# New Insights on the Chemistry of Organic Peroxy Radicals from Speciated Monitoring with Chemical Ionization Mass Spectrometry: Application to $RO_2$ + Alkene Reactions under Atmospheric Conditions

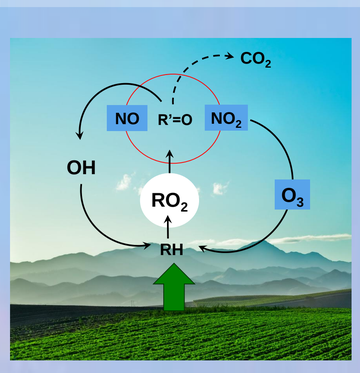

B. Nozière,[1*] O. Durif,[1] E. Dubus,[1] S. Kylington,[1] Å. Emmer[1] and F. Fache[2]

[1]Department of Chemistry, KTH, Royal Institute of Technology, Stockholm, Sweden

[2]Université Lyon 1, CNRS, UMR 5246, ICBMS, Villeurbanne, France

*noziere@kth.se


## Speciated Monitoring of gas-phase Organic Peroxy Radicals by proton-transfer Mass Spectrometry

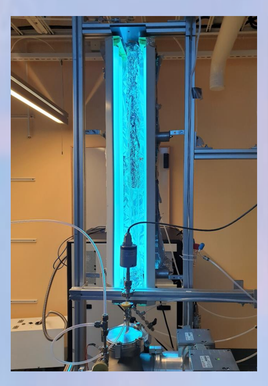


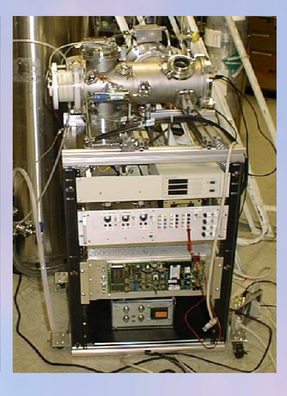

- Numerous ($RO_2$) in Earth's atmosphere from Volatile Organic Compound oxidation
- Many reactions of $RO_2$ identified but unknowns remain
- A major limit to understanding their chemistry is the inability to differentiate between different $RO_2$

⇒ Develop/apply proton-transfer ionization mass spectrometry for the detection of individual $RO_2$ under atmospheric conditions ("speciated detection"):

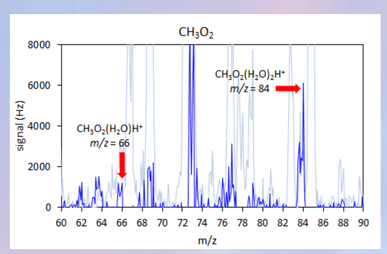
$$H_3O^+ + RO_2 \longrightarrow RO_2H^+ + H_2O$$

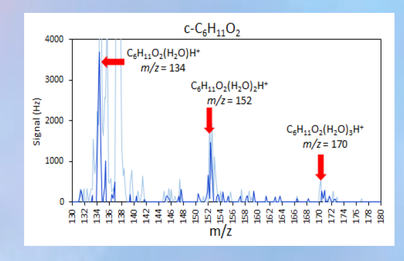
### I) Proof-of-concept with quadrupole Chemical Ionization Mass Spectrometer (CIMS)

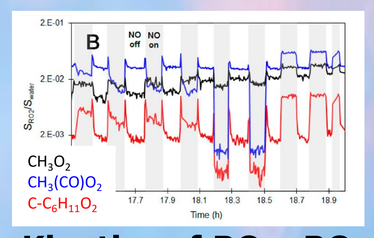




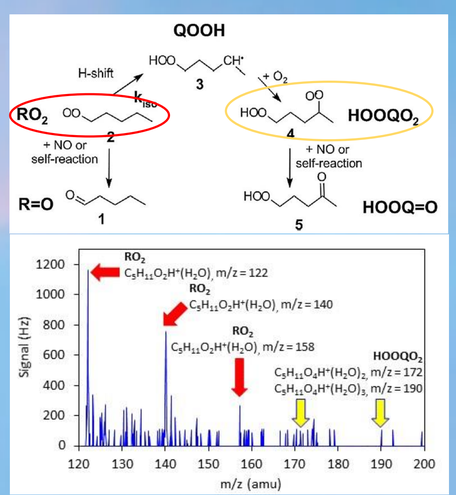
- $RO_2$ produced in flow rector from Cl + RH (UV-b) or R-I (UV-c)
- Add NO periodically to distinguish $RO_2$ from stable compounds



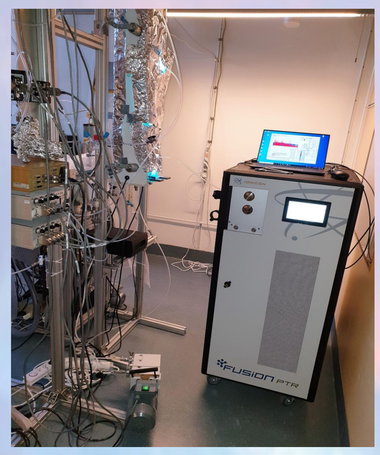




**Kinetics of $RO_2$+$RO_2$**
Nozière & Hanson, *J. Phys. Chem. A*, 2017, **121**, 8453




**Kinetics of autoxidation**
Nozière & Vereecken, *Angew. Chem. Int. Ed*, 2019, **58**, 13976

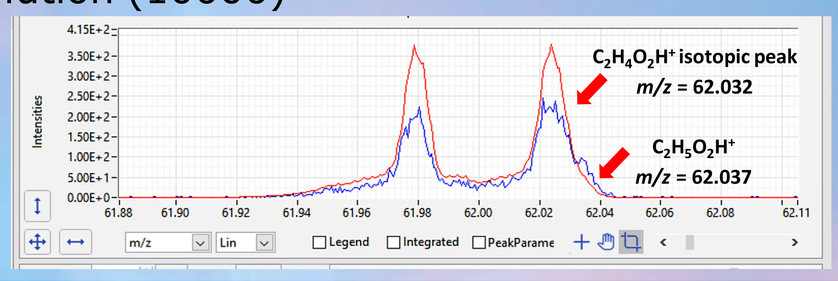
### II) High-resolution detection with PTR-ToF-MS




Start from FUSION PTR-TOF 10k (Ionicon Analytik, Gmbh)

- **On-going development** of ionization & sampling conditions
- High sensitivity (< ppt) + high resolution (10000)

⇒ separate $RO_2$ signal from isotopic ions for RC(O)OH

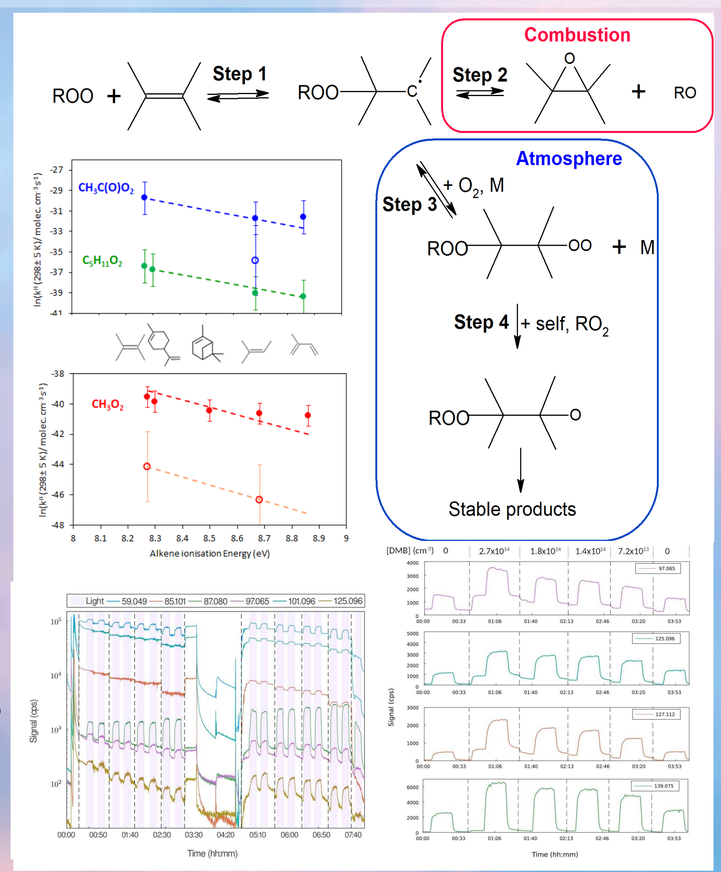



## Application to $RO_2$ + alkene reactions under atmospheric conditions

- Until recently $RO_2$ + alkene reactions only studied at T ≥ 360 K, expected slow at room temperature ⇒ ignored in atmospheric chemistry
- Only one reaction channel identified (step 1 + 2), step 2 limiting

- Recent kinetic study at 298 K monitoring $RO_2$ reports rate coefficients larger than expected (x10 – x100).

Nozière & Fache, *Chem. Sci.*, 2021, **12**, 11676




- Product study with PTr-ToF-MS FUSION at 298 K **shows epoxide channel negligible and reveals alternate peroxy radical channel**

⇒ under atmospheric conditions peroxy radical channel dominates, step 1 limiting (⇒ rates x 10 – x100)

⇒ $RO_2$+alkene possibly significant for some $RO_2$ in atmosphere

⇒ Monitoring $RO_2$ important even in laboratory studies

Nozière, Durif, Dubus, Kylington, Emmer, Fache, Piel & Wisthaler, *J. Phys. Chem. A*, 2022, submitted.


**ACKNOWLEDGMENTS**. This work is part of the **ERC Advanced Grant Project EPHEMERAL (grant agreement No 884532)** and has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme.