Rapid formation of aerosol precursors from *o*/*m*/*p*-Xylene and their contribution to secondary organic aerosol formation

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CENTRES OF EXCELLENCE IN RESEARCH

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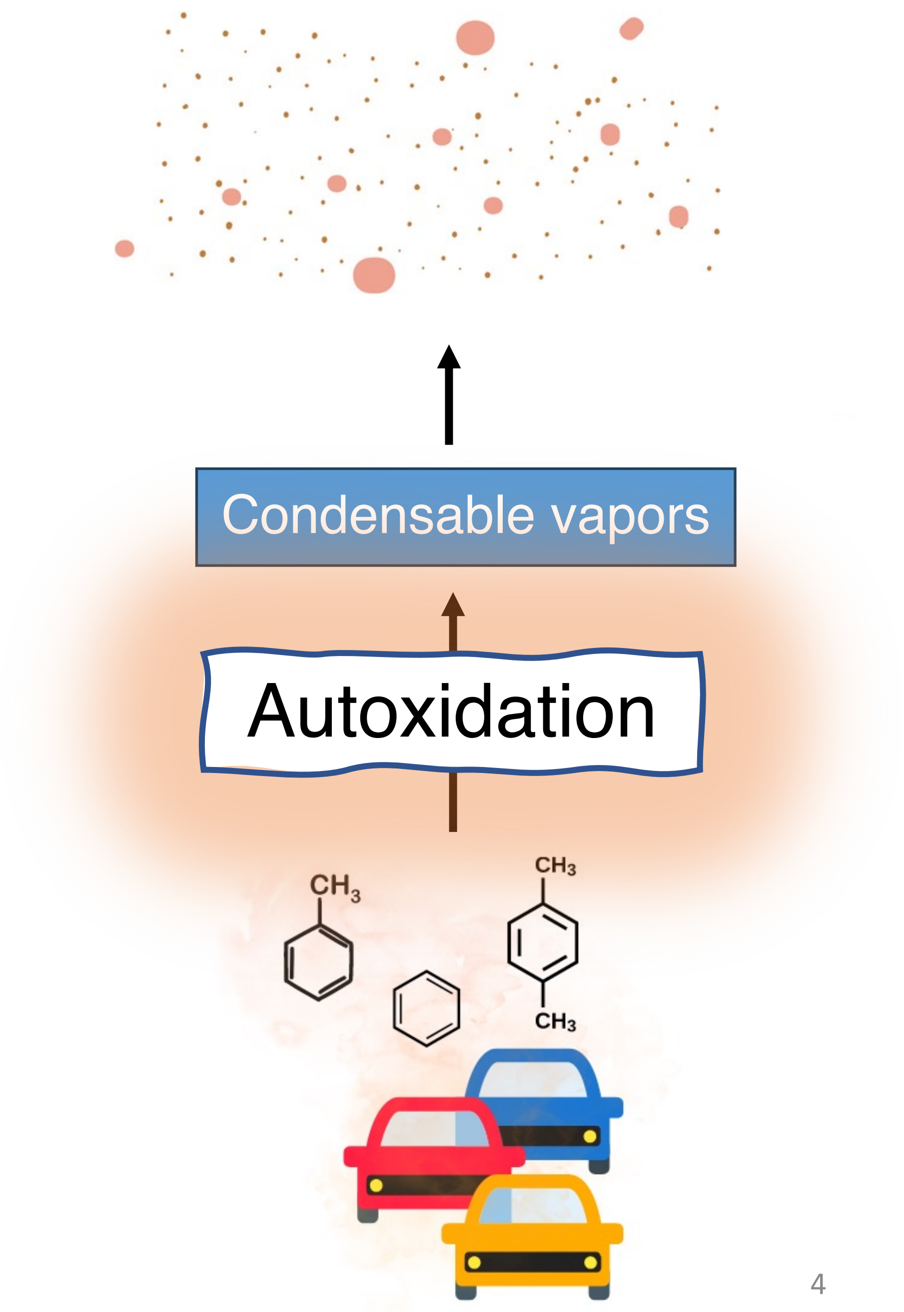
VIRTUAL LABORATORY FOR MOLECULAR LEVEL ATMOSPHERIC TRANSFORMATIONS

CSC

Oxidation of aromatics is a significant aerosol source

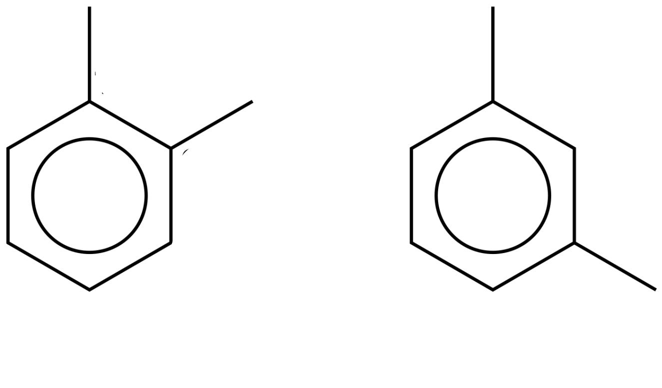
- Aromatics often comprise a dominant fraction of urban VOCs (=*Volatile organic compounds*)
- Recently we showed how toluene oxidation leads to low-volatility aerosol precursors in subsecond timescales (Iyer, S. et al. *Nat. Comm.* **14**, 4984, **2023**)
- **Tracking the explicit gas-phase (*aut-*)oxidation mechanisms is the key to developing better secondary aerosol models**



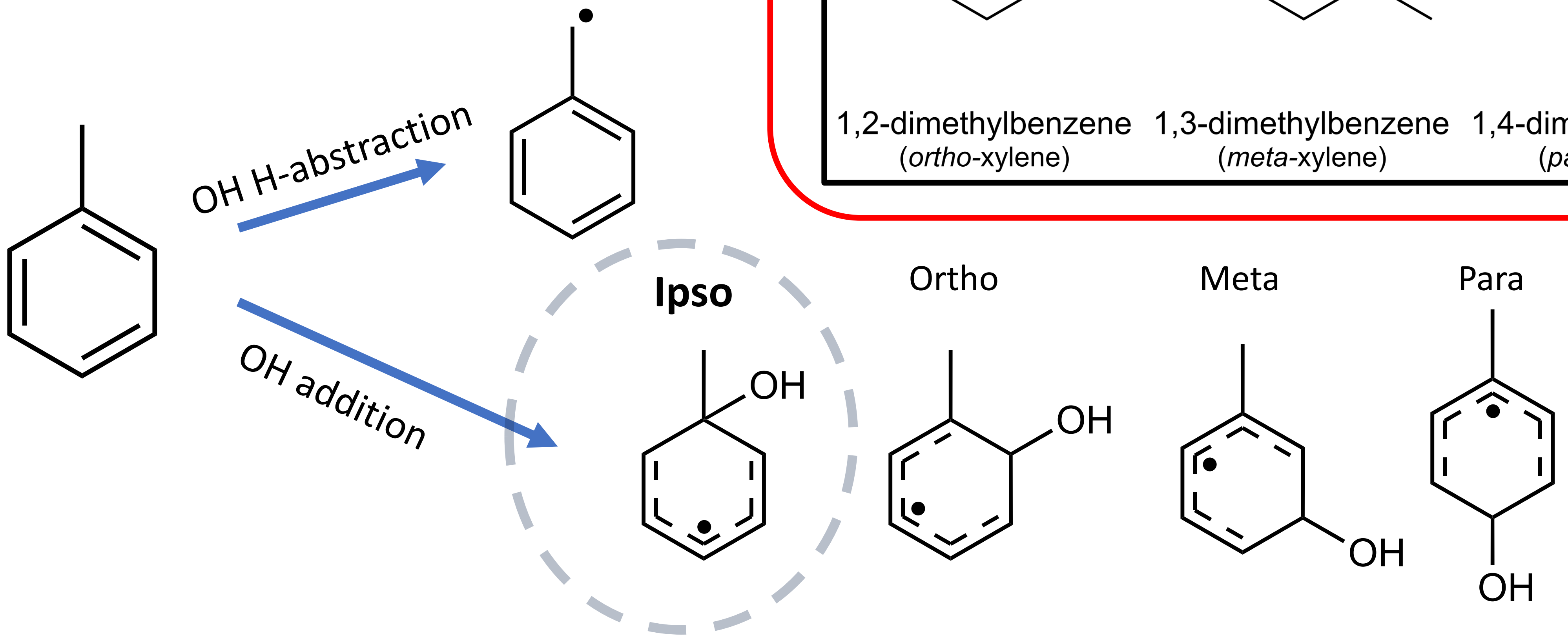
Aromatic oxidation

Toluene example

Xylene isomers used in this work



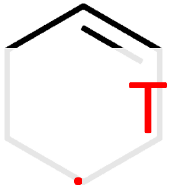
1,2-dimethylbenzene (*ortho*-xylene) | 1,3-dimethylbenzene (*meta*-xylene) | 1,4-dimethylbenzene (*para*-xylene)



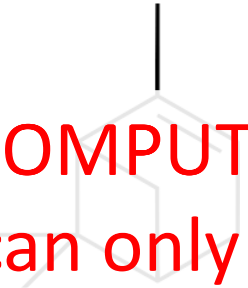
4 x hydroxyalkyl isomers from OH addition

HOMs = Highly Oxygenated organic Molecules

From cyclohexene



From α-pinene



From toluene

THESE ARE ALL COMPUTATIONALLY PREDICTED

Experimental methods can only give clues about the structure

Rissanen, M. et al., *JACS* **136**, 15596, **2014**

Iyer, S. et al., *Nat. Comm*. **12**, 878, **2021**

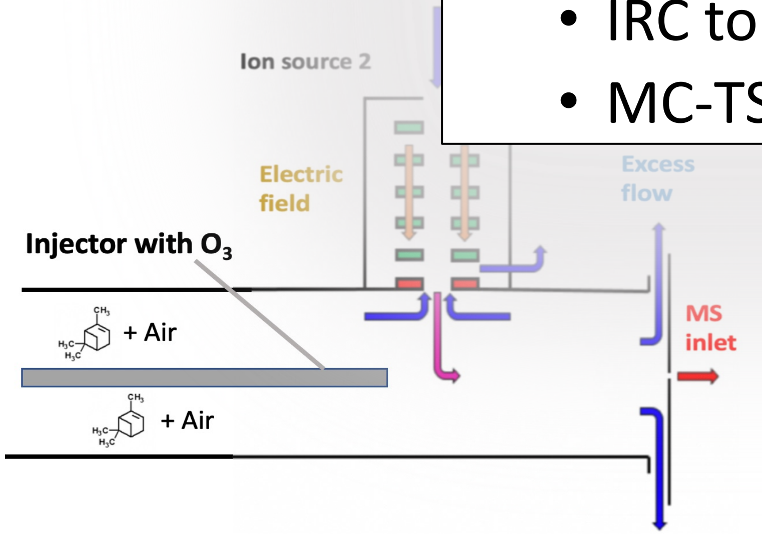
Iyer, S. et al., *Nat. Comm.* **14**, 4984, **2023**

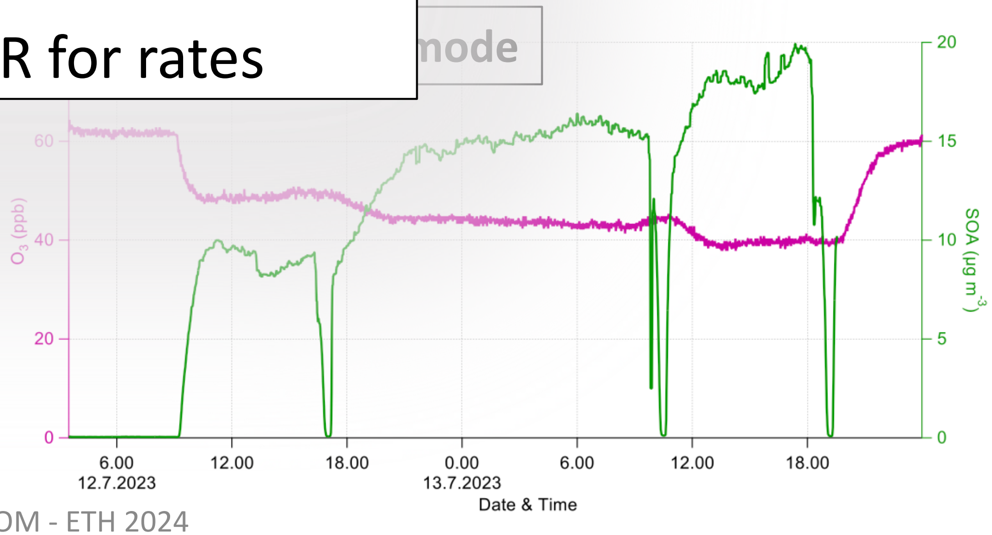
Experimental (& computational work)

- **Chemistry – RAPC flow reactor**
  - NO_3^- CIMS & MION inlet
  - 1-2 inch o.d. reacto
  - ~0.4 s to 10 s reacti
  - Injector for VOC int
  - $(CH_3)_2C=C(CH_3)_2$ + O
  - Xylene + OH

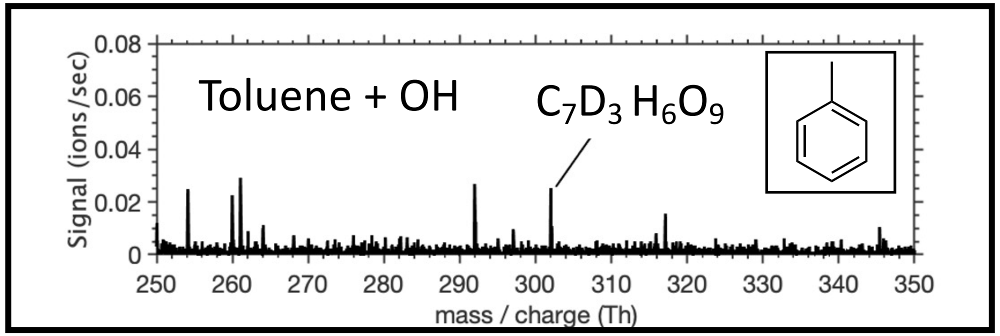
- **Computational**
  - Doodling on a paper
  - Force field conformer search
  - DFT geometry optimization(s)
  - CCSD(T) corrections (for all)
  - IRC to connect paths
  - MC-TST and MESMER for rates

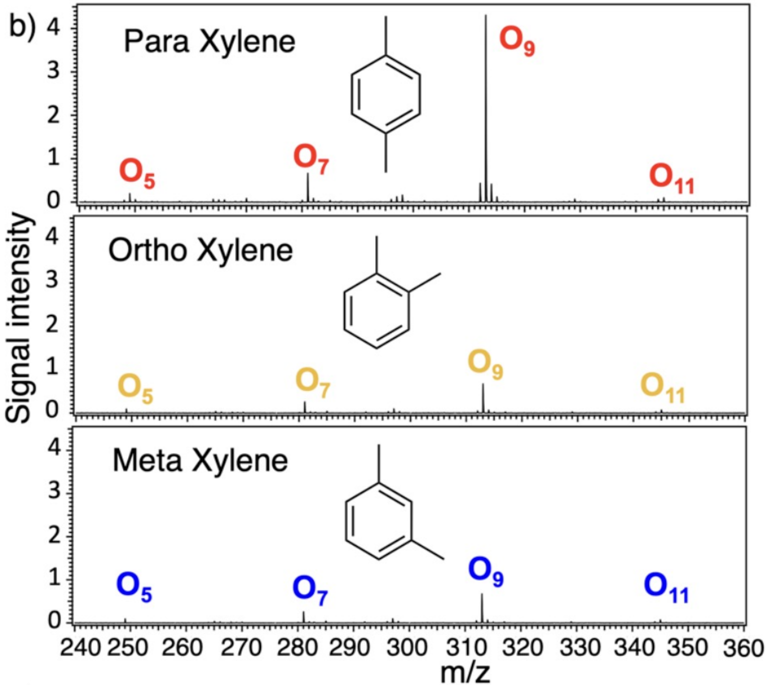
- **SOA yield – COALA chamber**
  - NO_3^- CIMS, AMS, etc.
  - n bag, 1 atm & 295 K
  - eaction time
  - ons
  - $(CH_3)_2$ + O_3 → OH + other
  - H (+$(NH_2)_4SO_4$ seed)

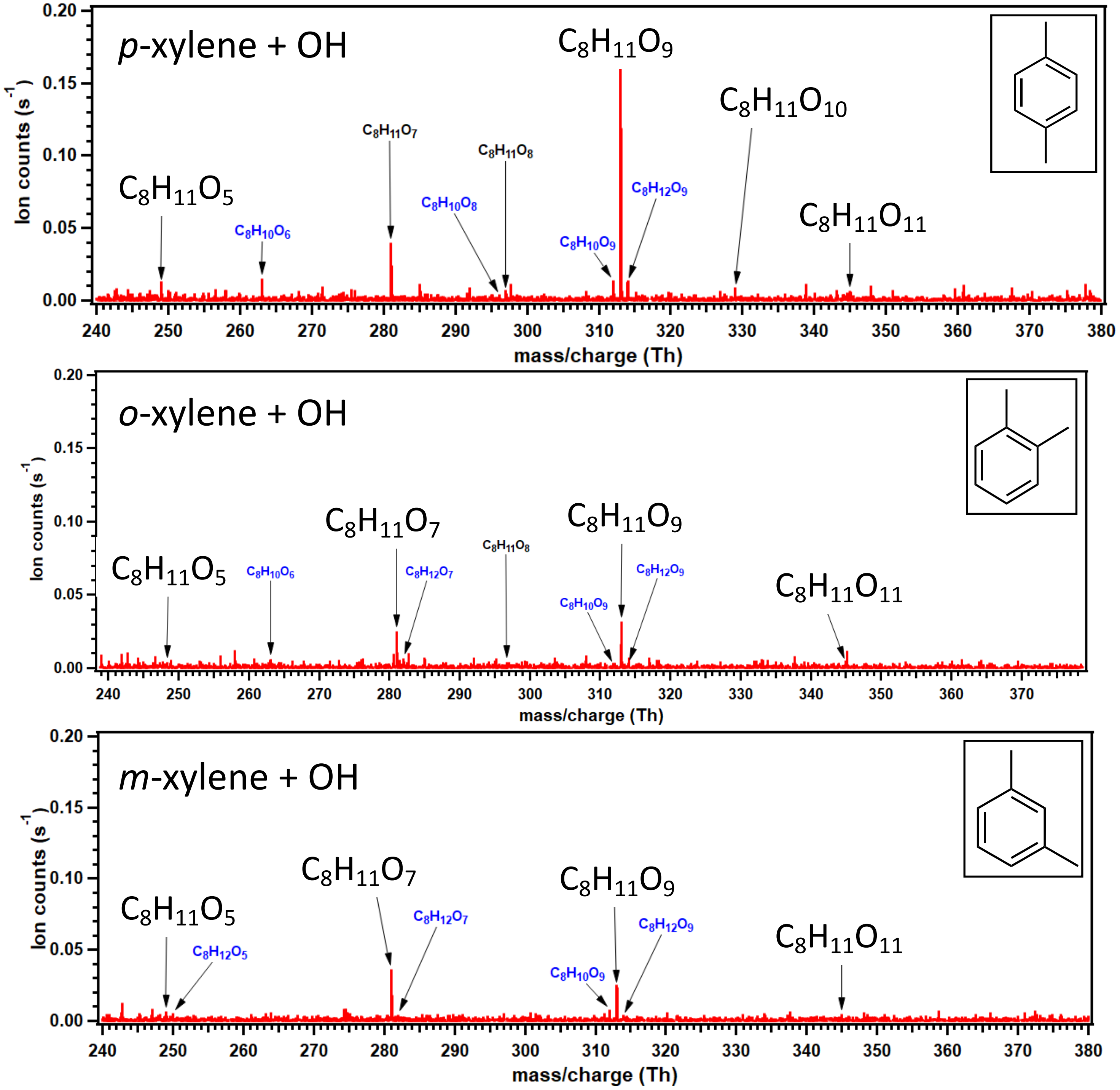




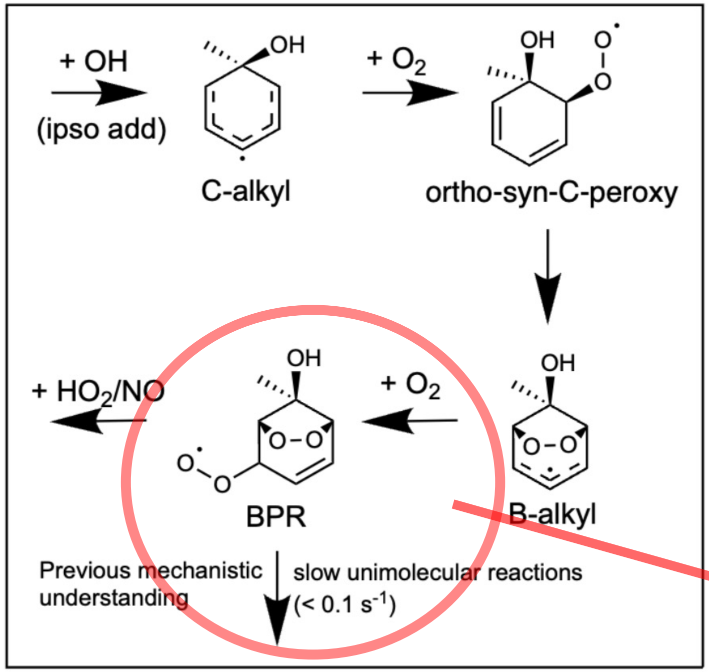
Subsecond (0.8 s) conversion of aromatic to HOM in flow reactor

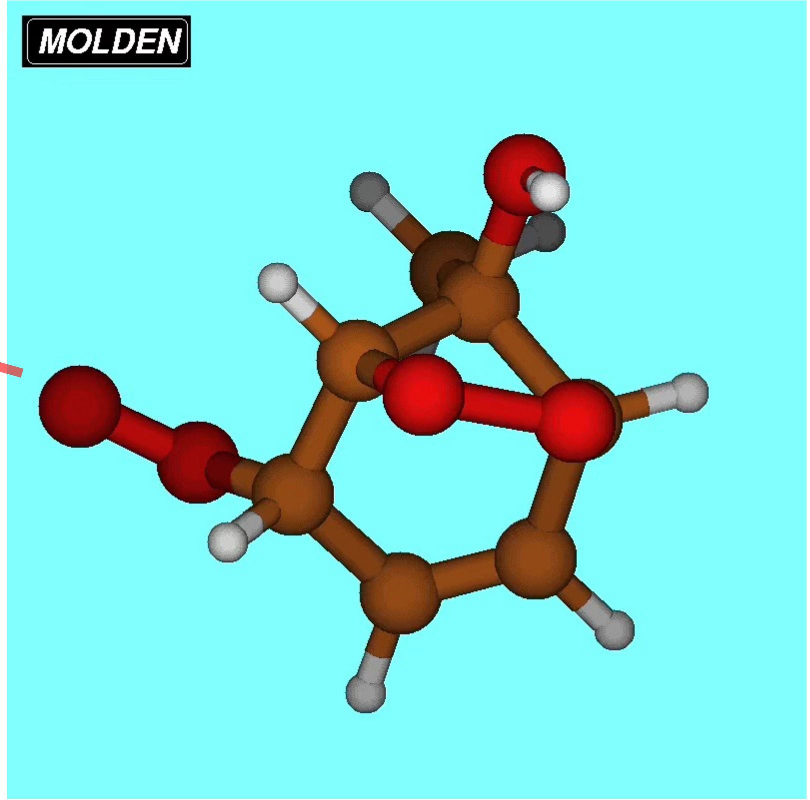






First steps of aromatic oxidation that lead to HOM
(*toluene oxidation*)

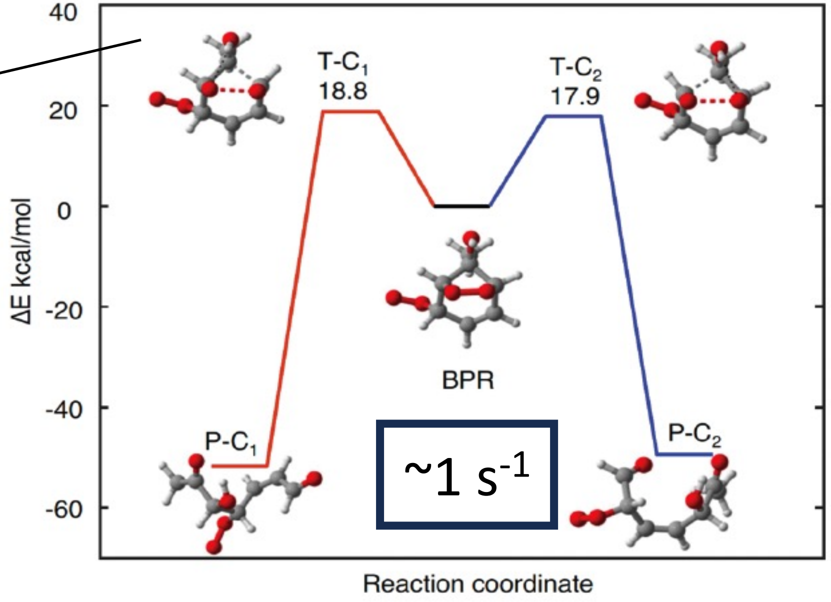




Molecular rearrangement

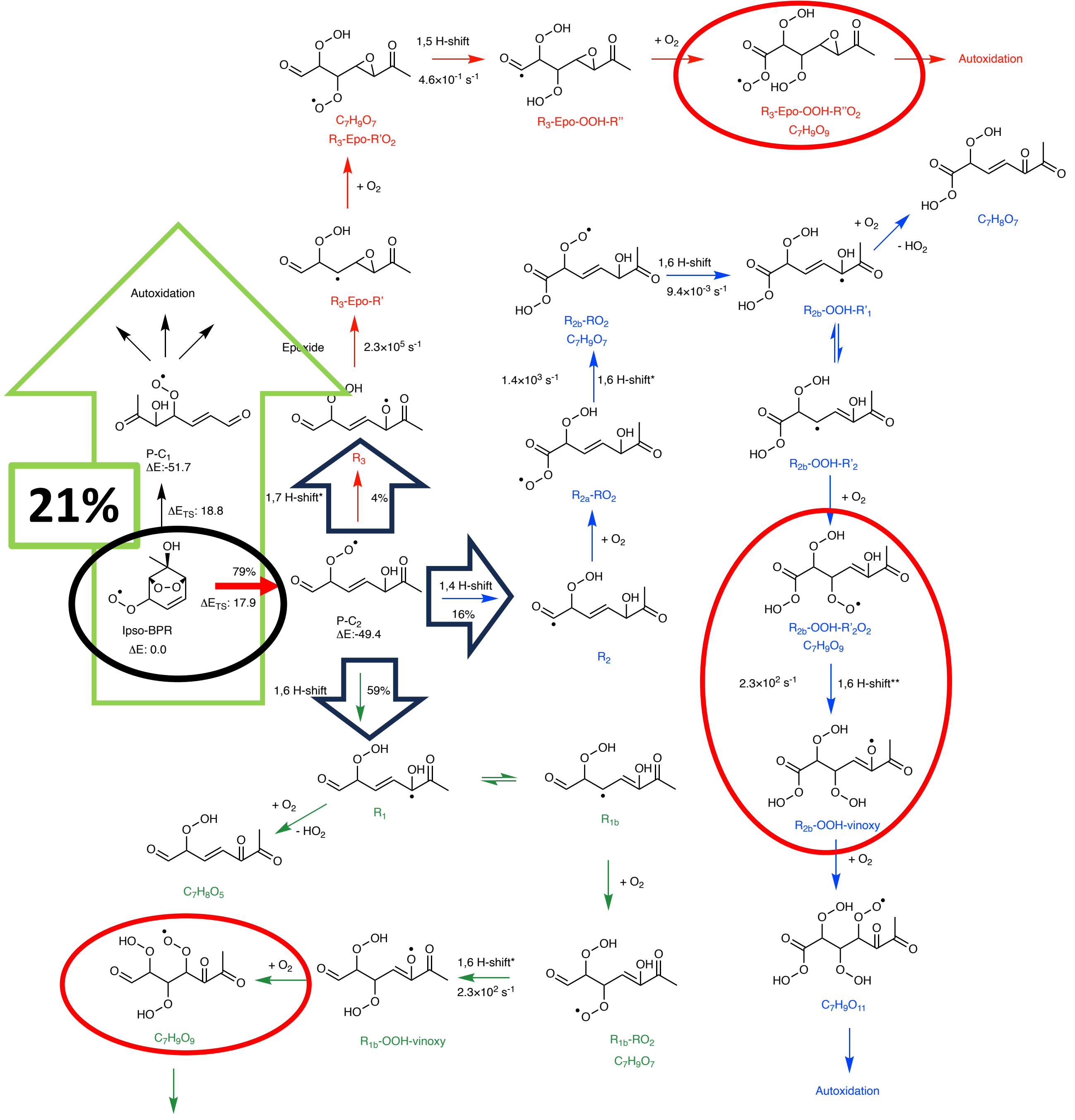
Iyer et al. *Nat. Comm.* **14**, 4984, **2023**

Around 0.1 s^{-1} rearrangement rate is needed to be competitive with other RO_2 loss processes



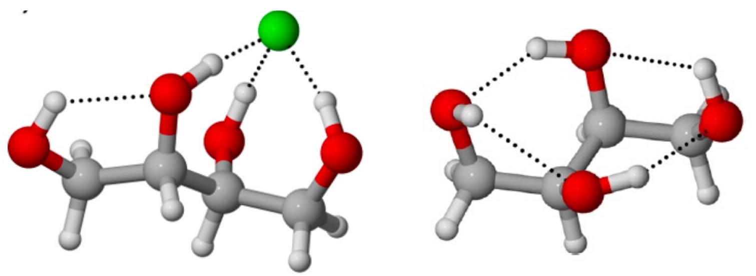
Rapid autoxidation

- Ring opened peroxy radicals rapidly autoxidize to 9-oxygen containing HOM



Structures critical for condensation properties
(=vapor pressures)

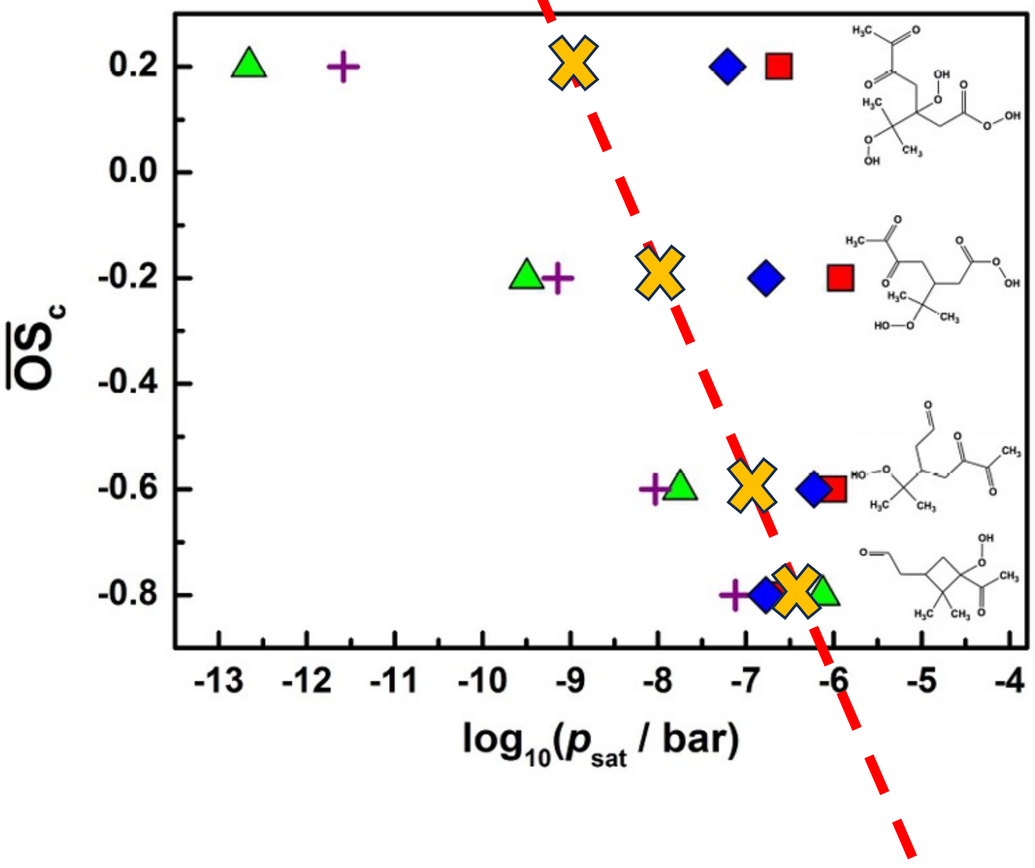
- Vapor pressures from i) functional group contributions or ii) quantum chemistry
  - SIMPOL vs COSMO-RS
  - i.e., i) fast and easy OR ii) slow and tedious
- Subsequent chemical box modelling to get the SOA yields



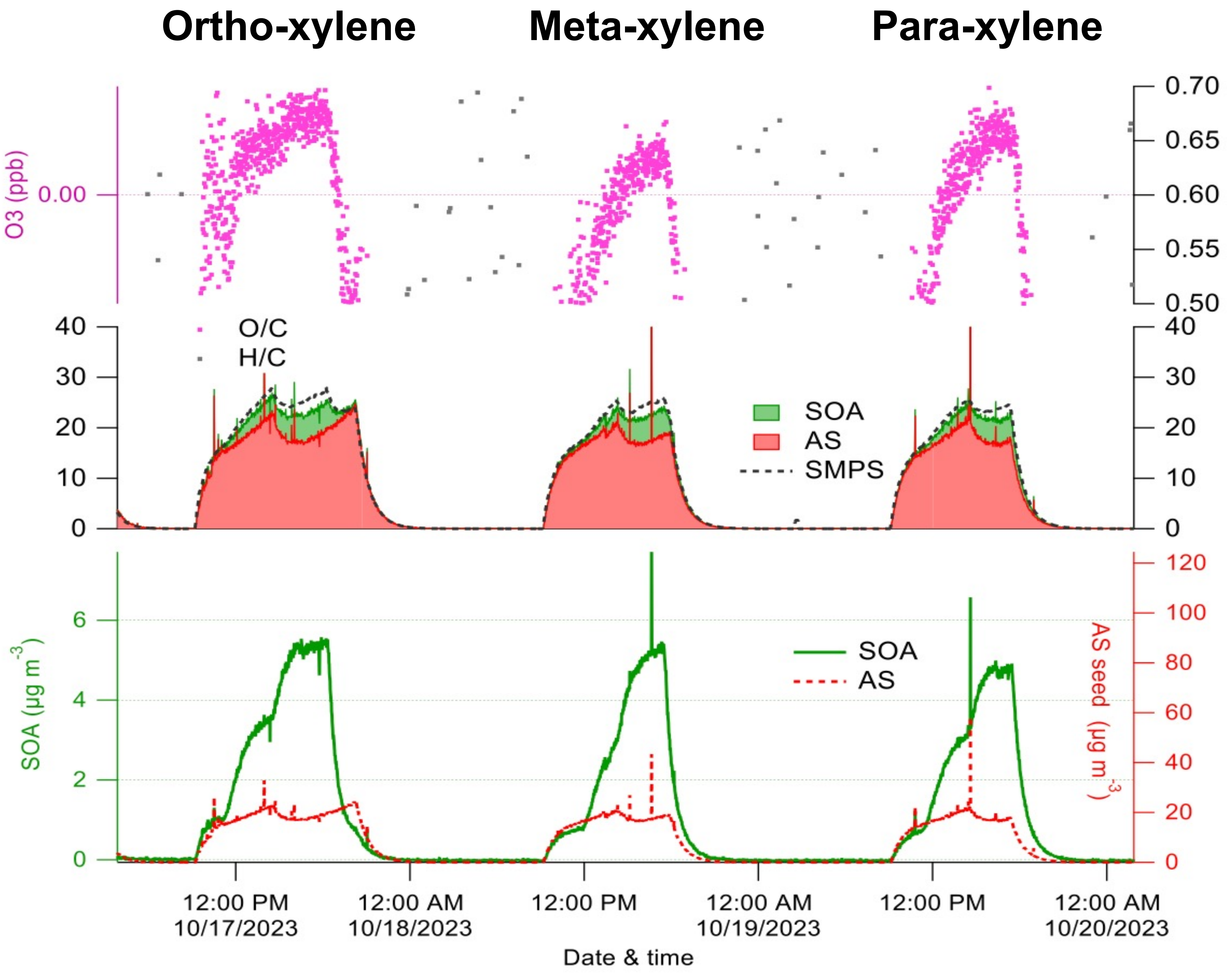
Hyttinen, N. et al., JPCA 2018, 120, 2569.

Average value closest to truth??

Kurtén, T. et al., JPCA 2016, 120, 2569.

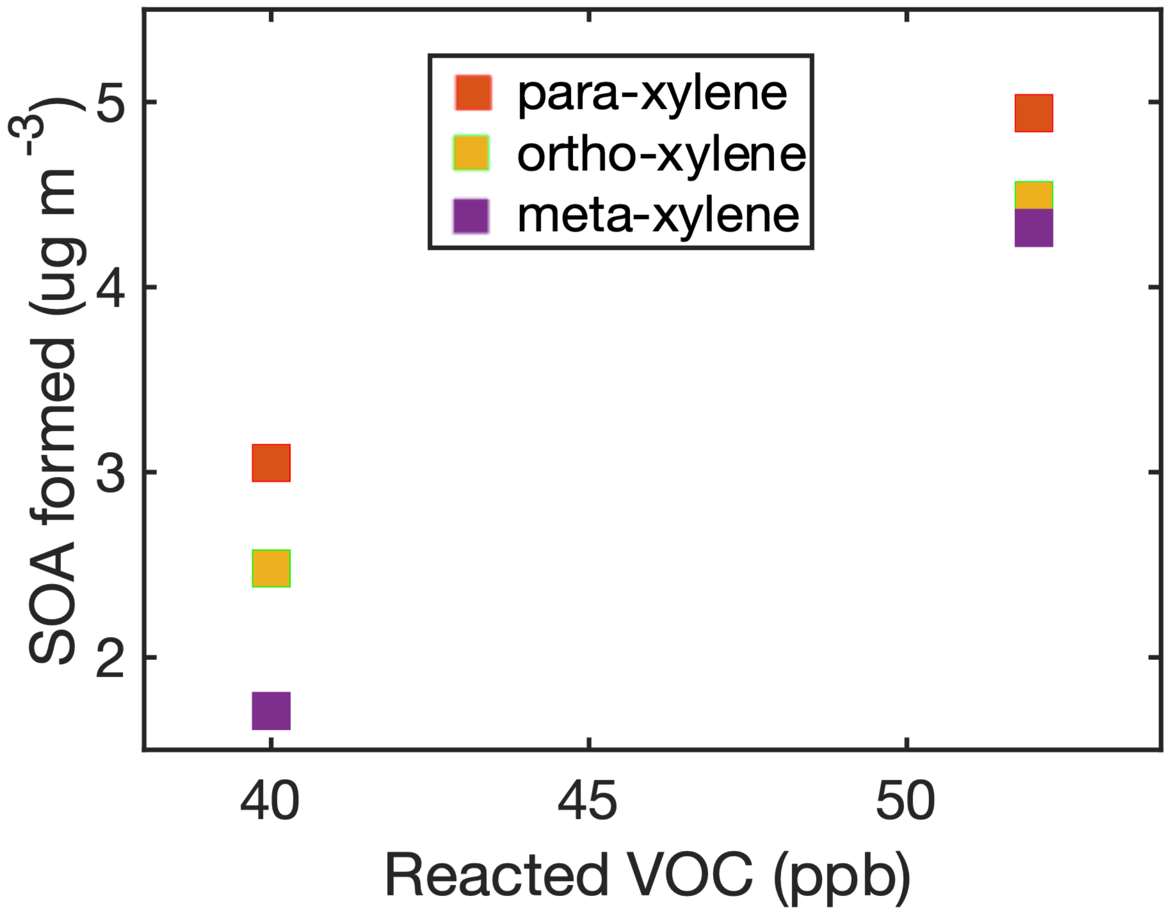


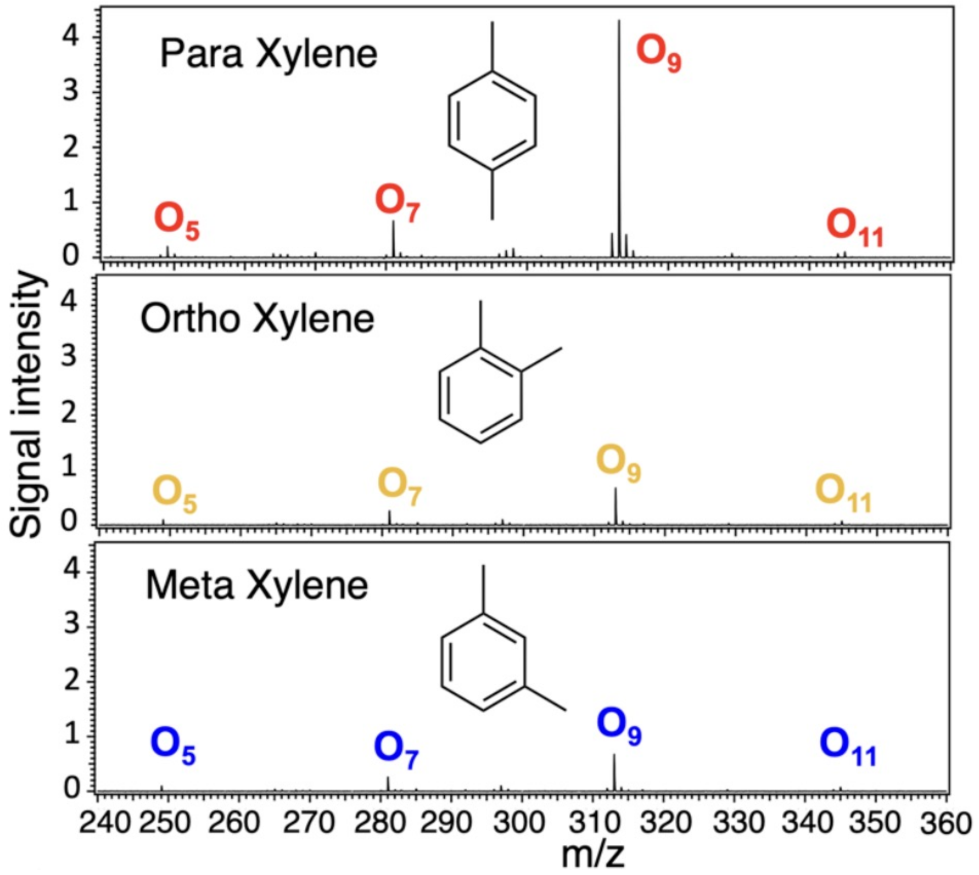
SOA yields. Only subtle differen-ces?



But there’s a difference!

HOM and SOA yields for the different xylene isomers



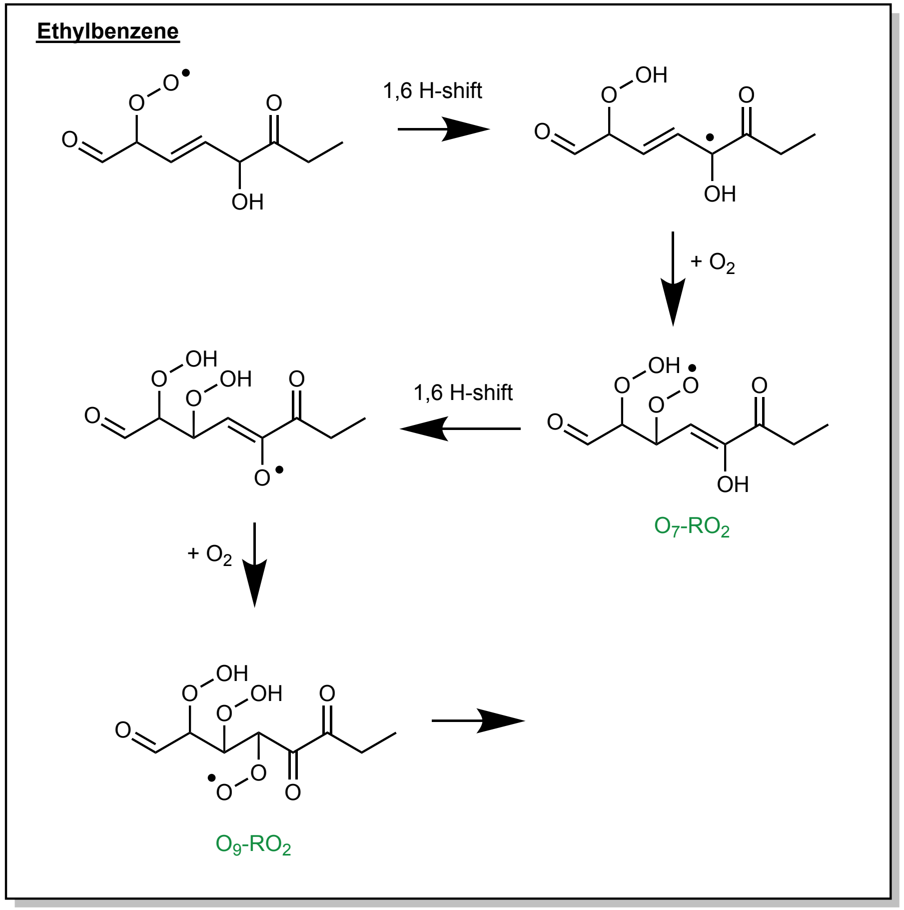


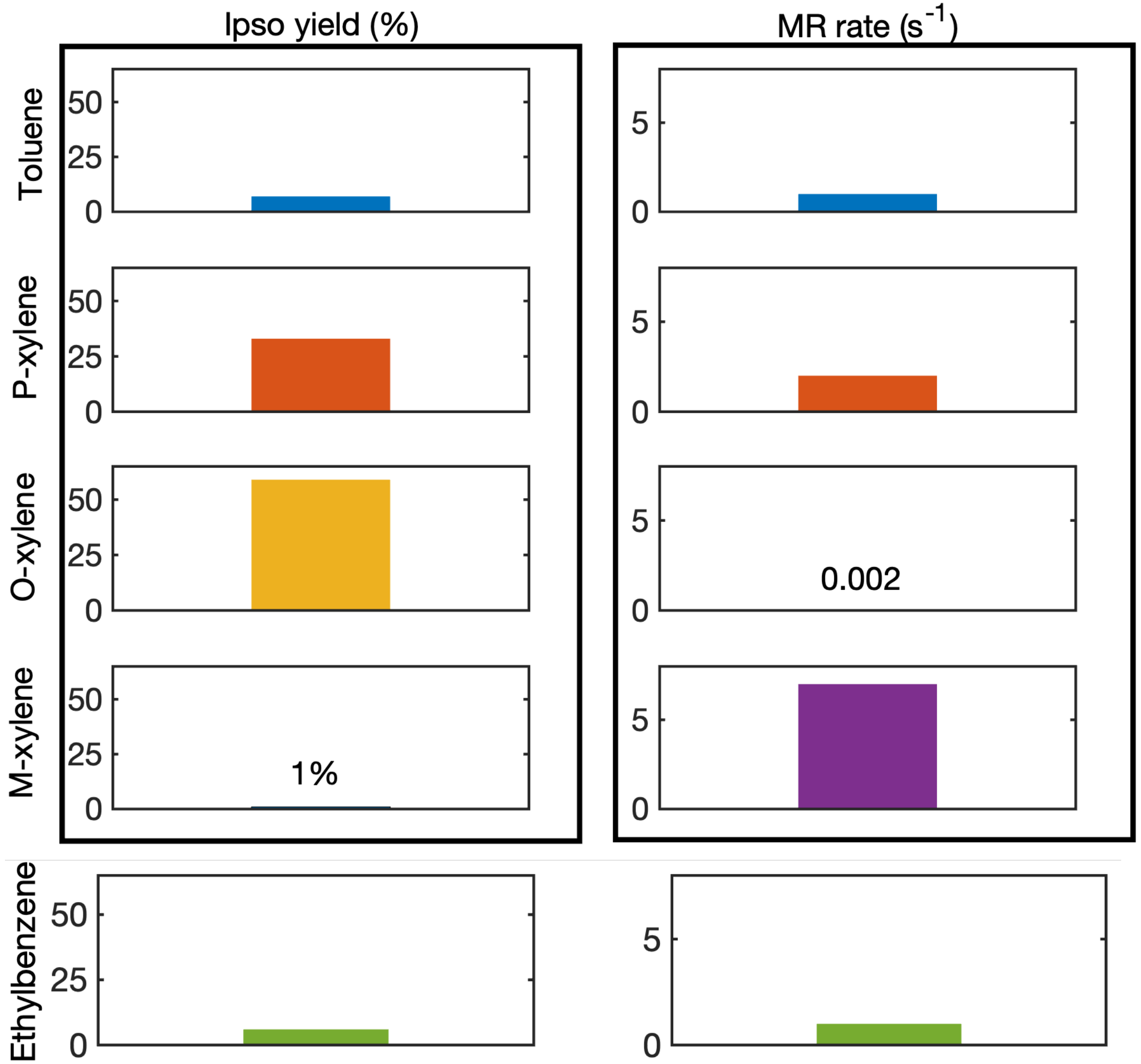
Summary

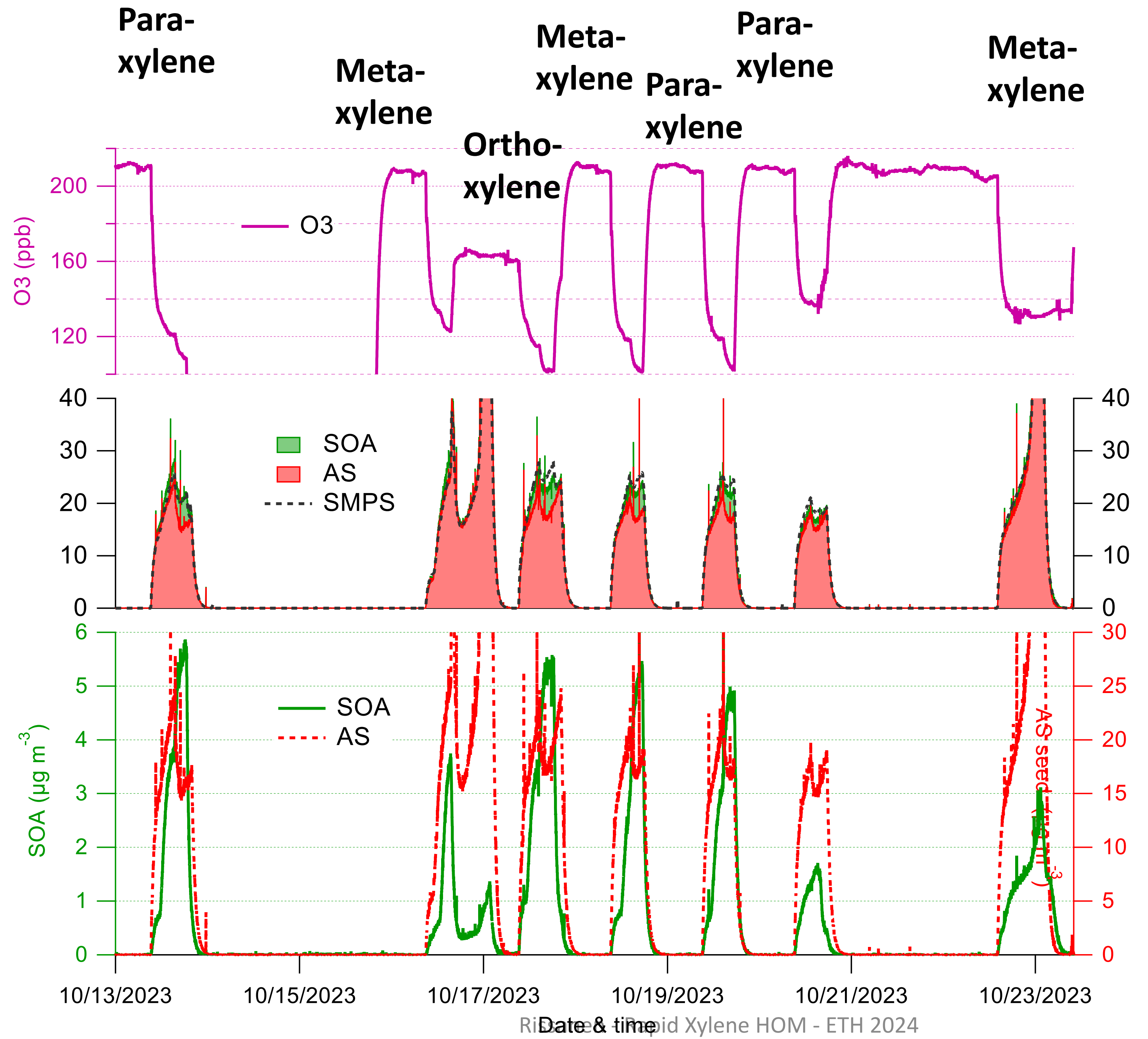
- The new molecular rearrangement mechanism explains sub-second O9-HOM formation in Xylenes.
  - *p*-Xylene has the highest yield of O9 HOM, others appreciable
- Only subtle differences in SOA yields…
  - Are we using too large seed particles?
- Explicit chemical mechanisms needed for molecular based aerosol modelling
  - Vapor pressures are the key for predicting SOA

Extra slides

What about ethylbenzene?






Para-
xylene
Meta-
xylene
Ortho-
xylene
Meta-
xylene
Para-
xylene
Para-
xylene
Meta-
xylene
O3 (ppb)
O3
SOA
AS
SMPS
SOA (µg m-3)
SOA
AS
AS seed
10/13/2023
10/15/2023
10/17/2023
10/19/2023
10/21/2023
10/23/2023
Date & time