SAND2013-5549C

Unconventional Peroxy Chemistry in Alcohol Oxidation: The Water Elimination Pathway

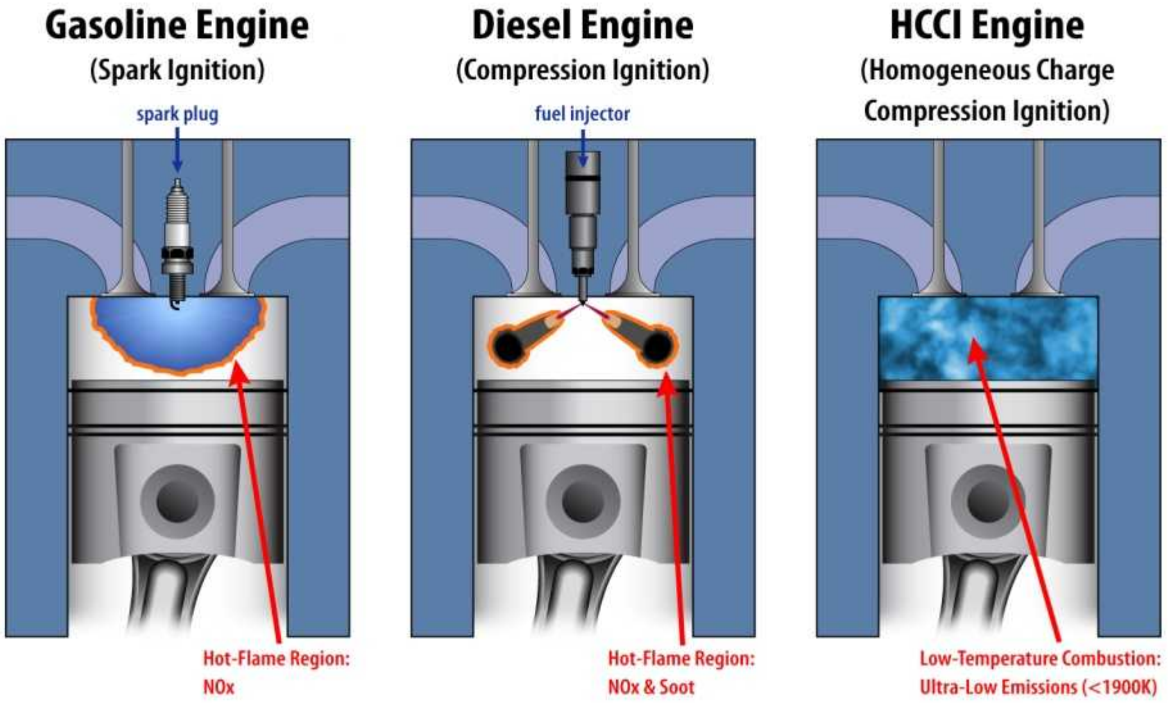
Judit Zádor
Oliver Welz
Craig A. Taatjes

Stephen J. Klippenstein
Lawrence B. Harding

8th International Conference on Chemical Kinetics
July 8-12, 2013, Seville, Spain

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



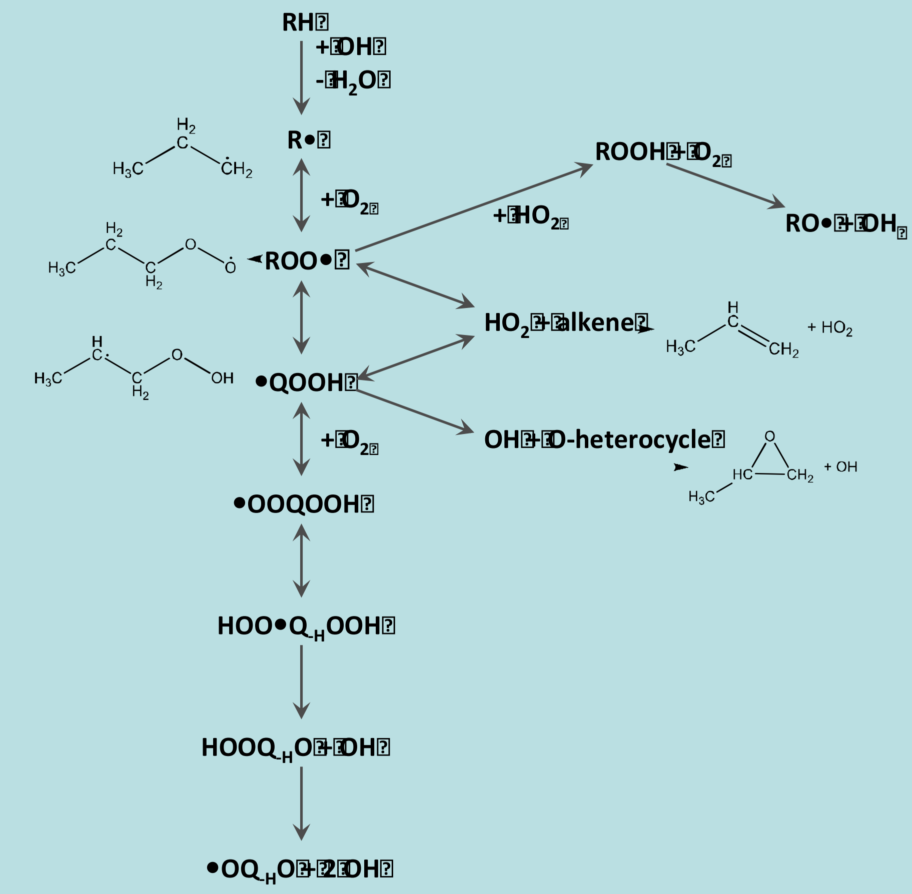
Manley et al. *Physics Today* 2008

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.

Low-temperature oxidation chemistry of alkanes is well known (or not? see parallel session)



RH

+ OH

- H_2O

R•

+ O_2

ROO•

+ HO_2

ROOH + O_2

RO• + OH

HO_2 + alkene

•QOOH

OH + O-heterocycle

+ O_2

•OOQOOH

HOO•Q_{-H}OOH

HOOQ_{-H}O + OH

•OQ_{-H}O + 2OH

Zádor, Fernandes, Taatjes, PECS, 2011

Most of these reactions happen on a multiwell PES:
➔ Complex pressure and temperature dependence.

What happens during the low-temperature chemistry of oxygenates?

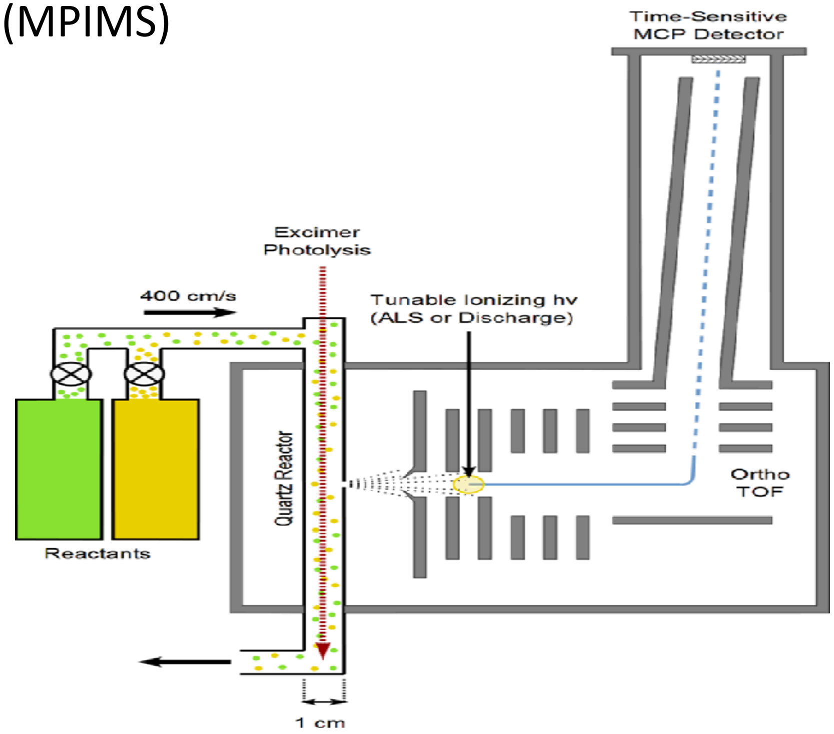
➔ **dramatic change in barrier heights**
very low direct-HO_2 elimination barrier in α-hydroxyalkyl radicals
$CH_3CH(OO^\bullet)OH = CH_3CHO + HO_2$
barrier: -23.6 kcal mol^{-1}
(cf. $C_2H_5 + O_2$: -3 kcal mol^{-1})

➔ **Waddington mechanism**:
β-scission is favored over cyclic ether formation in alkoxy type QOOH radicals formed from β-hydroxyalkyl radicals
$^\bullet OOCH_2CH_2OH = HOOCH_2CH_2O^\bullet$
$HOOCH_2CH_2O^\bullet = 2\ CH_2O + OH$

➔ **Are there fundamentally new pathways present for oxygenates?**
Welz et al., 2013, J. Phys. Chem. Lett.

Recent experiments on low-temperature alcohol oxidation showed evidence of unknown pathways

Laser photolysis reactor coupled to time-of-flight multiplexed photoionization mass spectrometry (MPIMS)



3-D data:

time – *m/z* – hv

➔ *m/z* – time

time dependent mass spectra

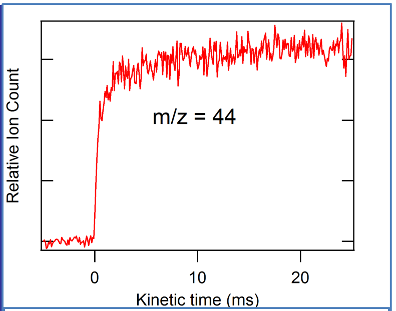
- ❖ kinetics of each mass channel

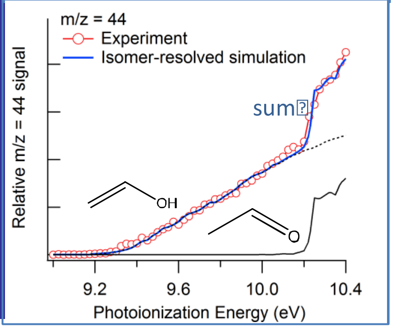
➔ *m/z* – hv

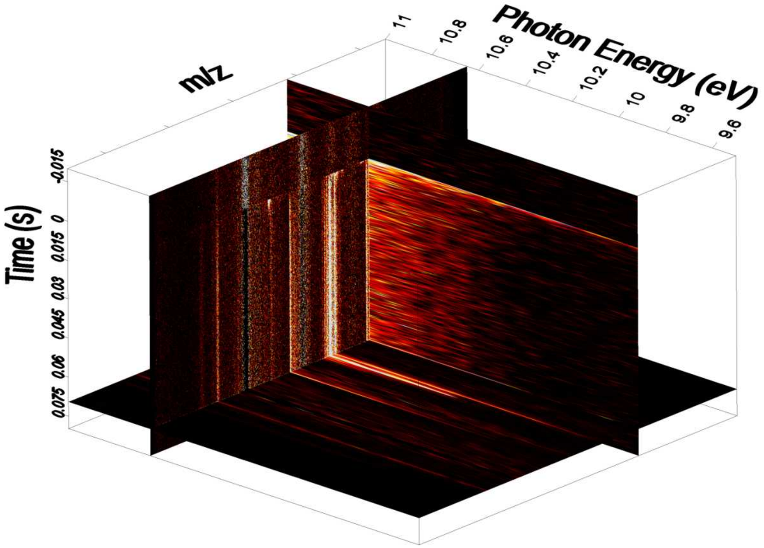
PIE curves

- ❖ isomeric resolution

➔➔ **isomer-resolved kinetics**







Cl-atom initiated low-T oxidation of alcohols

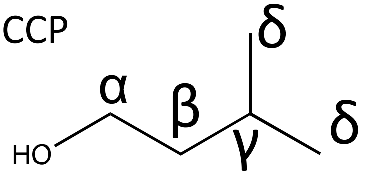
Cl + alcohol = hydroxyalkyl radicals (R_α, R_β, R_γ, etc.)

R + excess O_2 = products

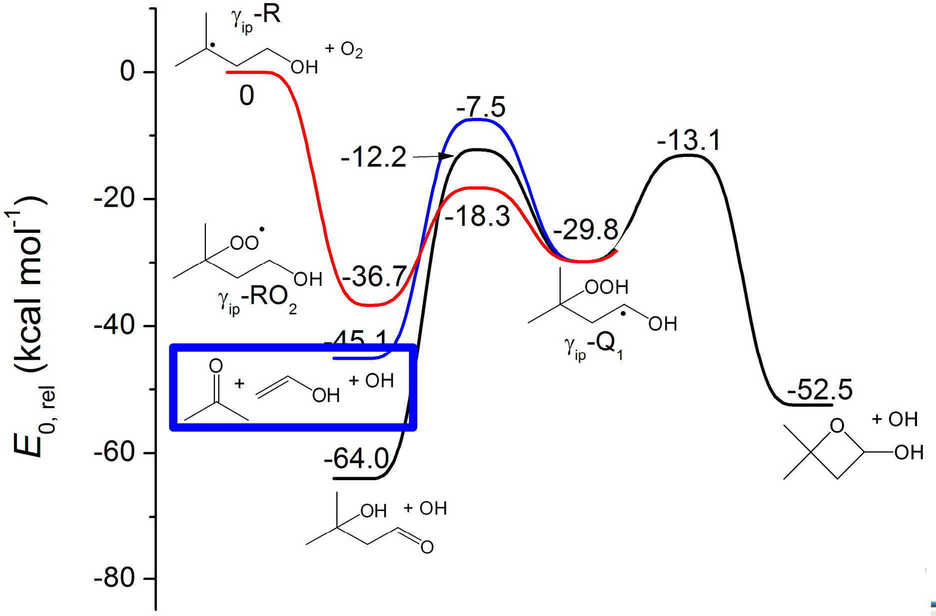
Recent experiments on low-temperature alcohol oxidation showed evidence of unknown pathways

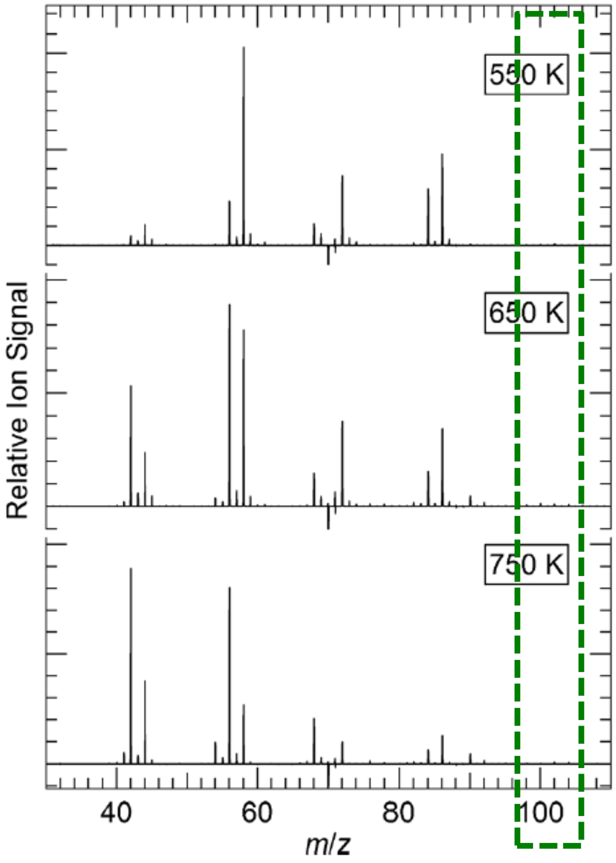
Chlorine-initiated oxidation of isopentanol

Welz et. al, 2012, PCCP



- cyclic ethers (*m/z* = 102) are absent
- relative position of –OOH, –OH and radical are important
- **observed acetone:ethenol ratio is 3:1**
- γ radical + O_2 produces acetone:ethenol in 1:1 ratio
- no acetone or ethenol pathway in α-, β-, or δ-R





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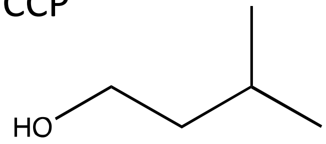
Chlorine-initiated oxidation of isopentanol

Welz et. al, 2012, PCCP



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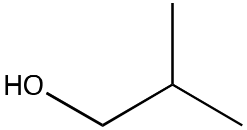
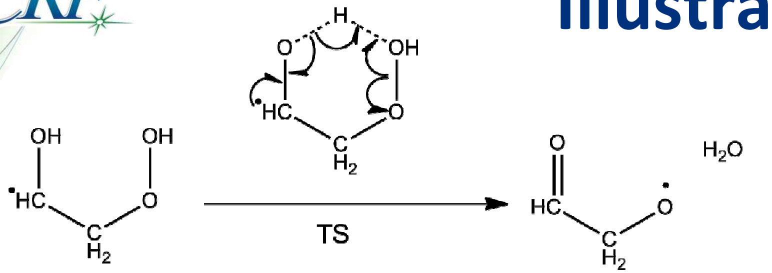
Chlorine-initiated oxidation of isobutanol

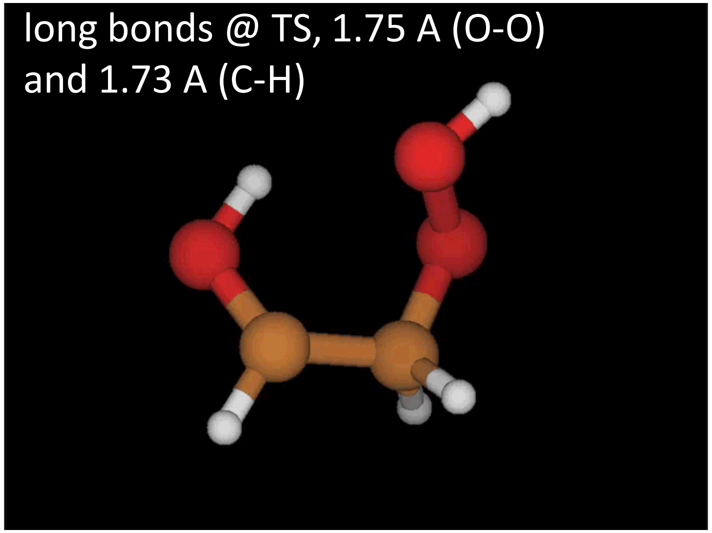
Eskola, 2013, Proc. Combust. Inst.

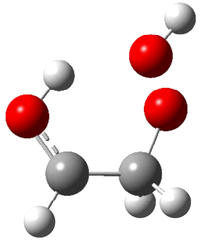


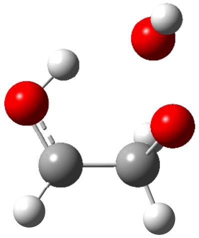
large amounts of acetaldehyde could not be accounted for

The water elimination pathway – Illustrated on ethanol



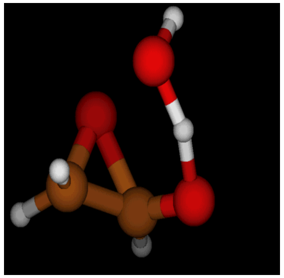

long bonds @ TS, 1.75 A (O-O) and 1.73 A (C-H)


TS


TS’

B3LYP/6-311++G*

- 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 is similar in energy, but has small probability



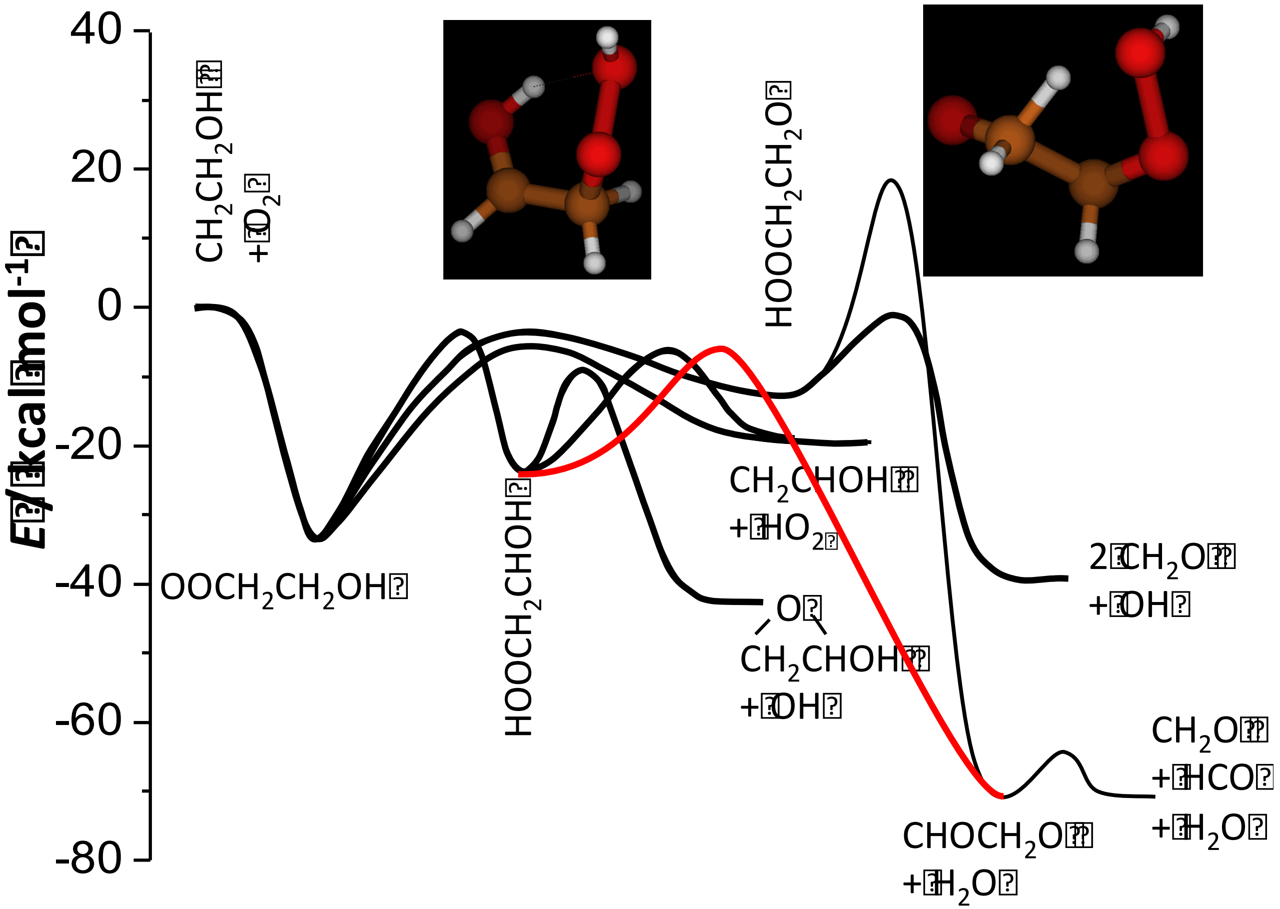
- the ordinary, two-step version of the above process does not play a role in the experiments because of the small radical and large precursor concentrations

Slide 7

A7 See my next comment -- I'd probably introdice the water elimination pathway for the gamma-QOOH. That connects better to the isopentanol and isobutanol systems.

Administrator, 7/5/2013

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



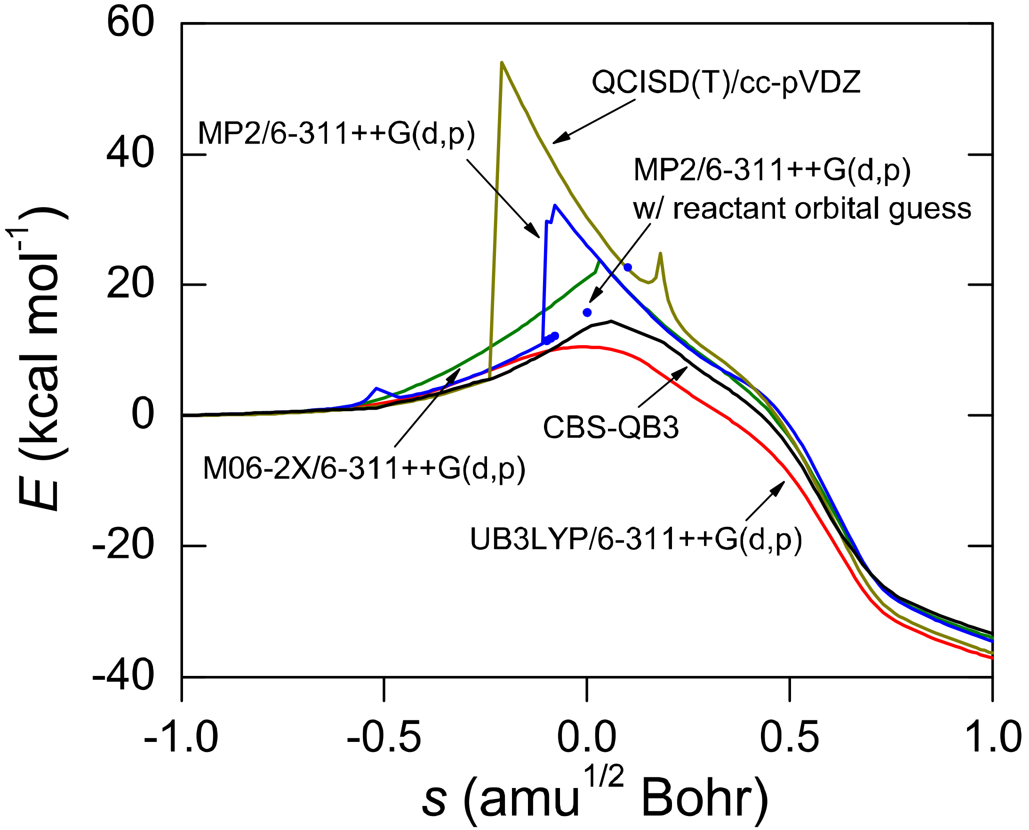
RQCISD(T)/cc-pV∞Z//B3LYP/6-311++G(d,p)

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

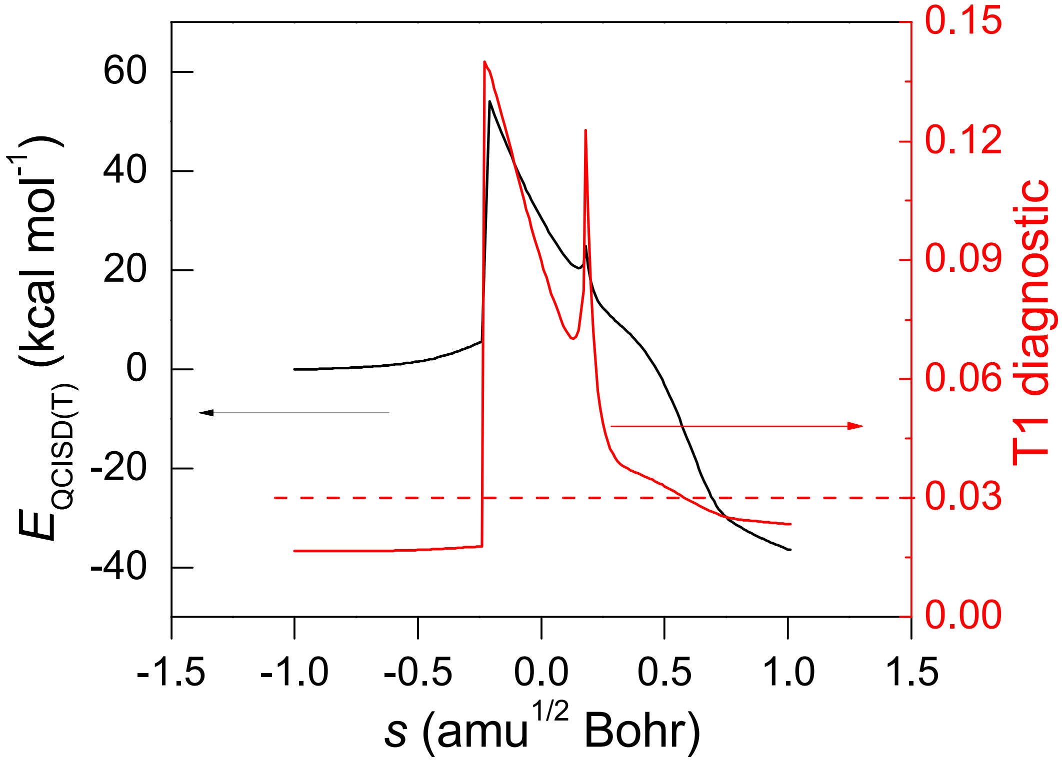
For one of the conformers of the water elimination pathway in ethanol, MP2 and M06-2X was unable to locate a saddle point.
QCISD(T) also was problematic.



Calculated energies along the B3LYP IRC.

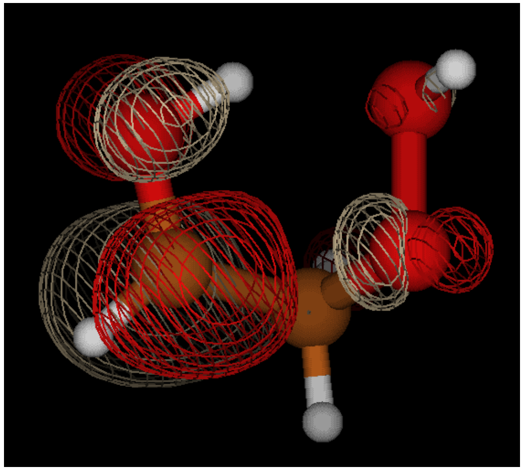
QCISD(T) energies and T1 diagnostic along the B3LYP IRC

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



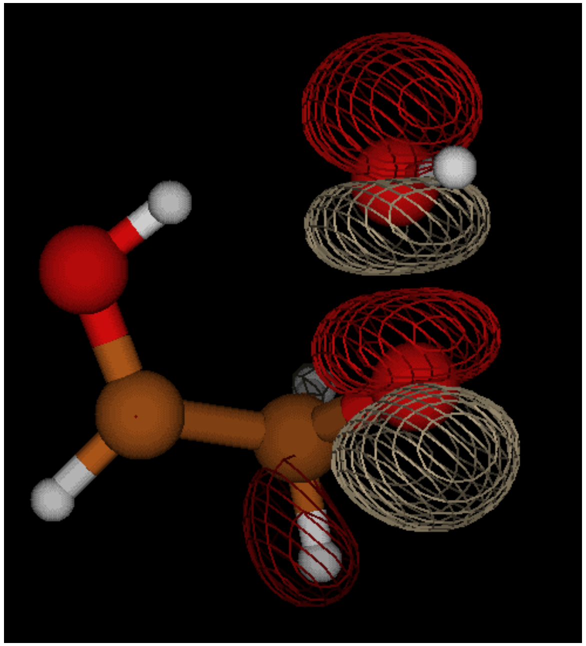
➔ **Multireference treatment of the electronic structure is necessary in the vicinity of the saddle point.**

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.

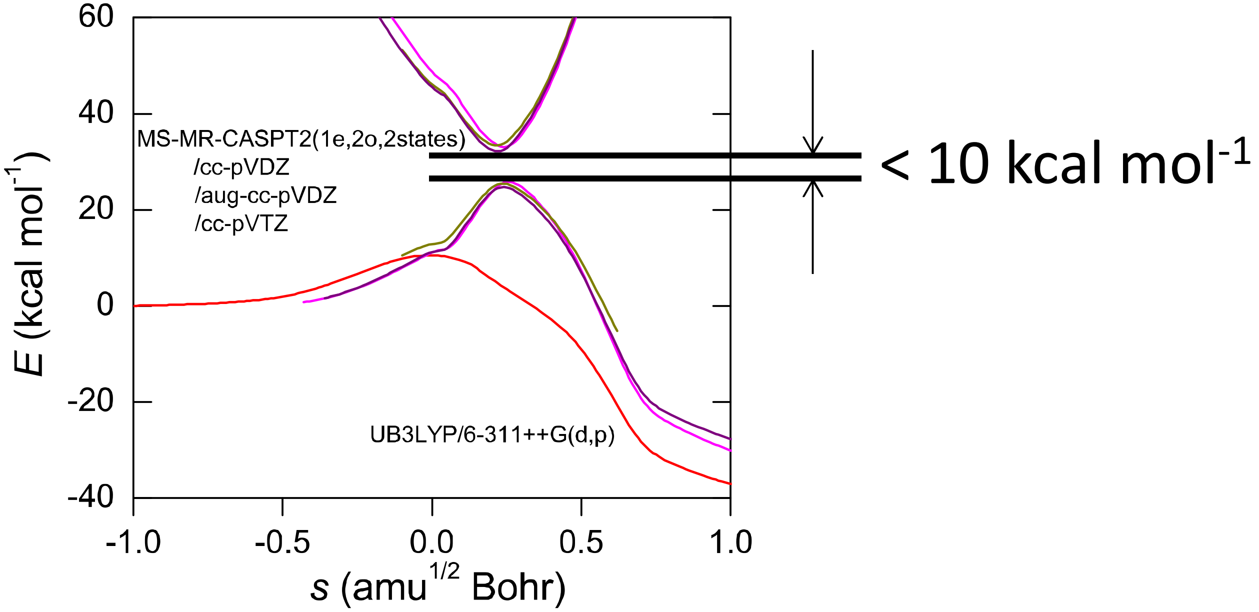
The simultaneous pathway involves the mixing of weakly interacting, spatially orthogonal orbitals.

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)

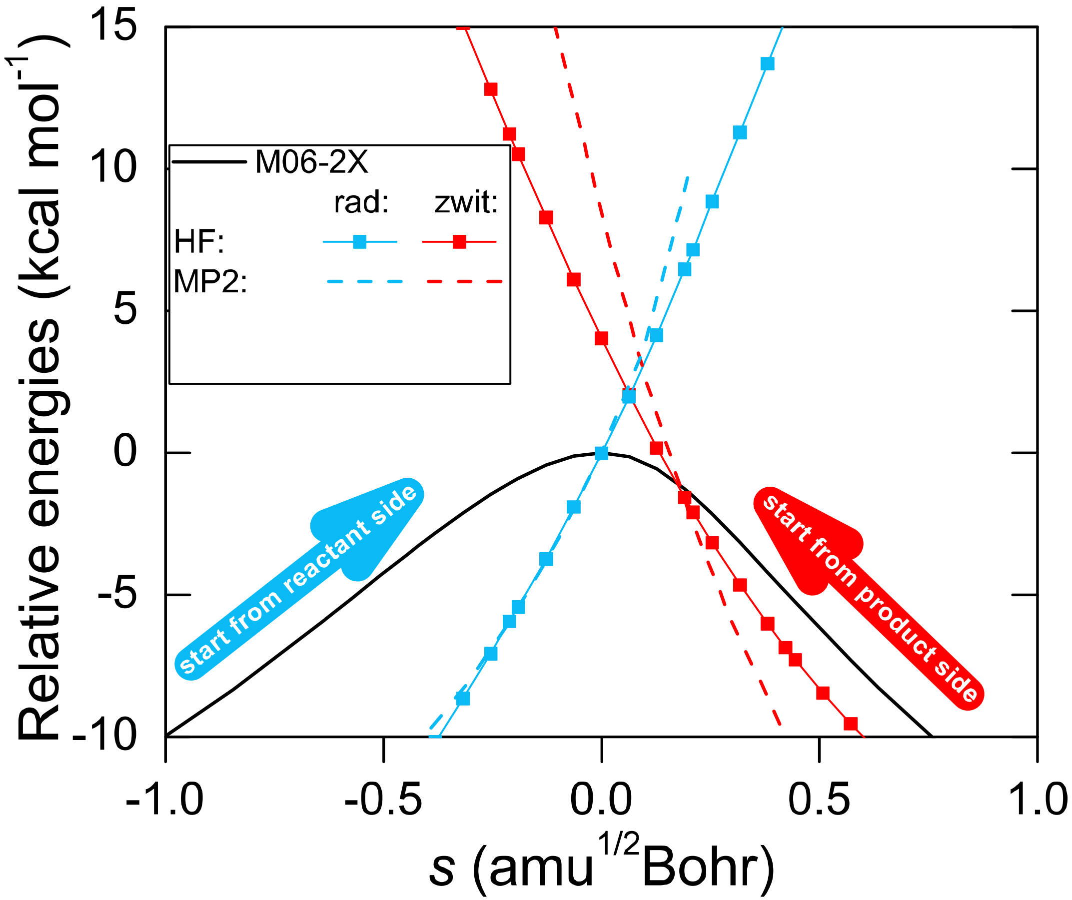
→ does not map smoothly to product space

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

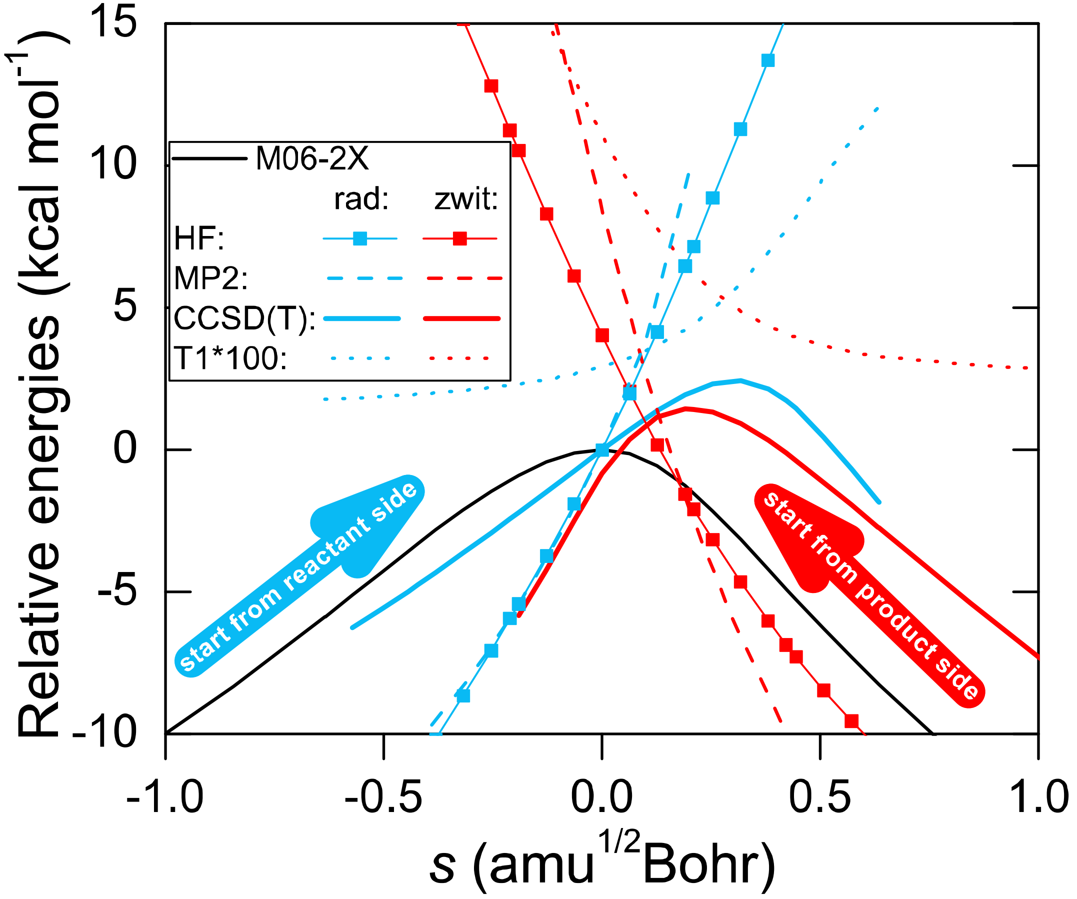
In the single reference framework two weakly interacting states can be found



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



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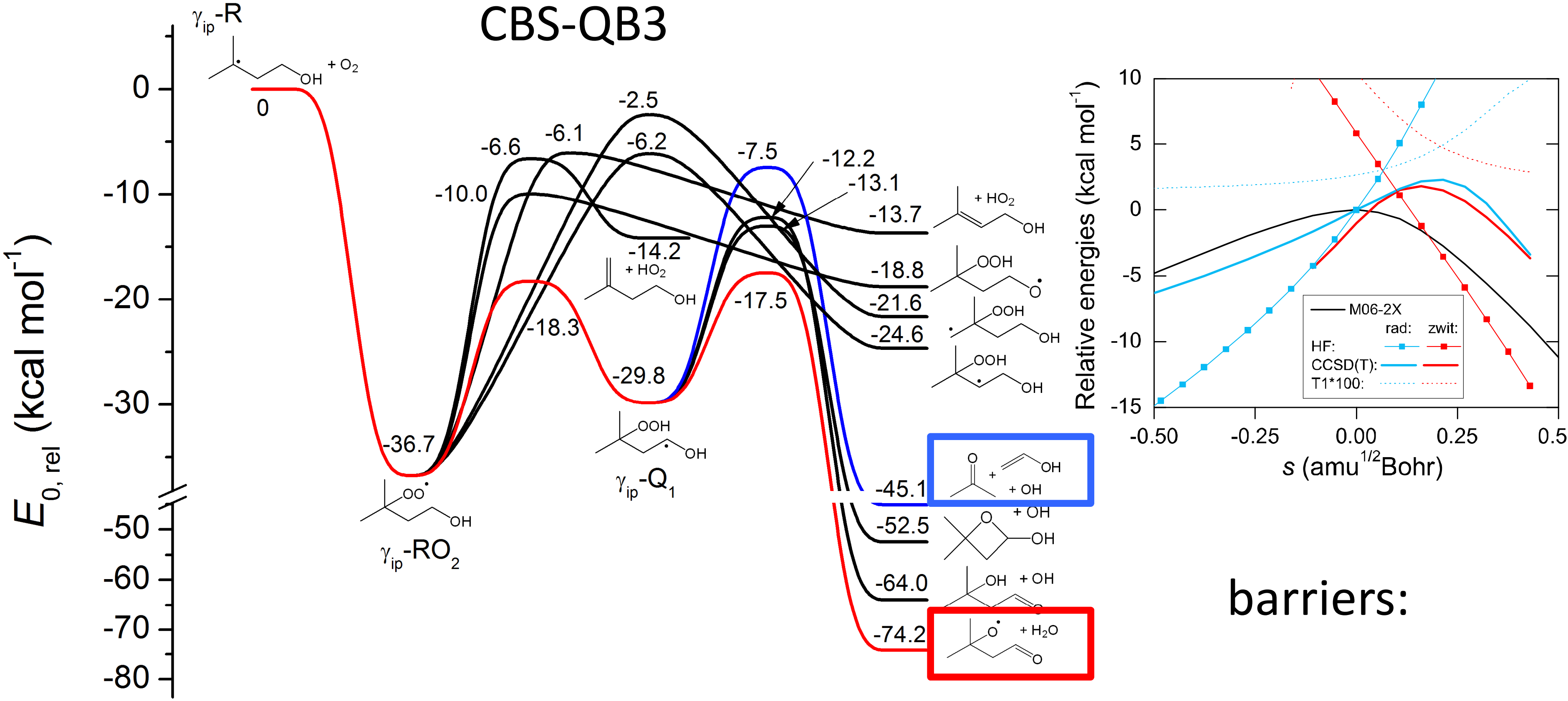
dipole moments (D)

	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

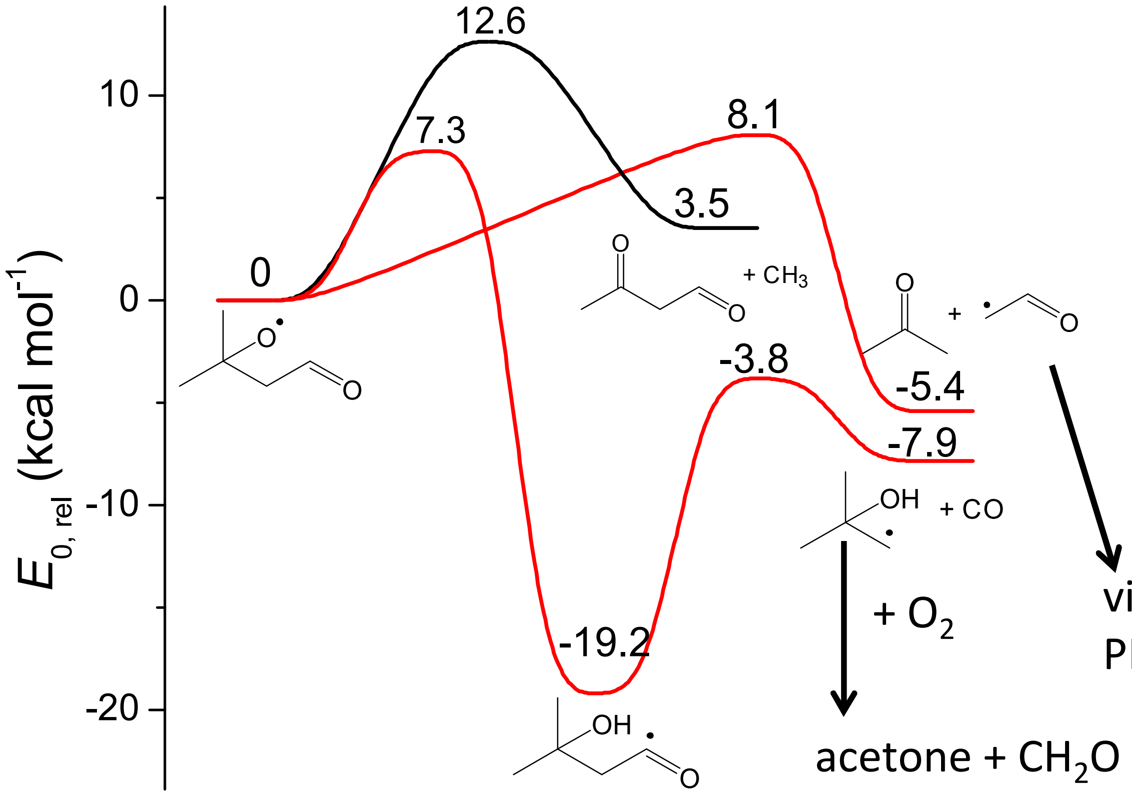


barriers:

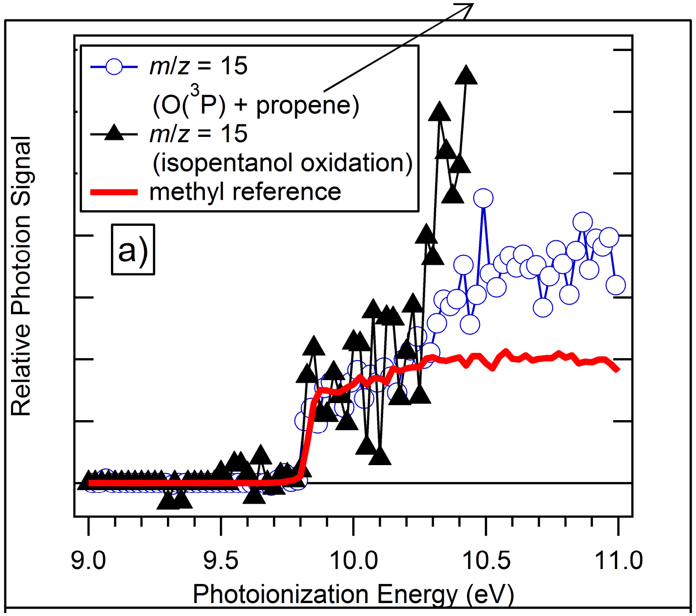
The **water elimination channel** is **the lowest overall** pathway to bimolecular products on the γ-R + O_2 surface.

Fate of the alkoxy radical

β-scission leads to acetone + vinoxy
isomerization leads to CO + …



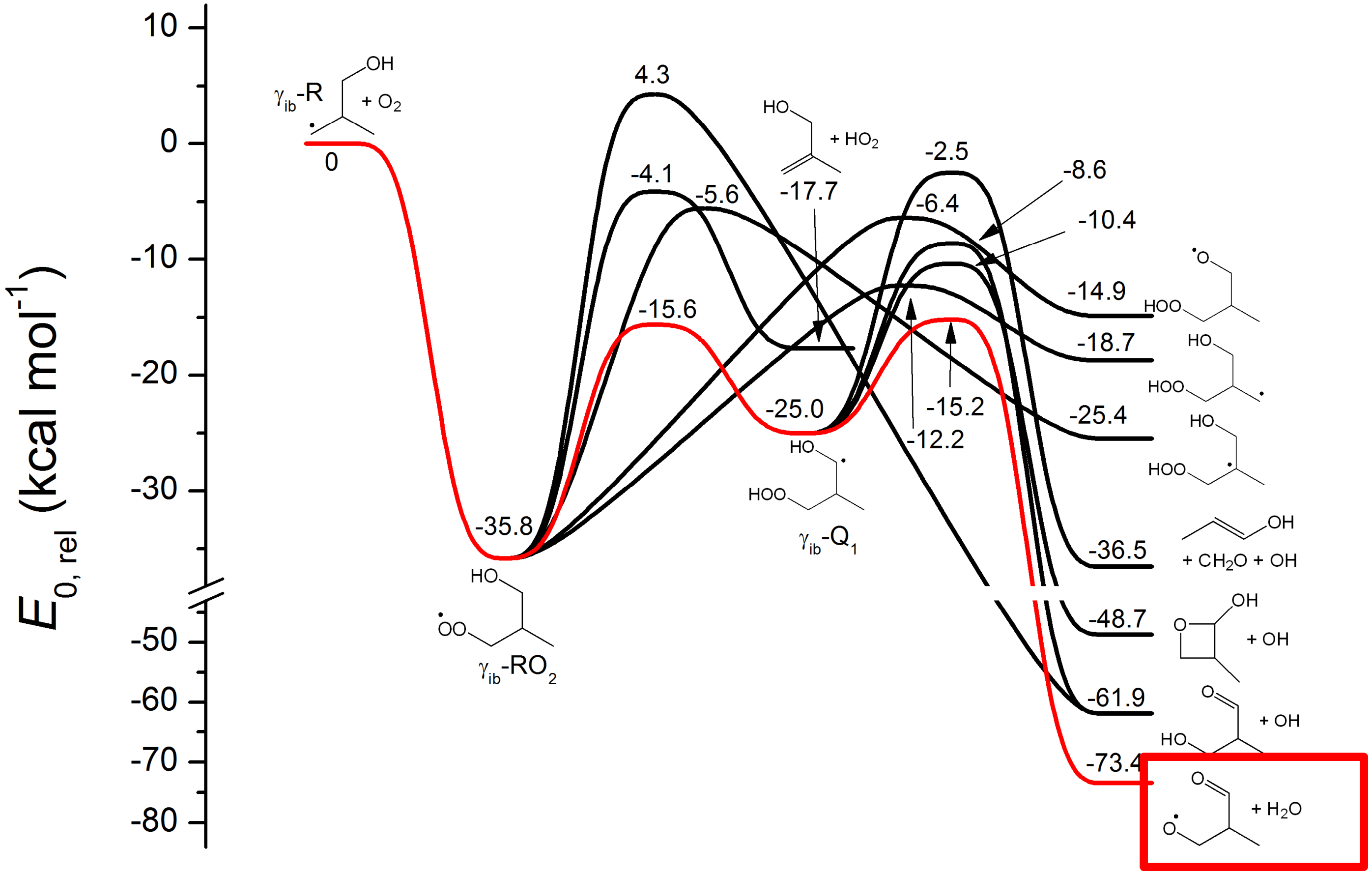
Savee et al., 2012, PCCP



vinoxy radical fragments to m/z = 15
PIE proves the presence of vinoxy

Decomposition of the alkoxy radical produces acetone, but no ethenol.

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



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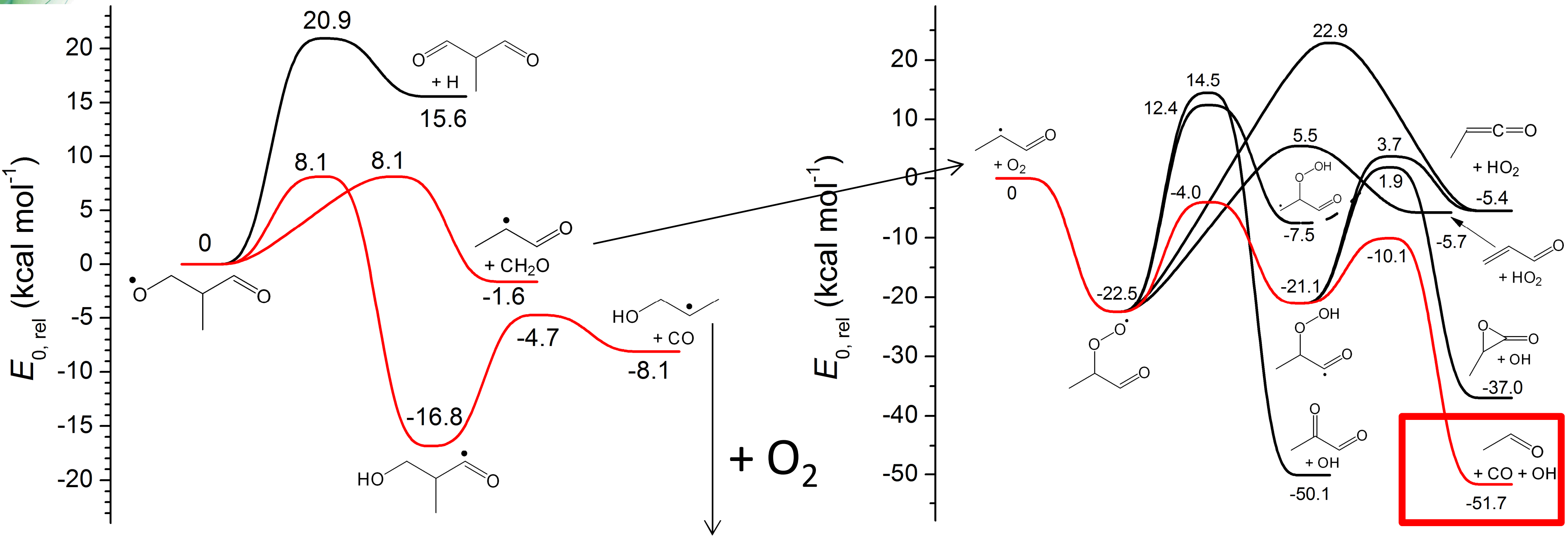
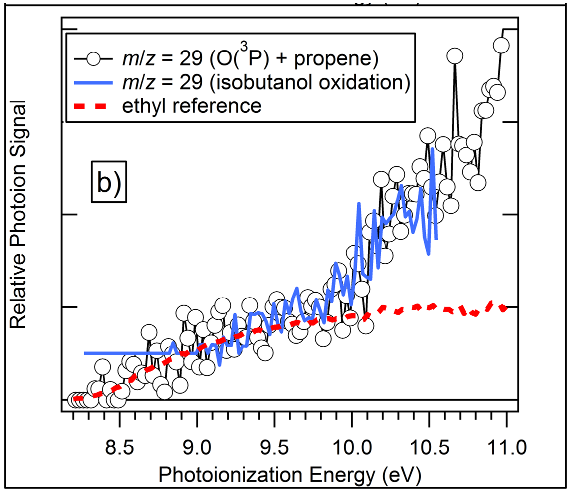


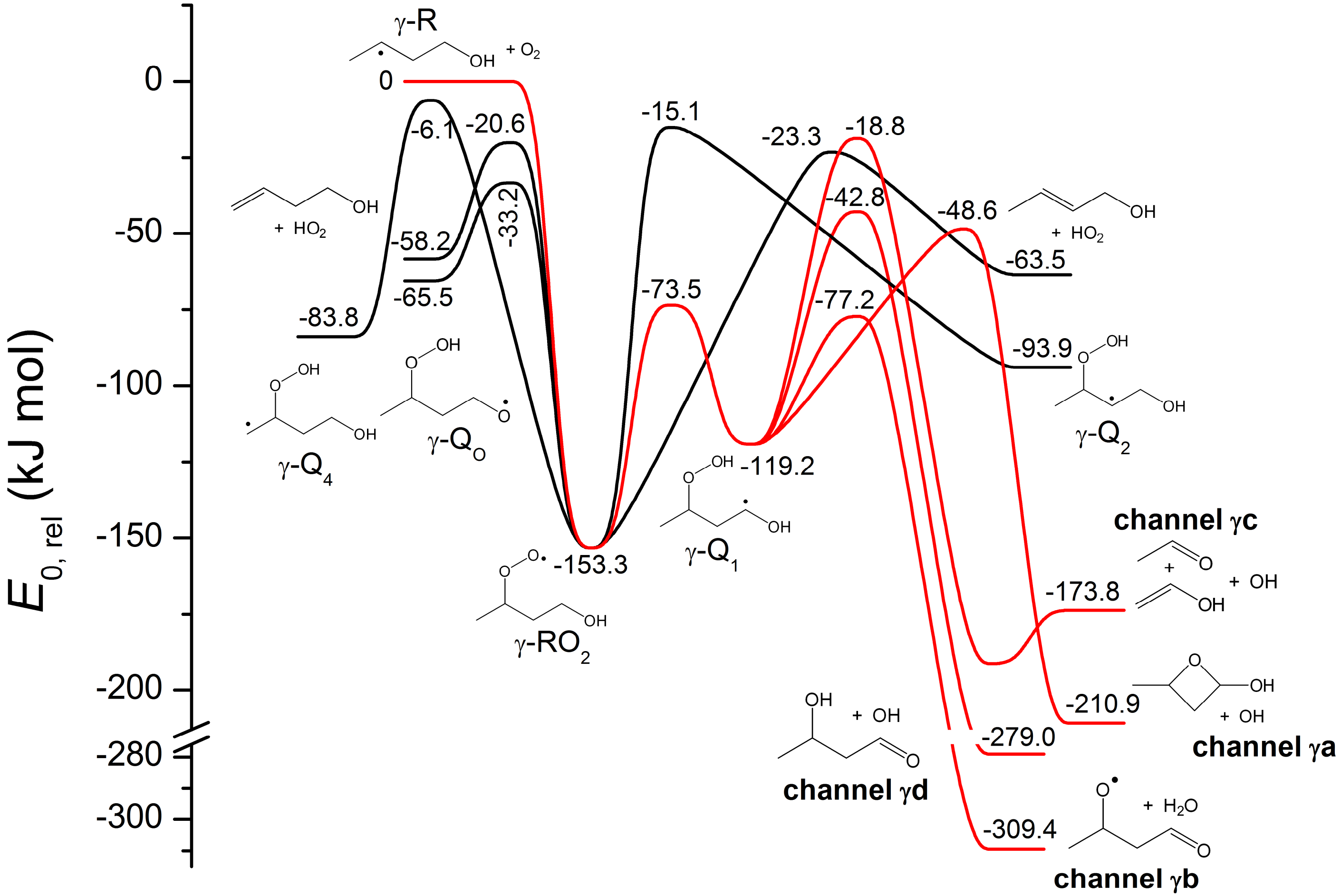
CH$_3$CHO + CH$_2$O + OH

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.

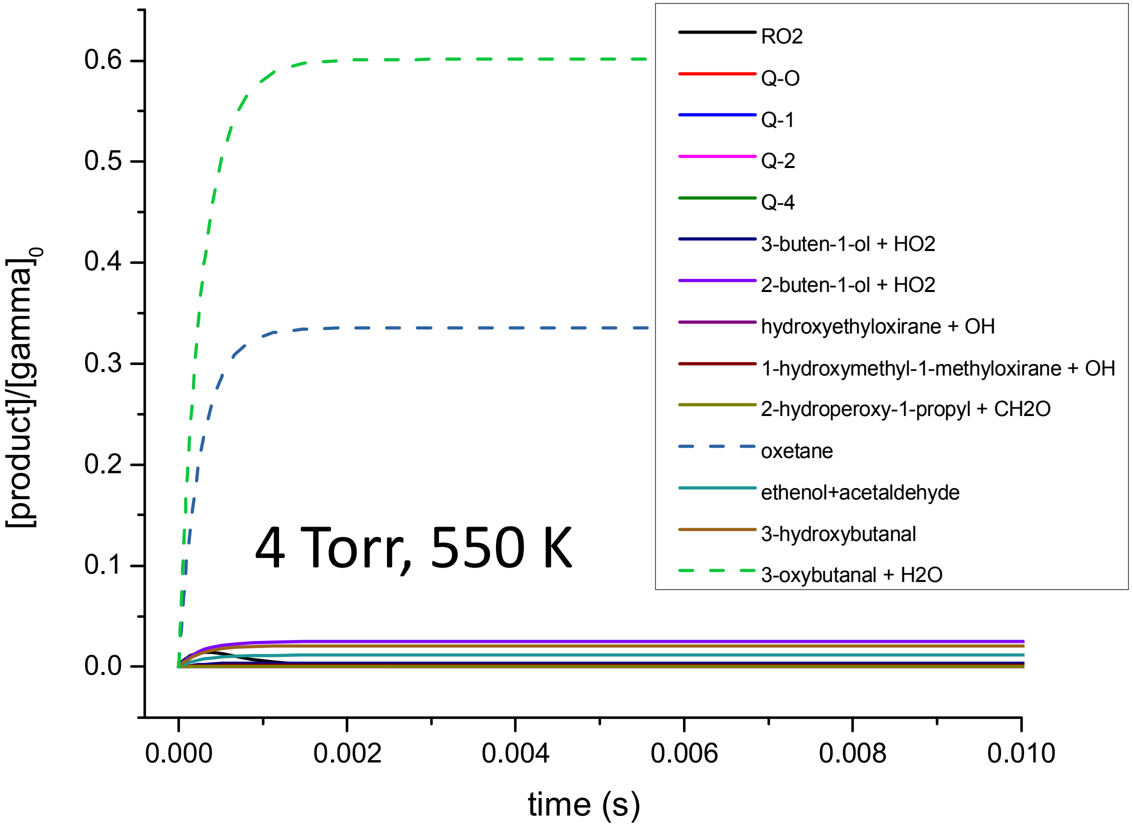
Water elimination in *n*-butanol: PES and experiments



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.

General relevance of the H_2O elimination channel in low-temperature alcohol oxidation

- Our calculations suggest that this channel is one of the or the most important pathway in γ-hydroxyalkyl radicals.
- For β-hydroxyalkyl radicals this channel is less important.
- The reaction is exotherm by ~75 kcal mol^{-1}

→ contributes significantly to heat release

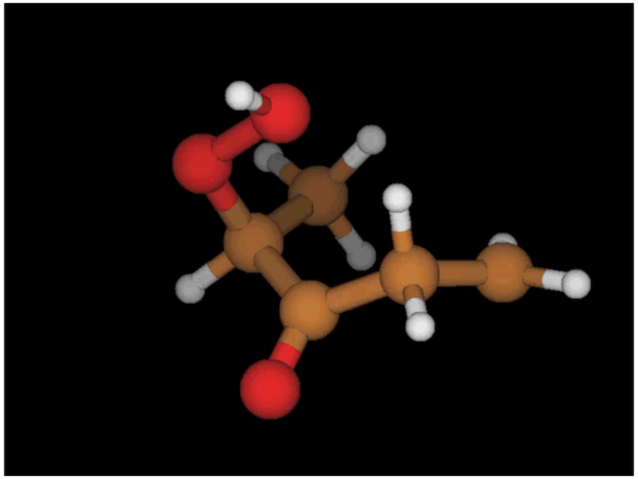
→ hot radicals can readily decompose to smaller fragments contributing readily to chain propagation

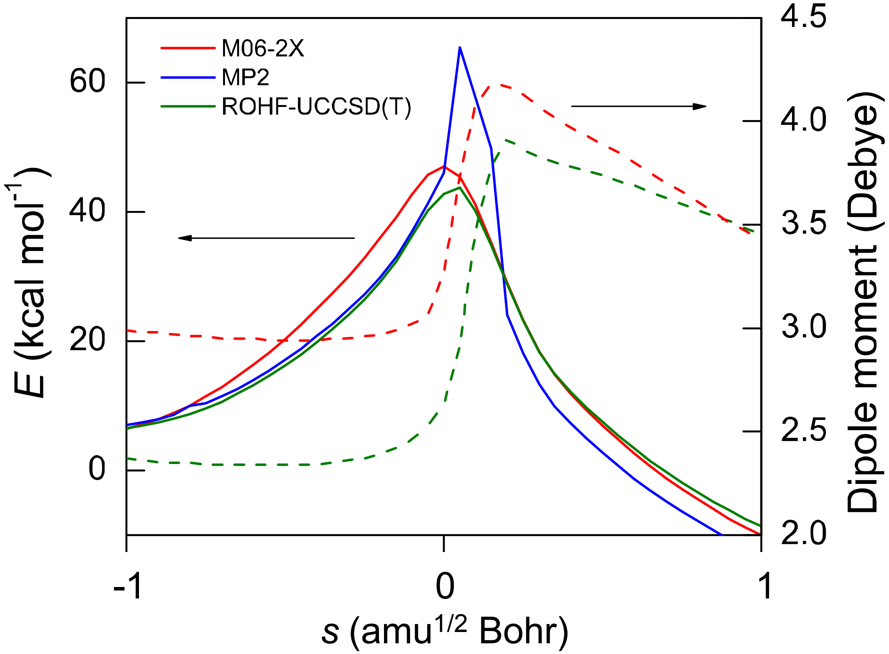
e.g. $HCO \rightarrow H + CO$

$HCO + O_2 = HO_2 + CO$

Can similar channels appear in other fuels?

Ketone oxidation



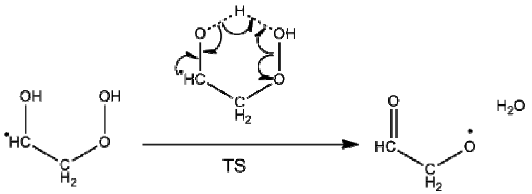


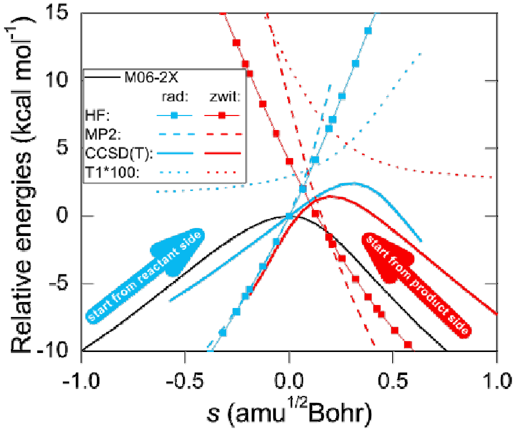
We located the corresponding saddle points, but they are too high (> 40 kcal mol^{-1}) to be important.

The TS shows some of the difficulties related to the electronic structure as for alcohols.

Summary and Outlook

- Characterized important new low-lying pathway in the low-T oxidation chemistry of alcohols.





- Water elimination is common, substantially altering current alcohol oxidation and ignition mechanisms.
- Theoretical methods have been developed for the general phenomenon of interacting radical and zwitterionic states.

- There are indications that similar pathways and low-lying zwitterionic states may play a role even in alkane oxidation.

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 under DOE Contract Numbers DE-AC04-94AL85000.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the National Nuclear Security Administration of the U.S. Department of Energy under Contract DE-AC04-94AL85000. The portion at Argonne was supported under Contract DE-AC02-06CH11357 as part of the Argonne–Sandia Consortium on High-Pressure Combustion Chemistry.