SPECIATED MONITORING OF ORGANIC PEROXY RADICALS ($\text{RO}_2$) WITH PROTON-TRANSFER MASS SPECTROMETRY:

REACTIONS OF $\text{RO}_2$ WITH ALKENES AT ROOM TEMPERATURE

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INTRODUCTION

- RO₂ key intermediates for VOC oxidation
  HOMs & aerosol formation

- Last ~ 15 years: H-shift (autoxidation) reactions
  ⇒ reduce observation / model discrepancies ([OH], [HO₂])

- Remaining discrepancies, even in laboratory
  Limited number of observables
  ⇒ more unknown reactions of RO₂?

- Detection in atmosphere based on chemical conversion / amplification ⇒ ΣRO₂

⇒ Useful to develop a technique to monitor individual RO₂ in the atmosphere («speciated monitoring»)
**PROJECT & OBJECTIVES**

Focus on small, aliphatic RO₂ (CH₃O₂, C₂H₅O₂ …) important for gas-phase chemistry

⇒ Proton-Transfer Ionization

AH⁺ + RO₂ → RO₂H⁺ + A

(H₂O)ₙH⁺ + RO₂ → RO₂(H₂O)ₙ₋ₘH⁺ + (H₂O)ₘ

**NSF–ATM0232057 (2003-2005):** collaboration D. R. Hanson, Augsburg College, MN  
**Proof-of-concept:** quadrupole CIMS to study RO₂ reactions laboratory

Cl₂ + hν (300 nm) → 2 Cl

Cl + RH → R + HCl

R + O₂ + M → RO₂ + M

R-I + hν (253 nm) → R + I

R + O₂ + M → RO₂ + M

**ERC-Adv-884532 (2021-2026):**
Adapt RO₂ detection to high resolution TOF-MS and apply to atmosphere

⇒ Optimize ionization conditions

⇒ Minimize losses (sampling line, MS inlet …)

⇒ Calibration

Detect CH₃O₂, C₂H₅O₂, i-C₃H₇O₂, t-C₄H₉O₂, CH₃C(O)O₂, 1-C₄H₉O₂, 1-C₅H₁₁O₂, 1-C₆H₁₃O₂, c-C₆H₁₁O₂ …
APPLICATIONS TO RO₂ CHEMISTRY IN LABORATORY

I) Cross reactions between RO₂s (Nozière & Hanson, 2017)

k² obtained from monitoring decay of R₁O₂ when R₂O₂ added:
CH₃O₂+CH₃C(O)O₂; CH₃O₂+t-butylO₂; c-hexylO₂+CH₃O₂; t-butylO₂+CH₃C(O)O₂; c-hexylO₂+ t-butylO₂

II) Autoxidation of C4-C7 aliphatic RO₂ (Nozière & Vereecken, 2019)

kᵢₒ obtained from observed ratios [HOOQO₂]/[RO₂]

RO₂ → HOOQO₂ (kᵢₒ)

If dominates, kᵢₒ ~ 1/tᵢₒ x [HOOQO₂]/[RO₂]
**REACTIONS RO$_2$ + ALKENE AT ROOM TEMPERATURE**

Combustion studies only (mostly $T \geq 360$ K)

Epoxidation of Alkenes by Peroxyl Radicals in the Gas Phase: Structure–Activity Relationships


- $k''$ increases with double bond substitution
  
P $<$ 2MP $<$ 2M2B $<$ 2,3DM2B

- $k''$ varies strongly with RO$_2$ structure
  
t-C$_4$H$_9$O$_2$ $<$ i-C$_3$H$_7$O$_3$ $<$ CH$_3$O$_2$ $<$ CH$_3$C(O)O$_2$

Suggest $k''$ negligible at 298 K

$k''(\text{CH}_3\text{O}_2+\text{2,3DMB}) = 6.6 \times 10^{-20}$ cm$^3$ molec. s$^{-1}$

$k''(\text{CH}_3\text{C(O)O}_2+\text{2M2B}) = 2.8 \times 10^{-16}$ $\Rightarrow \sim 10^{-15}$ for 2,3DM2B?
A) Kinetic study

RO₂ produced continuously, alkene added periodically

\[ \ln\left(\frac{\text{[RO}_2]}{[\text{RO}_2]_0}\right) = t_{\text{res}} \times k^{\text{II}} \times [\text{alkene}] \]

- \( k^{\text{II}} \) follows expected trends with RO₂ and alkene structure
- \( k^{\text{II}} \times 10^{-x} \times 100 \) expected values:
  - CH₃O₂ from CH₄ + Cl and CH₃I
  - 1-C₅H₁₁O₂ from I-C₅H₁₁
  - CH₃C(O)O₂ from H₃CCHO + Cl

\[ \Rightarrow \text{slow for alkyl RO}_2 \text{ in atmosphere but potentially non-negligible for acyl- or HO-substituted RO}_2? \]

Nozière & Fache, Chem. Sci. 12, 11676, 2021
B) Product study

- Alkene and RO₂ precursor flown continuously + RO₂ produced periodically (light ON/OFF) ⇒ differentiate products from impurities
- Irradiation window above reaction region ⇒ Reactions take place entirely in dark
- CH₃O₂ and 1-C₅H₁₁O₂ from iodinated precursors + UVc (253 nm)

Surprise!

- No measureable epoxide formation (<15 %), confirmed by GC/MS
- Other products, increasing with [alkene], observed
Product study

⇒ At room T, alkyl adduct produces RO₂ instead of epoxide

- “ROOR” not detected with PTR-TOF-MS
  Consistent with Li et al., ACP, 2021
  Fragmentation inside PTR-based mass spectrometers limits the detection of ROOR and ROOH peroxides
  Verified with standard t-butyl-OO-t-butyl

- Competition epoxidation vs R+O₂ consistent with Möller et al., 2019
  \[ r_{\text{epox}} \sim 3 \times 10^5 - 10^7 \text{ s}^{-1} < r_{R+O_2} = 4 \times 10^7 \text{ s}^{-1} \]

- Overall reaction kinetically limited by addition step, not by epoxidation step
  ⇒ consistent with \( k'' \times 10 \times 100 \) measured at 298 K

Nozière et al., submitted, 2023
Conclusions & Perspectives

Use proton transfer MS to monitor individual RO\textsubscript{2}, especially alkyl ones (CH\textsubscript{3}O\textsubscript{2} …)

Reactions RO\textsubscript{2} + alkene at room temperature: many surprises!

- Extrapolating combustion studies to room T not adequate?
  - rate coefficients underestimated due to different limiting steps
  - slow for many RO\textsubscript{2} (alkyl…) but potentially non negligible ($\geq 10^{-14}$ cm\textsuperscript{3}s\textsuperscript{-1}) for substituted ones (-OH, -C=O…)
    $\Rightarrow$ potentially competitive with other reactions in laboratory and NO\textsubscript{x}-free, biogenically-impacted regions of the atmosphere
    \[ [\text{alkene}] = 20 \text{ ppb} \times k^{ll} = 10^{-14} \text{ cm}^3\text{s}^{-1} \Rightarrow k^l = 5 \times 10^{-3} \text{ s}^{-1} \]
  - produce R’O\textsubscript{2} then ROOR instead of epoxide (from alkenes)

Thank you!