# Formation of Highly Oxidized Molecules from $NO_3$ Radical Oxidation of Δ-3-Carene: **A Computational Mechanism**

**Danielle Draper**

Nanna Myllys, Noora Hyttinen, Kristian Møller,
Henrik Kjaergaard, Julie Fry, Jim Smith, Theo Kurtén

ACM 2018

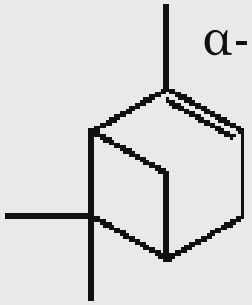
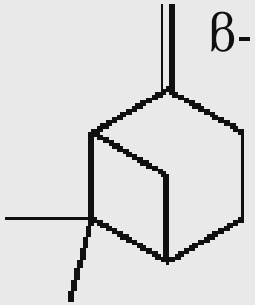
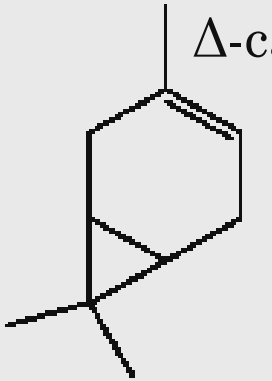
# introduction

- Pye et al. (2010) estimates that >50% monoterpene-derived SOA in the US comes from $NO_3$ oxidation
- Kurtén et al. (2017) compared $NO_3$ oxidation of α-pinene and Δ-3-carene mechanism computationally

  →Identified where the two diverge

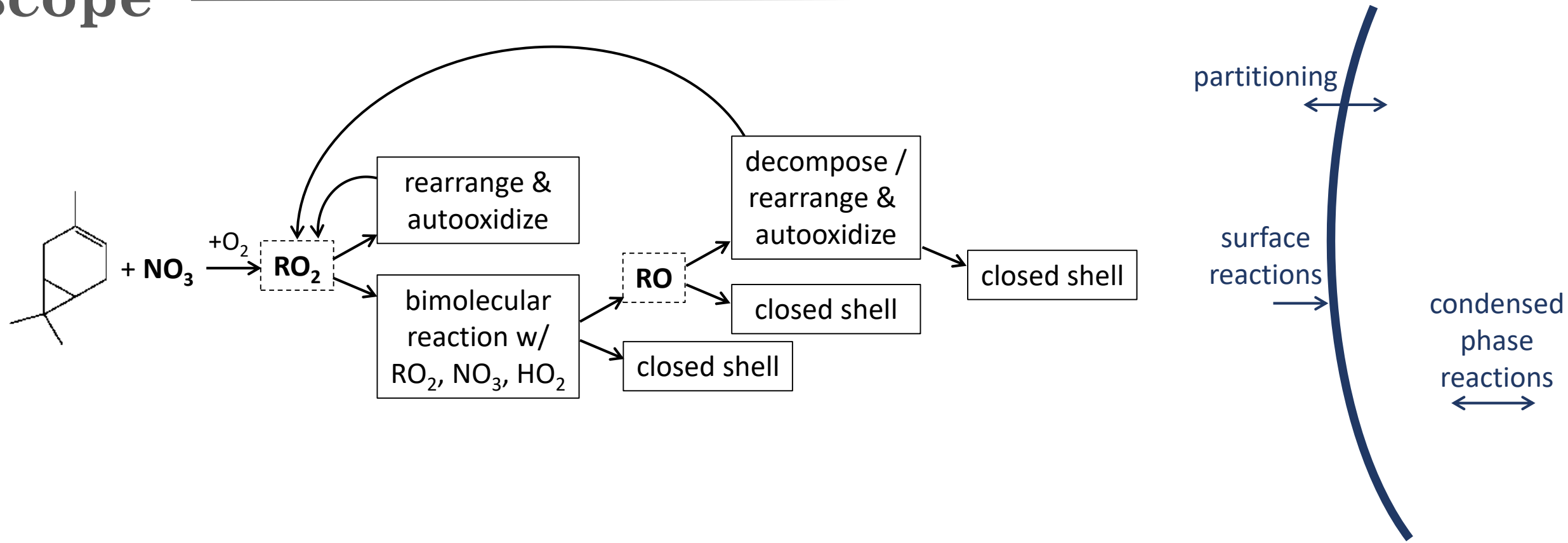
This work continues the Δ-3-carene + $NO_3$ mechanism leading to highly oxidized products

→likely important SOA precursors

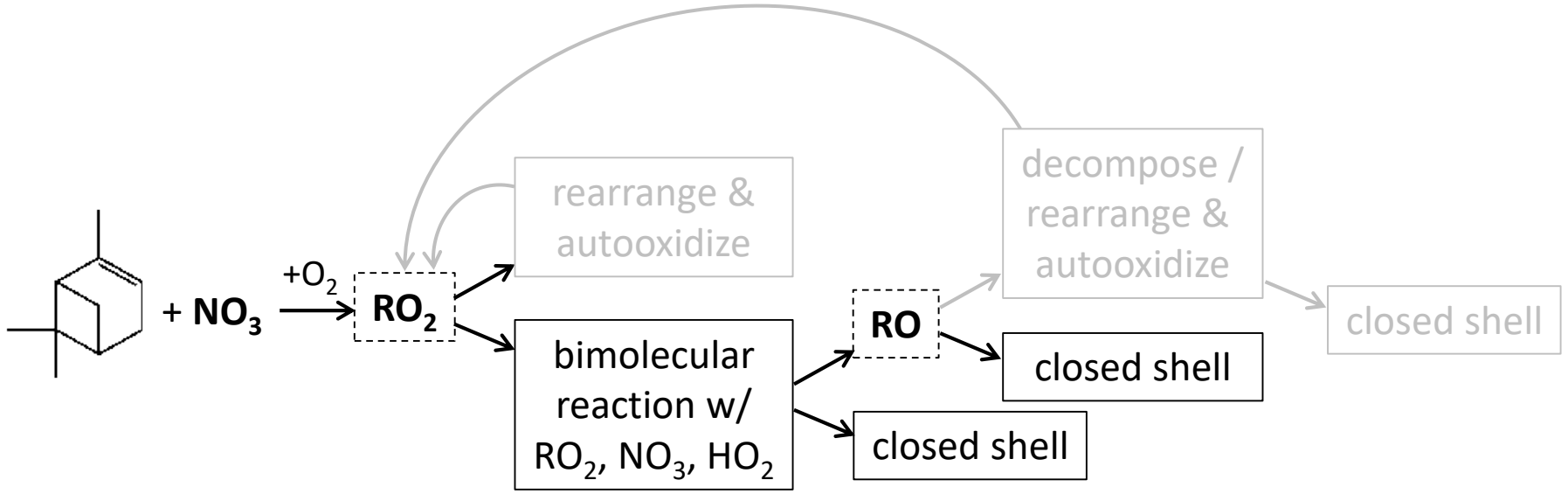
| Reaction | SOA mass yield |
|---|---|
| α-pinene  + $NO_3$ → | 0-16% (median ~4%) |
| ß-pinene  + $NO_3$ → | 7-104% (median ~37%) |
| Δ-carene  + $NO_3$ → | 12-72% (median ~44%) |

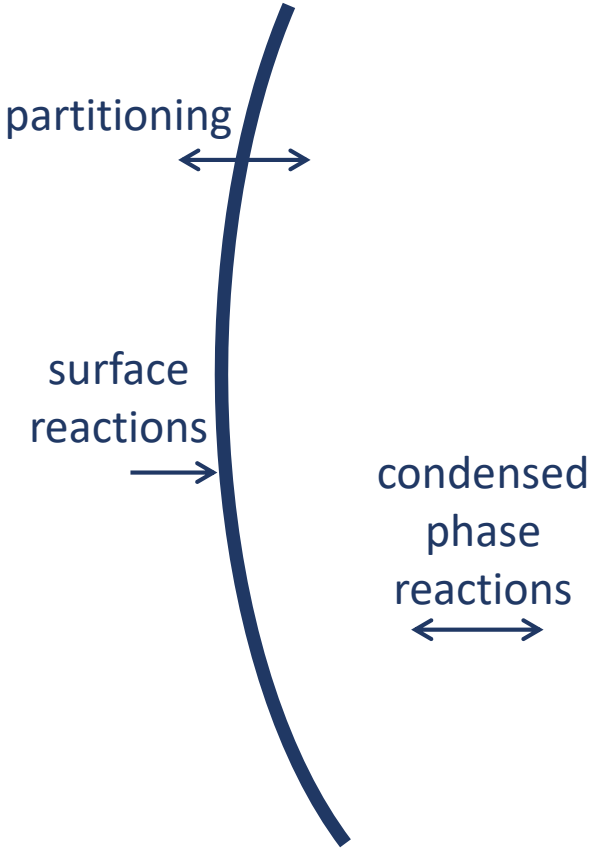
(Ng et al., 2017)

# scope


+ NO3
+O2
RO2
rearrange & autooxidize
bimolecular reaction w/ RO2, NO3, HO2
RO
closed shell
decompose / rearrange & autooxidize
closed shell
closed shell
partitioning
surface reactions
condensed phase reactions

# scope

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Theo Kurtén,[*,†] Kristian H. Møller,[‡] Tran B. Nguyen,[§] Rebecca H. Schwantes,[∥,◆] Pawel K. Misztal,[⊥] Luping Su,[#] Paul O. Wennberg,[∥,∇] Juliane L. Fry,[○] and Henrik G. Kjaergaard[*,‡]

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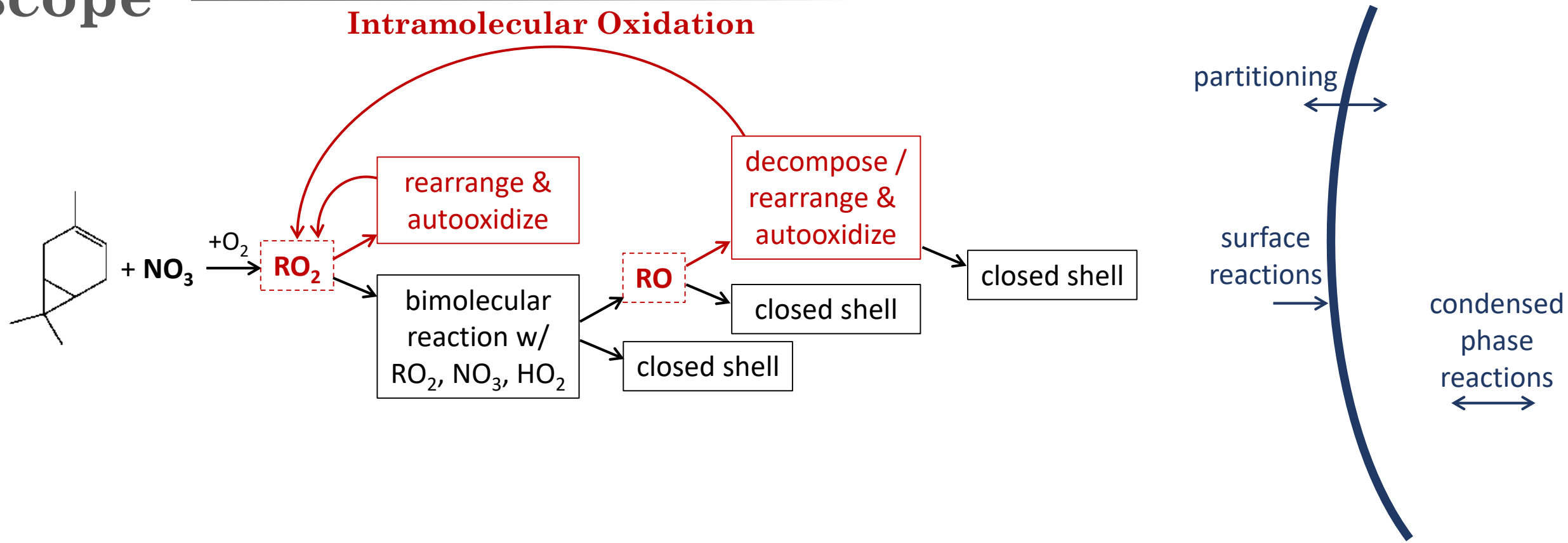


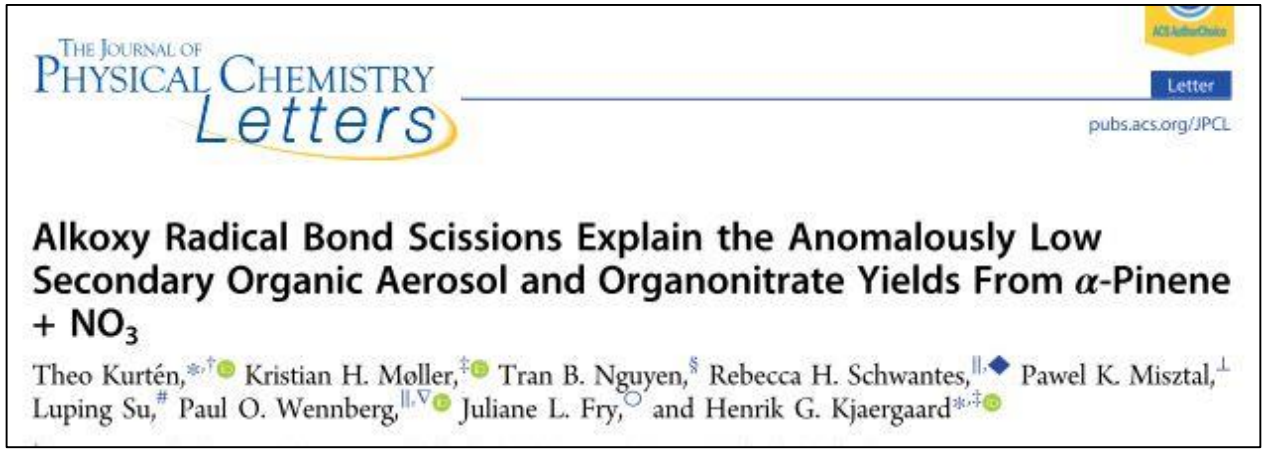

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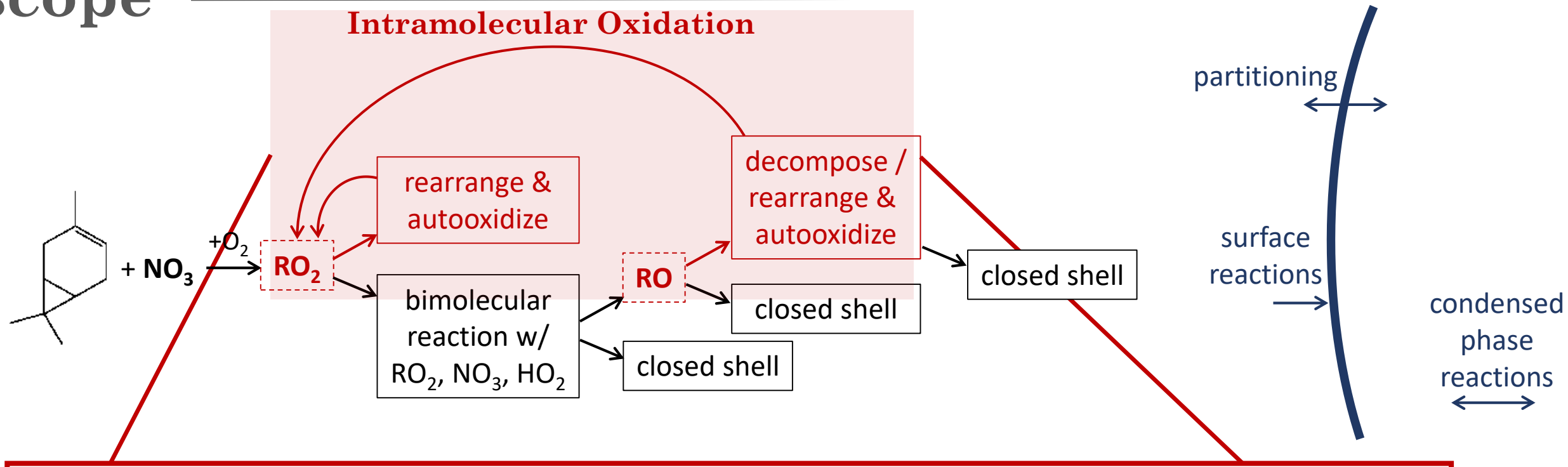
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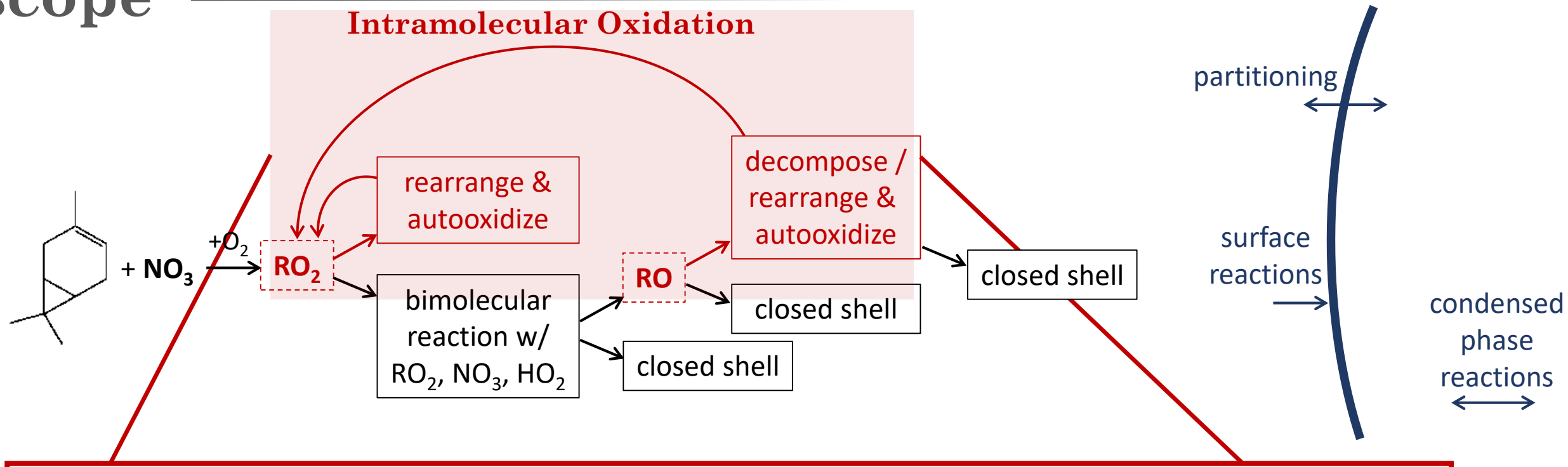
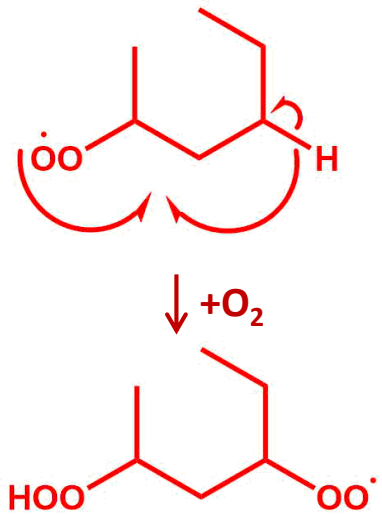



## H-shifts ($RO_2$ and RO)



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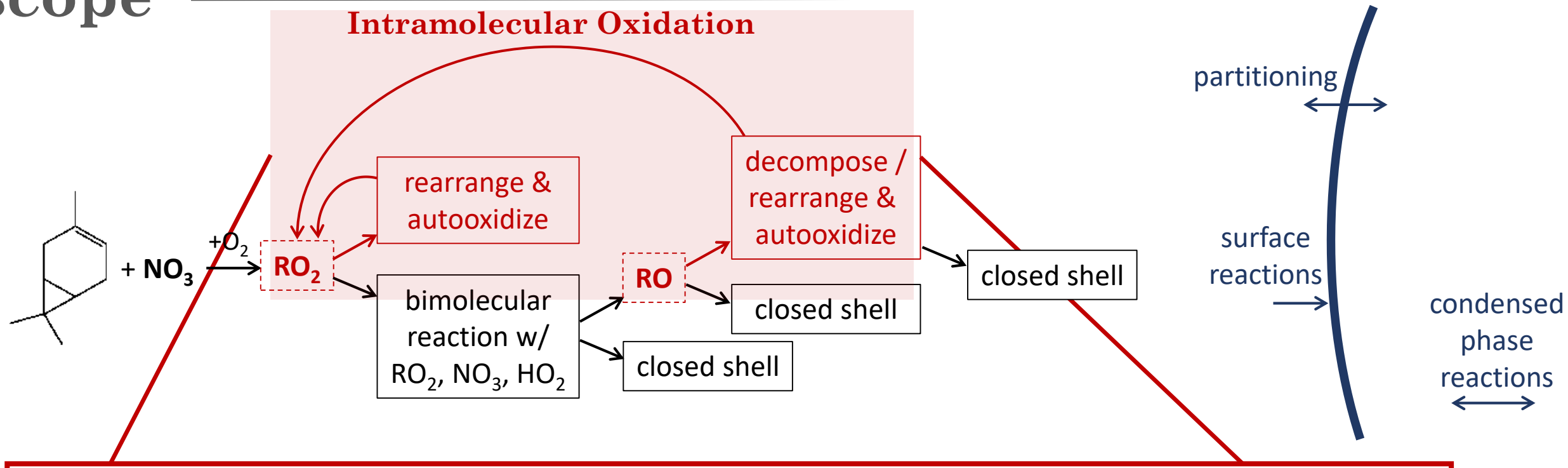


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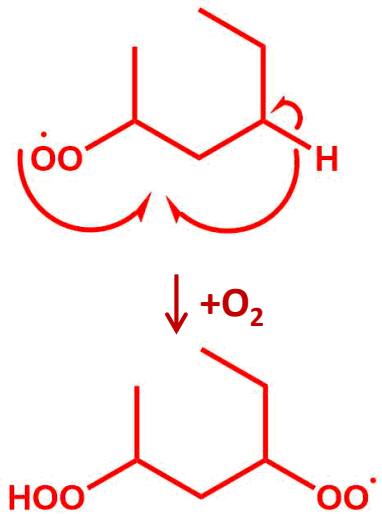
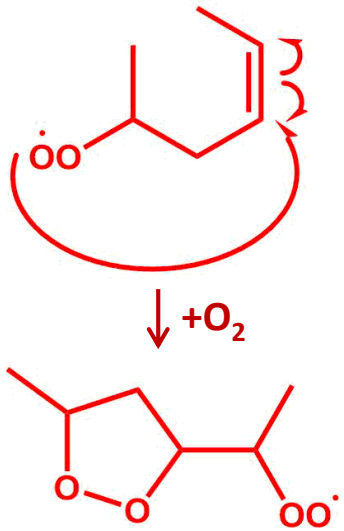
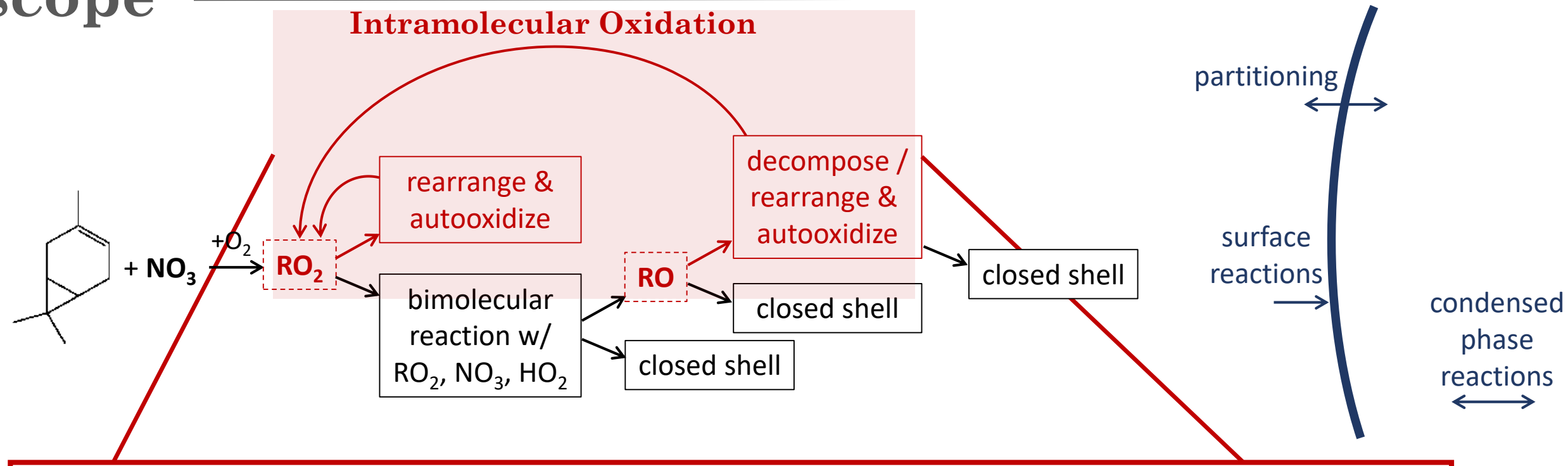



## Addition ($RO_2$ and RO)



# scope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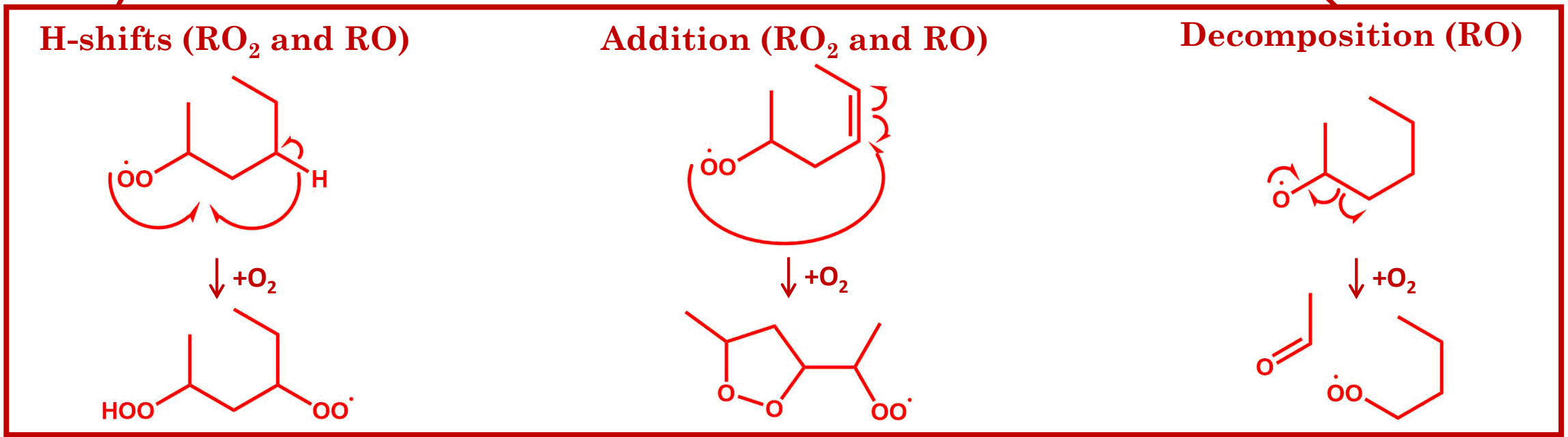
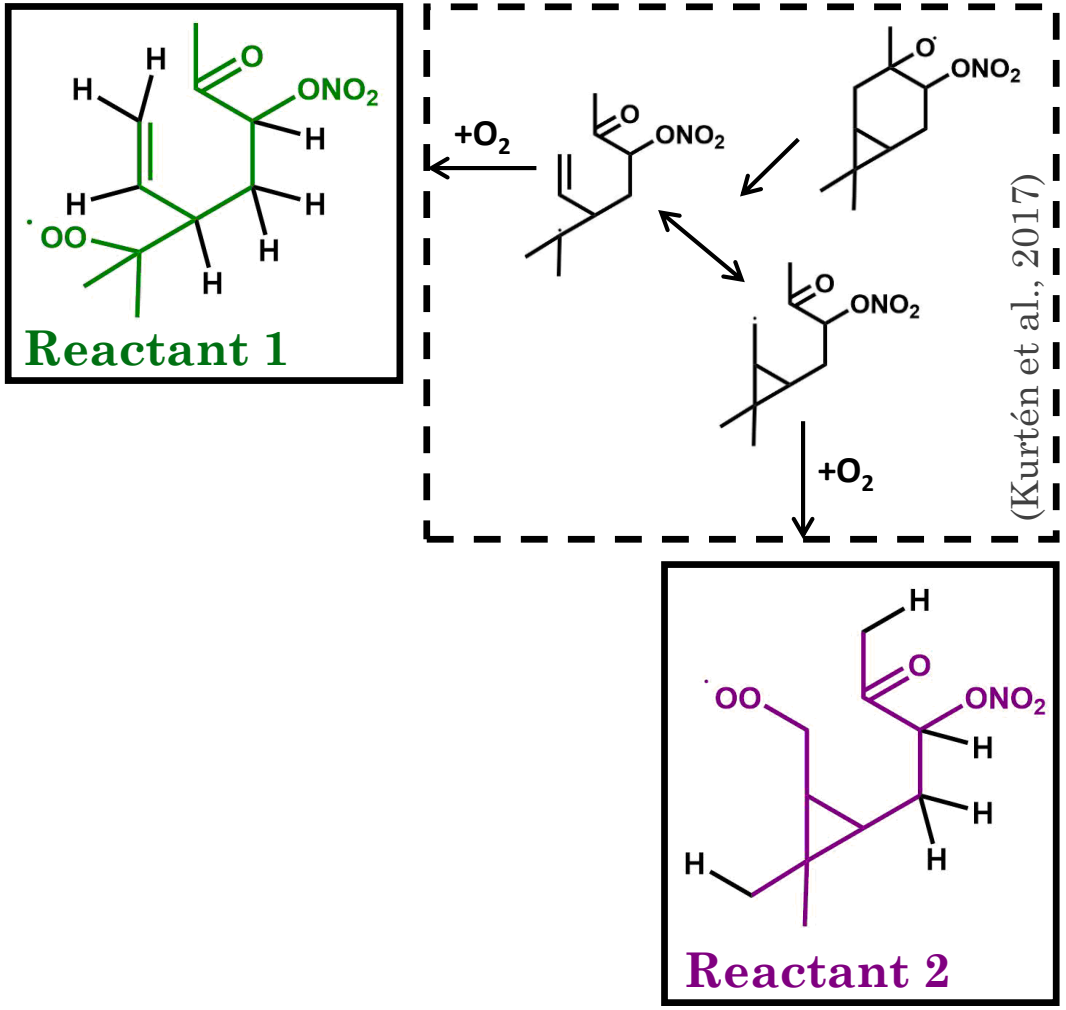

H-shifts (RO2 and RO)
Addition (RO2 and RO)
Decomposition (RO)
+O2
+O2
+O2
HOO
OO
OO
OO
O
O
OO
O

# computational methods

**For every reaction of interest:**

- Build structures & conformer sample (Spartan)
- Calculate energy optimization & frequency (B3LYP/6-31+G(d) → ωB97X-D/ aug-cc-pVTZ (Gaussian) → DLPNO-CCSD(T)/aug-cc-pVTZ (Orca)
- Calculate rate constant using Lowest Conformer – Transition State Theory (LC-TST)

[following the method described in Møller et al. 2016]



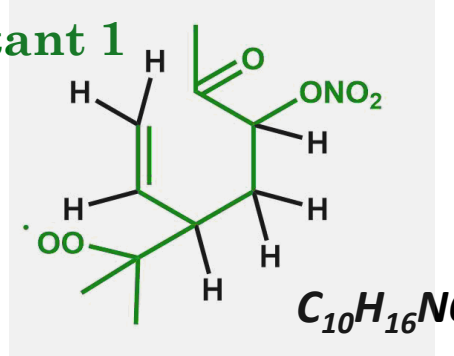

(Kurtén et al., 2017)

**Note: these structures are at the edge of computationally reasonable**

→ some modifications made to published method to balance accuracy and computational cost

# computational mechanism

**Reactant 1**

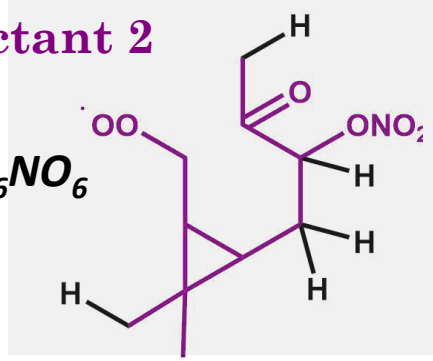



$C_{10}H_{16}NO_6$

$+RO_2$, $NO_3$
$+O_2$

~$10^{-2}$ $s^{-1}$

**Reactant 2**

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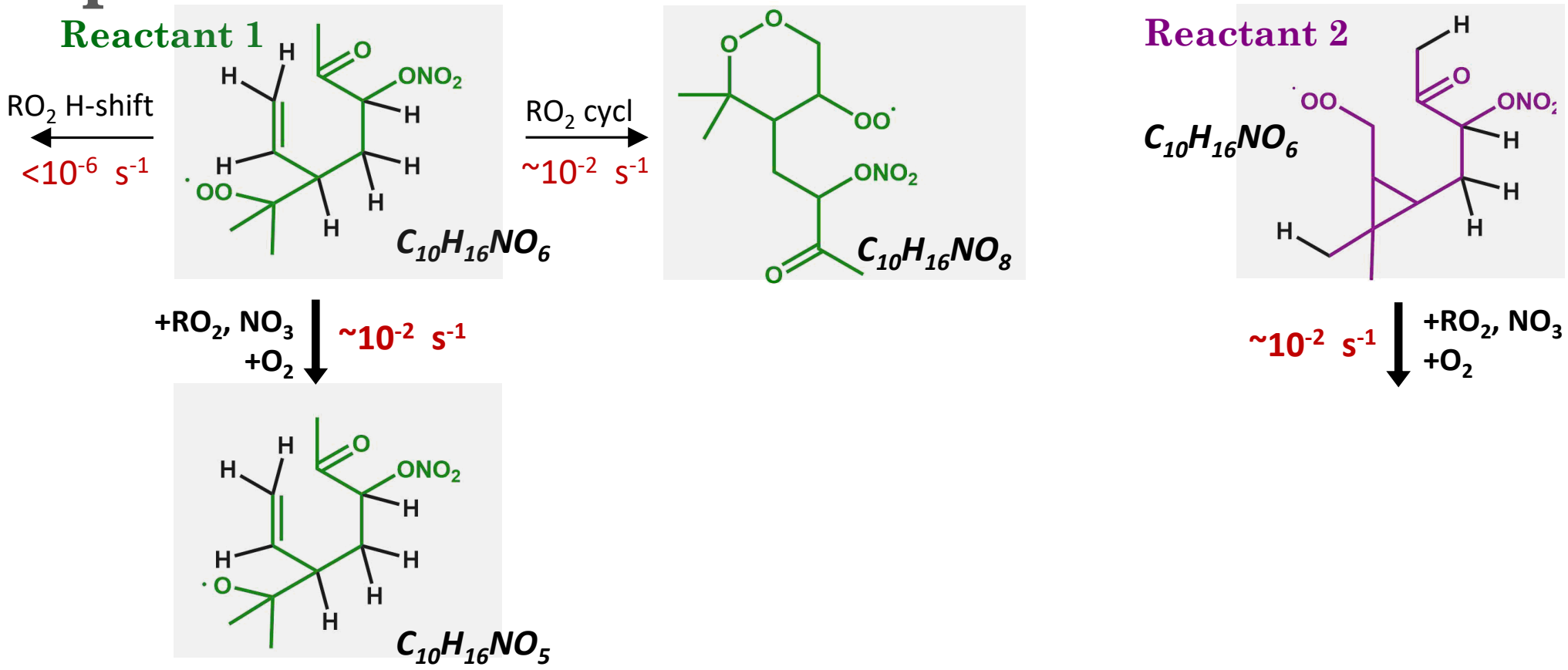
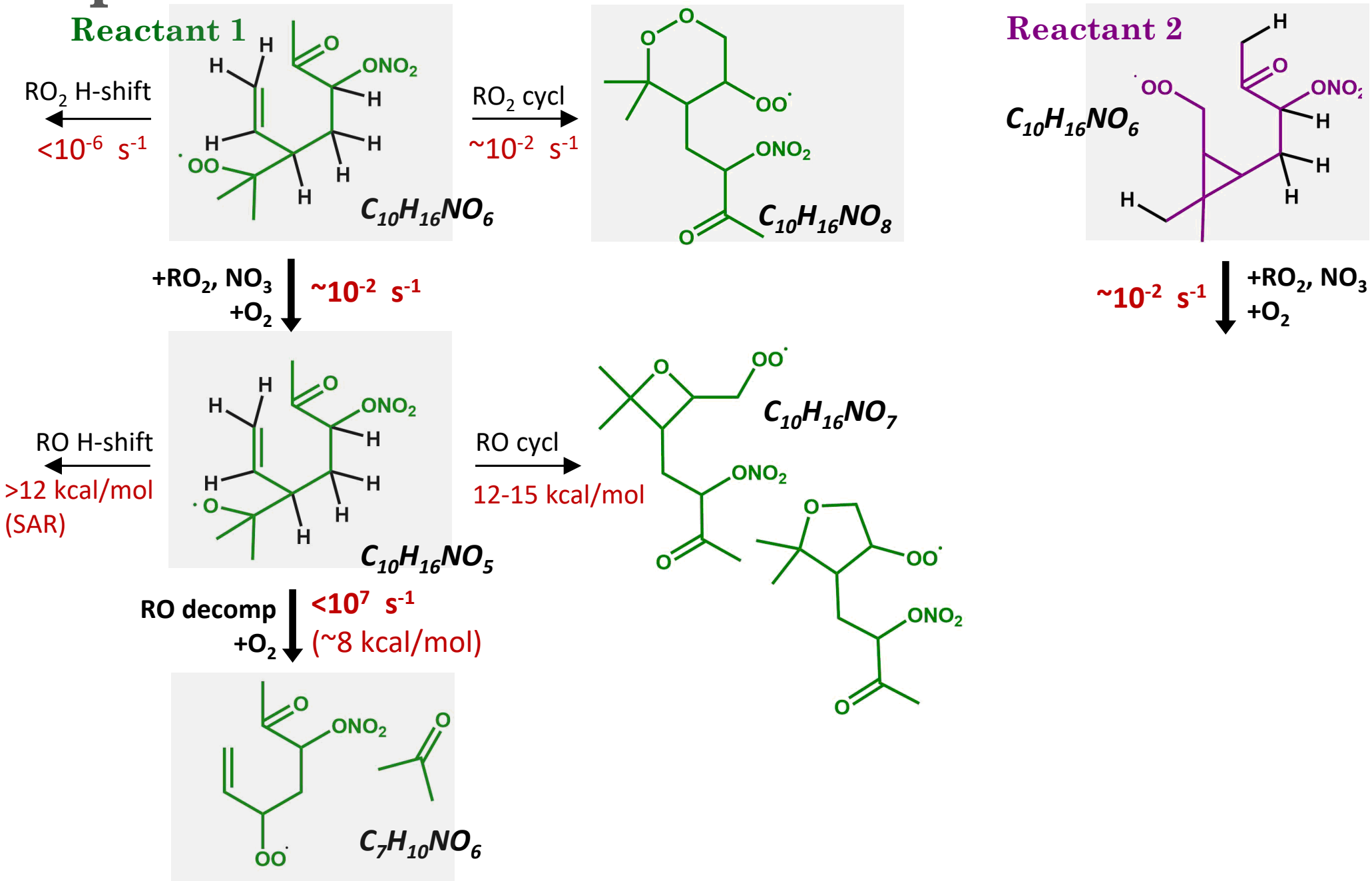
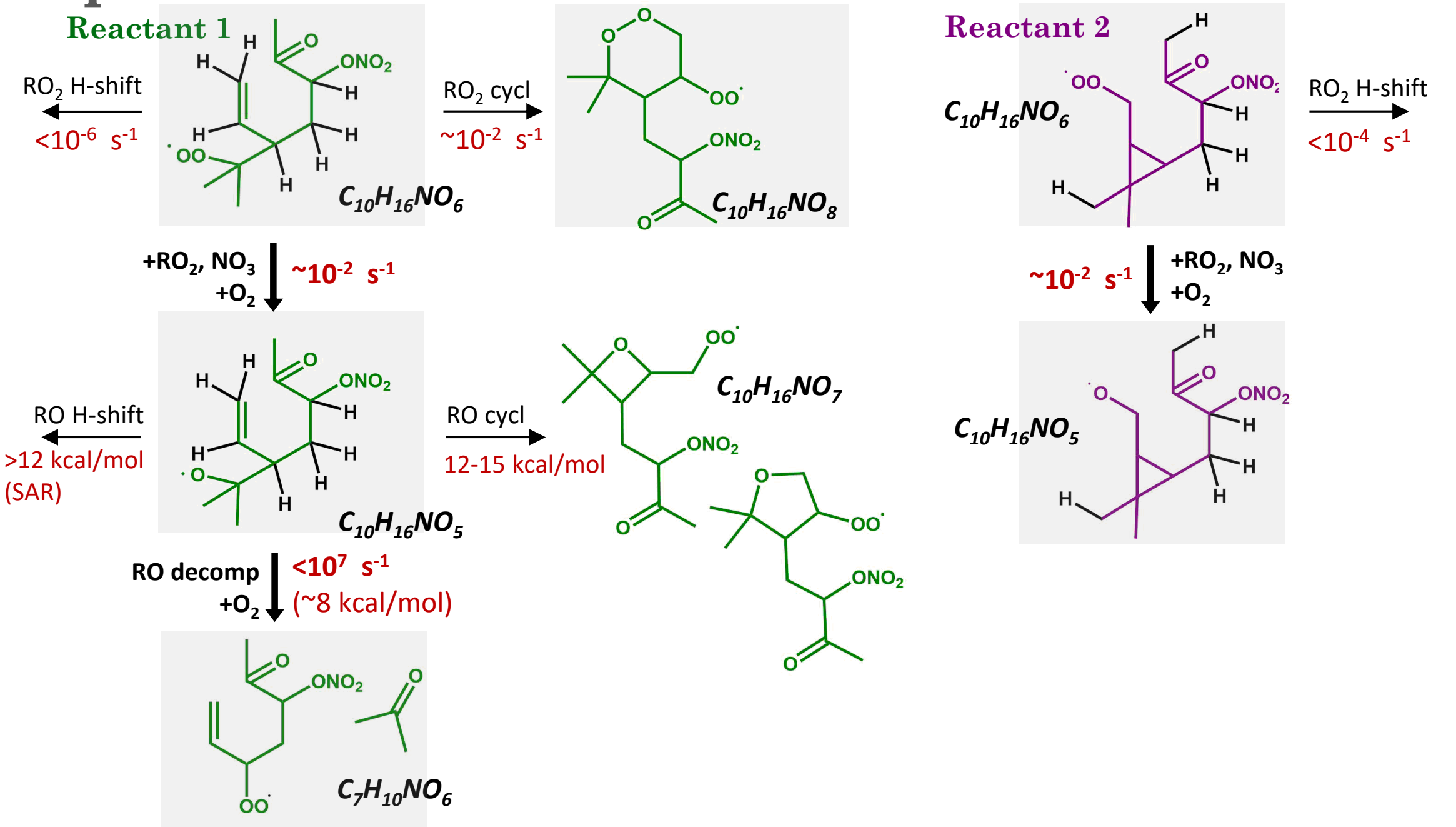


# computational mechanism




Vereecken & Peeters; PCCP 2009 & 2010)

# computational mechanism

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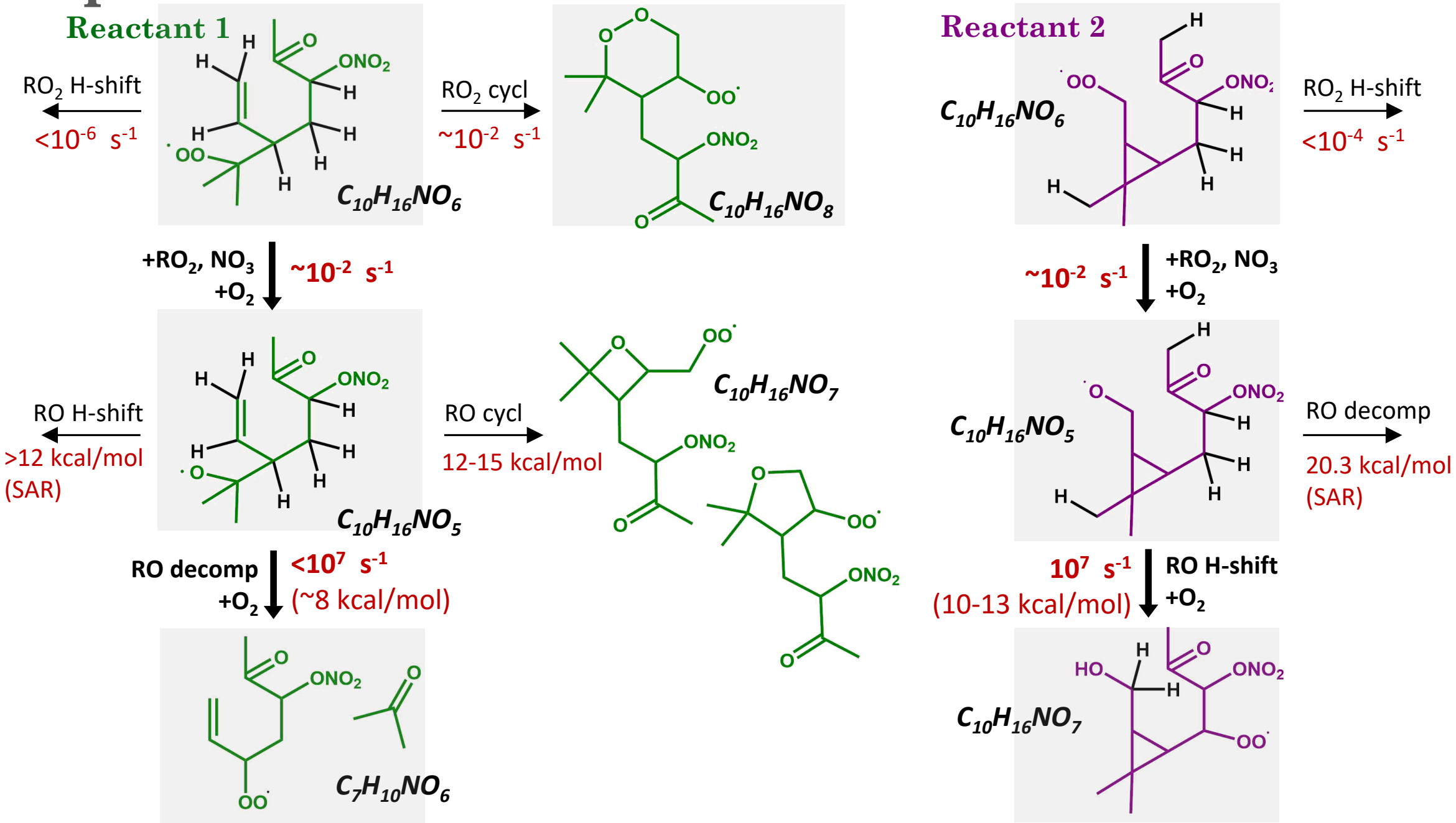


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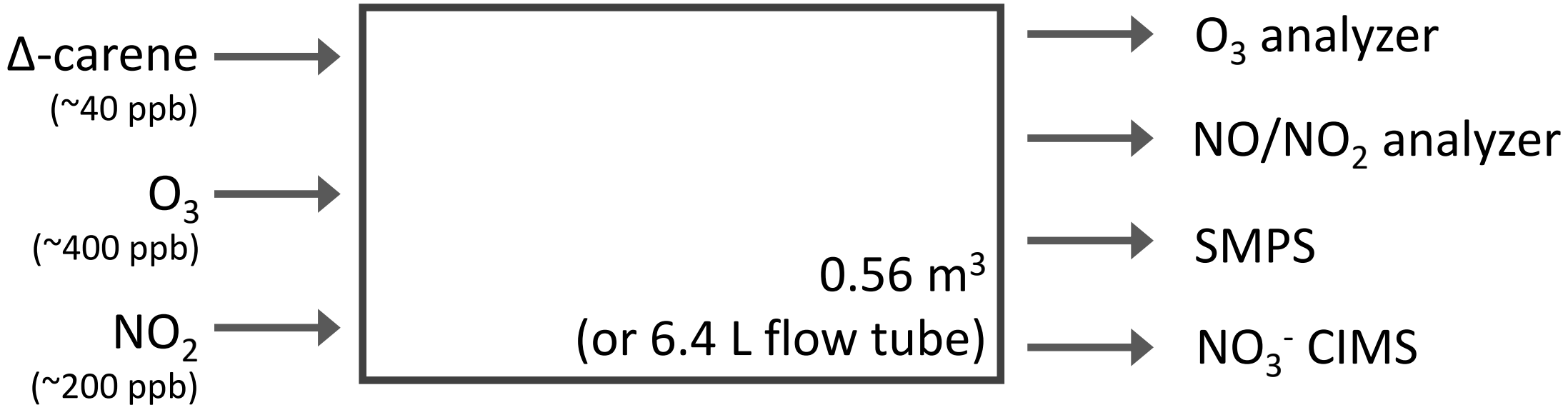
# experimental methods

Compare computational results to experimental observations:




$NO_3^-$ chemical ionization mass spectrometry (CIMS) is selective specifically to (many) highly oxidized, low volatility organic compounds

→ ideal to test validity of our mechanism

# $NO_3^-$ clustering calculations

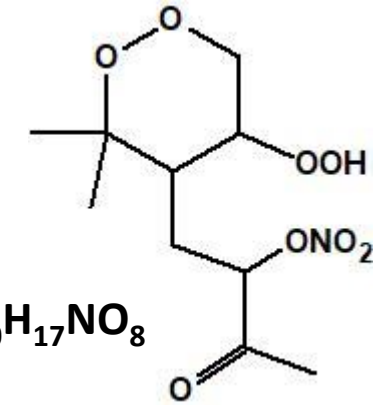
$NO_3^-$ is good at detecting highly oxidized molecules with H-bond donors

- formulas we see actually aren't THAT highly oxidized, given the $-ONO_2$
- structures we've calculated are fairly lacking in H-bond donors

closed shell + $NO_3^-$ → (closed shell)$NO_3^-$

$$\Delta E_{clustering} = E_{prod} - E_{react}$$

$$HNO_3 + NO_3^- \longrightarrow (HNO_3)NO_3^- \qquad \Delta E \approx -29 \text{ kcal/mol}$$



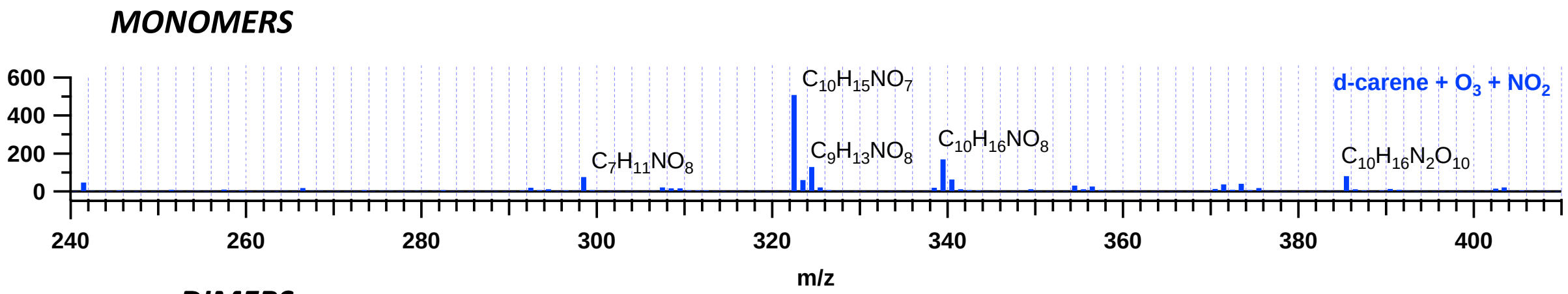

$C_{10}H_{17}NO_8$

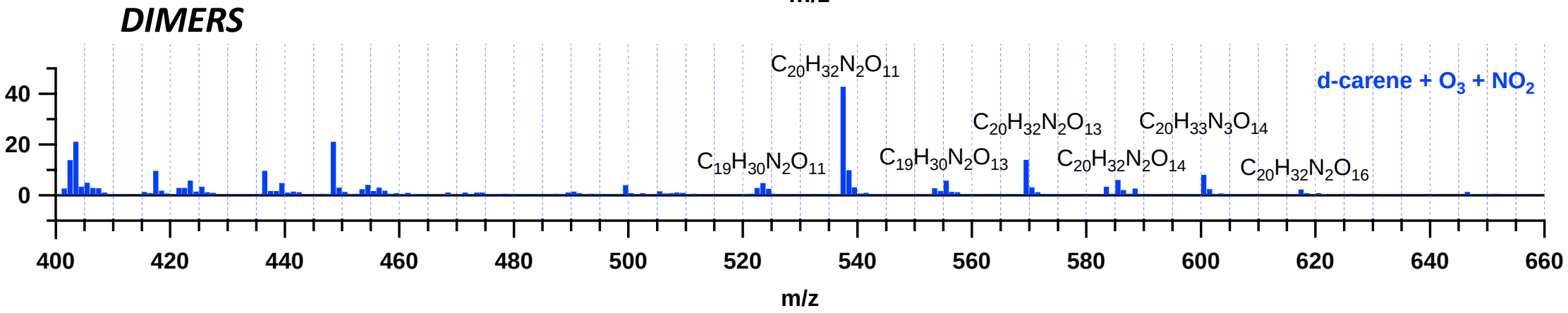
$$+ NO_3^- \longrightarrow (C_{10}H_{17}NO_8)NO_3^- \qquad \Delta E \approx -33 \text{ kcal/mol}$$

→ Quick $NO_3^-$ cluster calculations indicate we're sensitive to molecules of interest with at least 1 H-bond donor

# experimental data

At a glance:
- ✓ $C_{10}$ monomers & $C_{20}$ dimers
- ✓ primarily organonitrates
- ✓ monomers are building blocks of dimers



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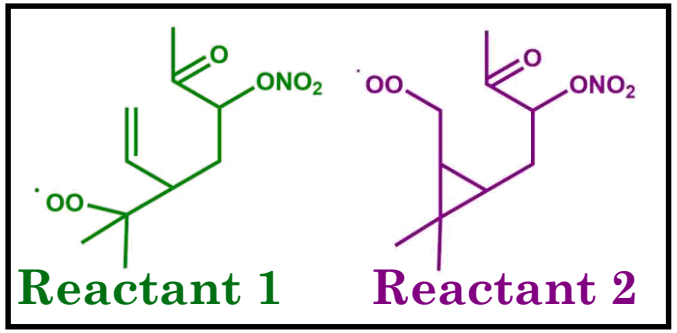
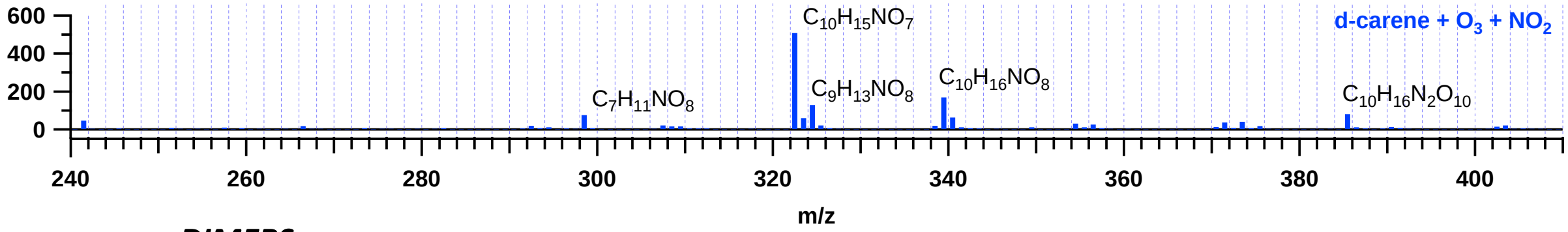
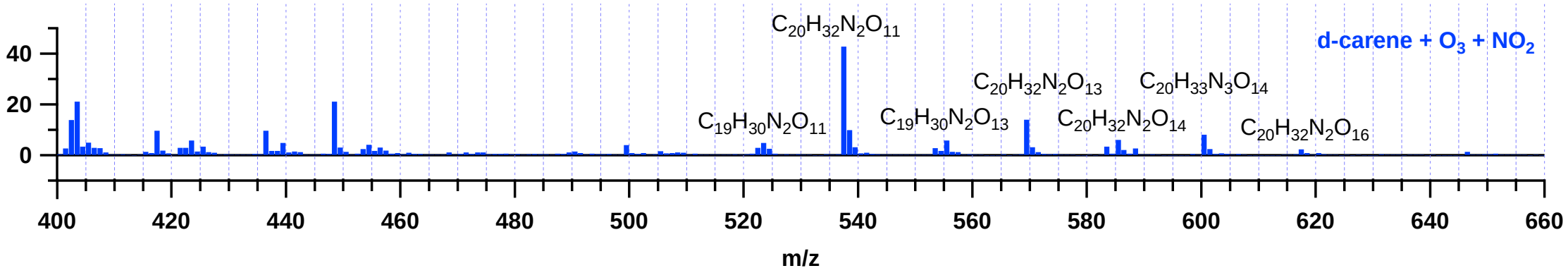



***MONOMERS***




***DIMERS***



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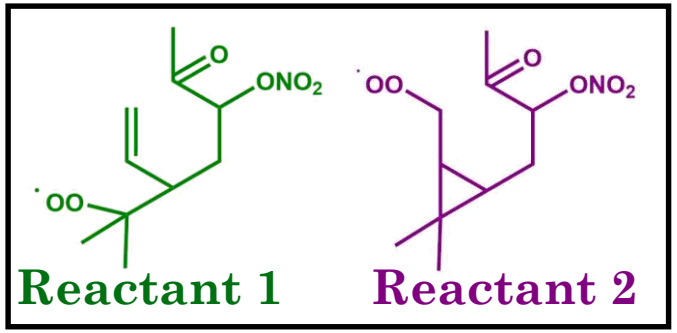


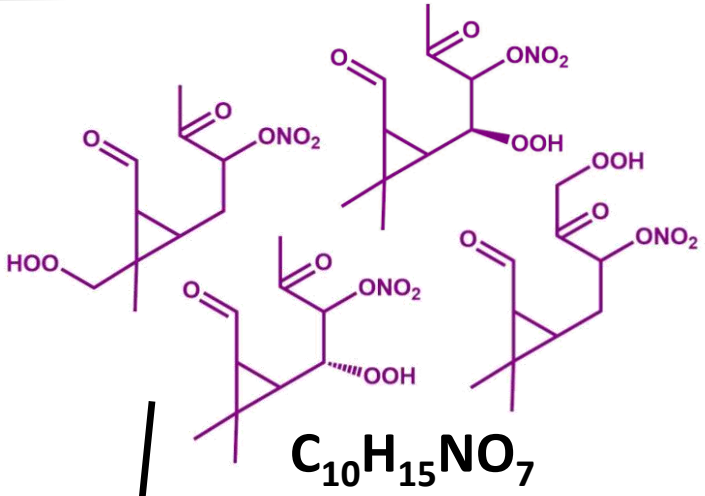


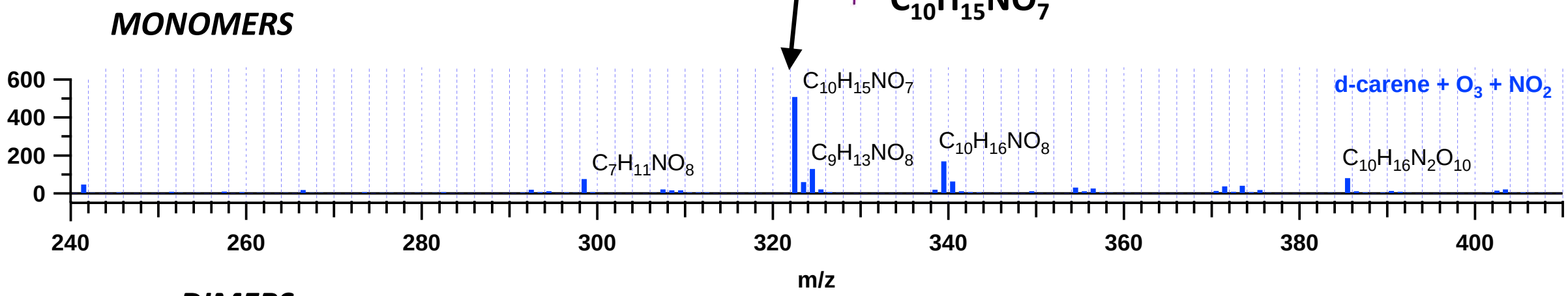


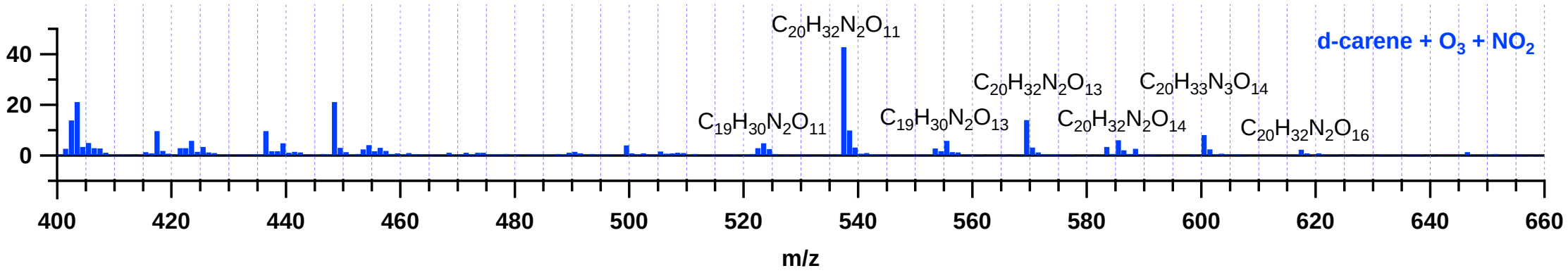

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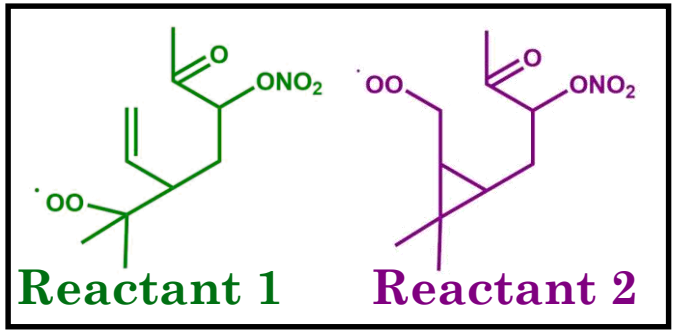


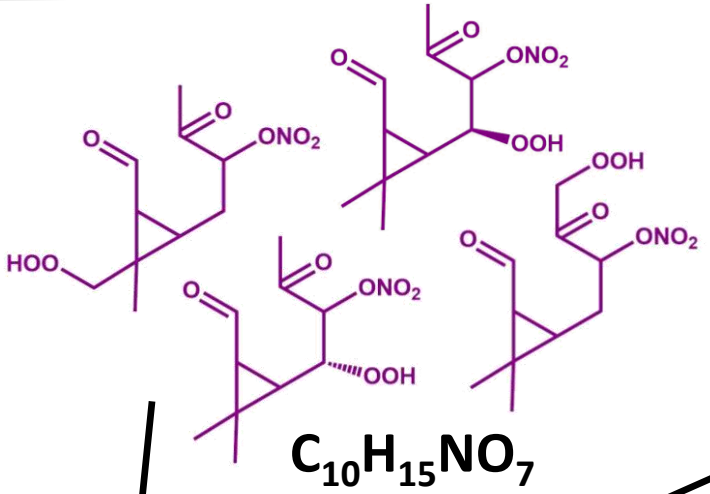


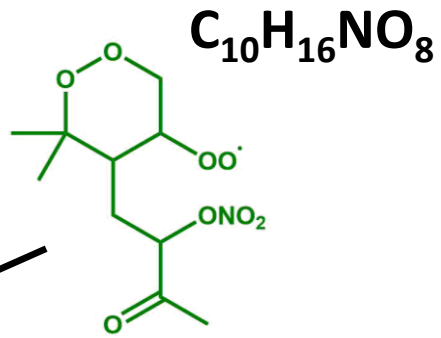


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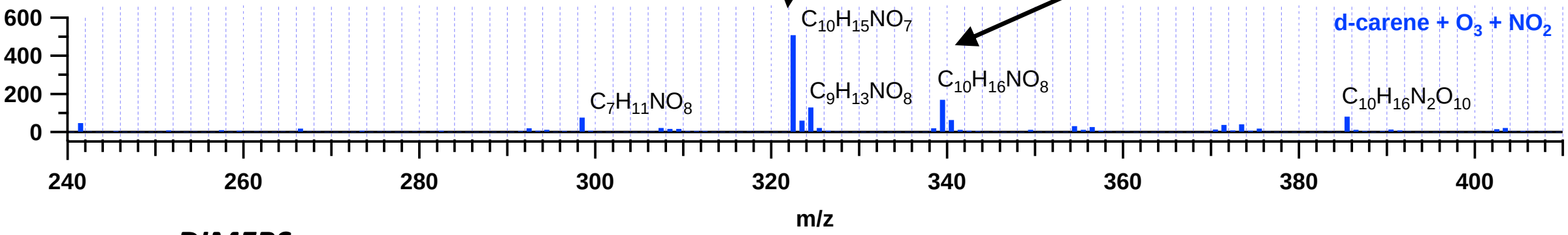


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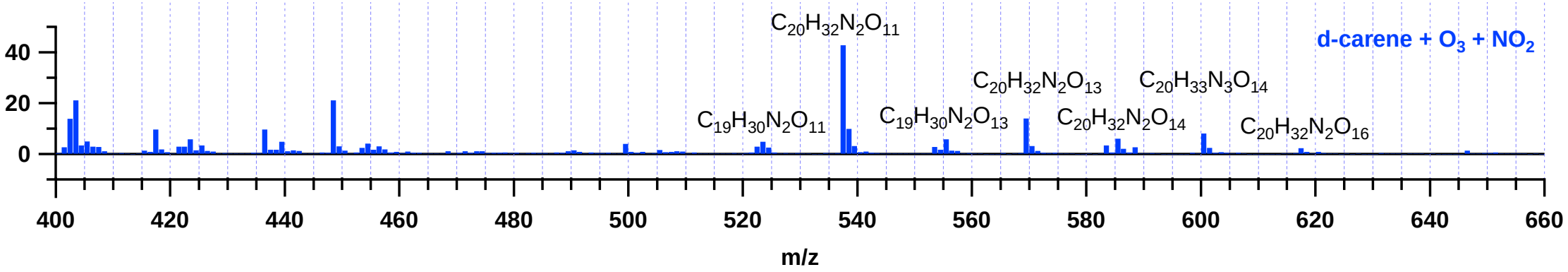

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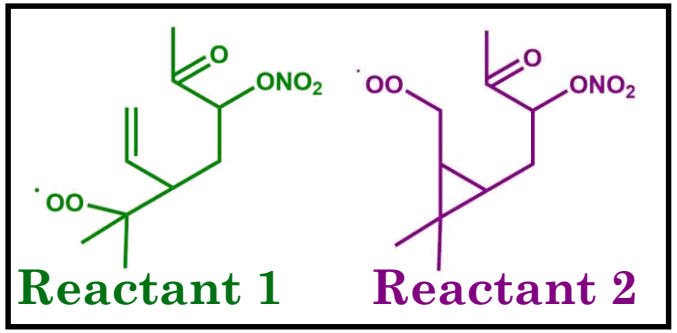


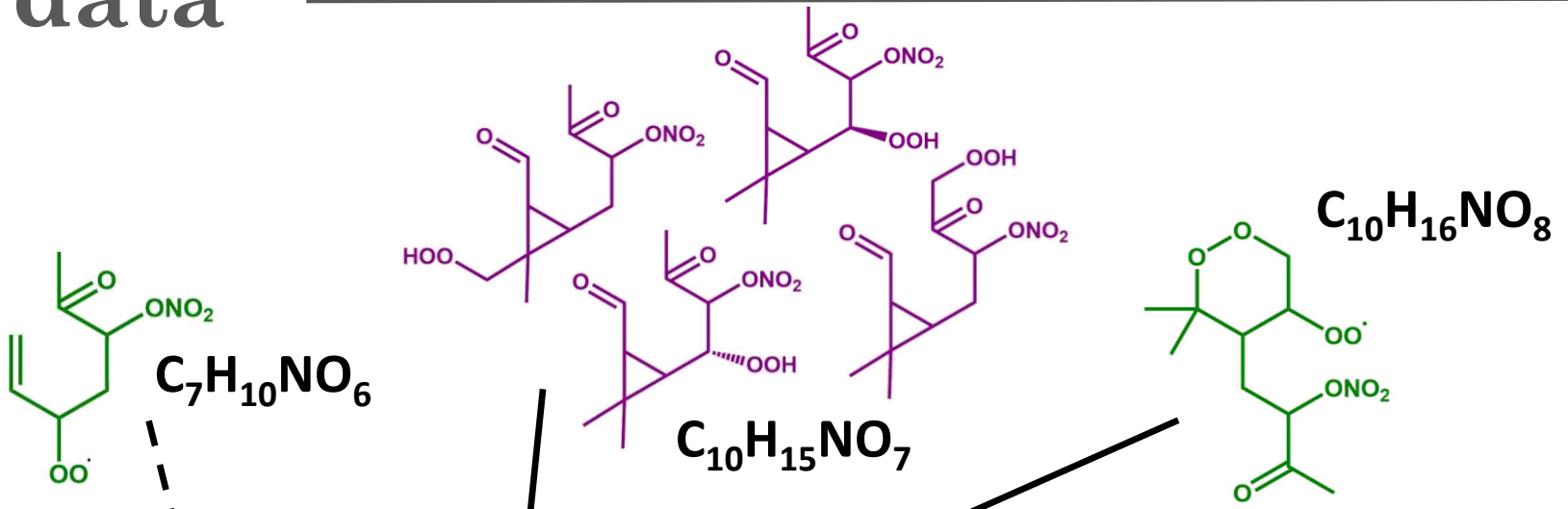


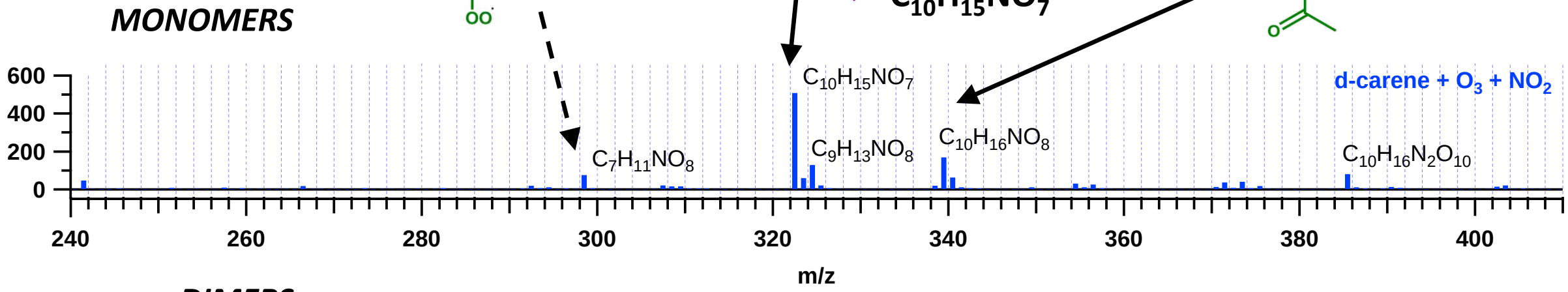


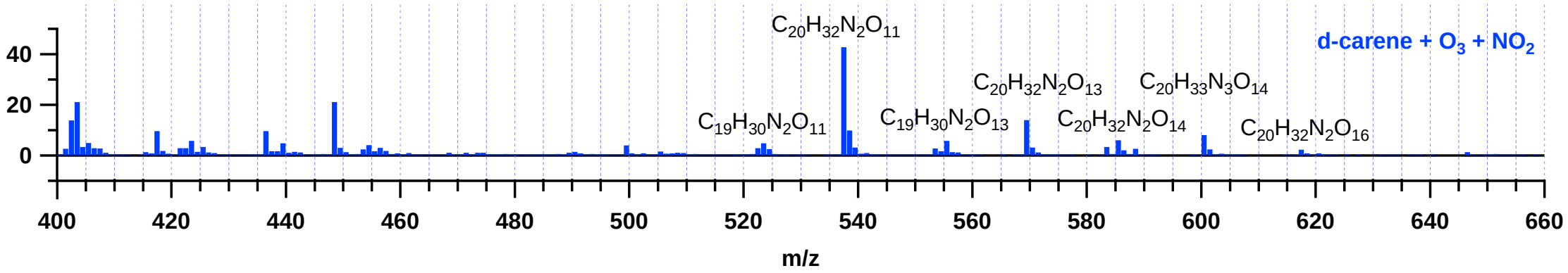

# conclusions

- Both intra- and bi-molecular reactions contribute to Δ-3-carene + $NO_3$ products
- We see many of our predicted highly oxidized products via $NO_3^-$ CIMS

  → Notably, our 3 dominant products predicted correspond to our highest intensity peaks
- While we have not yet made particle-phase measurements, we expect this portion of the mechanism to be an important link to particle formation from $NO_3$ oxidation of monoterpenes

# Thanks!

## Collaborators:

UNIVERSITY OF COPENHAGEN

HELSINGIN YLIOPISTO
HELSINGFORS UNIVERSITET
UNIVERSITY OF HELSINKI

REED COLLEGE

UCI University of California, Irvine

## Funding for this project:

NSF

ACADEMY OF FINLAND

CSC

# Questions?