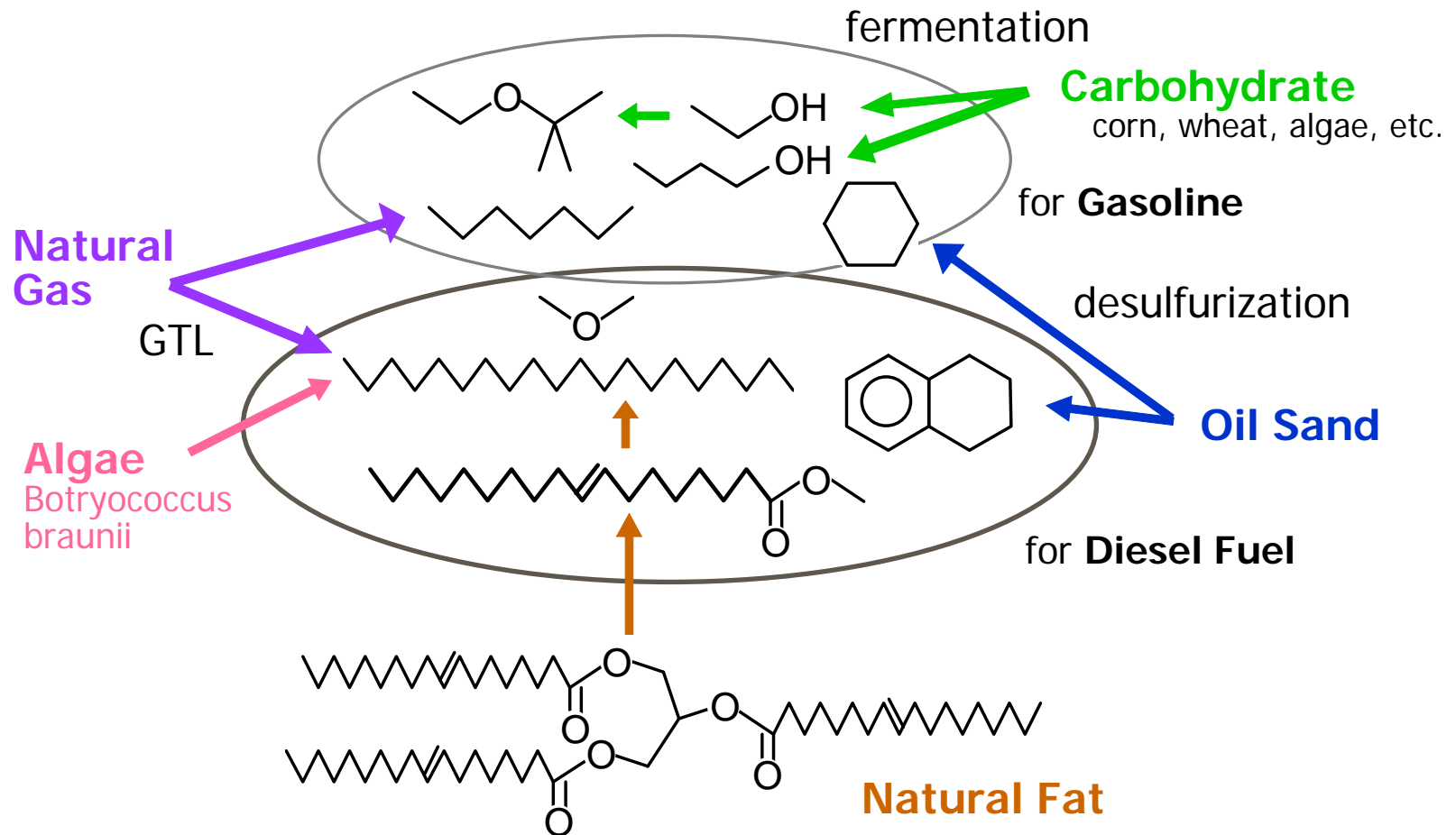 $RO_2 + fuel \rightarrow fuel\text{-}R + ROOH$
  $RO_2 + R'O_2 \rightarrow RO + R'O + O_2$
  for all R and RO_2 originated from fuels

Re-construction of Low-Temperature Oxidation Mechanism of Alkanes Based on Theoretical Investigations

Department of Chemical Systems Engineering, University of Tokyo

Akira Miyoshi

Special Session in IEA/TLM-Nara, July 29, 2010

Diversification of Fuel Sources

fermentation

Carbohydrate
corn, wheat, algae, etc.

for **Gasoline**

Natural Gas

GTL

desulfurization

Algae
Botryococcus braunii

Oil Sand

for **Diesel Fuel**

Natural Fat

Optimization Based on Chemical Kinetics !

Computational

Computational Method

❑ CBS-QB3 & CASPT2 calculations by using

- Gaussian 03 and MOLPRO 2008.1

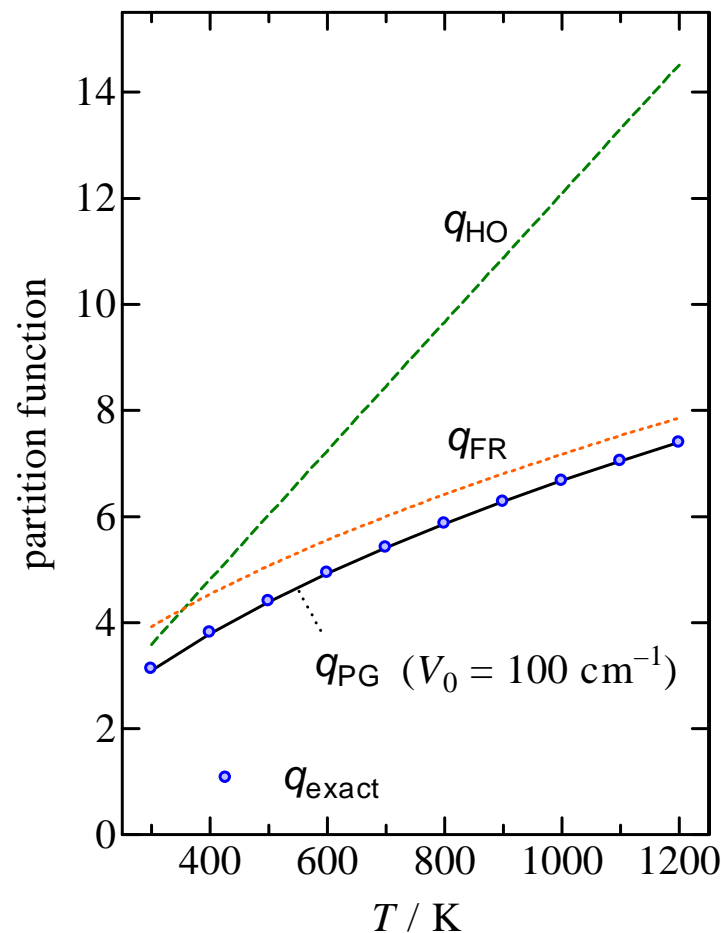❑ TST & VTST calculations with 1D-tunneling correction and hindered rotor treatment by using

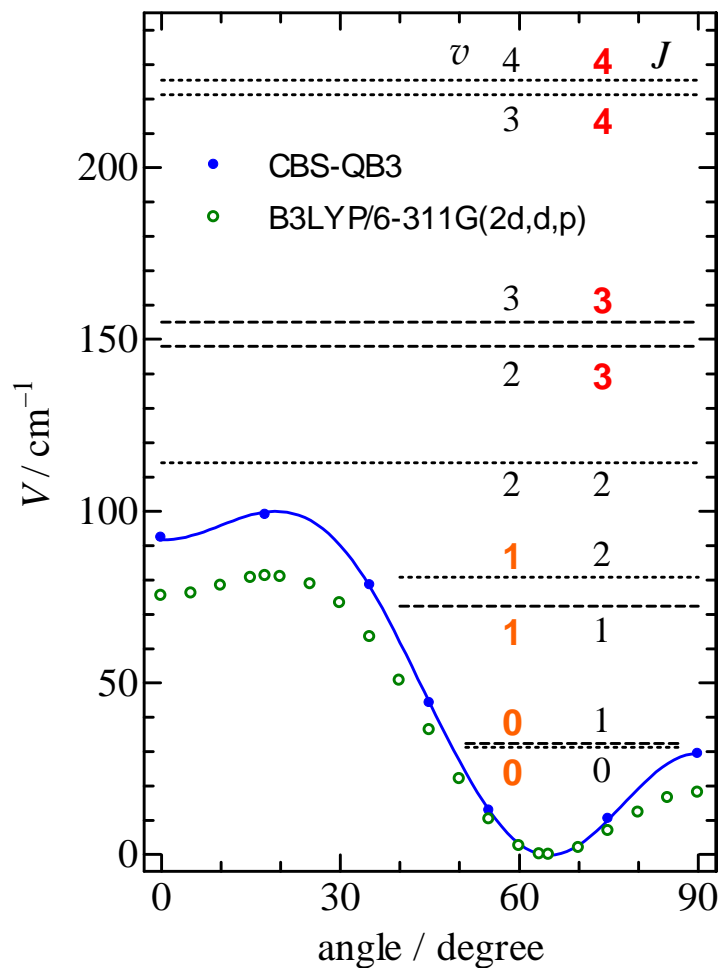- GPOP

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

❑ RRKM calculations
(thermal decomposition or chemical activation; multiple-well multiple-channel system) by using
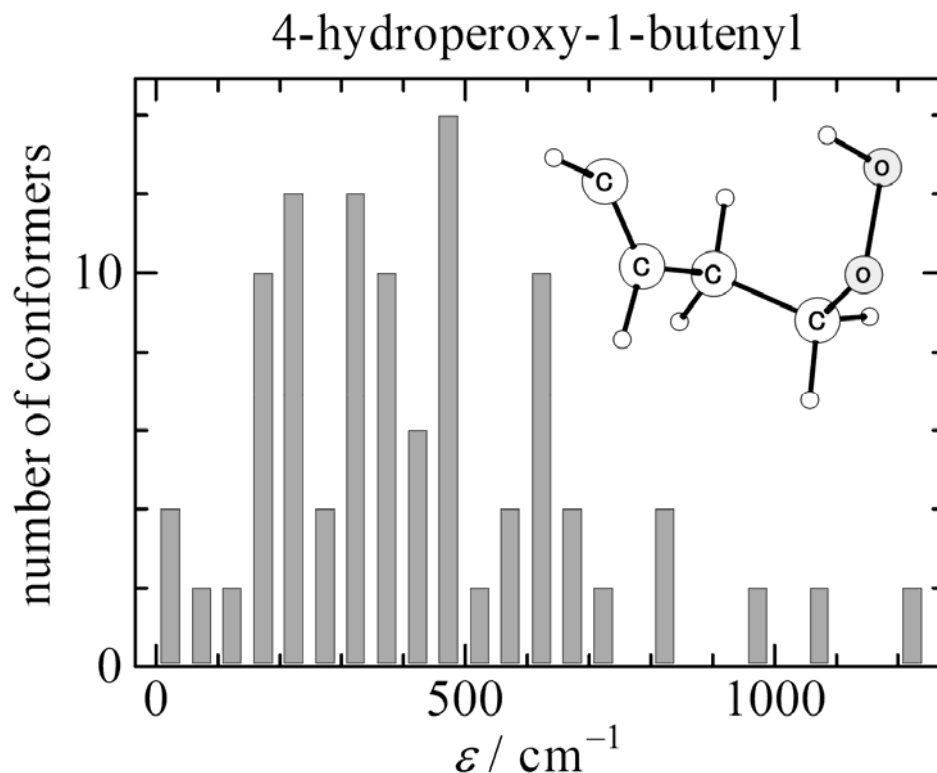
- SSUMES based on UNIMOL-RRKM and LAPACK/BLAS

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

Hindered Rotors

❑ Pitzer-Gwinn approximation after BEx1D analysis

http://www.frad.t.u-tokyo.ac.jp/~miyoshi/bex1d/

Rotational Conformers

❑ Rotational-Conformer Distribution Partition
Function: q_{RCD}

4-hydroperoxy-1-butenyl
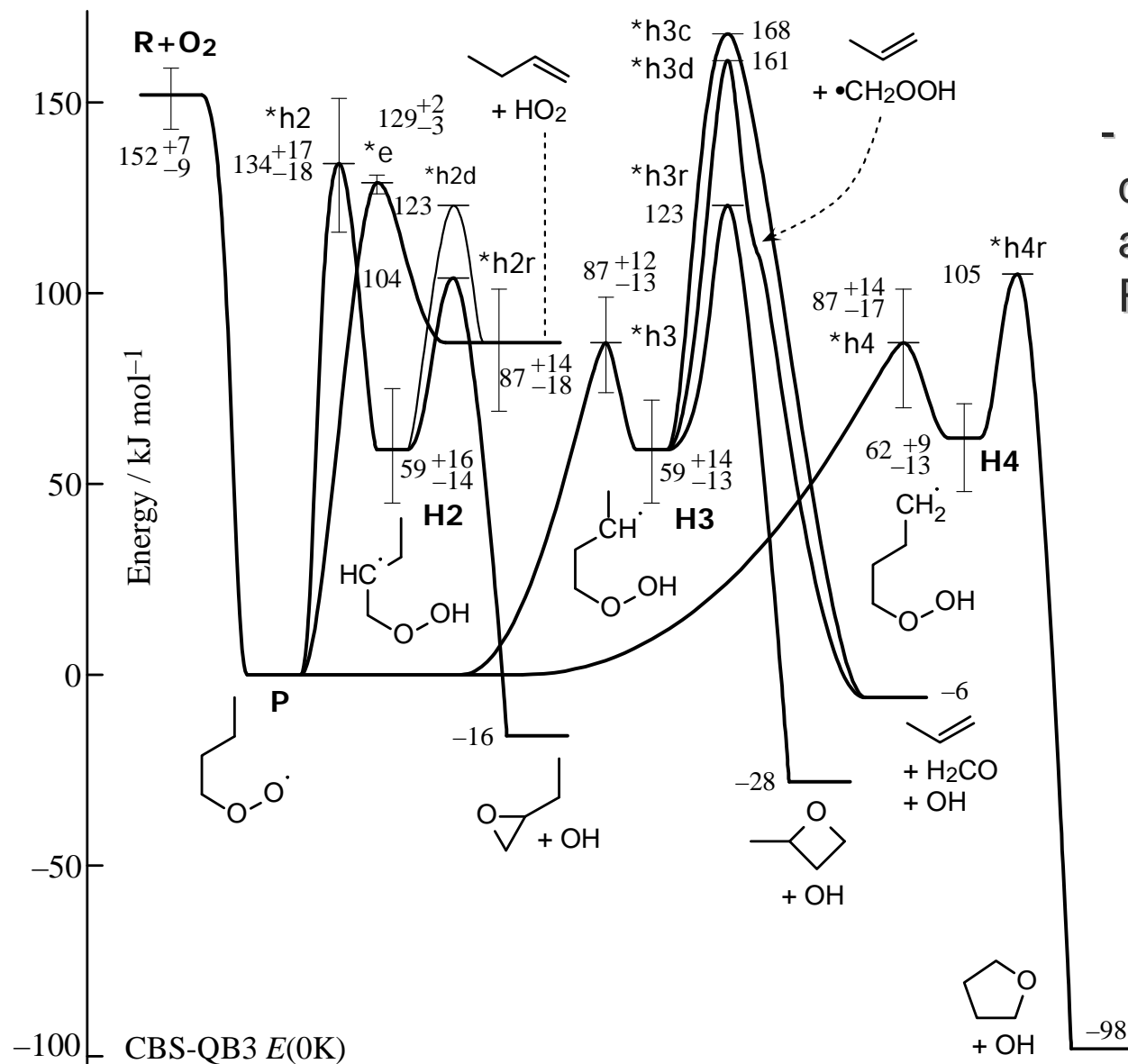

$$q_{tot} \approx q_{RCD}\, q_0$$

$$q_{RCD} = \sum_i g_i \exp\left(-\frac{\varepsilon_i}{k_B T}\right)$$
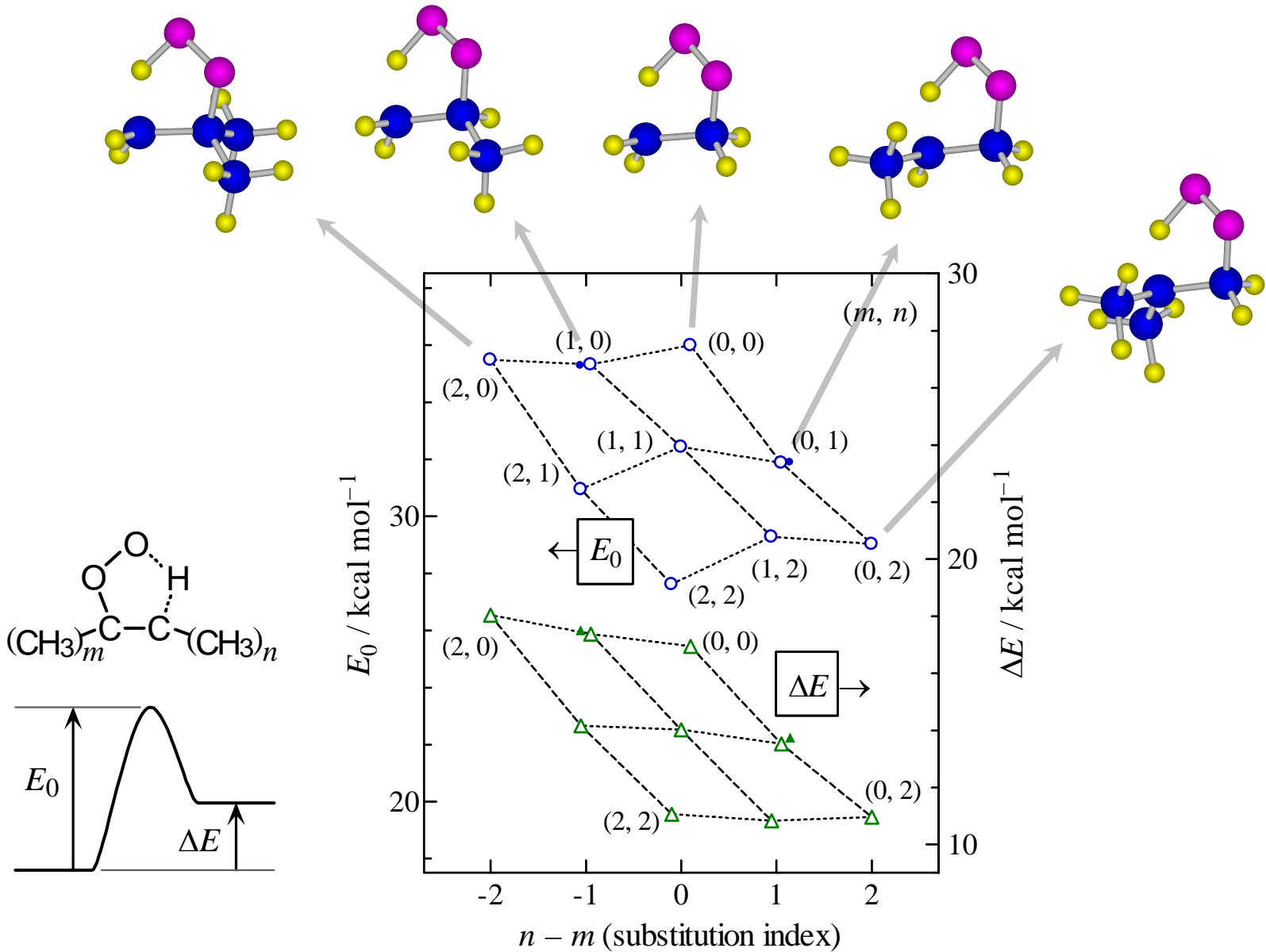
Isomerization Reactions of RO_2

Generalized Energy Diagram for RO₂ Reactions

Substitution Dependence

4,1-H shift reactions

$(CH_3)_m C \overset{O-O}{\underset{}{\diagup}} C (CH_3)_n$ ... H

E_0

ΔE

$E_0 / \text{kcal mol}^{-1}$

$\Delta E / \text{kcal mol}^{-1}$

(m, n)

$(2, 0)$ $(1, 0)$ $(0, 0)$

$(2, 1)$ $(1, 1)$ $(0, 1)$

$\leftarrow \boxed{E_0}$

$(2, 2)$ $(1, 2)$ $(0, 2)$

$(2, 0)$ $(0, 0)$

$\boxed{\Delta E} \rightarrow$

$(2, 2)$ $(0, 2)$

30

30

20

20

10

-2   -1   0   1   2

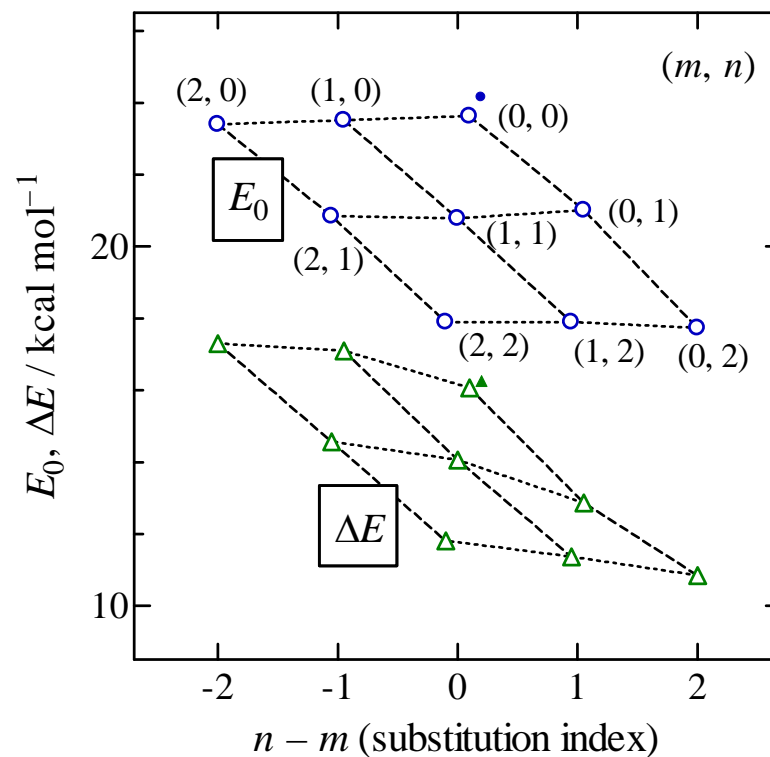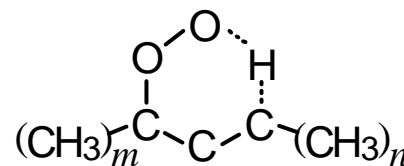$n - m$ (substitution index)

Reaction-Type Dependence
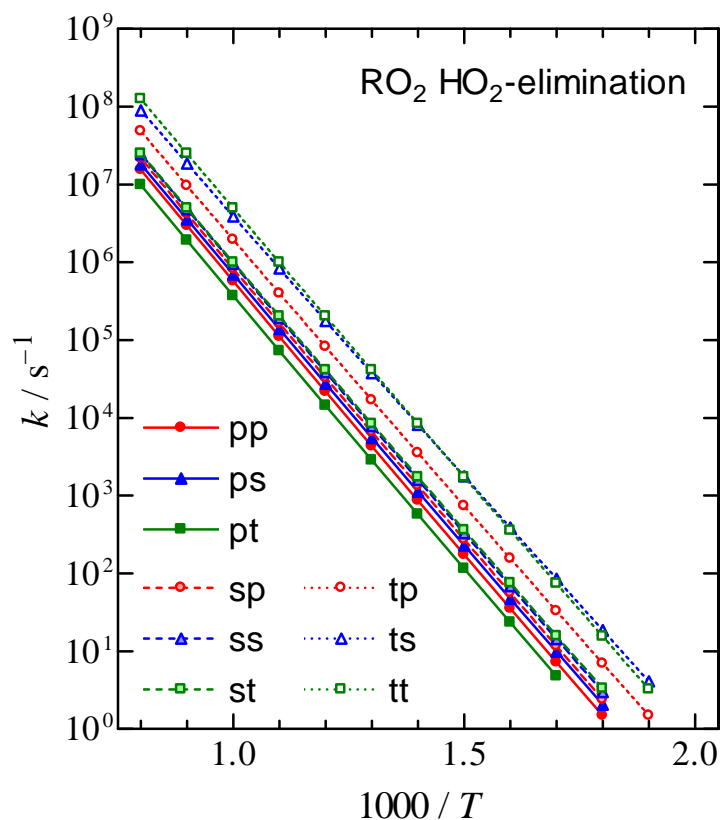
concerted HO$_2$ elimination reactions
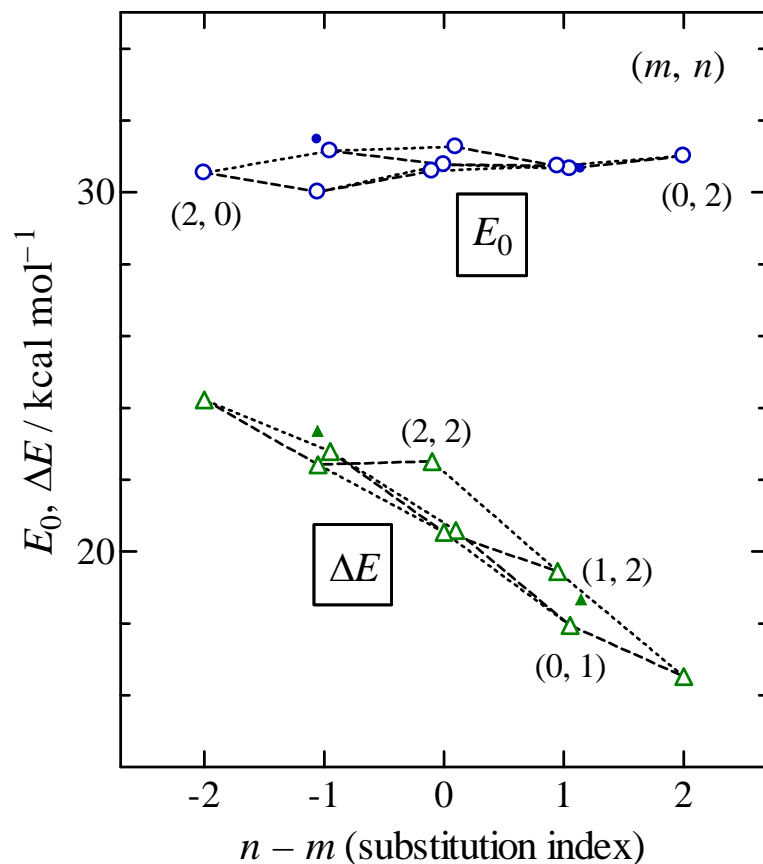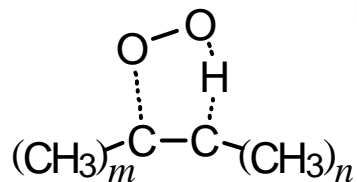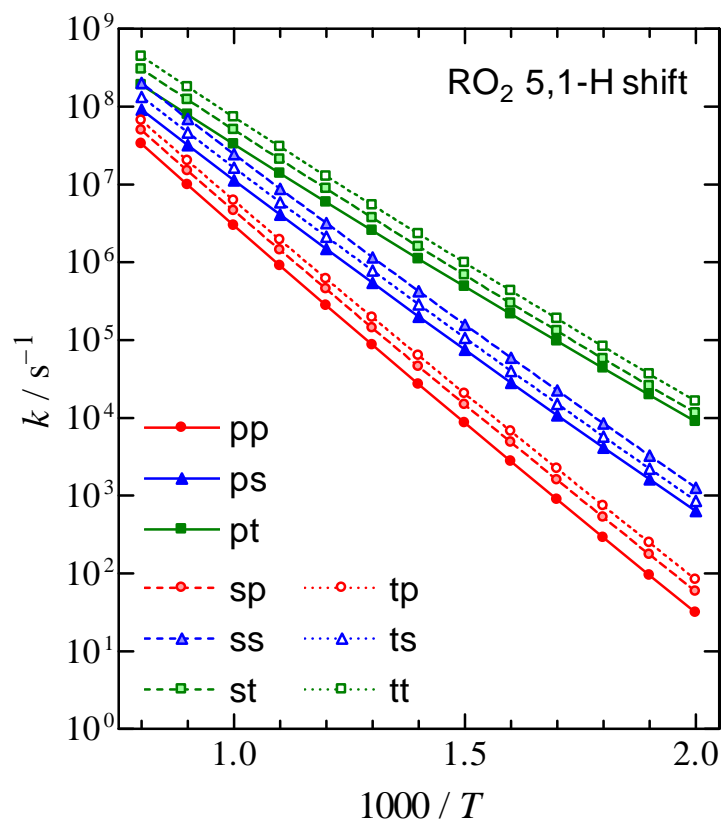

5,1-H shift reactions

'Unified' Rate Constants

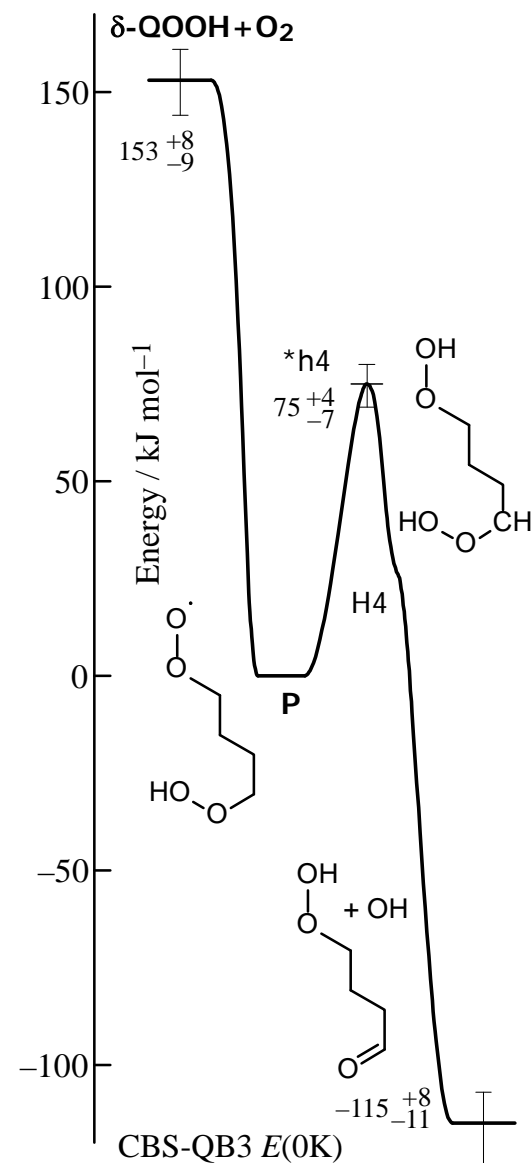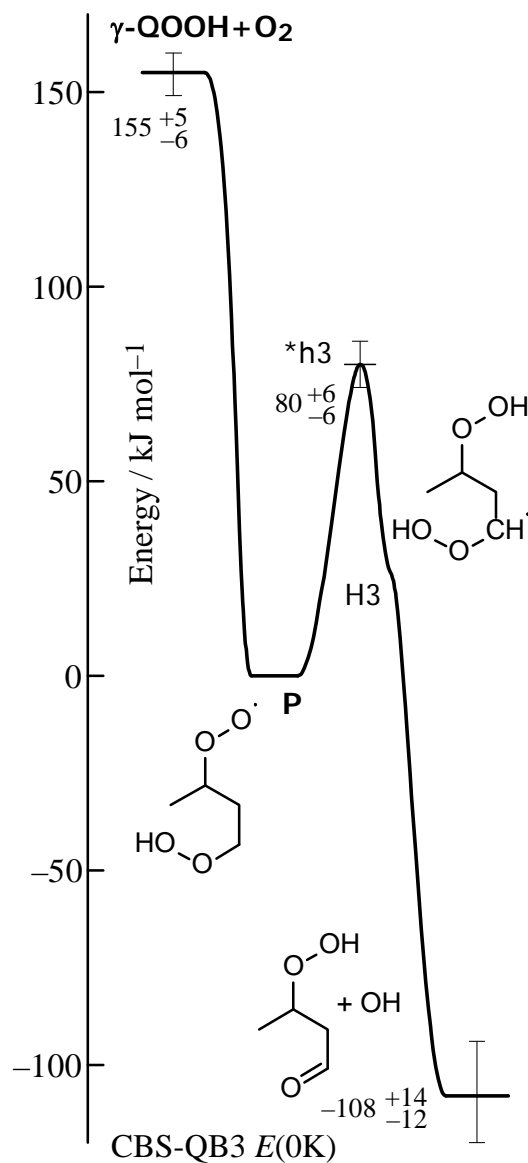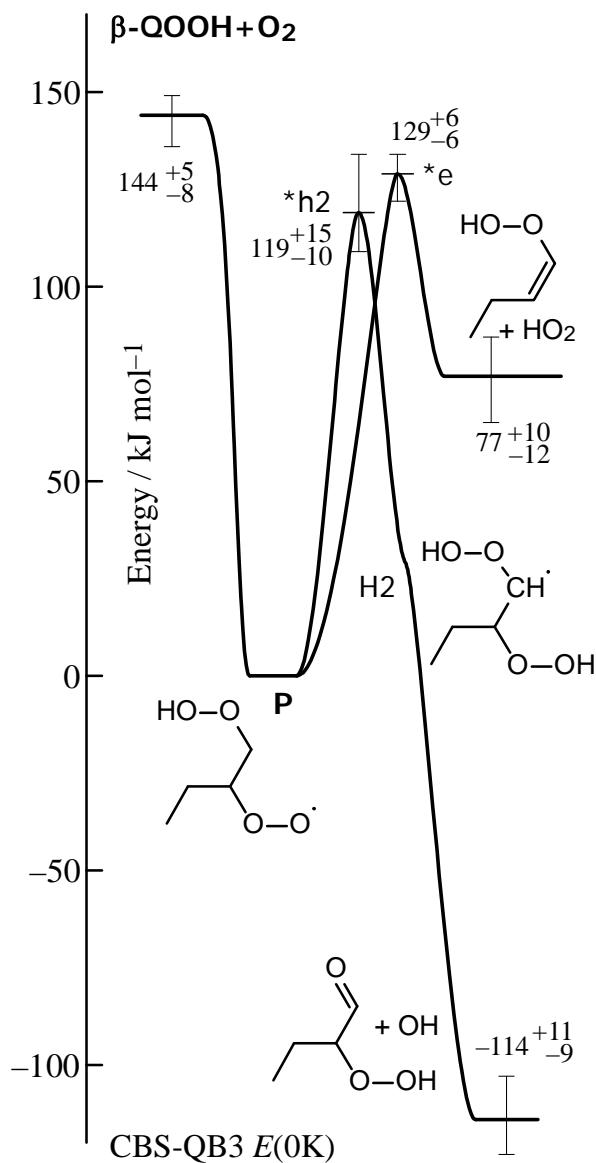concerted HO$_2$ elimination reactions

5,1-H shift reactions
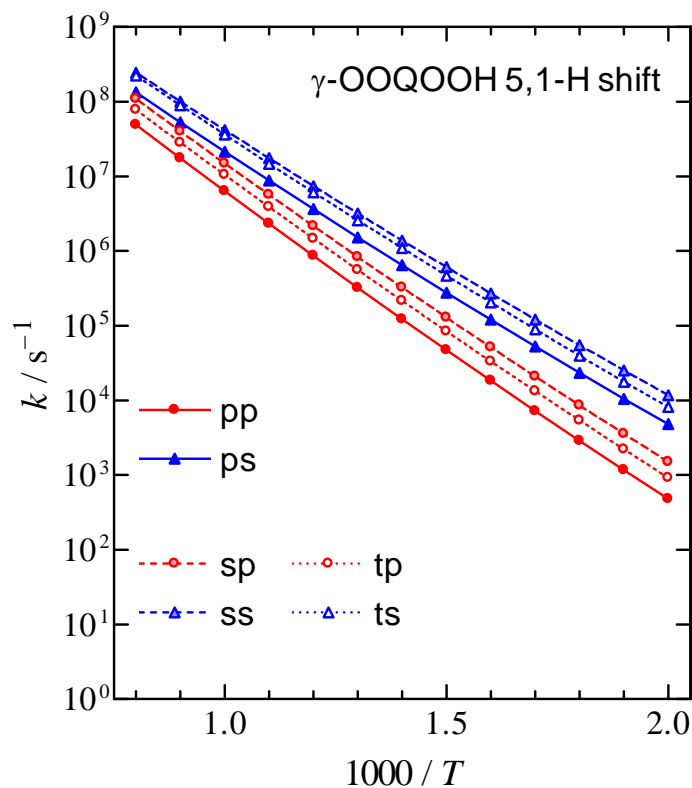
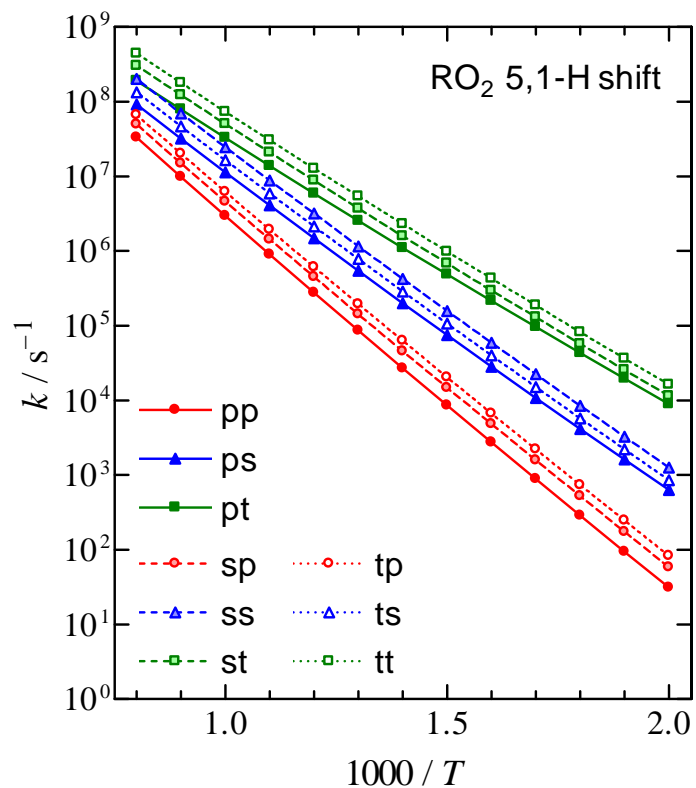# Reactions of OOQOOH

Generalized Diagram for OOQOOH Reactions

TST Rate Constants

Rate constants are nearly equal to (or slightly smaller than) those of isomerization of corresponding RO_2 with -OOH to -CH$_3$ replacement

γ-OOQOOH 5,1-H shift reactions

cf.) RO_2 5,1-H shift reactions

New Evaluations

```
Elim/HO2/RO2/pp    5.47E+12   0.    31960.
Elim/HO2/RO2/ps    5.73E+12   0.    31650.
Elim/HO2/RO2/pt    3.42E+12   0.    31890.
Elim/HO2/RO2/sp    6.96E+12   0.    31690.
Elim/HO2/RO2/ss    7.35E+12   0.    31500.
Elim/HO2/RO2/st    7.06E+12   0.    31350.
Elim/HO2/RO2/tp    1.26E+13   0.    31170.
Elim/HO2/RO2/ts    1.77E+13   0.    30450.
Elim/HO2/RO2/tt    3.82E+13   0.    31510.

Isom/RO2/5pp       1.26E+12   0.    33650.
Isom/RO2/5ps       1.02E+12   0.    30060.
Isom/RO2/5pt       6.95E+11   0.    27150.
Isom/RO2/5sp       1.54E+12   0.    33230.
Isom/RO2/5ss       8.50E+11   0.    30420.
Isom/RO2/5st       5.41E+11   0.    27210.
Isom/RO2/5tp       1.80E+12   0.    33410.
Isom/RO2/5ts       1.44E+12   0.    28840.
Isom/RO2/5tt       9.76E+11   0.    25800.

Isom/RO2/6pp       3.07E+11   0.    22960.
Isom/RO2/6ps       2.24E+11   0.    19670.
Isom/RO2/6pt       1.31E+11   0.    16490.
Isom/RO2/6sp       3.92E+11   0.    22570.
Isom/RO2/6ss       5.26E+11   0.    19820.
Isom/RO2/6st       2.42E+11   0.    16860.
Isom/RO2/6tp       5.05E+11   0.    22480.
Isom/RO2/6ts       3.48E+11   0.    19790.
Isom/RO2/6tt       3.57E+11   0.    16890.

Isom/RO2/7pp       4.36E+10   0.    21900.
Isom/RO2/7ps       3.39E+10   0.    18320.
Isom/RO2/7pt       1.53E+10   0.    15350.
Isom/RO2/7sp       9.27E+10   0.    22270.
Isom/RO2/7ss       7.93E+10   0.    19100.
Isom/RO2/7st       3.28E+10   0.    16100.
Isom/RO2/7tp       5.04E+10   0.    22700.
Isom/RO2/7ts       5.78E+10   0.    19450.
Isom/RO2/7tt       2.20E+10   0.    16450.

Dcmp/QOOH/cyc3QOpp 9.80E+12   0.    14930.
Dcmp/QOOH/cyc3QOps 6.22E+12   0.    13300.
Dcmp/QOOH/cyc3QOpt 1.07E+13   0.    12860.
Dcmp/QOOH/cyc3QOsp 7.43E+12   0.    12840.
Dcmp/QOOH/cyc3QOss 3.02E+12   0.    11860.
Dcmp/QOOH/cyc3QOst 4.61E+12   0.    11660.
Dcmp/QOOH/cyc3QOtp 5.73E+12   0.    11460.

Dcmp/QOOH/cyc3QOts 7.70E+12   0.    10740.
Dcmp/QOOH/cyc3QOtt 4.59E+12   0.    11200.

Dcmp/QOOH/cyc4QOpp 6.99E+11   0.    20150.
Dcmp/QOOH/cyc4QOps 6.05E+11   0.    17820.
Dcmp/QOOH/cyc4QOpt 6.03E+11   0.    15280.
Dcmp/QOOH/cyc4QOsp 1.26E+12   0.    18330.
Dcmp/QOOH/cyc4QOss 1.53E+12   0.    16630.
Dcmp/QOOH/cyc4QOst 3.75E+12   0.    15170.
Dcmp/QOOH/cyc4QOtp 1.06E+12   0.    16660.
Dcmp/QOOH/cyc4QOts 6.26E+11   0.    14910.
Dcmp/QOOH/cyc4QOtt 6.95E+11   0.    12860.

Dcmp/QOOH/cyc5QOpp 7.08E+10   0.    12780.
Dcmp/QOOH/cyc5QOps 1.26E+11   0.    10470.
Dcmp/QOOH/cyc5QOpt 1.15E+11   0.     8700.
Dcmp/QOOH/cyc5QOsp 5.48E+10   0.    13220.
Dcmp/QOOH/cyc5QOss 7.45E+10   0.    10240.
Dcmp/QOOH/cyc5QOst 2.80E+10   0.     7780.
Dcmp/QOOH/cyc5QOtp 3.65E+10   0.    12270.
Dcmp/QOOH/cyc5QOts 3.40E+10   0.     9360.
Dcmp/QOOH/cyc5QOtt 3.20E+10   0.     7360.

Elim/HO2/O2QOOH/pp 3.79E+12   0.    31250.
Elim/HO2/O2QOOH/ps 4.54E+12   0.    32740.
Elim/HO2/O2QOOH/sp 2.52E+13   0.    32430.
Elim/HO2/O2QOOH/ss 2.33E+13   0.    31370.
Elim/HO2/O2QOOH/tp 9.08E+12   0.    29810.
Elim/HO2/O2QOOH/ts 2.23E+13   0.    31050.

Isom/O2QOOH/5pp    1.83E+11   0.    26520.
Isom/O2QOOH/5ps    3.49E+11   0.    24160.
Isom/O2QOOH/5sp    8.96E+11   0.    30060.
Isom/O2QOOH/5ss    2.16E+12   0.    25710.
Isom/O2QOOH/5tp    1.21E+12   0.    28200.
Isom/O2QOOH/5ts    1.30E+12   0.    24900.

Isom/O2QOOH/6pp    9.35E+10   0.    19100.
Isom/O2QOOH/6ps    1.07E+11   0.    16940.
Isom/O2QOOH/6sp    1.67E+11   0.    18540.
Isom/O2QOOH/6ss    1.64E+11   0.    16470.
Isom/O2QOOH/6tp    1.32E+11   0.    18790.
Isom/O2QOOH/6ts    1.78E+11   0.    16920.

Isom/O2QOOH/7pp    1.47E+10   0.    17090.
Isom/O2QOOH/7ps    1.47E+10   0.    15140.
Isom/O2QOOH/7sp    2.48E+10   0.    17880.
Isom/O2QOOH/7ss    2.14E+10   0.    15990.
Isom/O2QOOH/7tp    2.40E+10   0.    17750.
Isom/O2QOOH/7ts    2.40E+10   0.    15830.
```
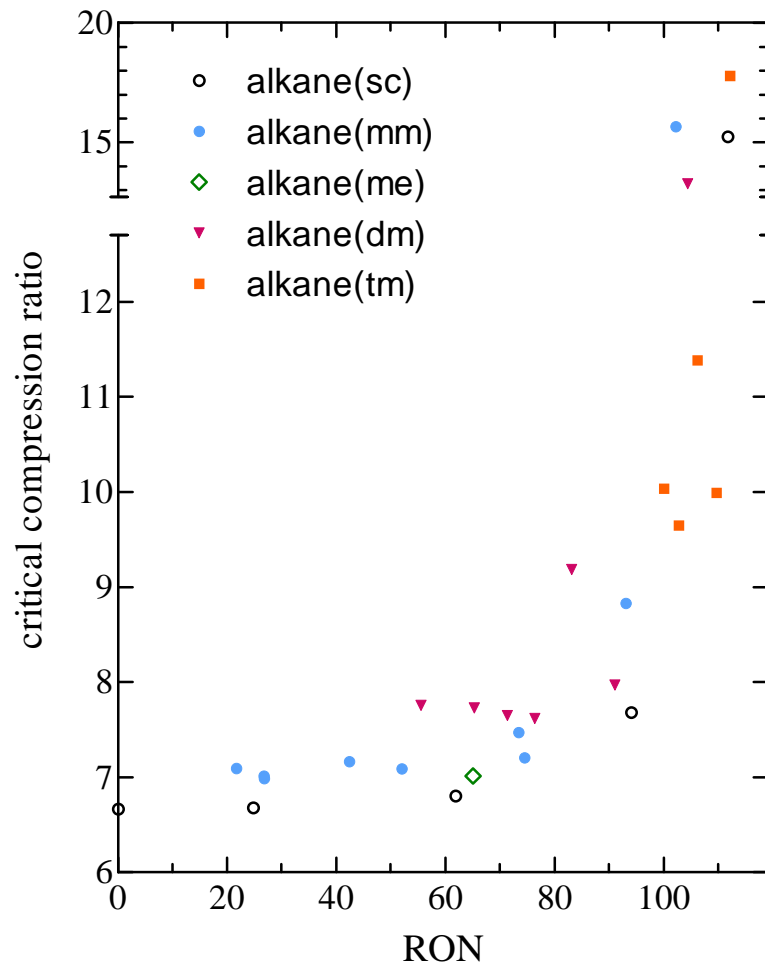
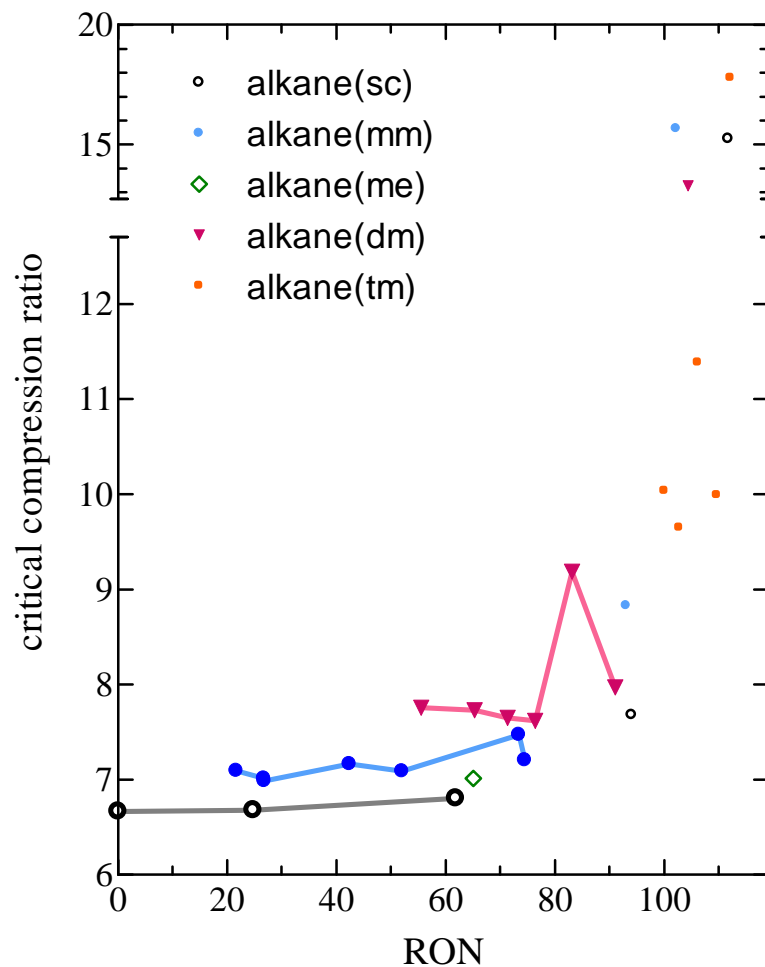# Molecular-Size Dependent Fall-off Rate Constants

Size Dependence?

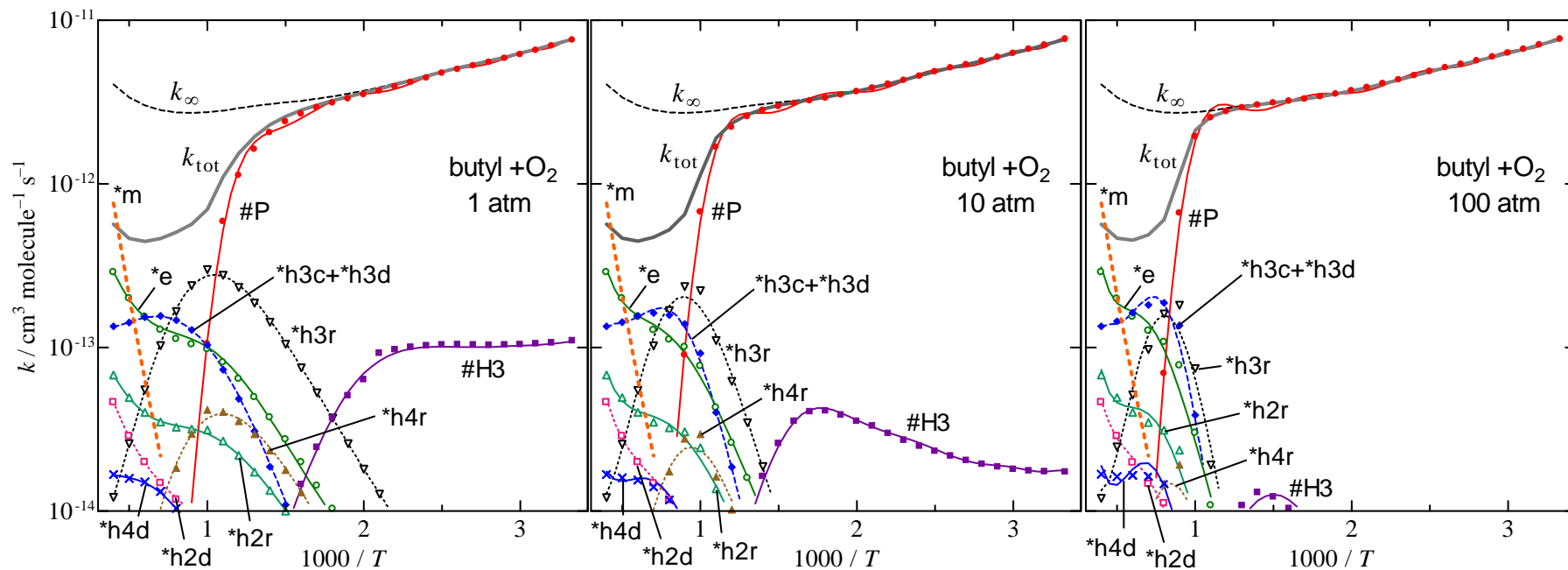- CCR predicted by previous KUCRS

Size Dependence?

- CCR predicted by previous KUCRS always showed
  systematic deviation between series of alkanes

Rate Coefficients for R + O$_2$

- Dominated by RO$_2$ formation at engine-cylinder pressure
  (> 10 atm) at least for C$_4$ and larger R
- Fall-off behavior at > 800 K is significant
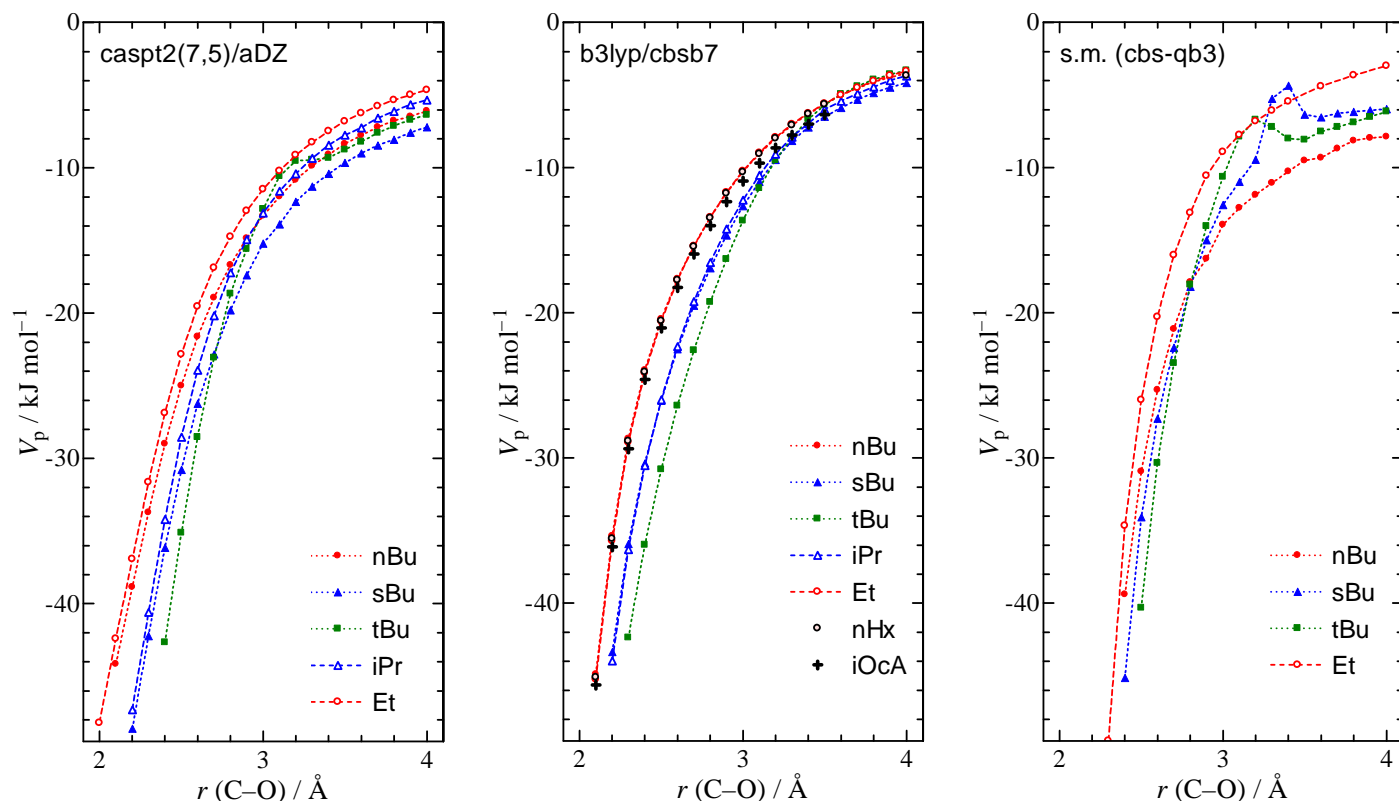
R + O$_2$: Potential Energy Curves

Table 3. Comparison of the Calculated and Experimental Rate Constants (cm^3 molecule^{-1} s^{-1})

	exp.		caspt2(7,5)/aDZ	(err)	b3lyp/cbsb7	(err)	s.m.(cbs-qb3)	(err)
ethyl	7.8×10^{-12}	[2]	7.28×10^{-12}	(–7%)	4.11×10^{-12}	(–47%)	2.93×10^{-12}	(–62%)
i-propyl	1.41×10^{-11}	[3]	1.25×10^{-11}	(–11%)	8.29×10^{-12}	(–41%)		
n-butyl	7.5×10^{-12}	[4]	9.21×10^{-12}	(+23%)	3.54×10^{-12}	(–53%)	1.59×10^{-11}	(+112%)
s-butyl	1.66×10^{-11}	[4]	1.26×10^{-11}	(–24%)	4.26×10^{-12}	(–74%)	4.24×10^{-12}	(–74%)
t-butyl	2.34×10^{-11}	[4]	2.50×10^{-11}	(+7%)	1.73×10^{-11}	(–26%)	8.03×10^{-12}	(–66%)

- caspt2(7,5)/aDZ potential curves predict rate constants at room temperature best.
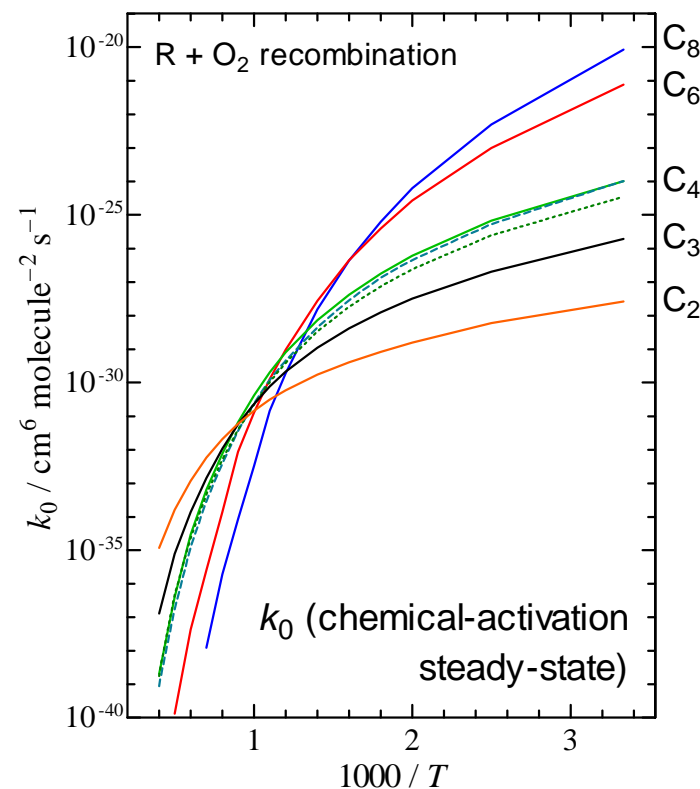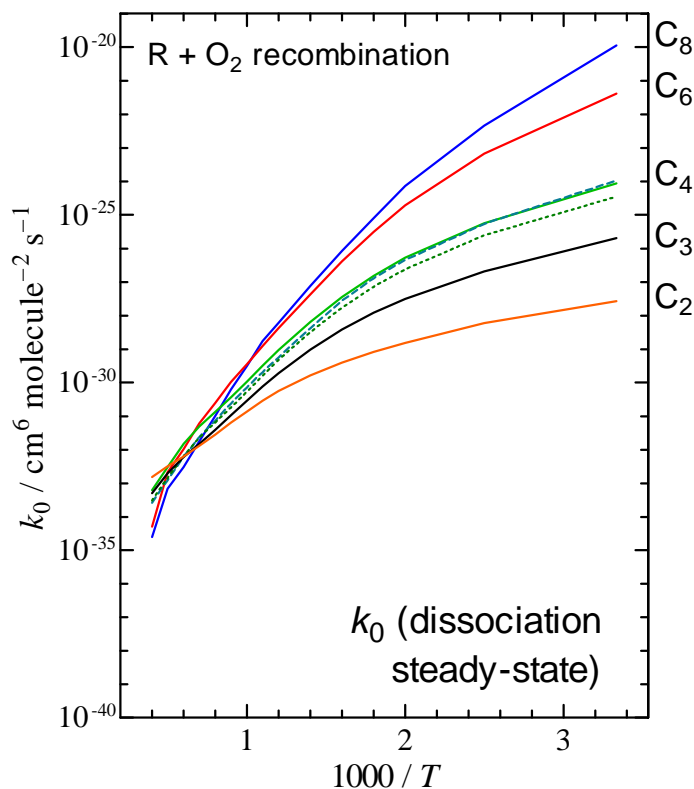
R + O$_2$: Variational TST

Size-Independent High-Pressure Limiting Rate Constants

- Similar VTST behavior for the same class of R
(primary / secondary / tertiary)
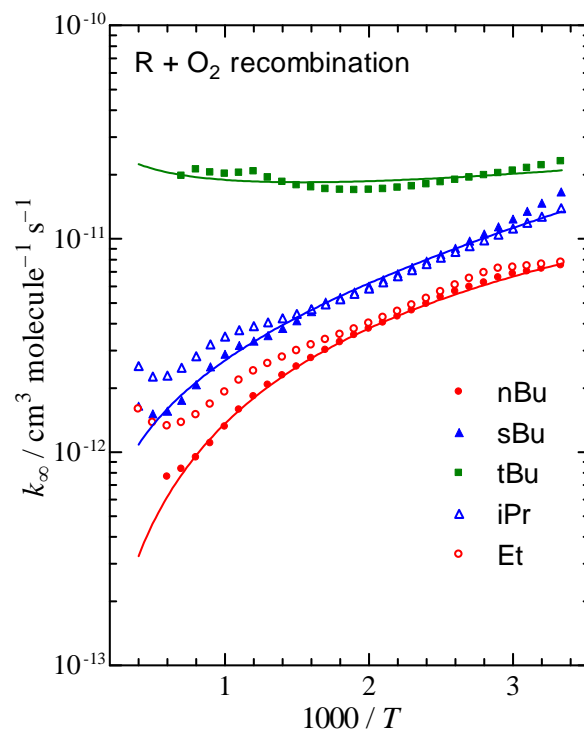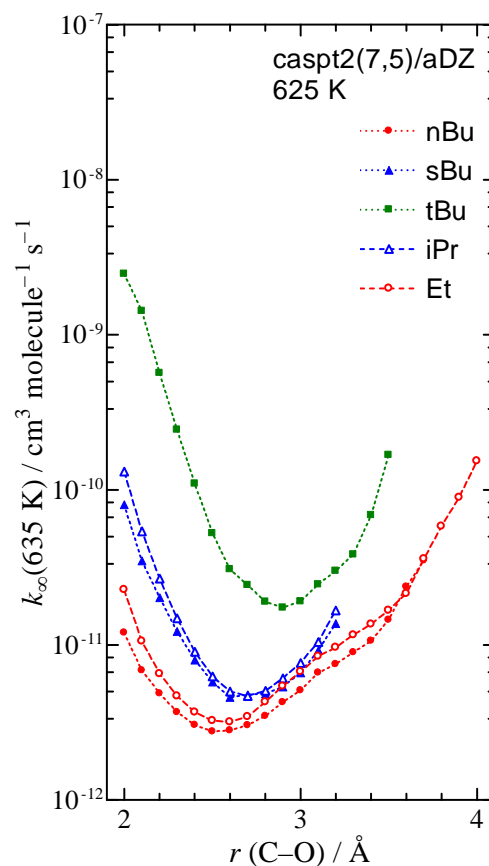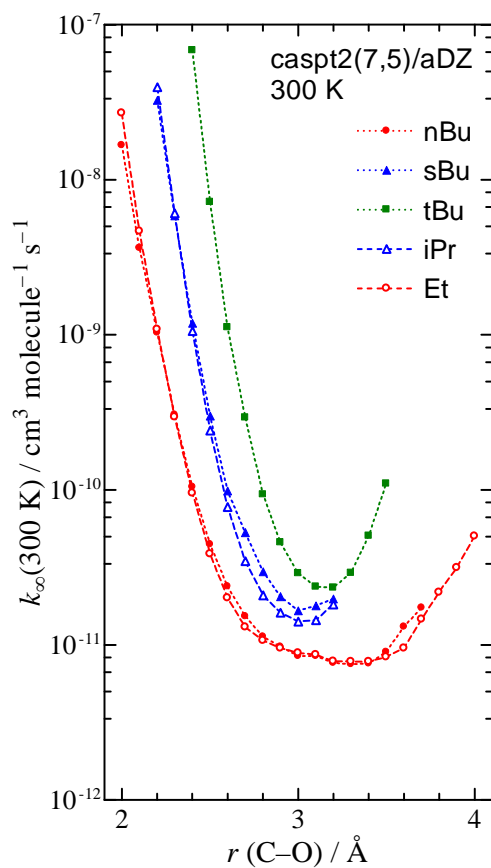
R + O$_2$: RRKM Fall-Off Analysis

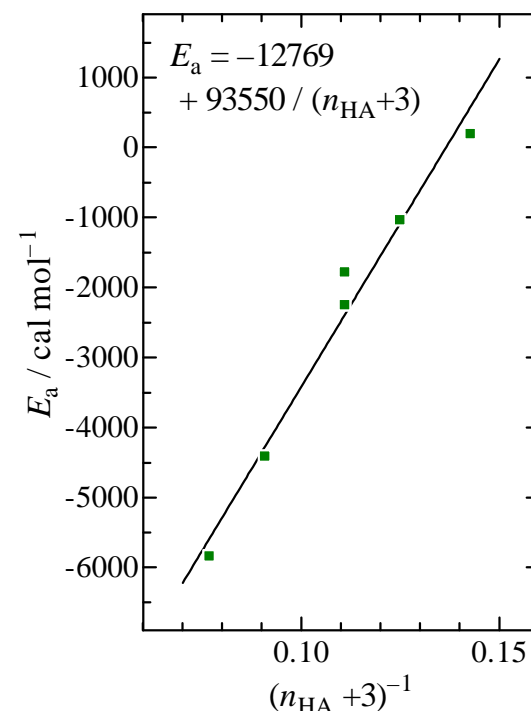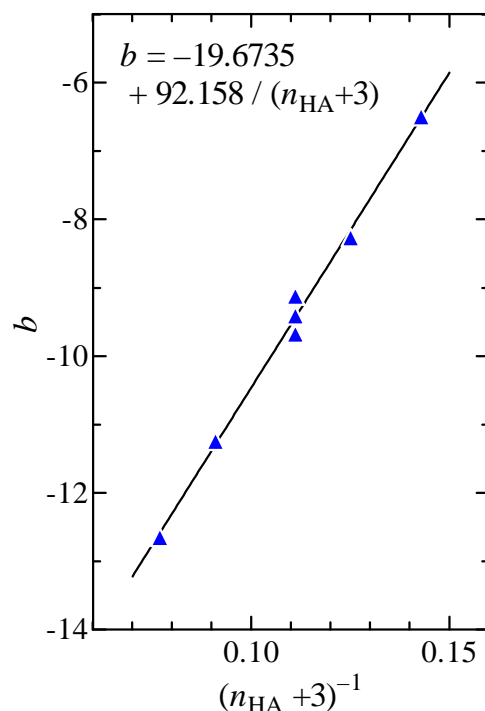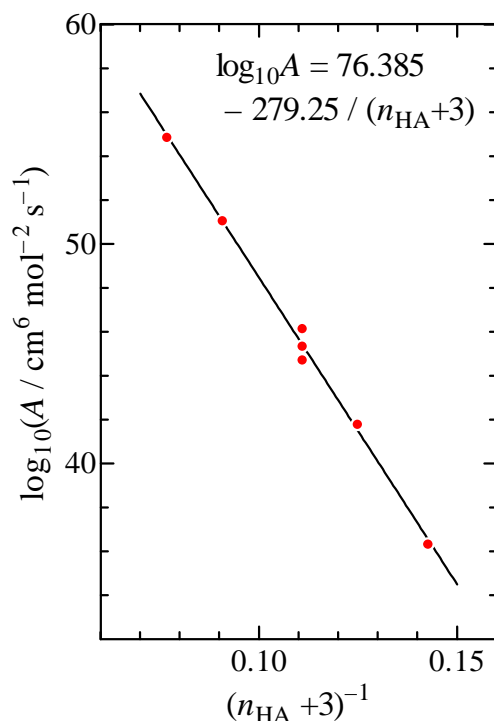## Size Dependent Low-Pressure Limiting Rate Constants

- Significant difference between dissociation steady-state and chemical-activation steady-state calculations at high-temperature suggests non-steady state behavior

R + O$_2$: Size-Dependent Formula for k_0

- Parameters for modified Arrhenius Expression:
$$k_0 = A \, T^b \exp(-E_a / RT)$$

Left plot:
$$\log_{10} A = 76.385 - 279.25 / (n_{HA}+3)$$
y-axis: $\log_{10}(A \, / \, cm^6 \, mol^{-2} \, s^{-1})$
x-axis: $(n_{HA}+3)^{-1}$

Middle plot:
$$b = -19.6735 + 92.158 / (n_{HA}+3)$$
y-axis: b
x-axis: $(n_{HA}+3)^{-1}$

Right plot:
$$E_a = -12769 + 93550 / (n_{HA}+3)$$
y-axis: $E_a \, / \, cal \, mol^{-1}$
x-axis: $(n_{HA}+3)^{-1}$

n_{HA} = number of heavy (non-hydrogen) atoms

Effect of Size Dependence
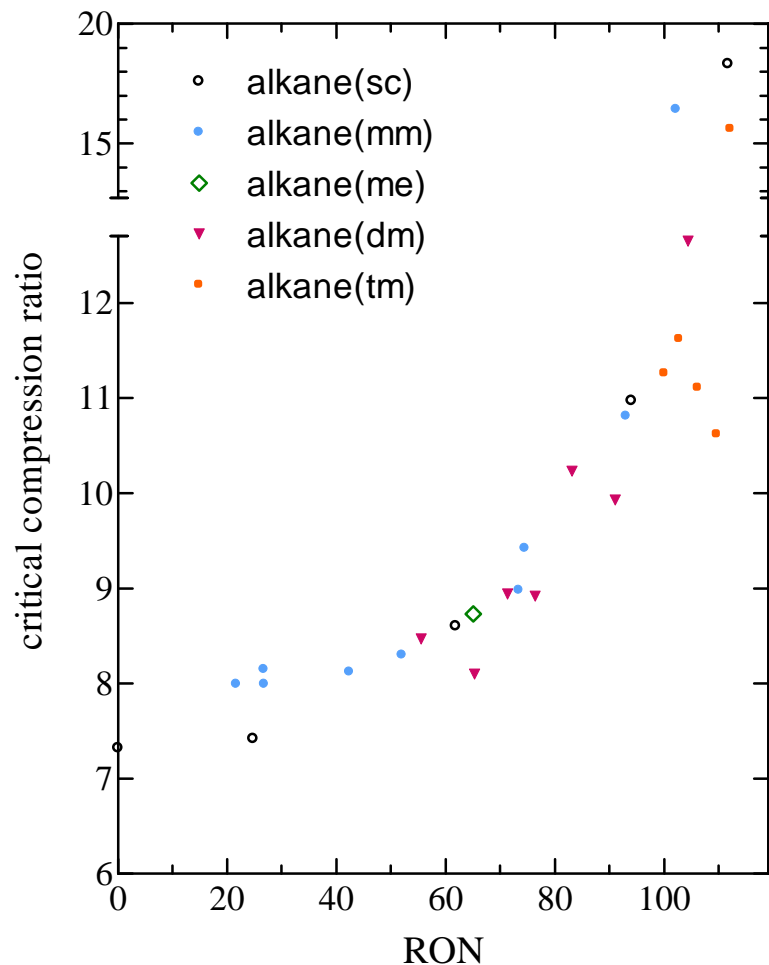
- **Systematic deviation disappeared !**

with:
- size-dependent fall-off rate constants for $R + O_2$
- size-dependent fall-off rate constants for KetOOH decomposition
- reduced OH-yields for alpha-H vinoxy + O_2

- **More validation is required**

Summary

— *Systematic Quantum Chemical Calculations for:*

- All important RO_2 isomerization reactions including:
  concerted HO_2 elimination
  4,1-, 5,1-, and 6,1-H shift
  cyclic ether formation from β-, γ-, and δ-QOOH
- Important OOQOOH isomerization reactions including:
  concerted HO_2 elimination & 4,1-H shift of β-OOQOOH
  5,1-H shift of γ-OOQOOH
  6,1-H shift of δ-OOQOOH

— *Size-Dependent Fall-Off Rate Evaluation for:*

- R + O_2 reactions based on the VTST and RRKM calculations for:
  R = C_2H_5, i-C_3H_7, n-C_4H_9, s-C_4H_9, t-C_4H_9, n-C_6H_{13}, i-C_8H_{17}
- Thermal decomposition reactions of KetOOH:
  based on k_0 for R + O_2
- More validation is required

— *Remaining Questions*

- Fall-off behavior of substituted vinoxy radical + O_2 reactions