

# Atmospheric Nanoparticle Growth from NO<sub>3</sub> Radical Initiated Oxidation of Monoterpenes

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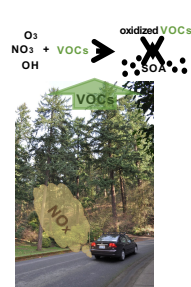
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## OBJECTIVES

- Implement computational chemistry methods for elucidating reaction pathways and developing CIMS detection strategies**
  - Calculate reaction rates for intramolecular reactions of NO<sub>3</sub> + monoterpene RO<sub>2</sub> and RO intermediates
  - Calculate ion-analyte binding enthalpies between predicted closed-shell products and relevant CIMS reagent ions (e.g. NO<sub>3</sub><sup>-</sup>, I<sup>-</sup>, and C<sub>2</sub>H<sub>5</sub>O<sub>2</sub><sup>-</sup>)
- Perform comparative laboratory studies of NO<sub>3</sub> 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

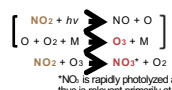
## BACKGROUND



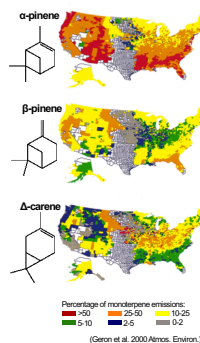
Monoterpenes account for about 10% of global VOC emissions and are potent SOA precursors (Guenther et al. 1995 JGR)

$\alpha$ -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<sub>x</sub> emissions in the US come from anthropogenic sources (Reis et al. 2009 ACP)



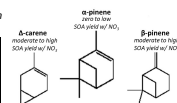
An estimated >50% monoterpene-derived SOA in the US comes from NO<sub>3</sub> oxidation, but NO<sub>3</sub> oxidation is only rarely explicitly treated in regional/global models (Pye et al. 2010 ACP)



In laboratory studies, NO<sub>3</sub> oxidation of monoterpenes is shown to have moderate to high SOA yields **except from  $\alpha$ -pinene** (compiled in N<sub>3</sub> et al., 2017 ACP)

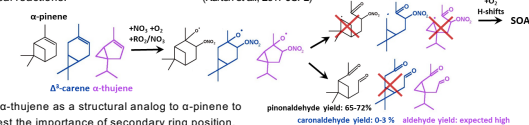
SOA and organonitrate yields from NO<sub>3</sub> oxidation of monoterpenes from Fry et al., 2014 EST

Precursor	SOA yield (g SOA/g reagent)	total (gas+particle) molar yield	fraction of total aerosol mass
$\alpha$ -pinene	7%	10%	2%
$\beta$ -pinene	33-44%	32%	55%
$\Delta^3$ -carene	38-65%	77%	55%



Members of current research team, Fry and Kurtén, investigated the anomalous behavior of  $\alpha$ -pinene vs.  $\Delta^3$ -carene computationally.

Concluded position of strained ring leads to different RO decomposition pathways, producing higher volatility pinonaldehyde in  $\alpha$ -pinene in high yield vs. a comparatively stable alkyl radical in  $\Delta^3$ -carene that can undergo additional radical reactions. (Kurtén et al., 2017 JCP)



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

## METHODS

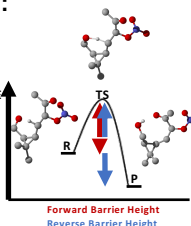
### I. Computational Chemistry:

#### Intramolecular Reaction Rate Constants

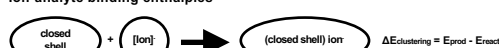
For RO<sub>2</sub> and RO H-shifts and intramolecular reactions of interest:

- 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 wB97X-D/aVTZ basis sets/functional
- 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 (Moller et al. 2016 JCPA)



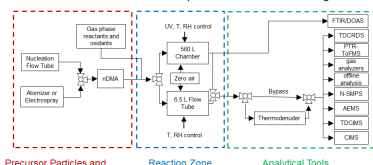
#### Ion-analyte binding enthalpies



- Compare  $\Delta E$  for each reagent ion clustering with itself vs. clustering with analyte
- E.g. for NO<sub>3</sub><sup>-</sup> CIMS, if  $\Delta E_{\text{Analyte}} < \Delta E_{\text{HNO}_3}$  we'd expect to detect it in NO<sub>3</sub><sup>-</sup> 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
$\alpha$ -pinene (0-100)	O <sub>3</sub> (0-100) + NO <sub>3</sub> (0-100)	none	T = 0.40 °C
$\alpha$ -thujene (0-100)	NO <sub>3</sub> (0-100)	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> (0-50 nm)	RH = 0.80%
$\Delta^3$ -carene (0-100)		BSQA (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)

$$GR = \frac{dD_p}{dt} \Big|_{\text{diffusion}} = k_{1,D_p}(p_i - p_{i,sat})$$

$$GR = \sum_i k_{1,D_p}(p_i - p_{i,sat}) + \sum_j A_{j,D_p} C_{j,sat,D_p} + \sum_k B_{k,D_p} C_{k,sat,D_p}$$

## EARLY RESULTS

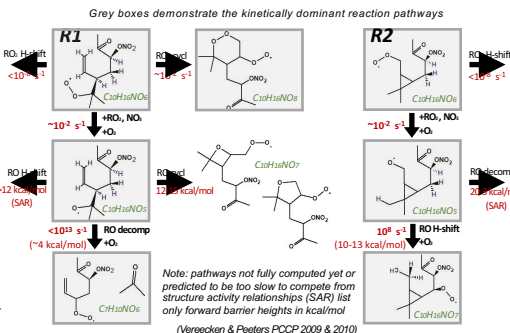
Computational work for this project has so far focused on what condensable products may form from  $\Delta^3$ -carene + NO<sub>3</sub>, focusing on RO<sub>2</sub>/RO intramolecular H-shift reactions, RO<sub>2</sub>/RO addition reactions, and RO decomposition reactions.

R1 and R2 are the

RO<sub>2</sub> radicals formed following the first, crucial RO decomposition for  $\Delta^3$ -carene + NO<sub>3</sub> (Kurtén et al. 2017 JCP)

Most intramolecular rate constants calculated from wB97X-D/aVTZ using LC-TST; absolute values not final, but relative values not expected to change significantly.

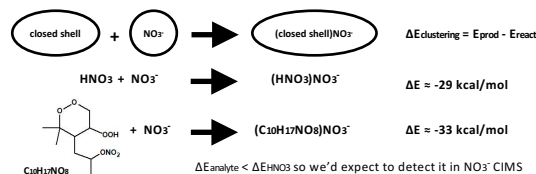
Bimolecular rate constants estimated from modeled chamber radical concentrations



Note: pathways not fully computed yet or predicted to be too slow to compete from structure activity relationships (SAR) list only forward barrier heights in kcal/mol (Vereecken & Peeters PCPP 2009 & 2010)

NO<sub>3</sub><sup>-</sup> reagent ions are selective for, e.g., highly oxidized organics and cluster with analyte molecules via H-bonding (Hytinen et al., 2017 JPCA)

Many closed-shell organonitrate products identified so far have only 1 H-bond donor



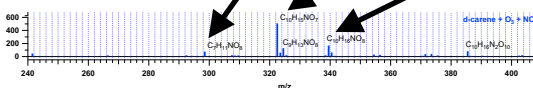
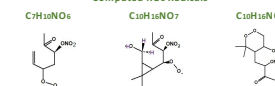
Quick ion-analyte clustering calculations for a product containing a single H-bond donor indicate NO<sub>3</sub><sup>-</sup> CIMS should be sensitive to these products

One  $\Delta^3$ -carene + NO<sub>3</sub> chamber experiment has been done at UCI, focusing on NO<sub>3</sub><sup>-</sup> CIMS measurements to qualitatively assess what highly oxidized products are forming

Dark, flow-through chamber; average residence time = 23 min  
400 ppb O<sub>3</sub> + 300 ppb NO<sub>2</sub> (O<sub>3</sub> + NO<sub>2</sub> → NO<sub>3</sub> + O<sub>2</sub>) + 50 ppb  $\Delta^3$ -carene (NO<sub>3</sub> responsible for >95% of oxidation according to kinetics modeling)

So far good agreement between computationally proposed products and observed products

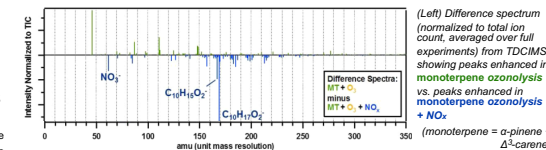
Highest Intensity CIMS Peaks  
C<sub>10</sub>H<sub>15</sub>NO<sub>3</sub><sup>+</sup>  
C<sub>10</sub>H<sub>17</sub>NO<sub>3</sub><sup>+</sup>  
C<sub>10</sub>H<sub>15</sub>NO<sub>3</sub><sup>+</sup>  
C<sub>10</sub>H<sub>17</sub>NO<sub>3</sub><sup>+</sup>



(Above) NO<sub>3</sub><sup>-</sup> 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<sub>3</sub>

NO<sub>3</sub> chemistry led to significant differences in nanoparticle composition, including dominant peaks C<sub>10</sub>H<sub>15</sub>O<sub>2</sub><sup>+</sup> and C<sub>10</sub>H<sub>17</sub>O<sub>2</sub><sup>+</sup> 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<sub>3</sub> (monoterpene =  $\alpha$ -pinene +  $\Delta^3$ -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 ability to share knowledge, and an increased understanding of meeting professional expectations, while mentees find near-peer mentors more relatable than faculty members

## ACKNOWLEDGEMENTS

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## RESEARCH TEAM

