

Atmospheric Nanoparticle Growth from NO₃ Radical Initiated Oxidation of Monoterpenes

James N. Smith,¹ Juliane L. Fry,² Theo Kurtén,³ and Danielle C. Draper¹

¹Department of Chemistry, University of California Irvine, Irvine, CA.

²Department of Chemistry, Reed College, Portland, OR.

³Department of Chemistry, University of Helsinki, Helsinki, Finland.

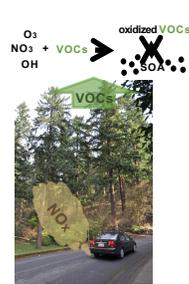
Correspondence: jimsmith@uci.edu, fry@reed.edu



OBJECTIVES

- Implement computational chemistry methods for elucidating reaction pathways and developing CIMS detection strategies**
 - Calculate reaction rates for intramolecular reactions of NO₃ + monoterpene RO₂ and RO intermediates
 - Calculate ion-analyte binding enthalpies between predicted closed-shell products and relevant CIMS reagent ions (e.g. NO₃⁻, I⁻, and C₂H₃O₂⁻)
- Perform comparative laboratory studies of NO₃ radical initiated oxidation of monoterpenes**
 - Chamber and flow tube experiments
 - Analyze gas- and particle-phase products with diverse suite of instrumentation
- Obtain chemical closure between gas phase precursors and nanoparticle physico-chemical properties**
 - Identify and quantify products observed in objective II
 - Develop mechanistic model for partitioning of these species, enabling prediction of particle growth rates and composition, given initial reaction conditions

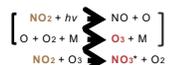
BACKGROUND



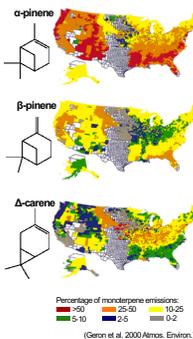
Monoterpenes account for about 10% of global VOC emissions and are potent SOA precursors (Guenther et al. 1995 JGR)

α-pinene is the most prevalent monoterpene emission globally, but other monoterpene emissions are significant and may dominate regionally (Guenther et al. 2012; Geron et al. 2000)

Nearly 90% of NO_x emissions in the US come from anthropogenic sources (Reis et al. 2009 ACP)



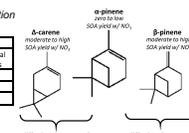
NO₃ is rapidly photolyzed and thus is relevant primarily at night
An estimated >50% monoterpene-derived SOA in the US comes from NO₃ oxidation, but NO₃ oxidation is only rarely explicitly treated in regional/global models (Pye et al. 2010 ACP)



In laboratory studies, NO₃ oxidation of monoterpenes is shown to have moderate to high SOA yields **except from α-pinene** (compiled in N₃ et al., 2017 ACP)

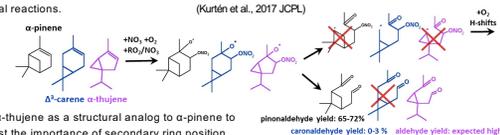
SOA and organonitrate yields from NO₃ oxidation of monoterpenes from Fry et al., 2014 EST

| Precursor | SOA yield (µg SOA per µg VOC) | total (gas+particle) molar yield | fraction of total aerosol mass |
|------------------------|-------------------------------|----------------------------------|--------------------------------|
| α-pinene | 7% | 30% | 2% |
| β-pinene | 33-44% | 27% | 55% |
| Δ ³ -carene | 38-63% | 77% | 55% |



Members of current research team, Fry and Kurtén, investigated the anomalous behavior of α-pinene vs. Δ³-carene computationally.

Concluded position of strained ring leads to different RO decomposition pathways, producing higher volatility pinonaldehyde in α-pinene in high yield vs. a comparatively stable alkyl radical in Δ³-carene that can undergo additional radical reactions. (Kurtén et al., 2017 JCL)



We have added α-thujene as a structural analog to α-pinene to experimentally test the importance of secondary ring position.

METHODS

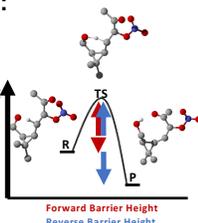
I. Computational Chemistry:

Intramolecular Reaction Rate Constants

For RO₂ and RO H-shifts and intramolecular reactions of interest:

- Generate all possible conformers for reactant (R), transition state (TS), and product (P)
- Optimize conformer geometries using density functional theory with B3LYP/6-31+G(d) and ωB97X-D/aVTZ basis sets/functionals
- Calculate rate constants using Lowest Conformer Transition State Theory (LC-TST)

Reactions with a **forward barrier <20 kcal/mol** are potentially competitive with bimolecular reactions in the atmosphere (Møller et al. 2016 JCPA)



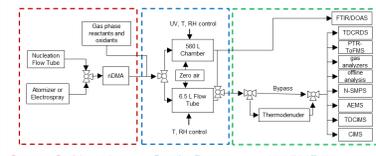
Ion-analyte binding enthalpies



- Compare ΔE for each reagent ion clustering with itself vs. clustering with analyte
- E.g. for NO₃⁻ CIMS, if ΔE_{analyte} < ΔE_{HNO₃} we'd expect to detect it in NO₃⁻ CIMS

II. Laboratory Experiments:

Perform chamber and flow tube experiments to characterize gas- and particle-phase products:



- Focus on:
- Size dependence (vary residence time)
 - Volatility of particle-phase products (thermometer)
 - Seed vs. no seed

| BVOC (ppb) | oxidant (ppb) | seed particle (diam.) | environment |
|--------------------------------|--------------------------------------------------|-----------------------------------------------------------|-------------|
| α-pinene (0-100) | O ₃ (0-100) + NO ₂ (0-100) | none | T = 0.60 °C |
| ω-pinene (0-100) | NO ₃ (0-100) | (NH ₄) ₂ SO ₄ (5-80 nm) | RH = 0.40% |
| Δ ³ -carene (0-100) | | BSSQA (0-50 nm) | |

III. Growth Rate Modeling:

Develop model to predict nanoparticle growth rates to demonstrate chemical closure, incorporating computational and experimental results.

- Characterize chamber losses and quantify observed products
- Compare experimental growth rates to the theoretical diffusion-controlled growth rate due to irreversible condensation of observed products
- If necessary, incorporate other growth mechanisms (e.g. surface or bulk reactive uptake)

$$GR = \frac{dD_p}{dt} \Big|_{\text{diffusion}} = k_{i,D_p} (p_i - p_{i,s})$$

$$GR = \sum_i k_{i,D_p} (p_i - p_{i,s}) + \sum_j A_{j,D_p} C_{j,wall,D_p} + \sum_k B_{k,D_p} C_{k,wall,D_p}$$

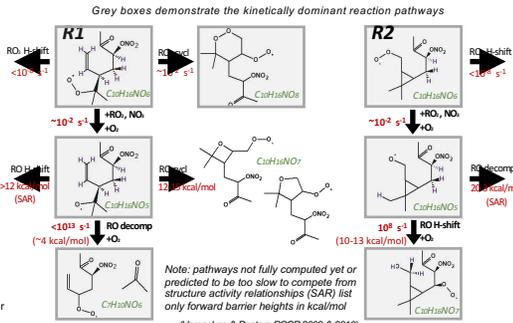
EARLY RESULTS

Computational work for this project has so far focused on what condensable products may form from Δ³-carene + NO₃, focusing on RO₂/RO intramolecular H-shift reactions, RO₂/RO addition reactions, and RO decomposition reactions.

R1 and R2 are the RO₂ radicals formed following the first, crucial RO decomposition for Δ³-carene + NO₃ (Kurtén et al. 2017 JPLCL)

Most intramolecular rate constants calculated from ωB97X-D/aVTZ using LC-TST; absolute values not final, but relative values not expected to change significantly.

Bimolecular rate constants estimated from modeled chamber radical concentrations



Many closed-shell organonitrate products identified so far have only 1 H-bond donor
Quick ion-analyte clustering calculations for a product containing a single H-bond donor indicate NO₃⁻ CIMS should be sensitive to these products

One Δ³-carene + NO₃ chamber experiment has been done at UCI, focusing on NO₃⁻ CIMS measurements to qualitatively assess what highly oxidized products are forming

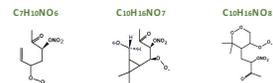
Dark, flow-through chamber; average residence time = 23 min
400 ppb O₃ + 300 ppb NO₂ (O₃ + NO₂ → NO₃ + O₂) + 50 ppb Δ³-carene (NO₃ responsible for >95% of oxidation according to kinetics modeling)

So far good agreement between computationally proposed products and observed products

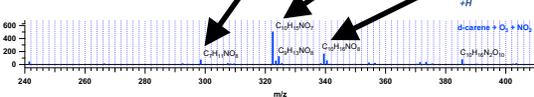
Highest Intensity CIMS Peaks

C₇H₁₁NO₈
C₈H₁₃NO₇ 1:17 N₁:0:6-12
C₁₀H₁₅NO₅ 1:18 N₁:0:7-12
C₁₁H₁₇NO₆ 1:11, 13
C₁₀H₁₅NO₃ 1:0:8-17

Computed RO₂ Radicals



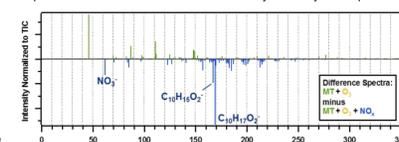
measure: C₇H₁₁NO₈ +H, +O₂
measure: C₈H₁₃NO₇ -H, +O₂
measure: C₁₀H₁₅NO₅ +H



(Above) NO₃⁻ CIMS spectrum highlighting the "monomer region" for comparison with computationally proposed products

Nanoparticle composition was analyzed with the TDCIMS during the CLOUD 10 campaign, including monoterpene ozonolysis chamber experiments with and without NO_x

NO_x chemistry led to significant differences in nanoparticle composition, including dominant peaks C₁₀H₁₅O₂⁻ and C₁₀H₁₇O₂⁻ that are likely thermally decomposed organonitrates



(Left) Difference spectrum (normalized to total ion count, averaged over full experiments) from TDCIMS, showing peaks enhanced in monoterpene ozonolysis vs. peaks enhanced in monoterpene ozonolysis + NO_x (monoterpene = α-pinene + Δ³-carene)

BROADER IMPACTS

Near-peer UCI / Reed College mentoring program

- Several undergraduate research assistants from Reed will be paired with UCI graduate students in "near-peer" mentoring pairs
- The group of mentor pairs will meet periodically throughout the academic year in organized video conferencing sessions with faculty moderators for discussions of themes related to scientific research and careers, focusing on everything from scientific topics (reading and discussing an article together) to career skills (preparing a cover letter)
- Mentor pairs will be encouraged to engage periodically outside of these organized sessions to informally discuss aspects of the graduate study experience
- This form of mentoring relationships has been demonstrated to promote belongingness and student retention. It benefits the mentor with teaching opportunities, the mentee to share knowledge, and an increased understanding of meeting professional expectations, while mentees find near-peer mentors more reliable than faculty members

ACKNOWLEDGMENTS

- Authors gratefully acknowledge funding from:
- National Science Foundation (AGS-1762098 and AGS-1762106)
 - Academy of Finland
 - NSF Graduate Research Fellowship program (DGE-1321846)
 - NSF Graduate Research Opportunities Worldwide (GROW) travel grant
 - CSC - IT Center for Science, Finland, for computational resources

RESEARCH TEAM

