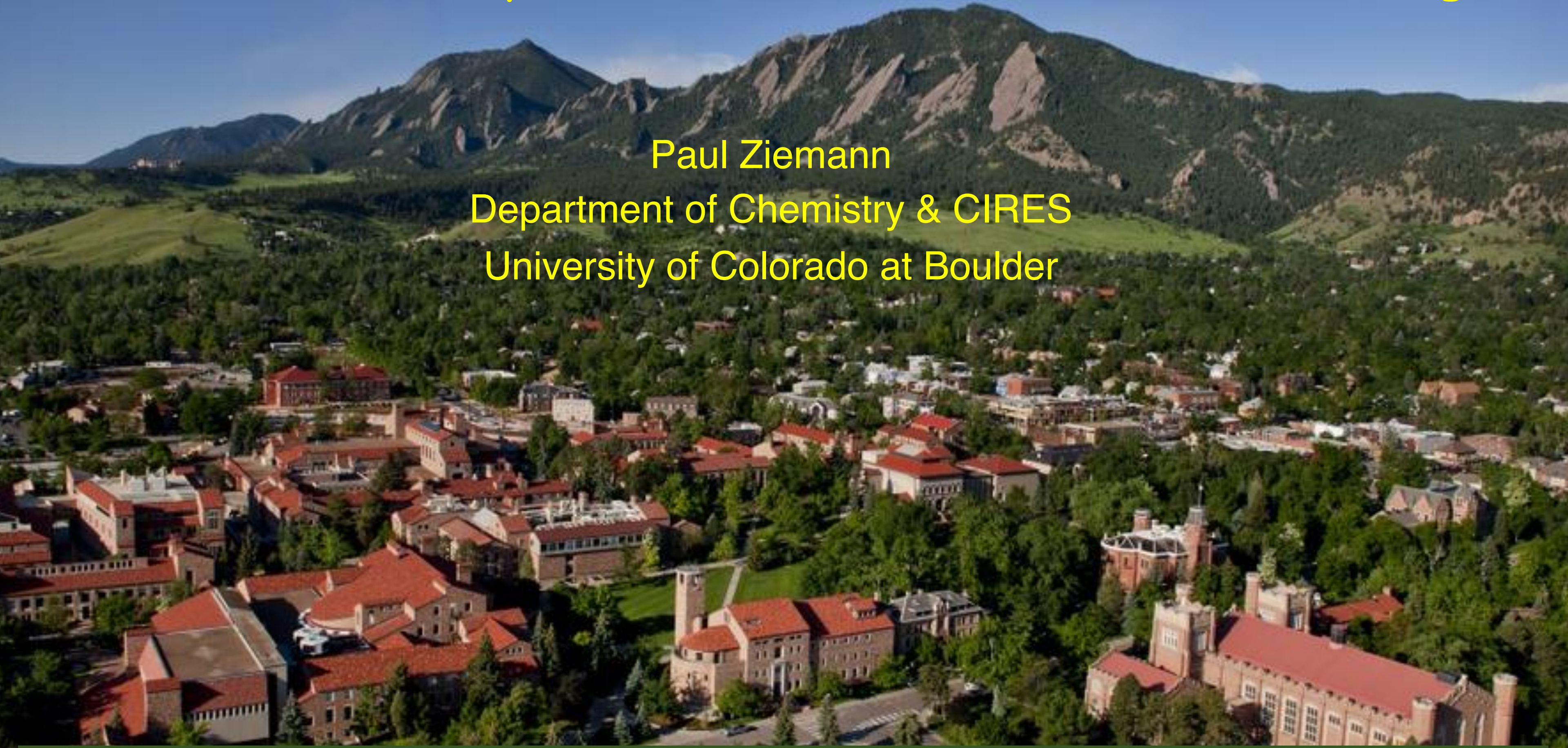
Gas- and Particle-Phase Products and their Mechanisms of Formation from the Reactions of Monoterpenes with NO_3 Radicals: Comprehensive Measurements and Modeling



Paul Ziemann
Department of Chemistry & CIRES
University of Colorado at Boulder

CIRES

This research is funded by
U.S. EPA - Science To Achieve Results (STAR) Program
Grant # 835408

Gas- and Particle-Phase Products and their Mechanisms of Formation from the Reactions of Monoterpenes with NO_3 Radicals: Comprehensive Measurements and Modeling

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Megan Claflin

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Southern Oxidant & Aerosol Study (SOAS)

Investigate the role of interactions among anthropogenic and biogenic emissions on air quality (O_3 and SOA)

- Biogenic VOCs are the most abundant class of VOCs emitted
- Isoprene and monoterpenes are ~ 70% of ~1000 Tg yr^{-1} global emissions
- Conducted lab studies of oxidation of monoterpenes & isoprene to determine functional group composition for SOAS-lab comparison

Ambient Organic Nitrates

Nighttime chemical evolution of aerosol and trace gases in a power plant plume: Implications for secondary organic nitrate and organosulfate aerosol formation, NO_3 radical chemistry, and N_2O_5 heterogeneous hydrolysis (*J. Geophys. Res.*, 2010)

Rahul A. Zaveri,[1] Carl M. Berkowitz,[1] Fred J. Brechtel,[2] Mary K. Gilles,[3] John M. Hubbe,[1] John T. Jayne,[4] Lawrence I. Kleinman,[5] Alexander Laskin,[6] Sasha Madronich,[7] Timothy B. Onasch,[4] Mikhail S. Pekour,[1] Stephen R. Springston,[5] Joel A. Thornton,[8] Alexei V. Tivanski,[9] and Douglas R. Worsnop[4]

Effects of anthropogenic emissions on aerosol formation from isoprene and monoterpenes in the southeastern United States (*PNAS*, 2015)

Lu Xu[a], Hongyu Guo[b], Christopher M. Boyd[a], Mitchel Klein[c], Aikaterini Bougiatioti[b,d], Kate M. Cerully[a,1], Gabriel Isaacman-VanWertz[e], Nathan M. Kreisberg[f], Christoph Knote[g], Kevin Olson[h], Abigail Koss[i,j], Allen Susanne V. Hering[f], Joost de Gouw[i,j], Karsten Baumann[k], Shan-Hu Lee[l], Athanasios Nenes[a,b,m], Rodney and Nga Lee Ng[a,b,2]

Nitrate radicals and biogenic volatile organic compounds: oxidation, mechanisms, and organic aerosol (*Atmos. Chem. Phys*, 2017)

ven S. Brown[3,4], Alexander T. Archibald[5], Elliot Atlas[6], Ronald C. Cohen[7], John N. Crowley[8], Neil M. Donahue[10], Juliane L. Fry[11], Hendrik Fuchs[12], Robert J. Griffin[13], Marcelo I. Guzman[14], nn[15], Alma Hodzic[16], Yoshiteru Iinuma[15], José L. Jimenez[9,4], Astrid Kiendler-Scharr[12], orah J. Luecken[18], Jingqiu Mao[19,20,a], Robert McLaren[21], Anke Mutzel[15], Hans D. Osthoff[22], nedicte Picquet-Varrault[24], Ulrich Platt[25], Havala O. T. Pye[18], Yinon Rudich[26],

Organic nitrate chemistry and its implications for nitrogen budgets in an isoprene- and monoterpene-rich atmosphere: constraints from aircraft (SEAC^{4}RS) and ground-based (SOAS) observations in the Southeast US (*Atmos. Chem. Phys.*, 2016)

Jenny A. Fisher[1,2], Daniel J. Jacob[3,4], Katherine R. Travis[3], Patrick S. Kim[4], Eloise A. Marais[3], Christopher Miller[4], Karen Yu[3], Lei Zhu[3], Robert M. Yantosca[3], Melissa P. Sulprizio[3], Jingqiu Mao[5,6], Paul O. Wennber John D. Crounse[7], Alex P. Teng[7], Tran B. Nguyen[7,a], Jason M. St. Clair[7,b], Ronald C. Cohen[9,10], Paul Romer Benjam Weiwei Thoma

Observations of gas- and aerosol-phase organic nitrates at BEACHON-RoMBAS 2011 (*Atmos. Chem. Phys*, 2013)

J. L. Fry[1], D. C. Draper[1], K. J. Zarzana[2,3], P. Campuzano-Jost[2,3], D. A. Day[2,3], J. L. Jimenez[2,3], S. S. Brown[4], R. C. Cohen[5], L. Kaser[6], A. Hansel[6], L. Cappellin[7], T. Karl[8], A. Hodzic Roux[8], A. Turnipseed[8], C. Cantrell[8], B. L. Lefer[9], and N. Grossberg[9]

Highly functionalized organic nitrates in the southeast United States: Contribution to secondary organic aerosol and reactive nitrogen budgets (*PNAS*, 2016)

Ben H. Lee[a,1], Claudia Mohr[a,1,2], Felipe D. Lopez-Hilfiker[a], Anna Lutz[b], Mattias Hallquist[b], Lance Le Ronald C. Cohen[c], Siddharth Iyer[d], Theo Kurtén[d], Weiwei Hu[e,f], Douglas A. Day[e,f], Pedro Campuza Jose L. Jimenez[e,f], Lu Xu[g], Nga Lee Ng[g,h], Hongyu Guo[h], Rodney J. Weber[h], Robert J. Wild[f,i], Steve Abigail Koss[i], Joost de Gouw[f,i], Kevin Olson[j,4], Allen H. Goldstein[j], Roger Seco[k], Saewung Kim[k], Ke Paul B. Shepson[l], Tim Starn[m], Karsten Baumann[n], Eric S. Edgerton[n], Jiumeng Liu[o], John E. Shilling William Brune[p], Siegfried Schobesberger[a], Emma L. D'Ambro[q], and Joel A. Thornton[a,5]

Aerosol characterization over the southeastern United States using high-resolution aerosol mass spectrometry: spatial and seasonal variation of aerosol composition and sources with a focus on organic nitrates (*Atmos. Chem. Phys*, 2015)

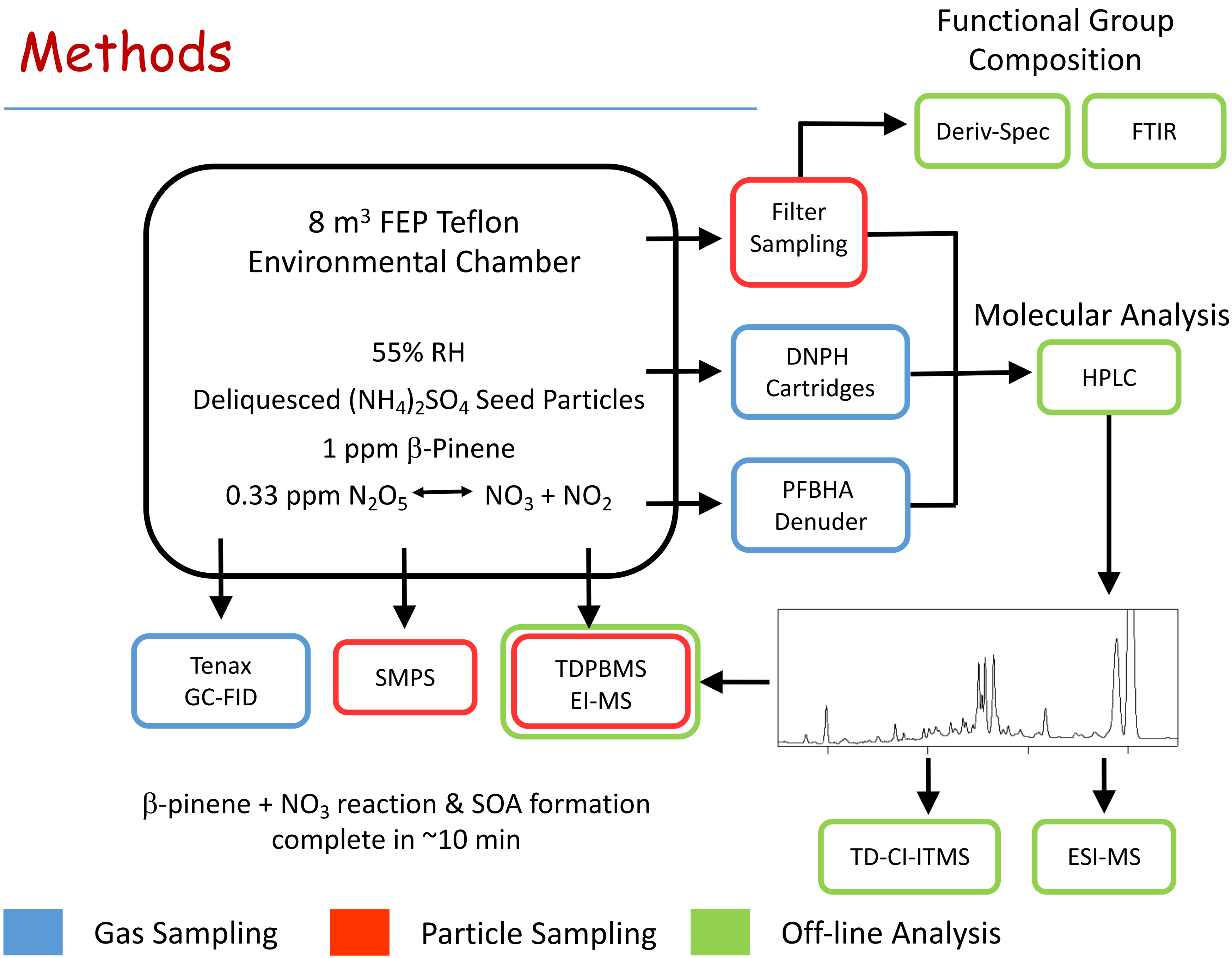
nd N. L. Ng[1,2]

Organic nitrate aerosol formation via NO_3 + biogenic volatile organic compounds in the southeastern United States (*Atmos. Chem. Phys*, 2015)

B. R. Ayres[1], H. M. Allen[1,2], D. C. Draper[1,3], S. S. Brown[4], R. J. Wild[4], J. L. Jimenez[5,6], D. A. Day[5,6], P. Campuzano-Jost[5,6], W. Hu[5,6], J. de Gouw[5,6], A. Koss[5,6], R. C. Cohen[7], K. C. Duffey[7], P. Romer[7], K. Baumann[8], E. Edgerton[8], S. Takahama[9], J. A. Thornton[10], B. H. Lee[10], F. D. Lopez-Hilfiker[10], C. Mohr[10,11], P. O. Wennberg[12], T. B. Nguyen[12], A. Teng[12], A. H. Goldstein[13], K. Olson[13], and J. L. Fry[1]

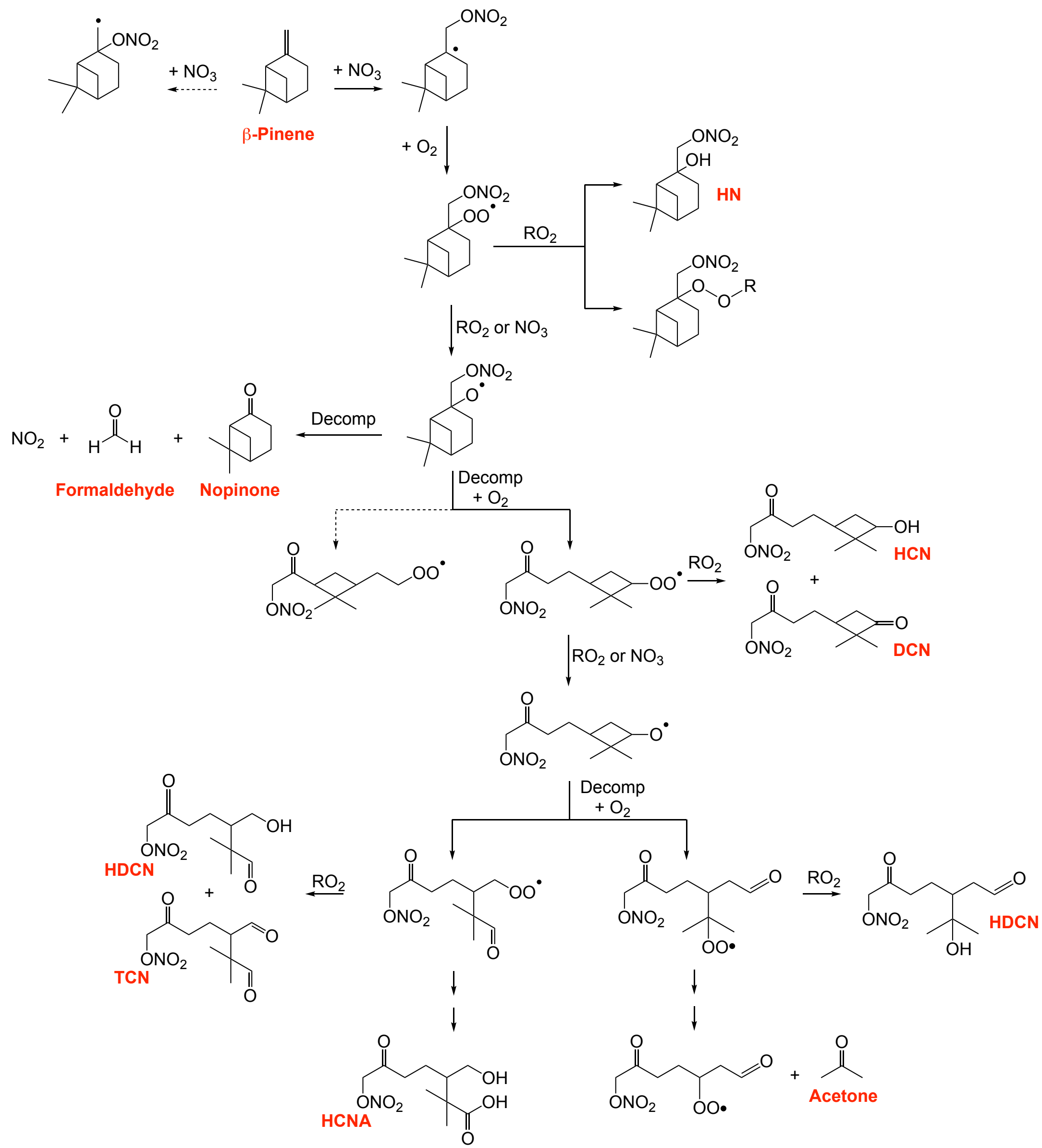
Reactions of Monoterpenes (mostly β-Pinene) + NO_3 Radicals

Methods

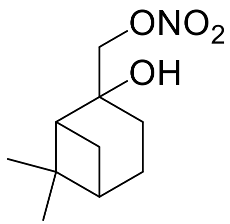


Functional Group Composition
Deriv-Spec
FTIR
8 m³ FEP Teflon Environmental Chamber
55% RH
Deliquesced $(NH_4)_2SO_4$ Seed Particles
1 ppm β-Pinene
0.33 ppm N_2O_5 ⟷ $NO_3 + NO_2$
Filter Sampling
DNPH Cartridges
PFBHA Denuder
Molecular Analysis
HPLC
Tenax GC-FID
SMPS
TDPBMS EI-MS
TD-CI-ITMS
ESI-MS
β-pinene + NO_3 reaction & SOA formation complete in ~10 min
Gas Sampling
Particle Sampling
Off-line Analysis

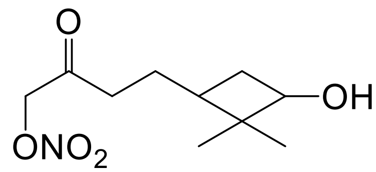
Mechanism of Reaction of β-Pinene + NO_3 Radicals



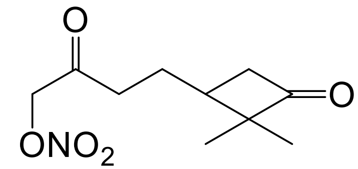
Multifunctional Gas-Phase Products



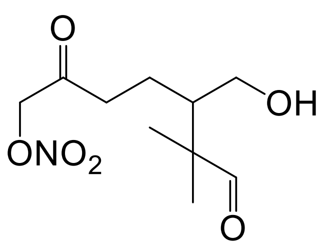
HN
MW = 215



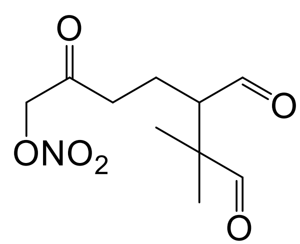
HCN
MW = 231



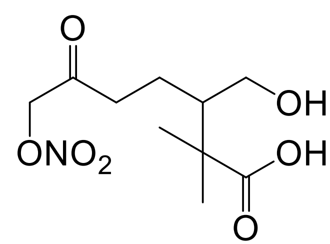
DCN
MW = 229



HDCN
MW = 247

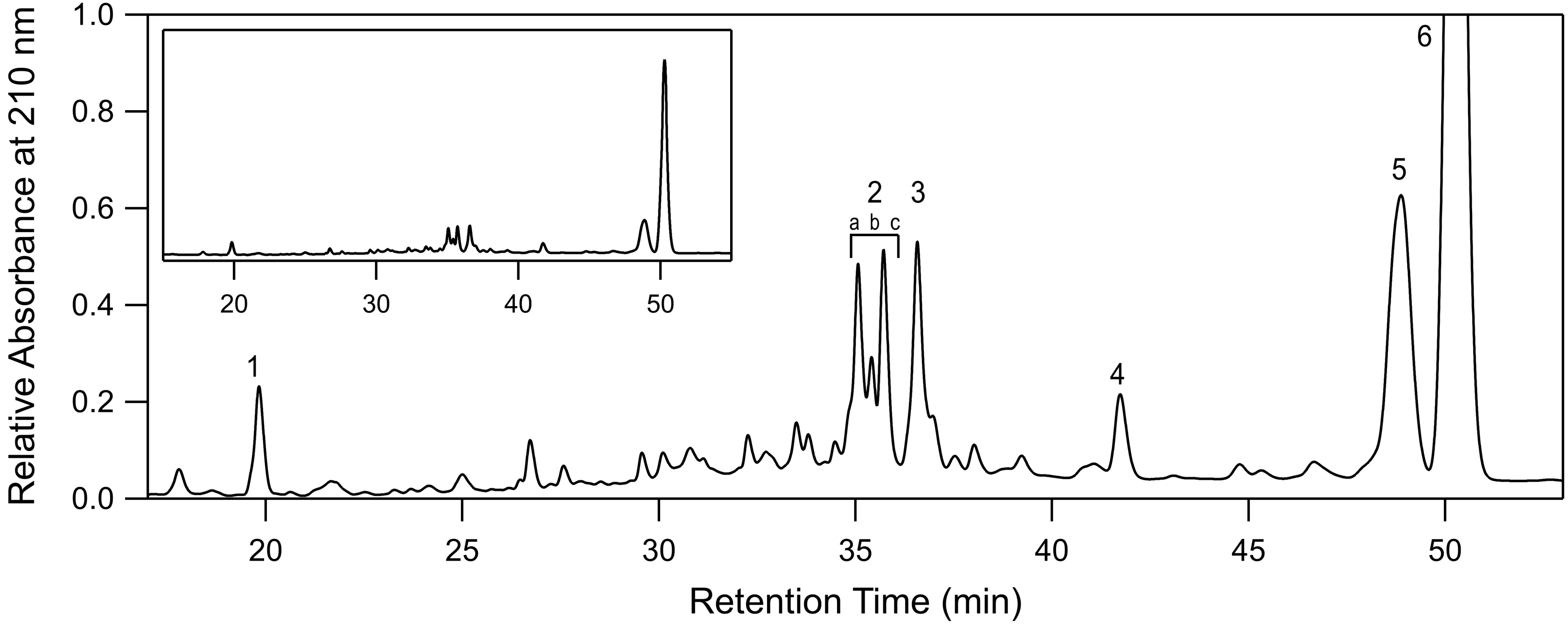


TCN
MW = 245



HCNA
MW = 263

SOA Product Separation & Quantitation: HPLC-UV

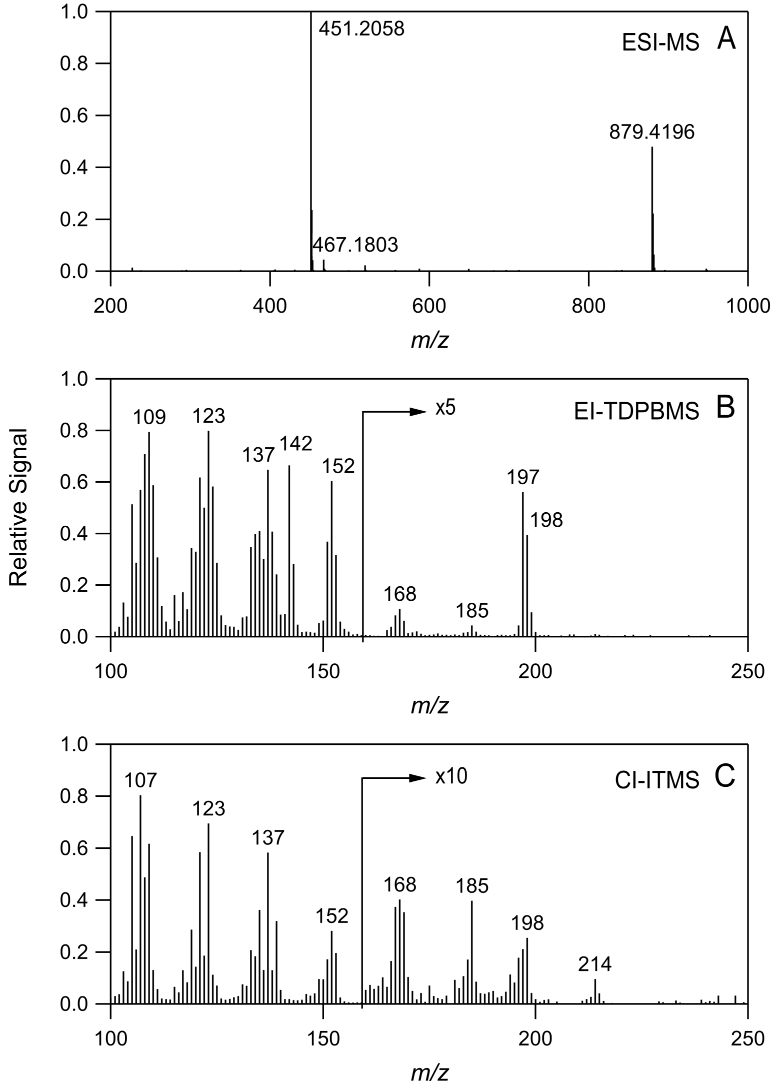


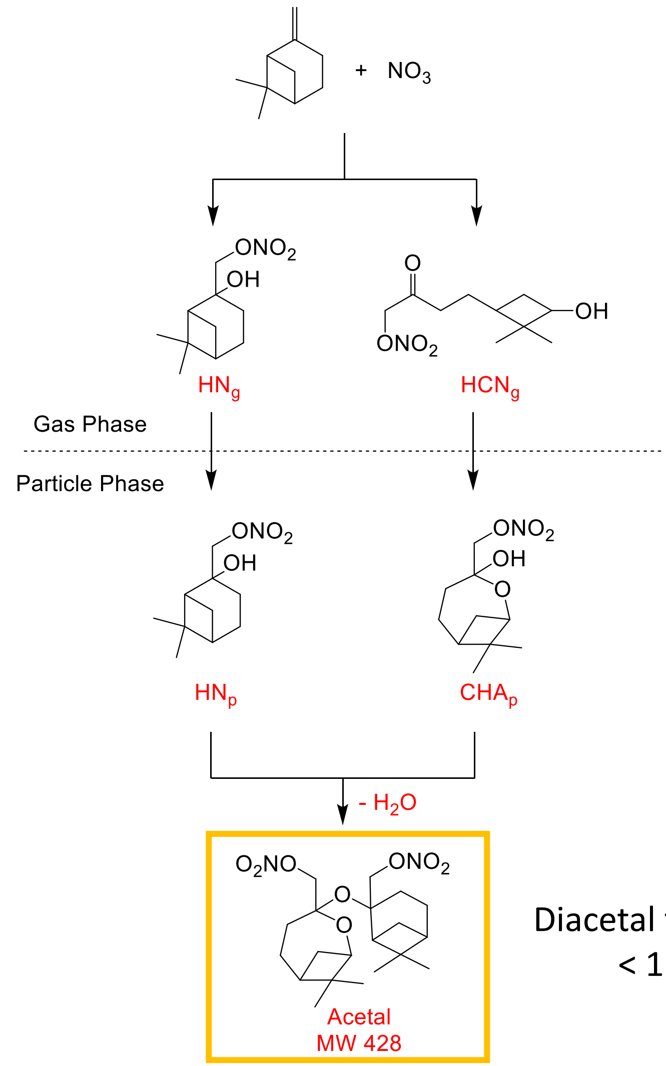
Measure nitrate absorbance at 210 nm

Quantify using authentic standard of Peak 6 compound

SOA Product Identification: Mass Spectrometry

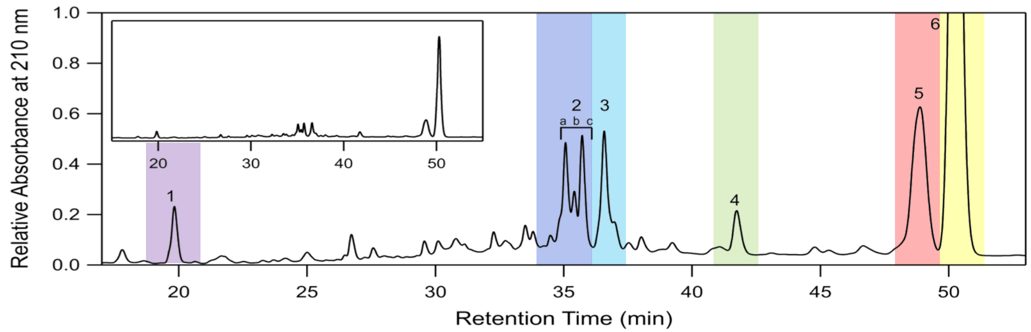
Peak 6

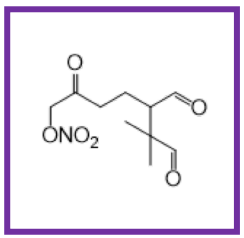
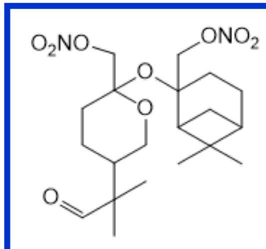
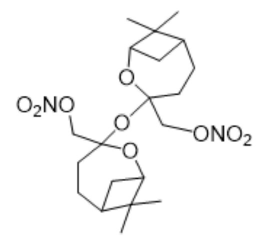
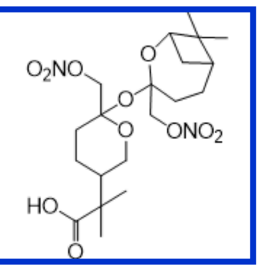
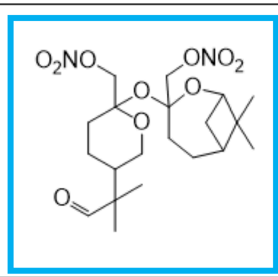
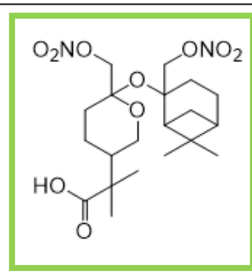
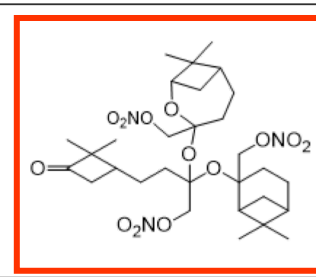
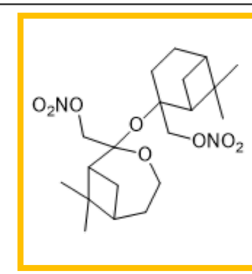




Diacetal formation
< 1 min

SOA Products & Mass Fractions



			
1 (6.5%)	2a (8.4%)	2b (3.6%)	2c (5.9%)
			
3 (7.3%)	4 (4.4%)	5 (9.5%)	6 (54.4%)

95% of SOA mass identified and quantified

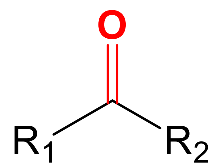
SOA Product Molar Yields

Monomer and Oligomers				Monomer Building Blocks			
Peak Number	MW of Product	Mole Fraction (%)	Molar Yield (%)	Monomer ID	MW of Monomer	Mole Fraction (%)	Molar Yield (%)
1	245	6.5	2.0	HN	215	37.8	23.6
2a	460	7.3	2.2	DCN	229	4.7	2.9
2b	444	3.6	1.1	HCN	231	41.5	25.9
2c	476	5.9	1.8	TCN	245	3.2	2.0
3	444	8.4	2.6	HDCN	247	7.7	4.8
4	460	4.4	1.4	HCNA	263	5.1	3.2
5	657	9.5	2.9				
6	428	54.4	16.7				

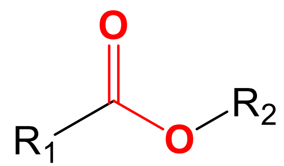
Total monomer molar yield = 62.4%

Based on 10–130 min filter samples corrected for particle wall loss

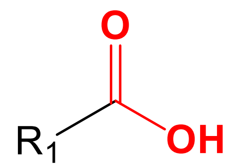
Deriv-Spec Functional Group Analysis



Carbonyl



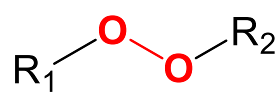
Ester



Carboxyl

ROH

Hydroxyl



Peroxide

$RONO_2$

Nitrate

Carbonyl, ester, carboxyl, hydroxyl: derivatize

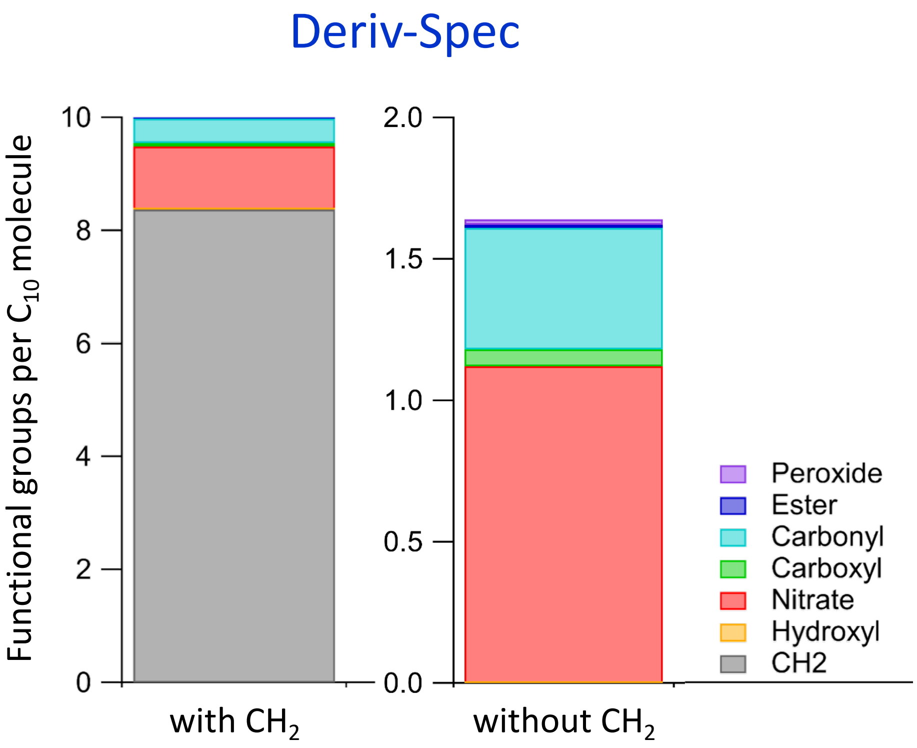
Peroxide: oxidize $2I^-$ to I_2

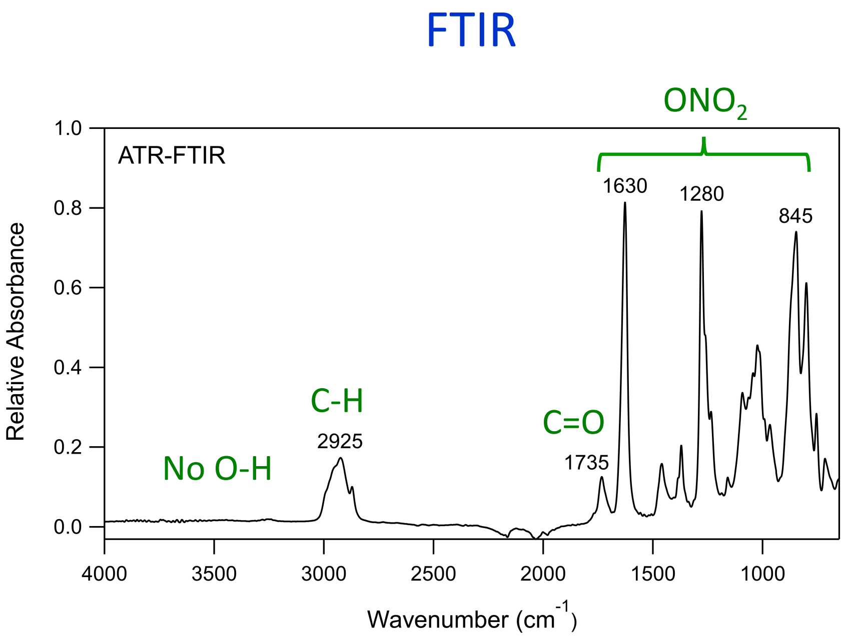
Nitrate

Measure UV-Vis absorbance

Quantify using surrogate standards

SOA Bulk Functional Group Analysis





SOA Functional Group Composition: Bulk vs. Molecular Analysis

Functional Group	Bulk	Molecular
	Deriv-Spec	HPLC-UV-MS
	FG/C_{10} Molecule	
Peroxide	0.02	0.00
Ester	0.01	0.00
Carbonyl	0.43	0.40*
Carboxyl	0.06	0.05
Hydroxyl	0.00	0.00
Nitrate	1.12	1.00
Methylene	8.37	8.55

*Estimated based on rate of sucrose hydrolysis at same pH

SOA results: Claflin & Ziemann, JPCA, 2018

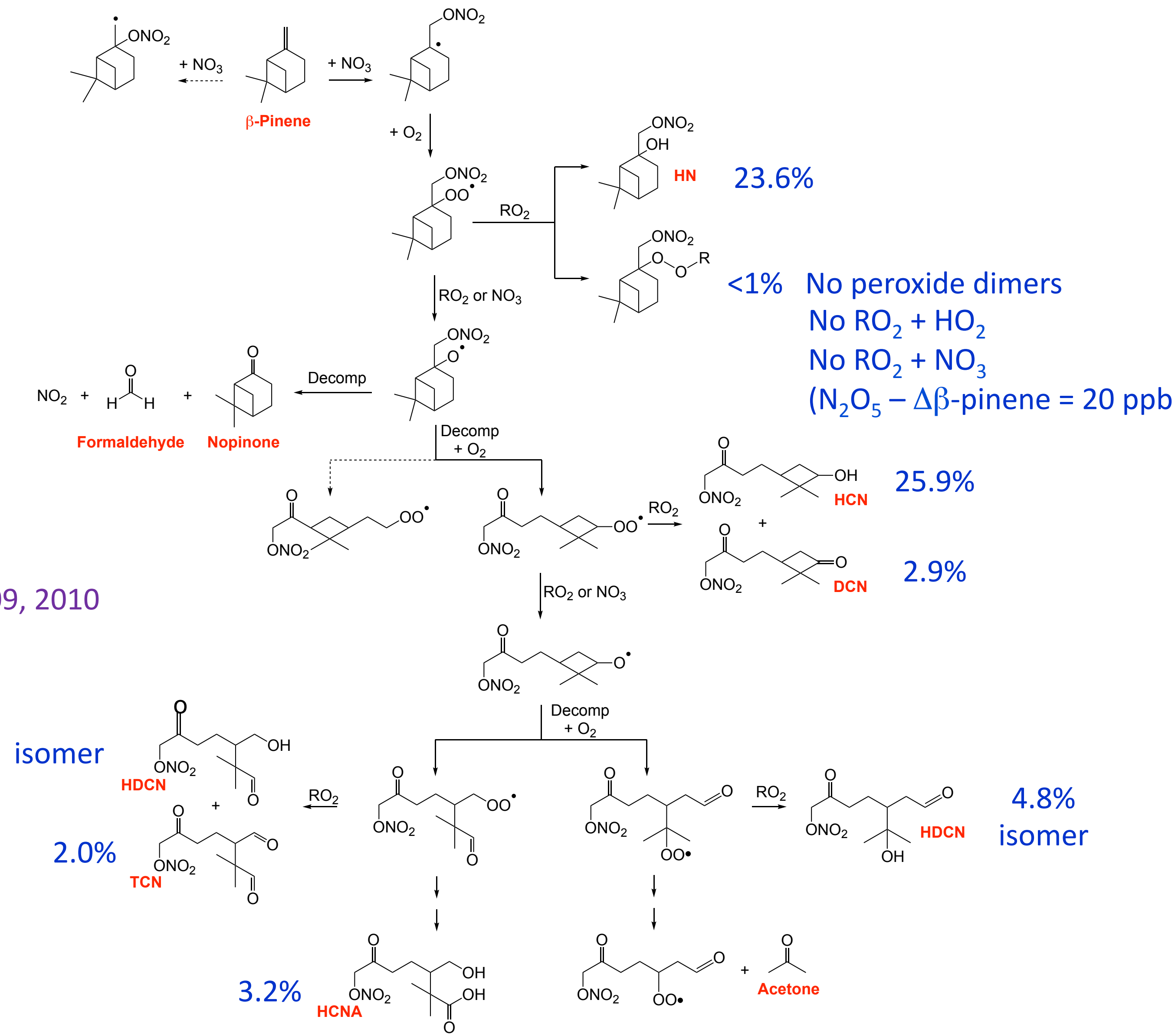
Mechanism of Reaction of β-Pinene + NO_3 Radicals

<u>Molar yields</u>

Particle phase = 62.4%

Yeh & Ziemann, JPCA, 2015

Vereecken & Peeters, PCCP, 2009, 2010



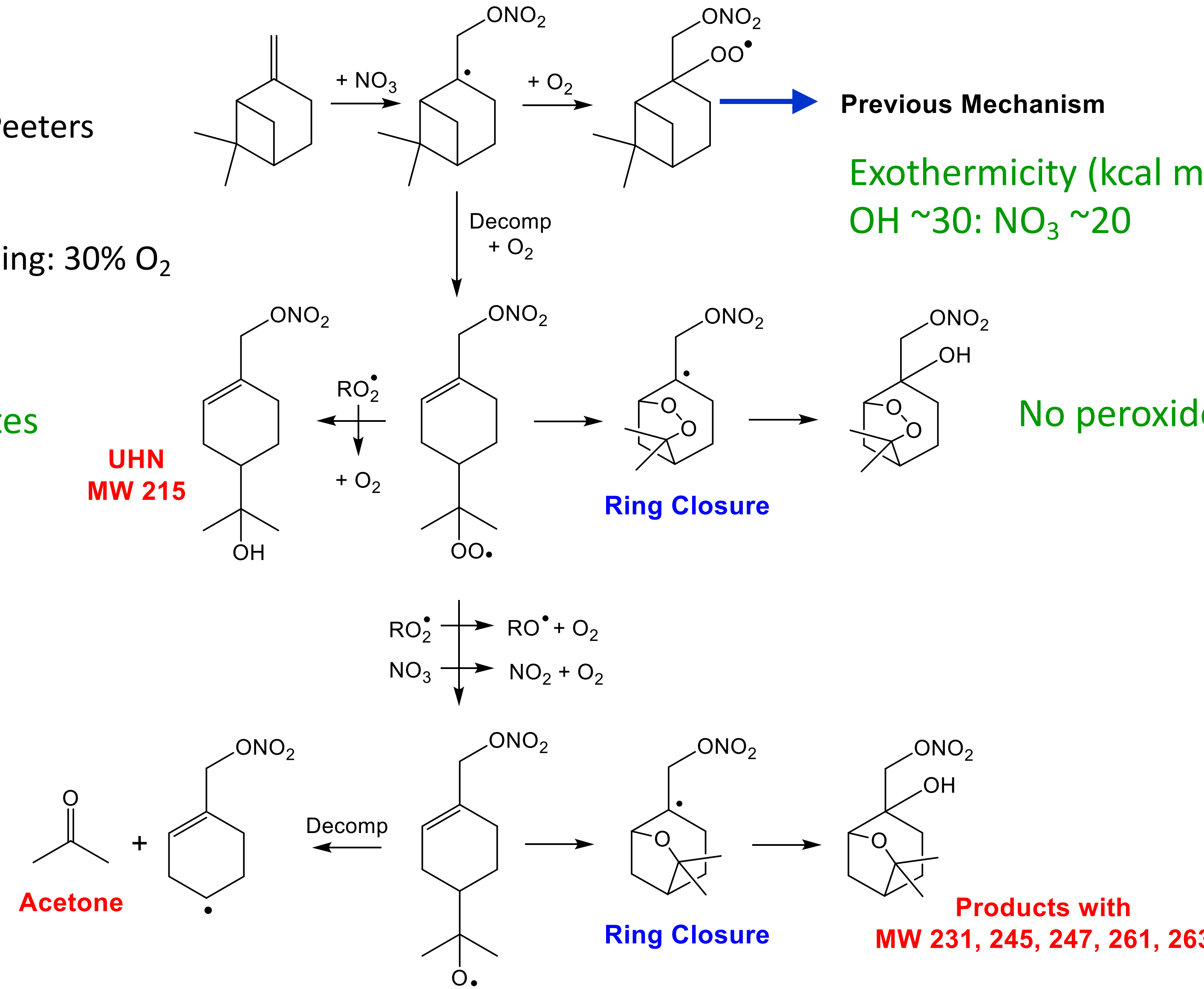
Unobserved Potential Additional Pathways

Vereecken & Peeters
PCCP, 2012
β-Pinene + OH
70% ring opening: 30% O_2

Exothermicity (kcal mol^{-1})
OH ~30: NO_3 ~20

No dinitrates

No peroxides



Conclusions

- Identified and quantified essentially all gas- and particle phase products from β-pinene + NO_3 radical reaction
- Developed quantitative gas- and particle-phase reaction mechanism and model
- Demonstrates importance of particle-phase reactions in SOA formation – needs to be in models
- May be similar chemistry for other monoterpenes
- Future work includes:

    > Other monoterpenes

    > High HO_2 and autoxidation conditions

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