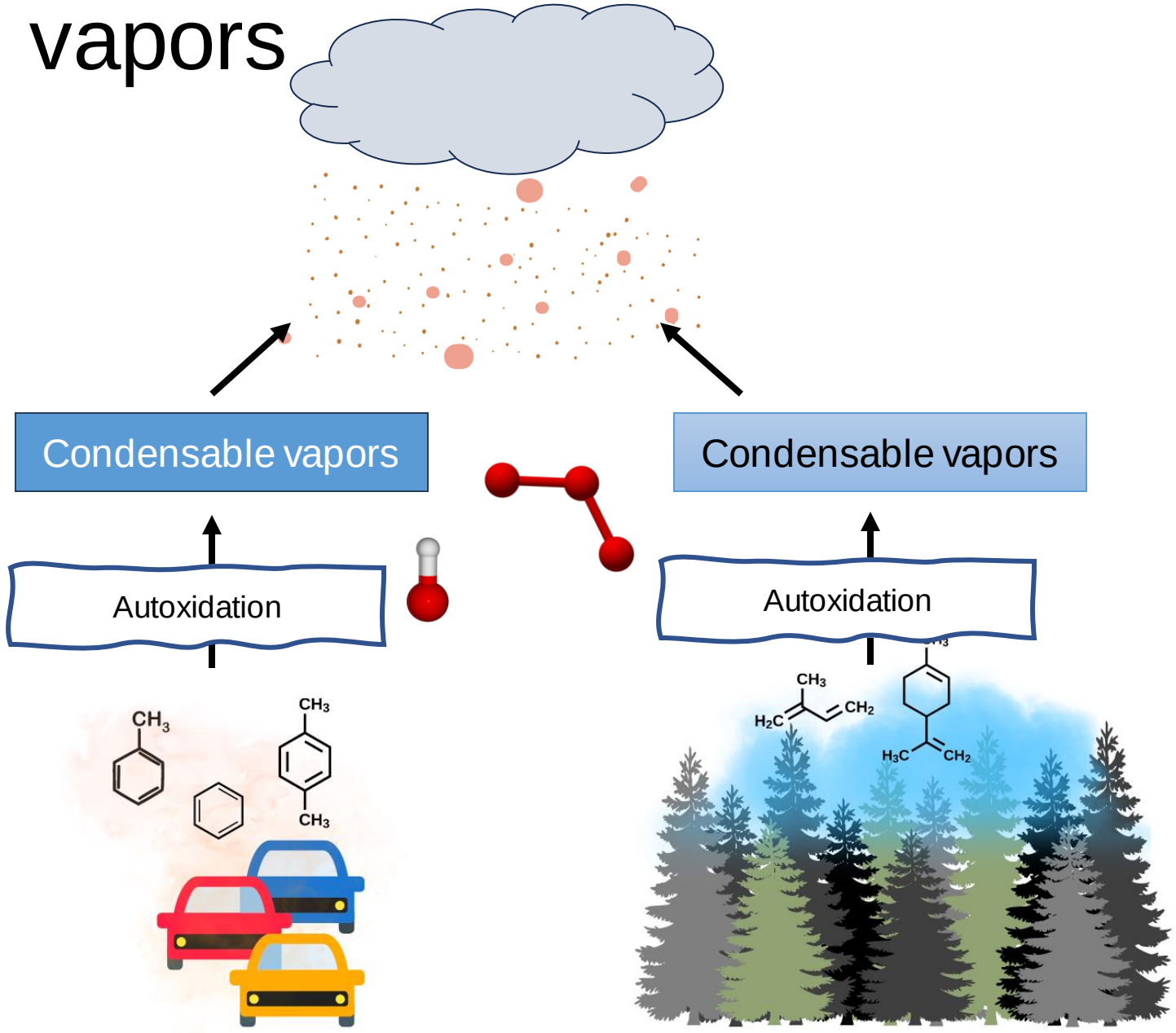
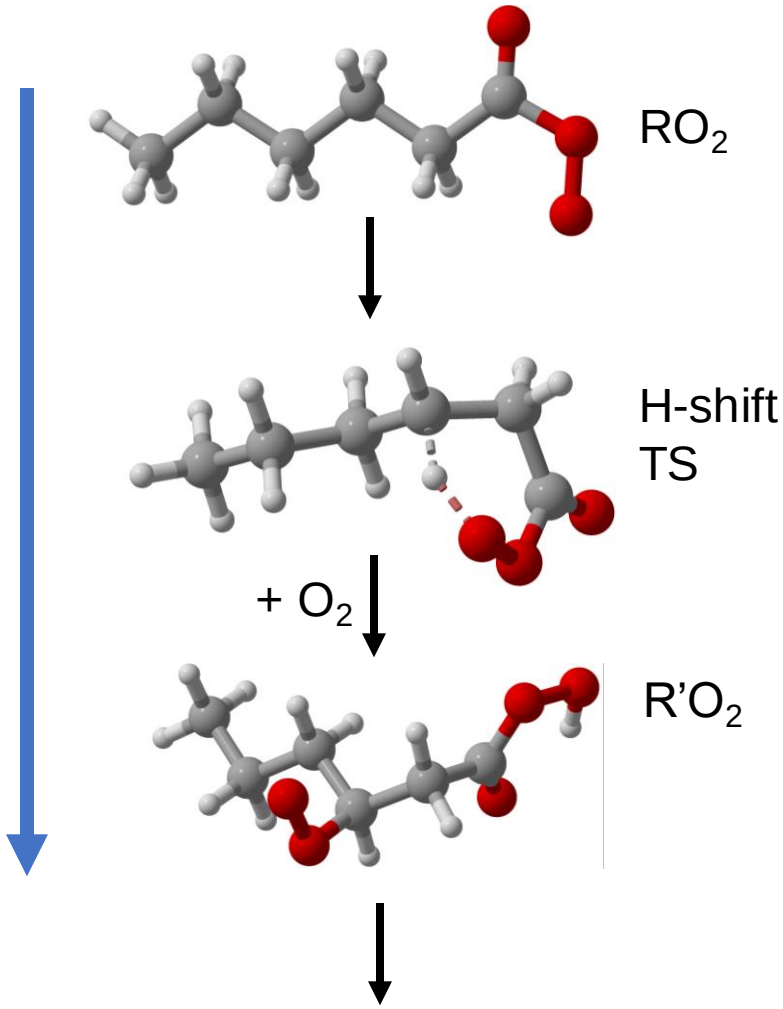
From vapors to aerosol: Excess energy and ring breaking in oxidation mechanisms

Siddharth Iyer

Research Council of Finland

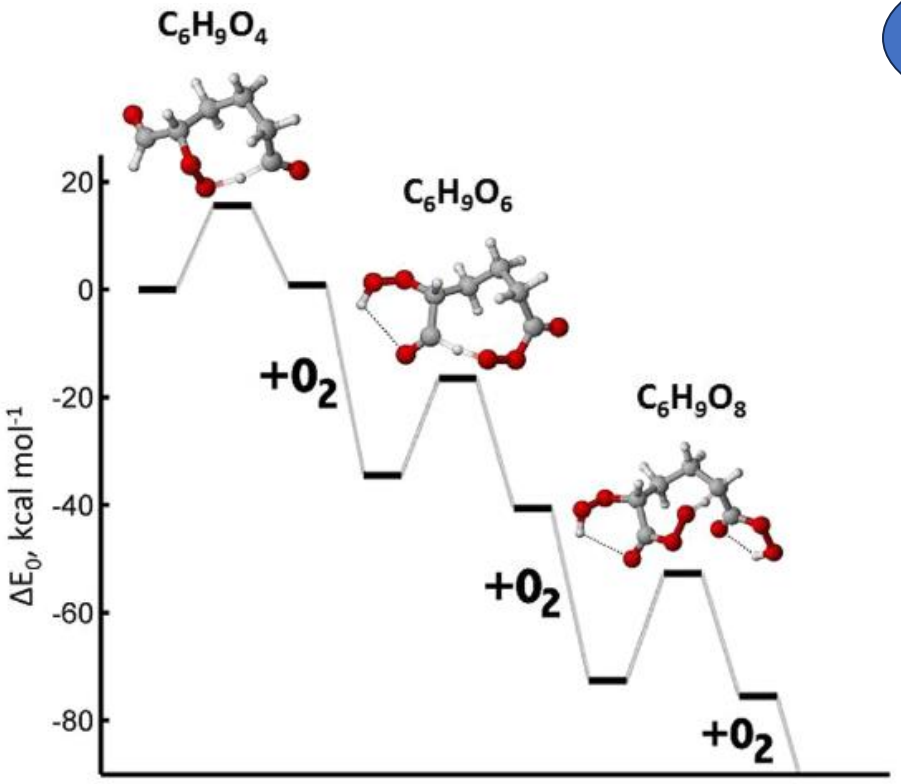
Volatile organic compounds to condensable vapors



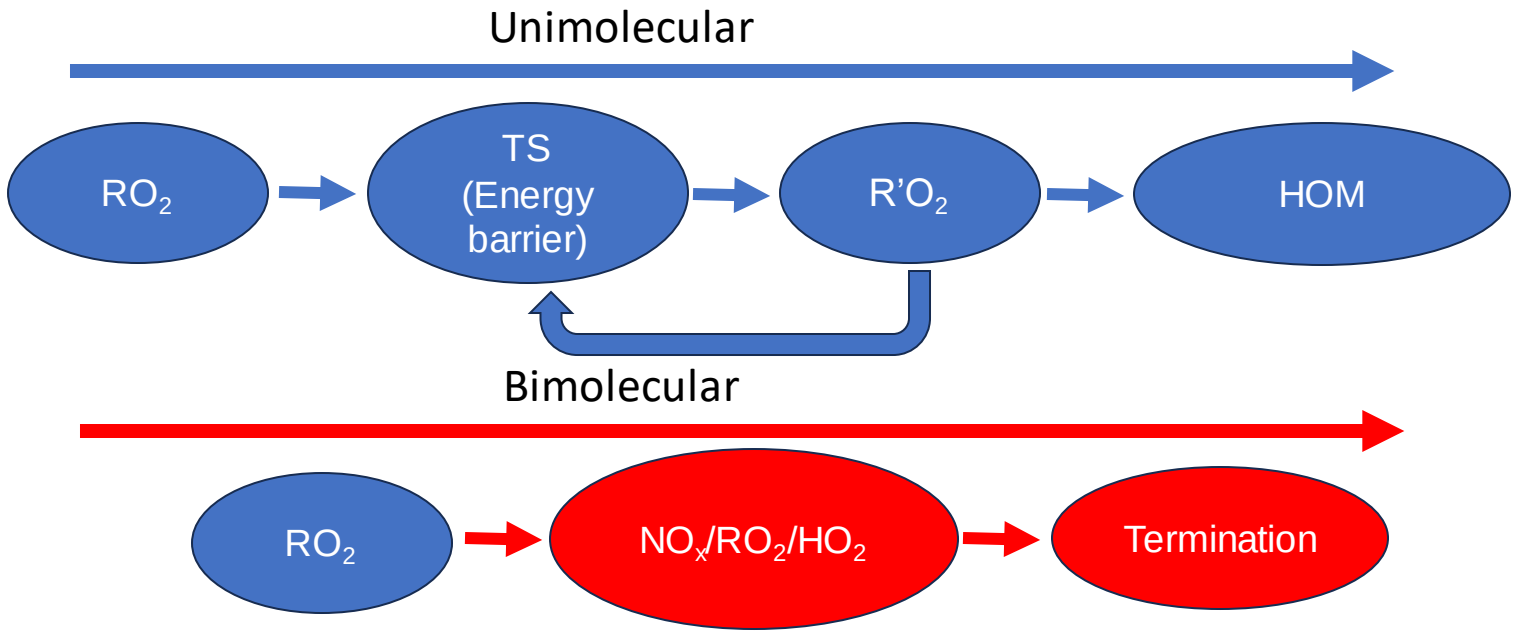


Leads to low-volatility HOM that are important for the initial formation of new particles

Autoxidation: be fast or be terminated



Rissanen et al. *J. Am. Chem. Soc.* **2014**, *136*, 15596-15606



- Unimolecular competes with bimolecular reactions.
- Low TS energy favors unimolecular, while higher TS energy favors bimolecular. Rule-of-thumb: unimolecular reactions should be >0.1 s^{-1}.

- **<u>The faster autoxidation is, less suspectible it is to termination, and more significant the VOC is as an aerosol source.</u>**

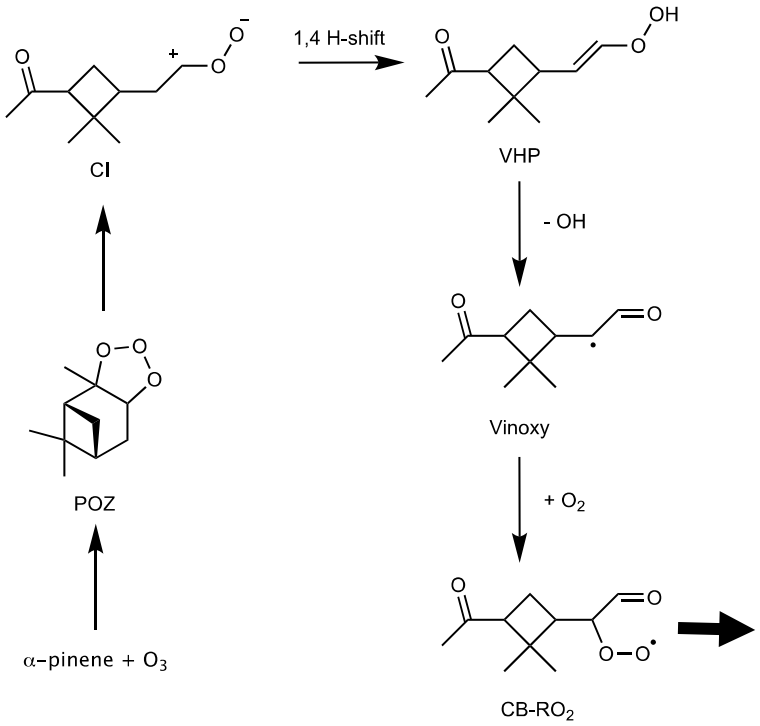
Note that not all bimolecular reactions lead to termination. Also, some termination products (ROOR) are condensable vapors

Previous discrepencies and recent breakthroughs

Case 1: α-pinene

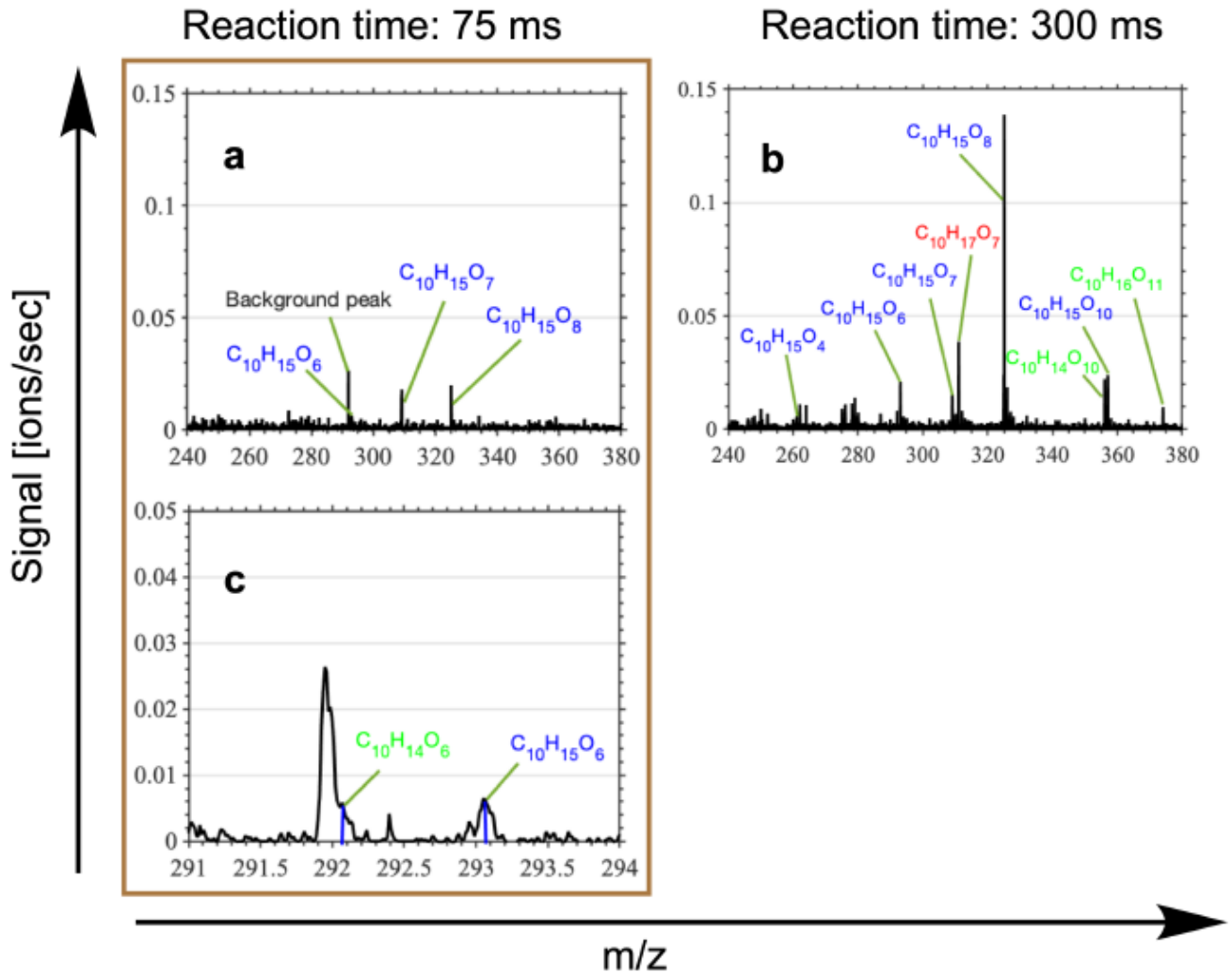
α-pinene ozonolysis

- α-pinene + ozone is one of the most efficient sources of aerosol precursors
- **On the right:** Products with 8 oxygen atoms with 100 ms of a-pinene meeting ozone.
- **Below:** "Computer says no."



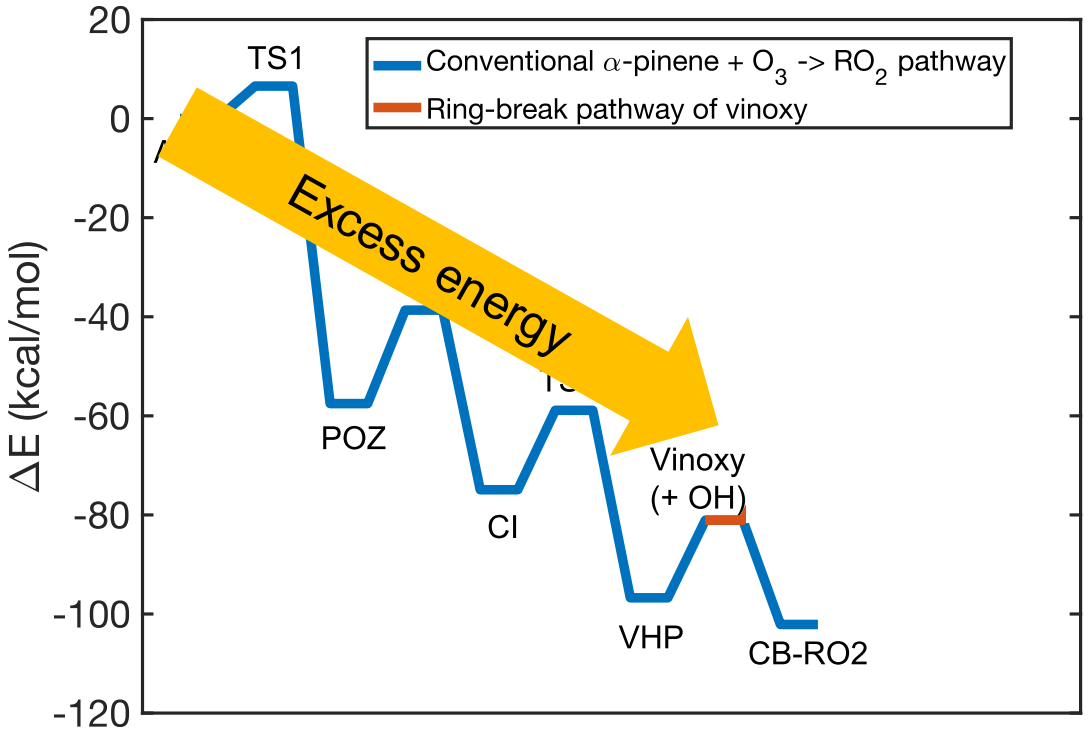
Slow unimolecular (<0.1 s^{-1})

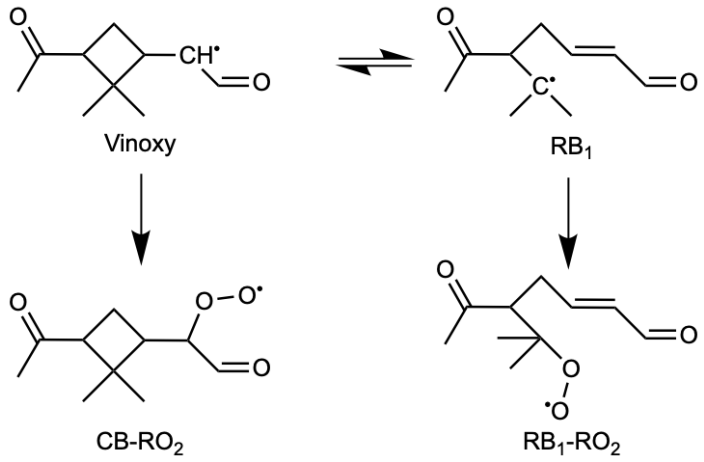
- Atmospheric pressure interface mass spec. A key instrument for measuring low-volatility condensable vapors

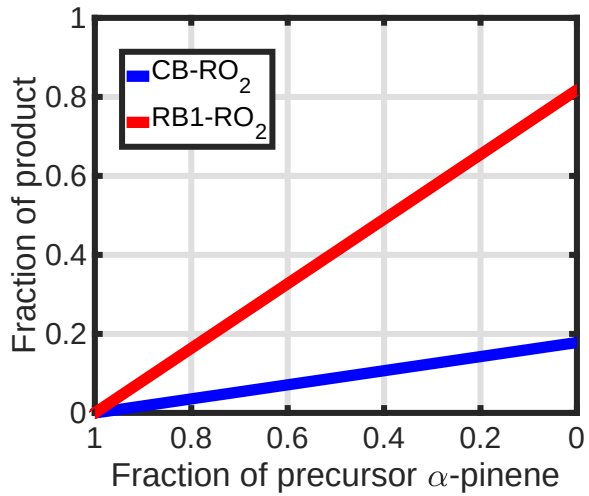


1) Molecular level mechanism of α-pinene ozonolysis

Initial steps of α-pinene ozonolysis



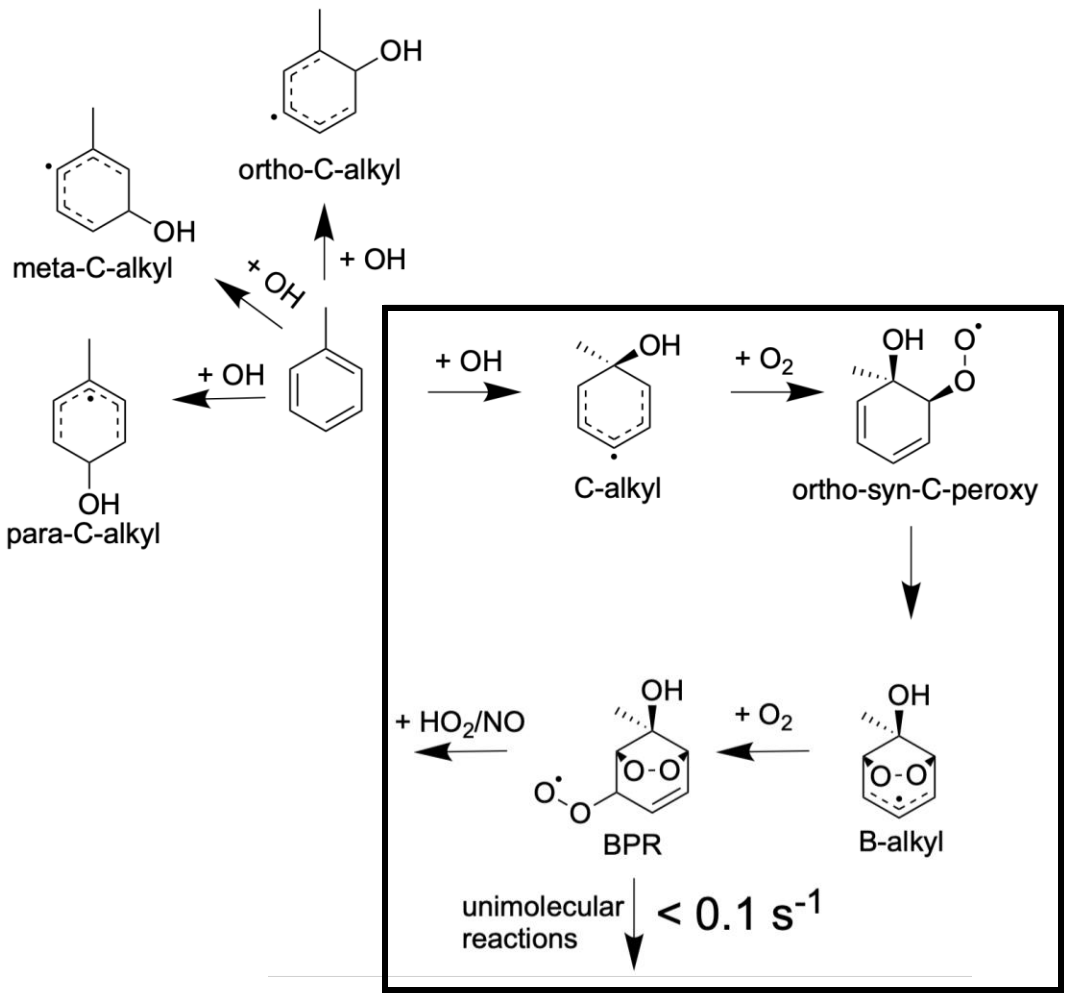




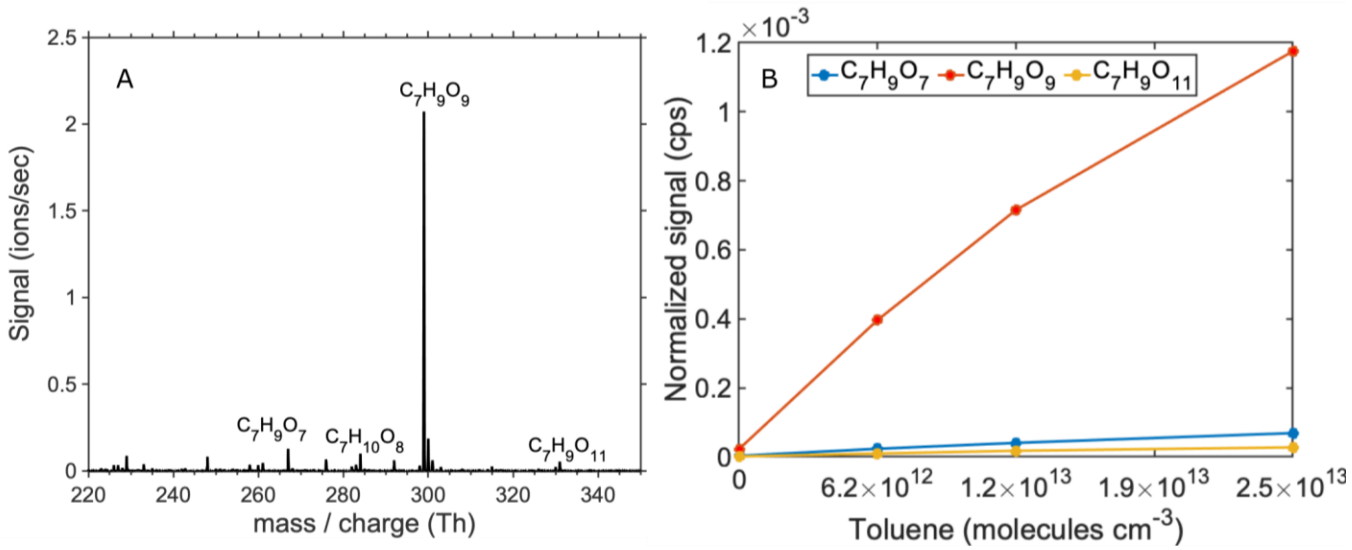
Previous discrepencies and recent breakthroughs

Case 2: Toluene

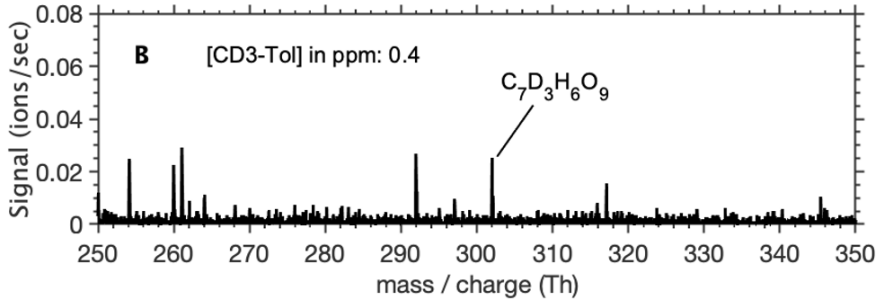
2) Molecular level mechanism of toluene oxidation



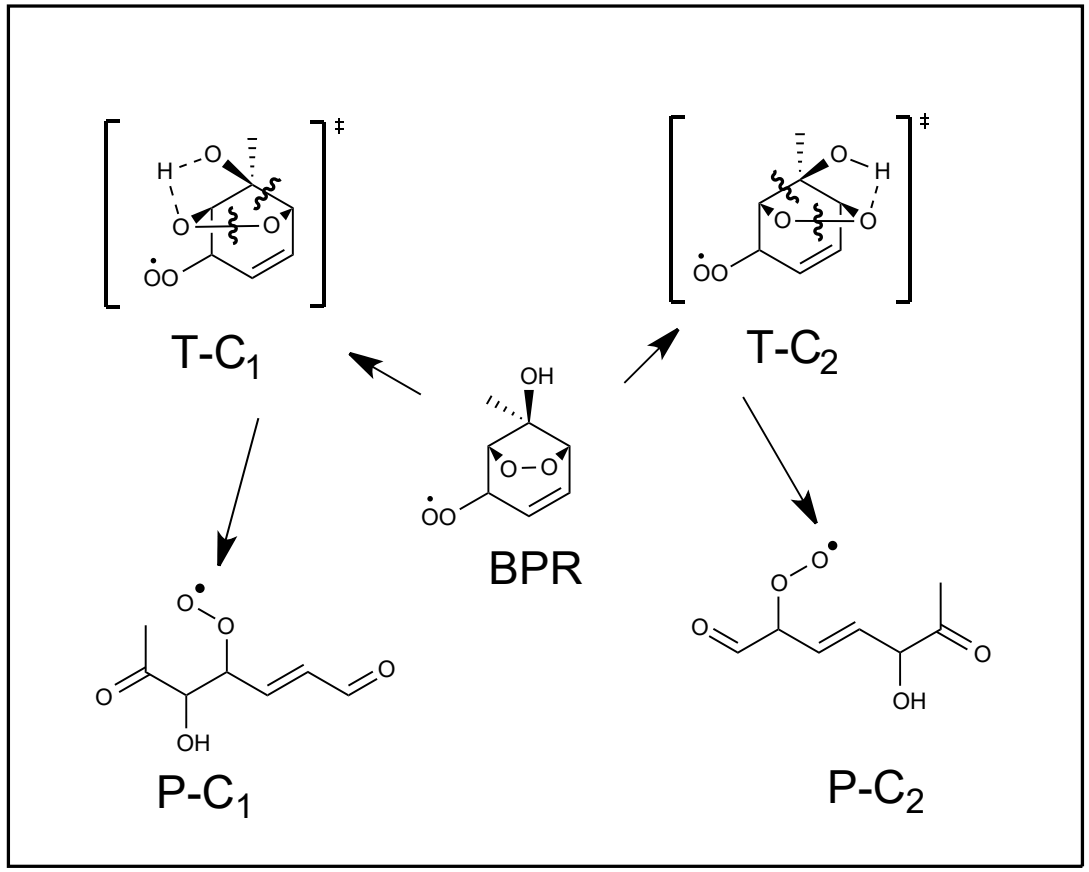
4 second toluene + OH residence time

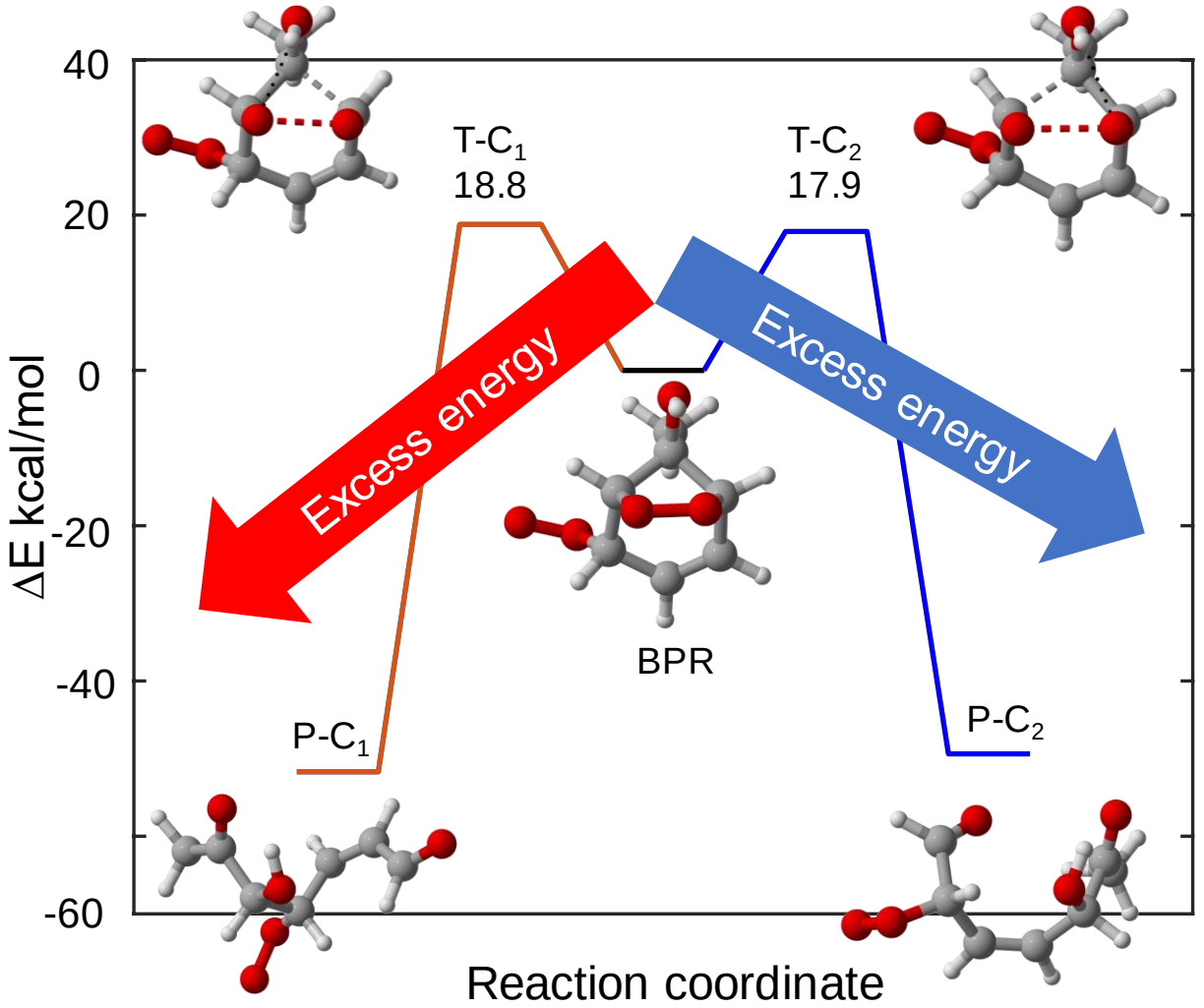


0.8 second toluene + OH residence time

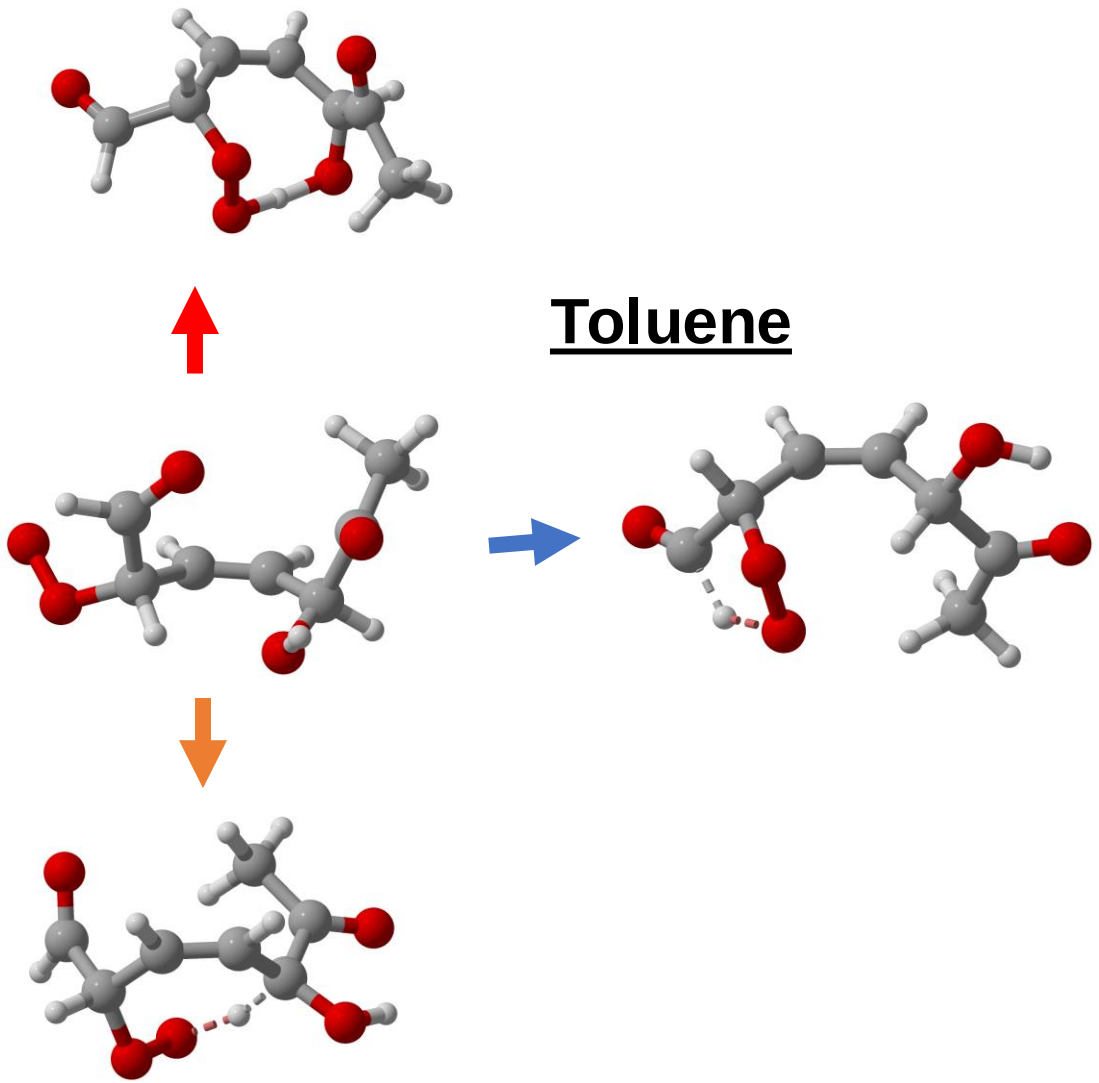


Molecular rearrangement of BPR



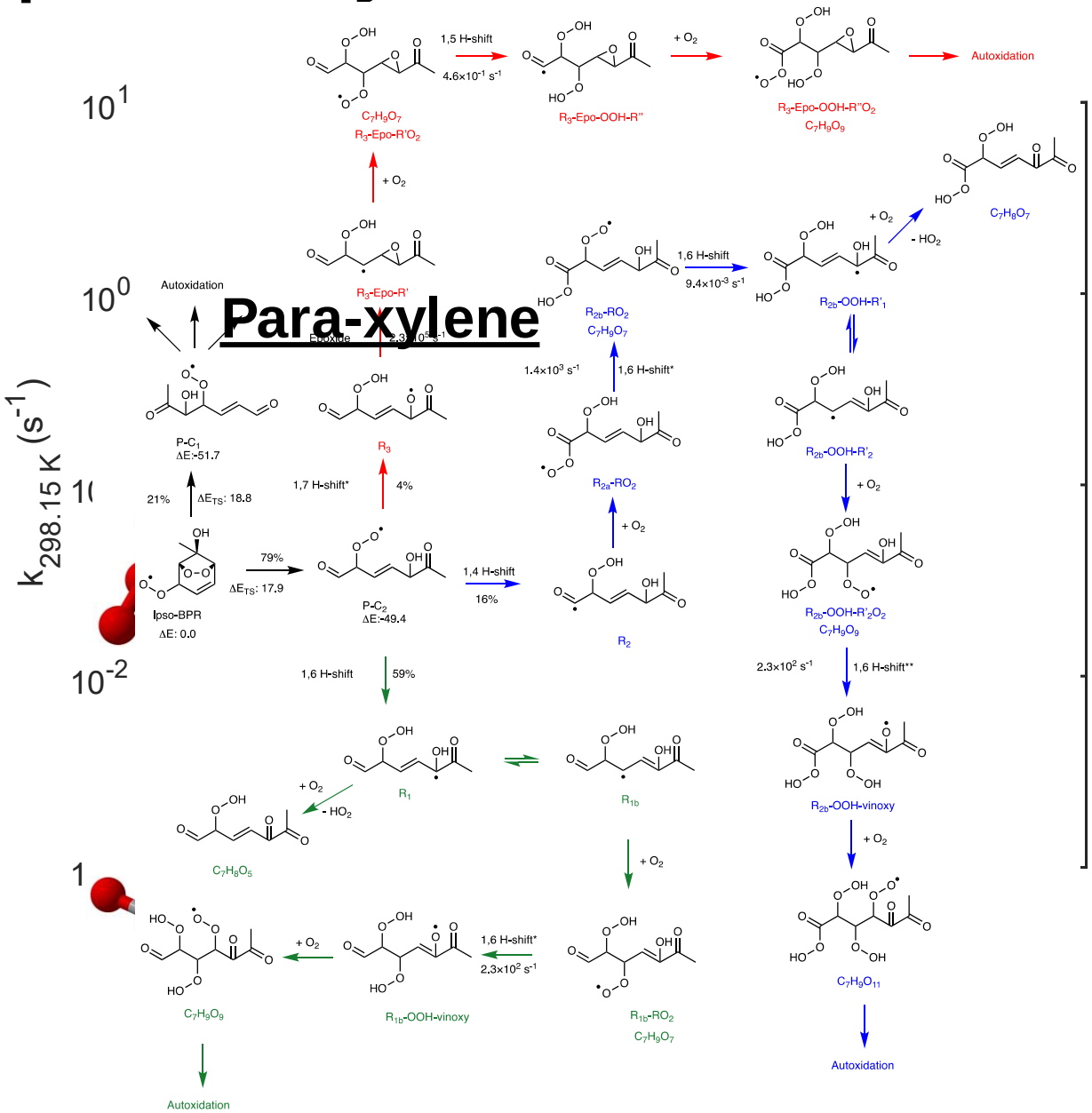


Multiple autoxidation pathways



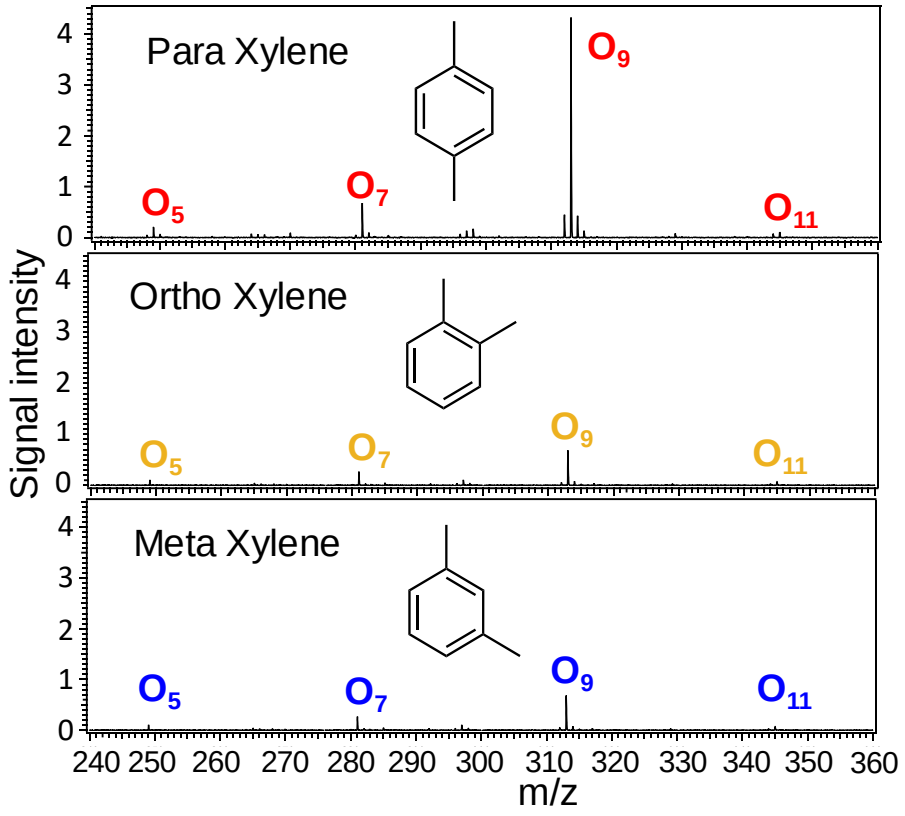
Toluene

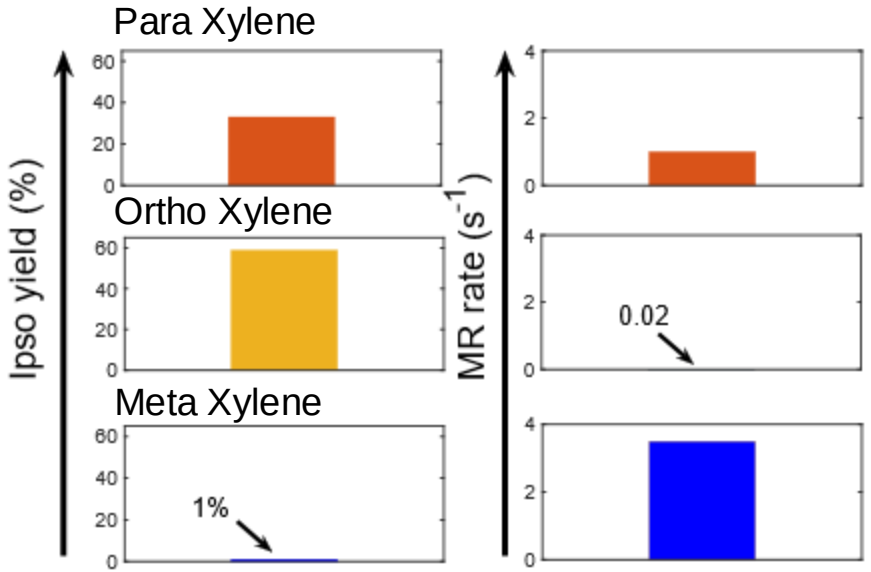
Para-xylene

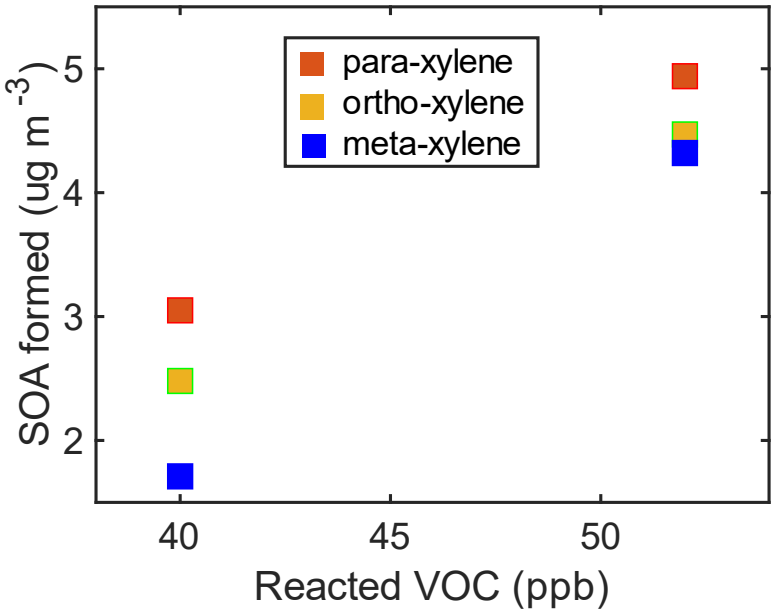


Different xylenes

5 second xylene + OH residence time







Summary

- Accurate understanding of autoxidation mechanisms is key modelling aerosol yields of different VOCs.
- Excess energy and ring breaking are key to the autoxidation of α-pinene, toluene and many other aromatics.
- For aromatics, high ipso yield and fast molecular rearrangement rates translate to higher HOM and higher SOA mass yield.
- Can we accurately model SOA mass yields of other aromatics using only ipso yield (in literature) and molecular rearrangement rates (relatively trivial to compute)? We are trying to find out.