NREL
Transforming ENERGY

Chemical Kinetics Underlying the Sooting Tendency and Auto-ignition Characteristics of Linear, Branched, and Cyclic Ether Compounds

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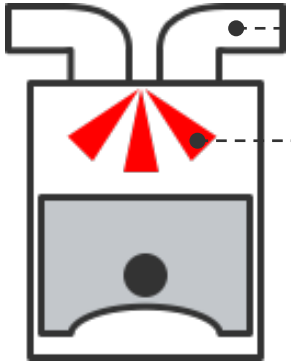
J. Luecke, J. Zhu, P. C. St John, B. T. Zigler,
C. S. McEnally, L. D. Pfefferle,
R. L. McCormick, S. Kim

The Effect of Chemical Structure on YSI and CN

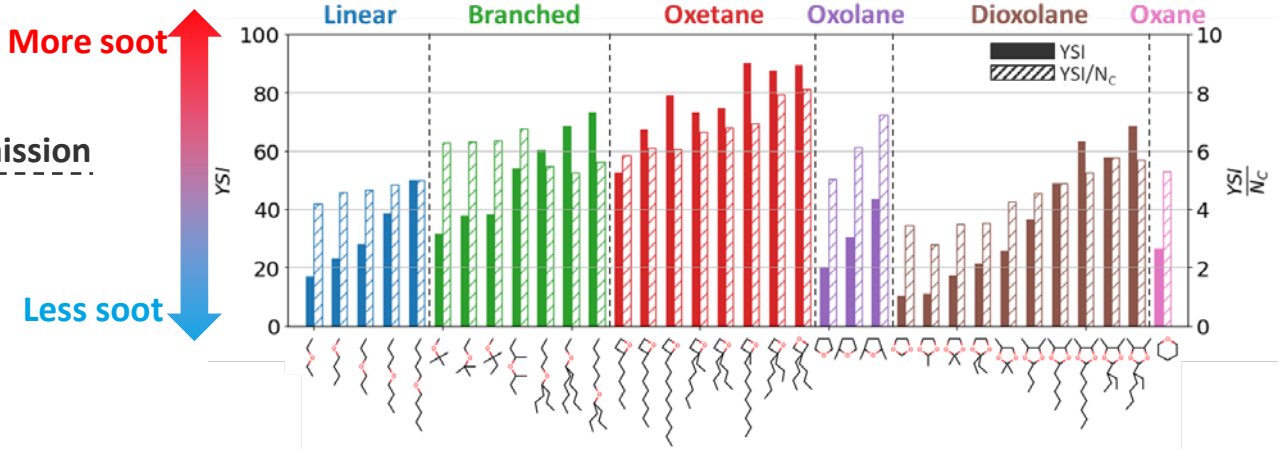


Compression ignition engine

Emission

More soot

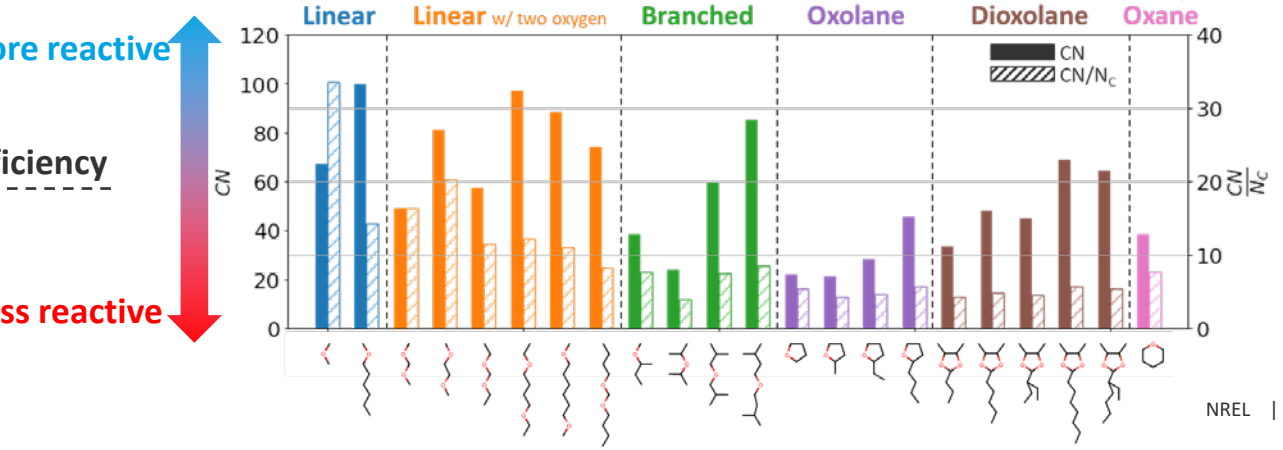
Less soot



Efficiency

More reactive

Less reactive



Structural effect on the sooting tendency

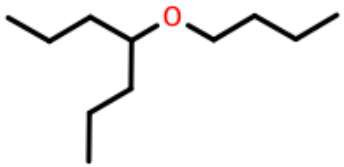
Research objective

1. Elucidate the chemical kinetics underlying the sooting tendency of various ethers
2. Elucidate the chemical kinetics underlying the autoignition char. of various ethers

Cyclic ether
3,3-dimethyl oxetane

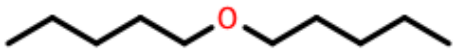
YSI_p=40.9±13.2
YSI_p/N_C=8.2±2.6

Branched ether
4-butoxy heptane



YSI_m=60.3±3.0
YSI_m/N_C=5.5±0.3

Linear ether
Di-n-amyl ether



YSI_m=49.8±2.5
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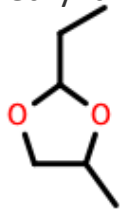
Cyclic ether
w/ two oxygen atoms
Ethyl-methyl dioxolane



YSI_p=23.6±9.2
YSI_p/N_C=3.9±1.5

More soot precursor formation
(Undesirable for low emission)

Less soot precursor formation
(Desirable for low emission)

p :predicted from model, m :measured from exp.

Flow reactor exp. @ high T and fuel-rich condition

3,3-dimethyl oxetane

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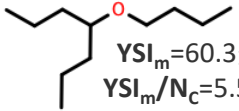
4-butoxy heptane



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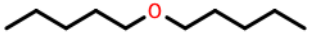

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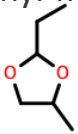

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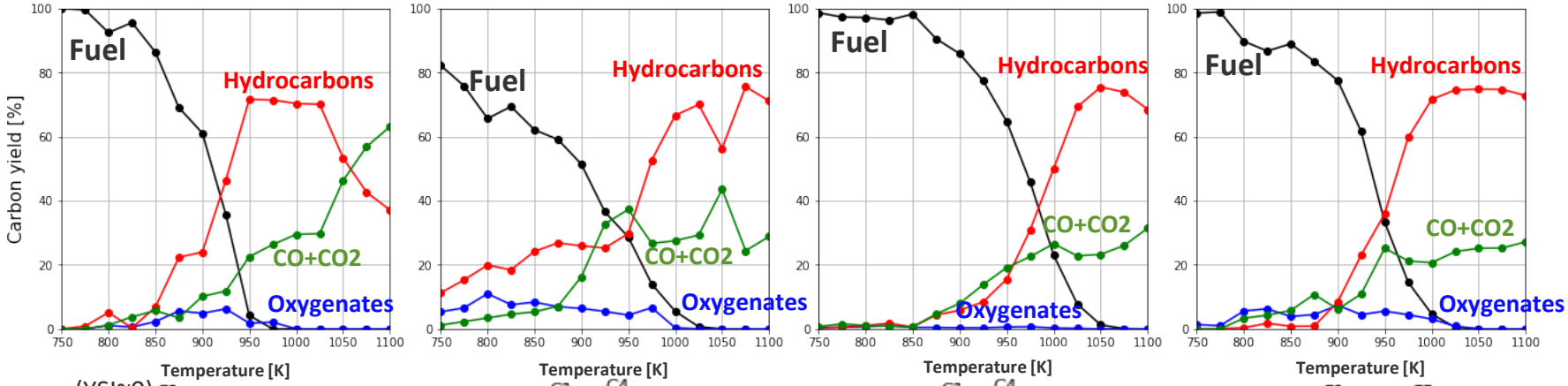
YSI_p/N_C=3.9±1.5

More soot

@ 750-1100K, atmospheric pressure, equiv. ratio=3

Less soot



YSI value is related to the size of product molecule from high T reaction.

QM calculation@ high T and fuel-rich condition

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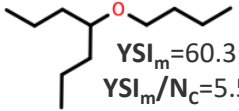

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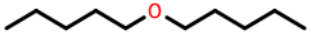

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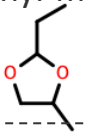

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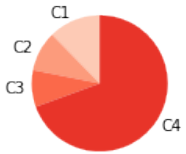
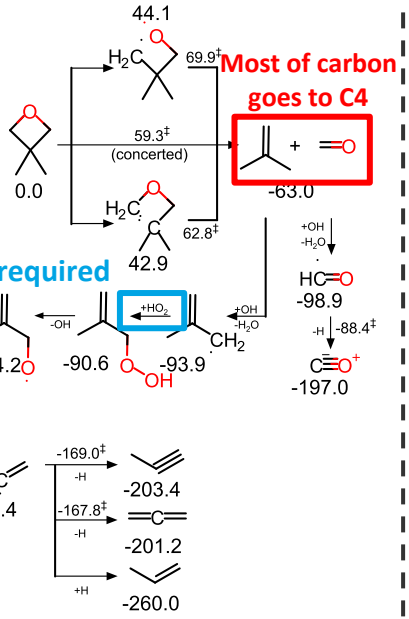
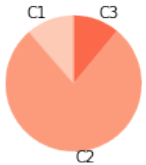




Most of carbon goes to C4

High radial conc. is required



Most of products are oxygenates

C2 compounds from propanal

Free energy [kcal/mol],
G4 composite, 1500K

QM calculation@ high T and fuel-rich condition

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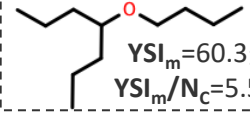
4-butoxy heptane



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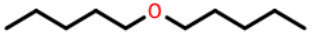

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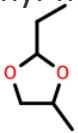

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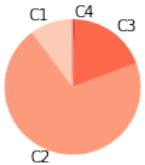
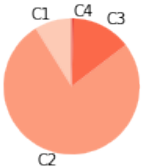
More soot



More pathway to C3.

Low dG‡ (23.7 kcal/mol)
From 5-heptanone to C3

Less soot



C2 compounds
pentanal

dG‡ to C3
(30.7 kcal/mol)

More pathway to C3. Free energy [kcal/mol], G4 composite, 1500K

Structural effect on autoignition characteristics

Research objective

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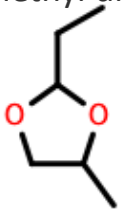

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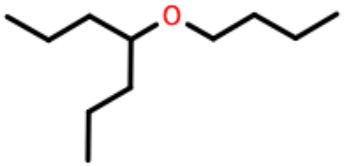
Branched ether
4-butoxy heptane



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Linear ether
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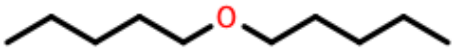


CN_p=90.2±5.1
CN_p/N_C=9.0±0.5

Less reactive
(Undesirable for thermal eff.)

More reactive
(Desirable for thermal eff.)

p :predicted from model, m :measured from exp.

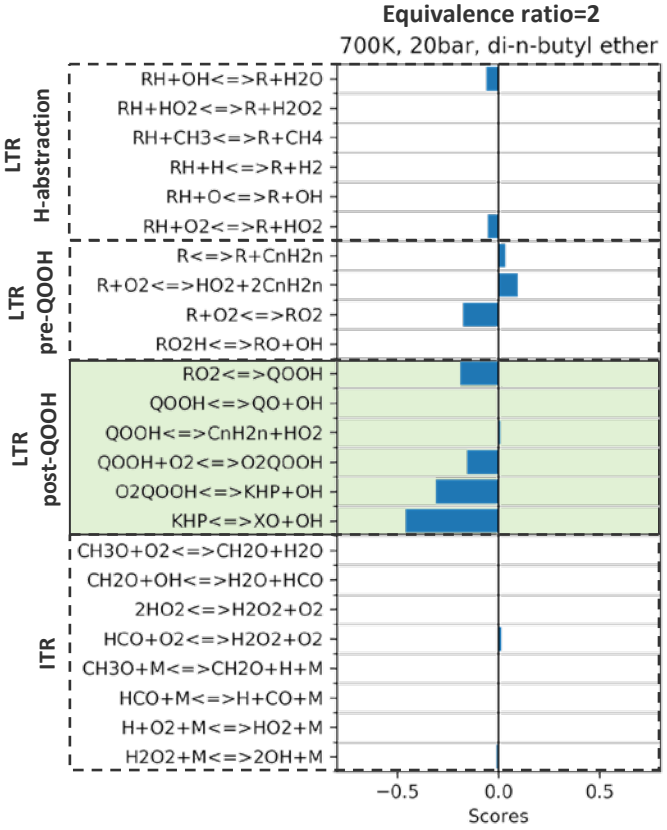
Key reaction step @Low Temperature

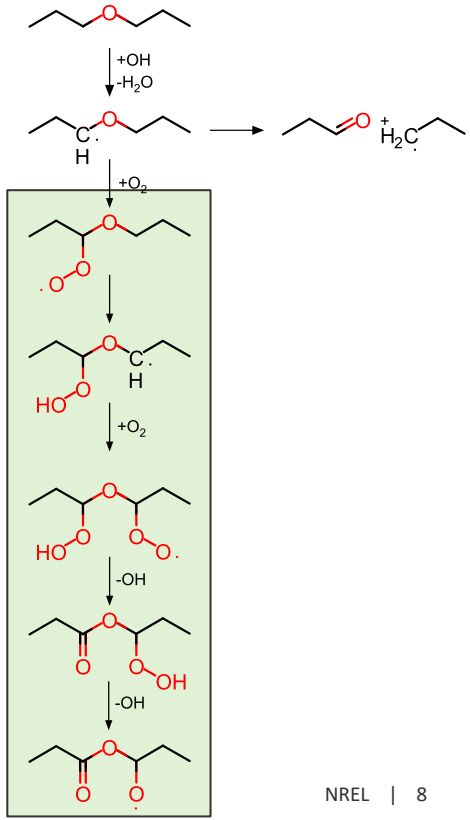
Q: What is the rate determining step for auto-ignition at engine relevant condition?

CFR engine

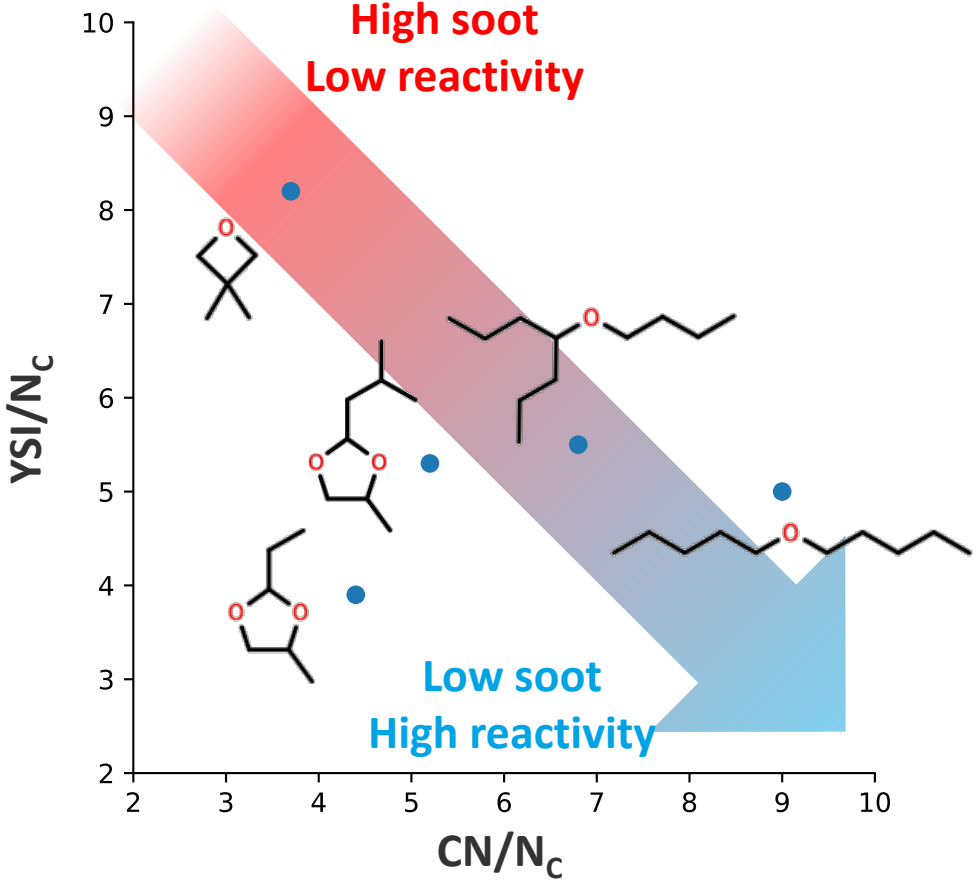
(standard engine for CN measurement)

Typical T, P, ϕ





Conclusion and future work



Soot characteristics

- Linear ether and dioxolane showed comparably low soot precursor formation.
- Flow reactor exp. revealed that YSI is related to the size of HC precursor

Autoignition characteristics

- Linear and branched ether showed high reactive characteristics

On-going work

- QM calculation on auto-ignition characteristics
- Extensive study on the structure effect including the fuel with high carbon #

Acknowledgements

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Yale University

Lisa Pfefferle

Charles McEnally

Junqing Zhu

National Renewable Energy Lab.

Robert McCormick

Gina Fioroni

Anna Thomson

Nimal Naser

Bradley Zigler

Jon Luecke

Peter St John

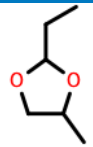
Brian Etz

Richard Messerly

Co-Optimization of
Fuels & Engines

QM calculation@ low T and stoich. condition

CN_p=18.7±8.2
CN_p/N_C=3.7±1.6



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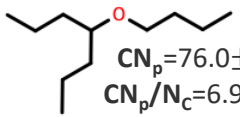

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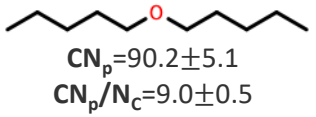

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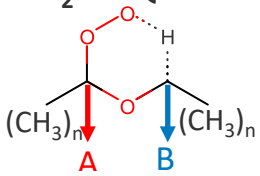
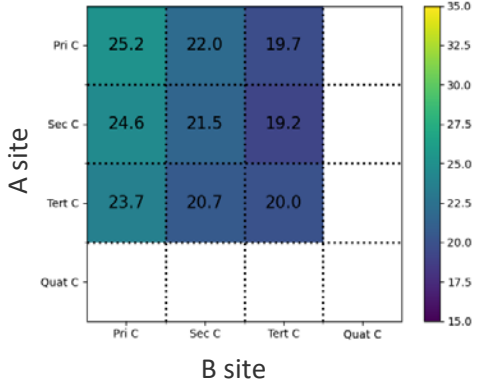
Less reactive → **More reactive**

Key reaction 1

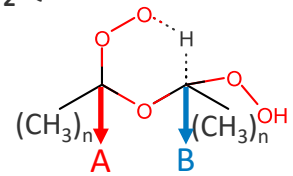
RO_2 ⇔ QOOH

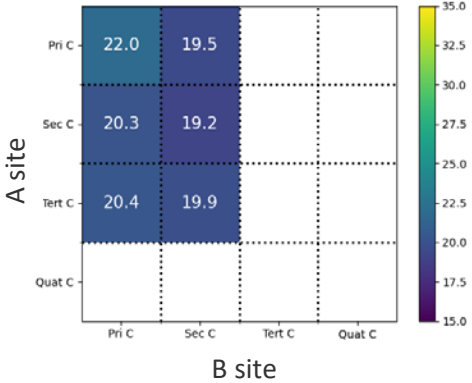




Key reaction 2

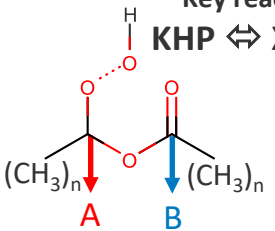
O_2QOOH ⇔ KHP+OH

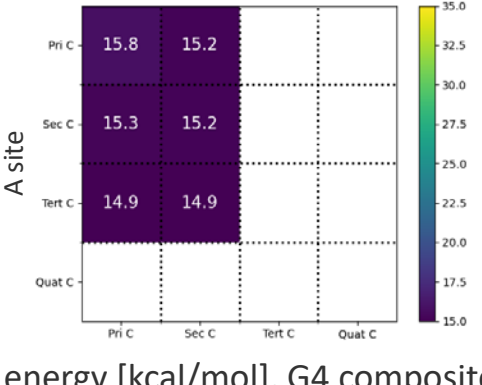




Key reaction 3

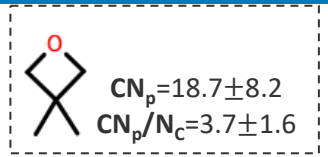
KHP ⇔ XO+OH





Free energy [kcal/mol], G4 composite, 700K

QM calculation@ low T and stoich. condition



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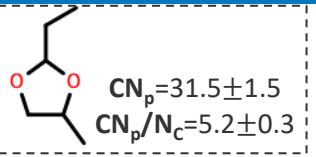

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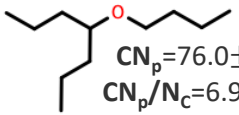

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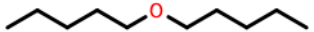

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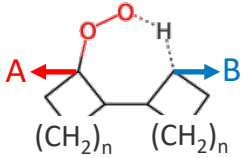
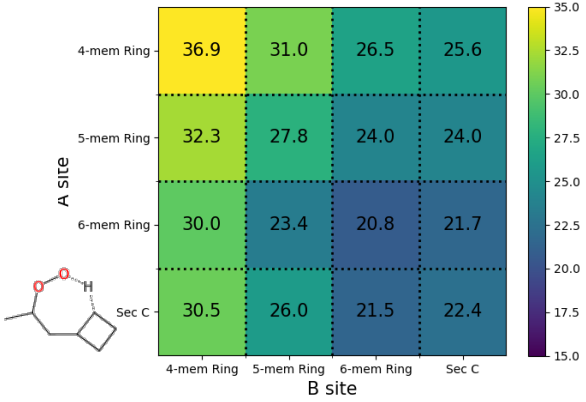
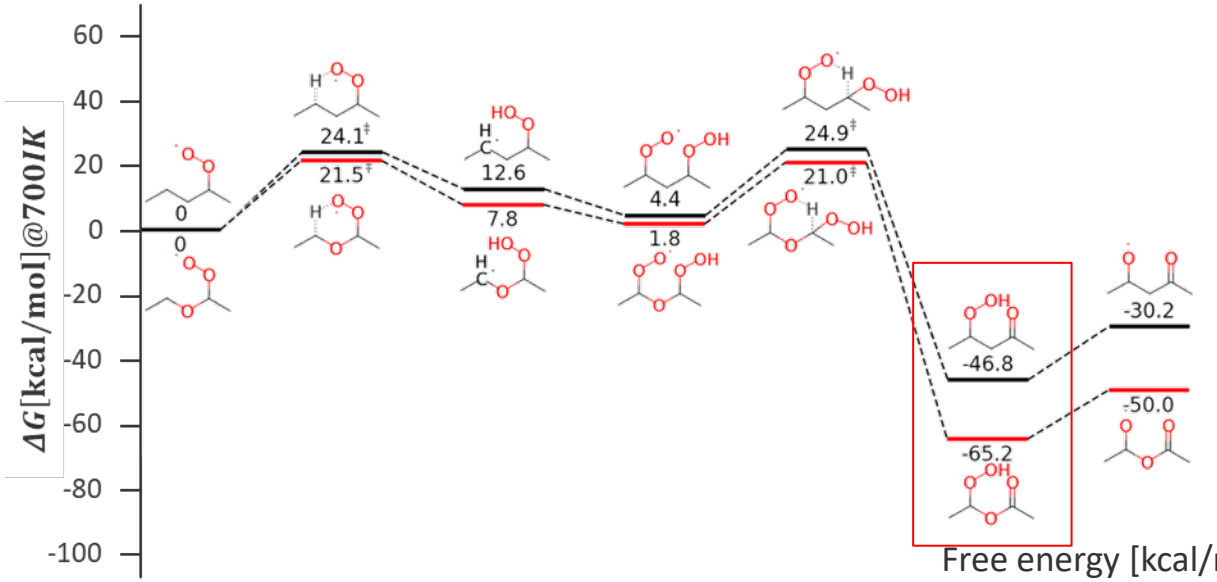
Less reactive → **More reactive**

Key reaction 1

$RO_2 \Leftrightarrow QOOH$







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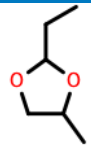

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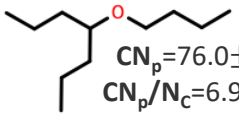

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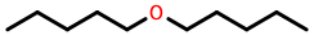
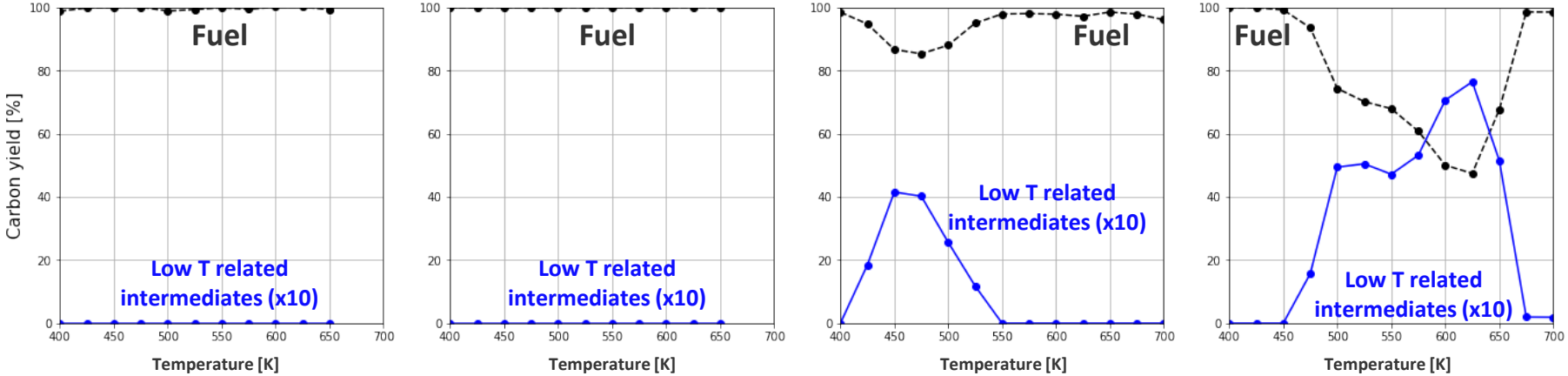


CN_p=90.2±5.1
CN_p/N_C=9.0±0.5

Less reactive → **More reactive**

N_{PriC}=2 N_{4mem}=2	N_{PriC}=2 N_{5mem}=1	N_{PriC}=3 N_{SecC}=7	N_{PriC}=2 N_{SecC}=8
N_{TertC}=0 N_{QuatC}=1	N_{TertC}=1 N_{QuatC}=0	N_{TertC}=1 N_{QuatC}=0	N_{TertC}=0 N_{QuatC}=0



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