COMBUSTION RESEARCH FACILITY

# Predictive Rate Coefficient Calculations for Combustion Modeling

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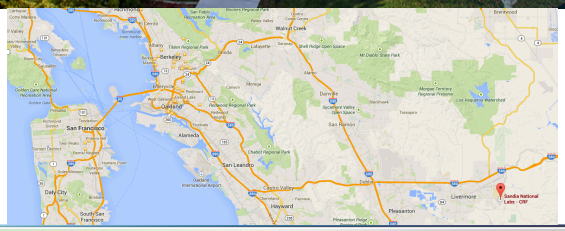
## Combustion Research Facility

*one of them…

2

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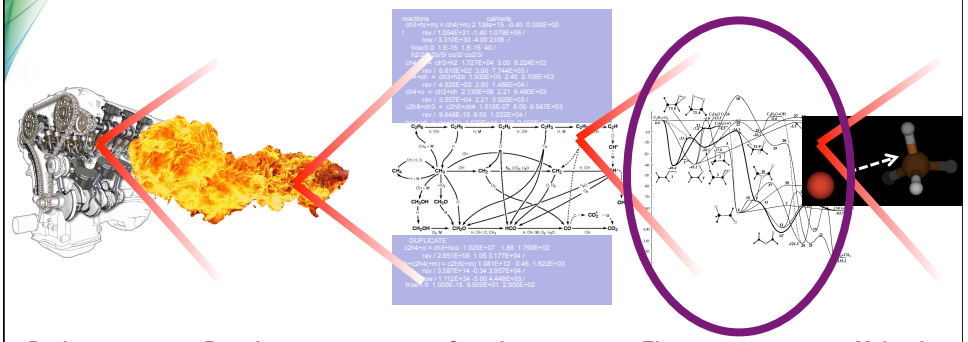
## The hierarchy of combustion chemistry and the role of theoretical kinetics



| Device scale | Reacting flows | Complex chemical mechanisms | Elementary chemical kinetics | Molecular dynamics |
|---|---|---|---|---|

**A bottom-up approach requires a set of efficient, flexible and rigorous tools.**

**Ideally, simplifications should be validated *a posteriori* !**

3



## What is combustion chemistry?

Fu → $H_2O$ + energy

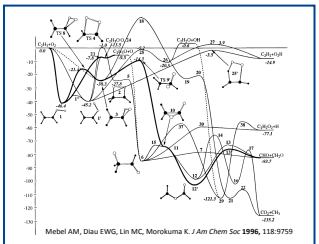
$NO_x$?

soot?

timing?

*P* and *T* dependence?

300 – 3000 K, 10 – $10^6$ Torr



Mebel AM, Diau EWG, Lin MC, Morokuma K. *J Am Chem Soc* **1996**, 118:9759

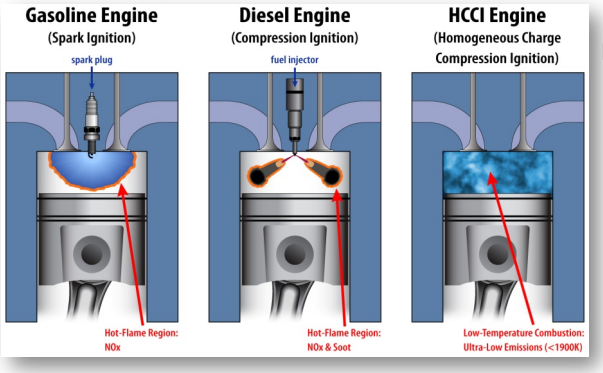
At least 8 papers on the reaction kinetics of vinyl + $O_2$!

***Details*** of combustion chemistry are critical in several areas.

4

# Importance of elementary chemical kinetics in combustion and engine development

In Homogeneous Charge Compression Ignition (HCCI) engines combustion is initiated by thermal autoignition → sensitive to molecular structure




Manley et al. *Physics Today* 2008

In practical fuels there are:

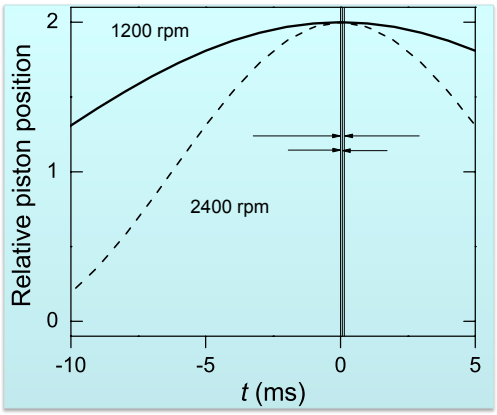
- alkanes
- olefins
- cycloalkanes
- aromatics
- oxygenates

Advanced engine concepts and the increasing use of alternative and non-traditional fuels present new challenges for combustion modeling.

5



# HCCI engine operation requires the precise knowledge of autoignition delay times



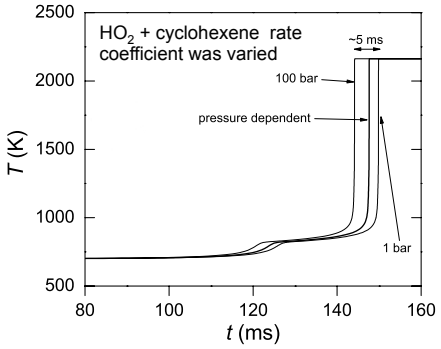

Ignition has to be timed at a minimum of 1 crank angle precision
@ 1200 rpm ~ 140 µs
@ 2400 rpm ~ 70 µs

Typical ignition time in HCCI: 2-4 ms ➔ Ignition delay predictions within ~3%.

Are chemical mechanisms capable of this?

6

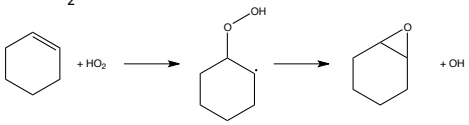
# One, very slow rate coefficient can make a few % difference on its own




- CHEMKIN simulation of homogeneous explosion
- 4:1 mixture of cyclohexane:cyclohexene (1/30 of all bonds is unsaturated)
- φ = 0.5
- Based on LLNL mechanism (1081 species and 4298 reactions)
- $T_0$ = 700 K and $P_0$ = 10 bar

Zádor, Klippenstein and Miller, J. Phys. Chem. A, 2011

The reaction is very slow (~$10^{-15}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ @ 700 K), but it converts unreactive $HO_2$ radicals into reactive OH radicals.

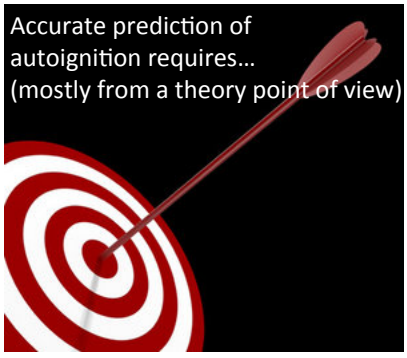



How can then a chemical kinetic model predict anything at all? ➔ Tuning!

7



# Overview




- Understanding of the underlying chemistry
- Calculation of rate coefficients rigorously for multiwell systems
- Reduction of uncertainties in our calculations
- Automation of reaction path searches
- Synergy with experimental work

8

## Reactions of alkyl radicals with $O_2$ control hydrocarbon autoignition at low *T* (< 900 K)

R• + $O_2$ → ROO•

alkene + $HO_2$•
chain termination

•QOOH

cyclic ether + •OH
chain propagation

+ $O_2$

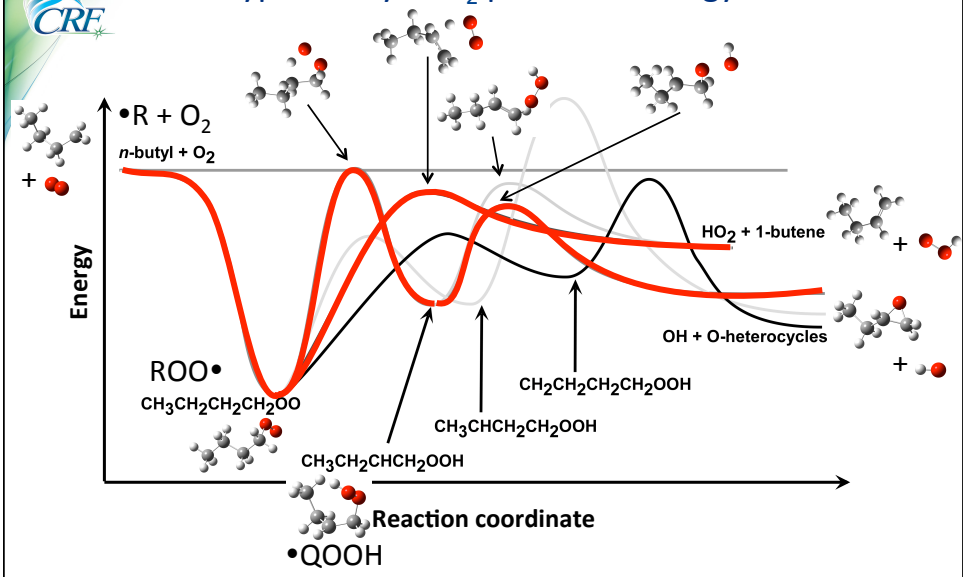
Challenges:
- Combined *P* and *T* dependence
- Isolation of individual steps is impossible

2 •OH Chain branching!

9



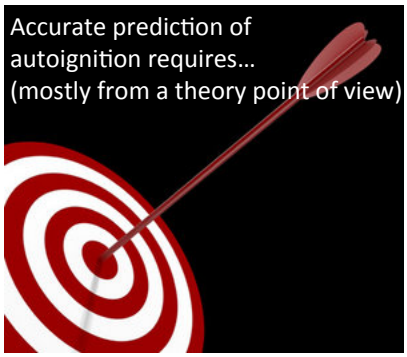
## A typical alkyl + $O_2$ potential energy surface




Prediction of rate coefficients and branching fractions require a coupled physical model that contains the full potential energy surface!

10

# Overview

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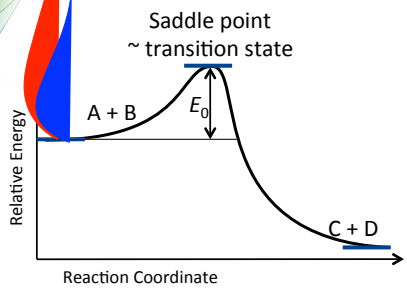
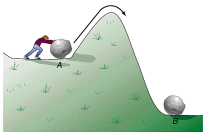
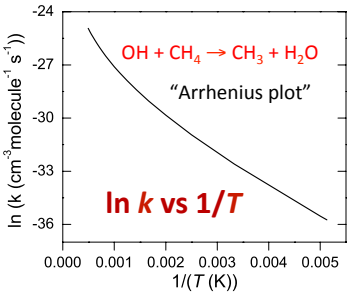
# Simple bimolecular reactions (A + B → C + D) have temperature dependence only



Rate coefficient is bound from above by the collision frequency, ~$10^{-9}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (~$10^{+10}$ collisions s$^{-1}$ at 1 bar per molecule)

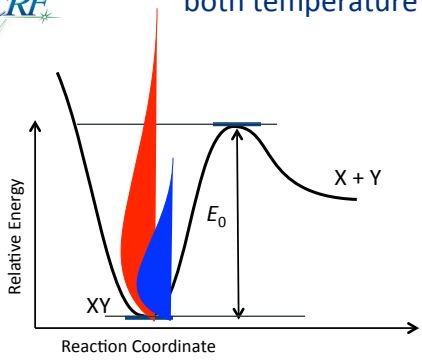
e.g. if $k$ = $10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ ➔ every 100$^{th}$ collision leads to a reaction.

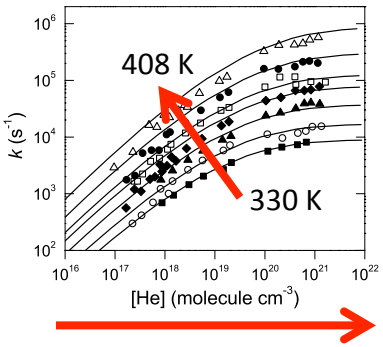



**Transition state theory** predicts the rate coefficient as a function of temperature:

$$k(T) = \kappa(T)\frac{Q^{TST}(T)}{Q^{reactant}(T)}\exp(-E_0 / k_B T)$$

## Simple unimolecular reactions (XY → X + Y) have both temperature and pressure dependence




0 $s^{-1}$ < $k$, no upper limit!

e.g. $10^6$ $s^{-1}$ ➔ lifetime is ~1 μs

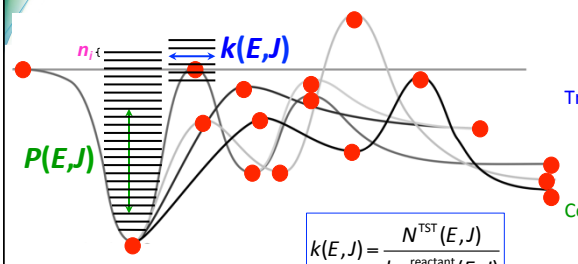
Low P: collisional control

High P: transition state control

A large fraction of important gas-phase reactions, however, feature multiple wells and multiple bimolecular exit channels, adding extra complexity to the system.



## The machinery of calculating rate coefficients: Time-dependent Master Equation




$$k(E,J) = \frac{N^{TST}(E,J)}{h\rho^{reactant}(E,J)}$$

Energy and other properties of stationary points are calculated from quantum chemistry.

Transition-state theory is used to compute energy and angular-momentum specific rate constants, $k(E,J)$.

Collisional energy transfer redistributes population among energy "levels".

Multiple-well master equation solution gives time-dependent populations for all species.

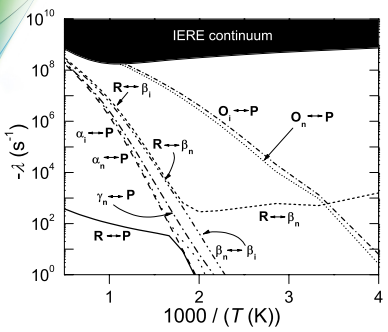
$$\frac{dn_i(E,J)}{dt} = Z_i \sum_{\mathcal{J}} \int_{E_{0_i}}^{\infty} P_i(E,J;E',J')\, n_i(E',J')\, dE' - Z_i n_i(E,J) - \sum_{j\neq i}^{M} k_{j_i}(E,J)\, n_i(E,J) + \sum_{j\neq i}^{M} k_{ij}(E,J)\, n_j(E,J) - k_{d_i}(E,J)\, n_i(E,J) + k_{a_i}(E,J)\, n_R n_m \rho_{Rm}(E,J) e^{-\beta E}/Q_{Rm} - \sum_{p=1}^{N_p} k_{p_i}(E,J)\, n_i(E,J)$$

$i = 1, \ldots, M$

$$\frac{d|w(t)\rangle}{dt} = \mathbf{G}|w(t)\rangle$$

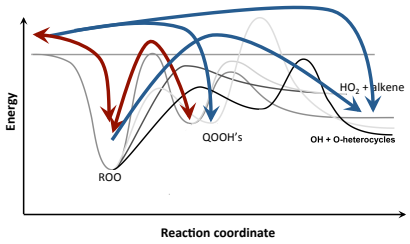
## The Master Equation is an eigenvalue-eigenvector problem

$$\frac{d|w(t)\rangle}{dt} = \mathbf{G}|w(t)\rangle$$




FAST eigenvalues: internal energy relaxation

SLOW eigenvalues: chemical reactions




The derived rate coefficients contain all possible combinations of species-to-species rate coefficients.

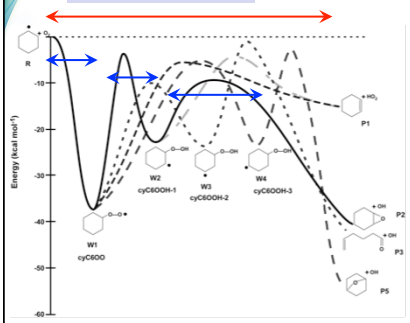
The solution accounts for both the **sequential** and the **well-skipping** pathways.

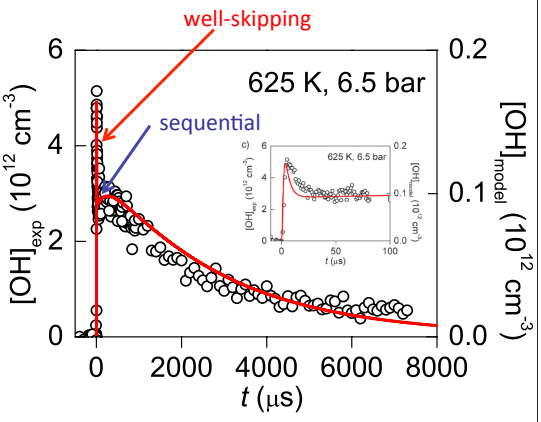
15



## Well-skipping processes are not merely theoretical constructs, but can be seen in experiments!

Cyclohexyl + $O_2$

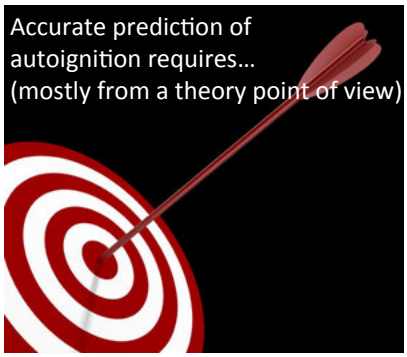





Well-skipping product formation is prompt, while sequential is delayed. Has a large effect on ignition delays – a "burst" of OH.

16

# Overview

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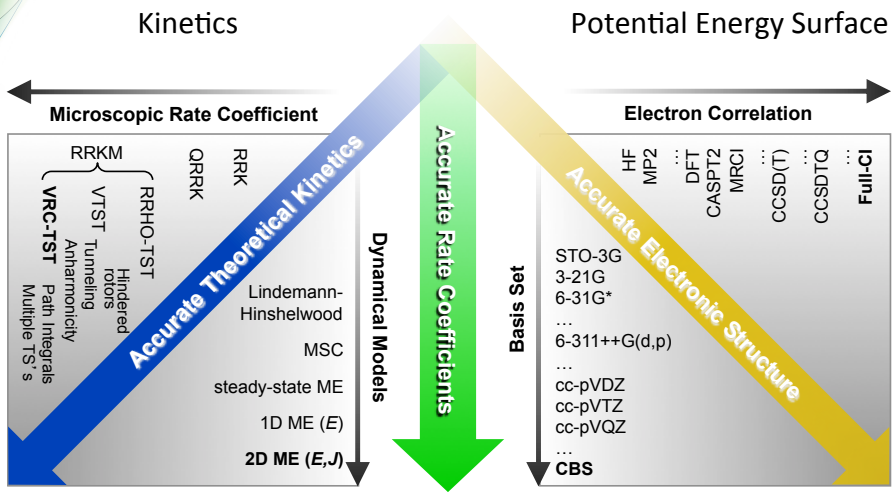
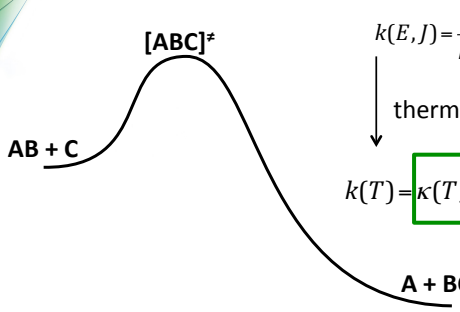
# A balanced approach is desirable for accurate kinetics.



## Sources of uncertainty for reactions with barriers




$$k(E,J) = \frac{N^{\neq}(E,J)}{h\rho_R(E,J)}$$

thermal averaging, canonical variational TST

$$k(T) = \kappa(T,s^*)\frac{k_B T}{h}\frac{Q^{\neq}(T,s^*)}{Q_R(T)}\exp(-E^{\neq}(s^*)/RT)$$

$s^*$: variationally determined, 3$N$-7 dimensional dividing surface, for reactions with a barrier often well approximated by a ridge including the saddle point(s) in question

$E^{\neq}$: barrier height, $E_{el}$ + *ZPE*

$Q$: electronic, rotational and vibrational (usually largely uncoupled) partition function

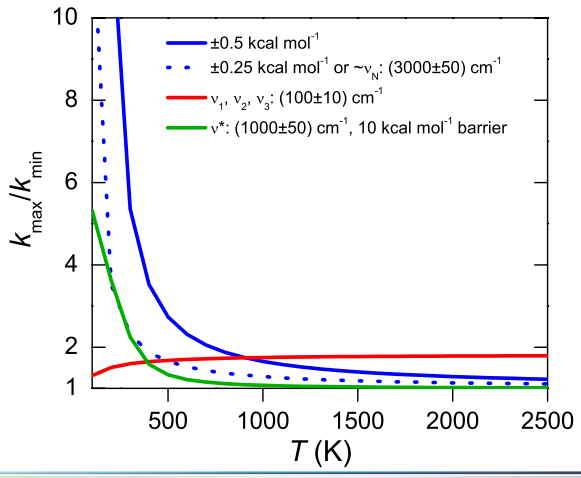
κ: tunneling, which cannot be factored out in a rigorous sense

19



## Sources of uncertainty for reactions with barriers

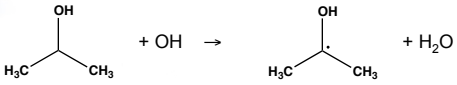
$$k(T) = \kappa(T,s^*)\frac{k_B T}{h}\frac{Q^{\neq}(T,s^*)}{Q_R(T)}\exp(-E^{\neq}(s^*)/RT)$$

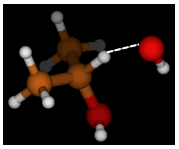



20

# Parametric uncertainty quantification in an *ab initio* rate-coefficient calculation

A simple abstraction reaction:



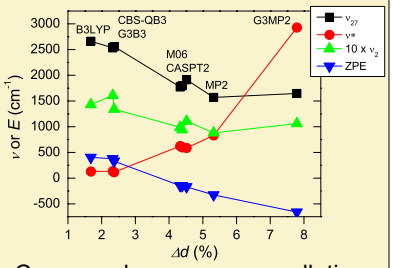



Significant variations in some of the calculated molecular parameters

| No. | Method | *E* kcal mol$^{-1}$ | ΔZPE kcal mol$^{-1}$ | $\nu_2$ cm$^{-1}$ | $\nu_{27}$ cm$^{-1}$ | $\nu^*$ cm$^{-1}$ | Δ*d*% |
|---|---|---|---|---|---|---|---|
| 1 | QCISD(T)/CBS//B3LYP/6-311++G(d,p) | -1.36 | +1.15 | 143 | 2663 | 129*i* | 1.68 |
| 2 | QCISD(T)/CBS//M062x/6-311++G(d,p) | -1.18 | -0.48 | 111 | 1912 | 588*i* | 4.52 |
| 3 | QCISD(T)/CBS//MP2/6-311++G(d,p) | -1.94 | -0.93 | 88 | 1571 | 832*i* | 5.32 |
| 4 | QCISD(T)/CBS//CASPT2/aug-cc-pVDZ | -1.18 | -0.42 | 99 | 1774 | 624*i* | 4.33 |
| 5 | QCISD(T)/CBS//CASPT2/aug-cc-pVTZ | -1.16 | -0.42 | 94 | 1797 | 598*i* | 4.39 |
| 6 | CBS-QB3 | -1.19 | +1.08 | 161 | 2534 | 135*i* | 2.33 |
| 7 | G3B3 | -0.41 | +0.94 | 134 | 2560 | 116*i* | 2.37 |
| 8 | G3MP2 | -1.89 | -1.89 | 106 | 1647 | 2929*i* | 7.79 |

What are the resulting parametric uncertainties?

Parameters are strongly correlated

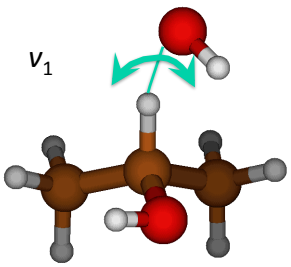


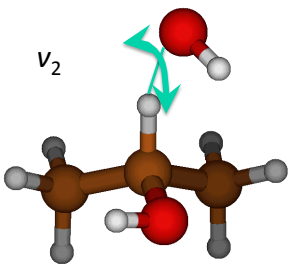

Can we rely on error cancellation and/or parameter correlation?

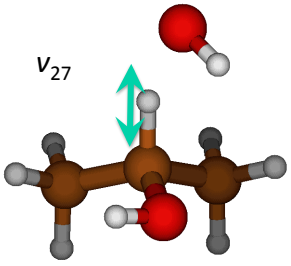
Prager, Najm and Zádor, *Proc. Comb. Inst.*, **2012** 21

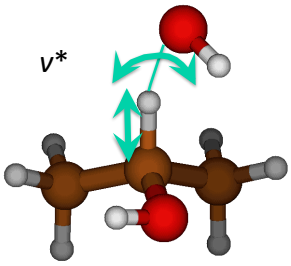


# The strong coupling between certain vibrational modes cause the correlation among the parameters



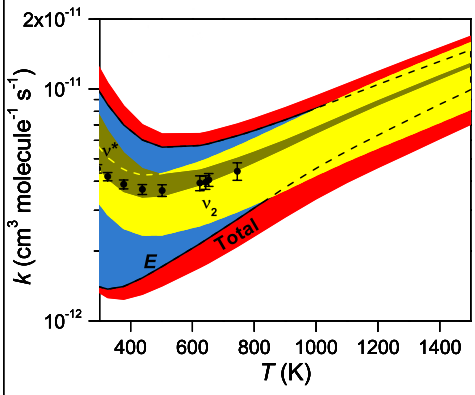




Prager, Najm and Zádor, *Proc. Comb. Inst.*, **2012** 22

# Forward uncertainty propagation of kinetics calculations

Dunlop and Tully (JPC 1993) measured site-specific abstraction rate coefficients (293-745 K) for isopropanol + OH.

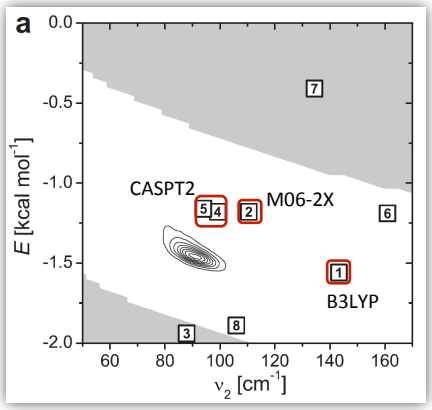



- 95% intervals
- Independent, uniform distribution
- Ratio of upper to lower bound:
  - (a) 10 at 300K
  - (b) 2.5 at 800K
- *E* dominates up to 800K
- $v_2$ small temperature dependence
- *v** minor importance, only to 500K
- reaction is challenging from theoretical/computational aspect

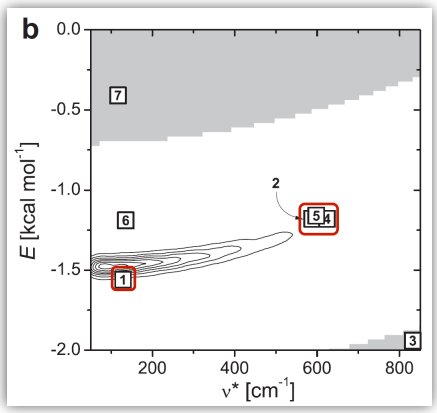


# Bayesian inference predicts best values and PDFs of parameters

PDF($v_2$, *E*)

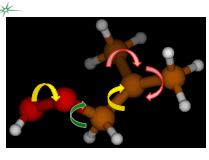


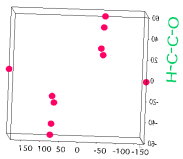

PDF(*v**, *E*)

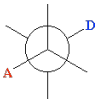



- Well defined PDF for *E* and $v_2$
- 'Map' for good QC parameter values
- Most methods are within factor of 2 of the parameter estimates

## Larger molecules: conformational entropy

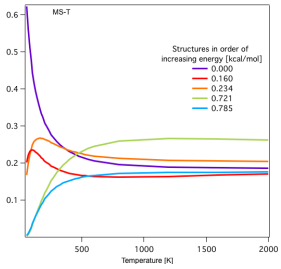





3 x 3 x 3 = 27 conformers ideally,
but only 10 in reality

Contribution of the conformers to the rovibrational partition function:



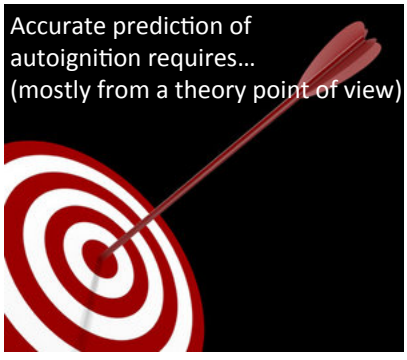

- Contributions change with temperature
- At high *T* all conformers contribute about equally

➔ determining accurate conformational partition functions for larger molecules is one of the largest problems to obtain accurate rate coefficients at combustion temperatures.

25



## Overview




- Understanding of the underlying chemistry
- Calculation of rate coefficients rigorously for multiwell systems
- Reduction of uncertainties in our calculations
- Automation of reaction path searches
- Synergy with experimental work

26

# Automation is necessary on all levels to meet the challenges of modern combustion chemistry

**Reaction Mechanism**

coupled concentrations

```
c2h4oh+o2=hoc2h4o2      1.00E+12  0.0  -1100.0  ! Marinov 1998
hoc2h4o2=ch2o+ch2o+oh   6.00E+10  0.0  24500.0  ! Marinov 1998
c2h4+oh=c2h3+h2o          2.02E+13  0.0   5936.0  ! Miller 1992
c2h4+o=ch3+hco            1.02E+07  1.88   179.0  ! Baulch 1994
c2h4+o=ch2hco+h       3.39E+06  1.88   179.0  ! Baulch 1994
c2h4+ch3=c2h3+ch4     6.62E+00  3.7   9500.0  ! Marinov 1995
c2h4+h=c2h3+h2        3.36E-07  6.0   1692.0  ! Dagaut 1990
c2h4+h (+m)=c2h5(+m)   1.08E+12  0.454 1822.0  ! Feng  1993
low / 1.112E+34  -5.0    4448.0 /                          ! Marinov 1996
troe / 1.0   1.0E-15   95.0  200.0 /
h2o /5.0/ h2/2.0/ co2/3.0/ co/2.0/
c2h4(+m)=c2h2+h2(+m)    1.8e14  0.0  87000.      ! Marinov 1997
low / 1.5e15 0.0  55443. /
c2h3+h(+m)=c2h4(+m)   6.1e12 0.27 280.        !GRI-Mech2.11
low/9.8e29  -3.86 3320 /
troe/ 0.782  208.  2663.  6095./
h2o/5.0/
c2h3+h=c2h2+h2          9.00E+13  0.0     0.0   ! Tsang 1986
c2h3+o=ch2co+h          3.00E+13  0.0     0.0   ! Miller 1992
c2h3+o=ch2o+hco         1.70E+29  -5.312 6500.0  ! Marinov 1997
c2h3+o=ch2hco+o         5.50E+14  -0.611 5260.0  ! Marinov 1997
c2h3+o2=c2h2+ho2        2.12E-06  6.0   9484.0   !cfm/nmm 1996
c2h3+oh=c2h2+h2o        2.00E+13  0.0     0.0   ! Miller 1992
c2h3+c2h=c2h2+c2h2      3.00E+13  0.0     0.0   ! Miller 1992
c2h3+ch=c2h2+c2h2       5.00E+13  0.0     0.0   ! Miller 1992
c2h3+ch3=ac3h5+h        4.73E+02  3.7   5677.0   ! Marinov 1996
c2h3+ch3=c3h6           4.46E+56 -13.0 13865.0   ! Marinov 1996
c2h3+ch3=c2h2+ch4       2.00E+13  0.0     0.0   ! Fahr  1991
c2h2+oh=c2h+h2o         3.37E+07  2.0   14000.0  ! Miller 1992
c2h2+oh=hccoh+h         5.04E+05  2.3   13500.0  ! Miller 1992
c2h2+oh=ch2co+h         2.18E-04  4.5   -1000.0  ! Miller 1992
dup
c2h2+oh=ch2co+h         2.00E+11  0.0     0.0   ! Vandooren 1977
dup
c2h2+oh=ch3+co          4.83E-04  4.0   -2000.0  ! Miller 1992
```

Combustion of real fuels involves thousands of elementary reactions.

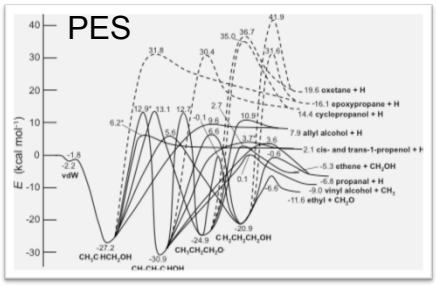
Automation is implemented, e.g. RMG or EXGAS.

Rules acting on symbols

Rules need to be made, tested, modified

**Elementary Reaction**

coupled concentrations AND rate coefficients




Elementary reactions involve several (dozens) of chemical species and hundreds of conformers.

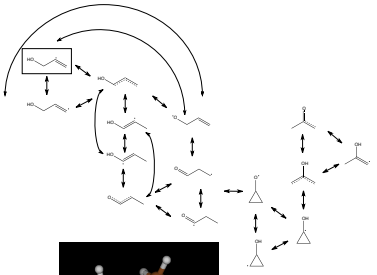
No commonly used efficient codes for automatic exploration.



# The 3-D realization of chemical structures is one of the major the bottle necks in theoretical kinetics calculations

Chemical "intuition" combined with literature and experimental evidence can predict almost all important pathways

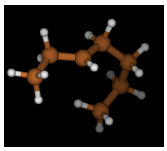
conceptually simple problem (pen + paper)

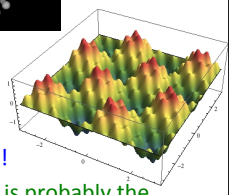


Realization of all chemical structures in 3-D

hard and tedious problem

- best guess structures are "hand-built" (sculpted in 3-D visualization programs)
- search for (lowest energy) conformers is also difficult
  ~$3^n$ conformers ($n$ is the number of heavy atoms)
  $n = 5 \rightarrow 243$
  typically 10 or more stationary points
- Combinatorial/bookkeeping problem
- Prone to human error

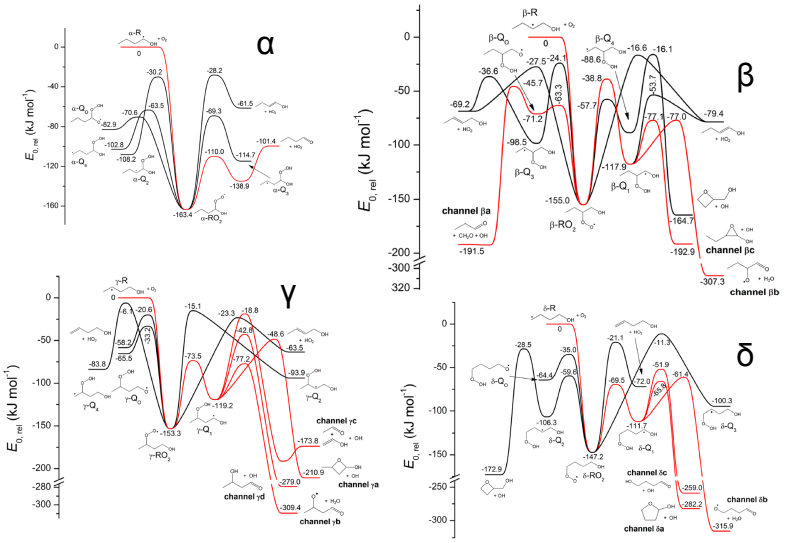




It is an extremely difficult task to search in this 3*N*-6 dimensional space!

In the application of modern TST theory, exploring all stationary points is probably the slowest process for molecules containing 4+ heavy atoms.

## Illustrative example: radicals derived from *n*-butanol reacting with $O_2$



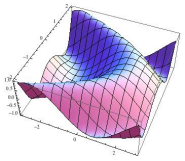

Welz et al., 2013, JPCA



## Strategies for finding minima on potential energy surfaces

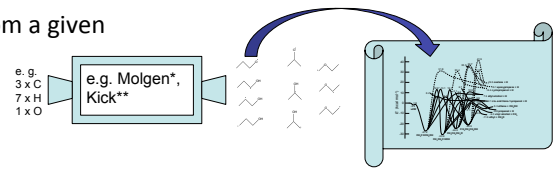
### I. Grid Approach

Calculate the full (or partial) PES using a dense enough coordinate grid.

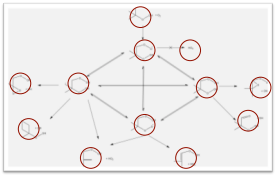


### II. Global Approach

Generate all stable species from a given constituency.




### III. Growing Network Approach



# Methods to find first-order saddle points

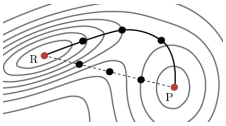
## I. Local Optimization Methods

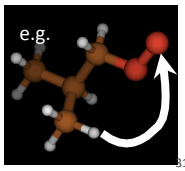
Uphill-walking methods, which can find the saddle-point starting at a reactant, without any knowledge about the product

N.B.: Once close to the real saddle point, Local Optimization Methods are efficient and accurate!

## II. Double-Ended Methods

~Morphing reactants into products, e.g. Nudged Elastic Band method, the Synchronous Transit-Guided Quasi-Newton method (implemented in Gaussian), the Ridge Method, etc.



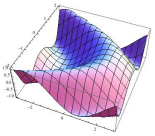

## III. Chemistry-Based Methods

Structural analysis using redundant internal coordinates
+ Chemical knowledge ("intuition") to generate good guesses

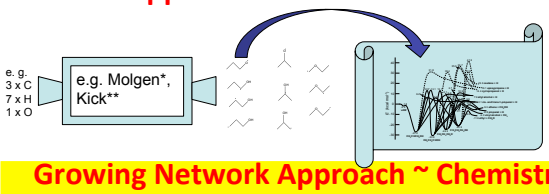


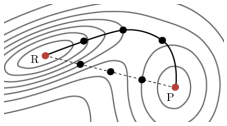
# Pairing of methods

## Grid Approach ~ Local Optimization Methods

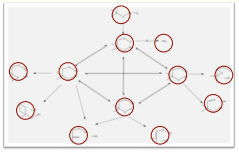


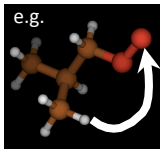
## Global Approach ~ Double-Ended Methods




## Growing Network Approach ~ Chemistry-Based Methods





## **KinBot**: a tool for the automated exploration of PES's relevant for gas-phase combustion chemistry

- Explores automatically the 3-D structure of stationary points on the underlying potential energy surface of elementary reactions in gas-phase combustion chemistry (C, H, O containing species currently), including the exploration of the conformational space.
- KinBot 1.0 combines a growing network approach for the network exploration with a chemistry-based approach for crawling in the network.
- The heart of the code are the algorithms that convert Cartesian coordinates into chemically meaningful information:
  - bonds
  - cycles
  - rotors
  - radical centers
  - motifs
  - symmetry numbers
  - identification of identical chemical structures
  - etc.
- Unimolecular reactions on complex, multiwell surfaces
- Bimolecular reactions (abstractions and additions)

33

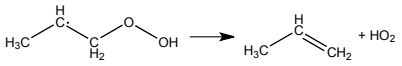


## Guiding principle: Bonds

All relevant reactions in gas-phase cobustion can be categorized based on the number of bonds broken (B) and/or made (M) in the course of the elementary step.

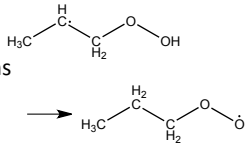
**1-bond reactions:**

B: scission
M: addition




**2-bond reactions:**

BM: transfer of parts of the structure, e.g. abstractions
BB/MM: certain elimination/addition reactions




**3-bond reactions:**

BMB/MBM: 1,*n*-eliminations/1,*n*-additions

**4-bond reactions:**

BMBM: cascade abstractions

**5-bond reactions:**

possible, but becomes VERY unlikely due to low entropy

34

# 1-bond example: Scission reactions

**β-scission:**

C-C bond cleavage: $C^{\bullet}$-C-C → C=C + $C^{\bullet}$

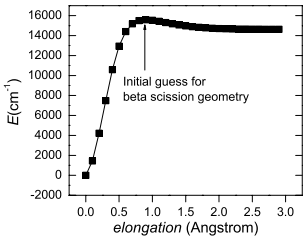
QOOH → $HO_2$ + alkene: $C^{\bullet}$-C-OOH → C=C + $HO_2^{\bullet}$

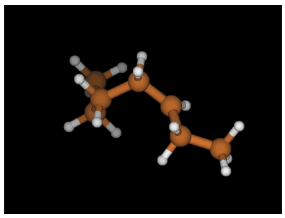
H-atom elimination: $C^{\bullet}$-C-H → C=C + $H^{\bullet}$

aldehyde/ketone formation: $O^{\bullet}$-C-C → C=O + $C^{\bullet}$

ROO dissociation: $O^{\bullet}$-O-C → $O_2$ + $C^{\bullet}$

- criterion: structure should contain **$X^{\bullet}$ – X – X** motif
- strategy: scan along all X-X bonds, and search for saddle point at the maximum, or identify barrierless cases



**non-β-scission:** all other bond breaking – no further search if barrierless

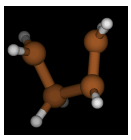


# 1-bond example: Internal addition of radical sites to multiple bonds

- criteria: structure should contain **$C^{\bullet}$ – *n*X – X*** motif, *n* = 1, …, 6

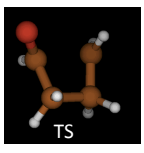
  X* has a multiple bond

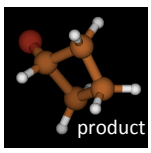
- strategy: fold molecule into a cyclic conformer in a series of steps

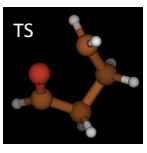


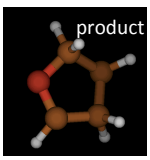
cyclization of but-3-ene-1-yl radical to cyclobutyl
(or ring opening of cyclobutyl)

Ketone/aldehyde radical isomerization step

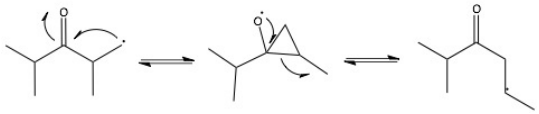



New ketone radical mechanism is a simple combination of this and a β-scission step.



## 2-bond example: Internal H-abstraction pathways

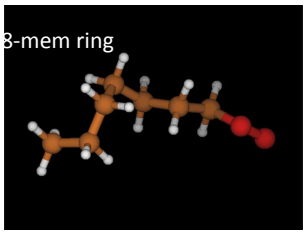
E.g. alkyl radical isomerization, ROO/QOOH isomerization

- criterion: structure should contain **X• – *n*X – H** motif, *n* = 3, …, 8
- strategy: fold molecule into a cyclic conformer in a series of steps to generate good initial guess

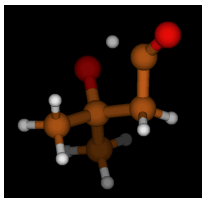
ROO/QOOH isomerization

5-mem ring

8-mem ring

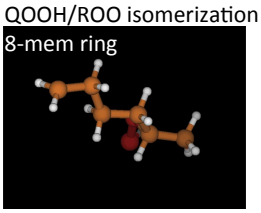


RO/RO isomerization



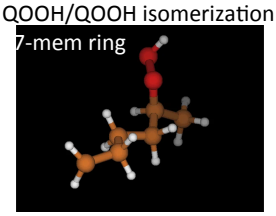
QOOH/ROO isomerization

8-mem ring



QOOH/QOOH isomerization

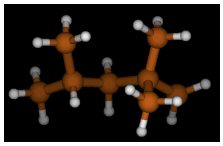
7-mem ring



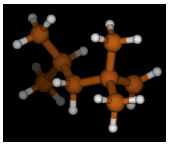
37



## Further 2-bond example: internal isomerization of an iso-octyl radical

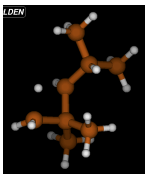


initial geometry (“seed”)

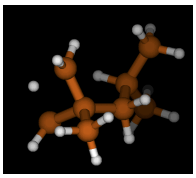


lowest energy conformer found

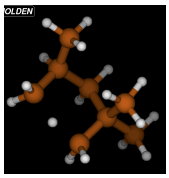
Transition states



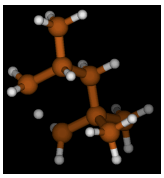
4-mem ring



4-mem ring



5-mem ring



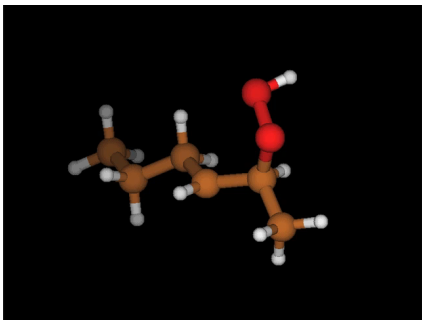
6-mem ring

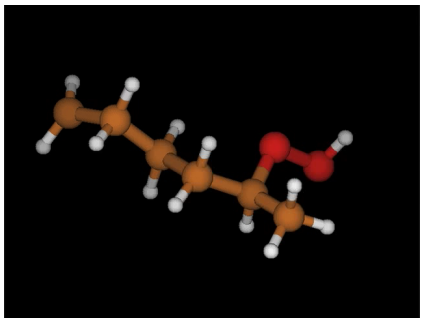
6-mem ring

38

## One more 2-bond example: Cyclic ether formation

- criterion: structure should contain **C• – *n*X – O – O – H** motif, *n* = 3, …, 8
- strategy: fold molecule into a cyclic conformer in a series of steps

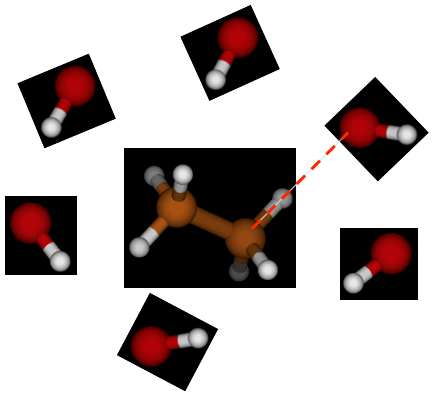


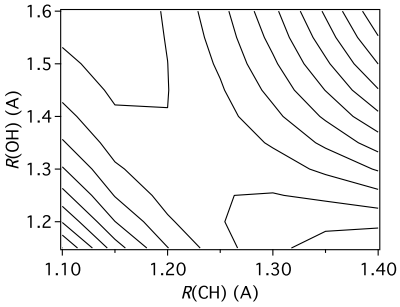




## Bimolecular abstractions (2-bond): RH + *X, *XY, *XYZ, *XYZW

Locating the saddle point, in principle, is straightforward using reduced dimensional scans:



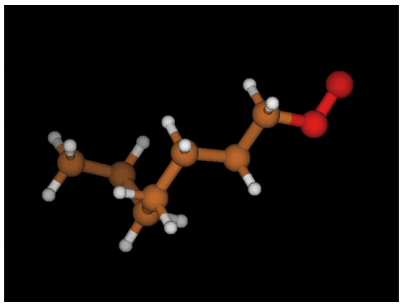



Saddle point can be found with a simple minmax algorithm very reliably.

# 3-bond example: Direct $HO_2$ elimination

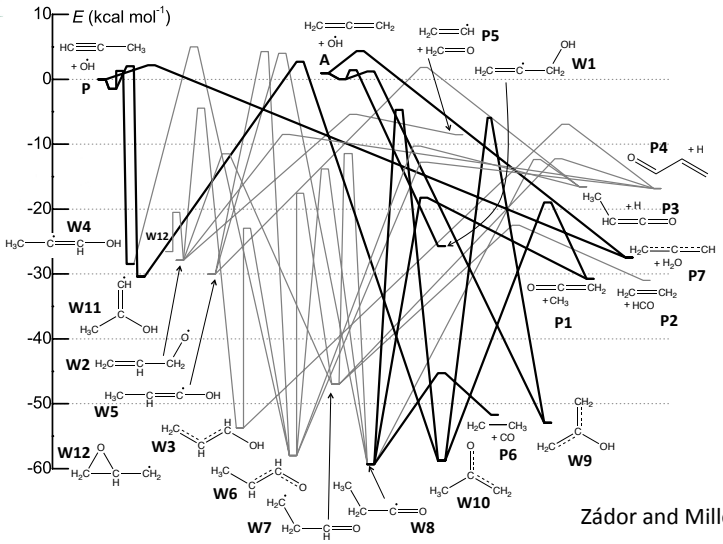
More specialized rule, can be thought of a special case of internal H-elimination

- criterion: structure should contain **H – C – C – O – O•** motif
- strategy: fold molecule into a cyclic conformer in a series of steps,
  - only the final step is different from a 4-mem ring elimination TS





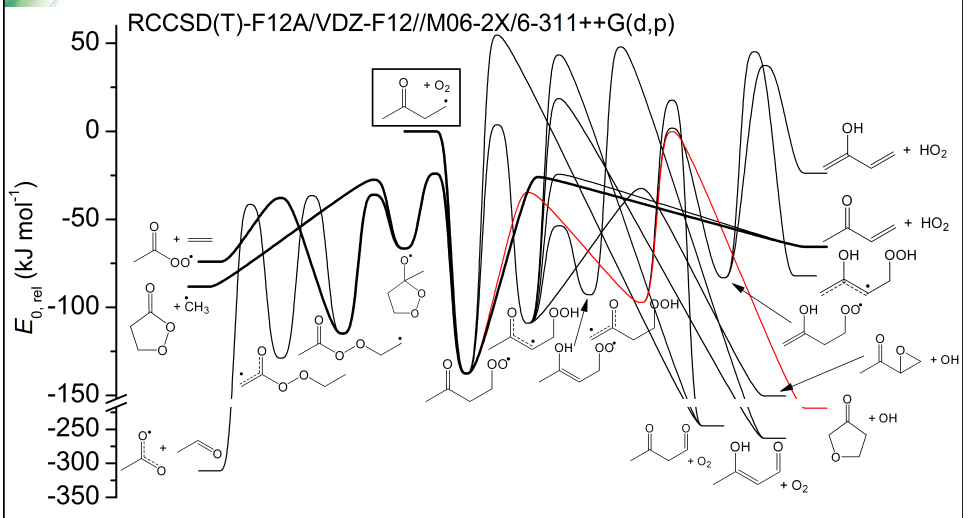
# A real example: $C_3H_5O$




Zádor and Miller, 2014 PCI

KinBot generated almost ready input for the kinetics code PAPER of Georgievkii and Klippenstein.

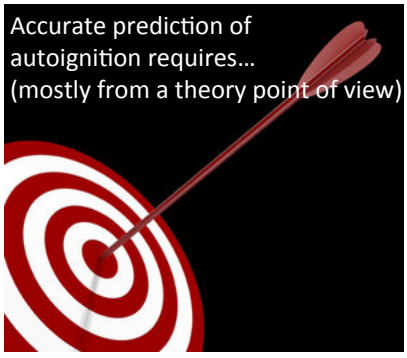
## Another example: Oxobutyl + $O_2$




Created by Oliver Welz using KinBot



## Overview

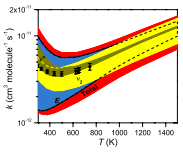



- Understanding of the underlying chemistry
- Calculating rate coefficients rigorously for multiwell systems
- Reducing uncertainties in our calculations
- Automating reaction path searches
- Characterizing key intermediates in synergy with experimental work

## Outlook

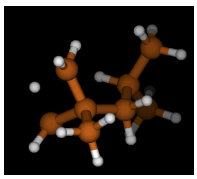
Only rigorous master equation methods can provide an accurate description of the physics. Simplified models are inadequate in many cases.

$$\frac{d|w(t)\rangle}{dt} = \mathbf{G}|w(t)\rangle$$




More systematic uncertainty studies are needed to further develop and better our theoretical framework.

In order to keep up with the pace of fuel-formulation and engine design improvements, the identification and exploration of chemical pathways should be automated. KinBot is an efficient tool for this.





# Thank You!

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