SAND2013-7515C

Combustion Research Facility

Theoretical reaction kinetics in combustion chemistry: Selected topics

Judit Zádor

Sandia National Laboratories

Chemistry Institute seminar

Eötvös Loránd University

September 2, 2012

What is a rate coefficient?

The rate coefficient of an elementary reaction is a quantity that satisfies the corresponding rate law of that reaction. ("Time is what clocks measure.")

one, irreversible, unimolecular channel: R → P $$-\frac{dr}{dt}=\frac{dp}{dt}=kr$$

one, reversible, unimolecular channel: R ↔ P $$-\frac{dr}{dt}=\frac{dp}{dt}=k_1 r-k_{-1}p$$

two, irreversible, unimolecular channels: $R \rightarrow P_1$, $R \rightarrow P_2$ $$-\frac{dr}{dt}=\frac{d(p_1+p_2)}{dt}=(k_1+k_2)r \qquad \frac{dp_1}{dt}=k_1 r$$

one, irreversible, bimolecular reaction: $R_1 + R_2 \rightarrow P$ $$-\frac{dr_1}{dt}=-\frac{dr_2}{dt}=\frac{dp}{dt}=kr_1 r_2$$

Rate coefficients are

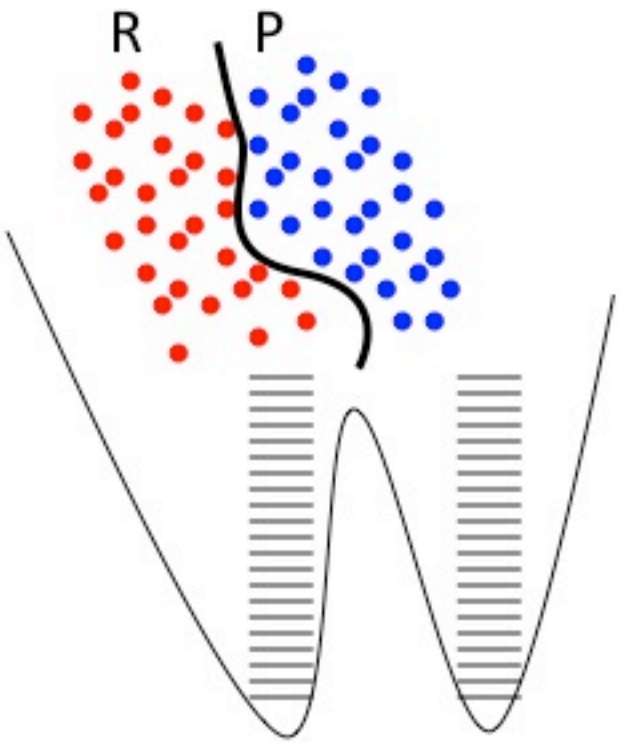
- phenomenological parameters
- depend almost always on temperature and very often on pressure
- never depend on time
- never depend on initial conditions (e.g. initial concentrations)
- and satisfy detailed balance, i.e. $k_1/k_{-1}=K$, the equilibrium constant

If a time-independent quantity satisfying the rate law cannot be found, the phenomenological rate description of a system breaks down.

There are things that can be done in this case, as we'll see later.

Shocking news

There are no such things in the physical world as reactants and products, only a large ensemble of quantum states of the system.
We like to call some of these many states as states of the reactant (i.e. reactant) and others as states of the product (i.e. product).

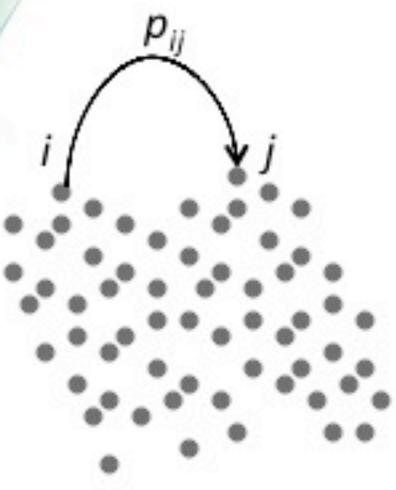


➔ A fundamental (first principle) physical model cannot predict directly the **phenomenological** *k*(R→P), only the so-called (state) **specific** transition probabilities

➔ The phenomenological *k* has to be constructed from the specific ones by averaging over all states

Let's assume we know how to calculate state-to-state transition probabilities per unit time in the system, p_{ij}...

How to obtain phenomenological rate coefficients from a microscopic description of a system?



$$dn_i / dt = \sum_j (p_{ji} n_j - p_{ij} n_i)$$

$$n_i = n_i(\infty) + \sum_l c_{il} \exp(-\lambda_l t)$$

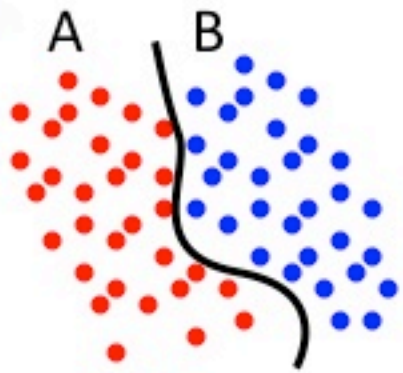
When all modes but the slowest, λ_1, are exhausted:

$$dn_i / dt = \lambda_1 [n_i - n_i(\infty)]$$

Widom, Science, 1965

How to obtain phenomenological rate coefficients from a microscopic description of a system?

$$dn_i / dt = \sum_j (p_{ji} n_j - p_{ij} n_i)$$



$$n_i = n_i(\infty) + \sum_l c_{il} \exp(-\lambda_l t)$$

When all modes but the slowest, λ_1, are exhausted:

$$dn_i / dt = \lambda_1 [n_i - n_i(\infty)]$$

$$dN_A / dt = dN_B / dt = \lambda_1 [N_A - N_A(\infty)] = \lambda_1 [N_B - N_B(\infty)]$$

The phenomenological description of the system:

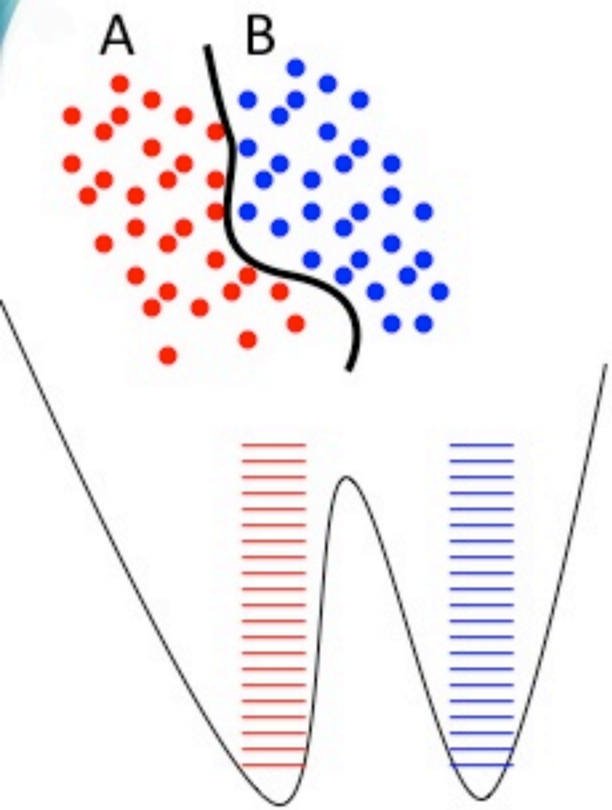
$$A \underset{k'}{\overset{k}{\rightleftarrows}} B$$

$$-dN_A / dt = dN_B / dt = kN_A - k' N_B$$

k and k' has to fulfill: $\lambda_1 = k + k'$ $\qquad k / k' = N_B(\infty) / N_A(\infty)$

Widom, Science, 1965

If there is no A and B in nature, just microstates, how can we divide them? And isn't everything arbitrary then?

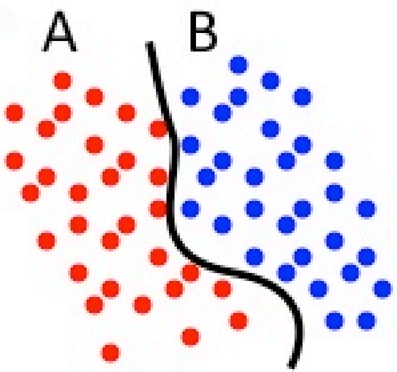


1. The boundary will influence what k and k' are, but $\lambda_1 = k + k'$ is invariant to this choice.

2. If the boundary is chosen chemically, then A and B are separated by high energy regions, which contribute little to the equilibrium population ➔ $N_A(\infty)$ and $N_B(\infty)$ will be practically independent of the exact choice of the boundary, therefore, k and k' also will be determined just as unambiguously.

Widom, Science, 1965

Further shocking news



$$A \underset{k'}{\overset{k}{\rightleftarrows}} B$$

k is not the probability of A making the A→B transition
k' is not the probability of B making the B→A transition

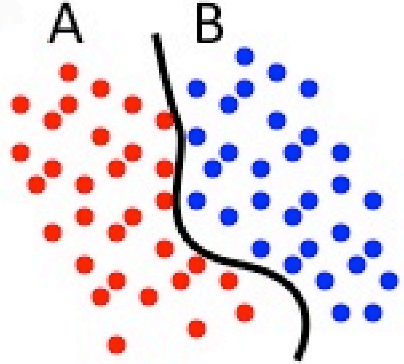
$$\lambda_1 = k + k' \qquad k / k' = N_B(\infty) / N_A(\infty) = K$$

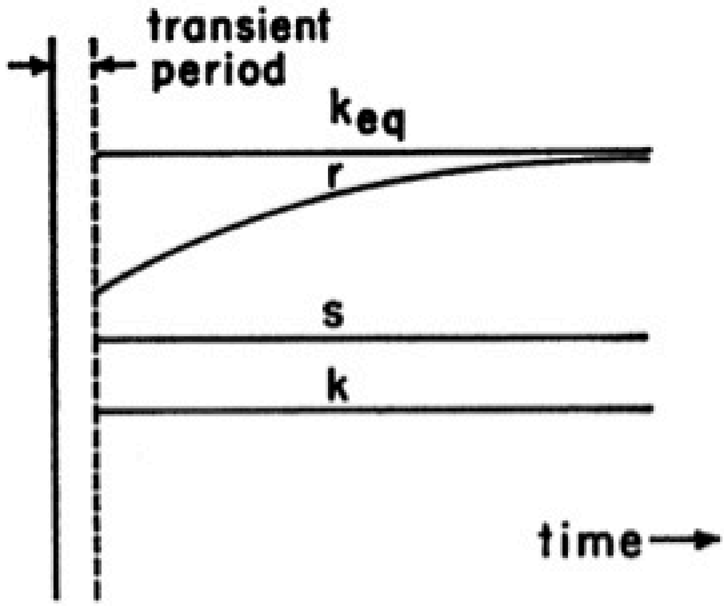
$$k = \lambda_1 \frac{K}{1+K} \qquad k' = \lambda_1 \frac{1}{1+K}$$

Both *k* and *k'* are fractions of λ_1, which depends on all transition probabilities (A→A, A→B, B→B, B→A)!

Widom, Science, 1965

Various flavors of “rate coefficients”





r: The A→B transition probability, depends on time and initial conditions

→ not a phenomenological rate coefficient

$\boldsymbol{k_{eq}}$: r at long time, $k_{eq}/k_{eq}'=K$, but $k_{eq}+k_{eq}'\neq\lambda_1$. Depends only on A→B transitions

→ not a phenomenological rate coefficient

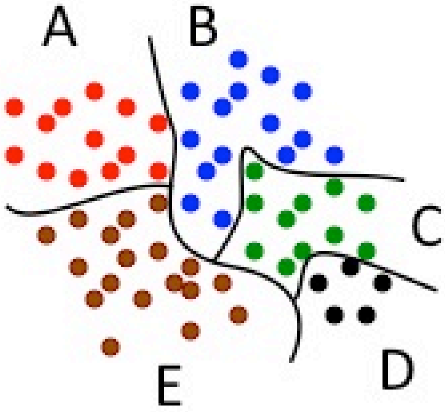
s: we assume that every time an A→B transition happens, B is removed, same as setting all B→A transitions to zero. It’s the A→B flux, but it’s an altered system

→ not the phenomenological rate coefficient of the original system

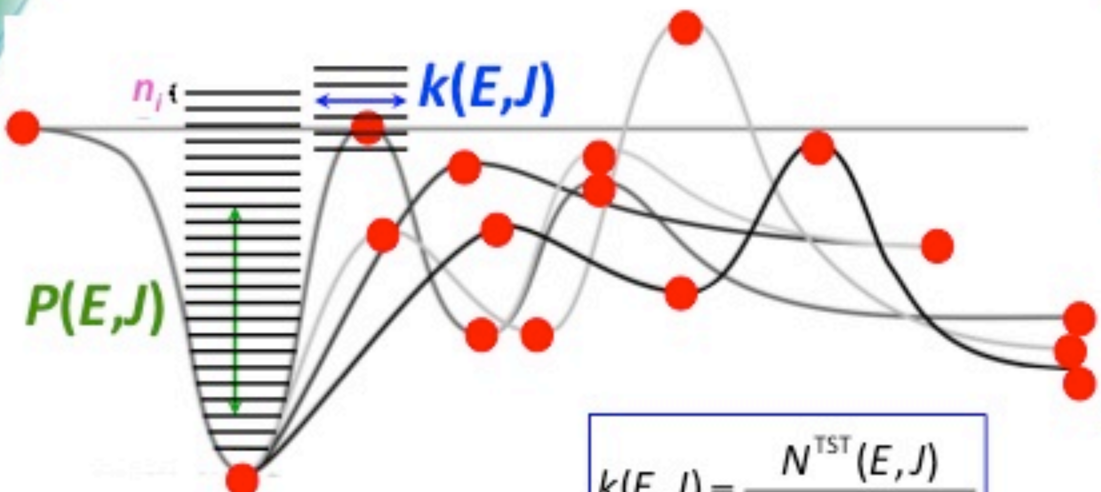
k: the phenomenological rate coefficient

Widom, Science, 1965

The machinery of calculating rate coefficients: Master Equation



The machinery of calculating rate coefficients: Master Equation



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

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.

$$\frac{\mathrm{d}n_i(E,J)}{\mathrm{d}t} = Z_i \sum_{J'} \int_{E_{0_i}}^{\infty} P_i(E,J;E',J')\, n_i(E',J')\, \mathrm{d}E' - Z_i n_i(E,J) - \sum_{j\neq i}^{M} k_{ji}(E,J)\, n_i(E,J) + \sum_{j\neq i}^{M} k_{ij}(E,J)\, n_j(E,J) - k_{d_i}(E,J)\, n_i(E,J) + k_{a_i}(E,J)\, n_R n_m \rho_{Rm}(E,J) e^{-\beta E}/Q_{Rm} - \sum_{p=1}^{N_p} k_{p_i}(E,J)\, n_i(E,J)$$

$$i = 1, \ldots, M$$

$$\frac{\mathrm{d}\left|w(t)\right\rangle}{\mathrm{d}t} = \mathbf{G}\left|w(t)\right\rangle$$

The machinery of calculating rate coefficients: Master Equation

the unknown *E* (or *E* and *J*) resolved population vector of wells and products

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

matrix for chemical exchange between wells and energy transfer within a well

This is an eigenvalue-eigenvector problem. **G** is Hermitian (real and symmetric) and nonpositive.

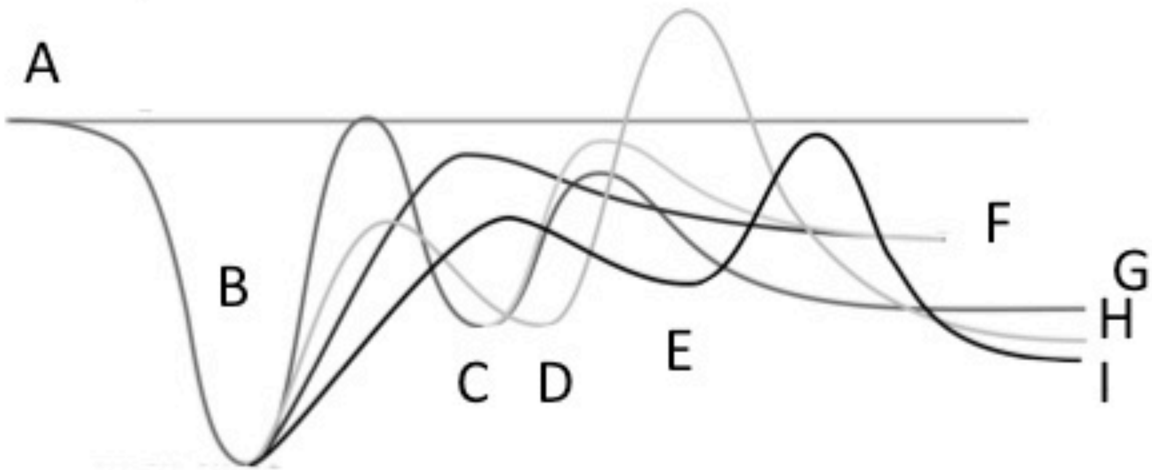
Slow eigenmodes
(the eigenvector with small absolute eigenvalue):
Chemically Significant Eigenvalues – **CSE**

Fast eigenmodes
(the eigenvector with large absolute eigenvalue):
Internal Energy Relaxation Eigenvalues – **IERE**

The machinery of calculating rate coefficients: Master Equation

The phenomenological rate equations also form a matrix:

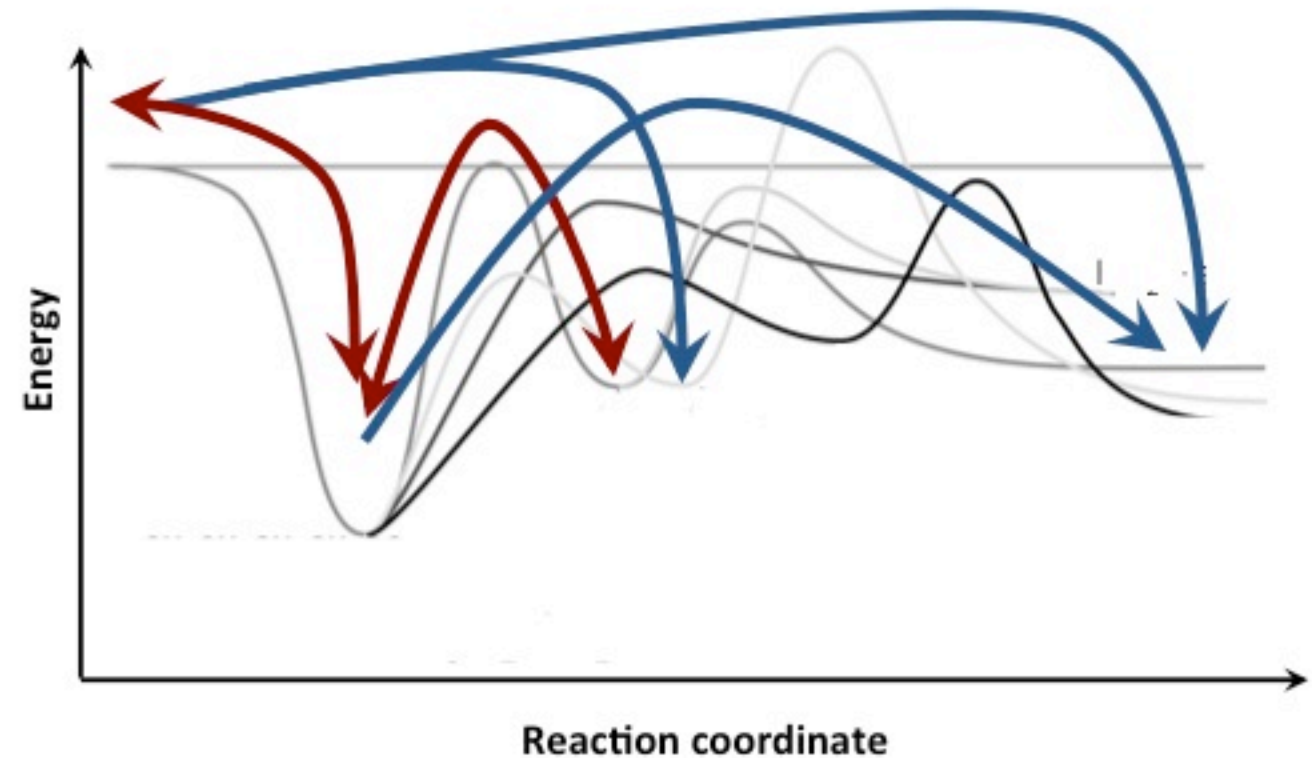
A→B k_1
A→C k_2
A→D k_3
…
B→A k_4
B→C k_5
B→D k_6
…
C→A k_7
…



This matrix also has eigenvalues, expressed in terms of *k*'s, and eigenvectors, expressed in terms of chemical concentrations (A, B, C, …).

λ_1 of the ME is the same as λ_1 of the kinetic equations, etc.
One needs to solve a set of algebraic equations (just as in the simple case of 2 wells). There are general solutions, see Miller & Klippenstein, JPCA 2006, 10528

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

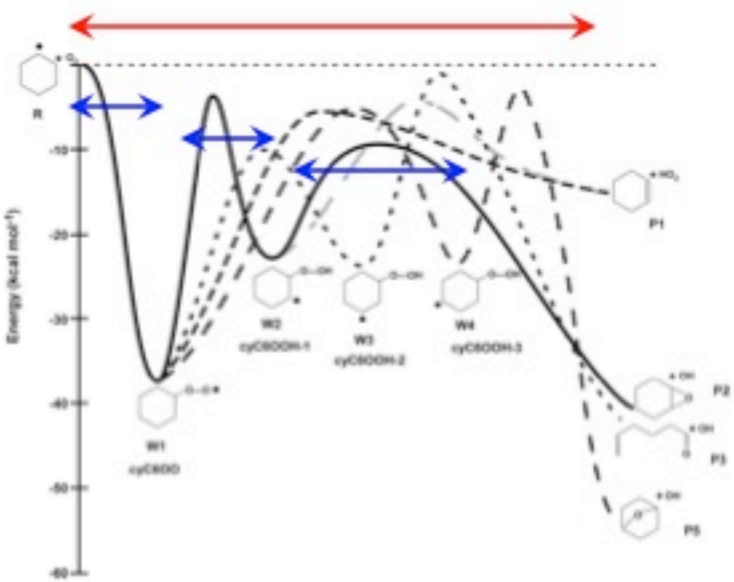


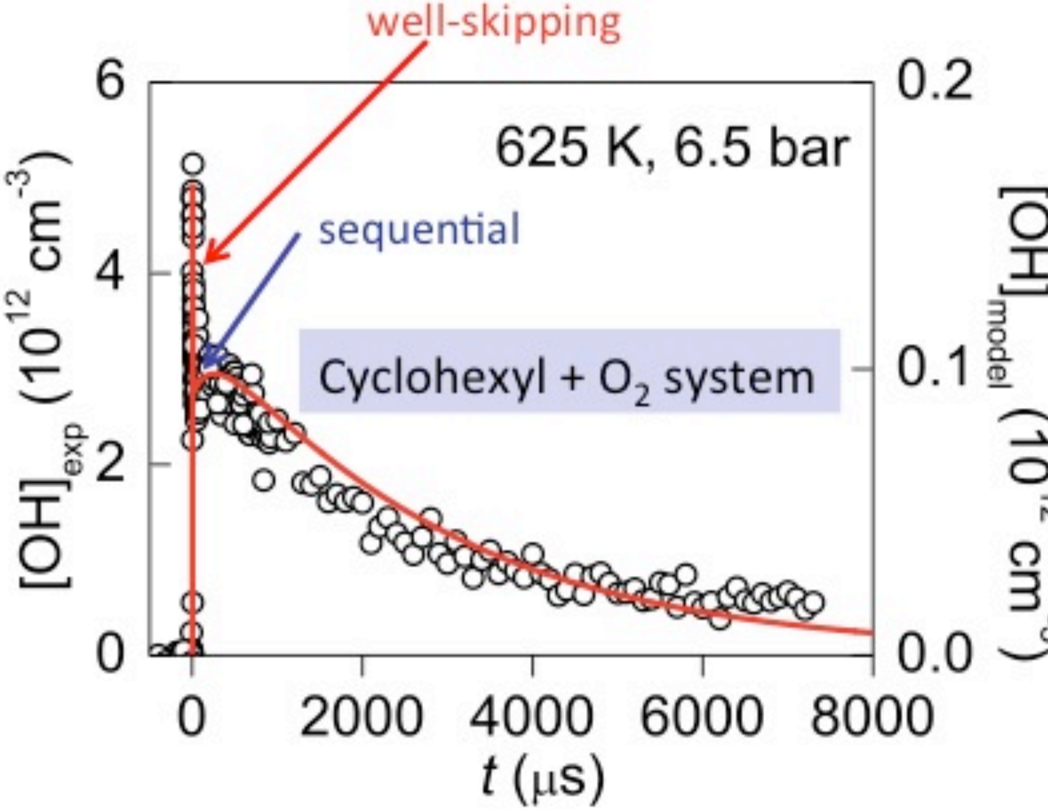
The eigenvalue-eigenvector method provides an internally consistent set of elementary rate constants, $k_i(T,P)$.

The solution accounts for both the **sequential** and the **well-skipping** (aka formally direct) pathways.

Chemical activation is a special case of well-skipping processes.

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



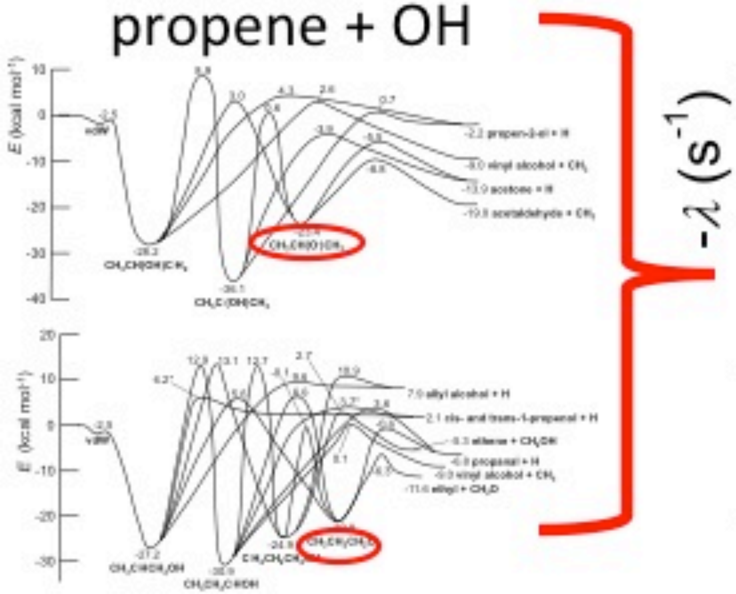


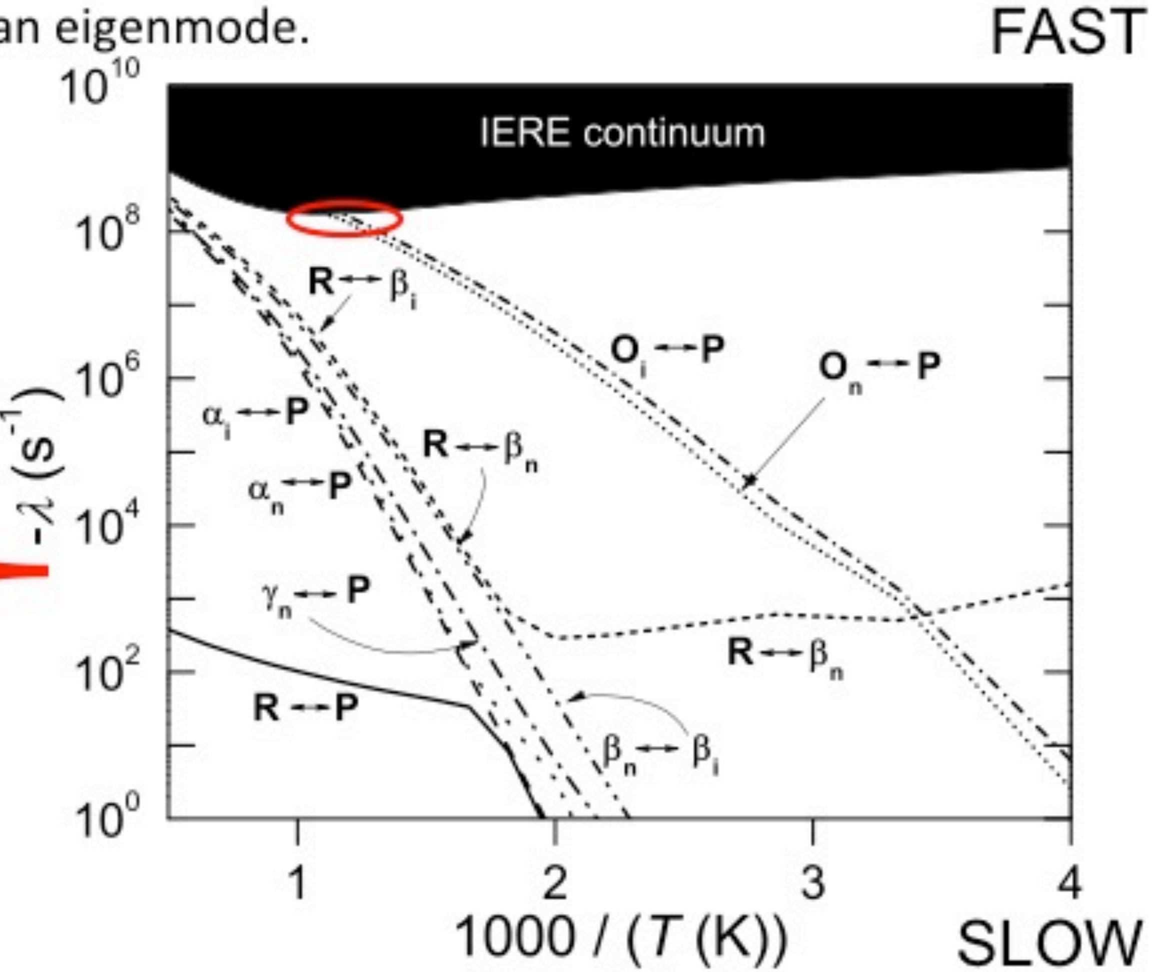
Well-skipping product formation is prompt, while sequential is delayed.

The eigenvalue spectrum of the ME

Equilibrium is reached in a series of steps, each corresponding to an eigenmode.

propene + OH

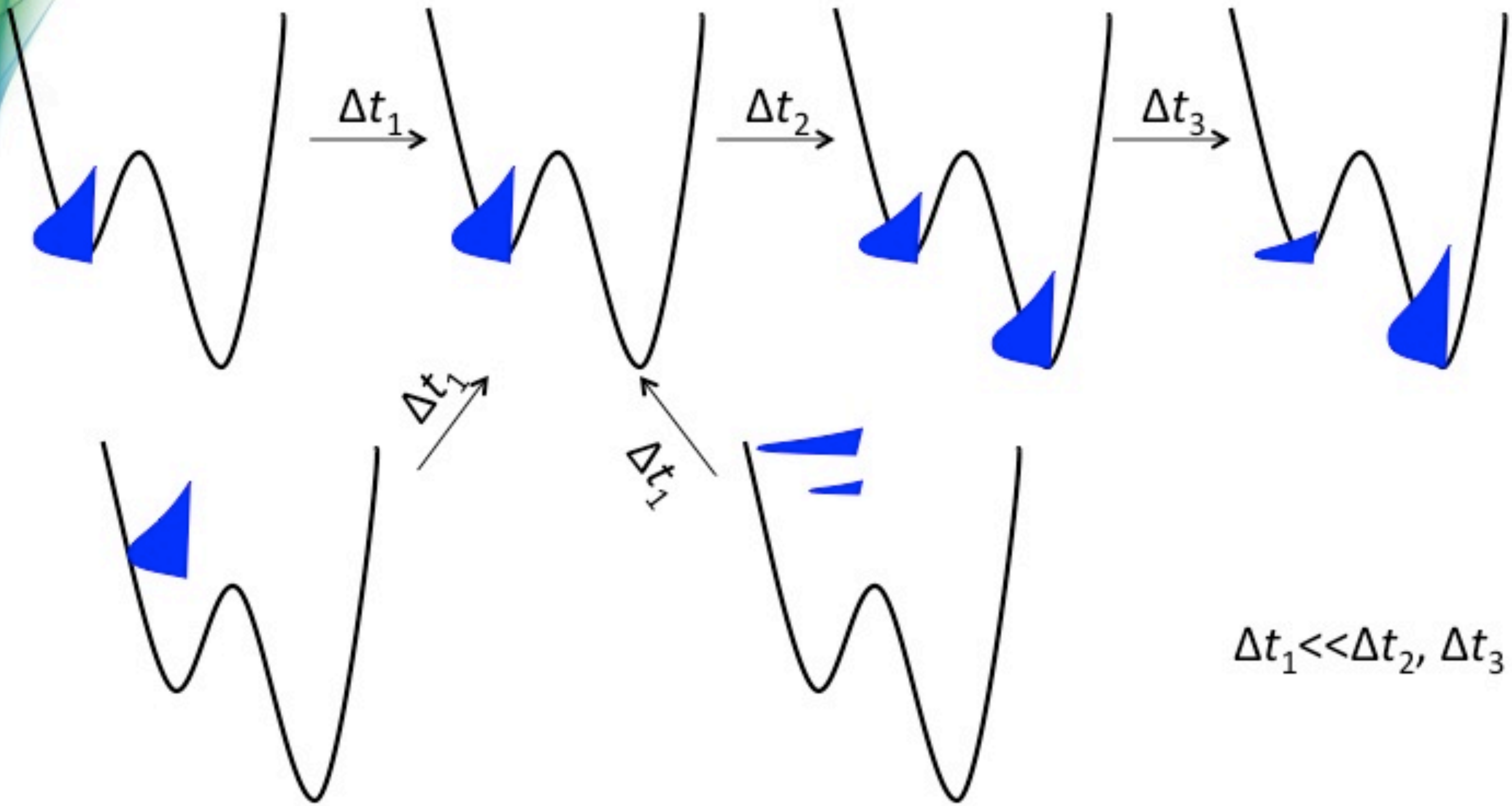




When CSE merge with IERE: the time scales of chemistry and internal energy redistribution do not separate → k will depend on the initial conditions → not a phenomenological rate coefficient any more

CSE merging IERE: what does it mean?

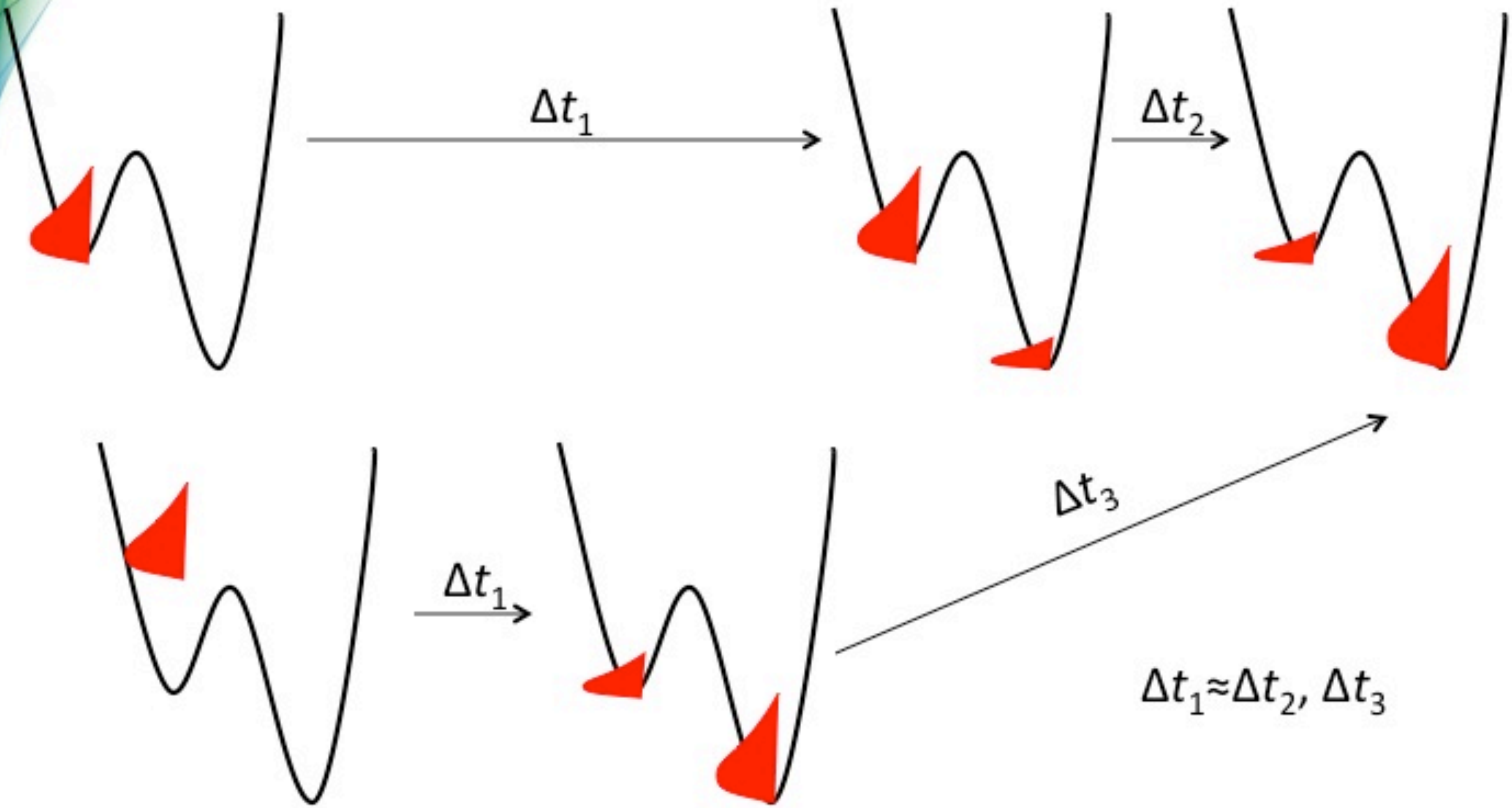
Low *T*, no merging:



$\Delta t_1 << \Delta t_2, \Delta t_3$

CSE merging IERE: what does it mean?

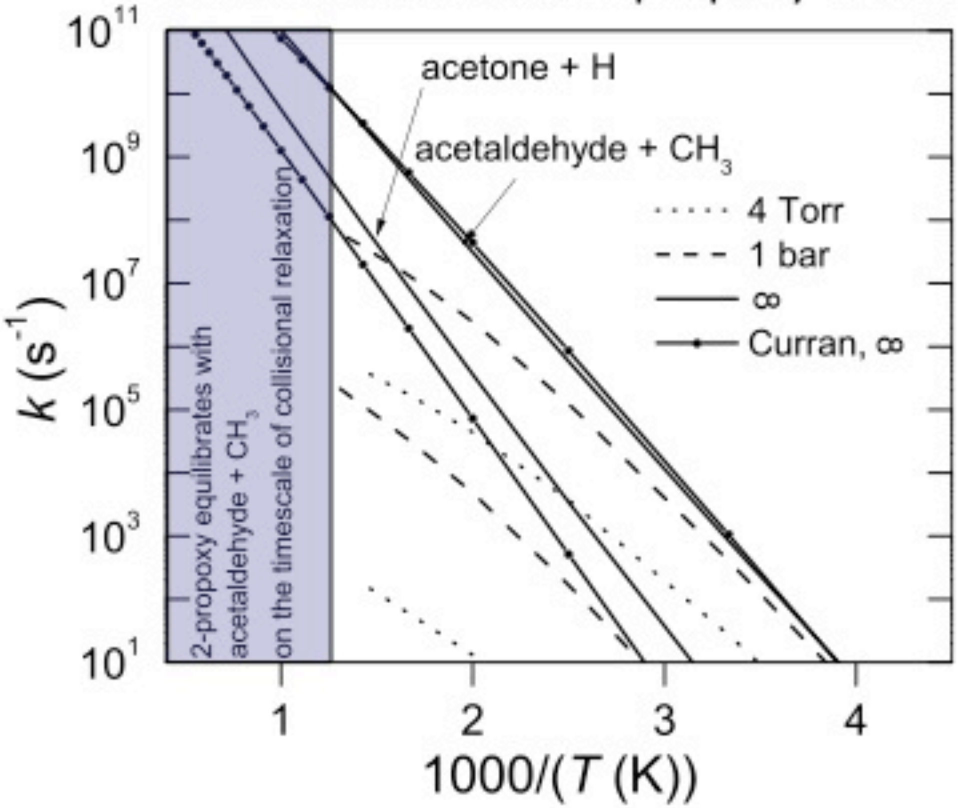
High *T*, merging:



The two wells do not represent separate species any more. (definitions of a species...)

The concept of superspecies

Dissociation of the isopropoxy radical



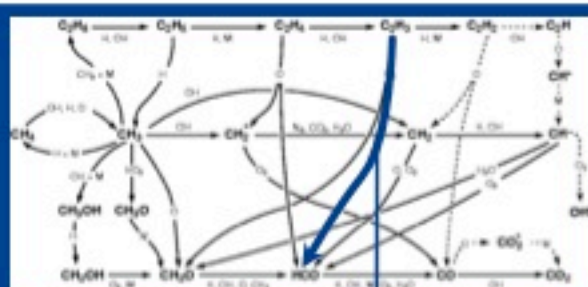
Equilibration of species happen BEFORE or WHILE vibrational relaxation takes place.

Treated as one species, sometimes referred to as “superspecies”.

In a chemical mechanism the concentration of the species involved should be determined by the equilibrium constant only.

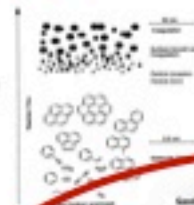
➔ Algebraic equations instead of differential equations

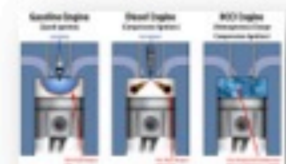
What is combustion chemistry?



Fu... H_2O + energy

NO_x? 

soot? 

timing? 

P and *T* dependence?

300 – 3000 K, 10 – 10^6 Torr

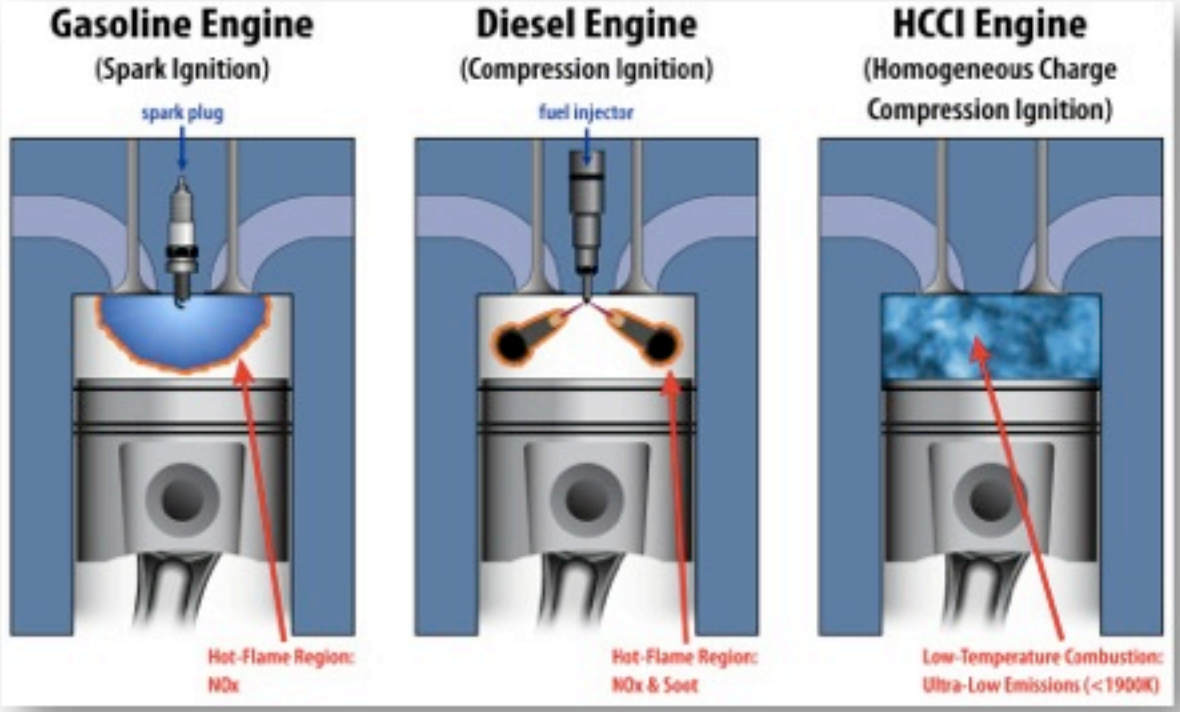
Mebel AM, Diau EWG, Lin MC, Morokuma K. *J Am Chem Soc* **1996**, 118:9759

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

Details of combustion chemistry are critical in several areas.

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

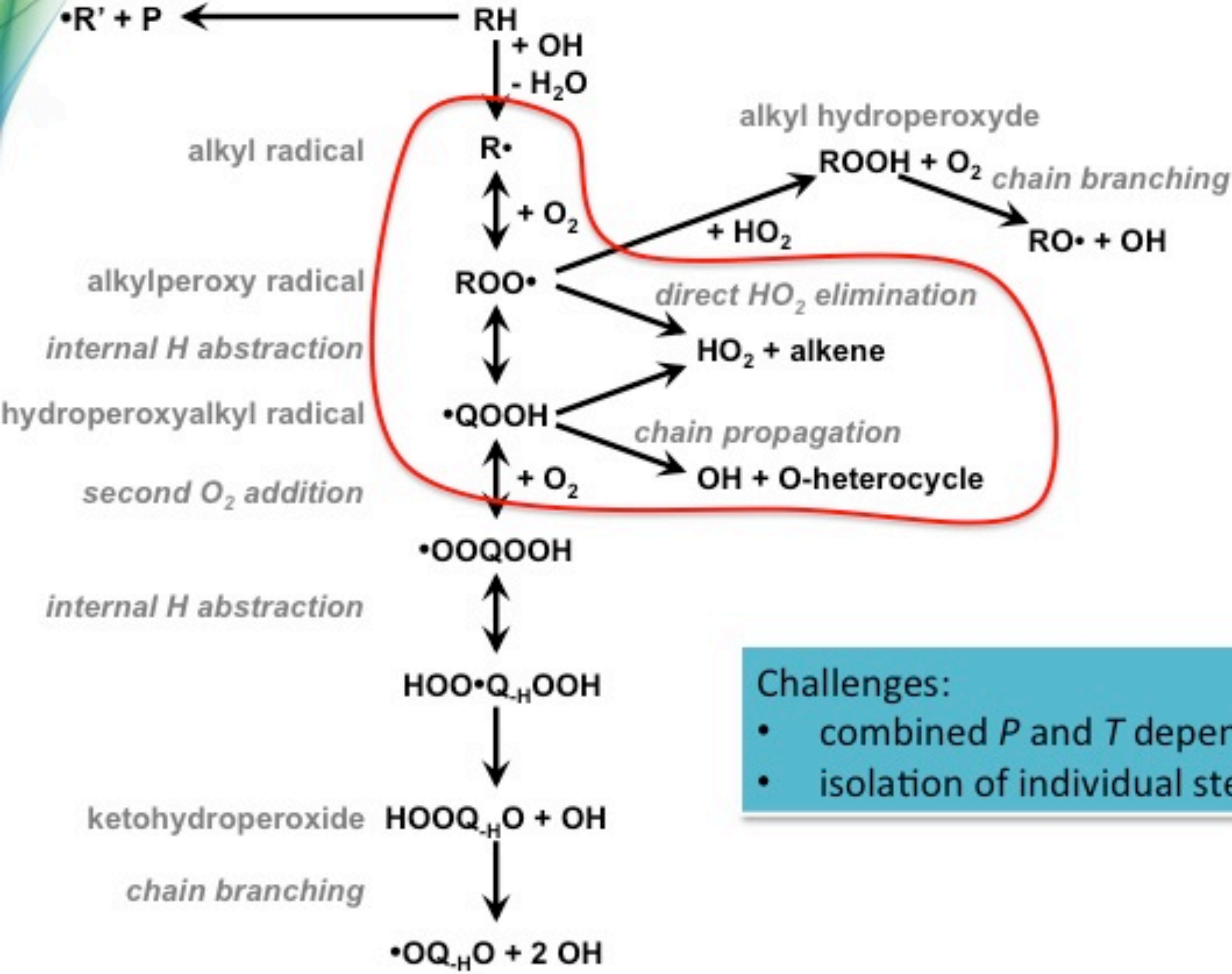


In practical fuels there are:

- alkanes
- olefins
- cycloalkanes
- aromatics
- oxygenates

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

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



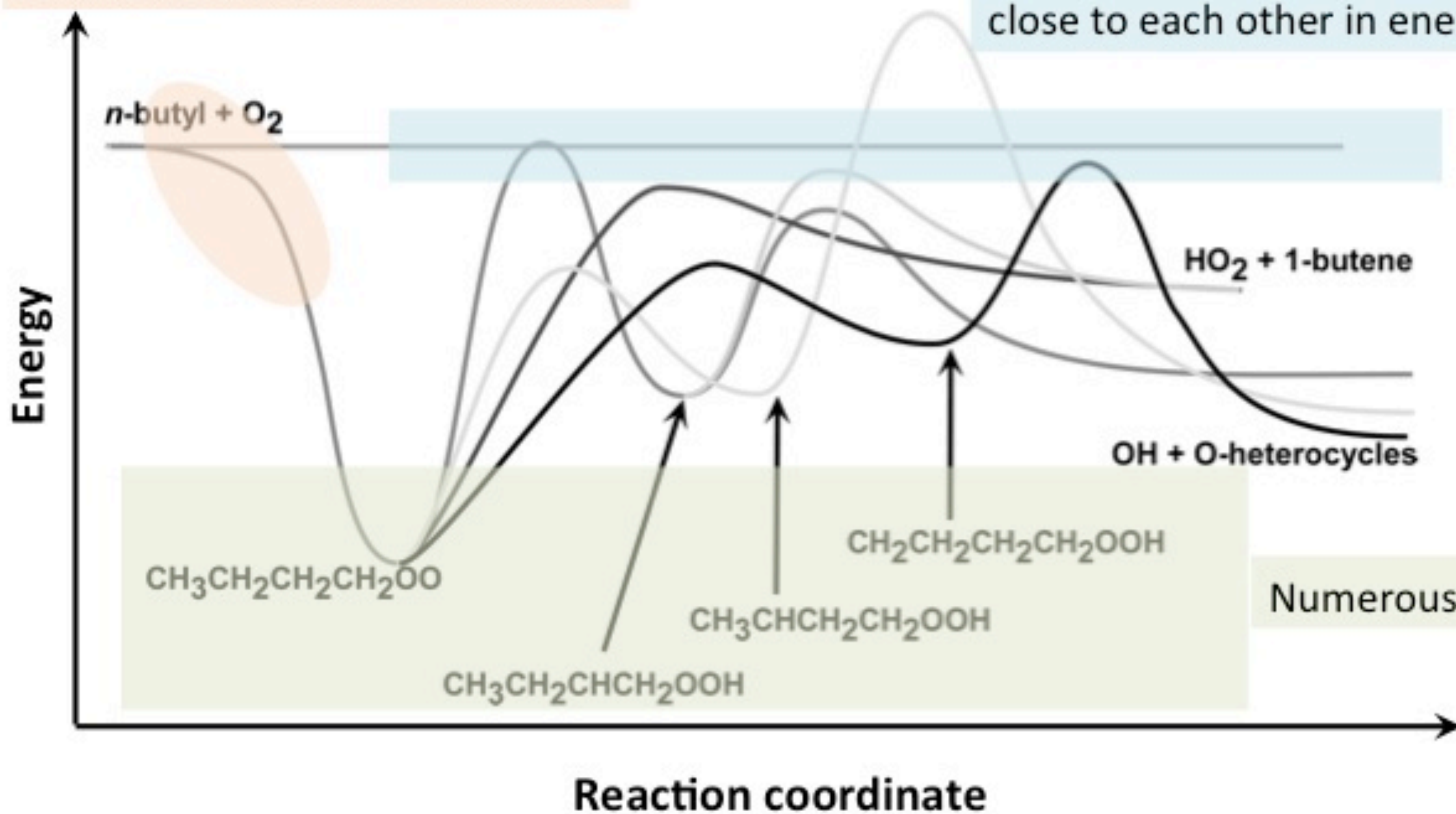
Challenges:

- combined *P* and *T* dependence
- isolation of individual steps is impossible

A typical alkyl + O_2 potential energy surface

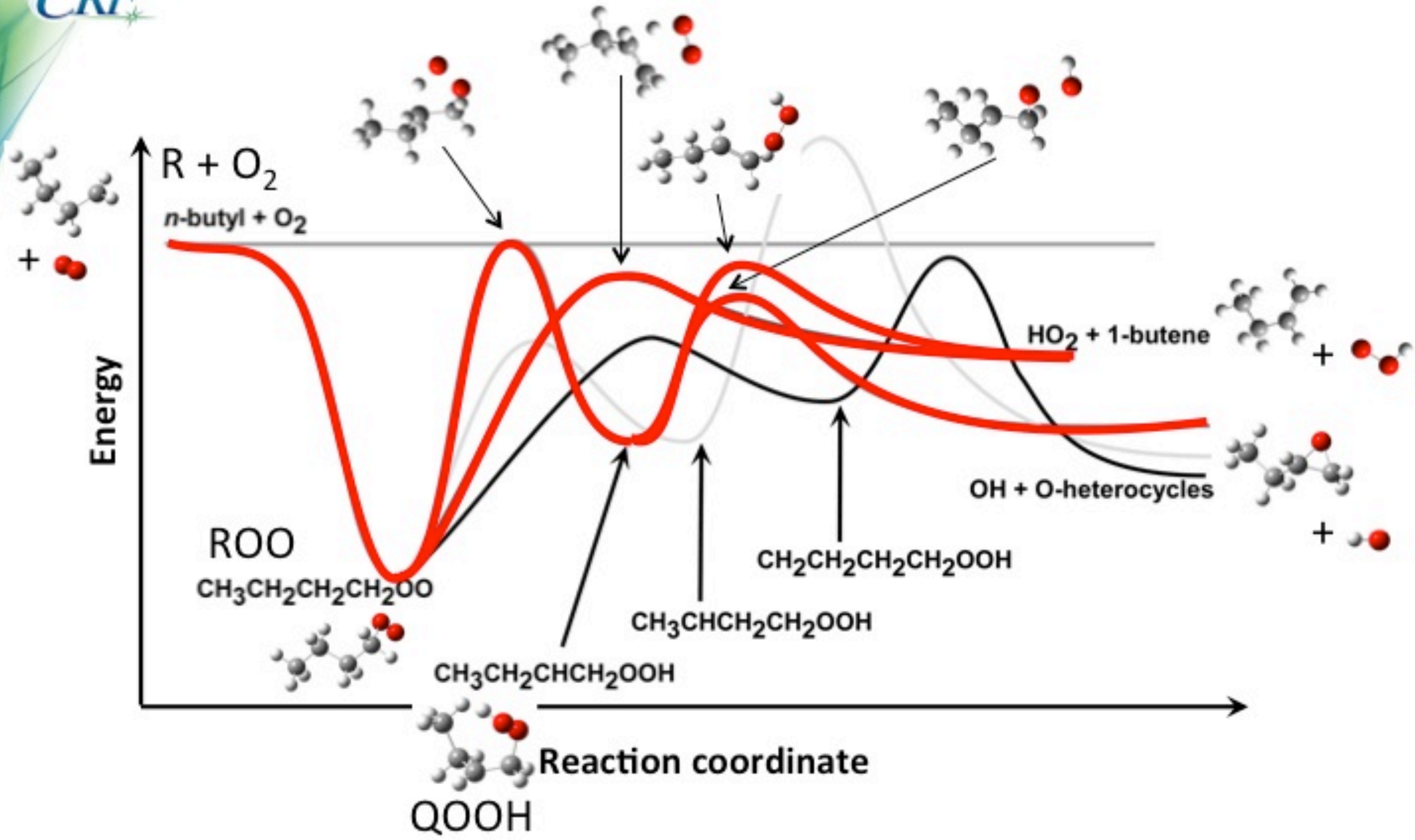
Barrierless entrance channel.

Channels are below the energy level of the reactants, and close to each other in energy.



Numerous wells.

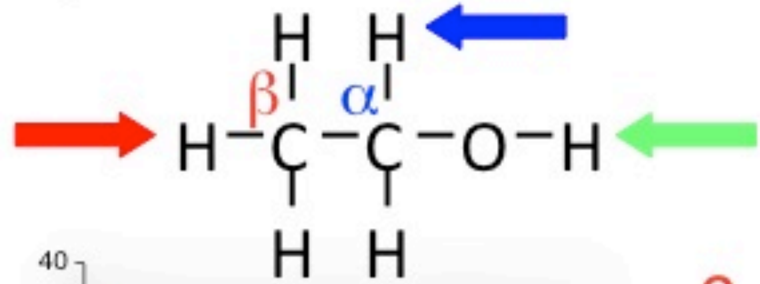
A typical alkyl + O_2 potential energy surface

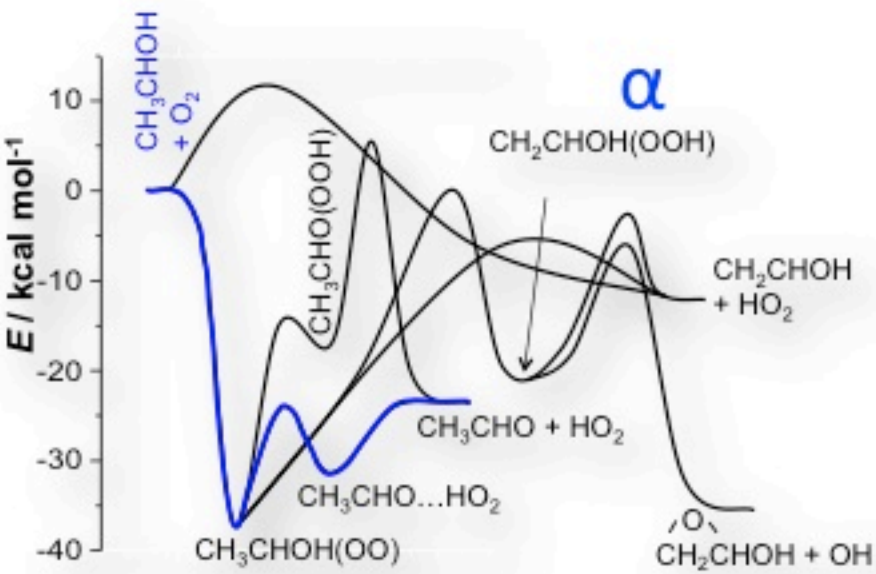


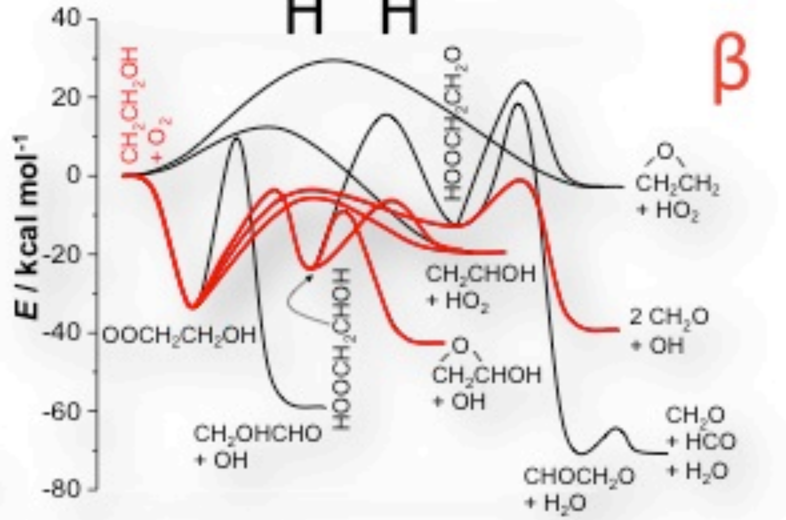
A carbon centered radicals derived from alcohols: α- and β-hydroxyethyl

Alcohols are one of the major biofuels.

Substituted alkyl radicals can have substantially shifted barriers as well as pathways not observed in alkyl radicals.



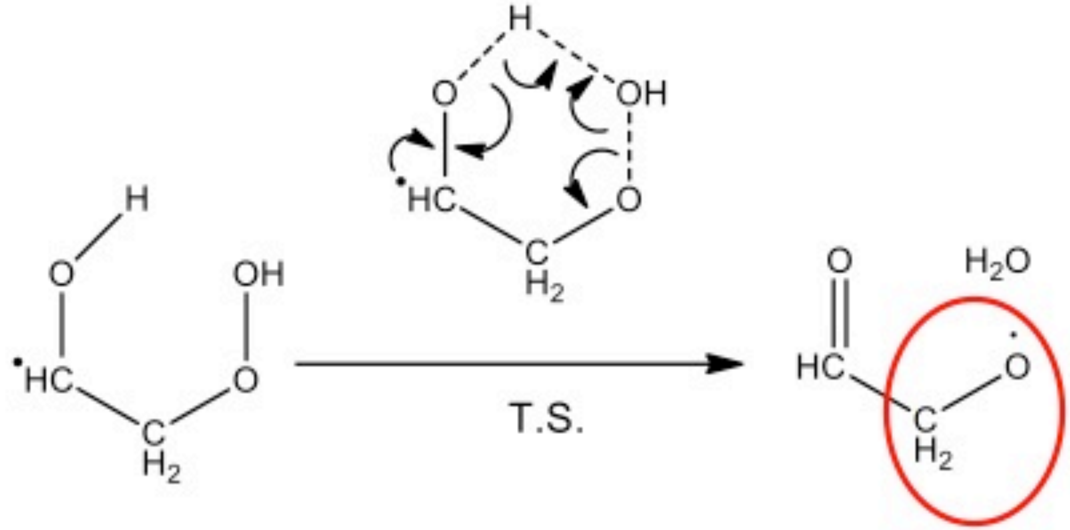




We could not explain the experimentally observed high formaldehyde concentration.

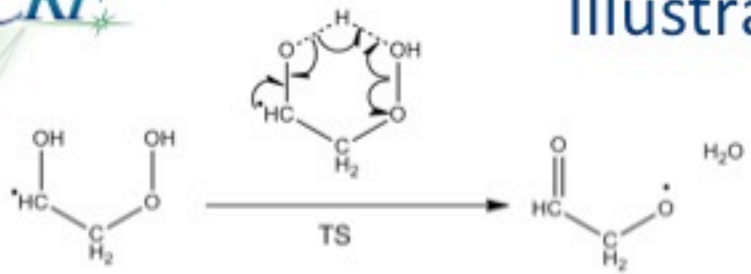
Unconventional peroxy chemistry in alcohol oxidation

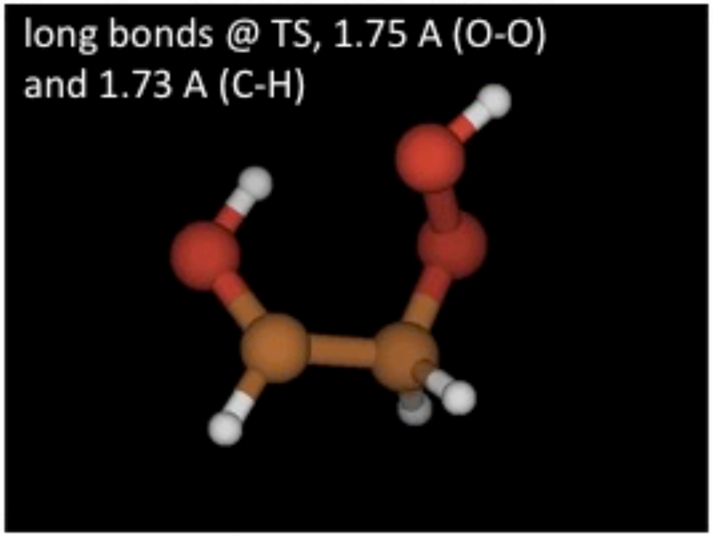
We recently discovered a new, low-lying water elimination pathway.
➔Resolves the discrepancy between the experimentally observed product spectrum and the predicted one for ethanol, isobutanol and isopentanol.



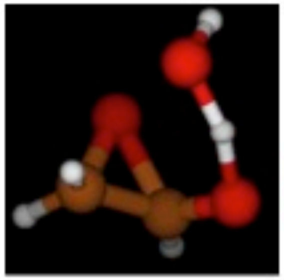
DFT (M06-2X or B3LYP) can locate the TS, but other single-reference methods fail to do so.
This is a hard problem for electronic structure methods.

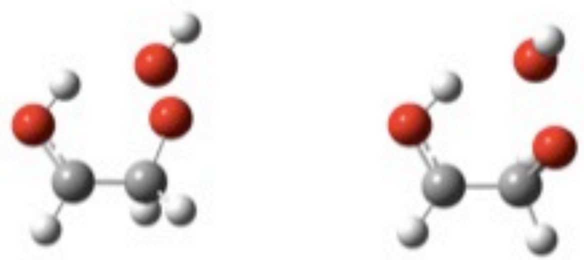
The water elimination pathway – Illustrated on ethanol





- happens via a single saddle point barrier
- concerted breaking of 2 bonds and making of 2
- product is weakly bound alkoxy carbonyl
- at the saddle point interatomic distances are larger than typical tight transition states, but smaller than roaming
- the alternative 2-step cyclic ether + roaming pathway has small probability



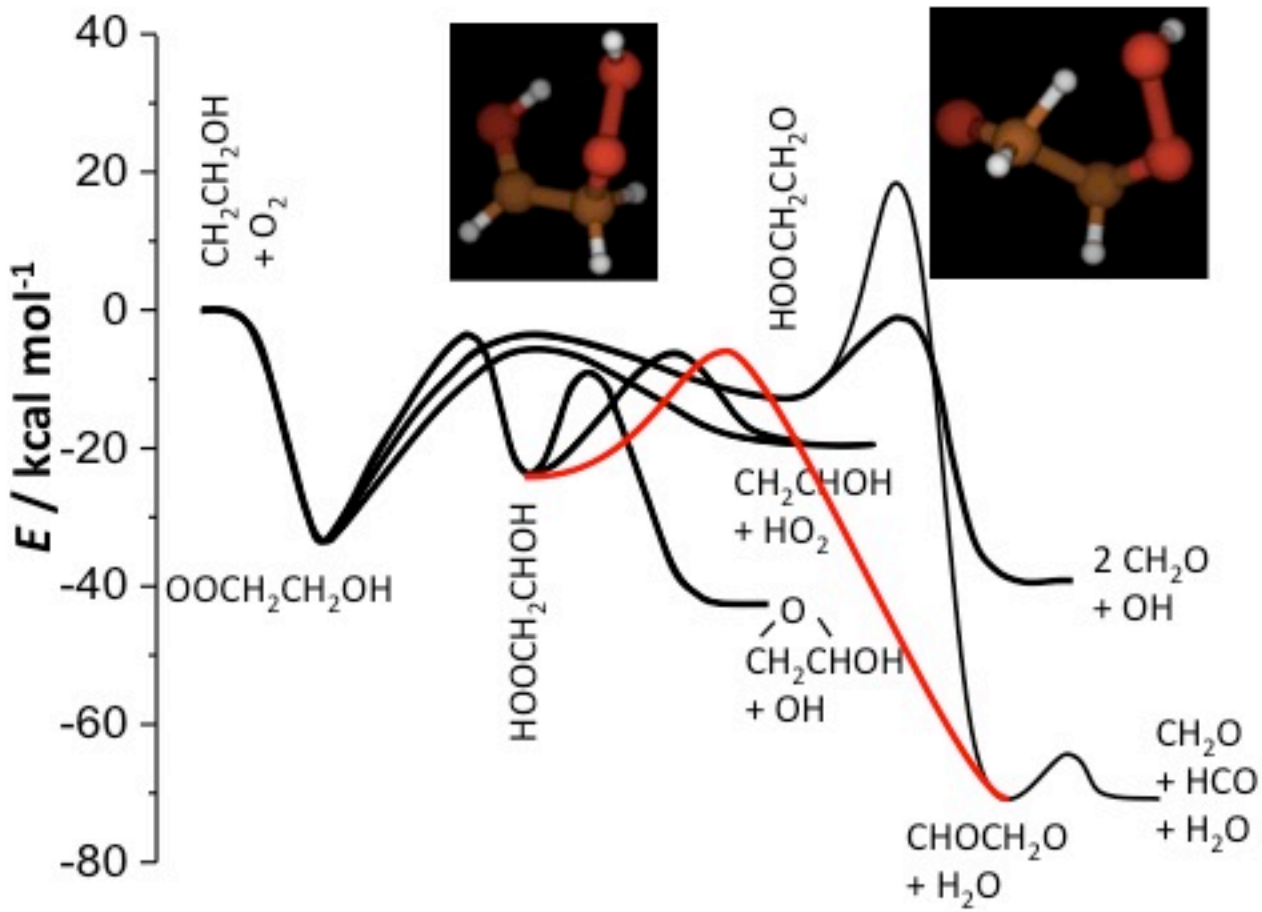


TS TS'

B3LYP/6-311++G*

- the ordinary, two-step version of the above process does not play a role in the experiments because of the small radical and large precursor concentrations

The water elimination channel in ethanol: B3LYP/6-311++G*



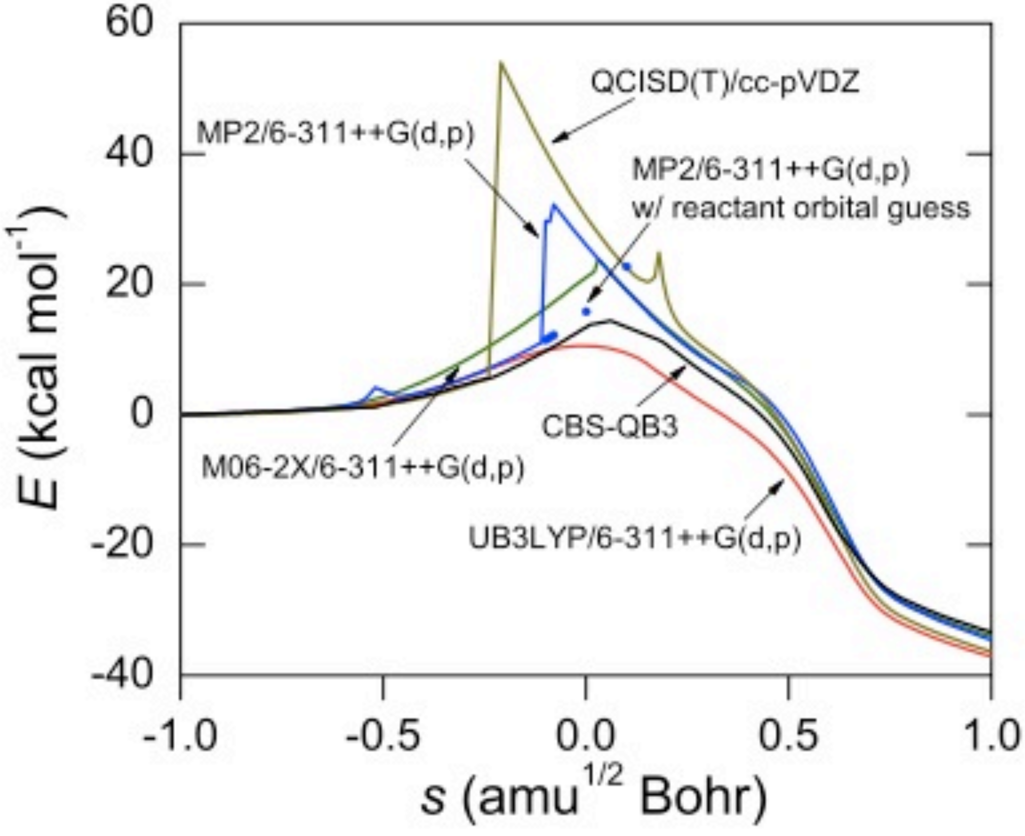
RQCISD(T)/cc-pV∞Z//B3LYP/6-311++G(d,p)

Zádor et al., PCI, 2008

What is the high-level energy, and is this pathway real or an artifact of B3LYP?

Problems finding the saddle point at other levels of theory

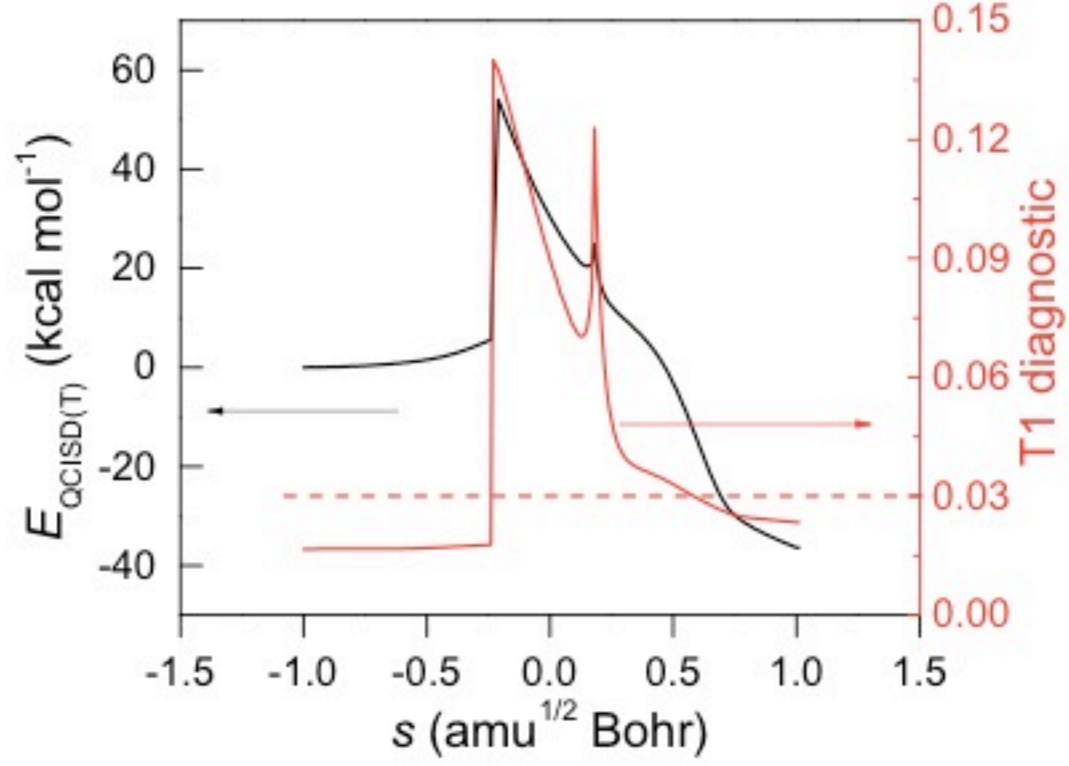
For one of the conformers of the water elimination pathway in ethanol, MP2 was unable to locate a saddle point. M06-2X also failed for TS'. QCISD(T) also was problematic.



Calculated energies along the B3LYP IRC.

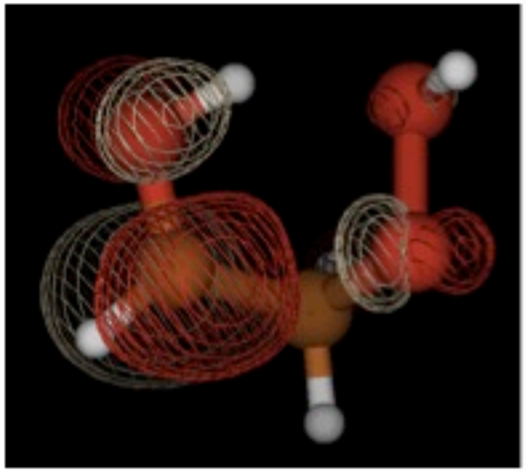
QCISD(T) energies and T1 diagnostic along the B3LYP IRC

Unphysical, sharp features in the potential are correlated with high T1 diagnostic values.

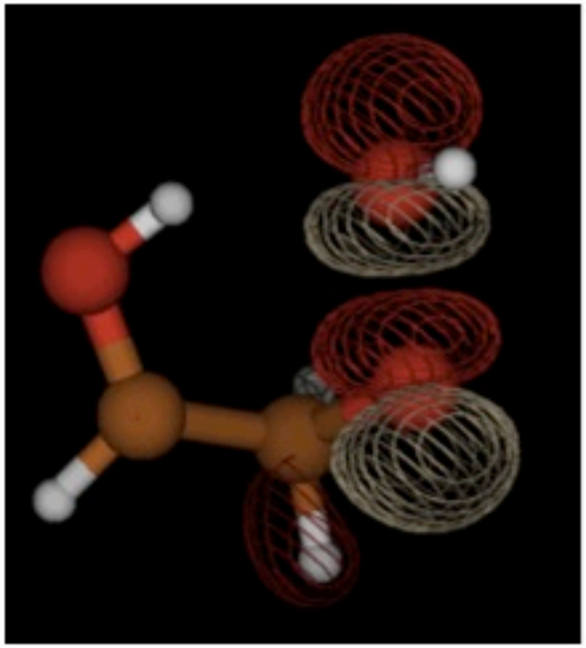


➔ Multireference treatment of the electronic structure is necessary in the vicinity of the saddle point.

HOMOs
on the two sides of the saddle point



reactant side HOMO
C-centered radical



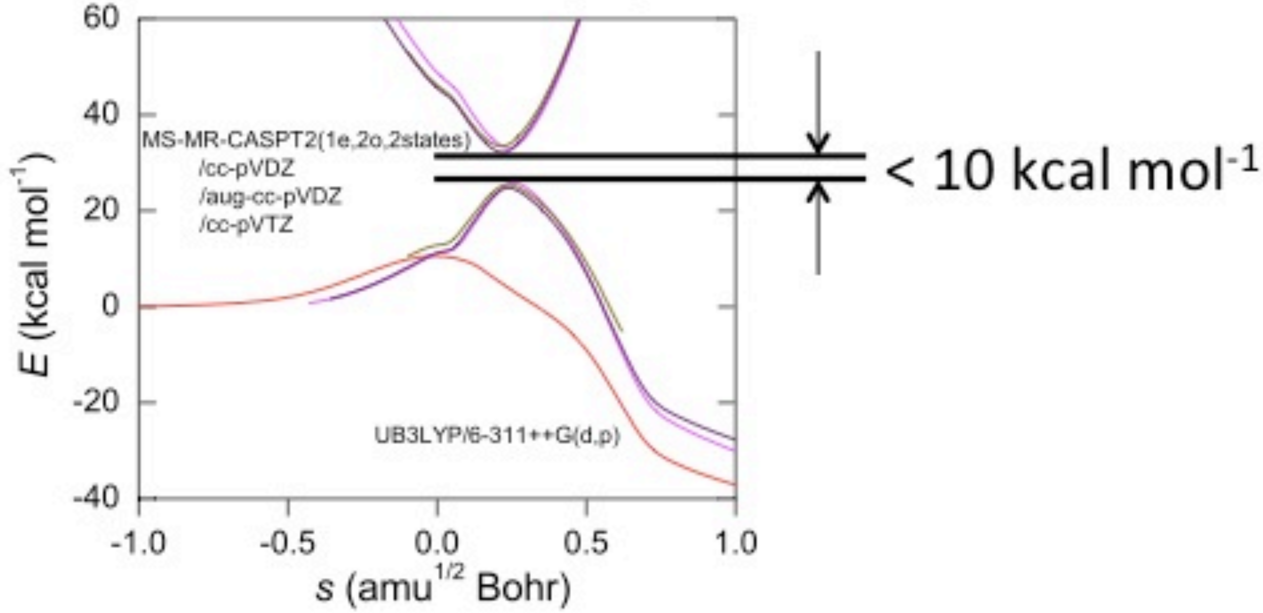
product side HOMO
O–O σ*

The consecutive process (breaking O–O bond and then abstracting the H atom) involves a doublet triradical, which is energetically unfavored.
The simultaneous pathway involves the mixing of weakly interacting, spatially orthogonal orbitals.
Antibonding orbital being the HOMO ➔ this is an electronic state with **zwitterionic character**

CASPT2 calculations require a large active space

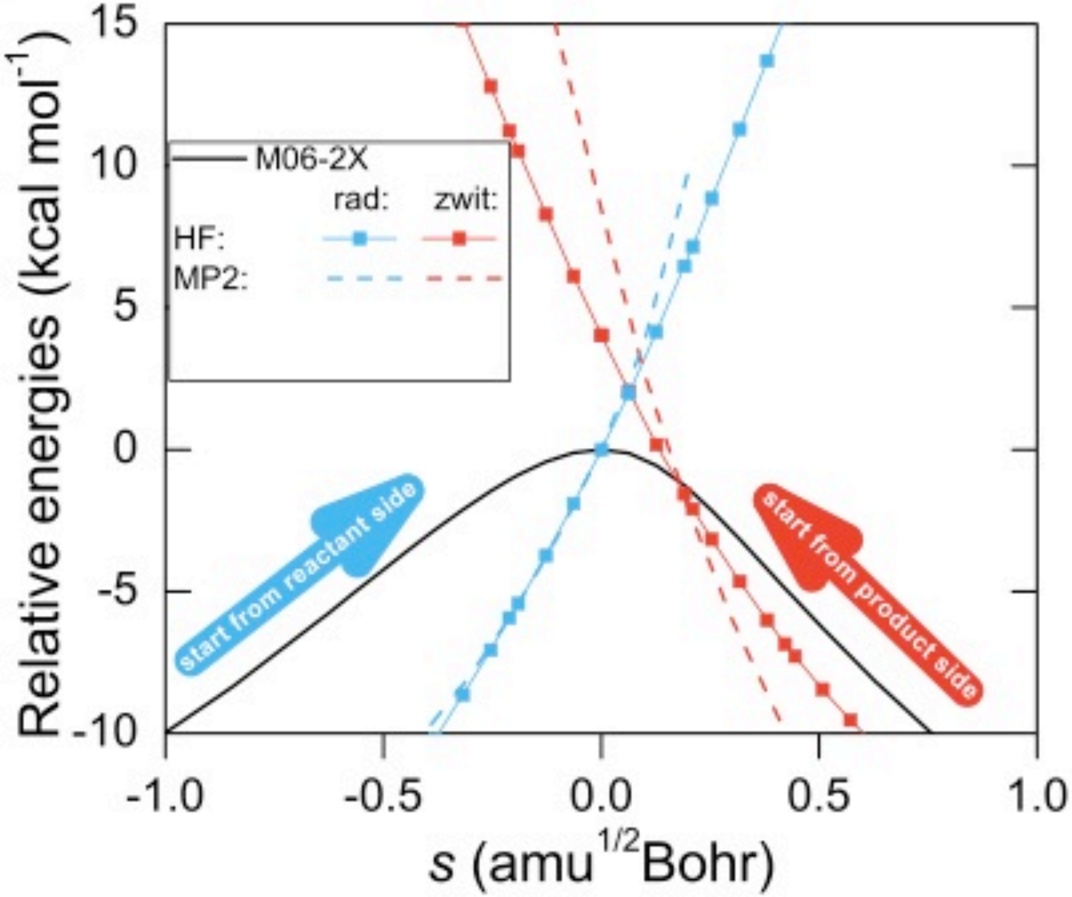
A simple **MS-MR-CASPT2(1e,2o,2states)** calculation:

- finds saddle point on ground state
- qualitatively shows the presence of two low-lying states



CASPT2(3e,3o)
→ does not map smoothly to product space
CASPT2(11e,8o,3states) is required
→ Very difficult and is plagued by convergence problems.
→ The barrier on the ground state is close to the M06-2X barrier height

In the single reference framework two weakly interacting states can be found



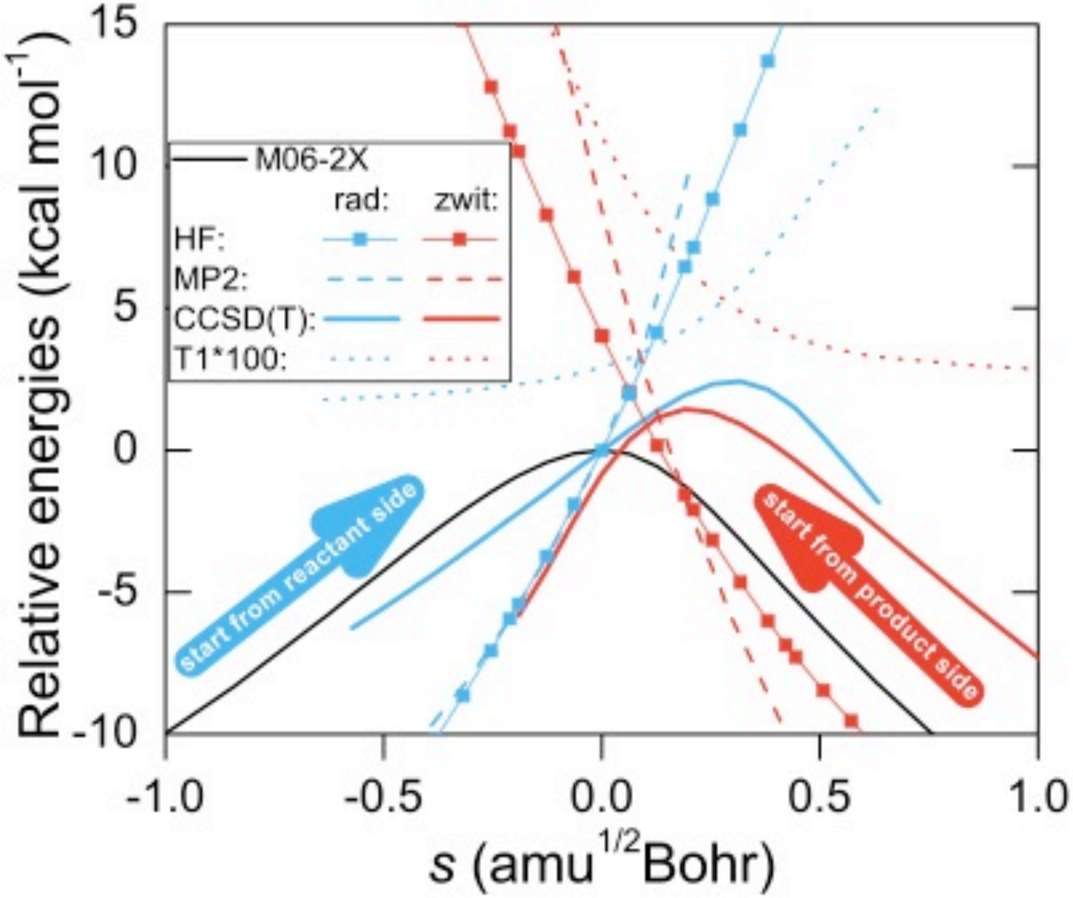
reactant side: **radical** character, small dipole moment

product side: **zwitterion** character, larger dipole moment

Orbital character depends on where the calculation is started

HF solutions do not mix

In the single reference framework two weakly interacting states can be found



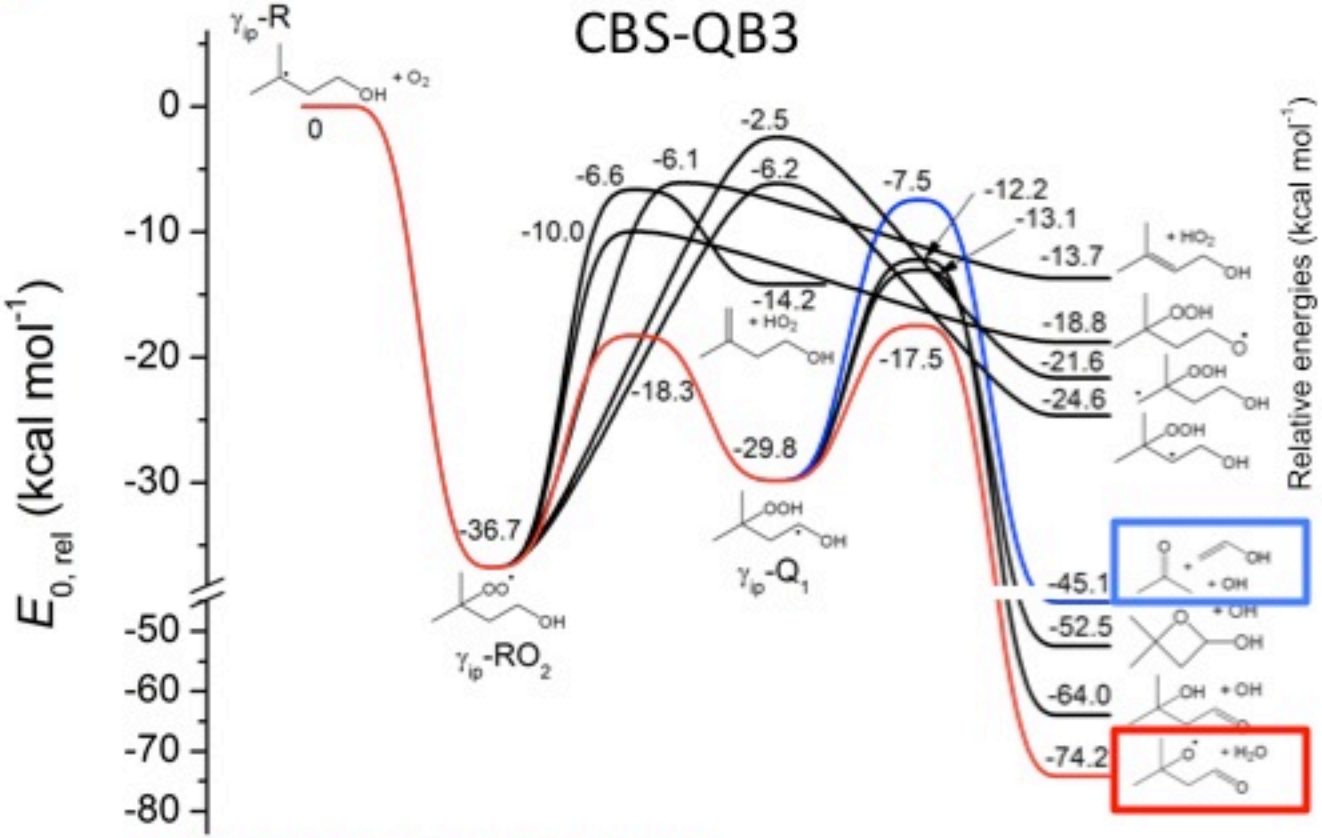
reactant side: **radical** character, small dipole moment
product side: **zwitterion** character, larger dipole moment

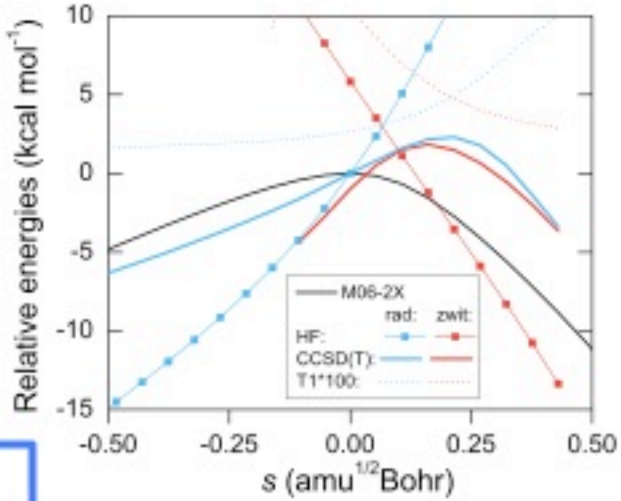
dipole moments (D)

	radical	zwitterion
ROHF:	2.1	4.9
RMP2:	1.3	4.9
UCCSD:	1.1	2.9
UCCSD(T):	1.4	1.6

UCCSD(T) energies become less dependent on initial orbital guesses
barriers for ethanol case: 18.2 and 17.2 kcal mol^{-1}
M06-2X barrier: 16.9 kcal mol^{-1} → close (within uncertainty) to the UCCSD(T) barriers.

The water elimination channel resolves the observed 3:1 acetone:ethenol ratio in isopentanol oxidation



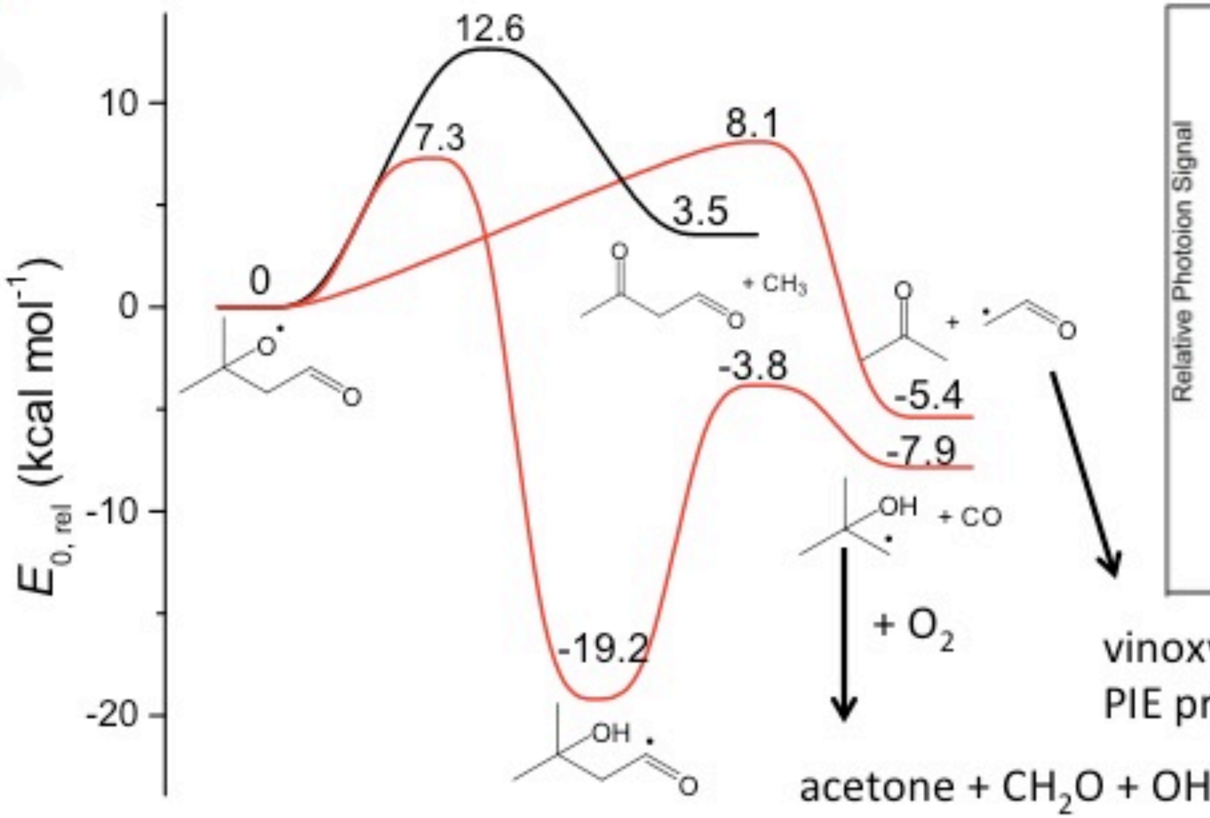


The **water elimination channel** is **the lowest overall** pathway to bimolecular products on the γ-R + O_2 surface.

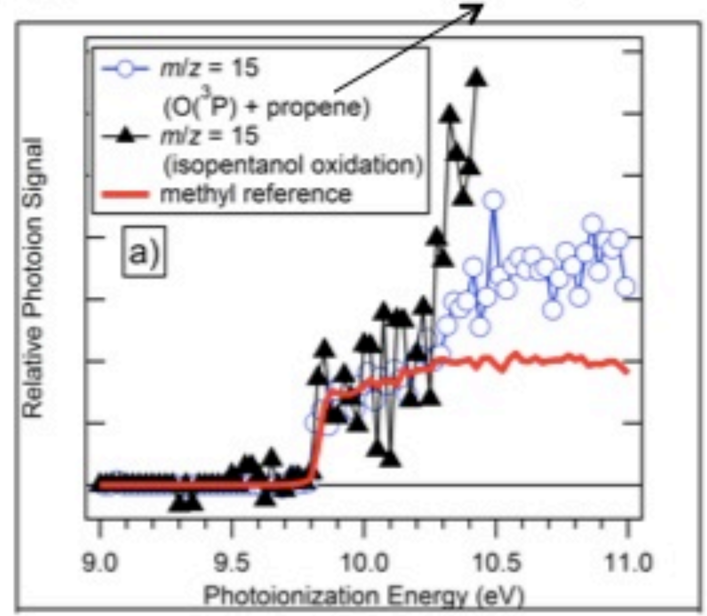
Fate of the alkoxy radical

β-scission leads to acetone + vinoxy

isomerization leads to CO + β-hydroxyalkyl radical



Savee et al., 2012, PCCP



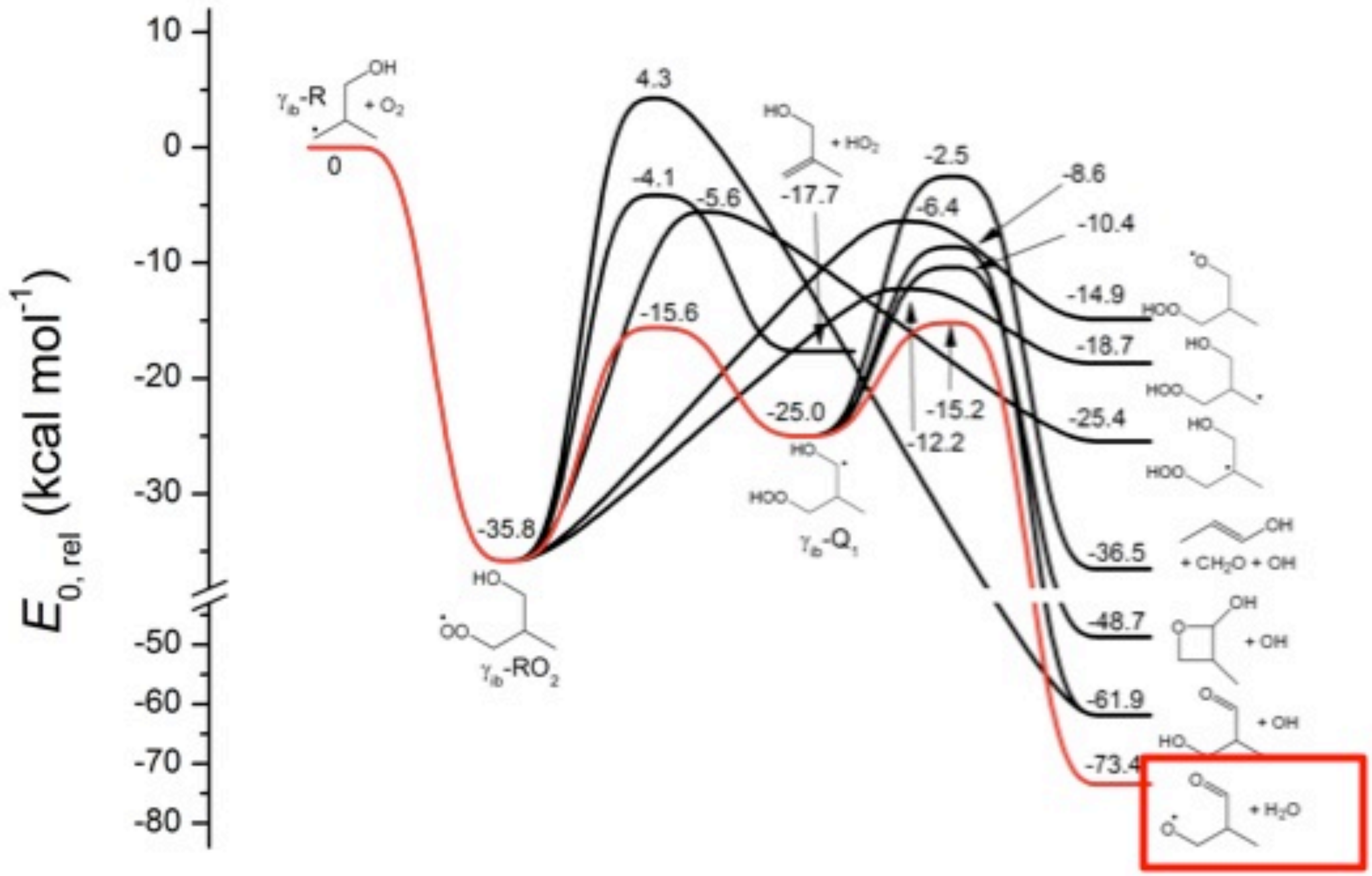
vinoxy radical fragments to m/z = 15

PIE proves the presence of vinoxy

Decomposition of the alkoxy radical produces acetone, but no ethenol

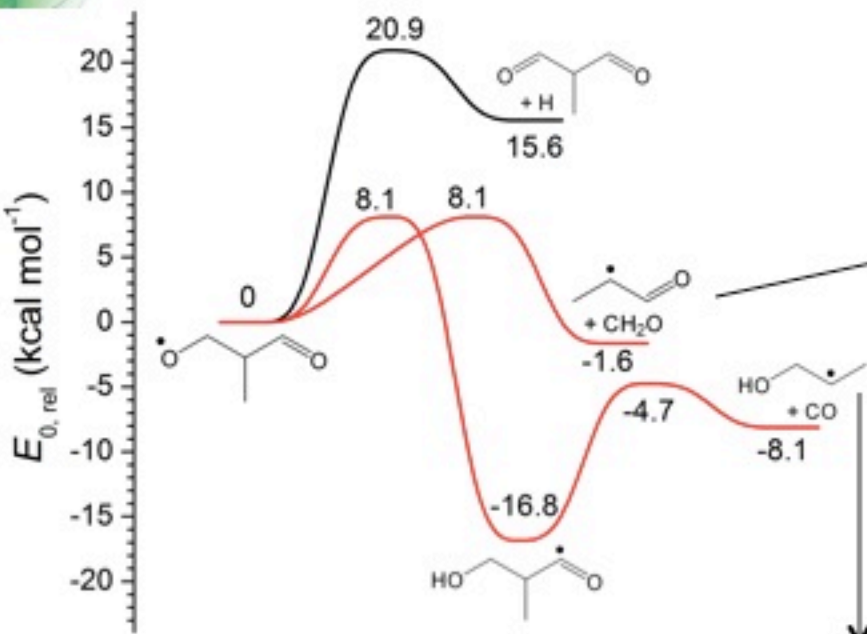
➔ This was the missing acetone source.

The water elimination pathway is responsible for the acetaldehyde formation in isobutanol oxidation

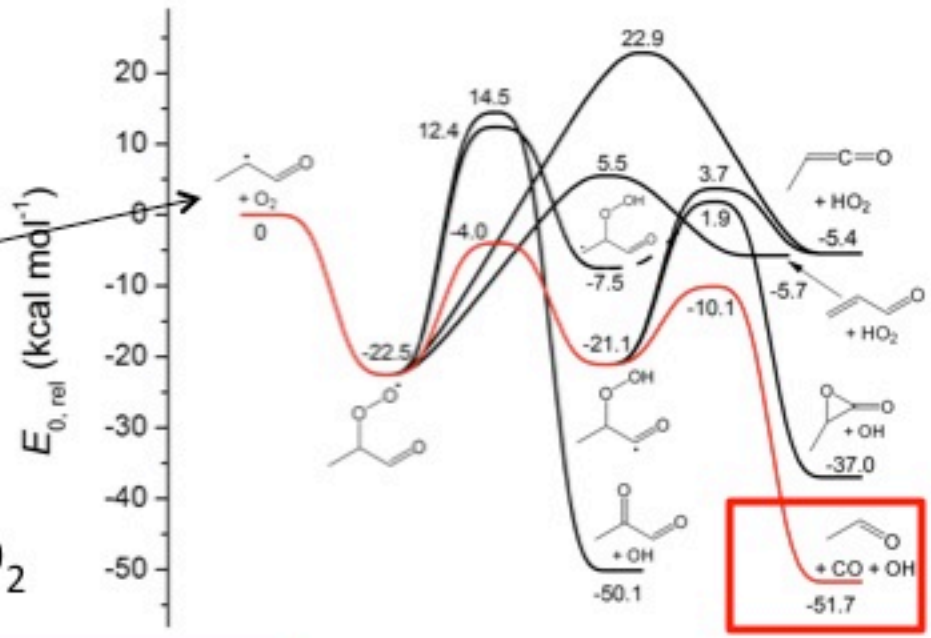


The **water elimination channel** is **the lowest overall** pathway to bimolecular products on the γ-R + O_2 surface.

Fate of the alkoxy radical

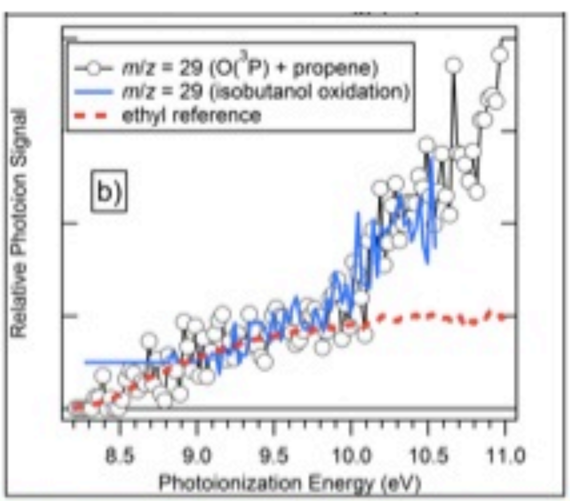


+ O_2



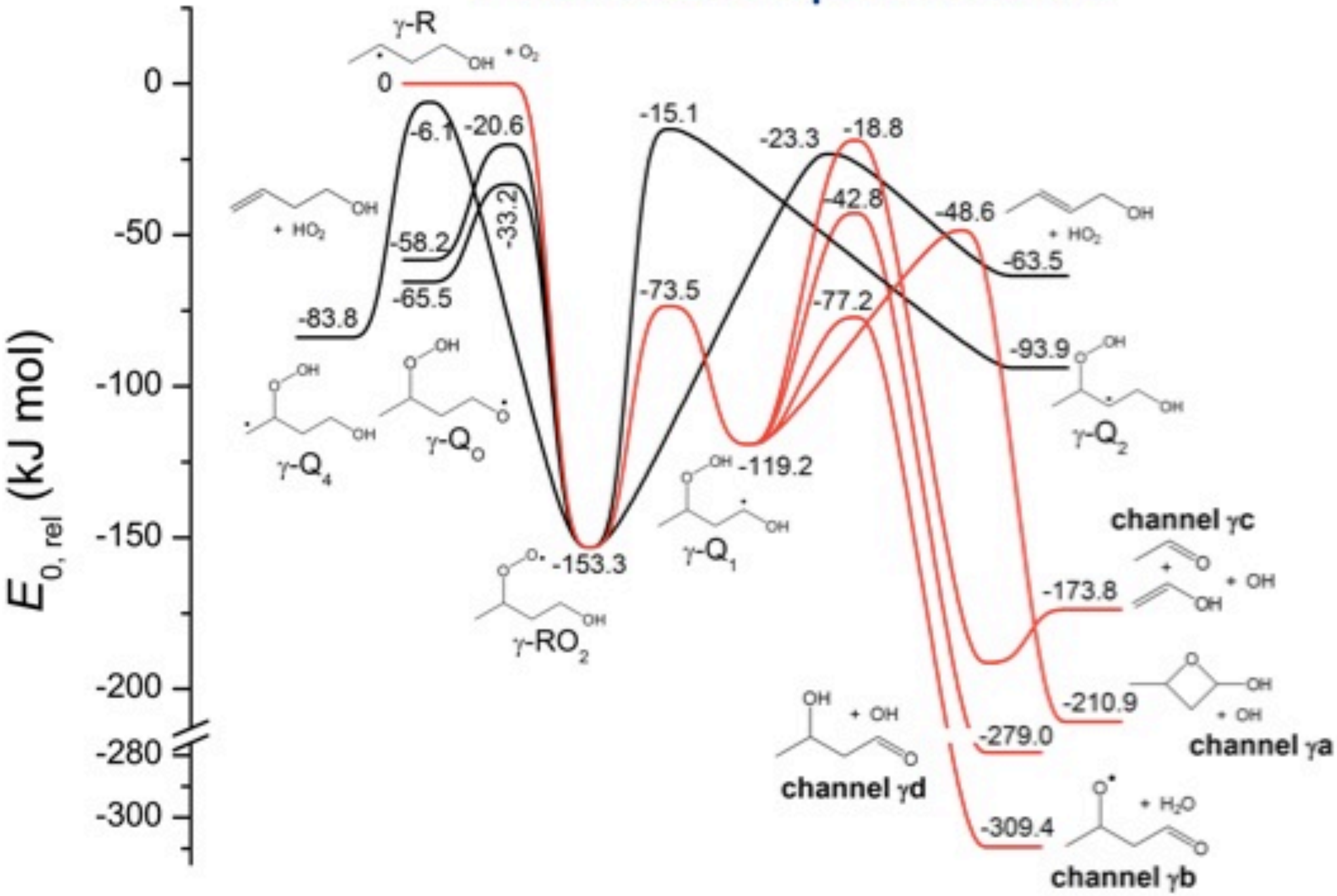
$CH_3CHO + CH_2O + OH$

Waddington



The m/z = 29 is suggested to arise due to the methylvinoxy daughter ions above ~10 eV, as also observed in the O(^{3}P) + propene experiment of Savee et al.

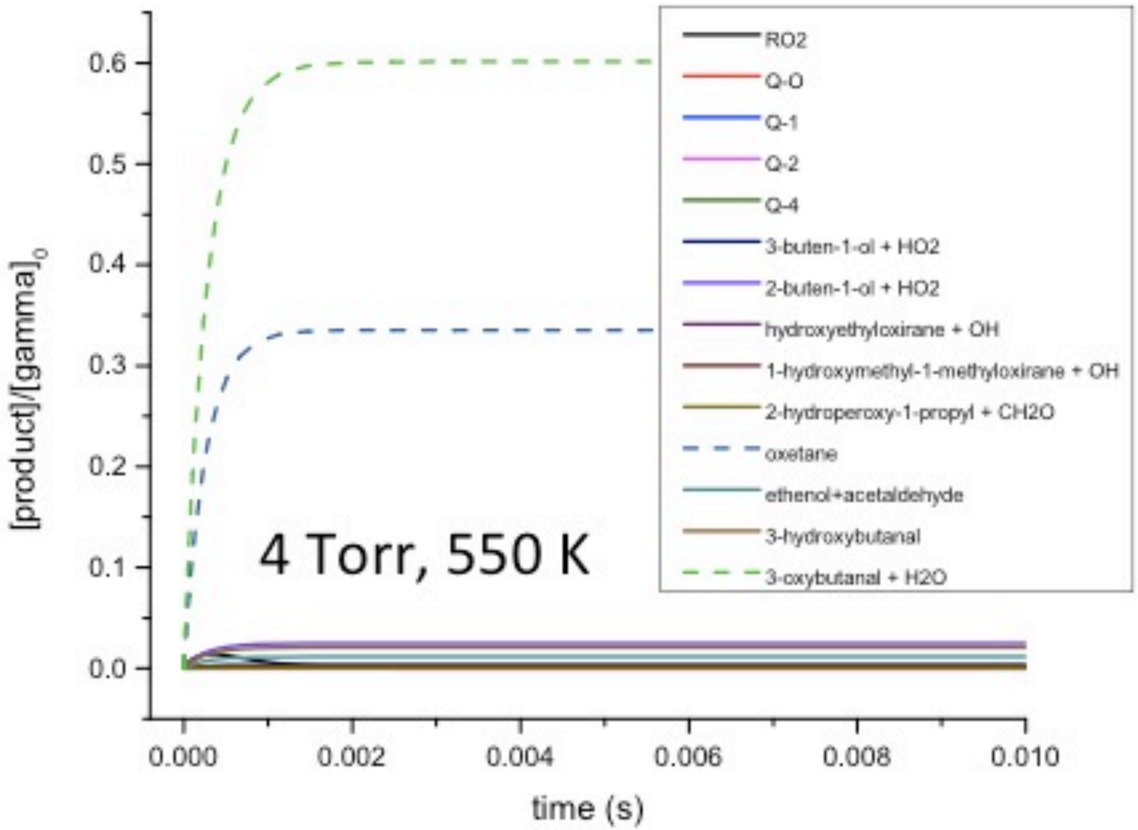
Water elimination in *n*-butanol: PES and experiments



γ-Q_1 is the most important QOOH for γ-ROO in *n*-butanol oxidation. Isotopically labeled experiments put a ~50% upper limit on the water elimination channel.

Welz et al., 2013 JPCA

Water elimination in *n*-butanol: Master Equation simulations



Our preliminary simulations of the kinetics suggest that the water elimination channel is the overall dominant channel for the γ radical. At higher pressures the reaction is more important.

Thank You!

and thank our sponsors:

Division of Chemical Sciences, Geosciences, and Biosciences, the Office of Basic Energy Sciences, the U.S. Department of Energy.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the National Nuclear Security Administration.