Isomerization and Decomposition of Isoprene's δ-(*Z*)-Hydroxyperoxyl Radicals

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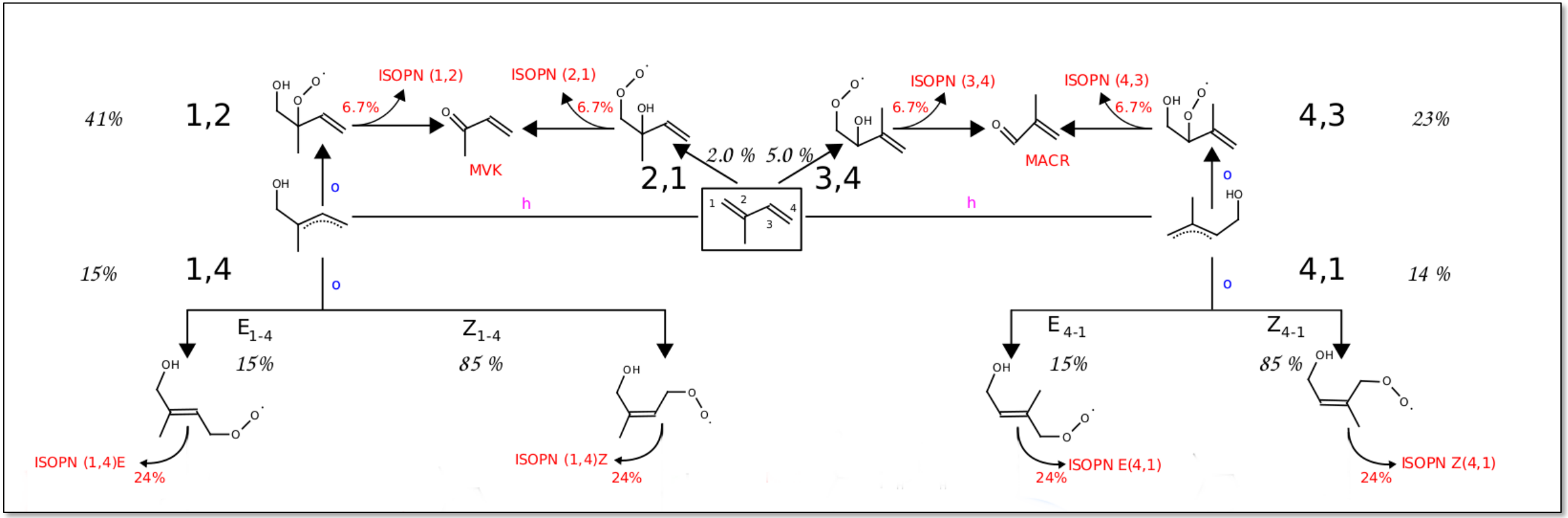
Isoprene is perhaps the most important VOC governing the chemistry of our atmosphere

- Rivals methane emissions
- Completely removed in planetary boundary layer (**where we live!**)
- Produces many generations of products
- Important interplay with aerosols and CCN
- Interacts with NO_x

Isoprene's atmospheric chemistry is complex…



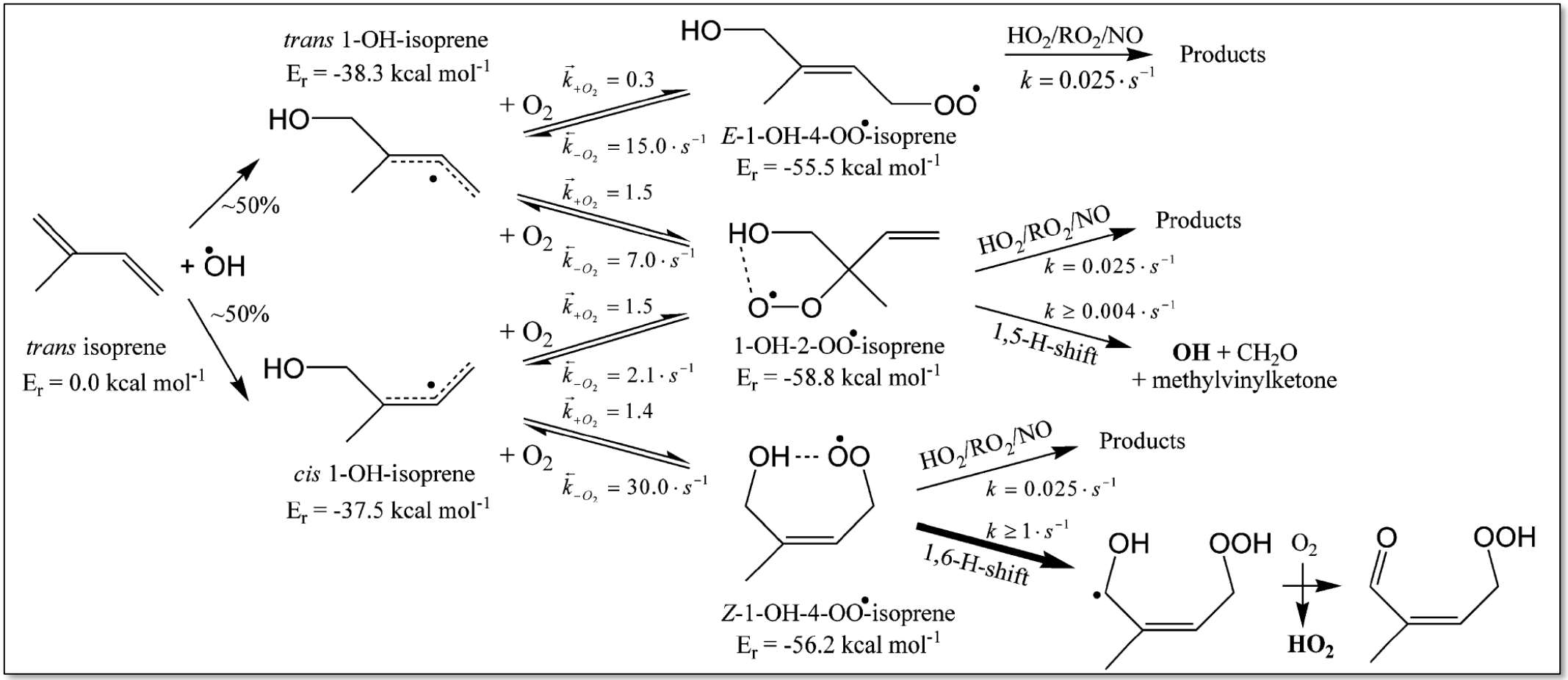
Paulot et al., *Atmos. Chem. Phys.* **2009**.

Isoprene Peroxyl Radicals

- Above forests, isoprene RO_2 can live for a long time.
- Atmospheric chemical models still struggle to reproduce this chemistry.
- Lab studies of isoprene RO_2 also disagree.

RO_2 Isomerization

- *Peroxyl radicals can scramble, isomerize, and decompose:*



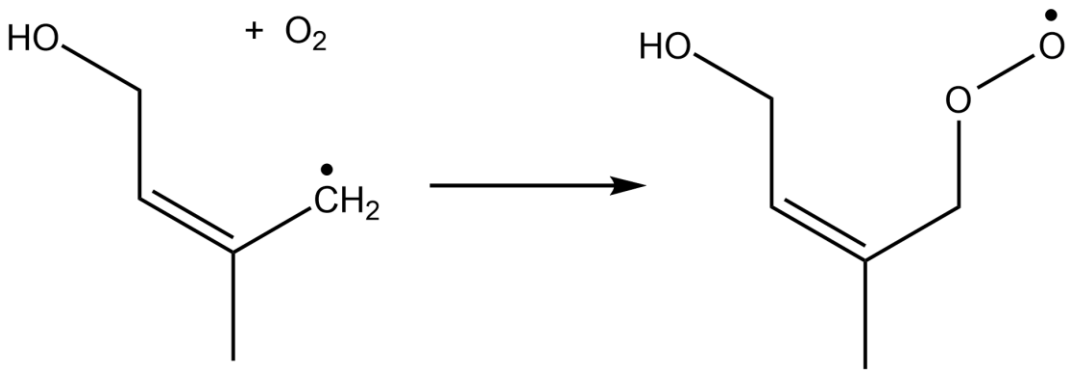
Peeters, Vereecken, and Nguyen, *Phys. Chem. Chem. Phys.* **2009**.

This work reports on a newly discovered decomposition channel of the isoprene δ-(*Z*)-hydroxyperoxyl radicals

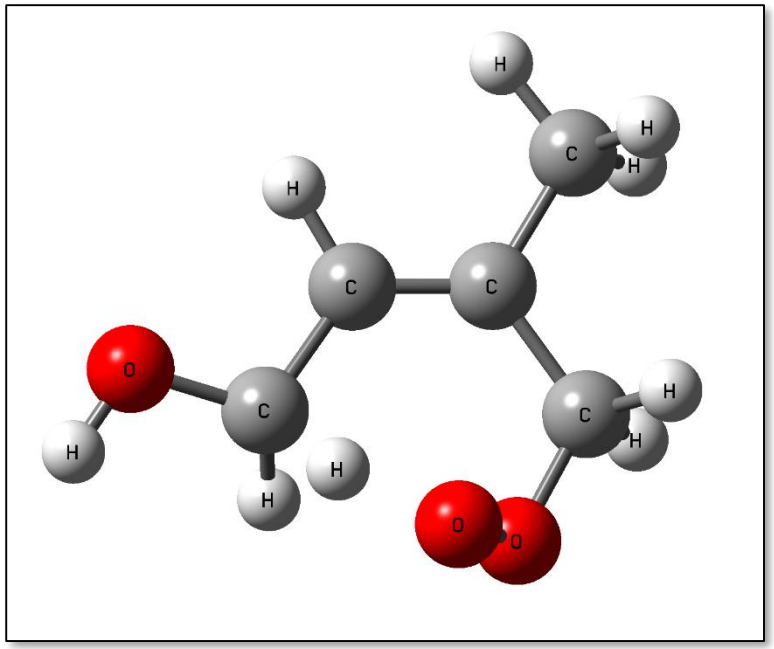
A New Mechanism…

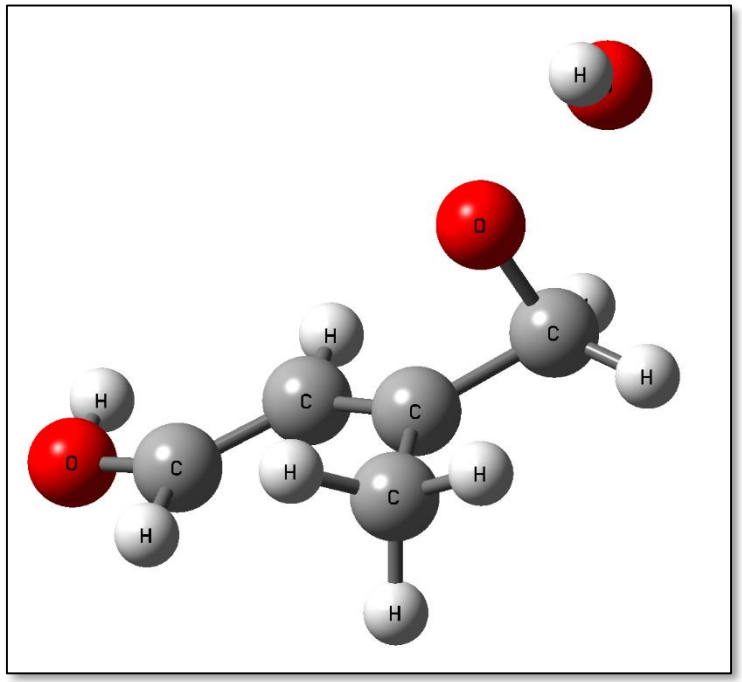
1 and 4 substituted ISOP-OH adducts can:

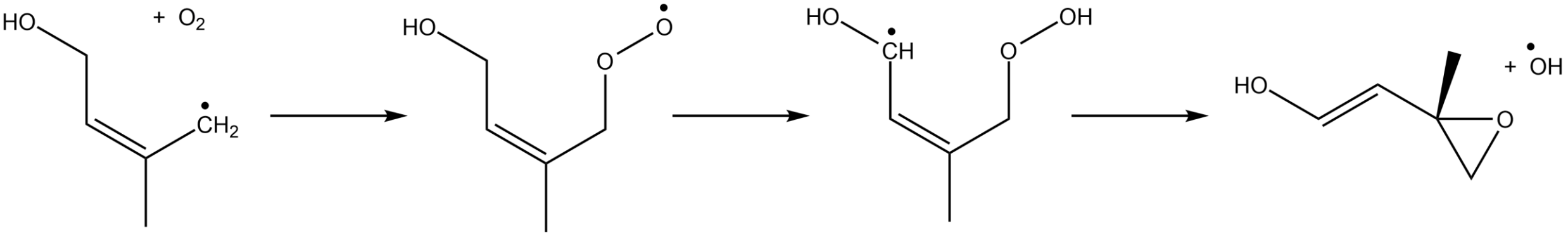
- Add O_2 to form 1,4- and **4,1-RO_2**,



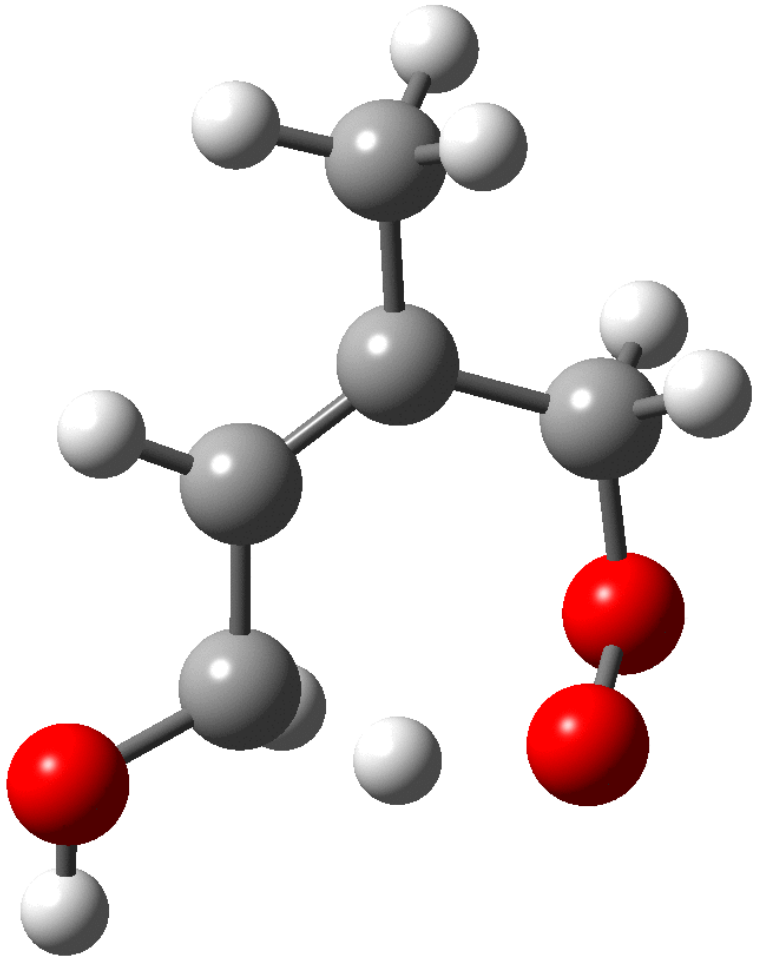
A New Mechanism…

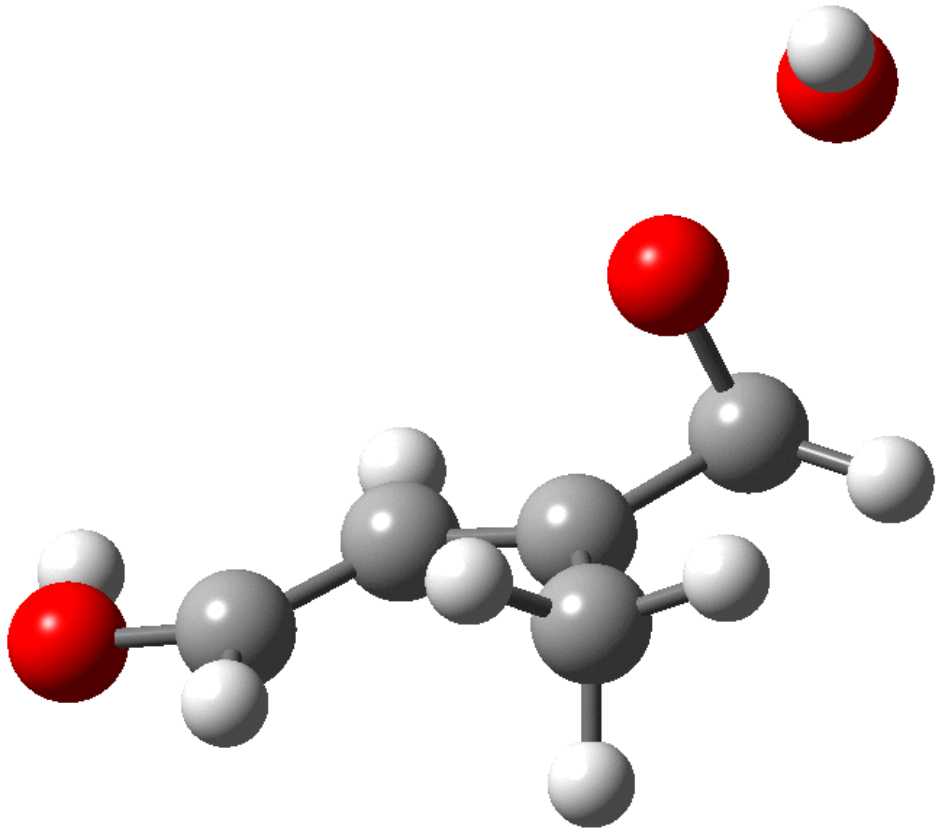


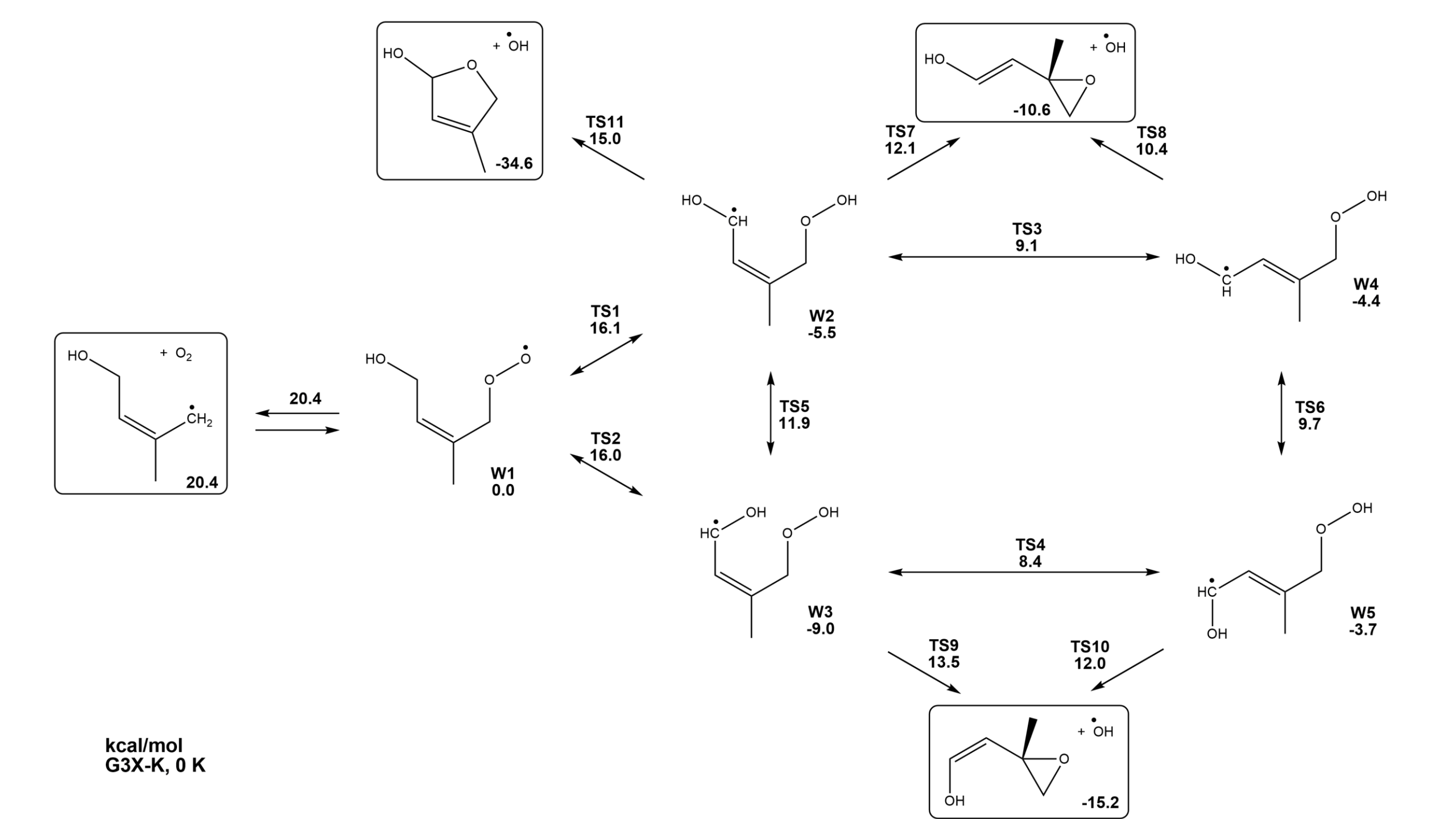




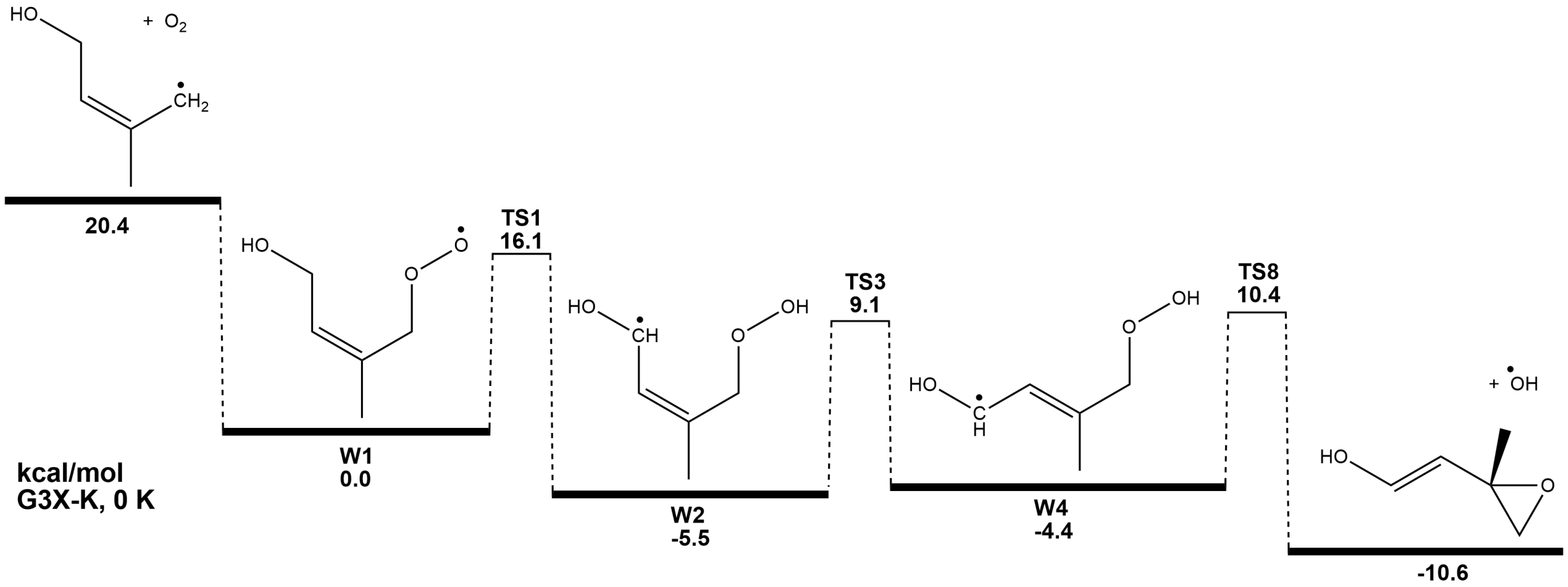
A New Mechanism…



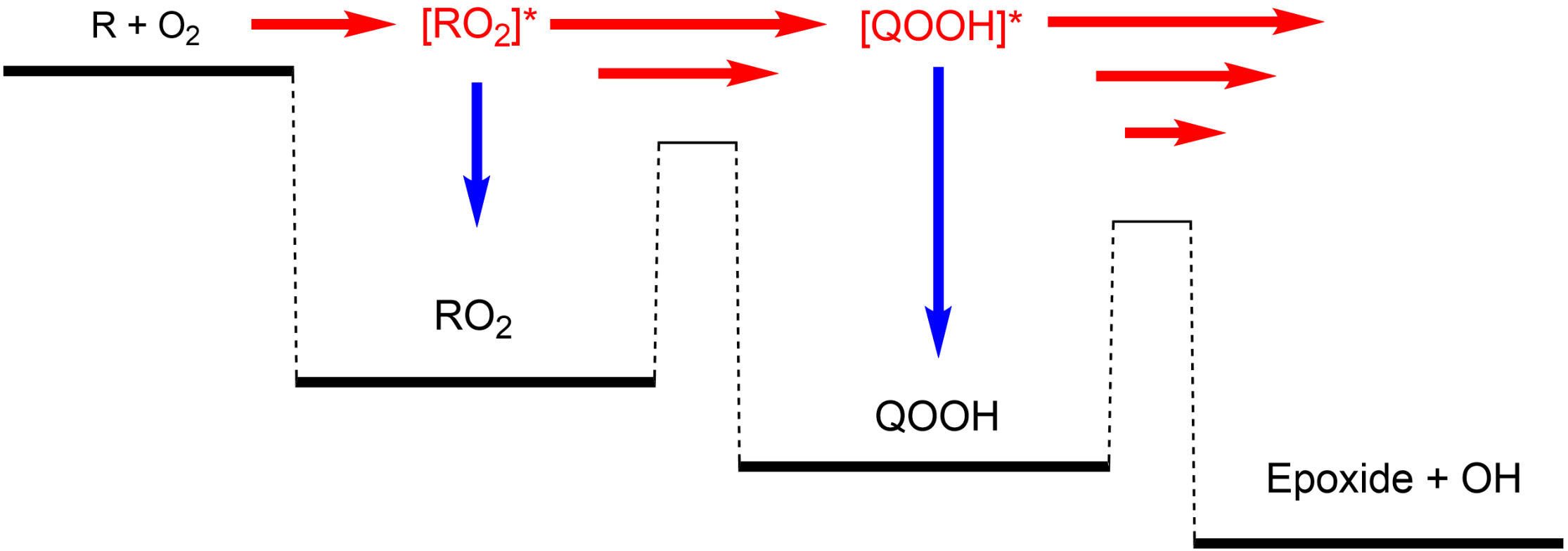



HO
+ OH
-34.6
TS11
15.0
HO
+ OH
-10.6
TS7
12.1
TS8
10.4
HO
OH
W2
-5.5
TS3
9.1
HO
OH
W4
-4.4
HO
+ O2
20.4
20.4
HO
W1
0.0
TS1
16.1
TS2
16.0
TS5
11.9
TS6
9.7
HC
OH
OH
W3
-9.0
TS4
8.4
HC
OH
OH
W5
-3.7
TS9
13.5
TS10
12.0
OH
+ OH
-15.2
kcal/mol
G3X-K, 0 K

4,1-(*Z*)-RO_2 Mechanism

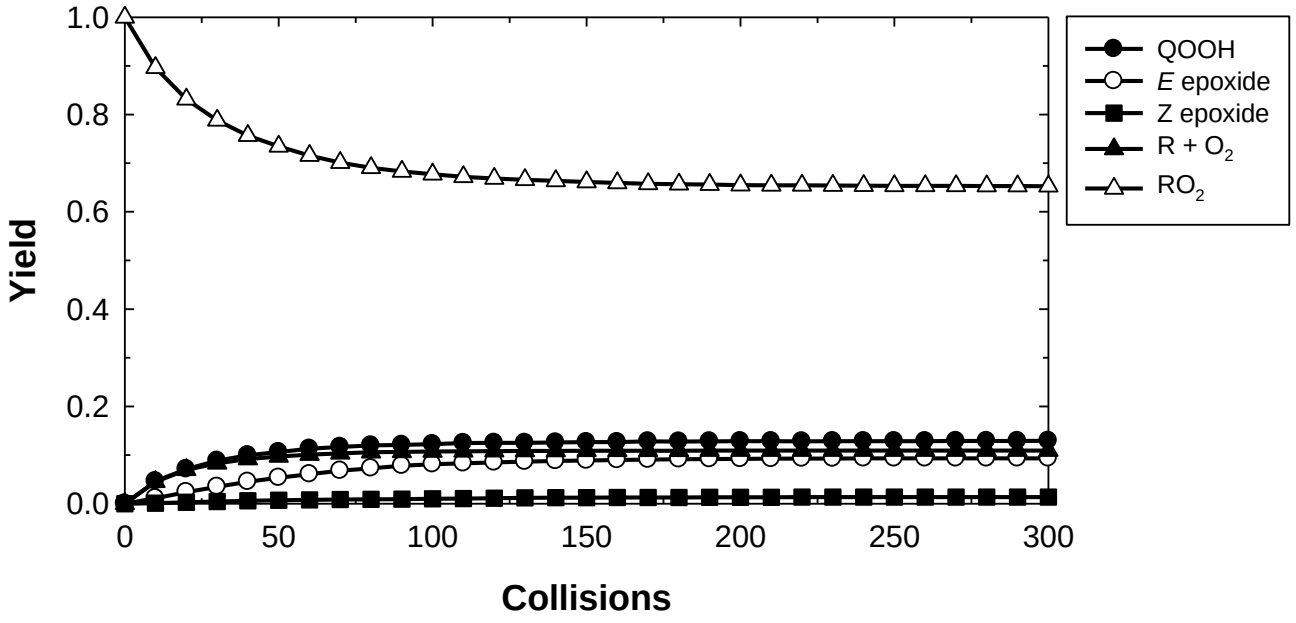


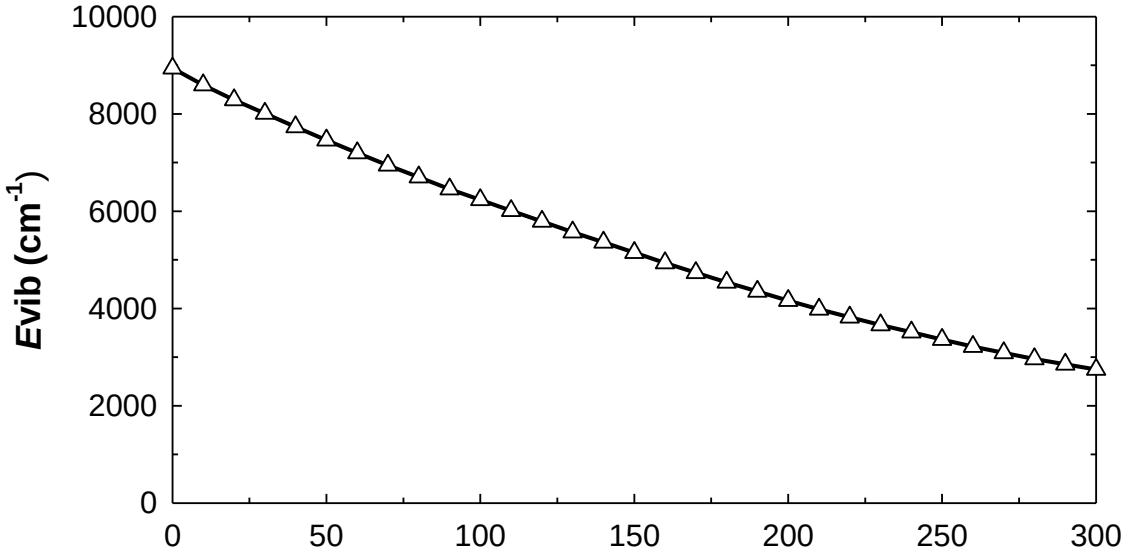
Reaction Schematic



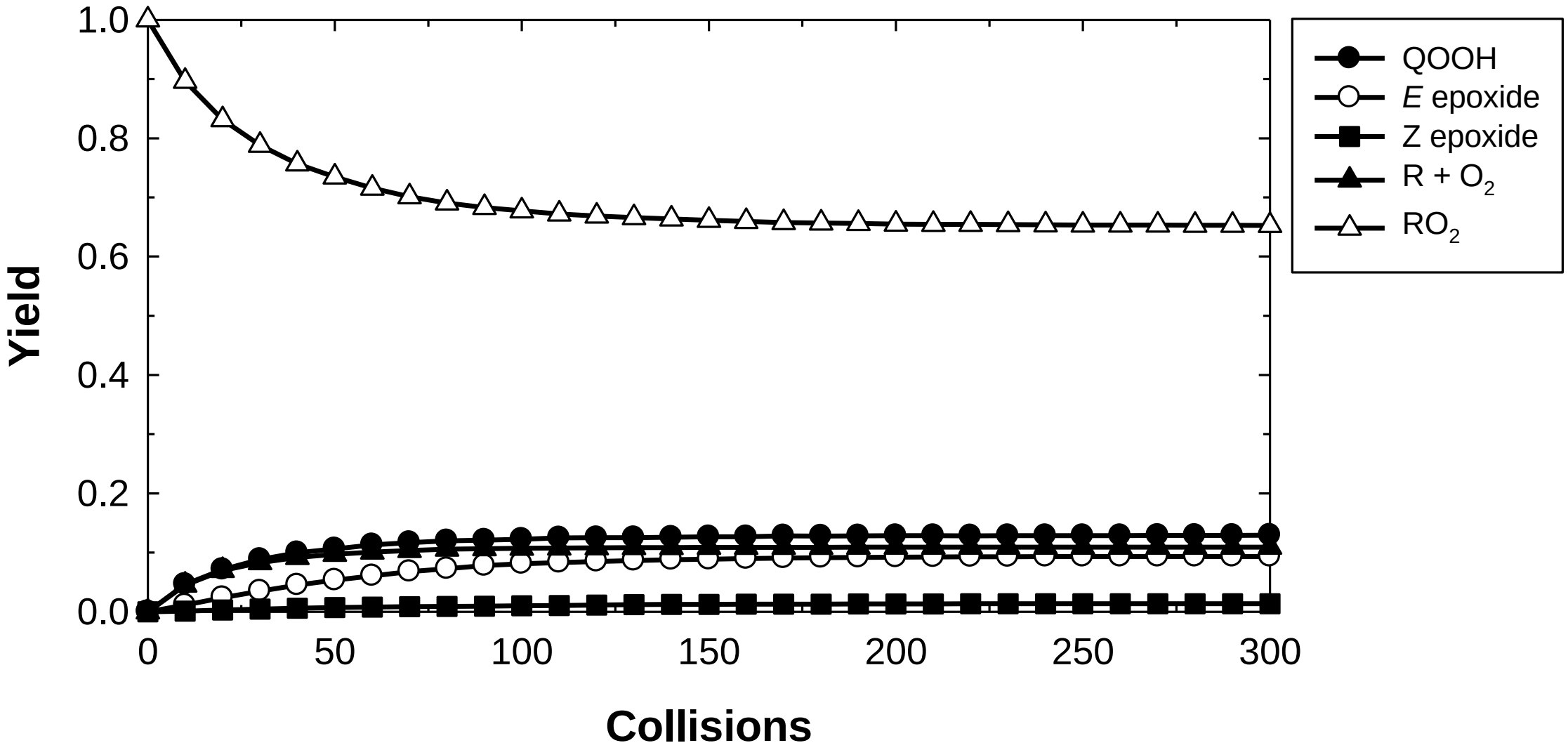
Master Equation Simulations

- EGME model developed in Multiwell
- 298 K and 1 atm N_2
- $\Delta E_d = 100 \pm 50\ cm^{-1}$
- Used to simulate R + O_2 on full surface
- Time (*i.e.*, collision) dependant product yields

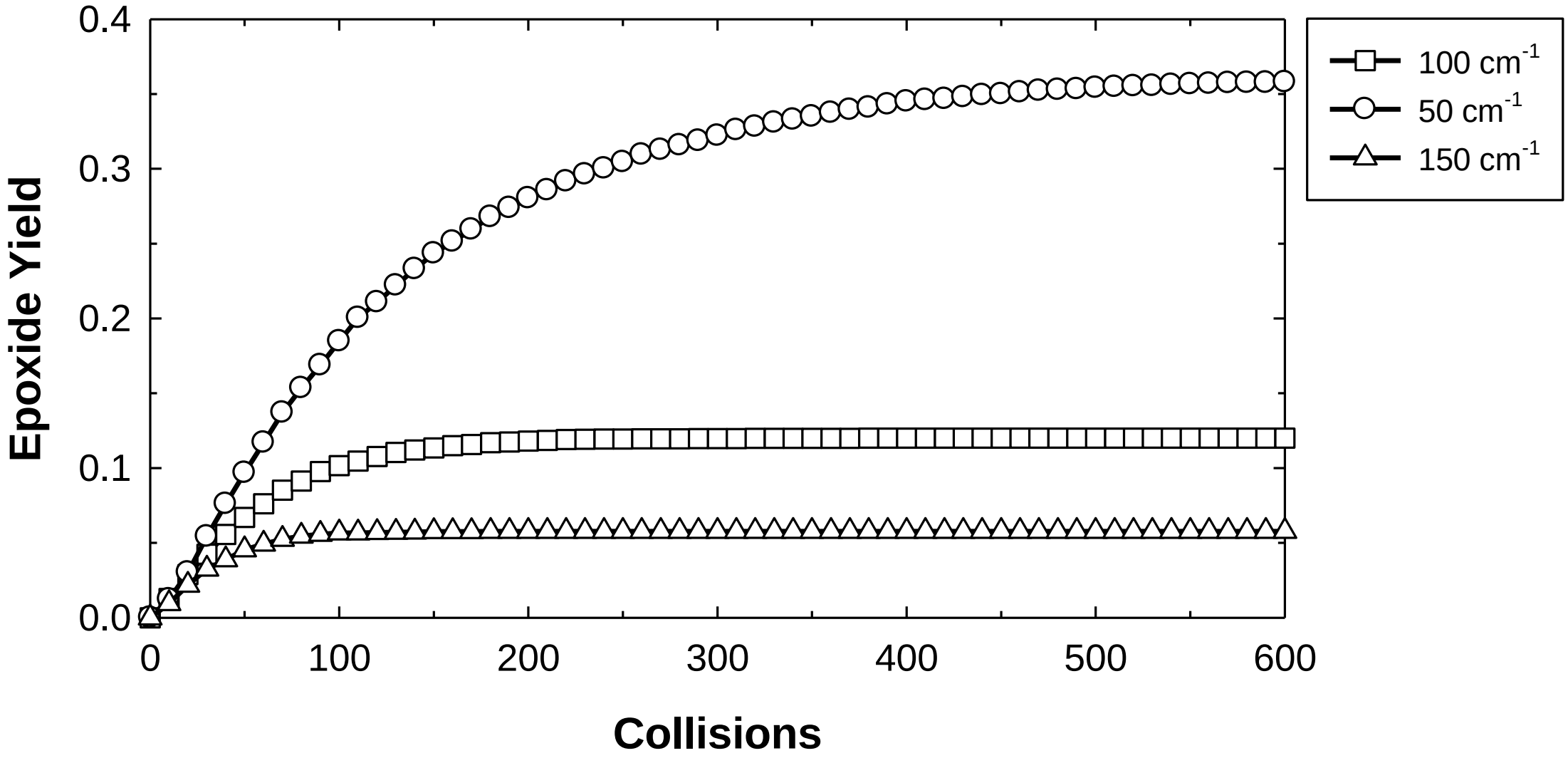




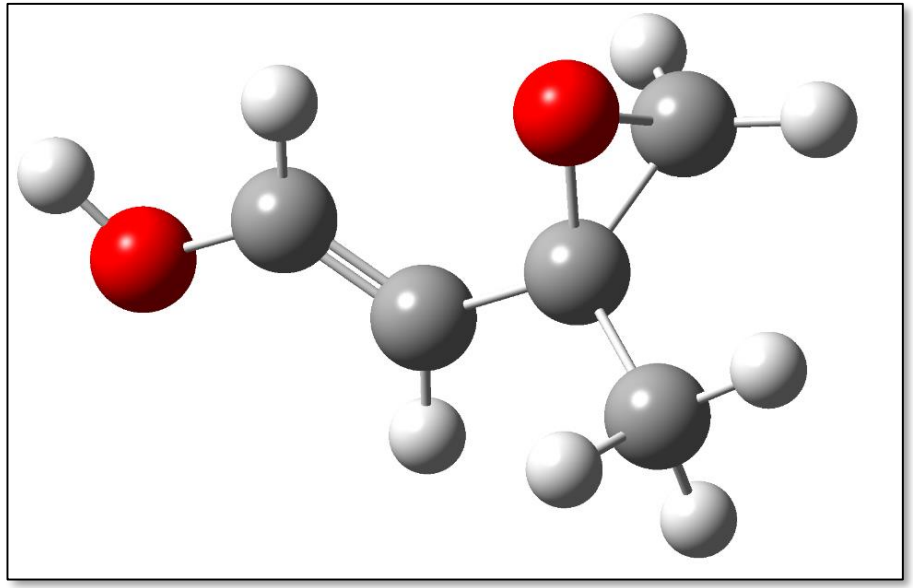
Master Equation Simulations: Product Yields



Master Equation Simulations: ΔE_d



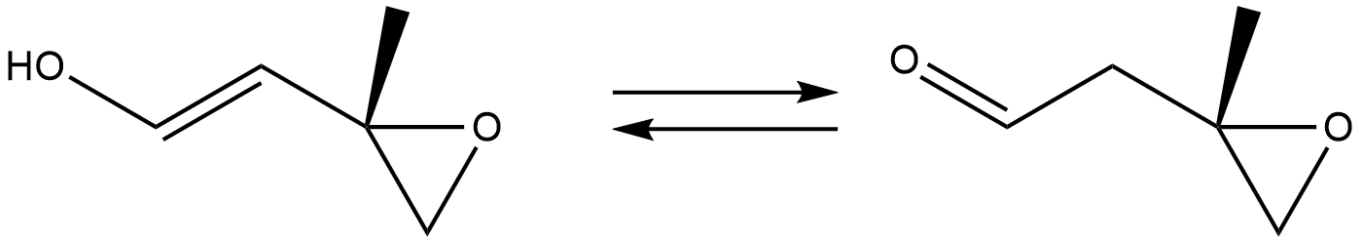
IsEnEpox



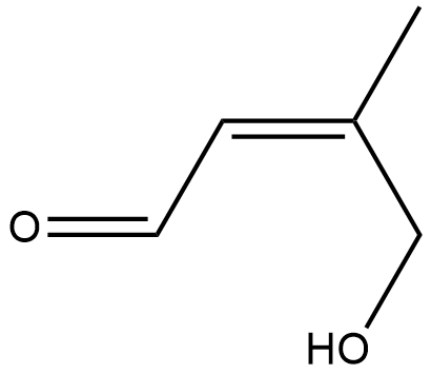
- Enols react rapidly with OH.

  So et al., *Environ. Sci. Technol.* **2014**; *J. Phys. Chem A* **2015**.

- Can tautomerize to aldehydes:



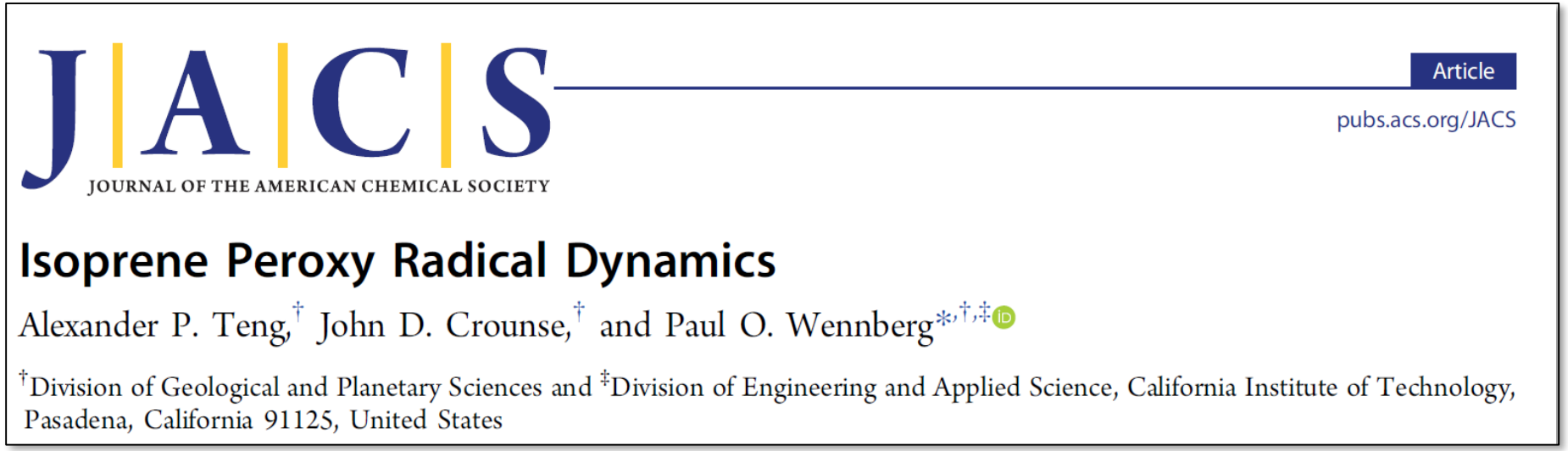
- Same mass as isoprene hydroxy carbonyls:



Kinetic *vs* Thermodynamic RO_2 Regimes

- At short lifetimes, δ-(*Z*)-$ISOPO_2$ may give a pulse of chemically activated products.
- At longer lifetimes:
  - Repeated "pulses" from O_2 addition/loss cycles.

    da Silva et al., *Environ. Sci. Technol.* **2010**.
  - Well skipping thermal decomposition possible.



THANK YOU!

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