COMBUSTION RESEARCH FACILITY

SAND2016-6945C

Competing first- and second-O_2 addition pathways in low-*T* autoignition of tetrahydrofuran

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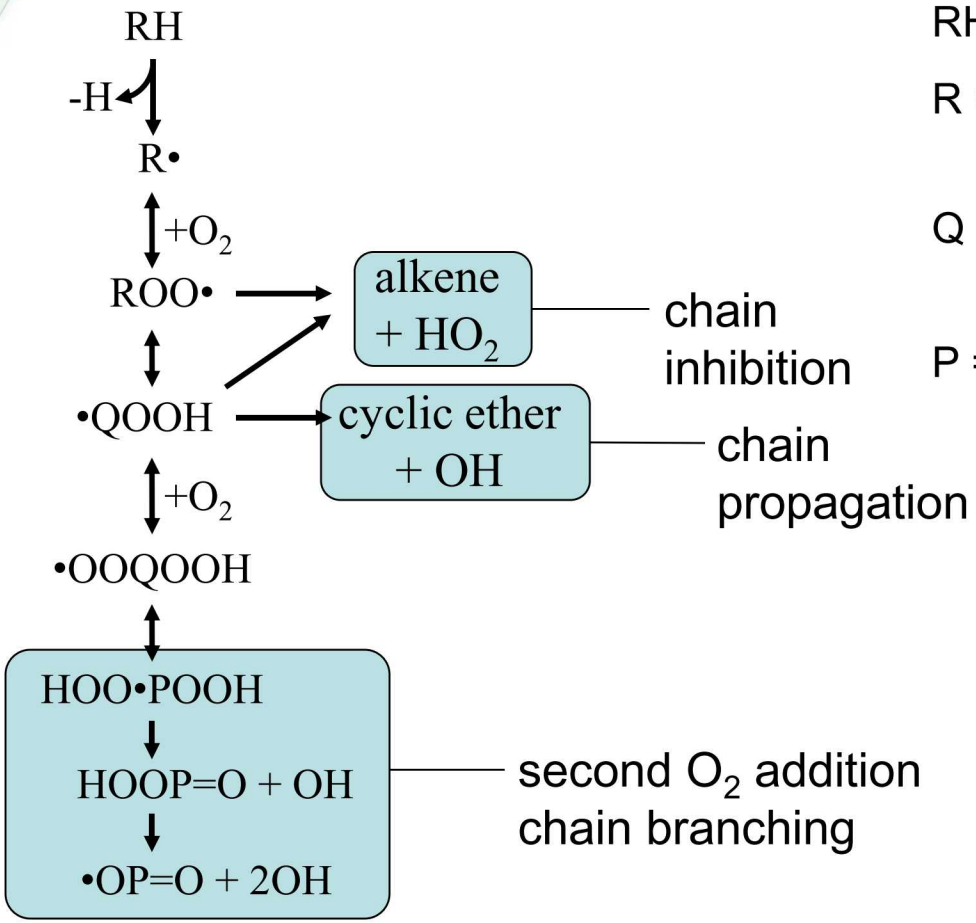


RH – organic fuel

R = RH_{-H}

R•
ROO•

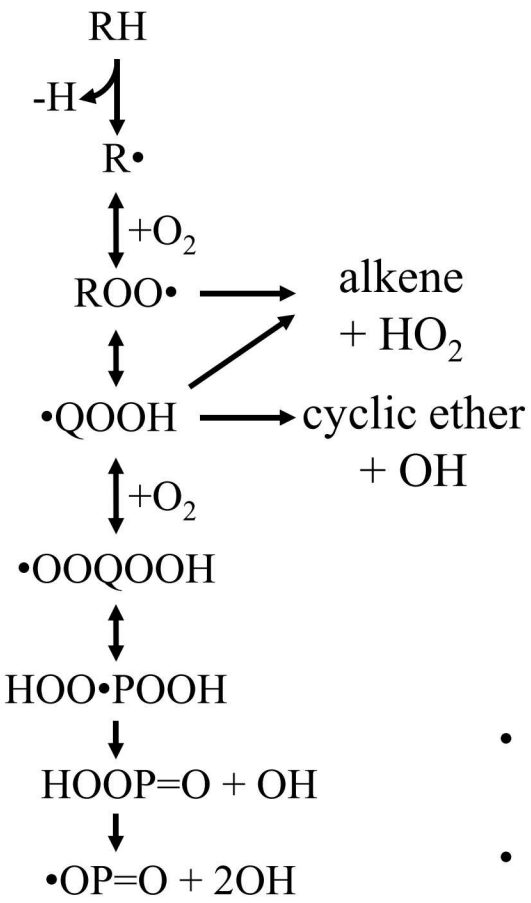
Q = R_{-H}

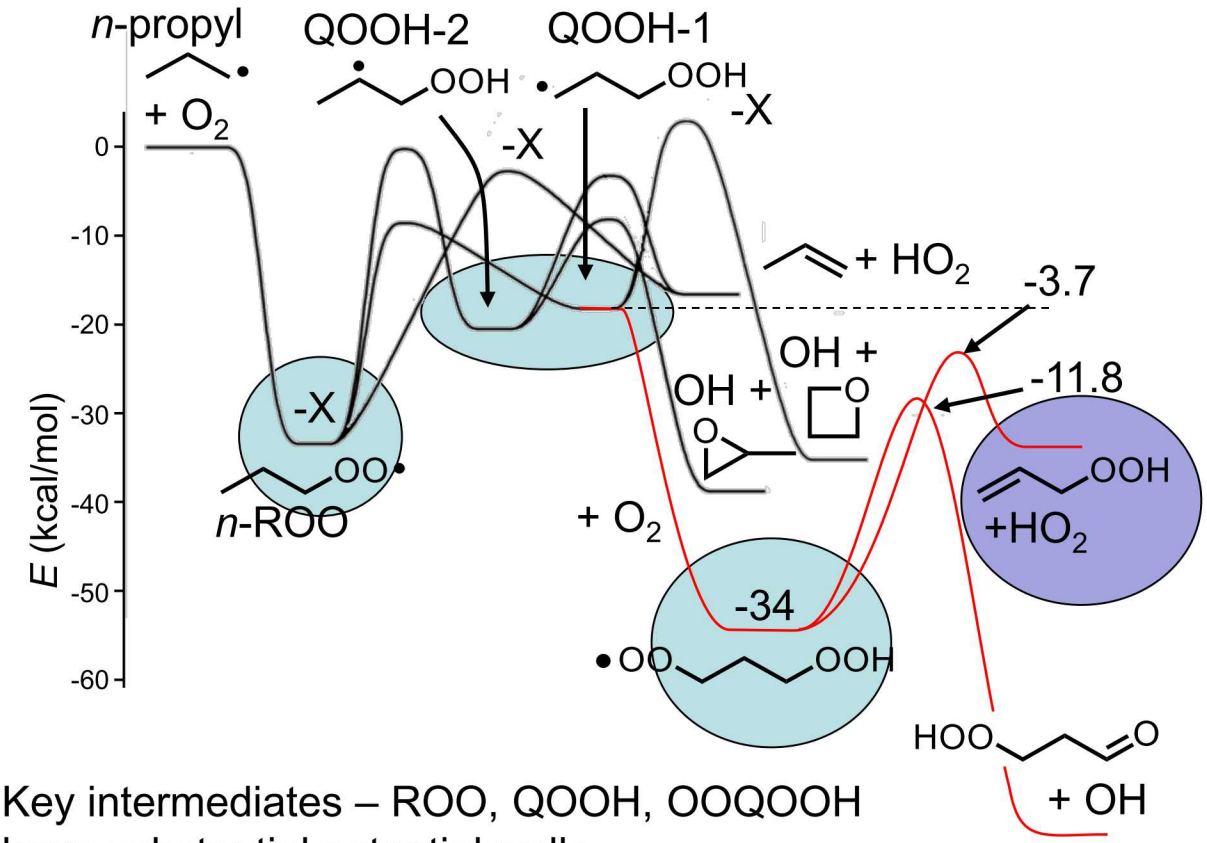
•QOOH
•OOQOOH

P = Q_{-H}

HOO•POOH
HOOP=O – ketohydroperoxide
•OP=O – oxy-radical

Example: propane oxidation





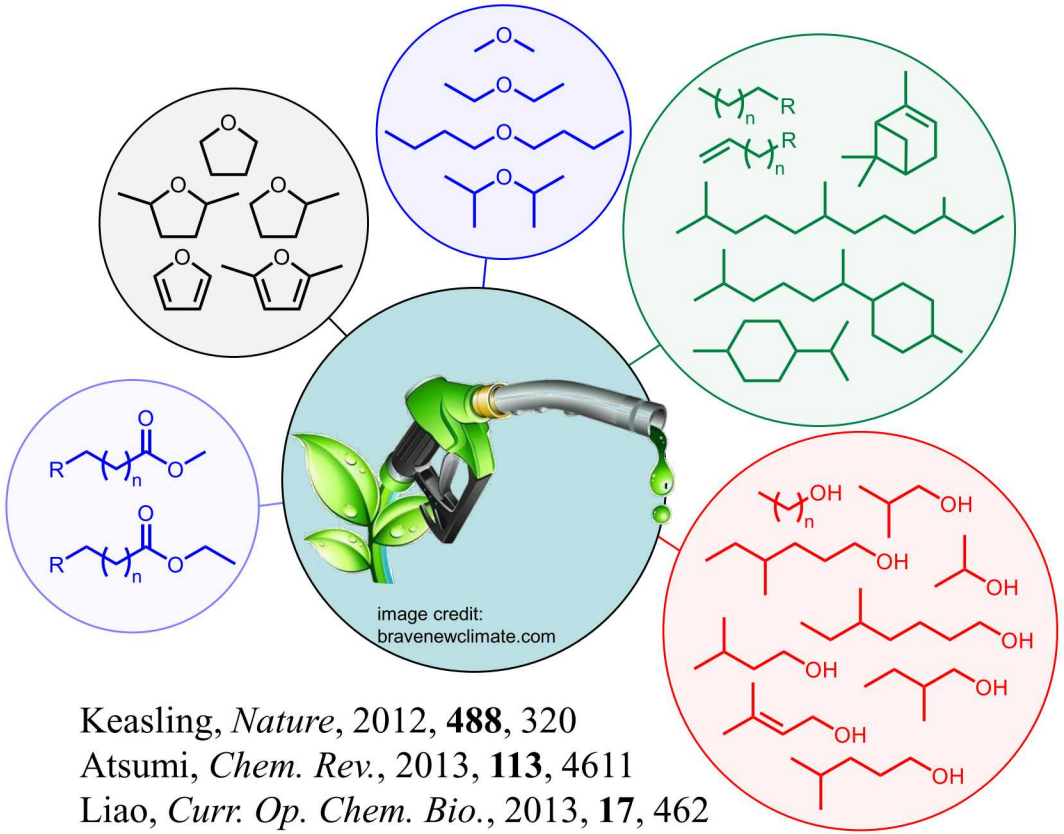
- Key intermediates – ROO, QOOH, OOQOOH have substantial potential wells
- Collisions activate and stabilize these species
- P-dependent chemistry

Next-generation biofuels

Numerous proposed 2nd and 3rd-gen. biofuels

- Promising synthetic routes
- Non-edible feedstock
- Existing infrastructure compatibility

- Diverse structural motifs
- Complex, largely unexplored chemistry



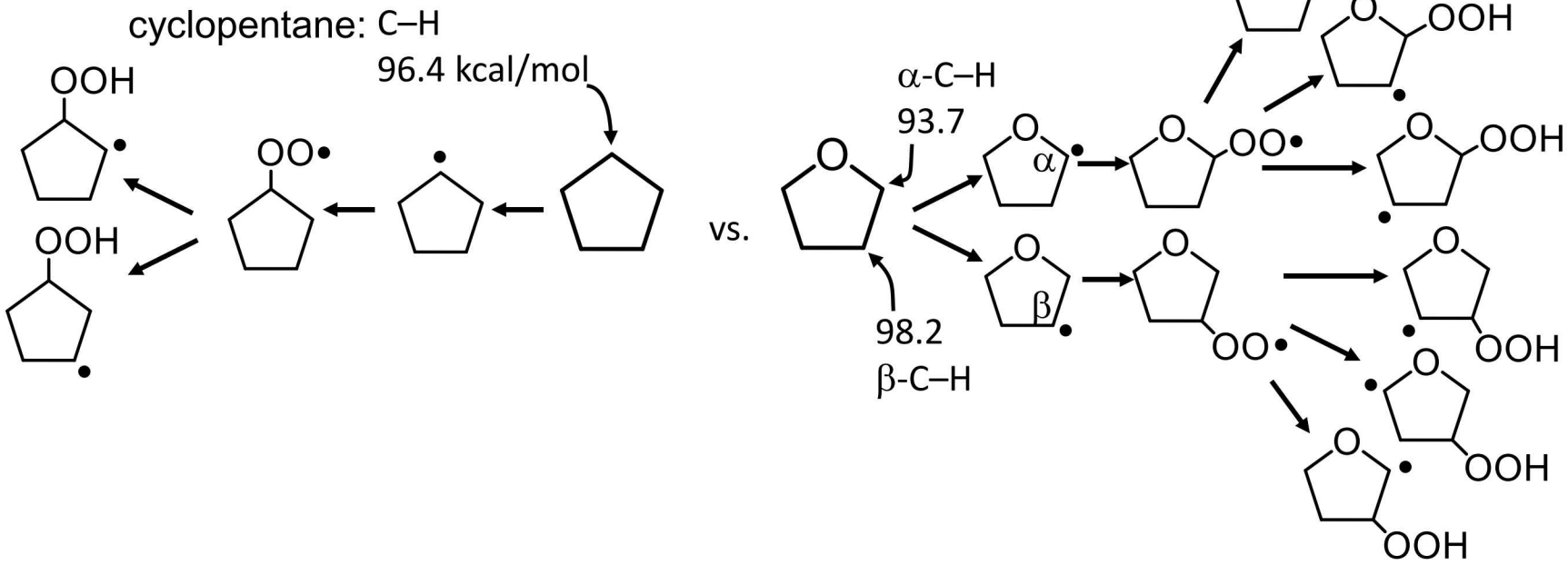
Keasling, *Nature*, 2012, **488**, 320
Atsumi, *Chem. Rev.*, 2013, **113**, 4611
Liao, *Curr. Op. Chem. Bio.*, 2013, **17**, 462

Effects of molecular structure on reactivity

- Chain length and branching
- Cyclic vs. acyclic
- Ether, ester, alcohol functional groups
- Unsaturation

THF is a cyclic ether…

- **C-H bond strength in THF**



- 1 ROO isomers, 2 QOOH isomers
- 2 ROO isomers, 6 QOOH isomers
- Site-selective H abstraction reactions

THF is a cyclic ether…

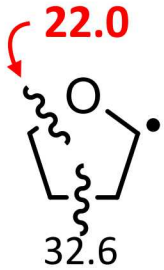
- C-H bond strength in THF

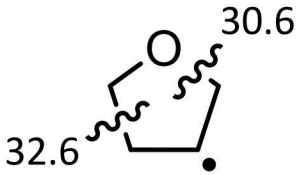
- C-O bond scission in α-THFyl

$k(700K) = 3.5 \times 10^3\ s^{-1}$

Manion, *PROCI*, 2011

vs.





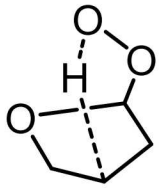
$k(700K) \sim 10^7\ s^{-1}$

Simmie, *JPC A*, 2012

- Rapid enough to compete with oxidation

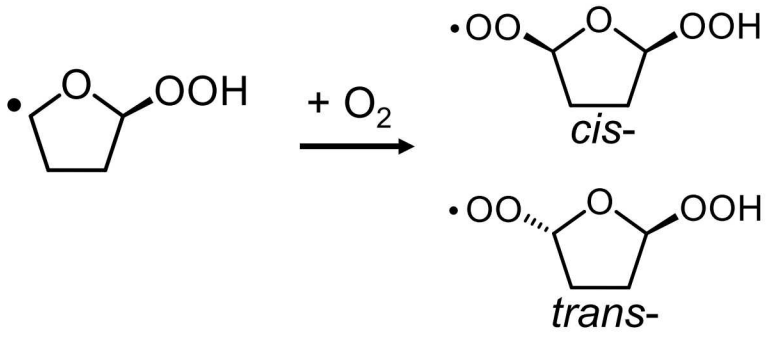
THF is a cyclic ether…

- C-H bond strength in THF
- C-O bond scission in α-THFyl
- Rigid ring structure
  - Ring strain



TS for ROO ↔ QOOH

  - Conformer-specific reactivity



Previous work

- **High temperatures (*T* > 1000K)**

Lifshitz *et al.*,	1980's	shock tube
Dagaut and co-workers	1990's	shock tube, JSR
Kasper *et al.*,	2011	low-P flame
Simmie	2012	ab initio, TST
Battin-Leclerc and co-workers	2015	shock tube, flames
	2015	ab initio, TST

- **Low temperature (*T* < 1000K)**

Molera *et al.*,	1988	static reactor
Battin-Leclers and co-workers	2015	JSR, RCM

Goals of this study

Initiation reactions in the low-*T* autoignition regime

- Laser photolysis initiation

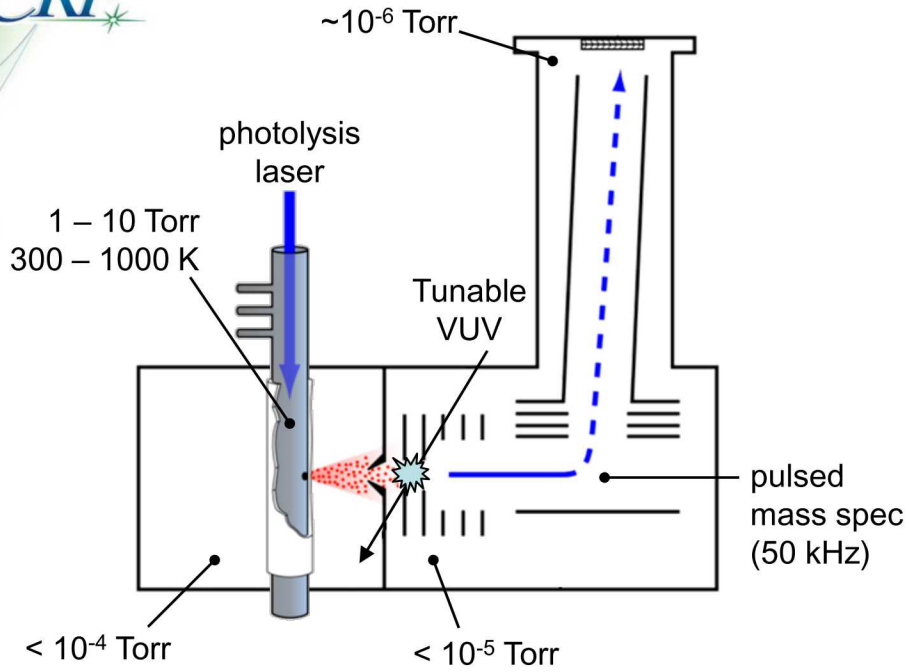
$(COCl)_2 \xrightarrow{266nm} 2\,CO + 2\,Cl\cdot$

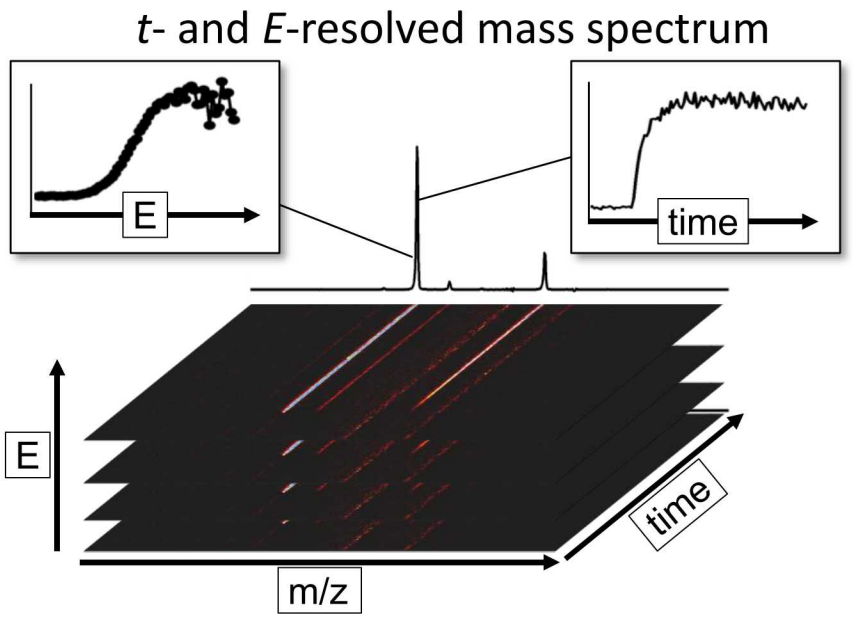
$Cl\cdot + \;\longrightarrow\; \begin{matrix}\alpha\text{-}R\cdot \\ \beta\text{-}R\cdot\end{matrix} \xrightarrow{+\,O_2}$ products

$\tau \sim 1\ \mu s$ 0 – 100 ms

- Homogeneous, constant-*T*, *P* flow reactor
  - *P* = 10 – 2000 Torr
  - *T* = 400 – 700 K
  - dilute, pseudo-1st-order conditions:
    - $[Cl]_0$ (~10^{13} cm^{-3}) << [THF] (~10^{15} cm^{-3}) << $[O_2]$ (>10^{17} cm^{-3})

- Time-resolved photoionization mass spectrometry (PIMS) probing
  - Photoionization spectra
  - Partially deuterated isotopologs (2,2,5,5-THF-d_4)



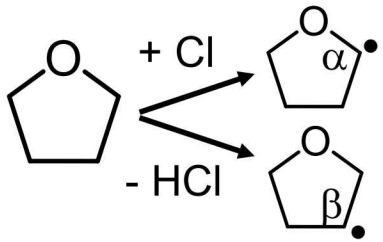


Multiplexed synchrotron-based PIMS

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

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

Initiation reactions



In 2,2,5,5-THF-d_4: α-R m/z = 74

β-R m/z = 75

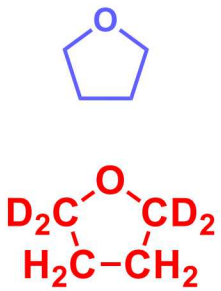
(using hν = 8.2 – 8.5 eV)

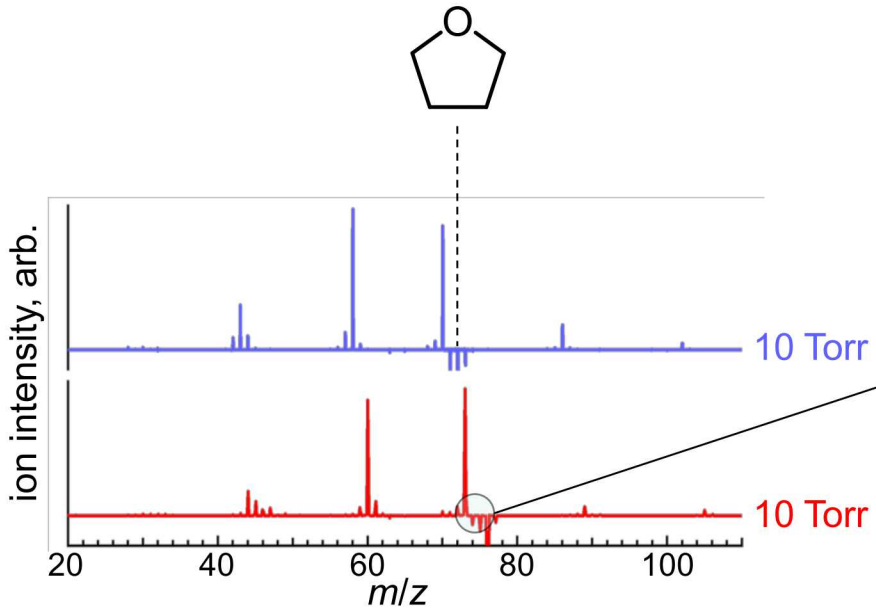
T = 650 K α/β ion signal ~ 10:1

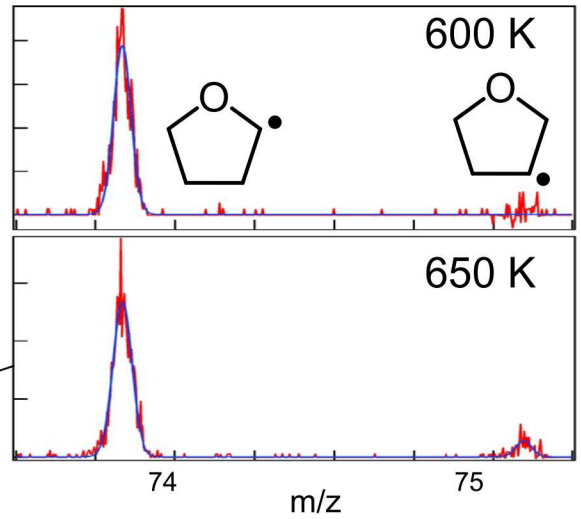
400K ≤ T ≤ 600K α/β > 25:1

- In our experiments, mostly α-R → α-ROO

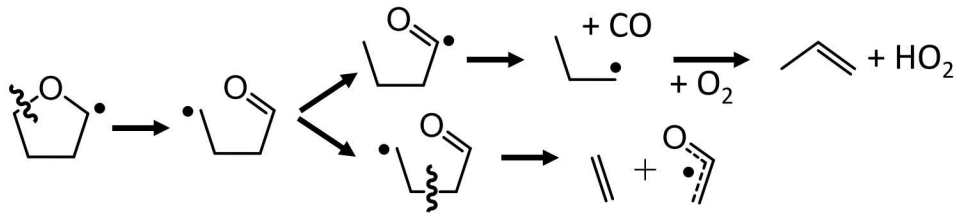
THF oxidation
600 K







THF-yl ring opening



Simmie, *JPC A*, 2012

propene m/z = 42

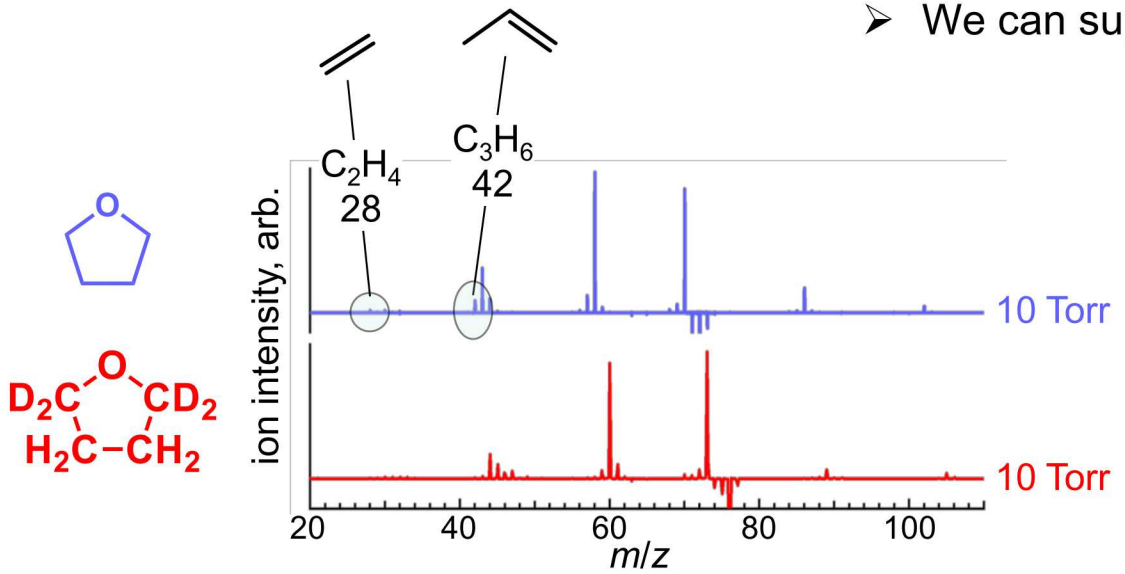
ethane m/z = 28

Yields:

T = 650 K ~ 5%

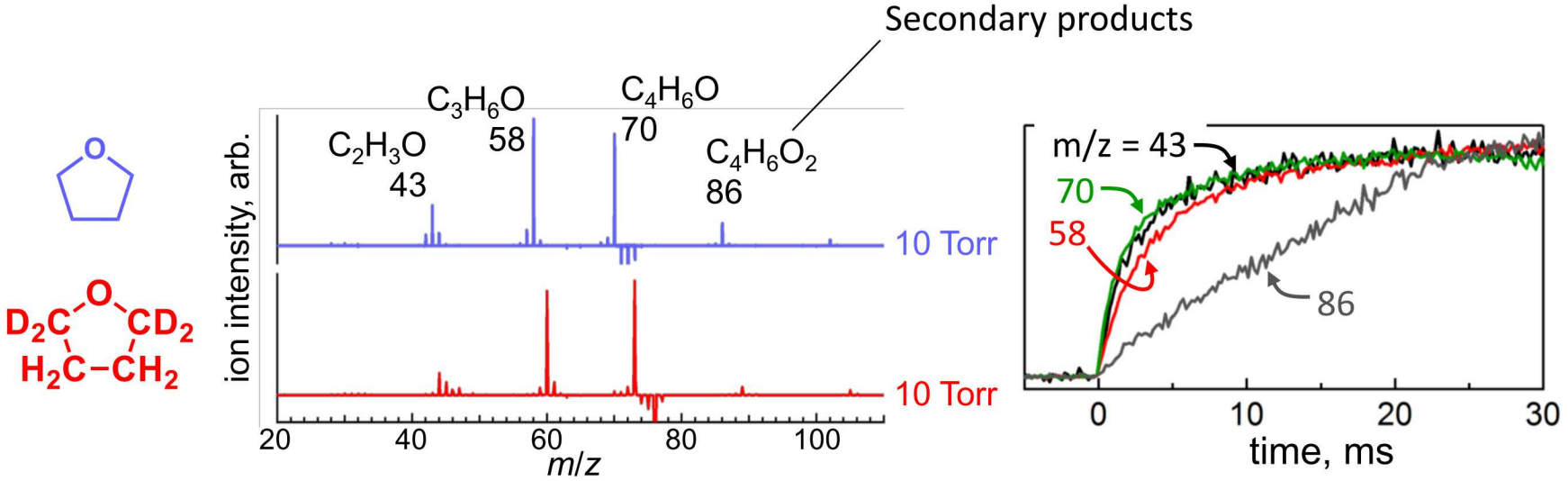
400K ≤ T ≤ 600K < 2%

- We can suppress ring-opening



First O_2 addition

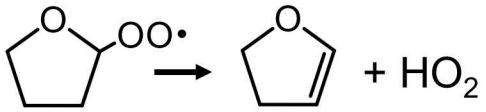
$R + O_2 \rightarrow ROO \rightarrow QOOH \rightarrow$ products

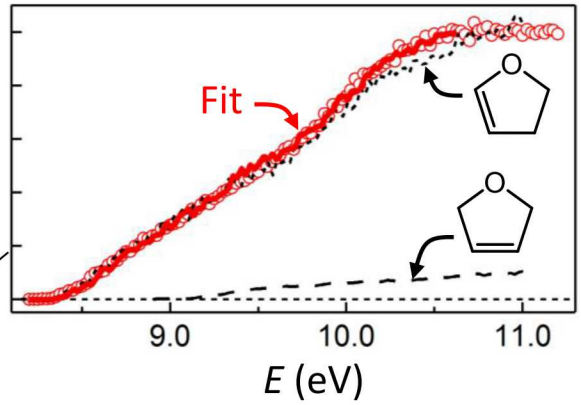


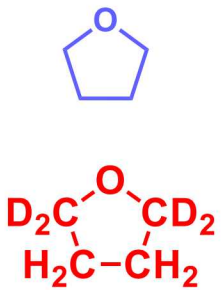
First O_2 addition

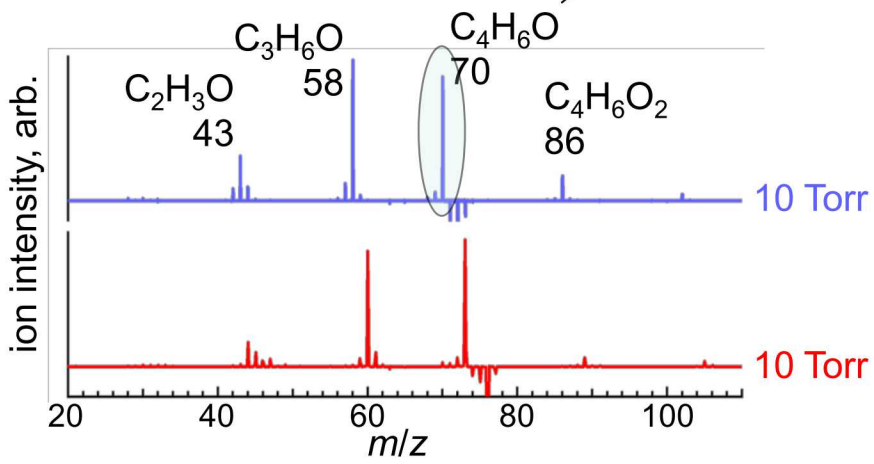
R + O_2 → ROO → QOOH → products

HO_2 + 2,5-DHF	m/z = 70	~1% at all *T*
HO_2 + 2,3-DHF	**m/z = 70**	**~20% at all *T***









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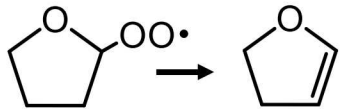
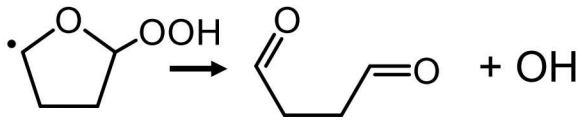
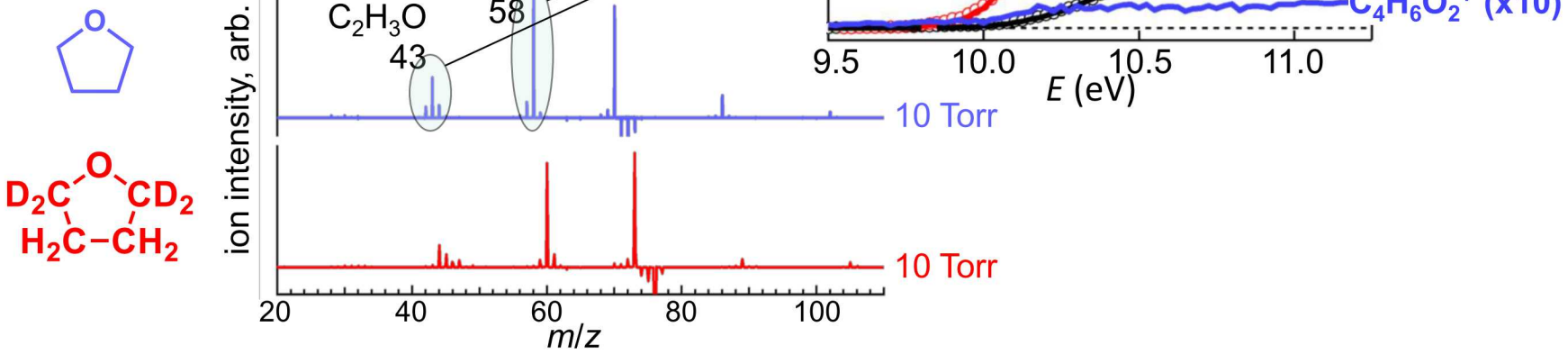


OH + butanedial	**m/z = 58, 43**	**??? (perhaps ~70%) ???**

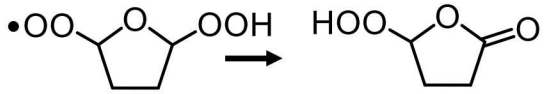


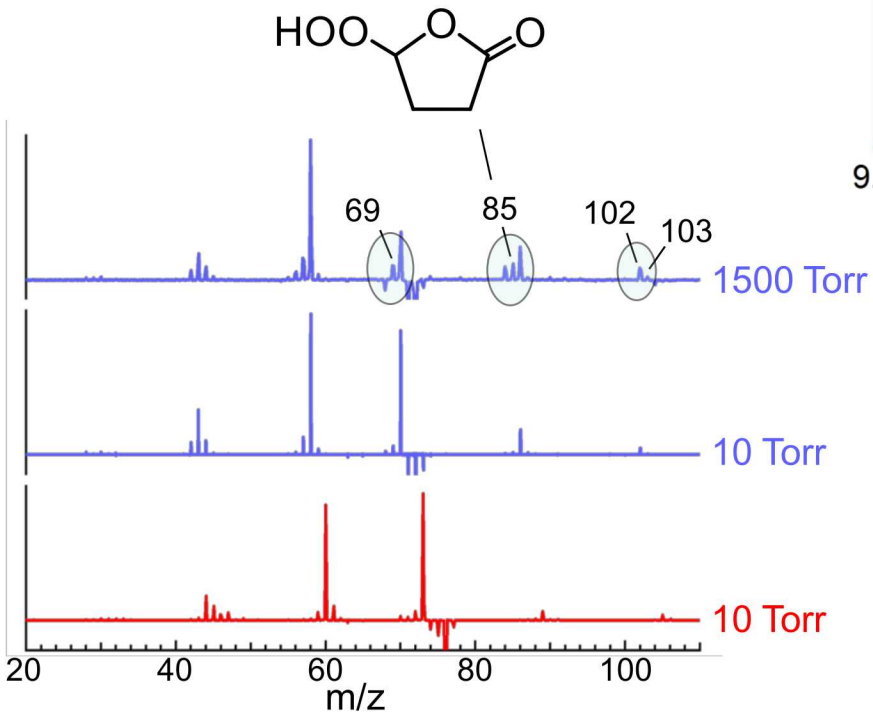


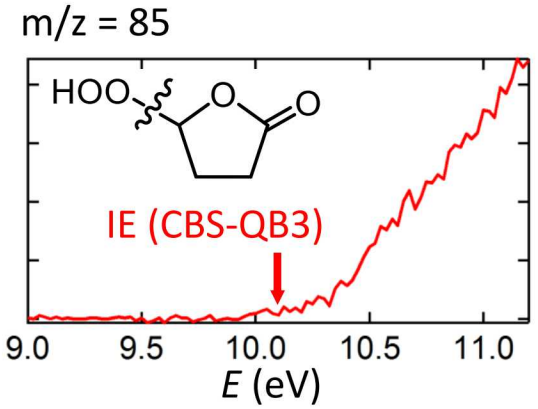
Second O_2 addition

QOOH + O_2 → OOQOOH → products

γ-butyrolactone-OOH (GBL-OOH) m/z = 85 (DI)



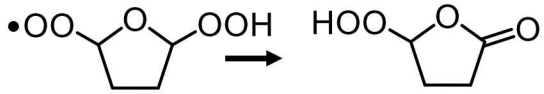




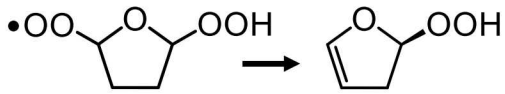
Second O_2 addition

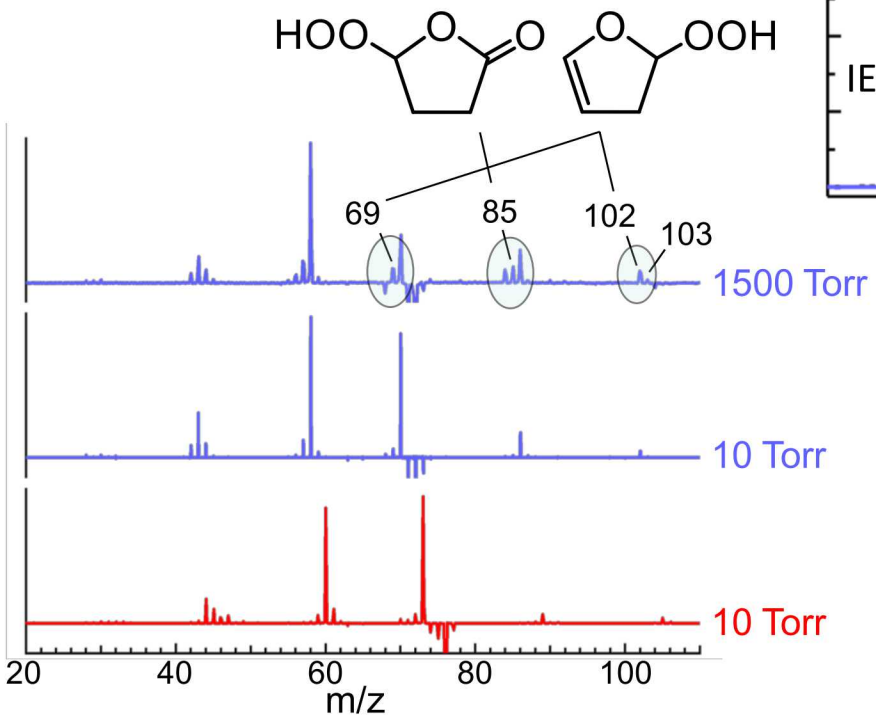
QOOH + O_2 → OOQOOH → products

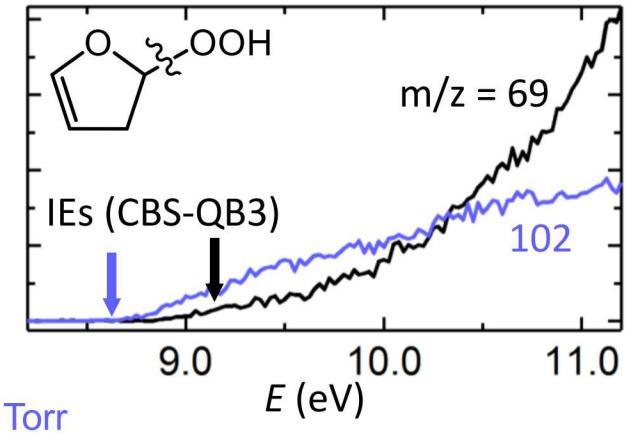
γ-butyrolactone-OOH (GBL-OOH) m/z = 85 (dissociative ionization)



2,3-DHF-OOH m/z = 102 (P), 69 (DI)







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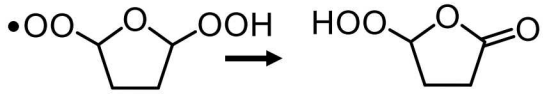

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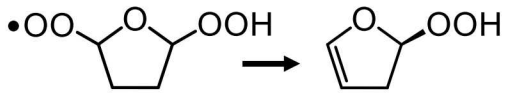
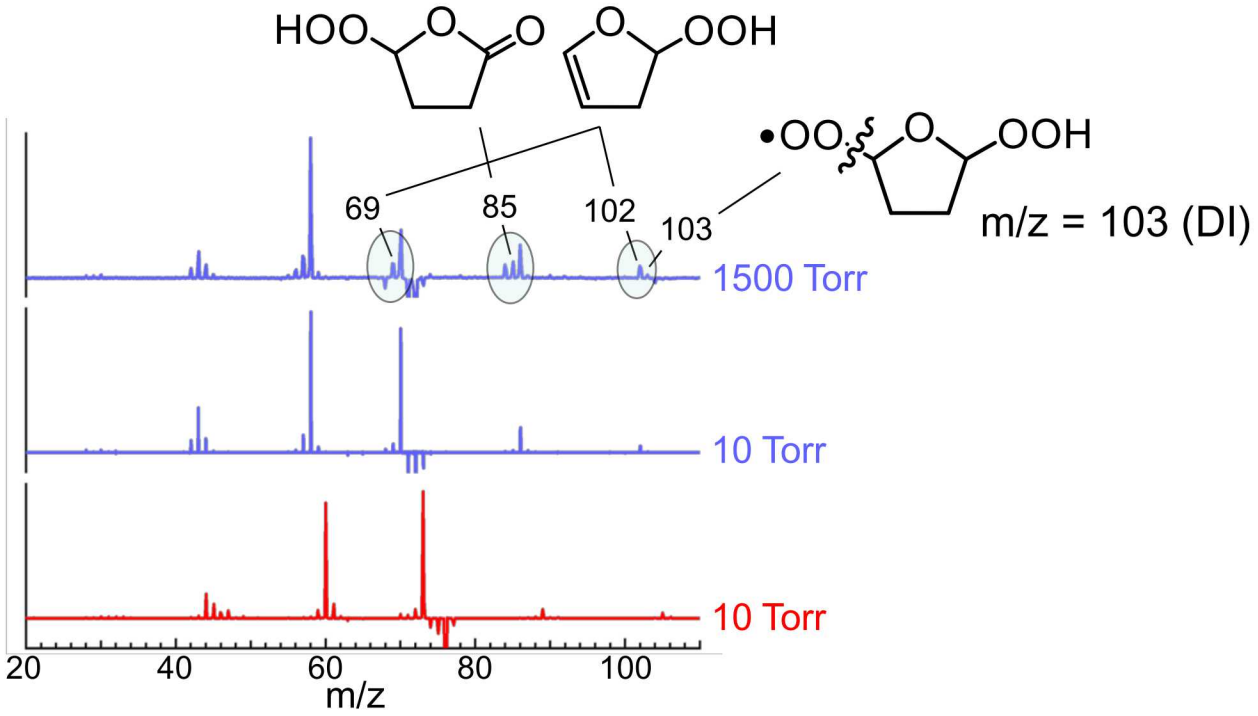
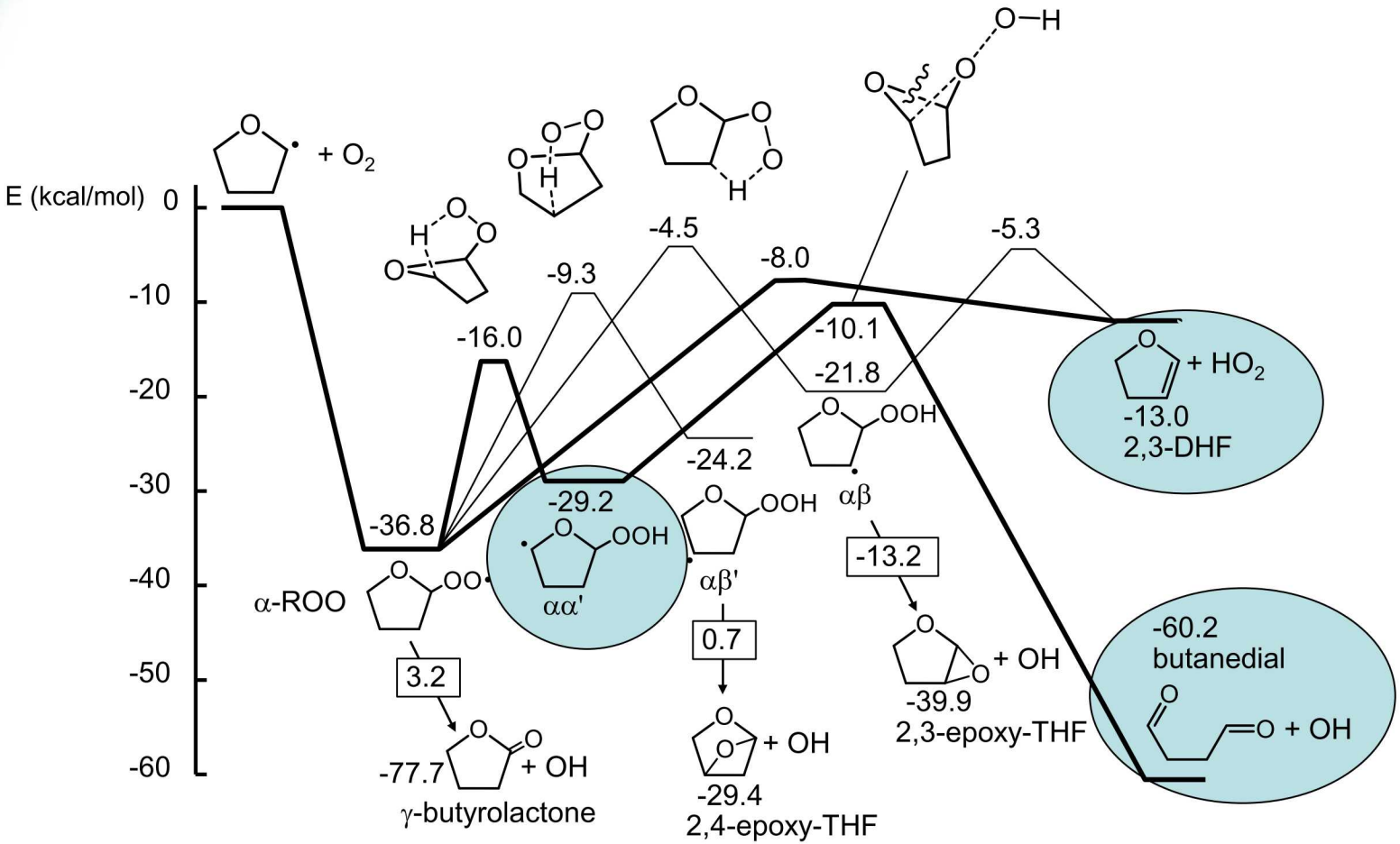




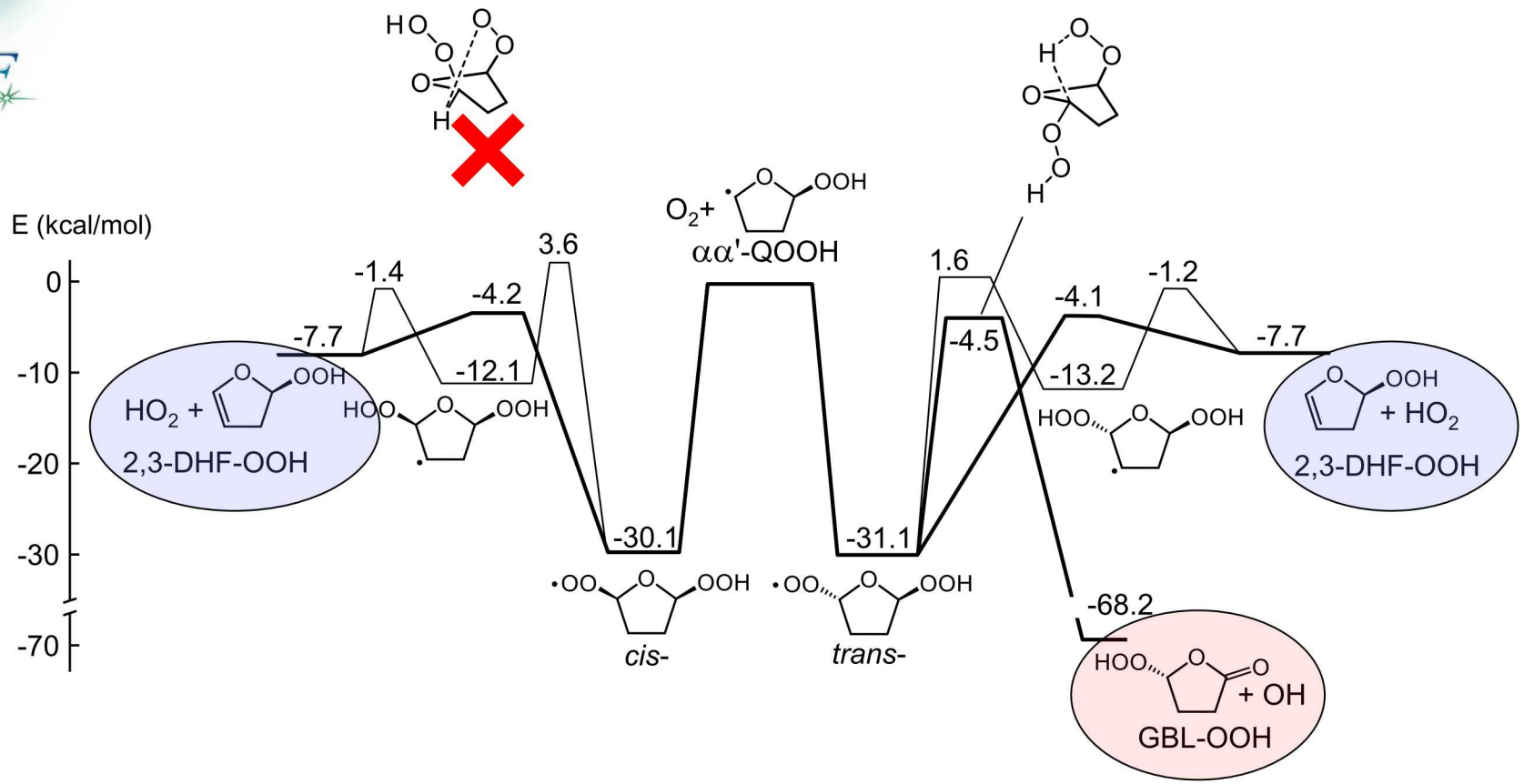


- αα'-QOOH dominant due to weak α-C–H
- butanedial yield 50 – 90% due to weak C–O

  propane oxidation – OH yield < 4%
  butane oxidation – OH yield <30%

PES exploration:
KinBot (J. Zádor)

Stationary points
optimized at CBS-QB3

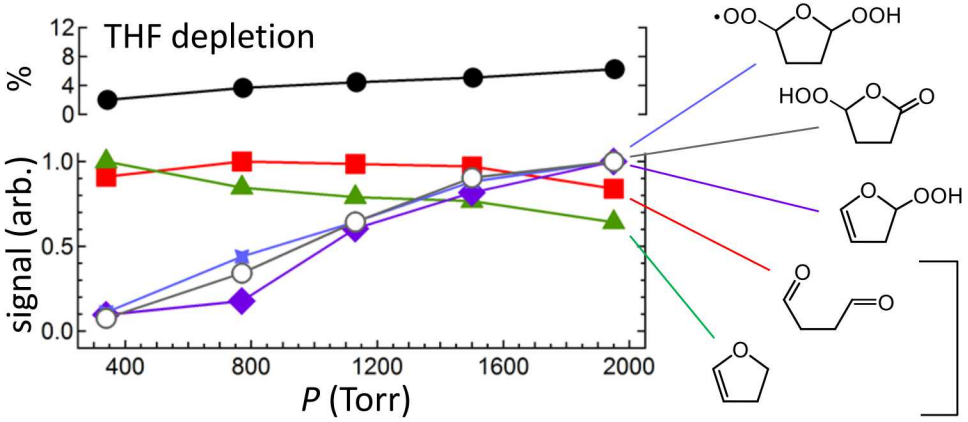


- ring structure gives rise to isomers with different reactivity

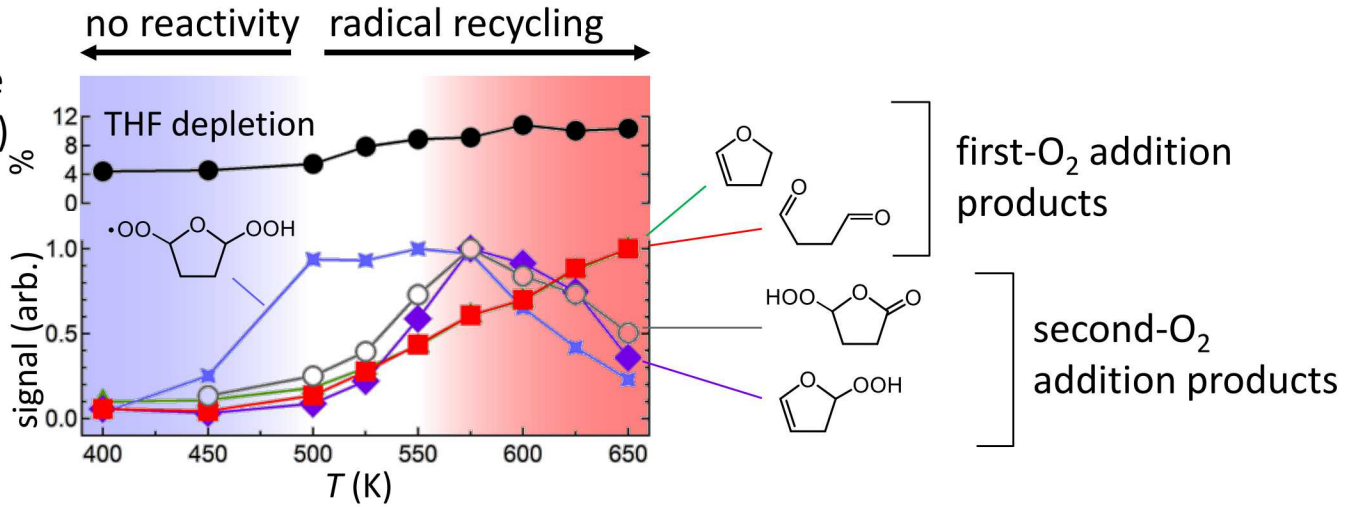
trans-αα'-OOQOOH	→ 2,3-DHF-αOOH	TS -4.1 kcal/mol	propane: -3.7
	→ GBL-OOH	TS -4.5 kcal/mol	propane: -11.8
cis-αα'-OOQOOH	→ 2,3-DHF-αOOH only		

- competition between DHF-OOH and GBL-OOH affects chain-branching

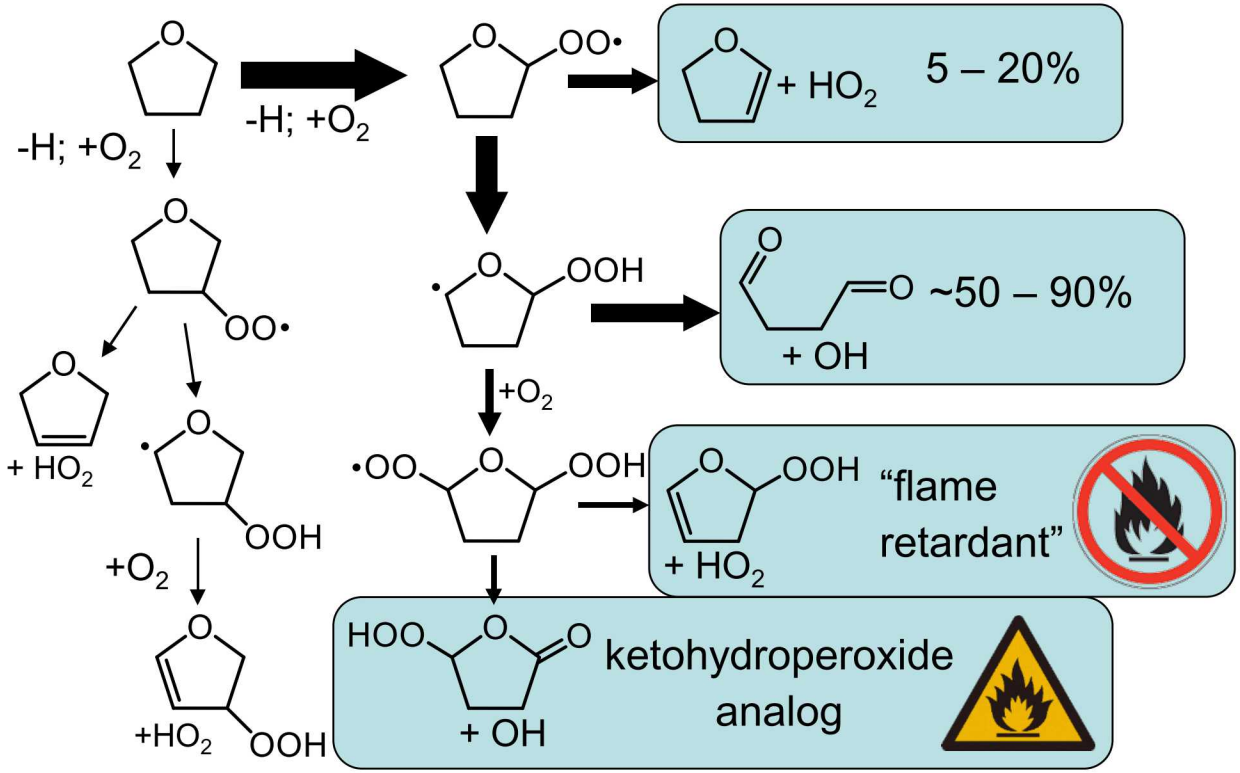
P-dependence
(*T* = 575 K)



T-dependence
(*P* = 1500 Torr)



Simplified THF autoignition mechanism



Conclusions:

- Low-*T* combustion chemistry of THF is relatively straightforward, dominated by products of α-ROO, $\alpha\alpha'$-QOOH, $\alpha\alpha'$-OOQOOH
- Unambiguous assignment of first- and second-O_2 addition products by mass spectrometry
- Strong *P*-dependence of pathways following second-O_2 addition

- **Autoignition models should be expanded to include HO_2 elimination from OOQOOH, maybe other competing pathways**

- Ongoing work:
  - Add OH, HO_2 probing – quantify second O_2 addition products
  - Develop a chemical model, based on ab initio kinetics
  - Expand to substituted THF derivatives

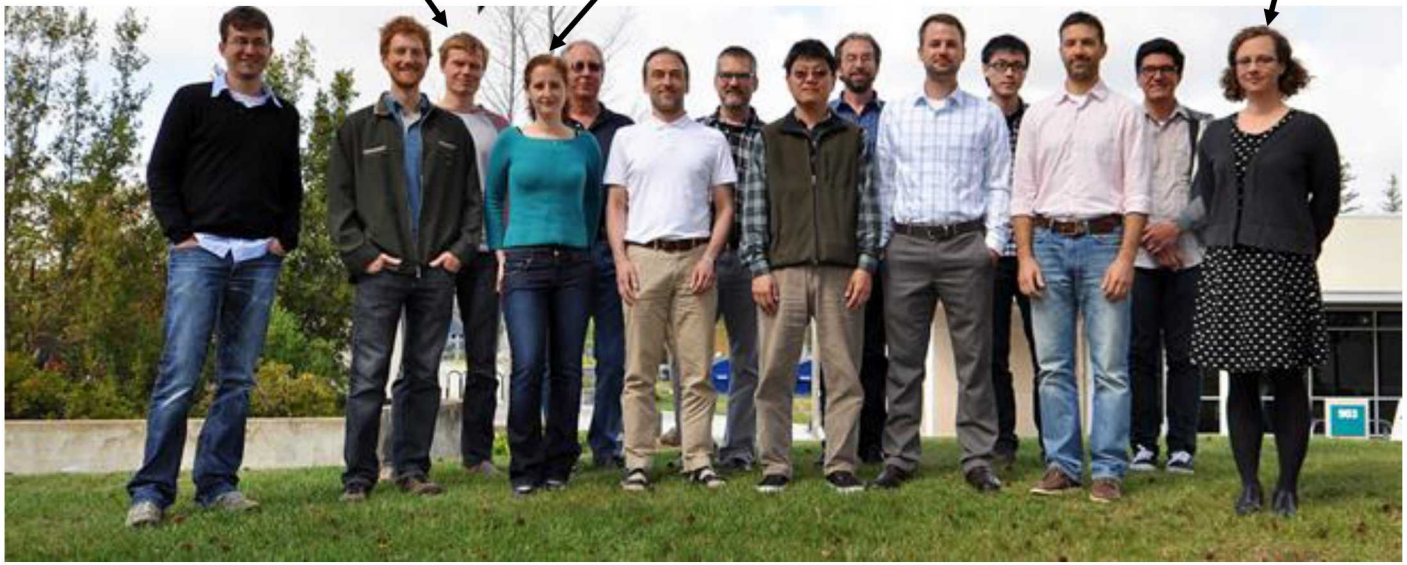
Thank you

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

Ivan Antonov (experiments)

Judit Zádor (theory)

Ewa Papajak



Funding: US DOE