

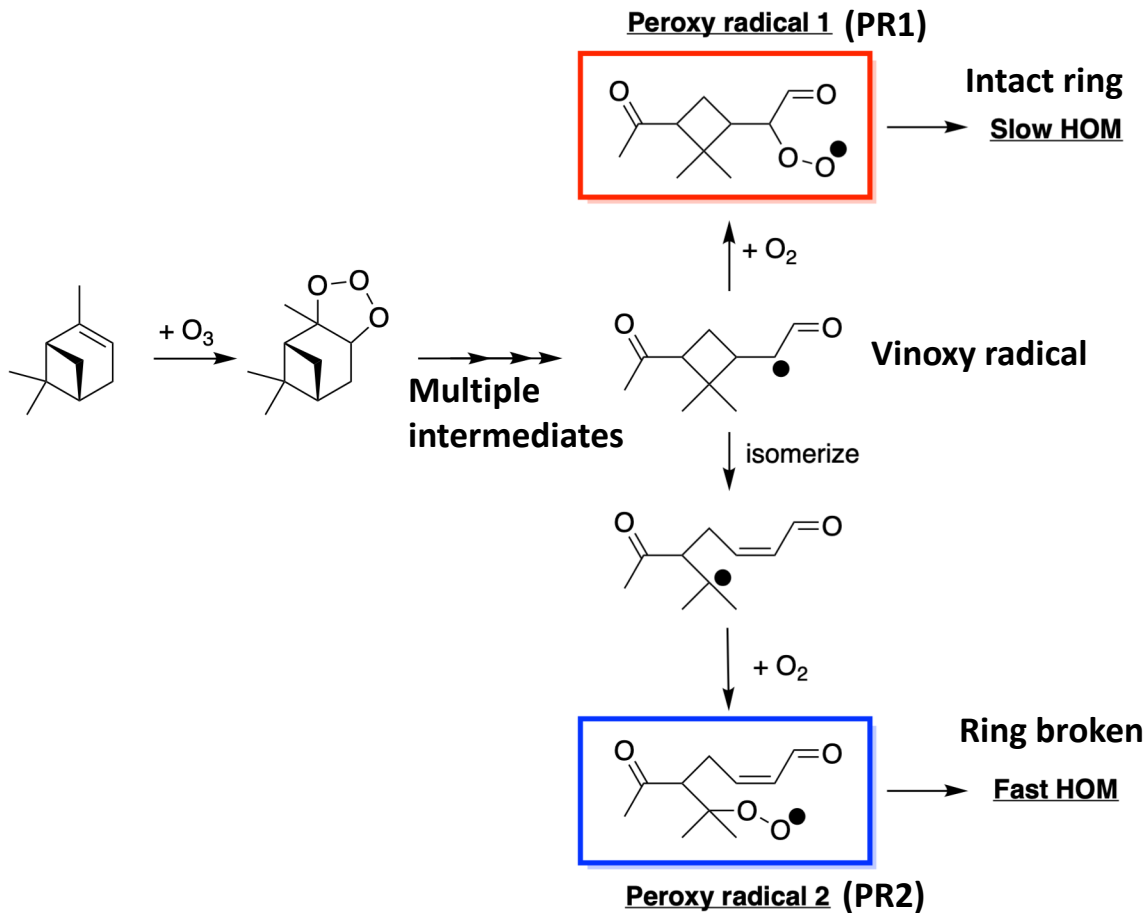
# Rapid formation of HOM from $\alpha$ -pinene ozonolysis

Siddharth Iyer, Matti P. Rissanen, Shawon Barua, Rashid Valiev, Joel Thornton, Theo Kurtén

# VOC oxidation → HOM → SOA

- Secondary organic aerosols (SOA) make up a major fraction of atmospheric aerosols.
- Highly oxygenated organic molecules (HOM) play a critical role in SOA formation. They are produced by the oxidation of volatile organic compounds (VOC), particularly monoterpenes. Following the initial oxidant attack, autoxidation, or the sequential addition of  $O_2$  to the hydrocarbon chain, rapidly converts VOC to HOM.
- $\alpha$ -pinene +  $O_3$  is one of the main SOA forming systems, but the mechanism is unknown.

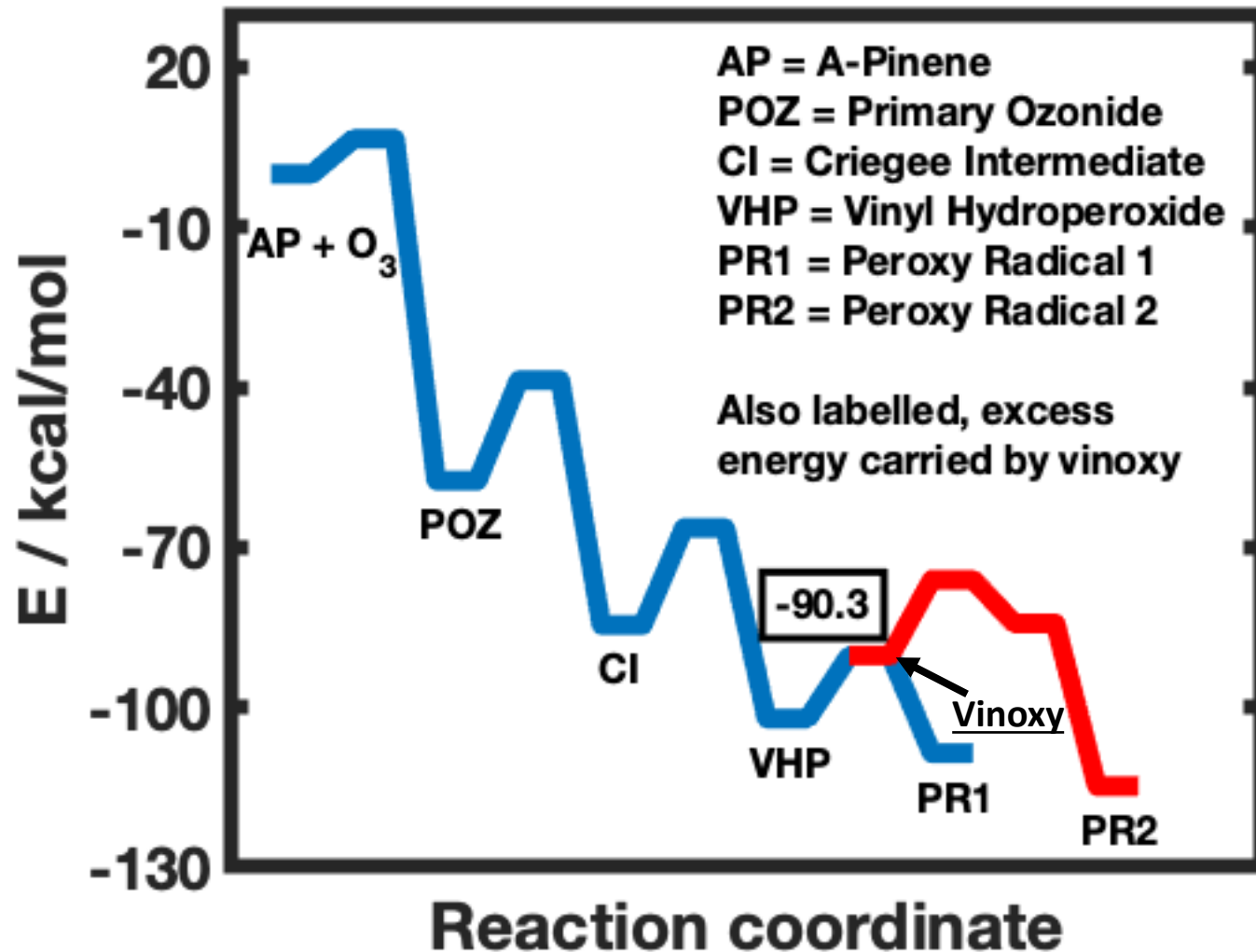
# $\alpha$ -pinene ozonolysis



However, isomerization step has a significant energy barrier

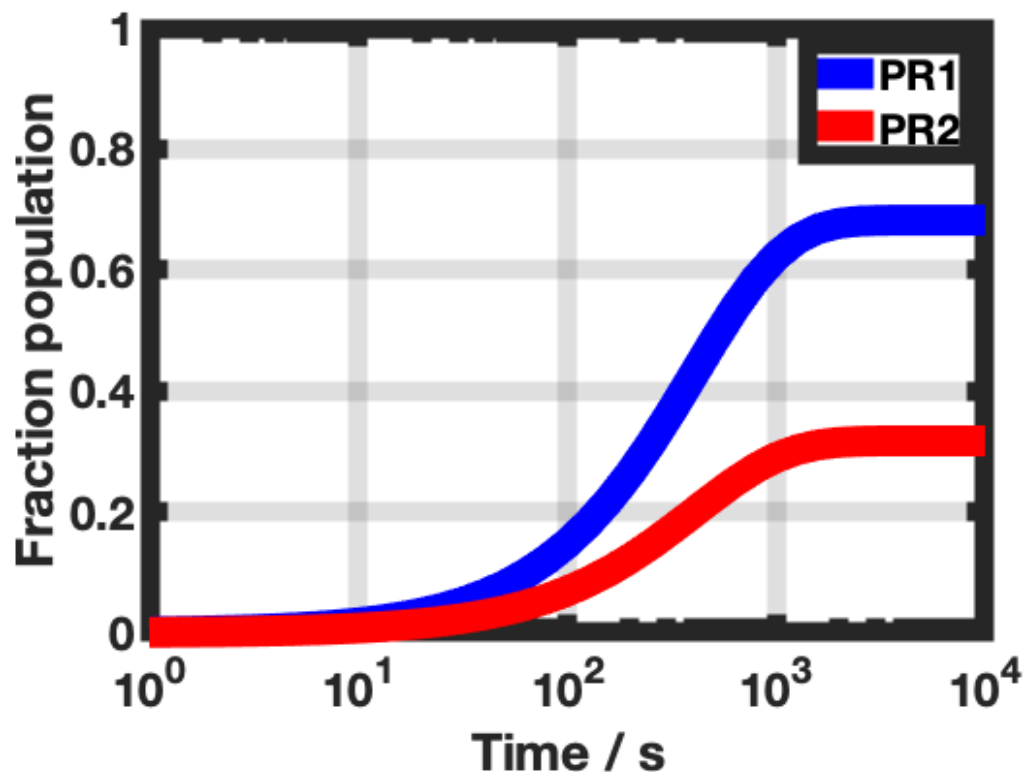
- $\alpha$ -pinene ozonolysis eventually leads to first-generation peroxy radical.
- Currently accepted mechanism leads to peroxy radical with intact 4-member ring (e.g. peroxy radical 1; PR1). Autoxidation is slow due to steric hindrance from ring = slow HOM formation.
- Isomerization step can break the 4-member ring to form Peroxy radical 2 (PR2). Fast autoxidation = fast HOM formation.
- **Take away:** Ring must break during  $\alpha$ -pinene ozonolysis to explain observed rapid HOM formation.

# Ozonolysis reaction = lots of excess energy



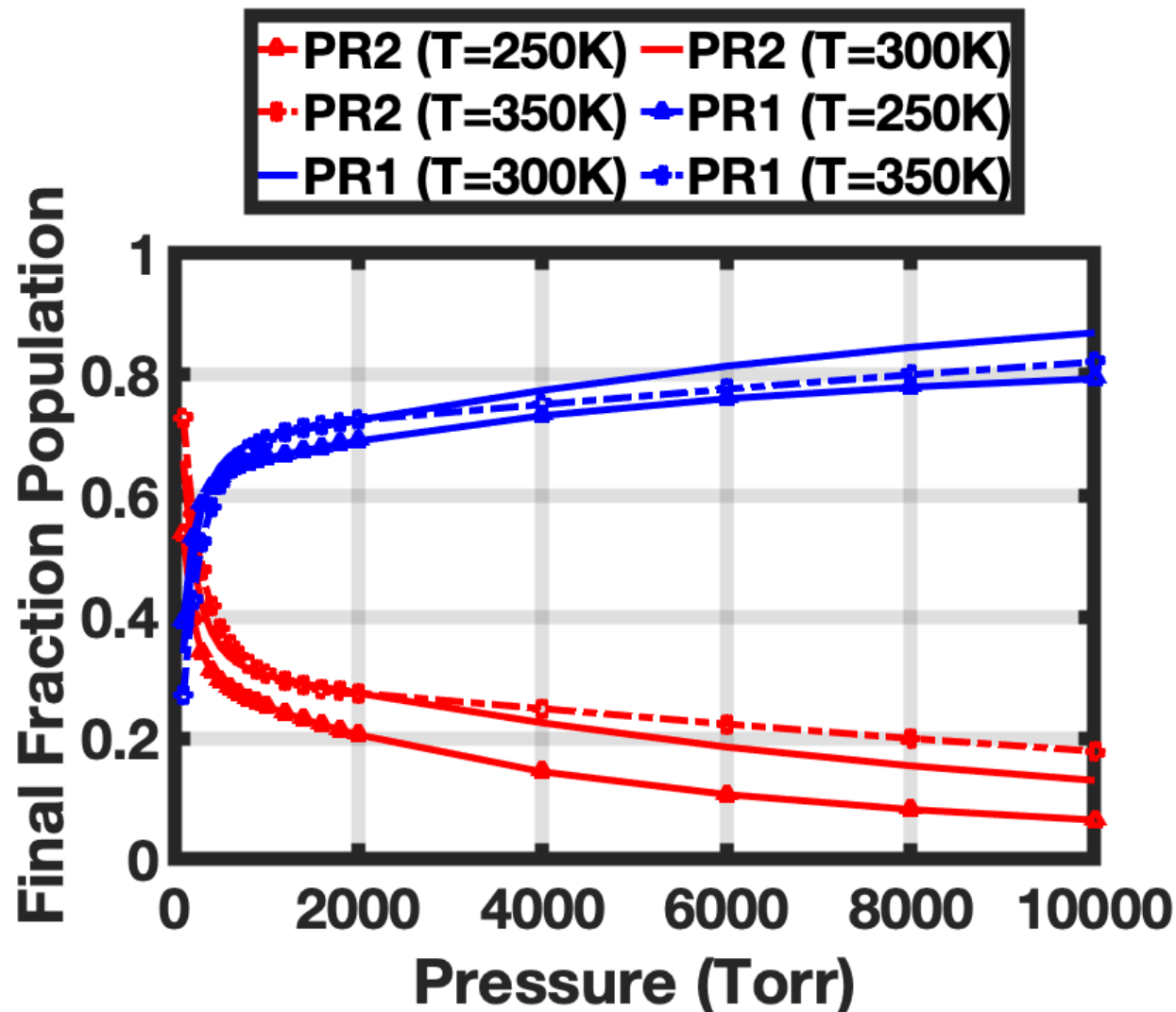
- Vinoxyl radical forms with a lot of excess energy = -90.3 kcal/mol.
- Excess energy is lost via collisions with air molecules.
- A fraction of vinoxyl could isomerize before losing the energy at normal temperature and pressure (NTP) conditions.
- **Take away:** Formation of ring-broken PR2 requires overcoming an energy barrier; -90.3 kcal/mol excess energy might help.

# Master equation simulation results



- RRKM simulation accounts for collisional stabilization of intermediates and products along reaction path.
- Time dependence is misleading – depends on assigned initial reactant concentration during simulation (kept unrealistically high to see rapid product yield; does not affect final population).
- **Take away**: Ring-broken **PR2 accounts for ~30%** product fraction; i.e. a significant fraction of vinoxy isomerizes to break ring.

# Master equation simulation results contd.



- Increase in pressure decreases PR2 fraction:

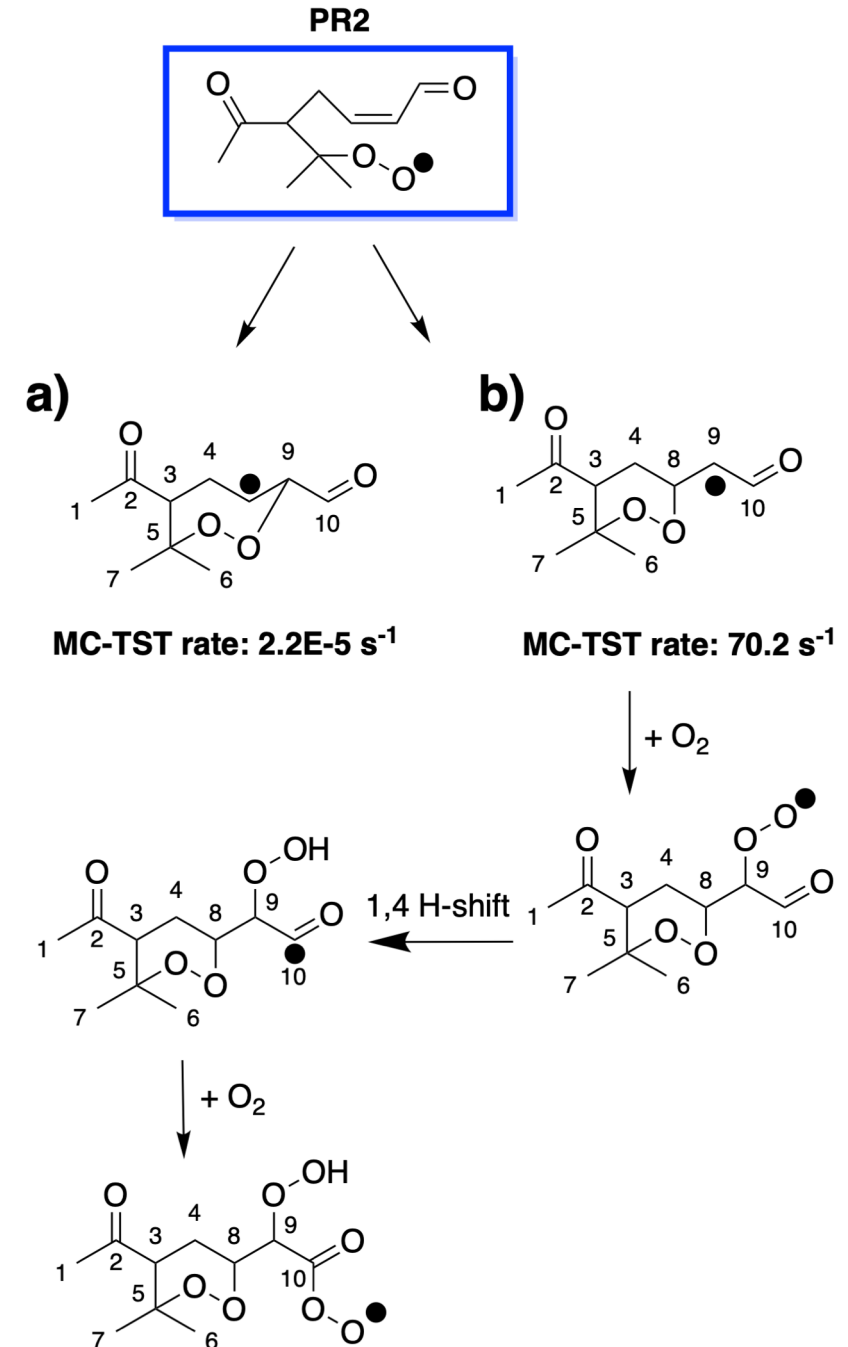
Because vinoxy is more efficiently collisionally stabilized at higher pressures, PR1 formation is preferred over PR2 in these conditions.

## Take away:

1. Sanity check -> product fraction show expected pressure dependence.
2. In NTP conditions, significant fraction of PR2 produced.

# What likely follows PR2 formation?

- PR2 can form an endoperoxide. The 6-member ring endoperoxide formation, figure **b**), is much more competitive than the 7-member ring, figure **a**). (Rates calculated at the b3lyp/6-31+g\* level).
- Following two rate-limiting steps (1 endoperoxide step and 1 H-shift step, both likely faster than  $1 \text{ s}^{-1}$  at NTP conditions), we form an 8-oxygen containing peroxy radical.
- Take away:** Mechanism for rapid HOM following  $\alpha$ -pinene ozonolysis.



# Summary

- The key to understanding the mechanism involved in the rapid formation of HOM from  $\alpha$ -pinene ozonolysis is accounting for the excess energy imparted to the vinoxy radical.
- Master equation simulations show that a significant fraction of the first-generation peroxy radical is completely ring-broken. This removes the hurdle for rapid autoxidation and HOM formation
- The ring-broken peroxy radical can undergo one endoperoxide step and one H-shift step, both likely faster than  $1\text{ s}^{-1}$ , to rapidly form a 8-oxygen containing peroxy radical. This can further autoxidate/react, leading to higher oxidized products.