Exploring the Impacts of Water Vapor on New Particle Formation Mechanisms

AirUCI

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Part A: Effect of water vapor on the mechanism of new particle formation from monoterpene oxidation

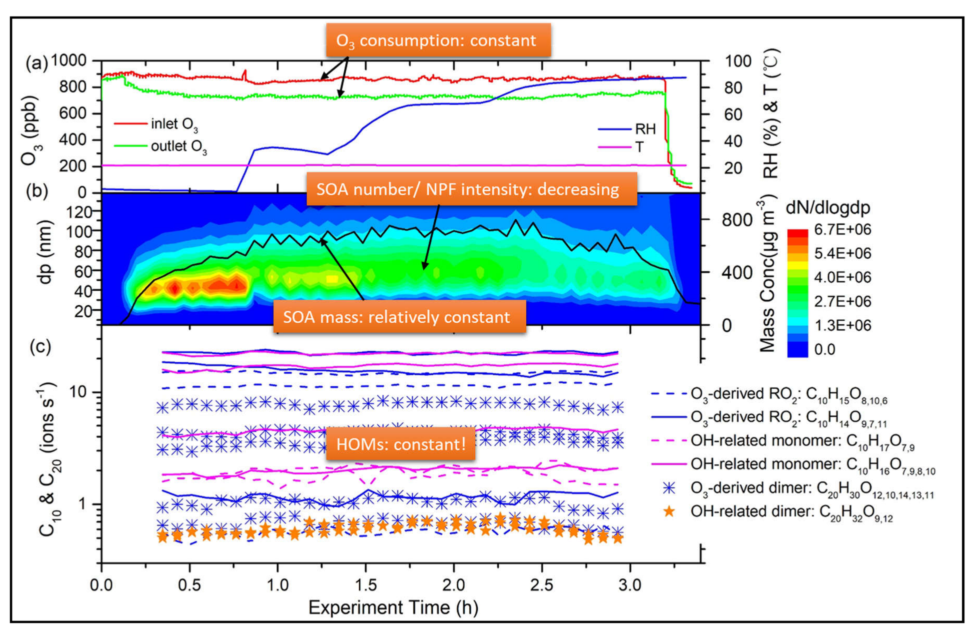
Background. Field studies suggest that NPF is suppressed during periods of high relative humidity (RH). A few mechanisms could be responsible:

- High RH is accompanied by increased condensation sink and decreased solar radiation, which decrease NPF.
- $H_2O_{(g)}$ directly influences the formation of NPF precursors or clusters.

Approach. Using a flow reactor and the newly-developed TI-CIMS, determine the mechanism by which $H_2O_{(g)}$ ***directly*** impacts the formation of NPF precursors: Highly Oxidized Molecules (HOMs). Experiments were performed at room temperature and 0 – 90% RH.

Precursor	Exp (#)	Monoterpene (ppbv)	O_3 (ppbv)	Cyclo-hexane (ppmv)
Limonene	1	1085	900±10	0
	2	1085	900±10	217
	3	54	350±5	0
α-pinene	4	1111	900±10	0
	5	1111	900±10	222
	6	54	350±5	0
△^{3}-carene	7	1111	900±10	0
	8	1111	900±10	222
	9	54	350±5	0

Results. For all systems studied, number concentrations decreased with increasing RH but ***detected HOMs did not change*** (see right). All identified peaks could be explained by autoxidation followed by RO_2+$R'O_2$ reactions. Clearly, ***NO_3^- TI-CIMS is not able to observe the reaction steps that are affected by $H_2O_{(g)}$***. This may indicate that accretion products from the stabilized Criegee Intermediate (sCI, see rxns IV and V below), or the formation of HOMs + H_2O clusters, are important steps in NPF.

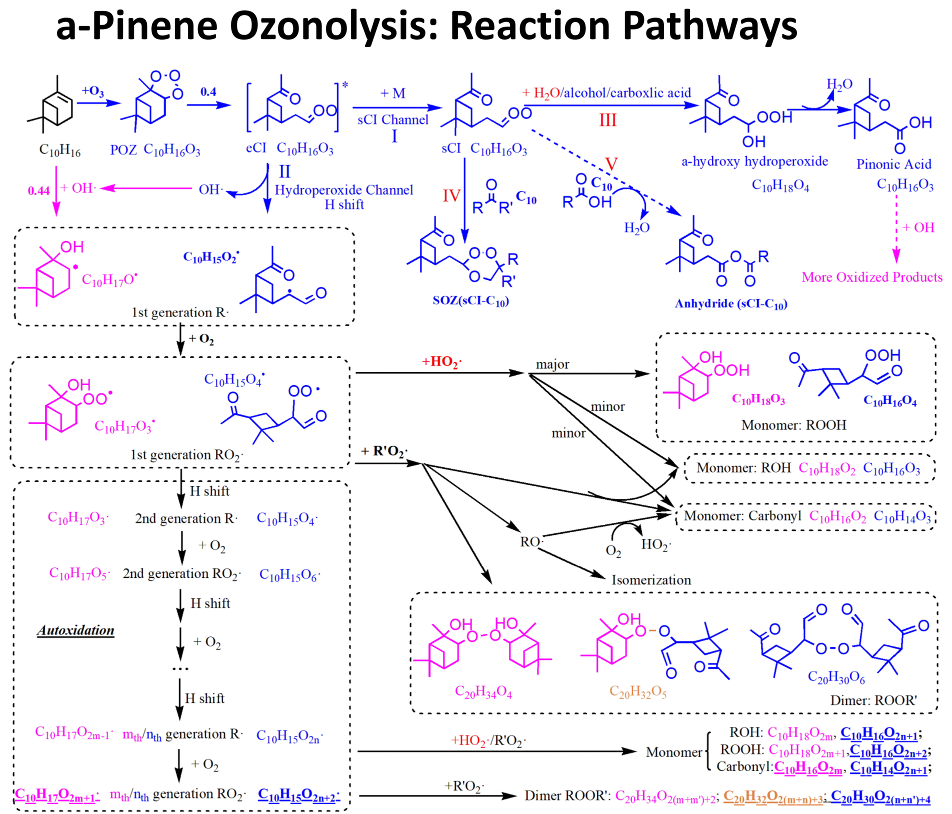


Discussion. sCI accretion products may explain the decreasing SOA number concentration and observed constant HOM formation. Another possibility is that water vapor somehow plays a role in hindering cluster growth and/or causing cluster fragmentation and evaporation. Additional studies are planned to explore these possibilities.

What NPF Mechanisms Are Explained by these Observations?

Conditions	RO_2 forms HOM	sCI further oxidized by OH	sCI forms SOZ (sCI-C_{10})	sCI forms anhydride (sCI-C_{10})
Formed in the gas phase	✓	✓	?	?
Contributes to nucleation/early growth	✓	✓	✓	✓
Suppressed by water vapor	⃠	⃠	✓	✓
NOT detected by nitrate-CIMS	⃠	⃠	✓	✓

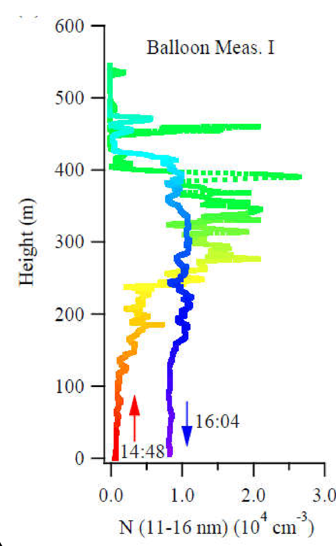
a-Pinene Ozonolysis: Reaction Pathways



Reference

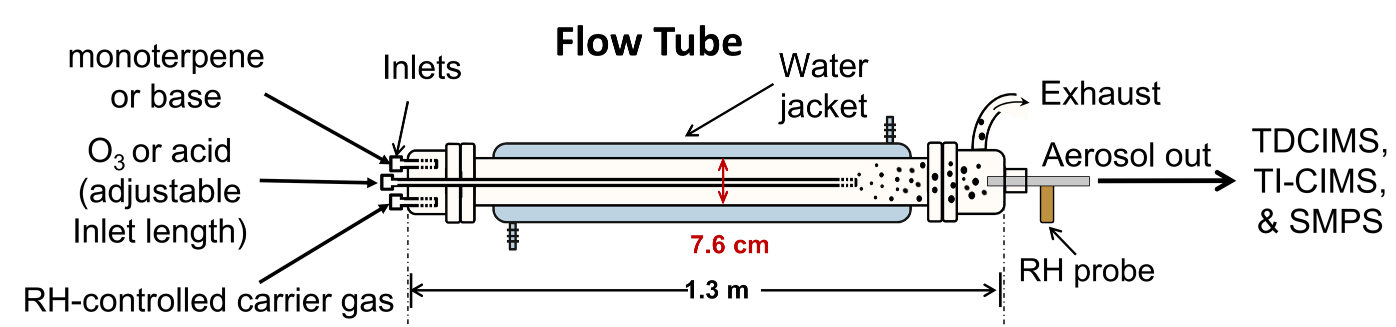
Li, X., Chee, S., Hao, J., Abbatt, J. P. D., Jiang, J., and Smith, J. N.: **Relative humidity effect on the formation of highly oxidized molecules and new particles during monoterpene oxidation**, Atmos. Chem. Phys., 19, 1555-1570, https://doi.org/10.5194/acp-19-1555-2019, 2019.

Motivation

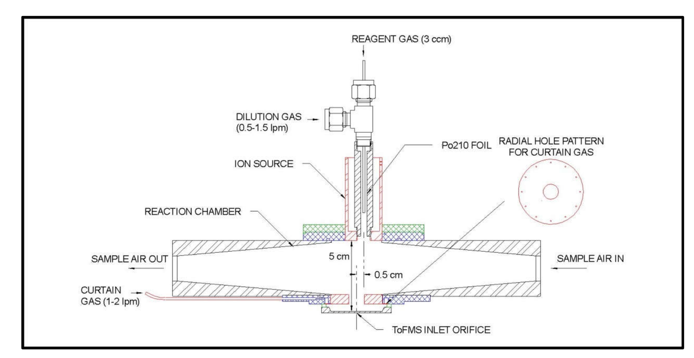


- In 2013 we measured vertical distributions of particles formed by new particle formation (NPF) at the Southern Great Plains ARM site (Chen, et al., ACP, 2017).
- Our measurements show that NPF events are likely initiated aloft, in an environment characterized by lower temperatures and higher relative humidity (RH) compared to the ground.
- These observations have motivated us to perform laboratory studies of the impact of water vapor on NPF mechanisms.

Instruments and Facilities

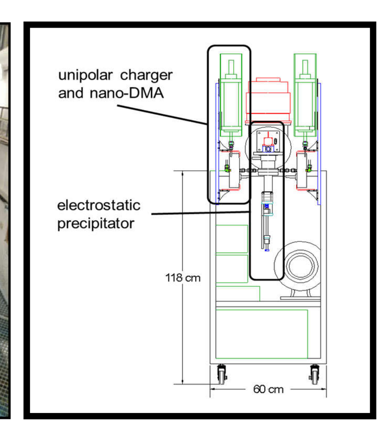


Transverse Ionization Chemical Ionization Mass Spectrometer (TI-CIMS)



TI-CIMS detects low volatility trace gases and clusters that likely serve as precursors to new particle formation. The inlet minimizes wall losses of sampled gases and clustering with neutral compounds in the ion source such as water vapor.

Thermal Desorption Chemical Ionization Mass Spectrometer (TDCIMS)



TDCIMS measures composition of nanoparticles by collecting, charging, and depositing them onto a Pt filament. The filament is resistively heated to evaporate the particles and the resulting vapors are analyzed by a chemical ionization time-of-flight mass spectrometer.

Conclusions

Monoterpene oxidation experiments show that:

- High RH suppresses NPF from monoterpene oxidation, but not by decreasing RO_2 autoxidation products.
- Cannot rule out the contribution of sCI accretion products, which are not visible using NO_3-TI-CIMS.
- Also possible that HOM clusters may react with water vapor in such a way as to suppress further growth

Acid-base reactive uptake experiments show that:

- For the **base + sulfuric acid** system, water stabilizes clusters and leads to higher concentrations from an increased nucleation rate. Water changes acid:base ratio for some bases (e.g., DMA).
- For the **base + nitric acid** system, water provides no stabilization to nascent clusters. High reactant volatilities mean that particles are only stable once acid and base undergo proton exchange.

Acknowledgement

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Part B: Effect of water vapor on the mechanism of new particle formation from acid-base reactive uptake

Background. Acid-base chemistry as a mechanism of reactive uptake into particles, while conceptually simple, is still poorly understood when applied to the formation and growth of clusters and nanoparticles.

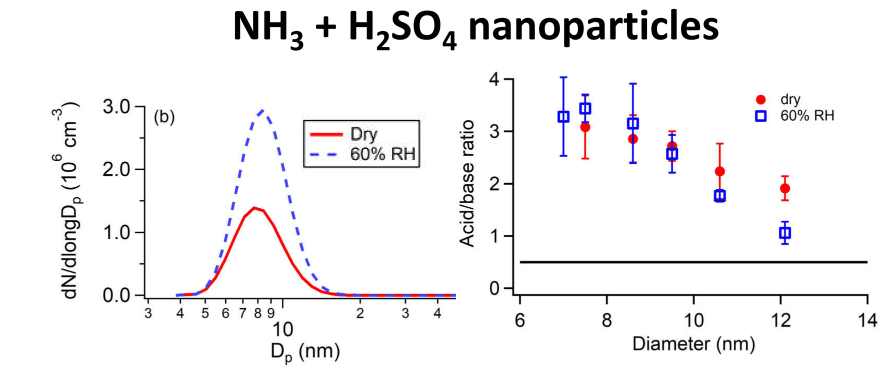
- For some systems, measurements show that as particles decrease in diameter below 20 nm they can become more acidic.
- The effect of water vapor on acid-base chemistry has not been studied for most acid-base systems.

Approach

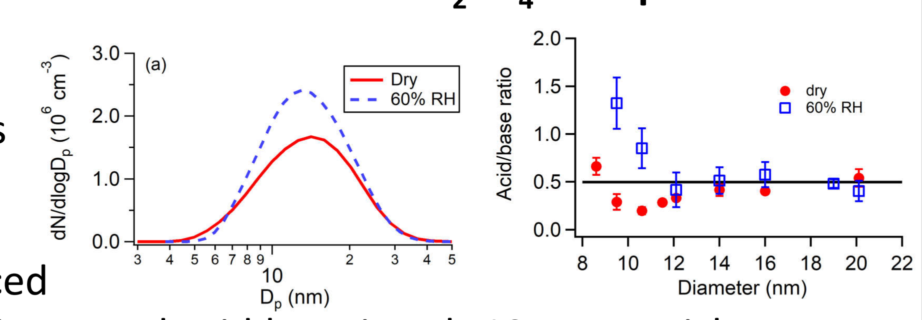
- Using a flow reactor and direct measurements of size-resolved nanoparticle composition using TDCIMS, determine the role of $H_2O_{(g)}$ in NPF and growth for various acid-base systems.
- Ultrapure N_2 carrier gas flow was set to 5 LPM in the flow tube.
- Experiments performed under dry (< 5% RH) and humid (55-60% RH) conditions.
- Ammonia (~100 ppbv) and dimethylamine (DMA, ~3.5 ppbv) were produced via perm tubes and mixed with sulfuric acid generated using a temperature-controlled saturator (~0.8 ppb) for the base + sulfuric acid experiments.
- For the base + nitric acid experiments, DMA (~12 ppb) was mixed with HNO_3 generated using a temperature-controlled (~35 ppm).
- Size-resolved nanoparticle composition (TDCIMS) and size distributions (SMPS) were measured.

Results. Plots of particle number-size distributions and TDCIMS-derived acid:base ratio are shown to the right.

NH_3 + H_2SO_4 nanoparticles

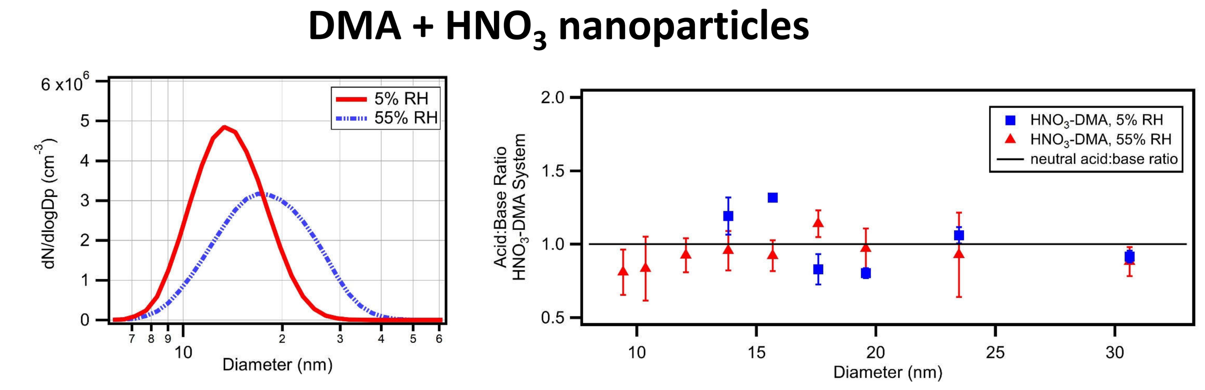


DMA + H_2SO_4 nanoparticles



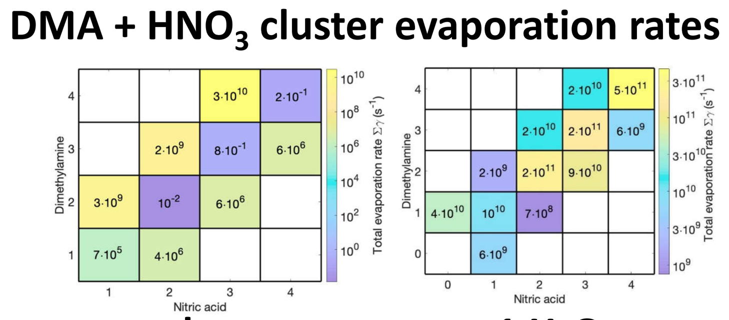
- **NH_3 + H_2SO_4**: The enhancing effect of $H_2O_{(g)}$ in nucleation is well-documented and supported by our size distribution measurements. Nanoparticles were acidic as they decreased in size and RH did not affect this.
- **DMA + H_2SO_4**: $H_2O_{(g)}$ enhanced nucleation and significantly increased acid:base in sub-12 nm particles.
- **DMA + HNO_3** : $H_2O_{(g)}$ enhanced growth somewhat, but number concentration was not affected. Unlike the H_2SO_4 system, acid:base was constant at 1:1 over all sizes measured.

DMA + HNO_3 nanoparticles



Discussion. Cluster stability calculations were performed on the HNO_3 system using ACDC cluster dynamics code. The addition of one H_2O to the cluster increased evaporation rates by a factor of 10^{11}. Water doesn't stabilize clusters.

DMA + HNO_3 cluster evaporation rates



References

Haihan Chen, Sabrina Chee, Michael J. Lawler, Kelley C. Barsanti, Bryan M. Wong & James N. Smith (2018) **Size resolved chemical composition of nanoparticles from reactions of sulfuric acid with ammonia and dimethylamine**, *Aerosol Science and Technology*, 52:10, 1120-1133, DOI: 10.1080/02786826.2018.1490005

Sabrina Chee, Nanna Myllys, Kelley C. Barsanti, Bryan M. Wong, and James N. Smith (2019) **An Experimental and Modeling Study of Nanoparticle Formation and Growth from Dimethylamine and Nitric Acid,** *The Journal of Physical Chemistry A* **Just Accepted Manuscript** DOI: 10.1021/acs.jpca.9b03326