

Organosulfate Formation in Biogenic Secondary Organic Aerosol

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Details of this study can be found online at [*J. Phys. Chem. A* AS&P Articles](#)

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Background

- Biogenic SOA formation enhanced in the presence of acidified sulfate seed aerosol
 - proposed source: acid-catalyzed particle-phase reactions
 - high-MW products

[Jang et al., 2002, *Science*]

[Iinuma et al., 2004, *Atmos. Environ.*]

[Tolocka et al., 2004, *ES&T*]

[Gao et al., 2004, *ES&T*]

[Surratt et al., 2006, *J. Phys. Chem. A*]

- Importance of particle-phase reactions to ambient aerosol remains uncertain

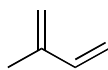
- Organosulfates of isoprene and α -pinene [Surratt et al., 2007, *ES&T*], as well as β -pinene [Iinuma et al., 2007, *ES&T*], have recently been observed in both laboratory-generated and ambient SOA

[Romero and Oehme, 2005, *J. Atmos. Chem.*]

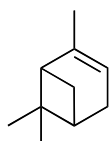
[Reemtsma et al., 2006, *Anal. Chem.*]

Objectives

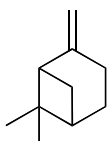
- Comprehensive laboratory investigation of organosulfate formation from the oxidation of 10 terpenes under dry conditions (RH < 9%):



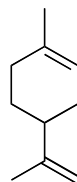
isoprene $\diamond\ddagger\text{c}\#$



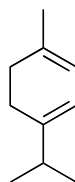
α -pinene $\diamond\ddagger\text{c}\#$



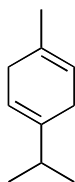
β -pinene $\diamond\ddagger\infty$



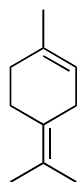
d- and *l*-limonene $\diamond\ddagger\infty$



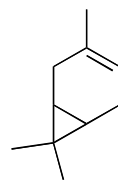
α -terpinene $\diamond\infty$



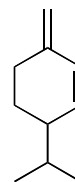
γ -terpinene $\diamond\infty$



terpinolene $\diamond\infty$



Δ^3 -carene $\diamond\infty$



β -phellandrene $\diamond\infty$

\diamond = photooxidation (i.e. OH-initiated oxidation) examined

\ddagger = nighttime oxidation (i.e. NO₃-initiated oxidation) examined

c = low-, intermediate-, and high-NO_x conditions examined

$\#$ = neutral, acidified, and highly acidified sulfate seed examined

∞ = intermediate-NO_x conditions and highly acidified seed only

Details of Chamber Operating Procedures:

[Kroll et al., 2006, ES&T]

[Surratt et al., 2006, *J. Phys. Chem. A*]

[Ng et al., 2007a, *ACP*]

[Ng et al., 2008, *ACP*]

- Analyze and compare composition of laboratory-generated and ambient aerosol using advanced ESI-MS techniques to evaluate atmospheric significance of organosulfates

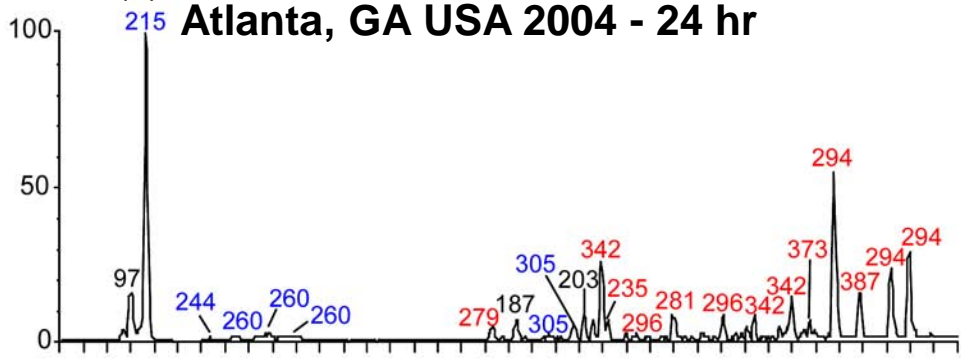
Caltech Indoor Chambers



- 2 Teflon chambers, 28 m³ each
- Scanning differential mobility analyzer (DMA)
- Teflon filters:
 - UPLC/(-)ESI-high resolution-TOFMS:
 - ❖ mass resolution ~ 12 000
 - ❖ accurate mass measurements (elemental compositions) - lock mass correction
 - HPLC/(-)ESI-Linear Ion Trap MS:
 - ❖ tandem MS measurements
 - ❖ structural elucidation & confirmation

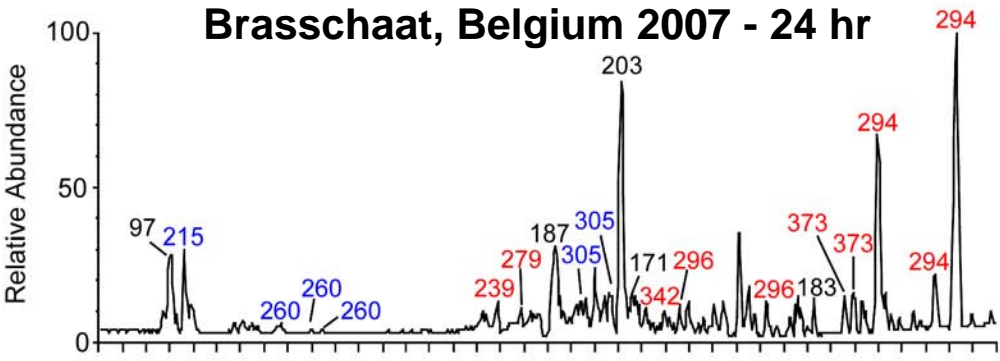
Organosulfates in Ambient Aerosol

• UPLC/(-)ESI-TOFMS TICs:



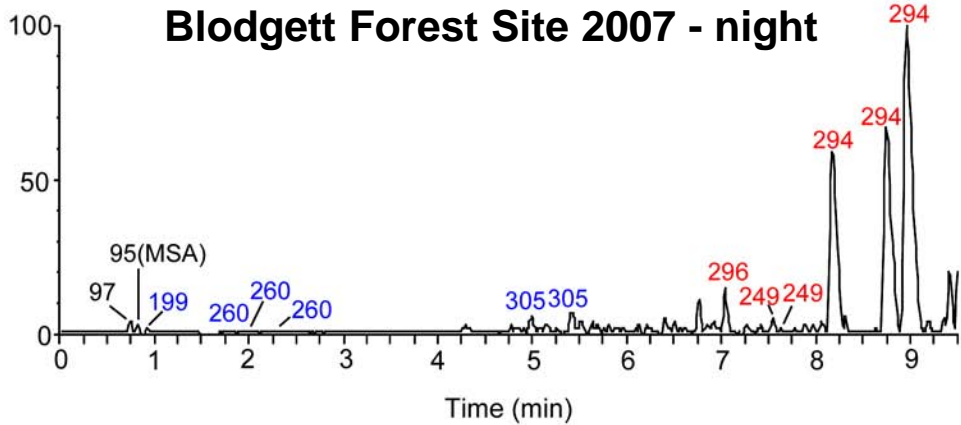
Organosulfates of Isoprene:

- m/z 199: $C_4H_7O_7S^-$
 - m/z 215: $C_5H_{11}O_7S^-$
 - m/z 260: $C_5H_{10}NO_9S^-$
 - m/z 244: $C_5H_{10}NO_8S^-$
 - m/z 305: $C_5H_9N_2O_{11}S^-$
 - m/z 331: $C_{10}H_{19}O_{10}S^-$
 - m/z 333: $C_{10}H_{21}O_{10}S^-$
- [Gómez-González et al., 2008, *JMS*]



Organosulfates of Monoterpenes:

- m/z 235: $C_9H_{15}O_5S^-$
- m/z 249: $C_{10}H_{17}O_5S^-$
- m/z 279: $C_{10}H_{15}O_7S^-$
- m/z 294: $C_{10}H_{16}NO_7S^-$
- m/z 296: $C_9H_{14}NO_8S^-$
- m/z 342: $C_{10}H_{16}NO_{10}S^-$
- m/z 373: $C_{10}H_{17}N_2O_{11}S^-$
- m/z 387: $C_{10}H_{15}N_2O_{12}S^-$



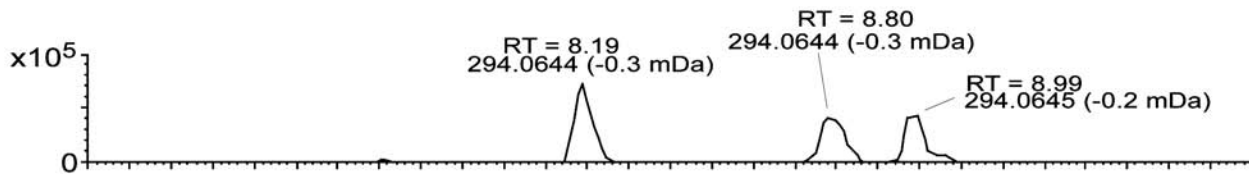
Other Identified Species:

- m/z 95: MSA ($CH_3O_3S^-$)
- m/z 97: inorganic sulfate (HO_4S^-)
- m/z 171: norpinic acid
- m/z 183: *cis*-pinonic acid
- m/z 187: unknown terpenoic acid
- m/z 203: 3-methyl-1,2,3-butanetricarboxylic acid [Szmigielski et al., 2007, *GRL*]

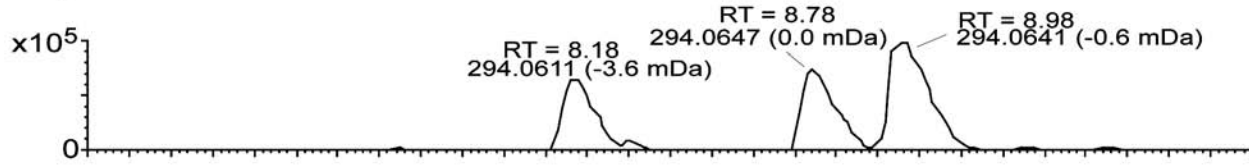
Source of m/z 294 Nitrooxy Organosulfates ($C_{10}H_{16}NO_7S^-$)

- Source previously proposed to be α -pinene but other monoterpenes could not be ruled out [Gao et al., 2006, *JGR*; Surratt et al. 2007a, *ES&T*; Iinuma et al., 2007, *ES&T*]

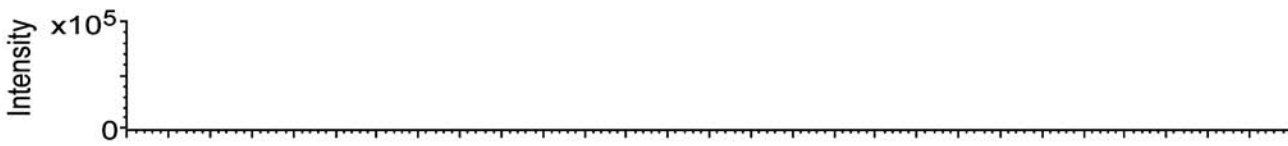
- UPLC/(-)ESI-TOFMS EICs of m/z 294:



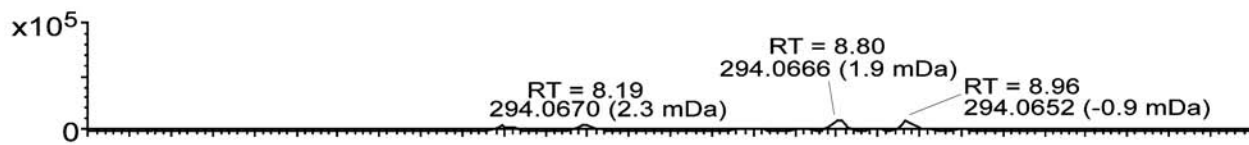
Centerville, AL USA 2004
24 hr-integrated Sample



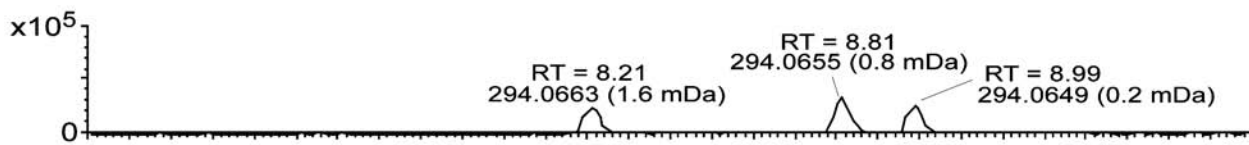
UC Berkeley Blodgett Forest Site 2007
Nighttime Sample



α -Pinene/ H_2O_2 /NO/neutral seed
CALTECH Photooxidation Experiment



α -Pinene/ H_2O_2 /NO/highly acidic seed
CALTECH Photooxidation Experiment

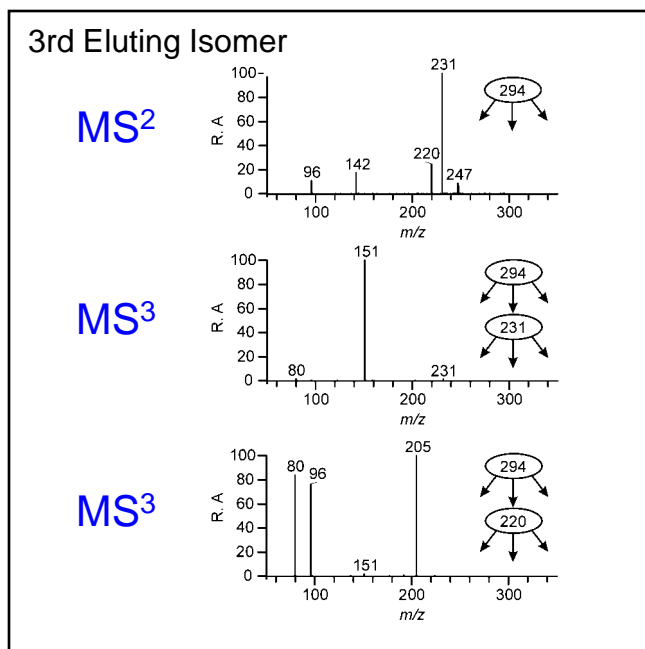


α -Pinene/ NO_3 /highly acidic seed
CALTECH Nighttime Oxidation Experiment

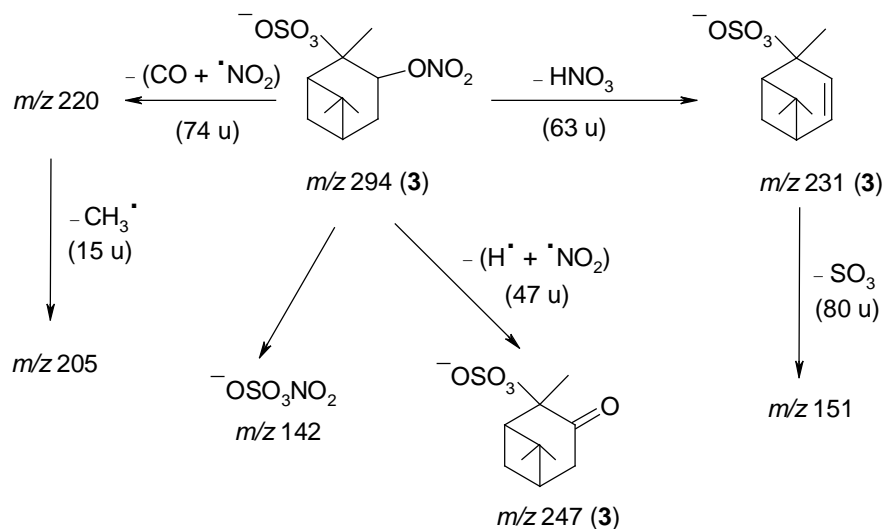
7.00 7.40 7.80 8.20 8.60 9.00 9.40 9.80
Time (min)

Structural Characterization of m/z 294 Nitrooxy Organosulfates

- Tandem MS experiments using the HPLC/(-)ESI-LITMS techniques:

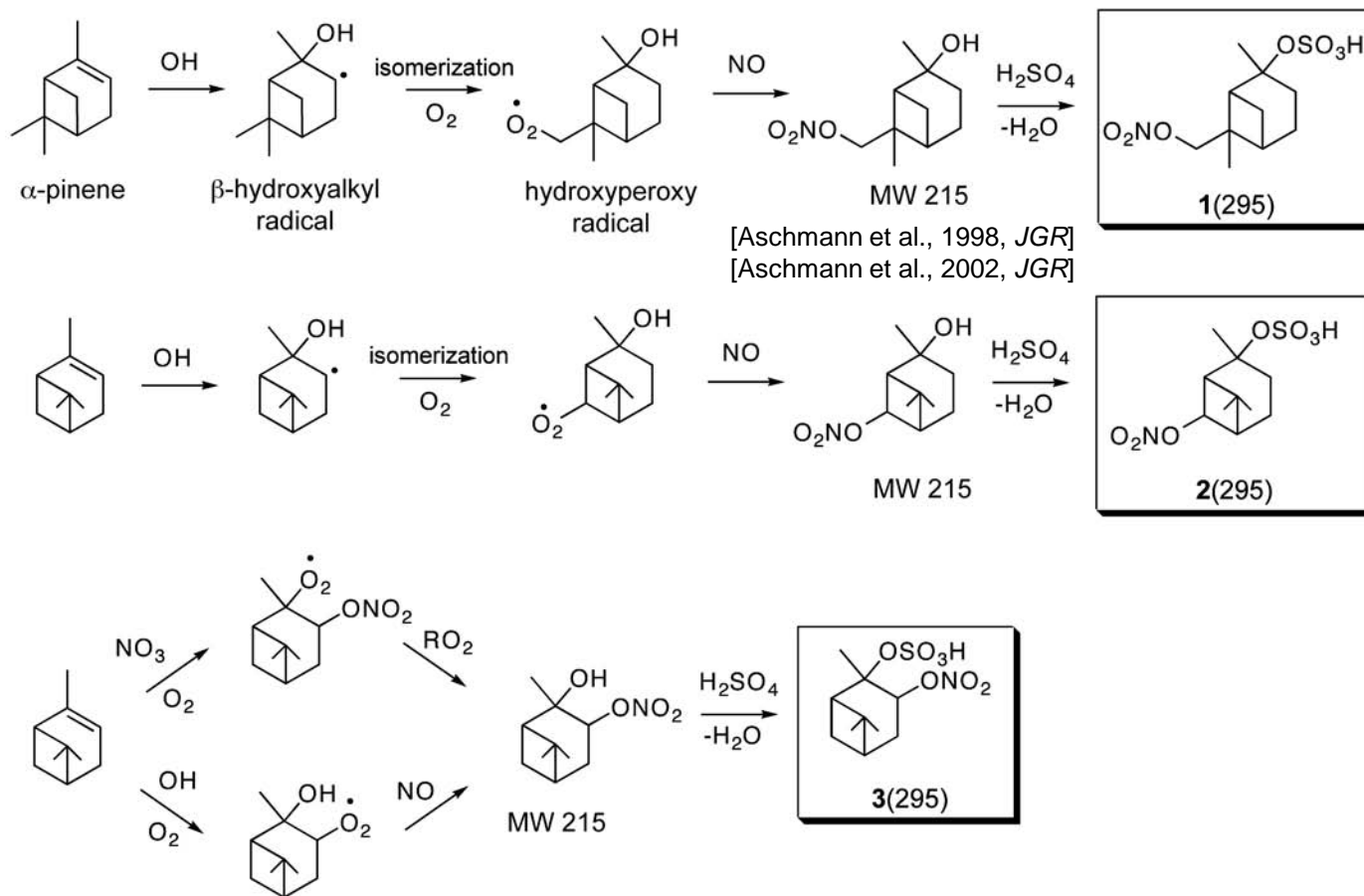


proposed explanations for observed product ions



Detailed tandem MS data for other two isomers available in Surratt et al. [2008, *J. Phys. Chem. A*]

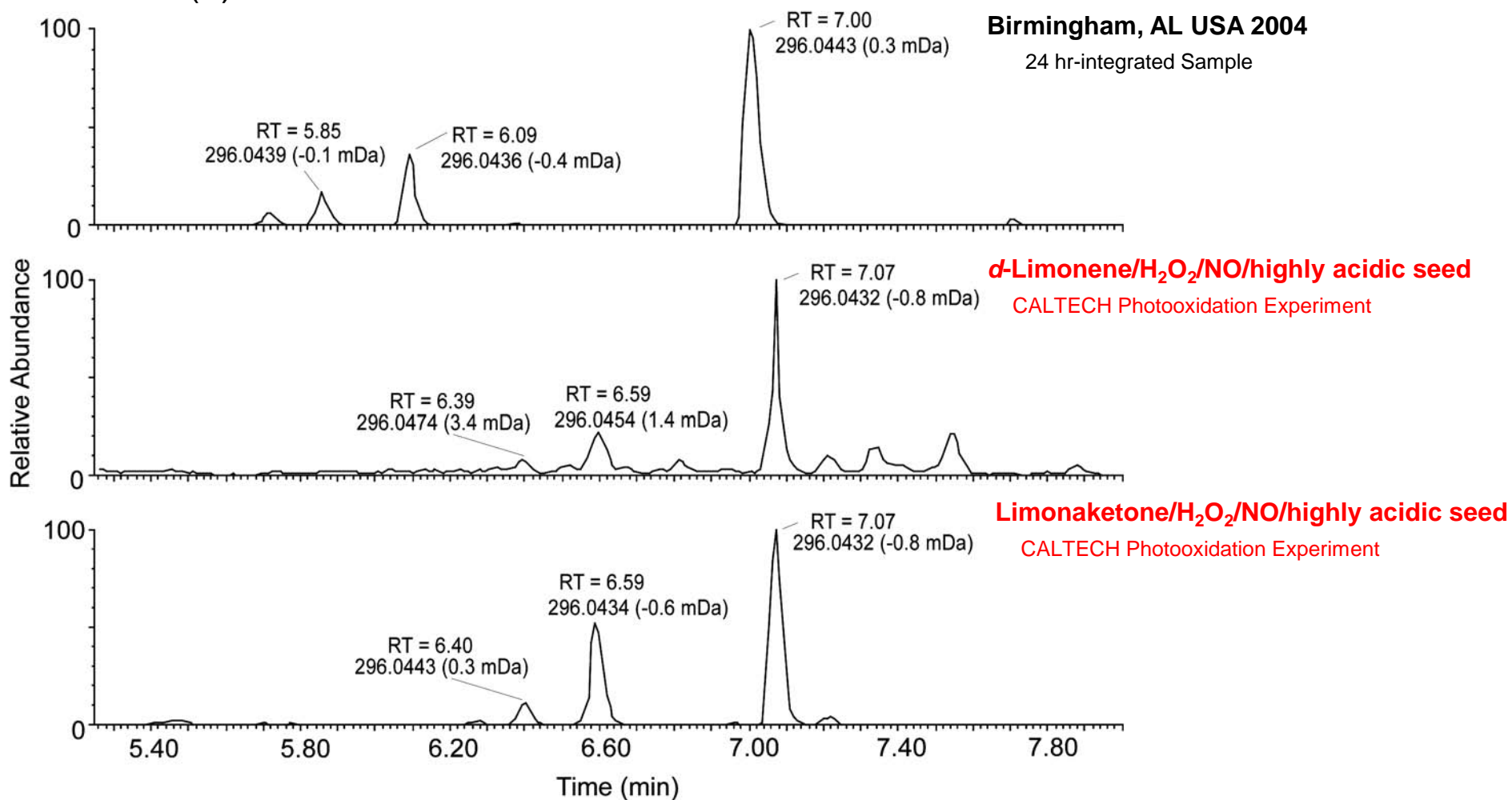
Proposed Formation of α -Pinene m/z 294 Nitrooxy Organosulfates



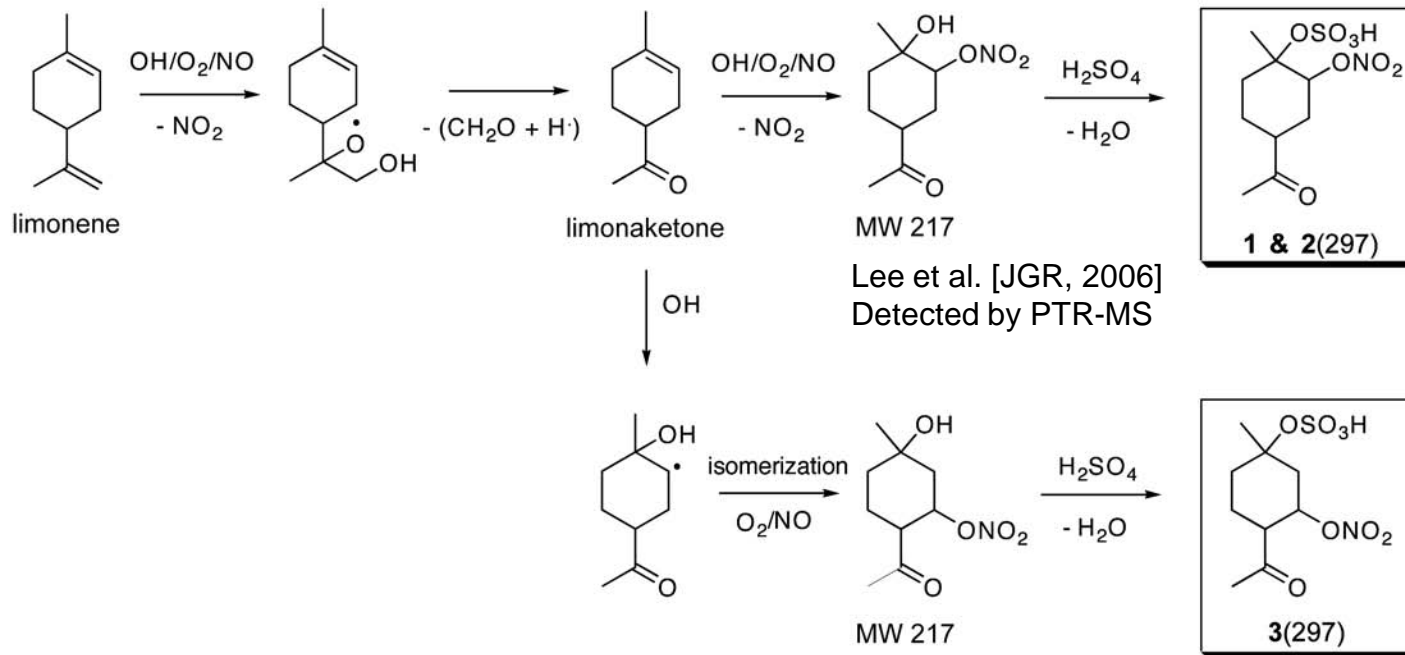
- Reactive uptake of gas-phase hydroxynitrates proposed to yield these products
 [Liggio et al., 2005, *ES&T*] [Liggio et al., 2006, *GRL*] - glyoxal and pinonaldehyde
- Recent bulk solution studies [Minerath et al., 2008, *ES&T*] suggested that alcohol sulfate esterification may not be kinetically feasible to explain observed organosulfates
- Reactive uptake experiments using **dihydroxypinane** and **α -pinene epoxide** needed

Source of m/z 296 Nitrooxy Organosulfates ($C_9H_{14}NO_8S^-$)

- Observed previously in S.W. and S.E. USA summer aerosol - source unknown [Reemstma et al., 2006, *Anal. Chem.*; Gao et al., 2006, *JGR*]
- UPLC/(-)ESI-TOFMS EICs of m/z 296:



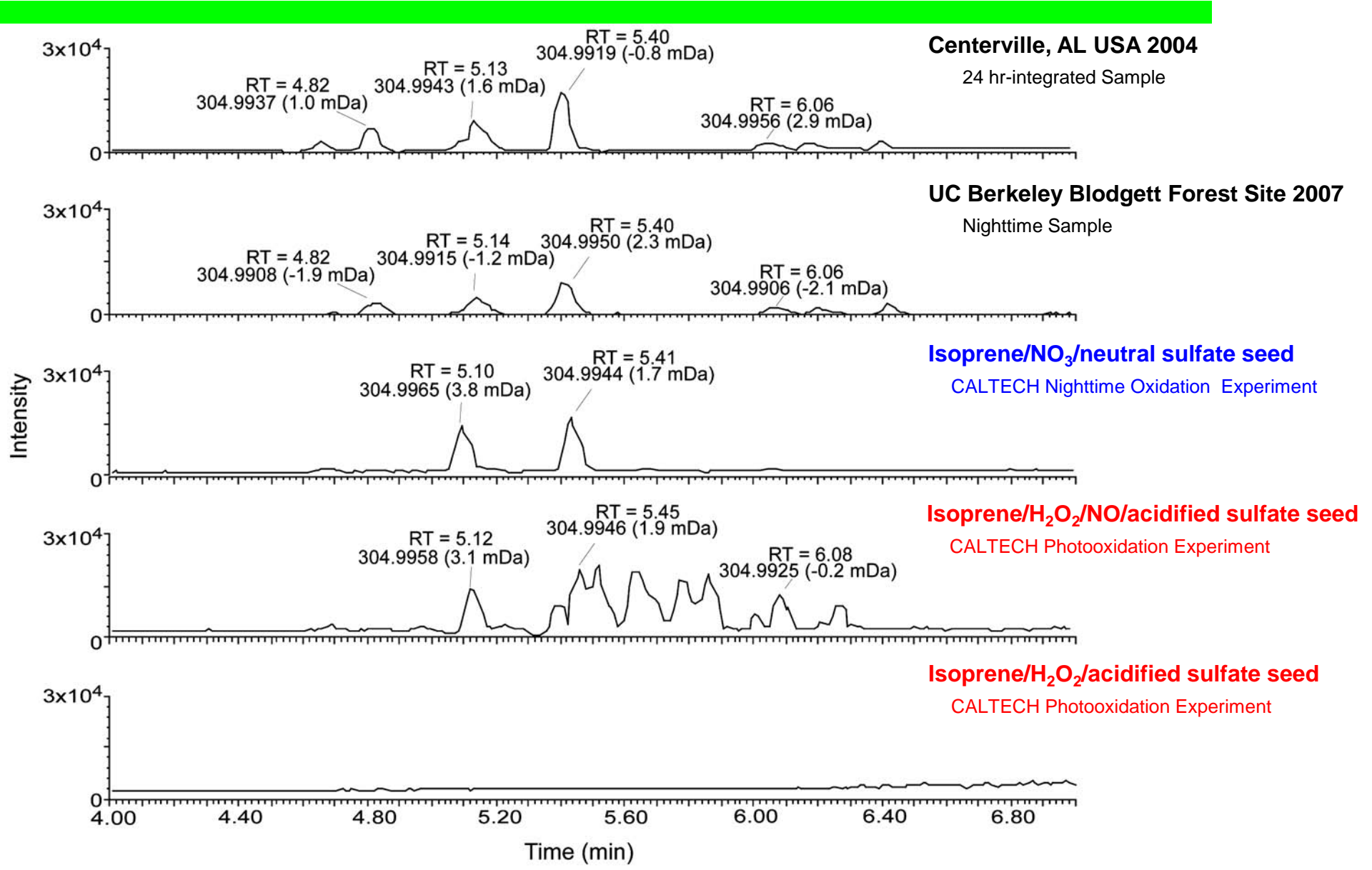
Formation of m/z 296 *d*-limonene Nitrooxy Organosulfates



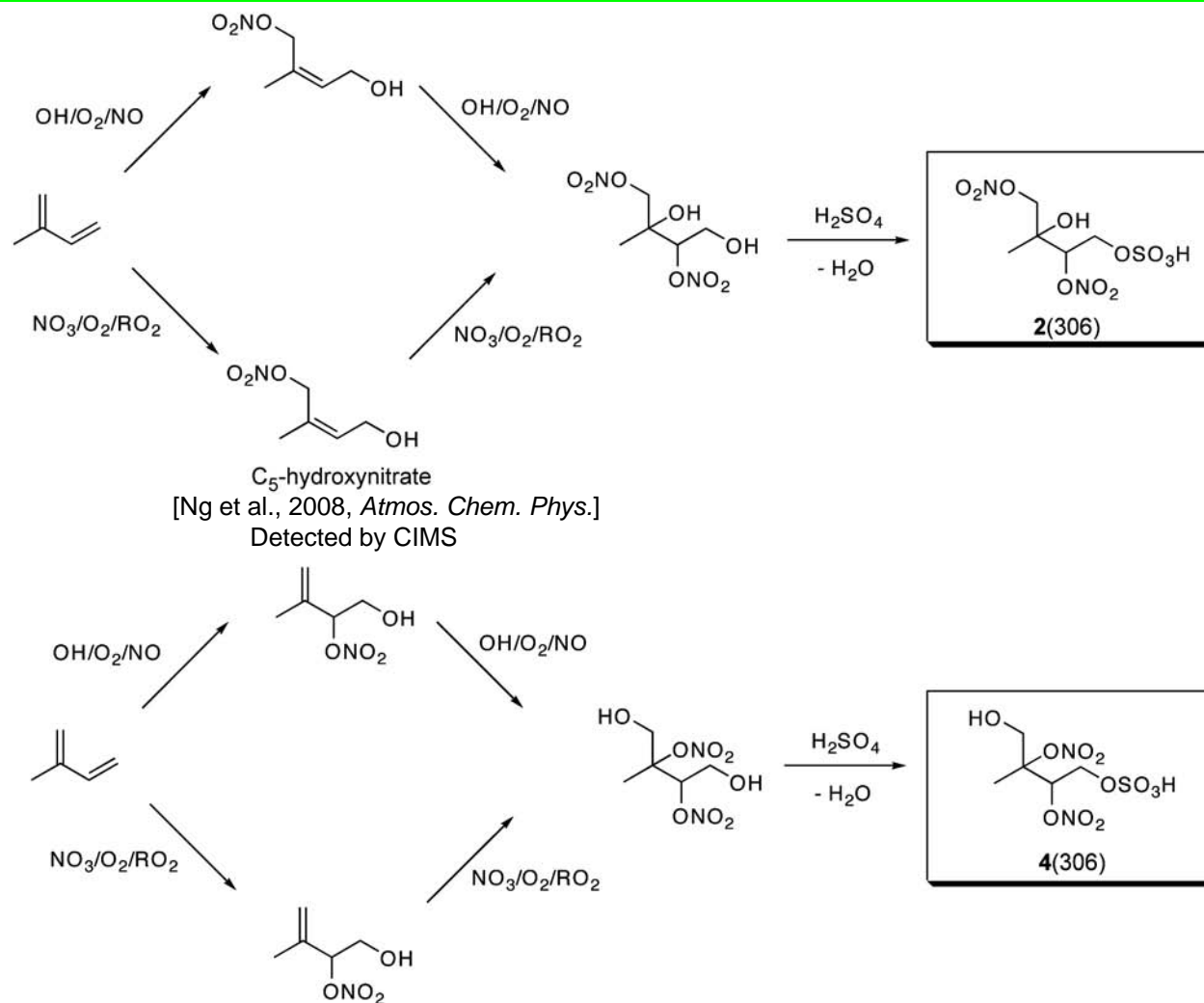
- Nighttime-oxidation of limonene in the presence of highly acidic seed:
No m/z 296 nitrooxy organosulfates produced - possibly due to large nucleation event
- None of the other monoterpenes with two double bonds examined in this study (i.e., α -/ γ -terpinene and terpinolene) were found to produce m/z 296 nitrooxy organosulfates
- RTs and Tandem MS data varied slightly between ambient and limonene m/z 296 compounds, suggesting a unknown “limonene-like” monoterpene as source

[Di Carlo et al., 2004, *Science*] - other unknown terpene-like compounds with substantial OH reactivity

Source of m/z 305 Nitrooxy Organosulfates ($C_9H_{14}NO_8S^-$)



Formation of *m/z* 305 Isoprene Nitroxy Organosulfates



- Please visit poster by Claeys et al. (SOA Formation/Mechanisms Session) for details of structural characterization
- Surratt et al. [2008, *J. Phys. Chem. A*] also contains further details

Atmospheric Significance of Organosulfates

- Upper limit estimate (i.e. subtraction of IC-sulfate from XRF/PIXE-total S) indicates that ~ 30% of the total ambient OM could be in the form of organosulfates for one site

[Lukács et al., 2008, *Atmos. Chem. Phys. Discuss.*] - organosulfates in WSOC contribute 6-12% to the total S concentration.

- Organosulfate formation from BVOCs appear to be ubiquitous in ambient aerosol collected from the USA and Europe
- Both the OH-initiated (in presence/absence NO_x) and NO_3 -initiated oxidation of BVOCs in the presence of acidified ammonium sulfate seed aerosol leads to organosulfates
- In continental aerosol, these compounds have a mixed biogenic and anthropogenic (i.e. NO_x and SO_x) origin
Aerosol from remote regions also appear to contain organosulfates - See Claeys et al. Poster (Marine Aerosols)
- Organosulfates can be regarded as humic-like substances - multifunctional compounds containing hydroxyl, carboxyl, sulfate, and nitrooxy groups

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- **Colleagues/Organizations:**

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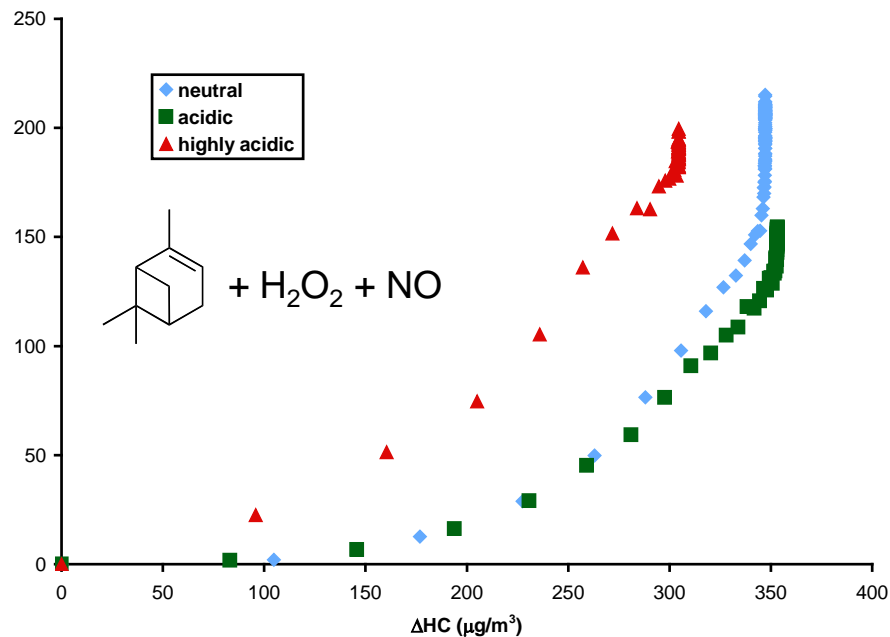
Research Foundation - Flanders

Questions??

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Organosulfates Observed in Chamber Experiments

- widest number/variety of organosulfates formed under the intermediate-NO_x and highly acidic condition - consistent with growth curves:



- highly acidic seed forms organic aerosol more quickly than other seed types - Mg:SO₄ molar ratio increased by 16-30% (indicates loss by reaction)

Characterization of Organosulfates

- Sample preparation
 - filters extracted in methanol by ultrasonic agitation
 - concentrated (via N₂ or rotavap)
 - reconstituted with 1:1 (v/v) methanol:water solvent mixture
- UPLC/ESI-high resolution TOFMS
 - instrument: Waters UPLC coupled to Waters LCT Premier XT TOFMS
 - negative ion mode; W reflectron (mass resolution ~ 12000)
 - accurate mass measurements - lock mass correction (leucine enkephalin; MW = 555)
 - Waters ACQUITY UPLC HSS column (reverse-phase)
- HPLC/ESI-Linear Ion Trap Mass Spectrometry (LITMS)
 - negative ion mode
 - tandem MS measurements - structural elucidation & confirmation
 - Waters Atlantis

Confirmation of Organosulfate Formation

Organosulfate Formation in Isoprene SOA:

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

neutral seed

acidic seed

- Although not evident in Figure A, SO_4^{2-} decays by **20%** over 9 hours (wall-loss)

- Shows SO_4^{2-} decays by **60%** over 6 hours - much faster than neutral seeded case (chemical reaction!)

[Surratt *et al.*, ES&T, 2007]

Organosulfate Formation in α -pinene SOA:

- highly acidic seed forms organic aerosol more quickly than other seed types - $\text{Mg}:\text{SO}_4$ molar ratio increased by 16-30% (indicates loss by reaction)

Photooxidation (OH-initiated) Experimental Conditions

- T ~ 25 °C, RH < 9%
- NO_x conditions [Ng *et al.*, ACP, 2007]
 - NO_x-free: $\text{H}_2\text{O}_2 + h\nu \rightarrow \text{OH} + \text{OH}$ (high HO₂/NO ratio)
 - intermediate-NO_x: $\text{H}_2\text{O}_2 + h\nu \rightarrow \text{OH} + \text{OH}$ (switch from high-NO_x to low-NO_x)
 - high-NO_x: $\text{HONO} + h\nu \rightarrow \text{OH} + \text{NO}$ (low HO₂/NO ratio)
- Seed Aerosol Acidities
 - neutral: 15mM (NH₄)₂SO₄
 - acidic: 15mM (NH₄)₂SO₄ + 15mM H₂SO₄
 - highly acidic: 30mM MgSO₄ + 50mM H₂SO₄
- α-Pinene examined over all NO_x conditions and aerosol acidities
- All other monoterpenes examined only under intermediate-NO_x and highly acidic conditions

Nighttime-Oxidation (NO₃-initiated) Experimental Conditions

- Nitroxy-organosulfates recently shown to form more readily under nighttime conditions in ambient aerosol [Iinuma *et al.*, ES&T 2007]
- T ~ 20 °C, RH < 9%
- NO₃ radical source: 600 ppb NO₂ + 200 ppb O₃
 - when O₃ drops to ~ 45 ppb monoterpene injected
 - theoretical calculations show [NO₃]_{initial} ~ 500 ppt (assuming no loss of N₂O₅)
 - NO₃ dominates initial oxidation
- α-pinene examined under neutral and highly acidic conditions
- *d*-limonene and *l*-limonene examined only under highly acidic conditions