COMBUSTION RESEARCH FACILITY

SAND2016-10565C

Measurements of Key Chemical Intermediates in Low-*T* Combustion

Leonid Sheps

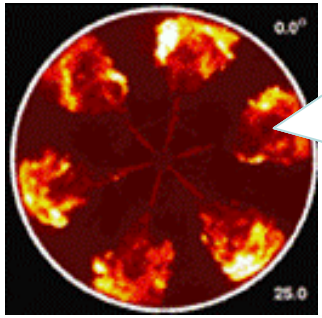
Combustion Research Facility, Sandia National Laboratories

Livermore, CA, USA

MACCCR

October 18, 2016

Complex chemistry



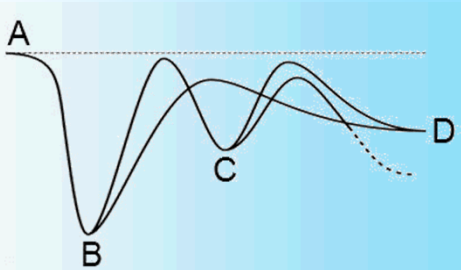
In-cylinder ignition

C. G. Mueller, CRF

Comprehensive kinetic mechanism

```
c7h15o2-1=c7h14ooh1-2 2.000e+11 0.000
26850.0 !12-I 5s c7h15o2-1=c7h14ooh1-3
2.500e+10 0.000 20850.0 !12-I
c7h15o2-1=c7h14ooh1-4 3.125e+09 0.000
19050.0 !12-I 7s c7h15o2-1=c7h14ooh1-5
3.912e+08 0.000 22050.0 !12-I 8s
c7h15o2-2=c7h14ooh2-1 3.000e+11 0.000
29400.0 !12-I 5p c7h15o2-2=c7h14ooh2-3
2.000e+11 0.000 26850.0 !12-I 5s
c7h15o2-2=c7h14ooh2-4 2.500e+10
```

Elementary reaction kinetics



When do we need to understand detailed chemistry?

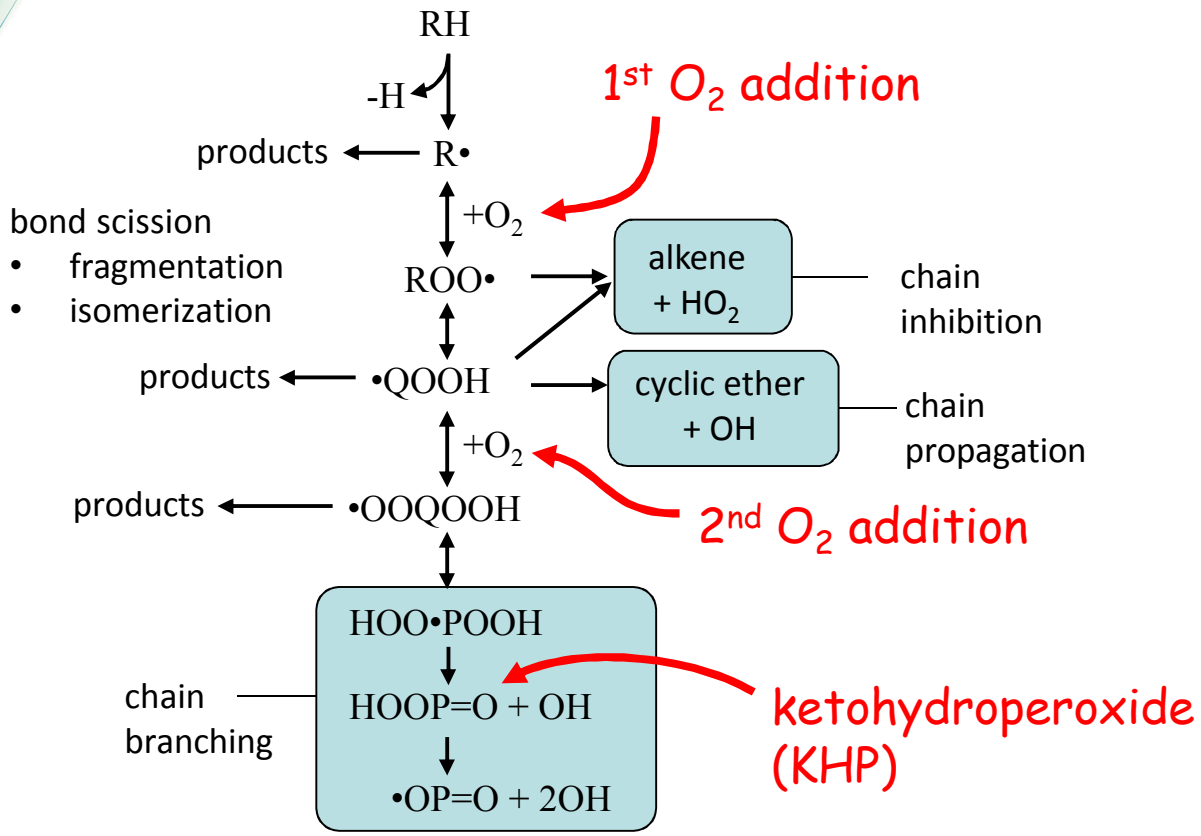
- Pollutant formation
- Autoignition

Why do we need it?

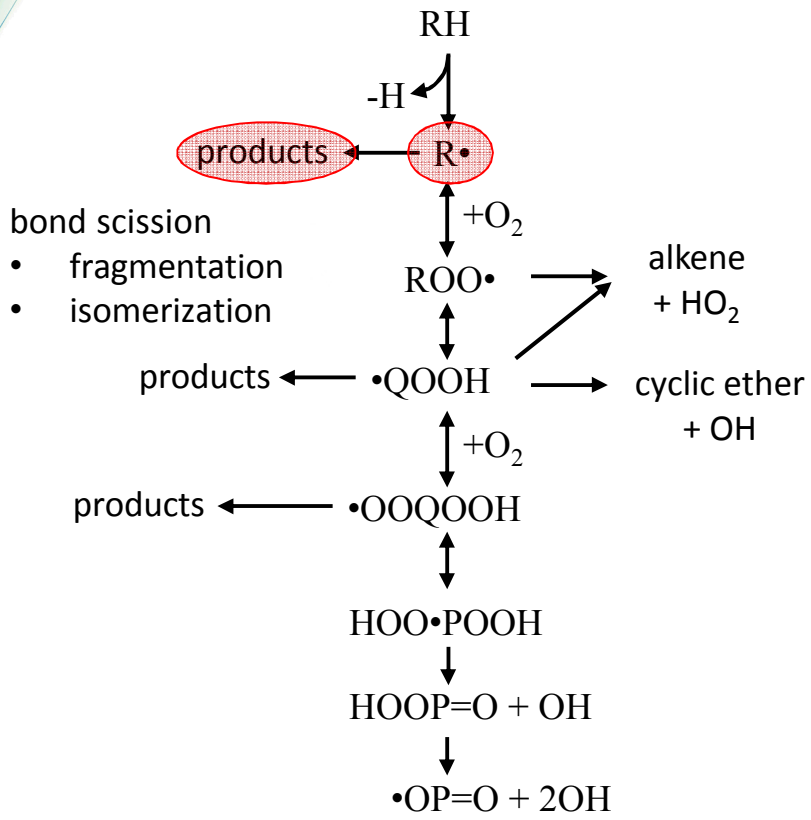
- Model extrapolation
- Model development for new fuel class (biofuels…)

Low-*T* oxidation chemistry

(a moderately – detailed view)



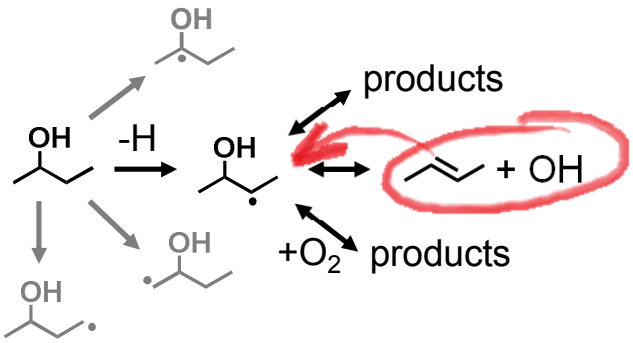
- Detailed probing of primary products and intermediates is key to constraining models
- Many unstable or metastable species – time-resolved probing is important

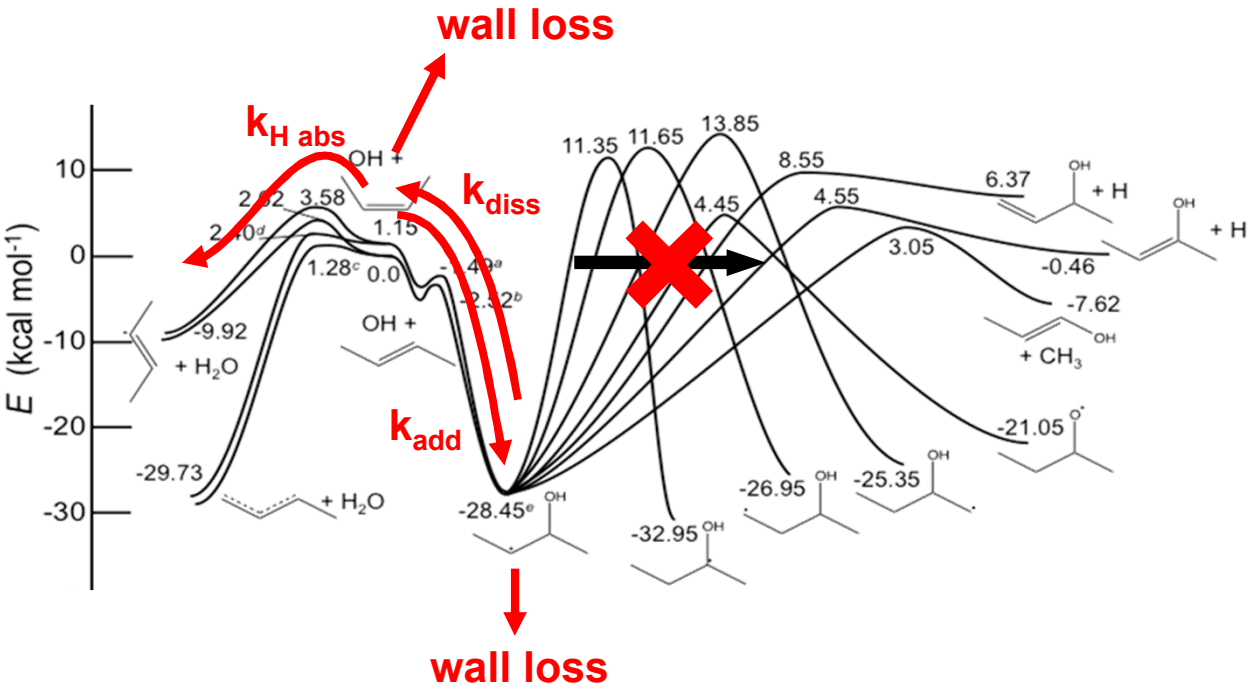


- Thermal decomposition of β-hydroxybutyl radicals
- QOOH decomposition pathways in propane oxidation
- Competing channels in the 1st- and 2nd-O_2 addition reactions in THF oxidation

How to study isomer-specific reactivity of radical intermediates?

- start with OH + 2-butene
- probe by time-resolved OH LIF



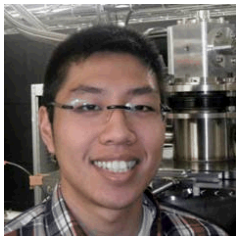


theory:

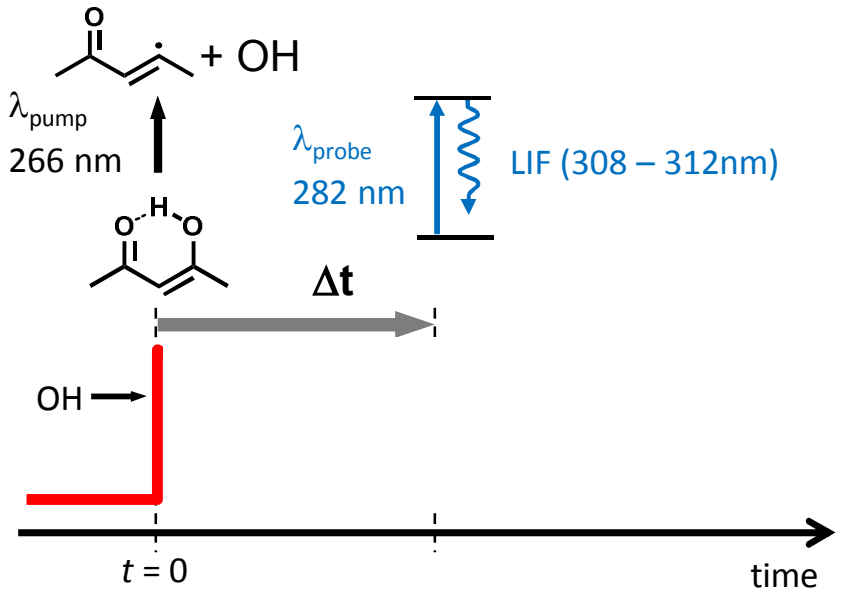
Judit Zádor

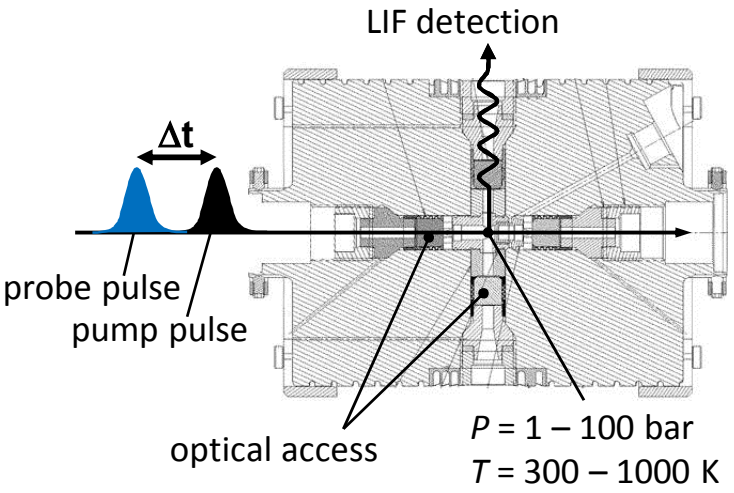
High-*P* laser-induced fluorescence OH probing

Justin Kwok



Ivan Antonov





- OH produced by 266-nm photolysis of acetylacetone in He bath
- OH kinetics probed by LIF

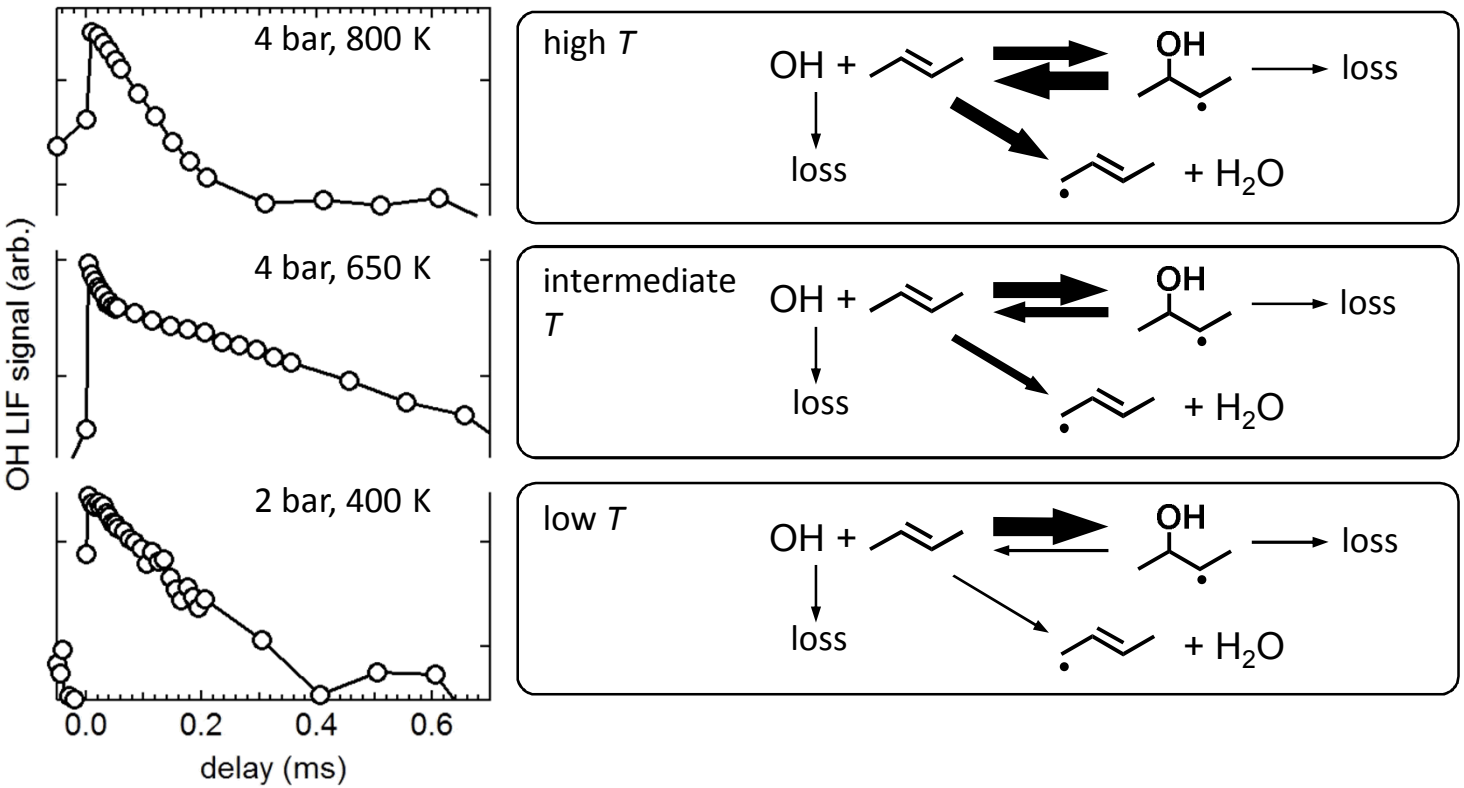
  excite (0,1) $A^2\Sigma^+ \leftarrow X^2\Pi$ 282 nm

  LIF (0,0) and (1,1) 308 – 312 nm
- Experimental conditions

  P = 1 – 20 bar

  T = 400 – 800 K

OH + *cis*-2-butene



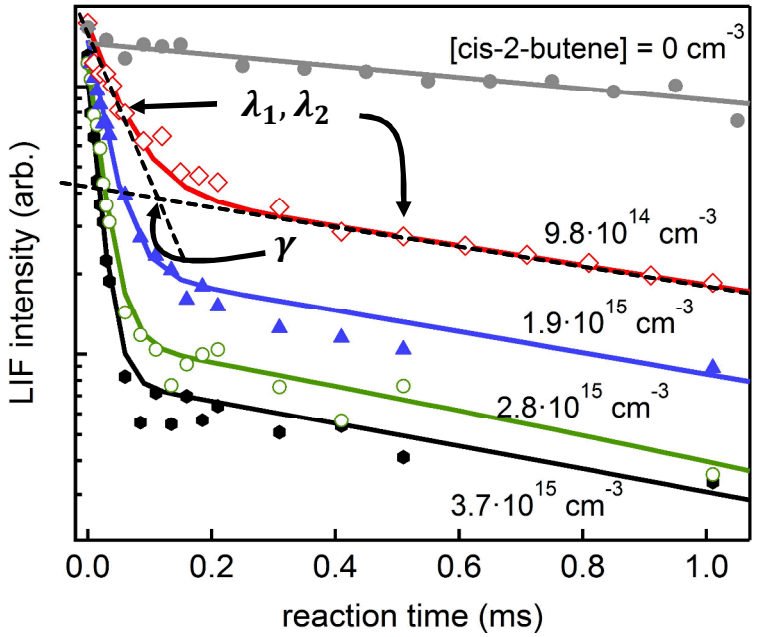
- OH LIF probing reveals competition between

  Irreversible loss
  (H abstraction, wall losses)

  vs.

  Establishing equilibrium
  OH + butene ⇄ 3-hydroxy-2-butyl

OH + *cis*-2-butene, P = 2 bar, T = 600 K

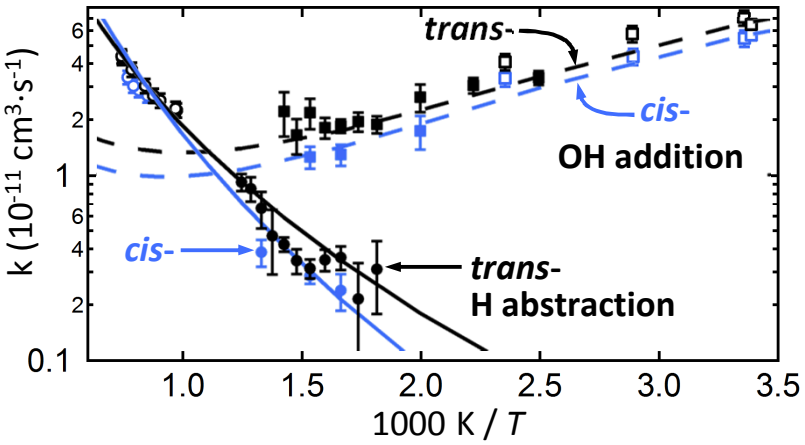


$$\frac{OH_t}{OH_0} = \frac{(\gamma - \lambda_1)\exp(-\lambda_1 t) - (\gamma - \lambda_2)\exp(-\lambda_2 t)}{\lambda_2 - \lambda_1}$$

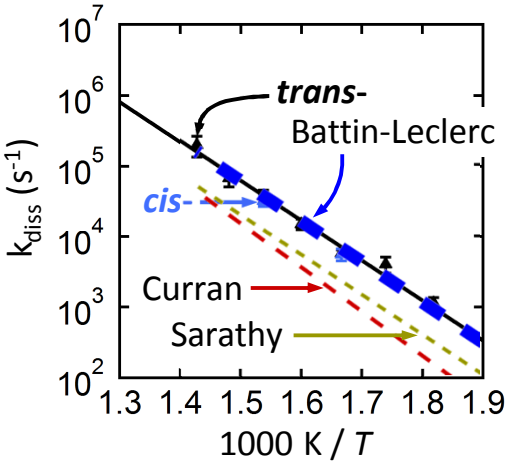
- 3 fit parameters ↔ 5 rate coefficients
- Vary experimental conditions, constrain fits
  - k_{add} – depends on *T*, *P*, [butene]
  - k_{diss} – depends on *T*, *P*
  - $k_{H\ abs}$ – depends on *T*, *P*, [butene]
  - wall loss – depends on *P, T (weakly)*

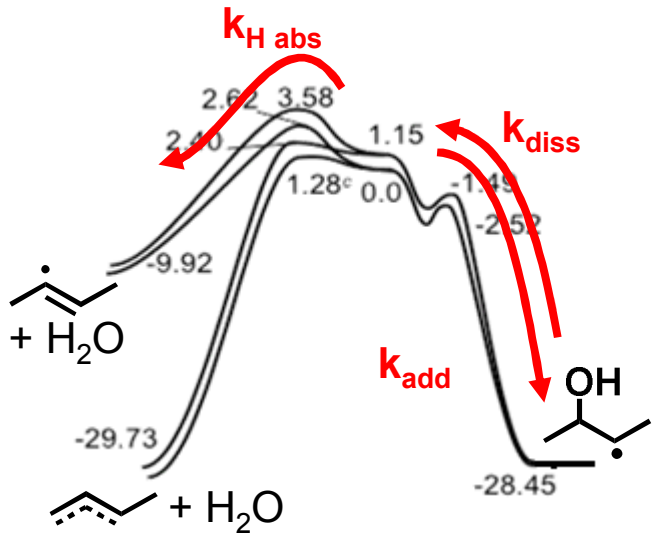
T (K)	P (bar)	[2-butene] 10^{14} cm^{-3}	# traces
trans-2-butene			
400	2	0 – 83	37
450	2	0 – 42	44
500	2	0 – 21	35
550	2	0 – 4.3	19
575	1,3	0 – 35	35
600	2	0 – 59	31
625	2	0 – 31	30
650	1,3	0 – 26	56
675	2,4	14 – 80	22
700	2,4	0 – 140	47
725	4	72 – 41	11
750	4	72 – 40	12
775	4	72 – 21	12
800	4	0 – 22	18
cis-2-butene			
500	1	0 – 88	24
600	2	0 – 37	10
650	2	0 – 110	31
750	2	0 – 19	15

Total OH + 2-butene reaction rate coefficient



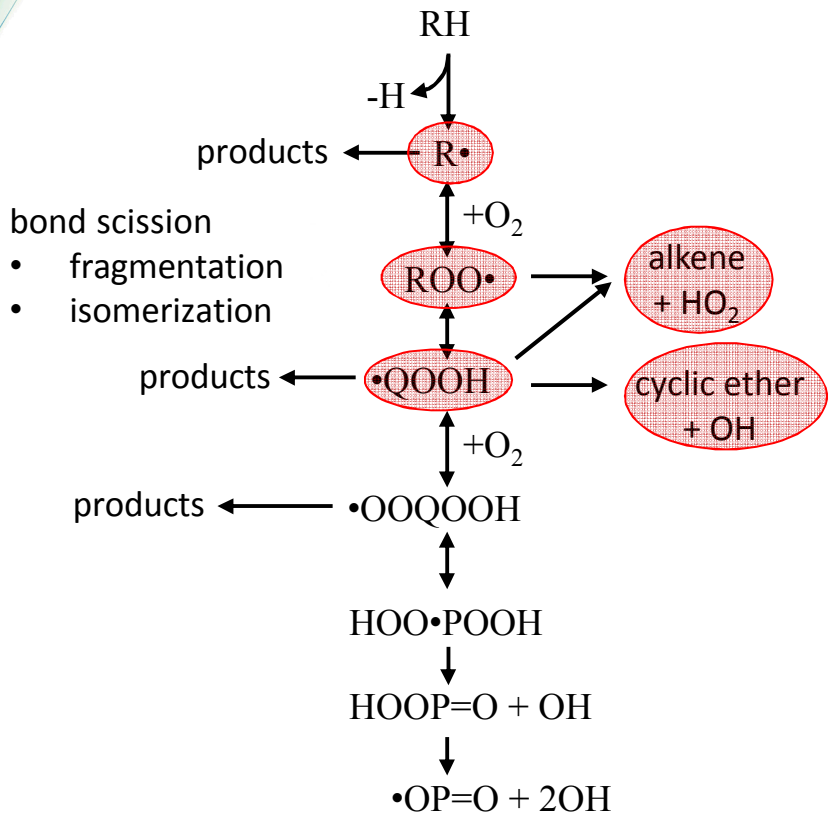
3-hydroxy-2-butyl dissociation





Combination of experiments and theory

- Calculations guide the construction of a core sub-mechanism
- Experimental fitting provides high-*P* limit reaction rate coefficients
- Experiments benchmark master-equation calculations



- Thermal decomposition of β-hydroxybutyl radicals
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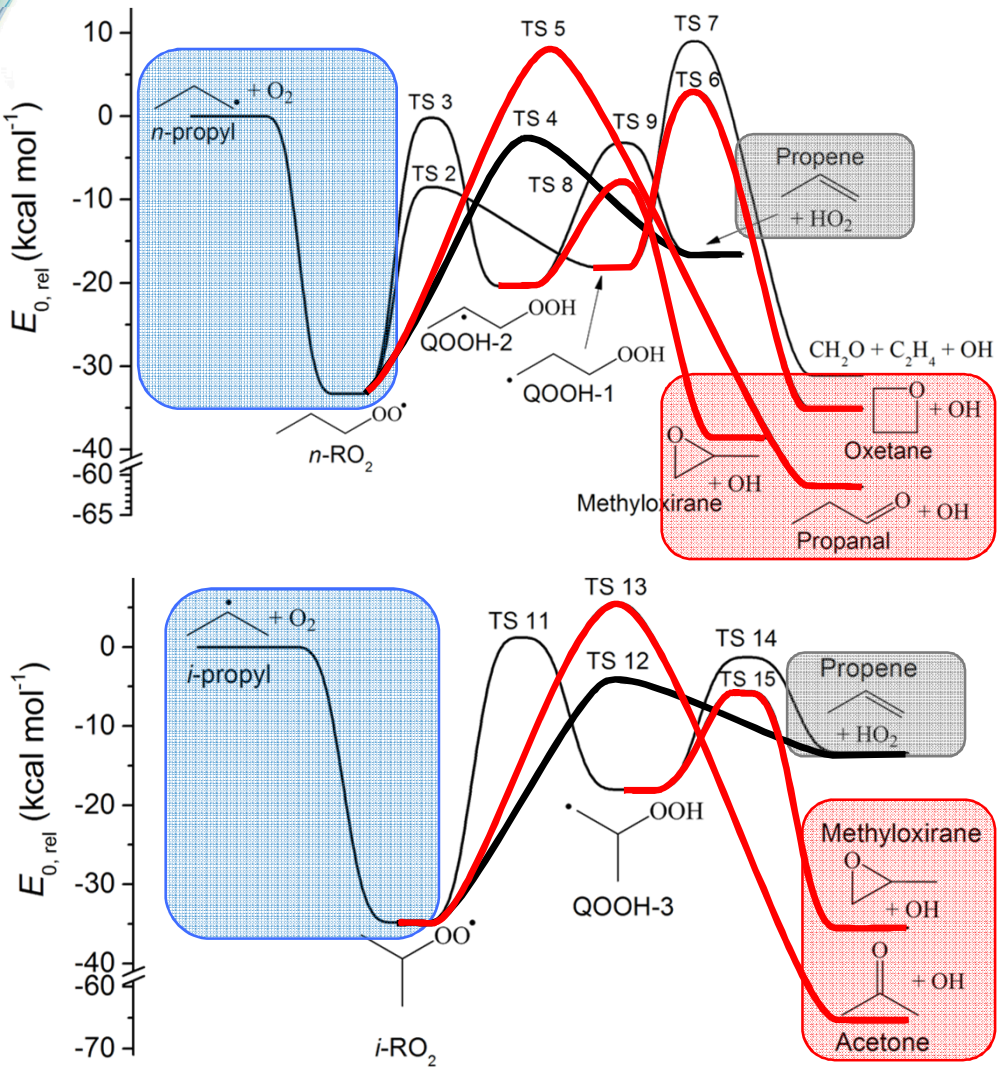
- Competing channels in the 1st- and 2nd-O_2 addition reactions in THF oxidation

Propane: target fuel for Argonne-Sandia HPCC

Low-*T* propane oxidation



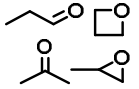
R + O_2

***n*-propyl,** ***i*-propyl**	*t*-resolved mass spectrometry (*Slagle, Gutman*)

HO_2 elimination

propene	*t*-resolved mass spectrometry (*Gutman*) GC (*Walker, Battin-Leclerc*)
HO_2	*t*-resolved laser absorption (*Taatjes*)

OH elimination

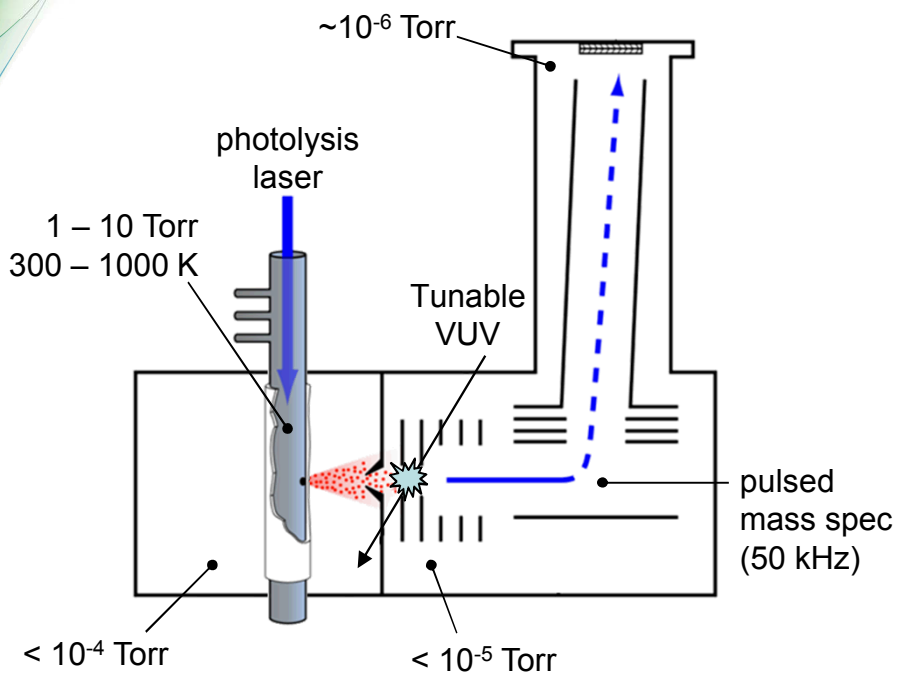
OH	*t*-resolved laser absorption (*Taatjes*)
	GC (*Walker, Battin-Leclerc*)

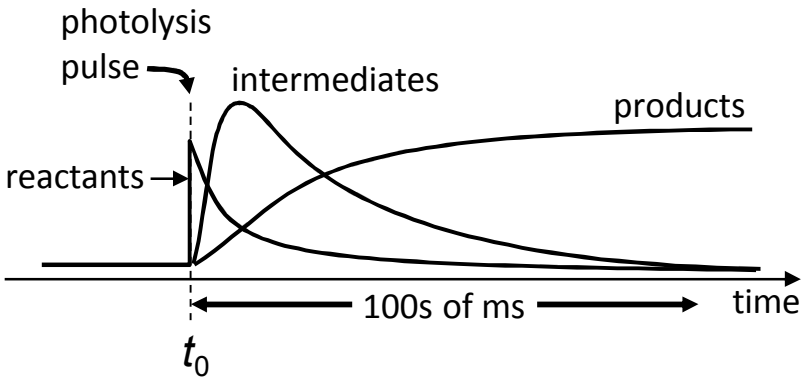
Outstanding questions:

- Conflicting experimental data on C_3H_6O
- Models don't capture *T*-dependence of OH

C. F. Goldsmith, W. H. Green, S.J. Klippenstein, *J. Phys Chem. A*, **2012**, 116, 3325

Multiplexed Photoionization Mass Spectrometry (PIMS)



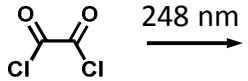


Multiplexed synchrotron PIMS

- Developed by Sandia NL, in collaboration with Lawrence Berkeley Lab's Advanced Light Source
  D. Osborn, C. Taatjes, S. Leone, M. Ahmed

Experimental scheme

- Homogeneous flow reactor at constant *T*, *P*
- Laser photolysis Cl – initiated oxidation reactions



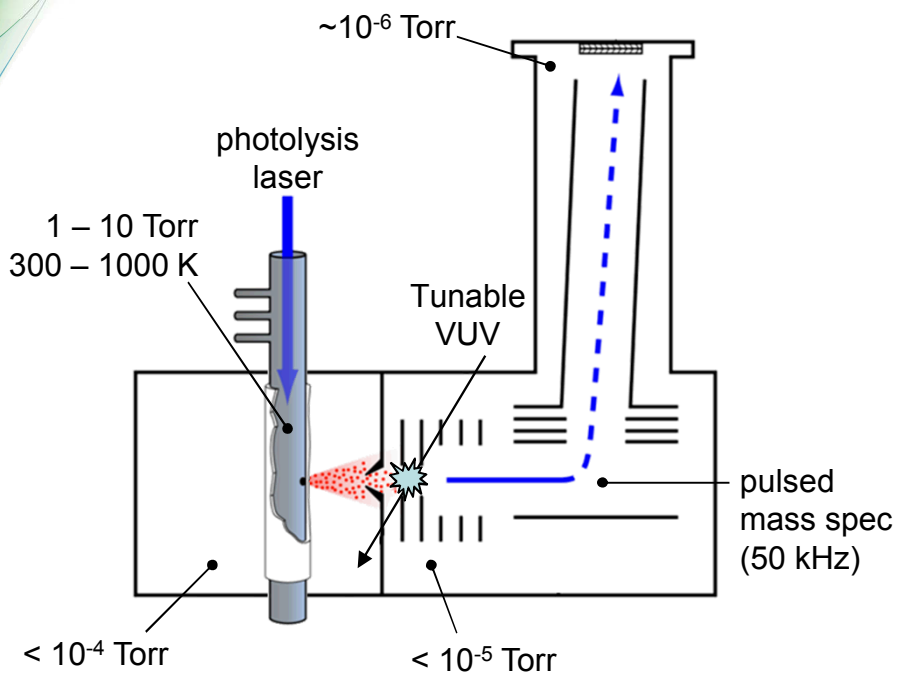
$Cl\cdot + C_3H_8 \longrightarrow$ *n*-$C_3H_7\cdot$ ~50%, *i*-$C_3H_7\cdot$ ~50% ($\tau < 10$ µs)

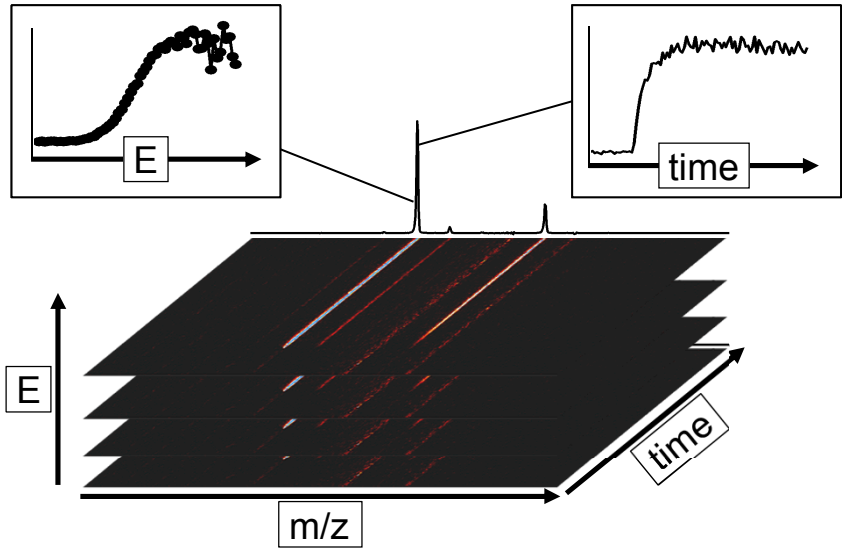
$C_3H_7\cdot + O_2 \longrightarrow$ products (0 – 100s ms)

- Continuous 50-kHz sampling by orthogonal TOF mass spectrometry

  Sensitive (single-ion) near-universal detection
  Multiplexed – complete mass spec every 20 µs
  Time-resolved – can see chemical intermediates
  Tunable VUV ionization – isomer selectivity

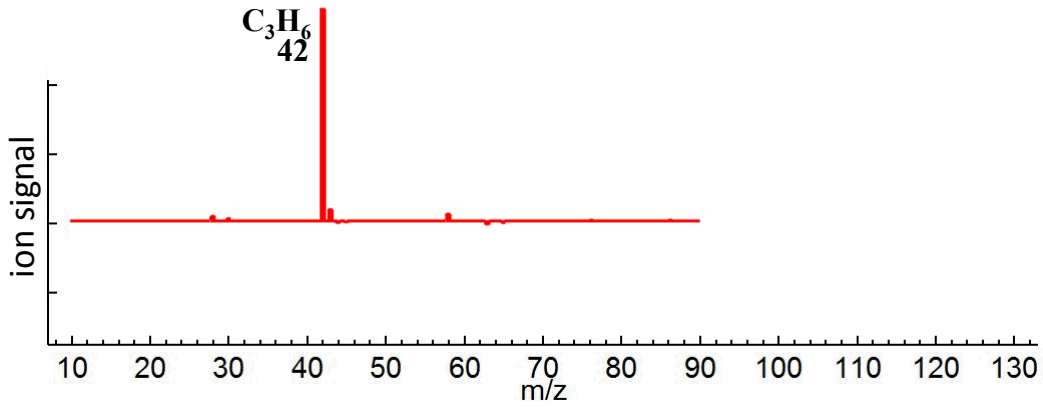
Multiplexed Photoionization Mass Spectrometry (PIMS)





"3-D" experimental dataset

- Ion intensity as a function of *m/z*, *t*, *E*
- photoionization spectra for species identification
- time evolution for kinetics measurements

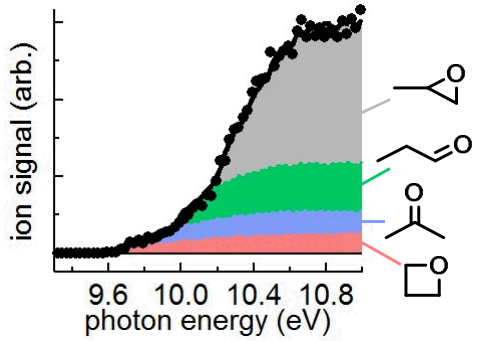


Primary products:

43 *i-*, *n*-propyl
i-, *n*-propyl peroxy

42 propene

58 oxetane
methyloxirane
acetone
propanal



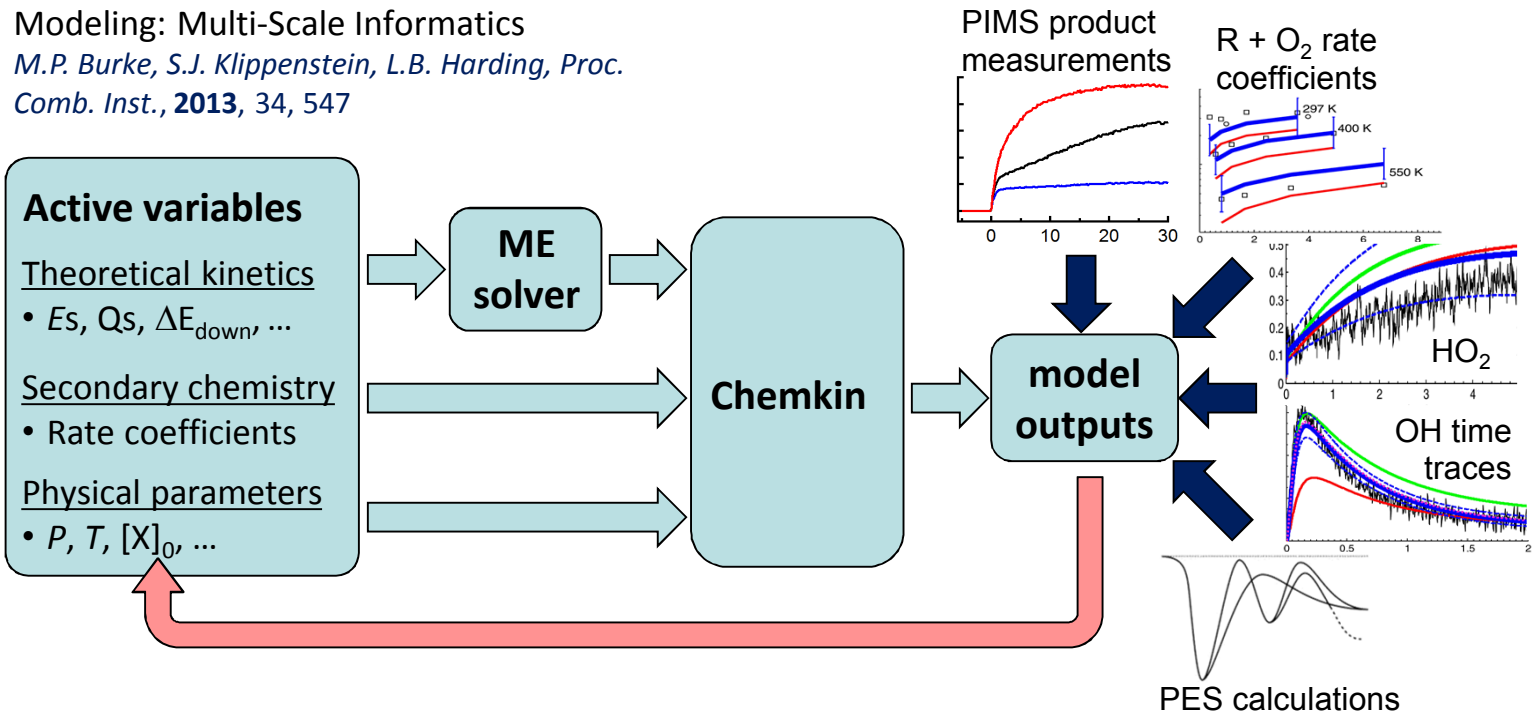
Secondary products:

15 methyl
28 ethene
29 ethyl
ethyl peroxy
30 formaldehyde
34 H_2O_2
44 acetaldehyde
47 methyl peroxy
60 *i-*, *n*-propanol
76 *i-*, *n*-propyl hydroperoxide
86 C_6H_{14} isomers

Multi-Scale Informatics (MSI) Modeling

Modeling: Multi-Scale Informatics

M.P. Burke, S.J. Klippenstein, L.B. Harding, Proc. Comb. Inst., **2013**, 34, 547



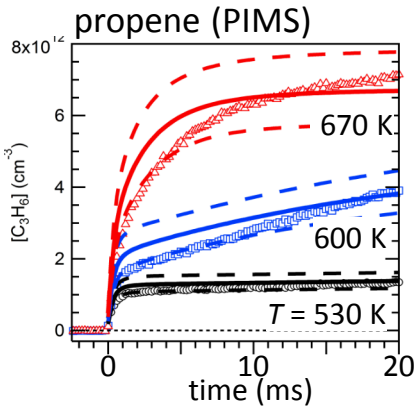
Modeling advances:

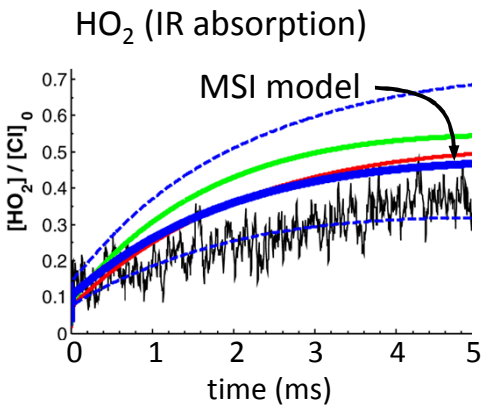
- global optimization against a diverse set of targets
- includes oxetane + OH pathway
- non-Boltzmann energy distribution of reactants and products
- QOOH + O_2 pathways

Michael Burke

Multi-scale modeling solution:

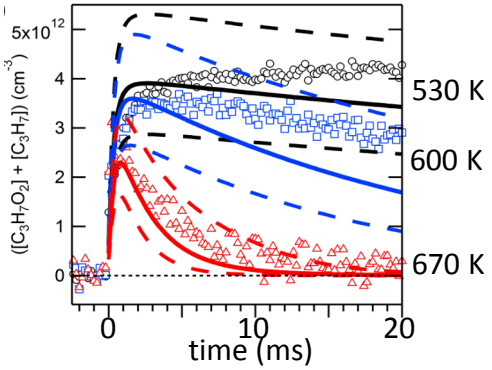
- Major product – propene + HO_2
  - abs. concentration
  - time evolution



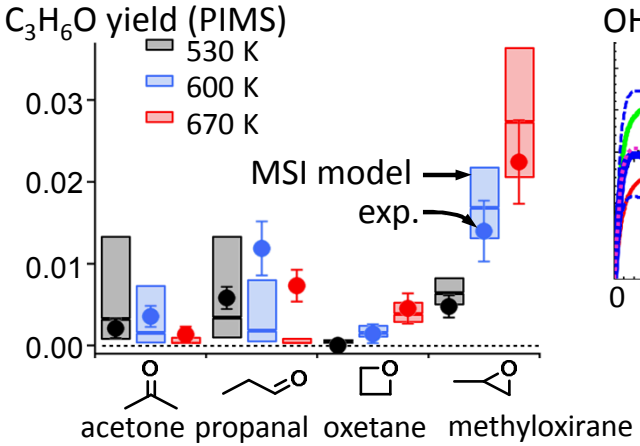


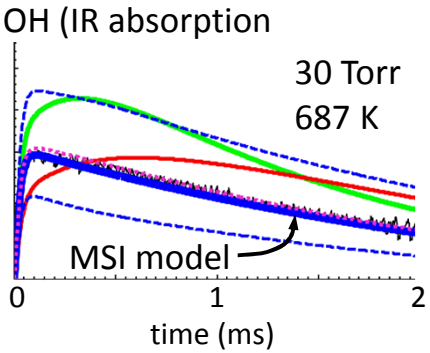
- propyl peroxy
  - no abs. concentration
  - time evolution
  - *T*-dependence

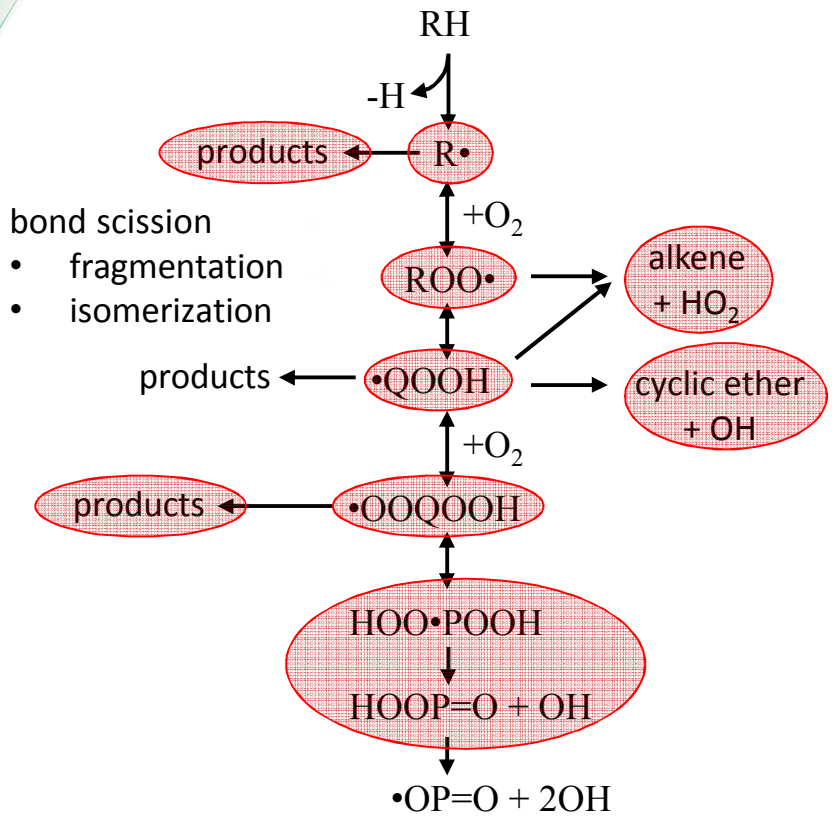
i-RO_2 + *n*-RO_2 (PIMS)



- critical measurement – product yields of C_3H_6O + OH
  - primary products: oxetane, methyloxirane
  - individual probing of OH elimination channels



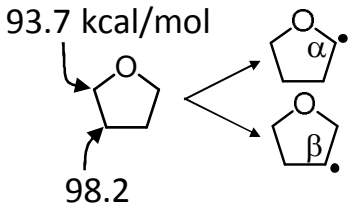




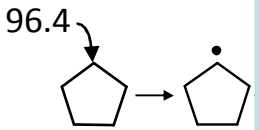
- Thermal decomposition of β-hydroxybutyl radicals
- QOOH decomposition pathways in propane oxidation
- Competing channels in the 1st- and 2nd-O_2 addition reactions in THF oxidation

C-H bond strength

- α-CH bond is 4.5 kcal/mol weaker than β-CH

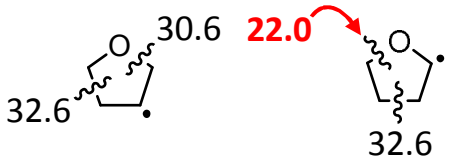


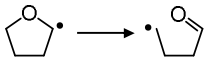
- in cyclopentane all CH bonds equivalent



Ring-opening

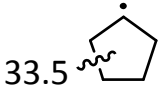
- lowest ring opening barrier ~22 kcal/mol in α-CH

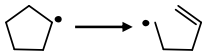




k(700K) ~ 10^7 s^{-1}
Simmie, JPC A, 2012

- ring opening barrier ~33.5 kcal/mol in cyclopentane

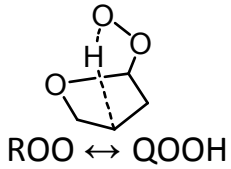




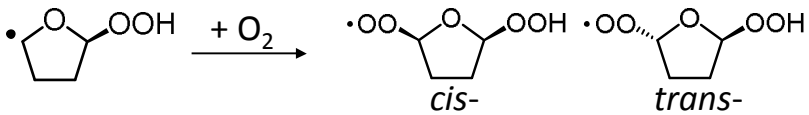
k(700K) = 3.5×10^3 s^{-1}
Manion, PROCI, 2011

Rigid ring structure

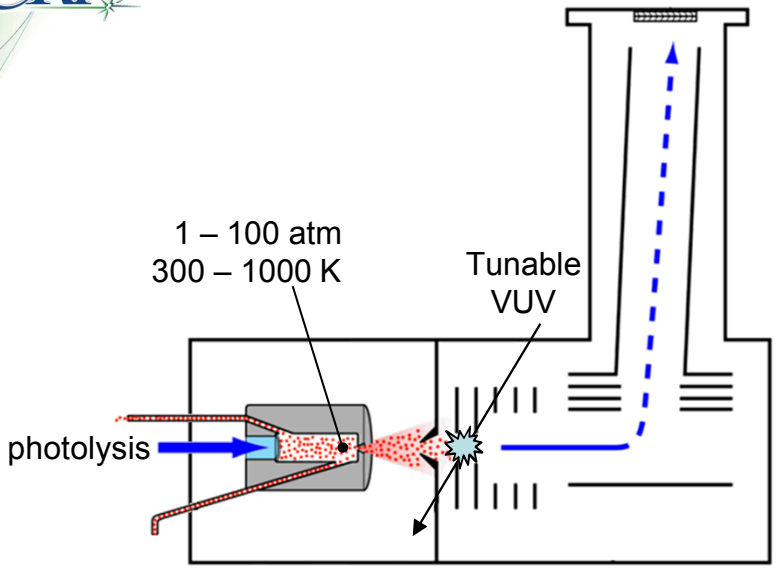
- effects of ring strain on TS energies



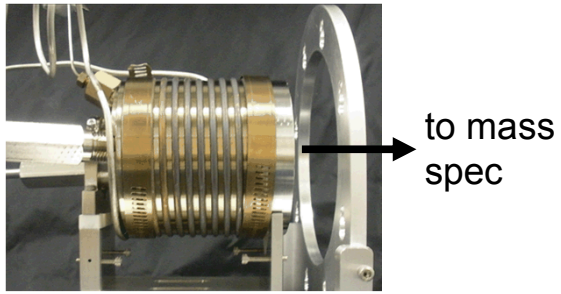
- conformer-dependent reactivity

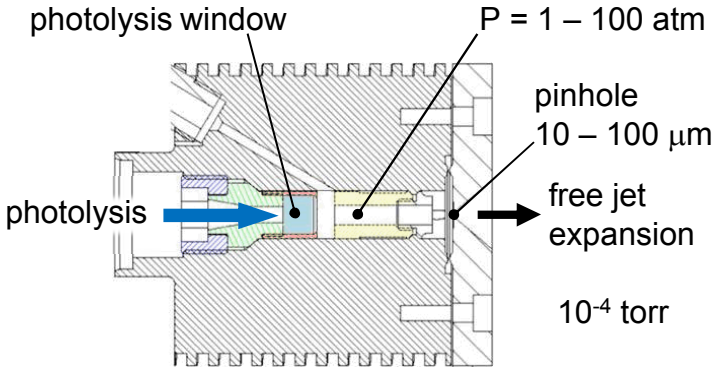


Photoionization Mass Spectrometry at Elevated Pressures

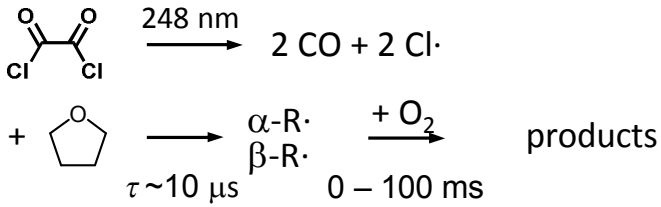


High-*P* reactor (version 1.0)





Cl – initiated oxidation of THF



Experimental conditions

- *P* = 10 – 2000 Torr
- *T* = 400 – 700 K

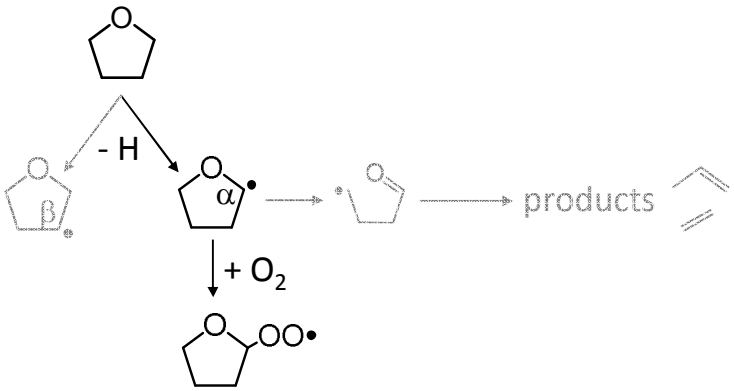
Ivan Antonov

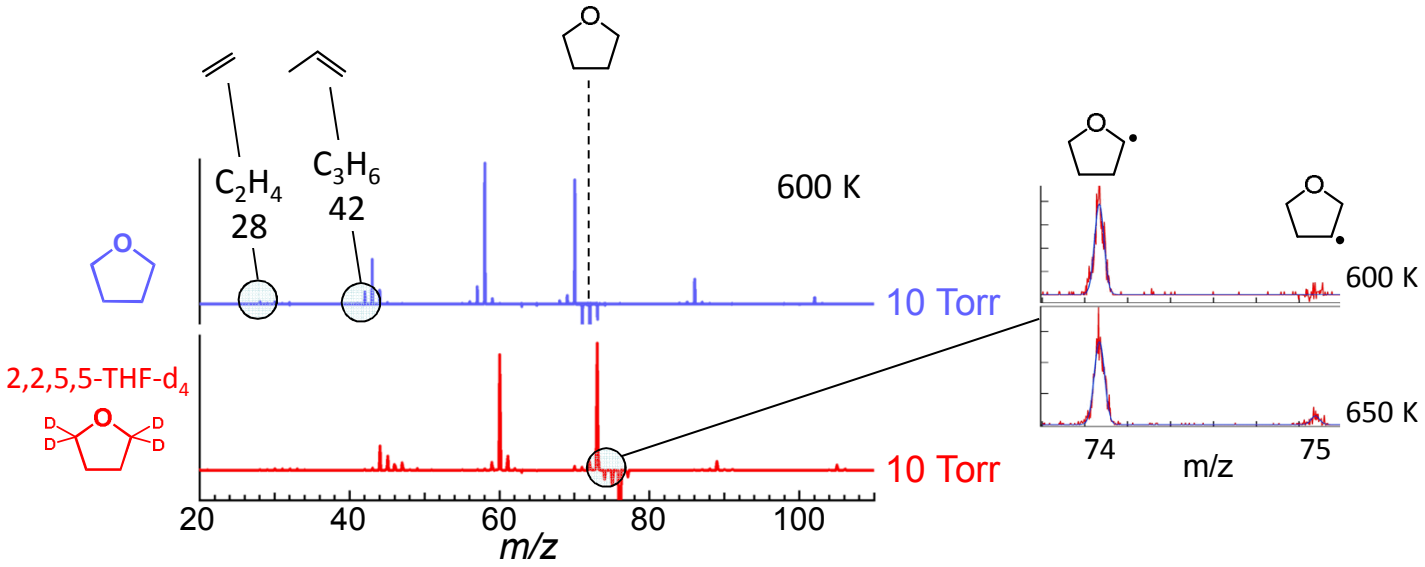
initiation reactions

- almost exclusively α-THF-yl at $T \leq 700K$

ring-opening

- < 5% at $T \leq 650K$





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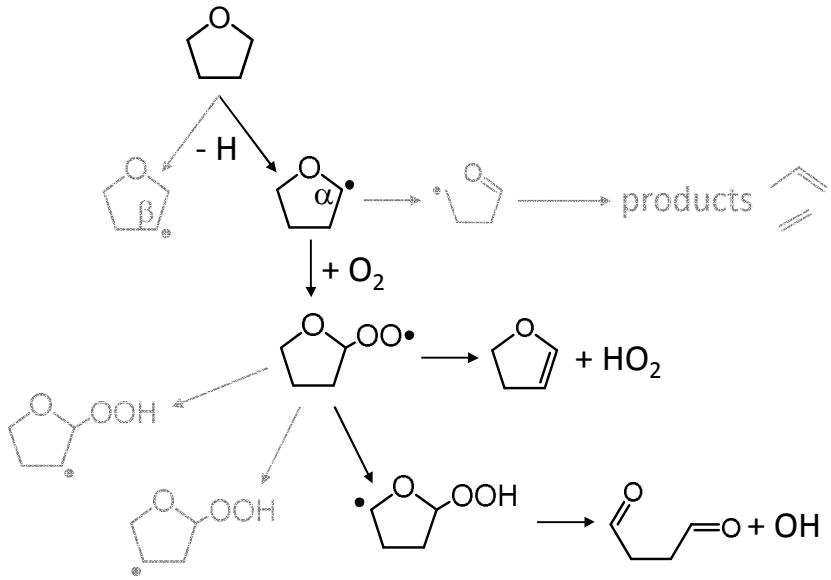
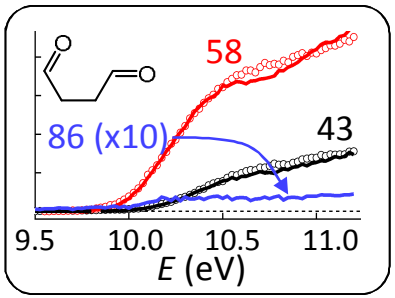
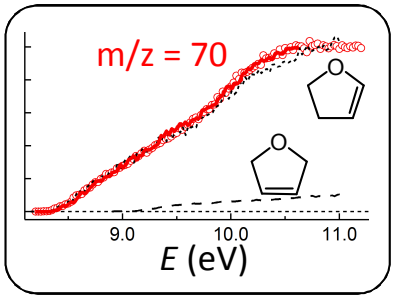
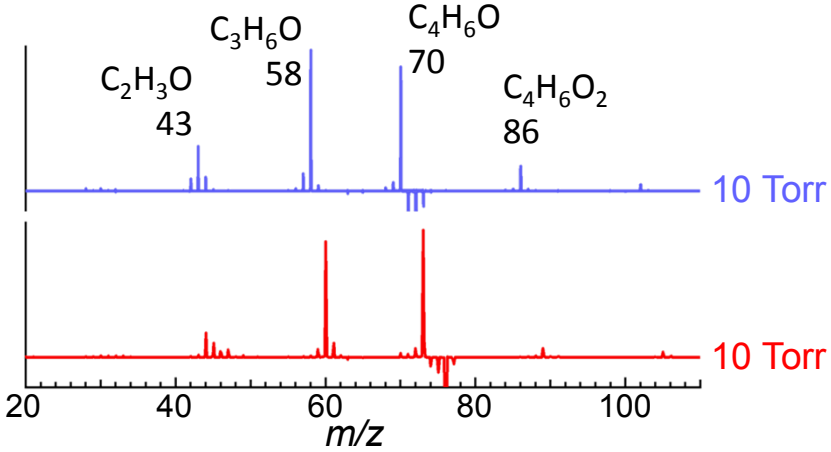
α-R + O_2 products

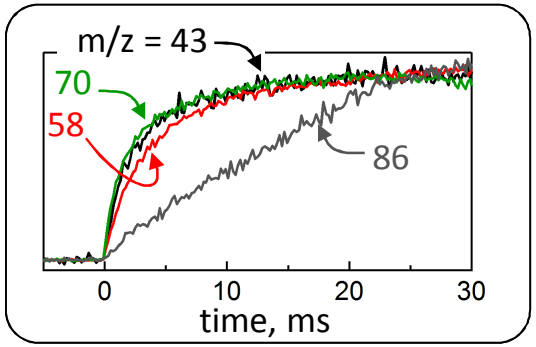
- α-ROO → 2,3-DHF + HO_2 ~20%
- α-ROO → αα'-QOOH → butanedial + OH ~70%











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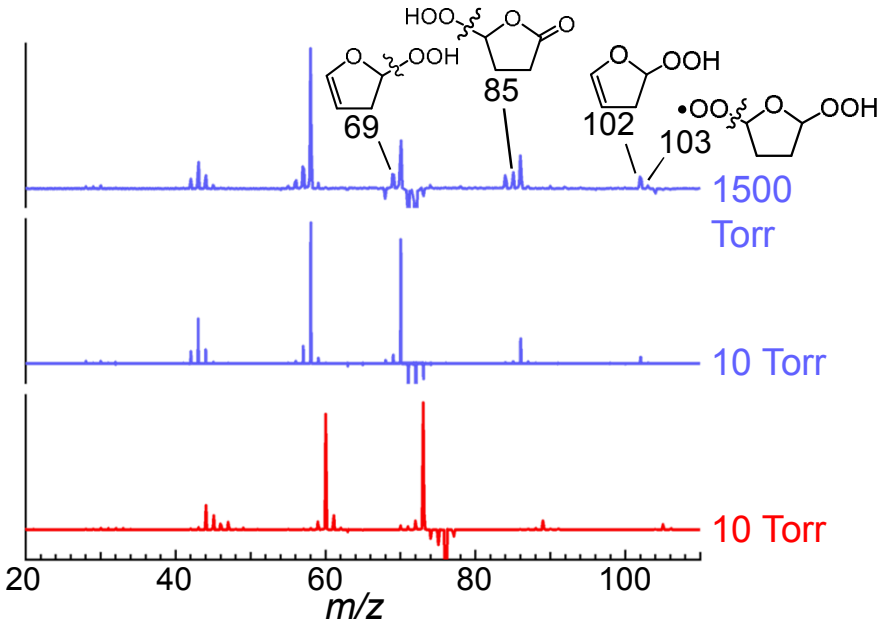
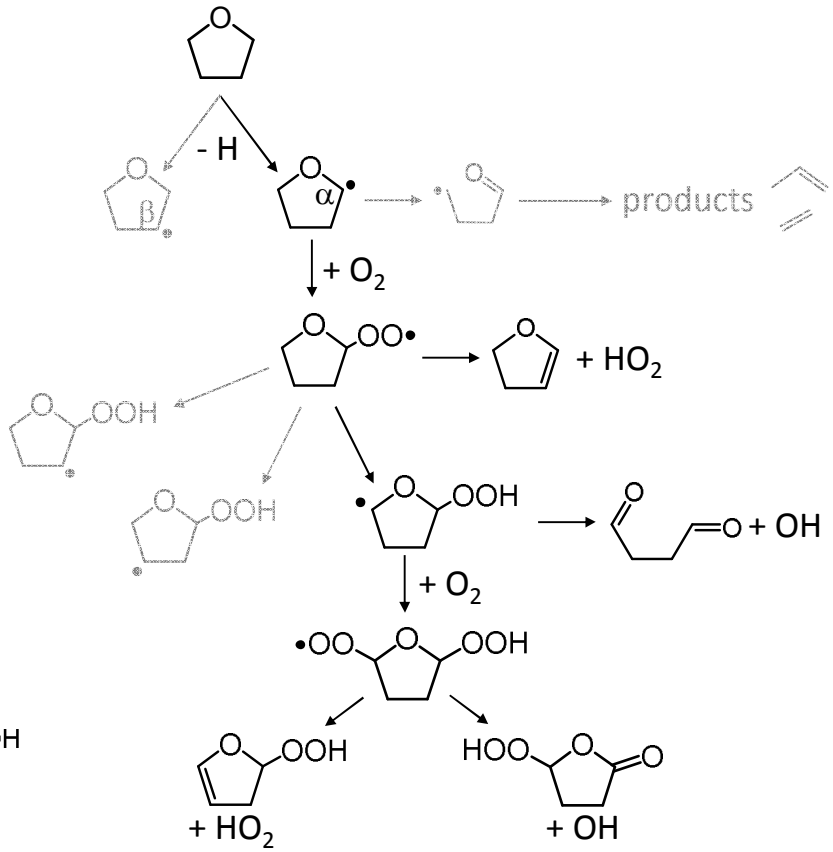
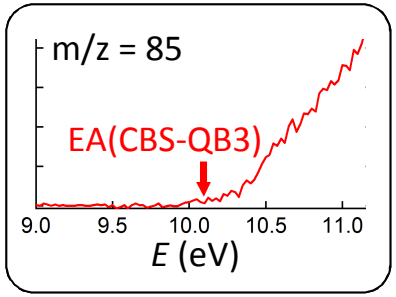
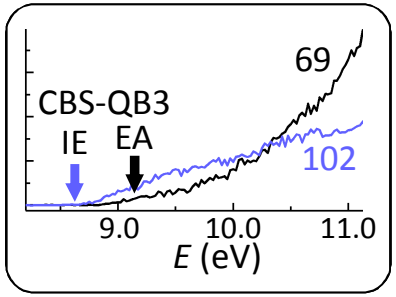
αα'-QOOH + O_2 products

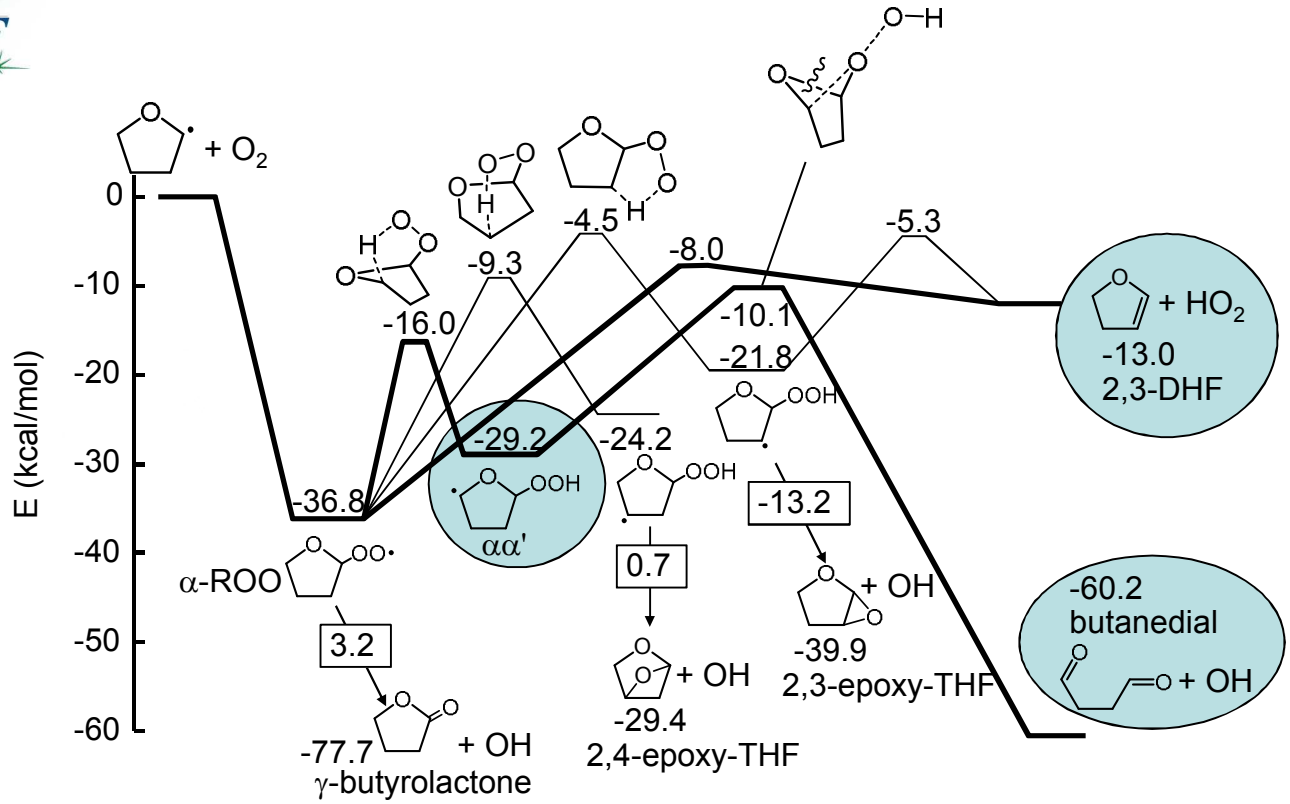
- αα'-QOOH + O_2 → GBL-OOH + OH
- αα'-QOOH + O_2 → 2,3-DHF-OOH + HO_2









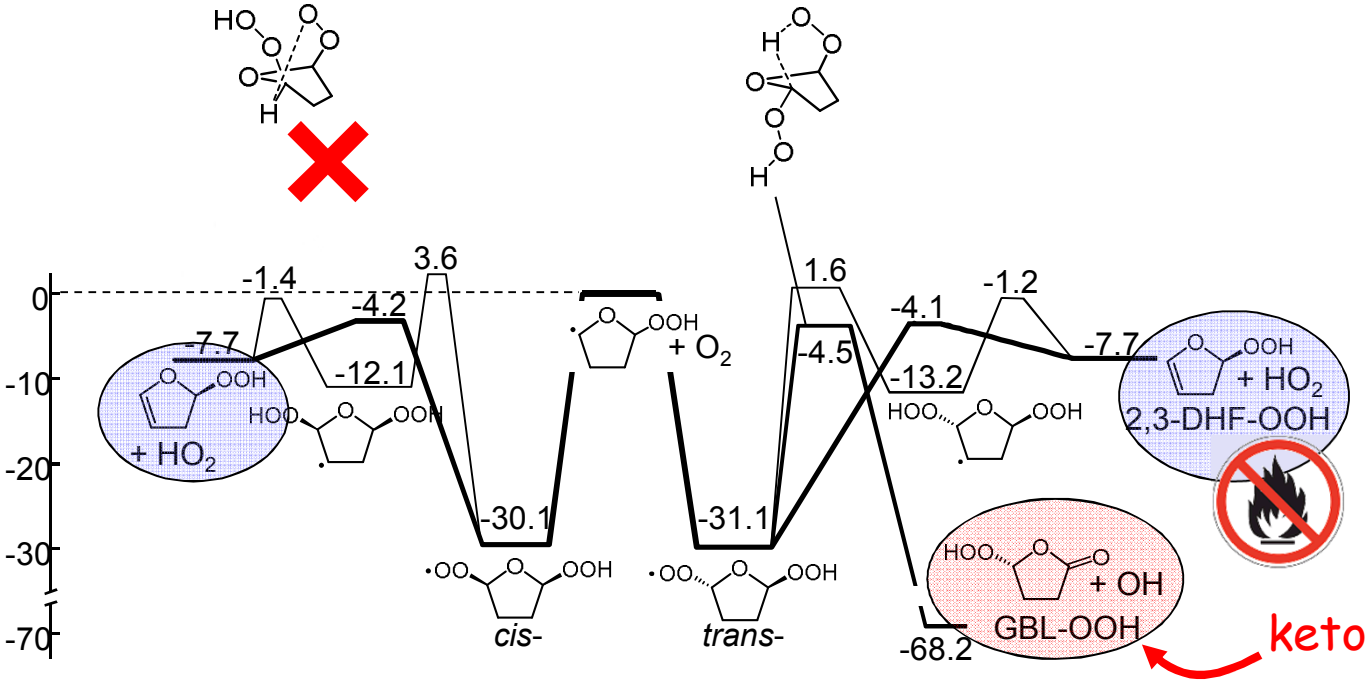



Ivan Antonov


Judit Zádor

Automated PES exploration using Kinbot (J. Zádor)

- Nearest-neighbor search with high-energy cut-off
- Stationary points optimized at CBS-QB3
- α-R + O_2: main products – 2,3-DHF + HO_2
  butanedial + OH
- αα'-QOOH dominant due to weak α-C–H bond
- low butanedial formation barrier (~5 kcal/mol lower than in alkanes)



ketohydroperoxide analog

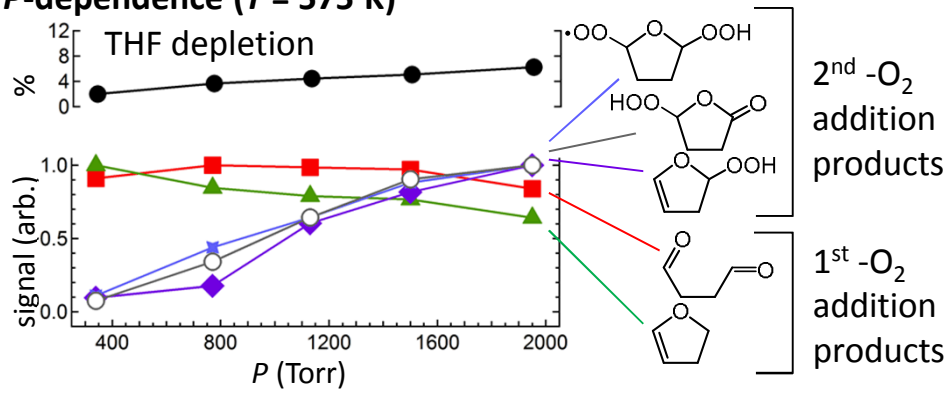
- αα'-QOOH + O_2 main products – 2,3-DHF-OOH + HO_2
  GBL-OOH+ OH
- distinct reactivity for *cis*-OOQOOH and *trans*-OOQOOH
- DHF-OOH + HO_2 directly competes with GBL-OOH + OH
- expanding studies on 2-methyl- and 3-methyl THF
  competing pathways are a general feature of cyclic ethers, must be included in low-*T* oxidation models

Model development targets

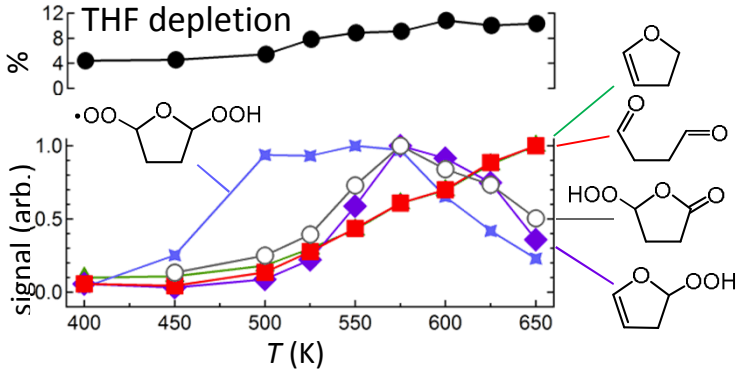
- Incorporate competing OOQOOH reaction pathways
- *P*-, *T*- dependence

- OH, HO_2 probing
- quantification of major products: butanedial, GBL-OOH, DHF-OOH

***P*-dependence (*T* = 575 K)**

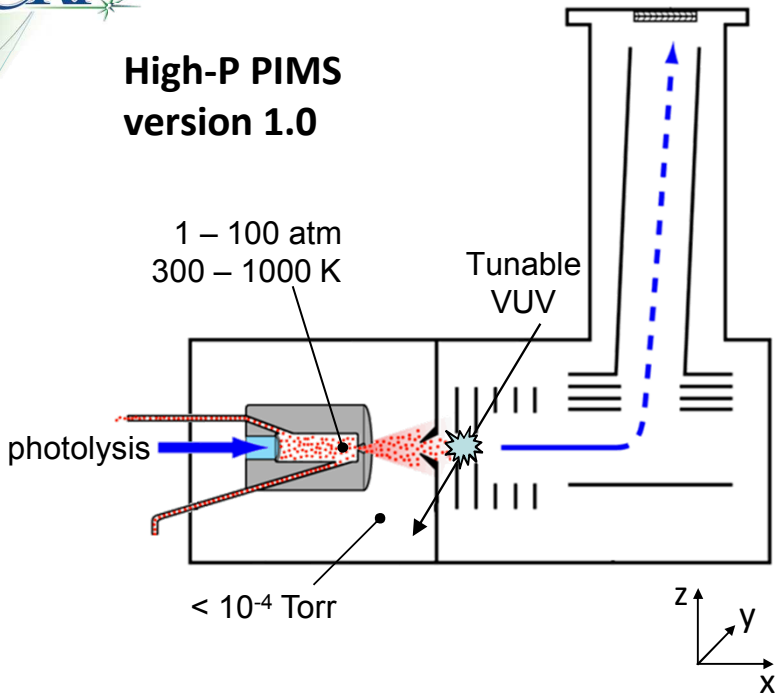


***T*-dependence (*P* = 1500 Torr)**



Extending High-P PIMS measurements to engine-relevant pressures

High-P PIMS version 1.0



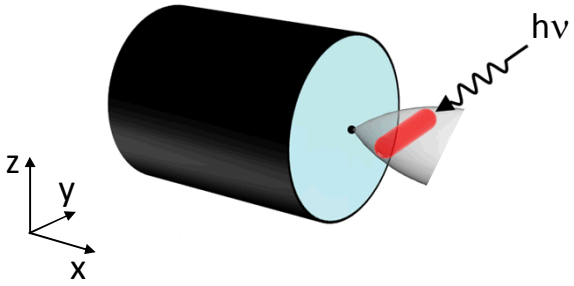
Experimental challenge:

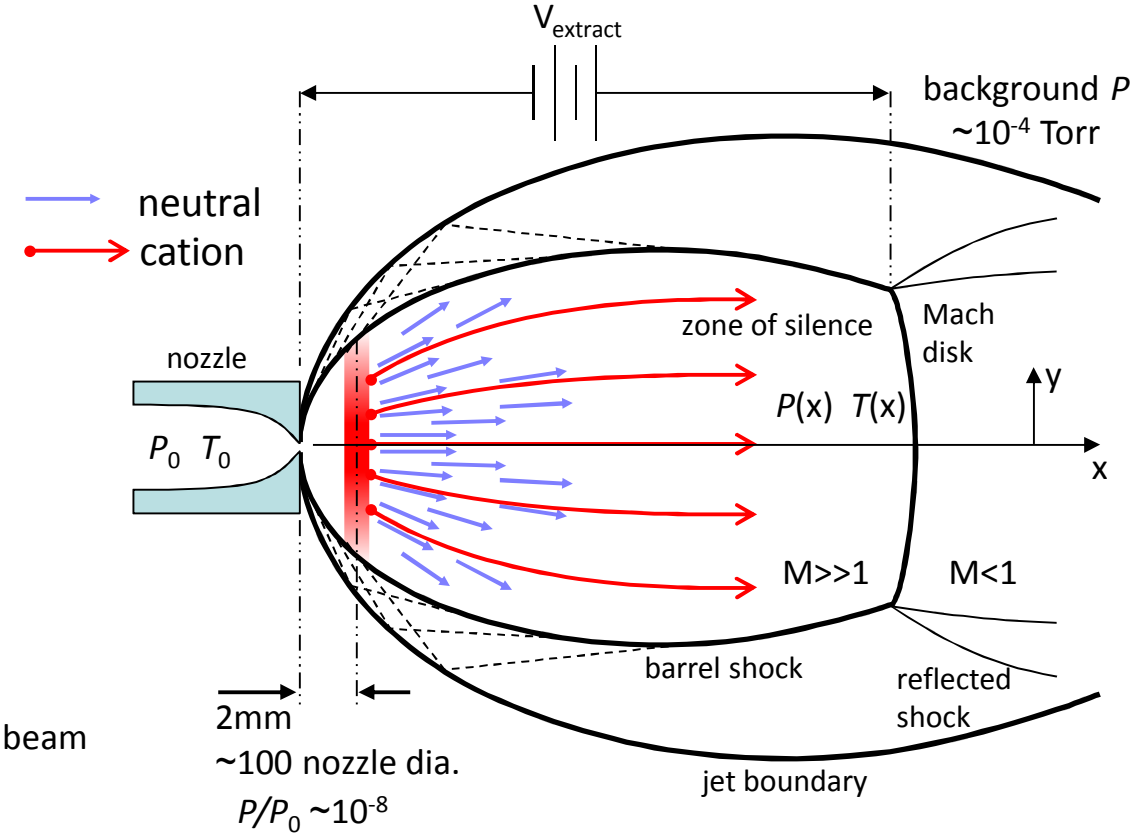
- Instrument sensitivity
  detection limit of ~10^{11} cm^{-3} (~1% product yields)
  - ~3 ppm at 1 Torr
  - ~4 ppb at 1 atm ← current limit
  - ~40 ppt at 100 atm

Solution: high-density ionization

- increase ion yields
  $\rho \sim 1/x^2$ (x – distance from nozzle)

- extract ions without inducing collisions
  custom ion guides
  custom time-of flight mass spectrometer
  collisional simulation of gas expansion

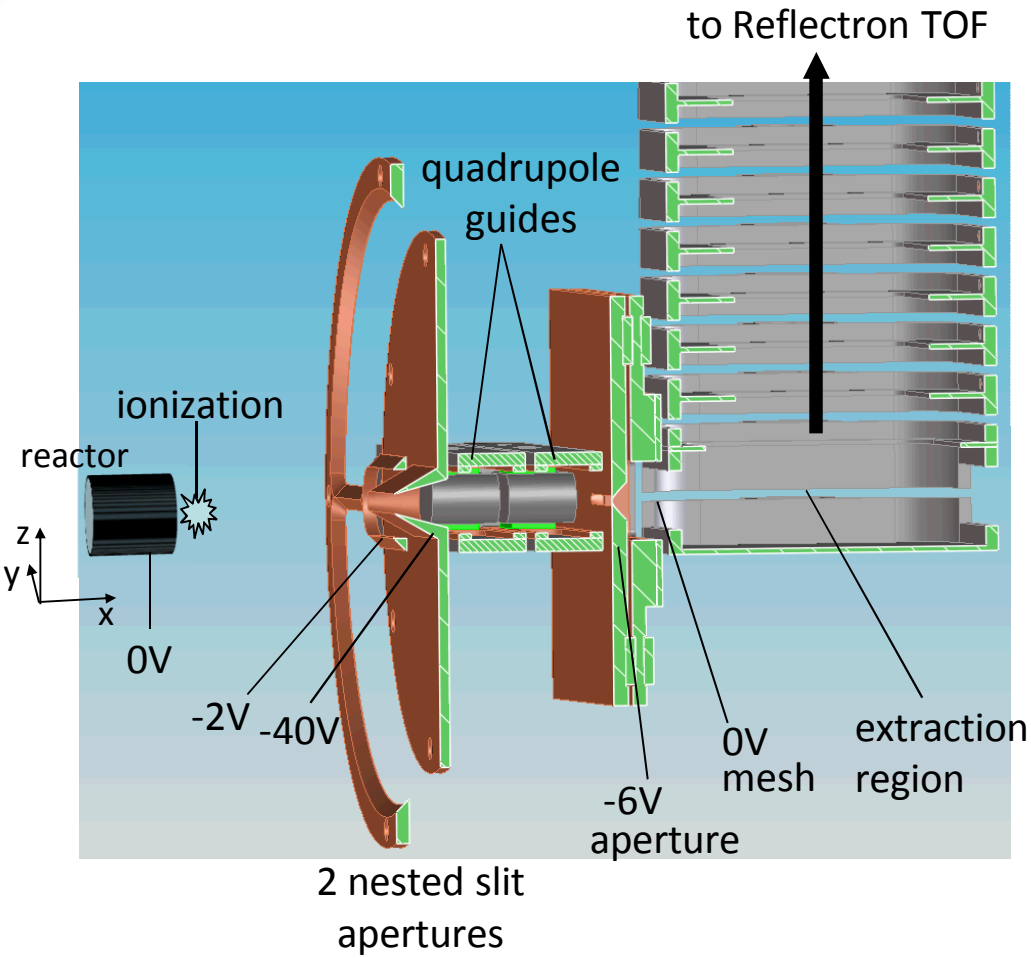


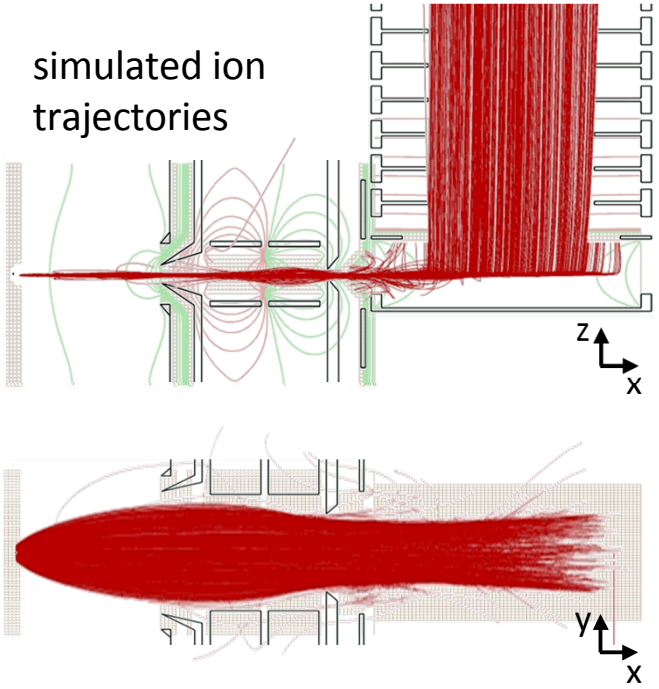


Collisional simulation in free jet expansion

- ion trajectories modeled in SIMION 8
- neutral (bath gas) ρ, T, $\vec{v}$ based on empirical molecular beam formulae
- ionization creates highly divergent ion beam
  large Δy, Δv_y
- "soft" ion extraction by electrostatic field
- additional Monte-Carlo simulations of collisions with bath gas

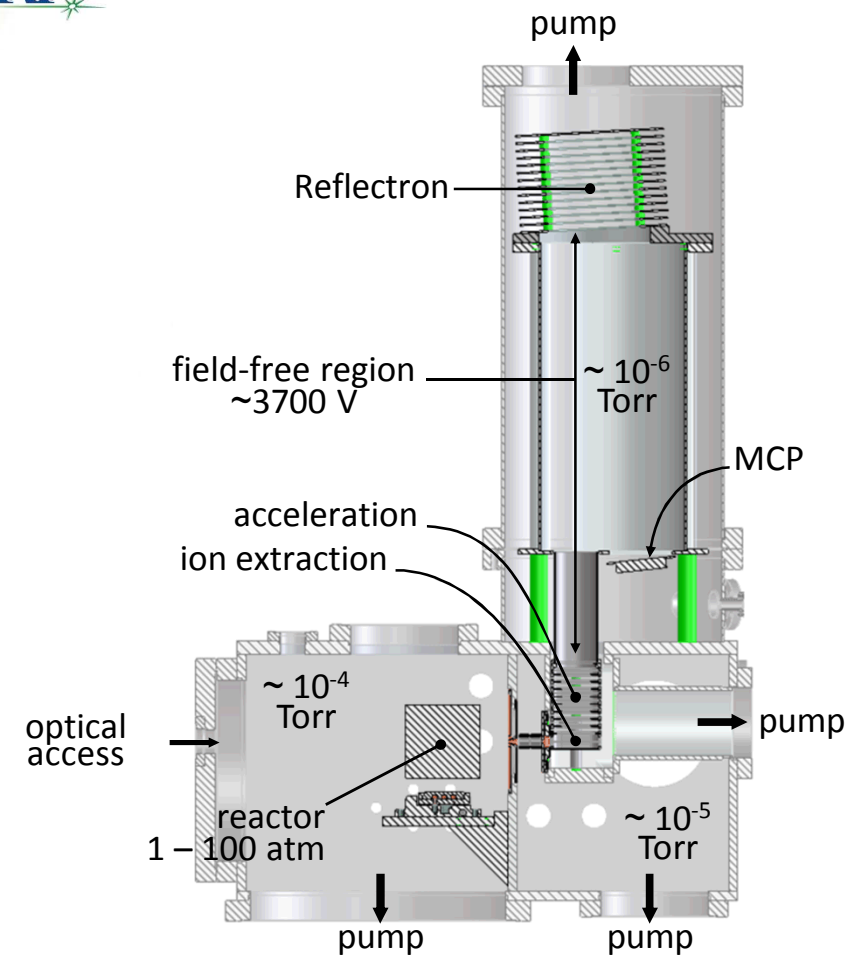
Optimized Mass Spectrometer Design

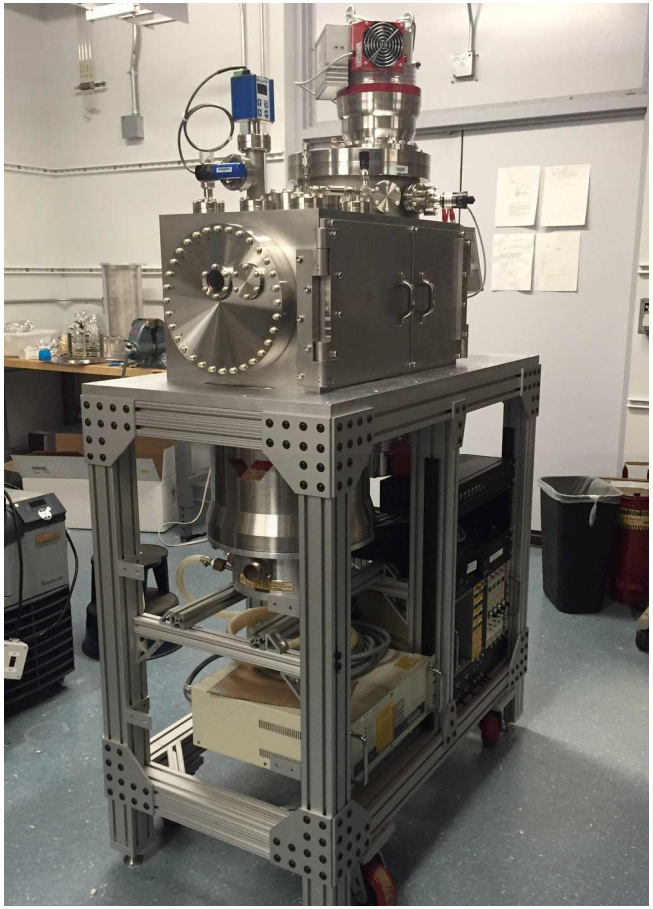




- compromise between signal intensity and mass resolution
- "typical" molecule of mass 56:
  - average # of collisions ~0.2
  - m/Δm = 1600
  - collection efficiency ~0.5

Optimized Mass Spectrometer Design





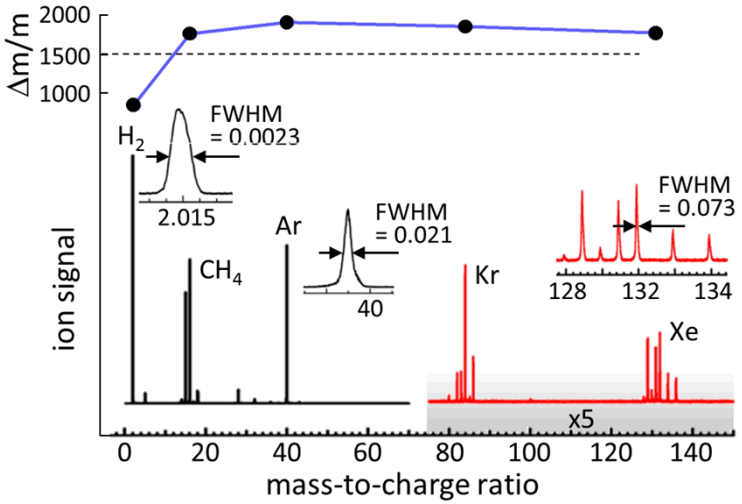
in preparation for first field campaign at LBL, January 2016

- Self-contained, mobile experiment
- Interfaces with Lawrence Berkeley Lab's Advanced Light Source – tunable VUV ionization at Beamline 9.0.2
- can be operated in a lab using discharge lamps

High-P PIMS, version 2.0

- Commissioned at Sandia, January 2016
- First successful test at LBL, January 2016

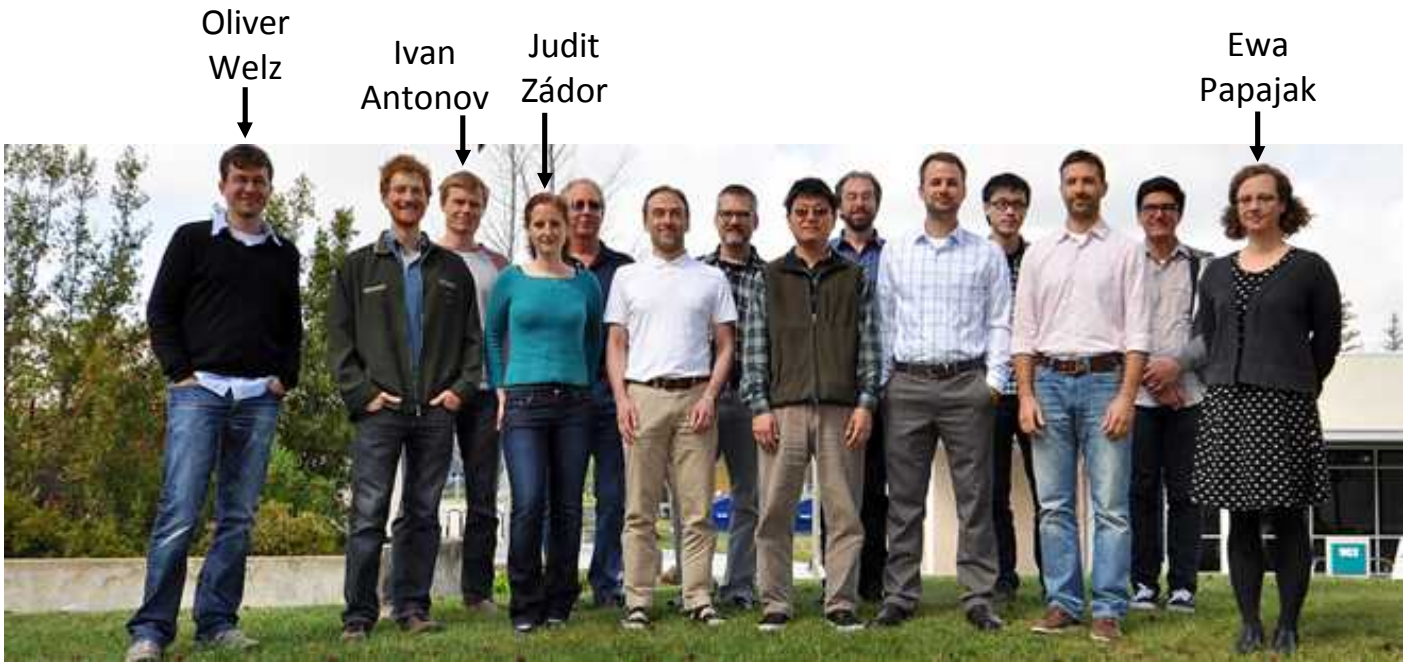
- Performance benchmarks – mass resolution, detection sensitivity
  - ➢ Factor of 100 signal increase over first-generation prototype
  - ➢ m/Δm >1800 for up to m/z = 128 – 136 (Xe isotopes)



- Extends the range of accessible experimental conditions to *P* ~100 atm
- Next field campaign – December 2016

Thank you

Collaborators (CRF, Sandia NL, and ALS, Lawrence Berkely Lab, US)



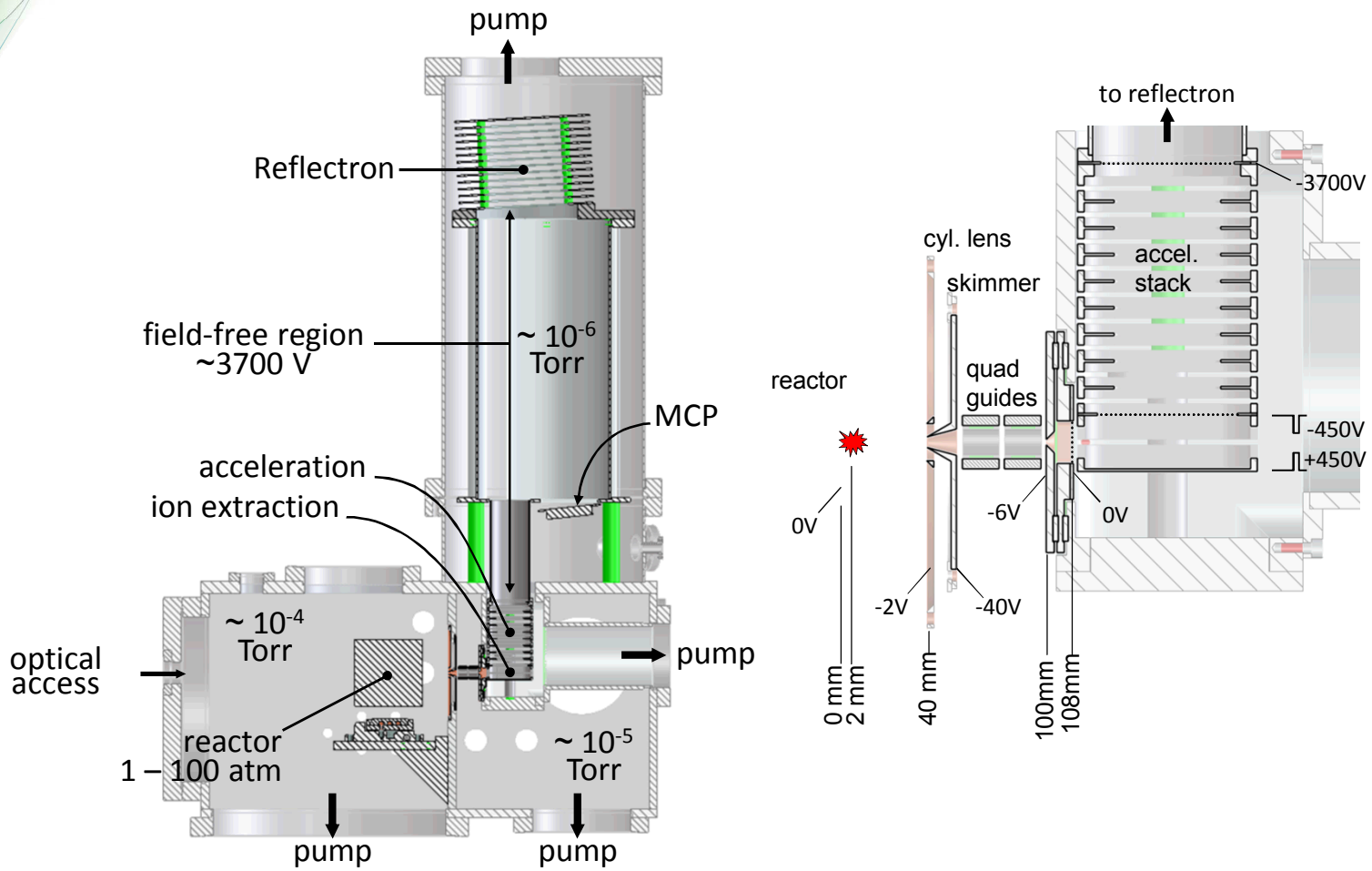
Funding: Argonne-Sandia High-Pressure Combustion Chemistry program
US DOE, Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences

Sandia National Laboratories

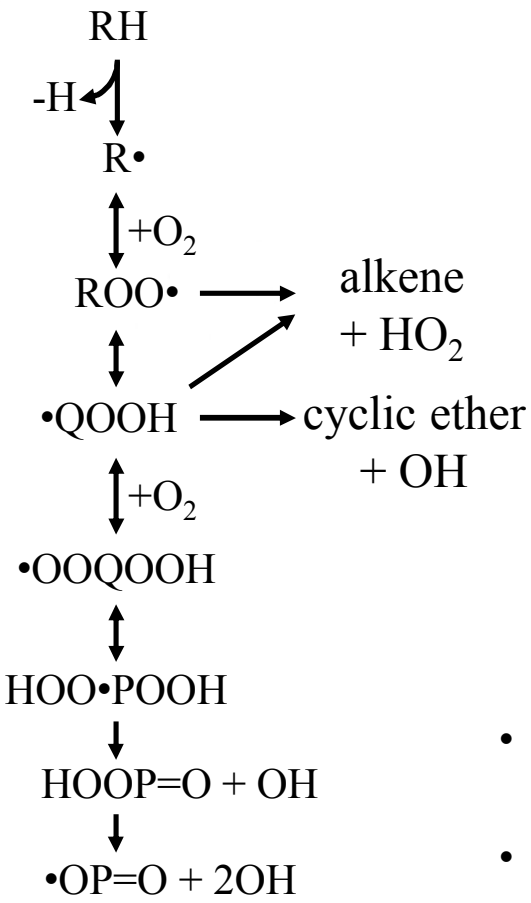
ALS ADVANCED LIGHT SOURCE

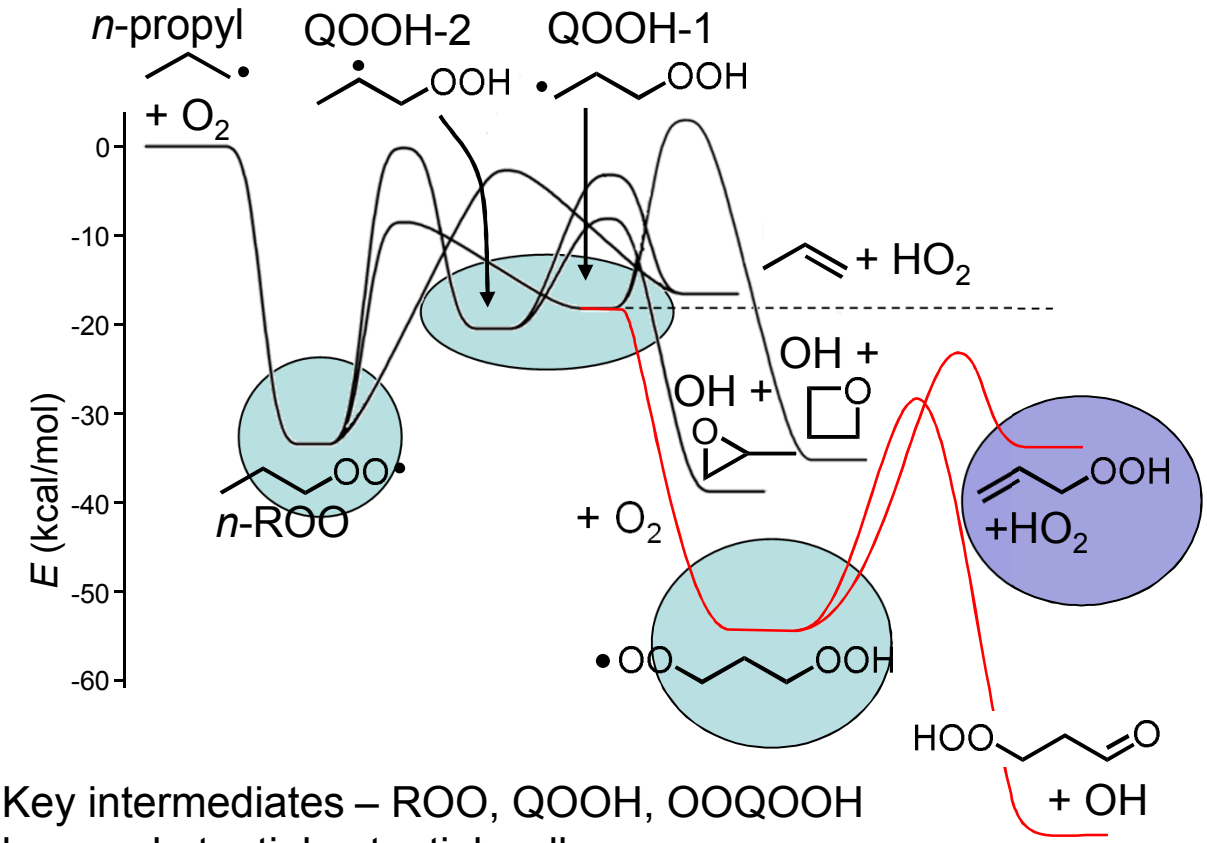
9.2 CHEMICAL DYNAMICS BEAMLINE


CRF

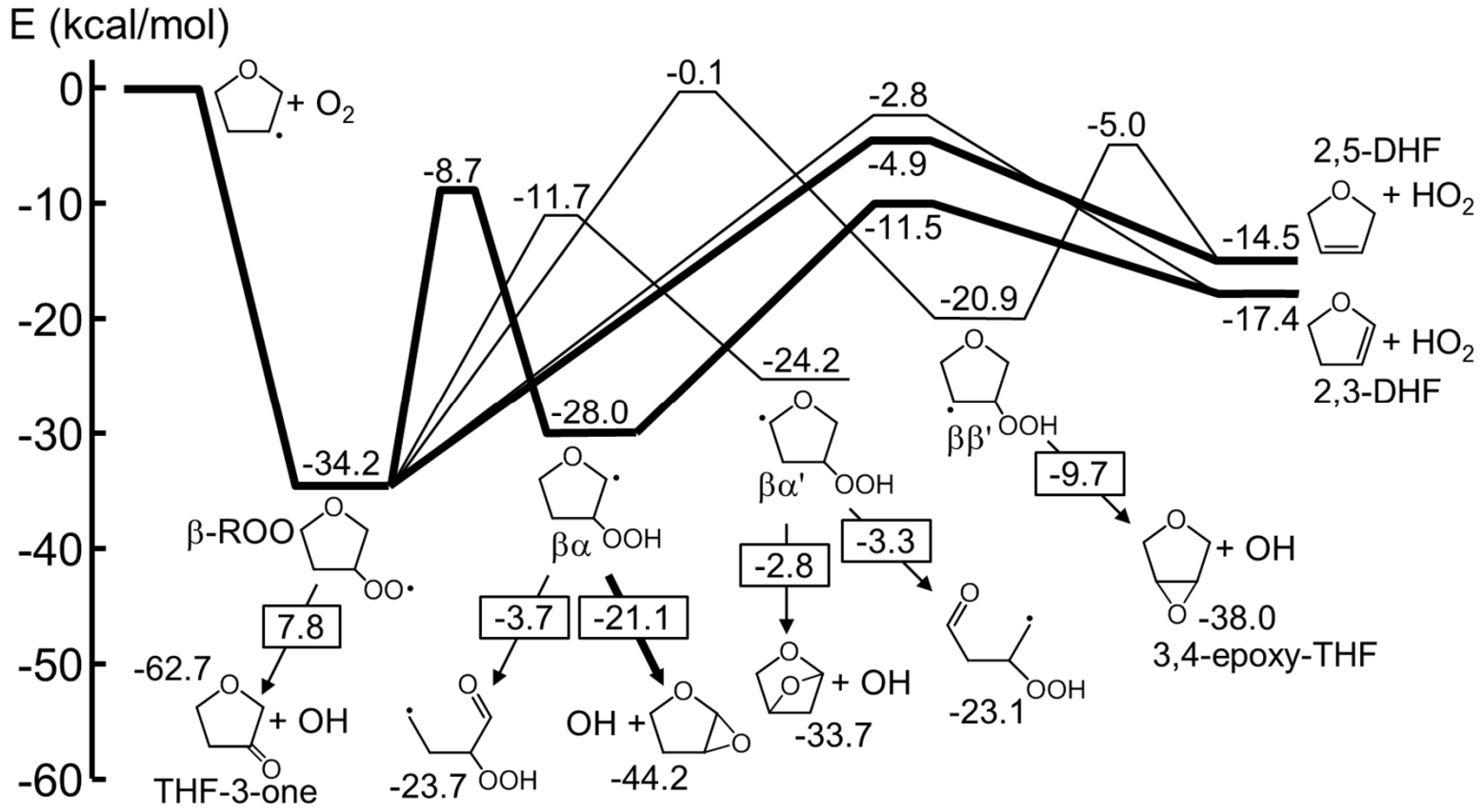

pump
Reflectron
field-free region
~3700 V
~ 10-6
Torr
MCP
acceleration
ion extraction
~ 10-4
Torr
optical
access
reactor
1 – 100 atm
~ 10-5
Torr
pump
pump
pump
reactor
0V
0 mm
2 mm
cyl. lens
skimmer
quad
guides
-2V
-40V
40 mm
to reflectron
-3700V
accel.
stack
-6V
0V
-450V
+450V
100mm
108mm

Example: propane oxidation

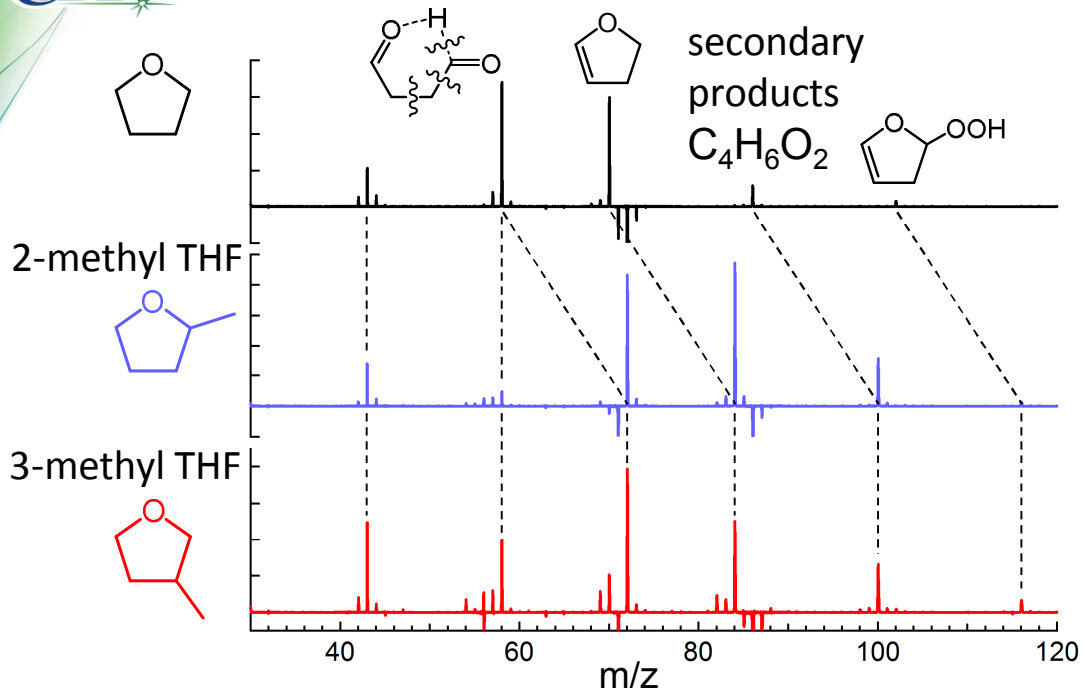




- Key intermediates – ROO, QOOH, OOQOOH have substantial potential wells
- Collisions activate and stabilize these species
- P-dependent chemistry

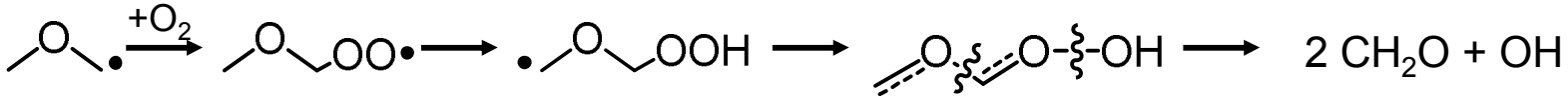

E (kcal/mol)
0
-10
-20
-30
-40
-50
-60
+ O_2
-34.2
-8.7
-11.7
-0.1
-28.0
-2.8
-4.9
-11.5
-5.0
-20.9
-24.2
-14.5
-17.4
2,5-DHF
+ HO_2
2,3-DHF
β-ROO
$OO\cdot$
7.8
-62.7
+ OH
THF-3-one
βα OOH
-3.7
-21.1
-23.7 OOH
OH +
-44.2
βα' OOH
-2.8
-3.3
+ OH
-33.7
ββ' OOH
-9.7
-23.1
+ OH
-38.0
3,4-epoxy-THF

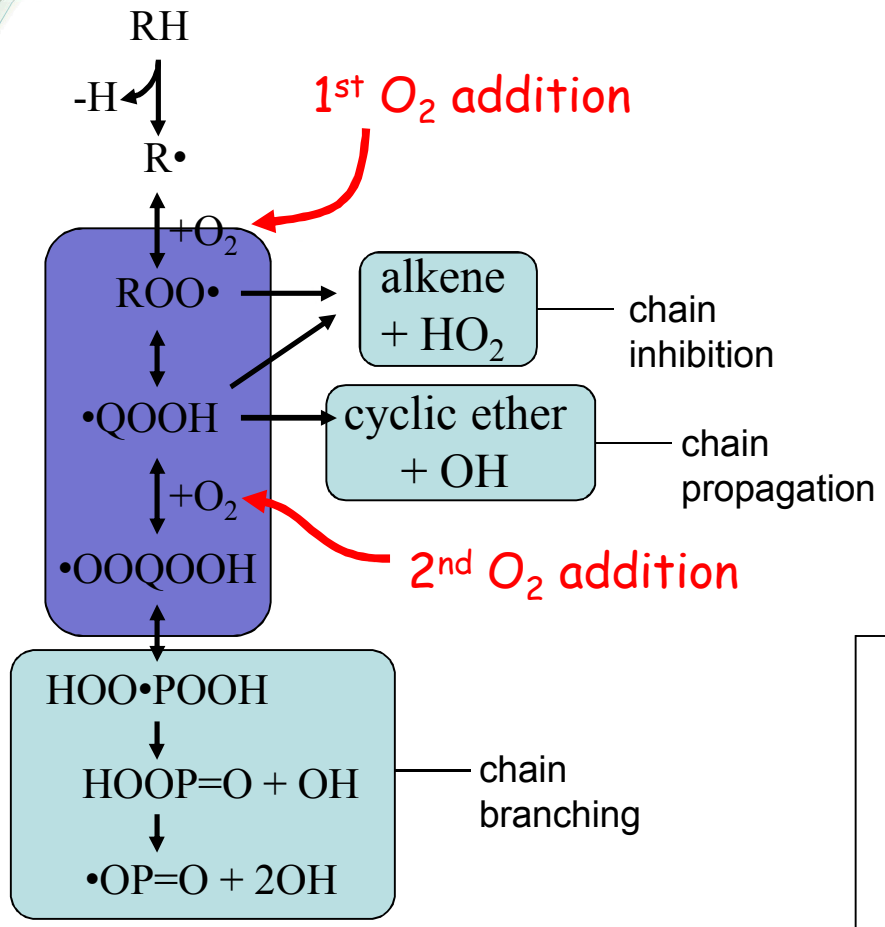
Similarities with THF derivatives

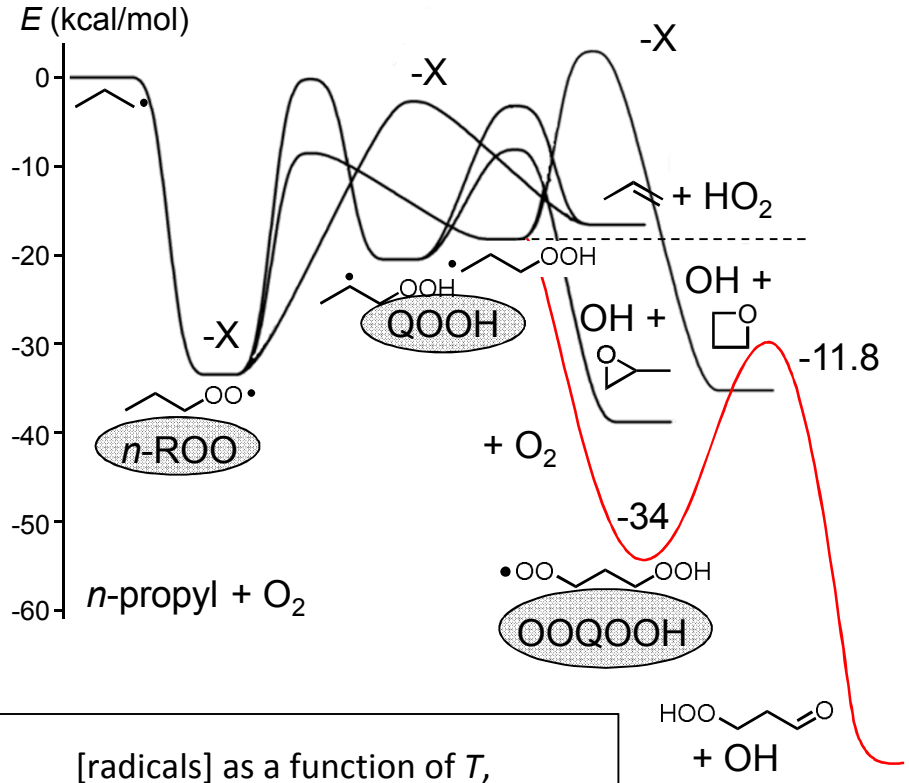


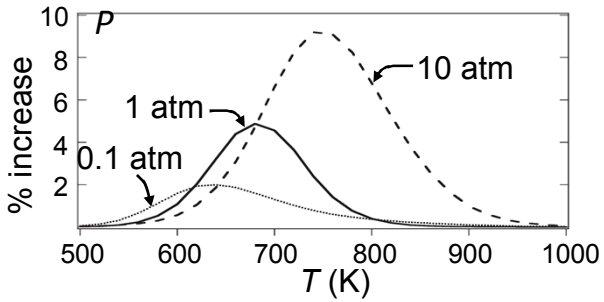
- 2MTHF and 3MTHF oxidation potentially much more complex
- Many pathways analogous to THF
- α-R are primarily active

Similarities with DME oxidation









Goldsmith, Green, and Klippenstein
JPC A, 2012, **116**, 3325

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