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 afloat, 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.

Part A: Effect of water vapor on the mechanism of new particle formation from monoterpenes 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.
- H2O2 directly influences the formation of NPF precursors.
- H2O2 may explain the formation of NPF precursors.

Approach. Using a flow reactor and the newly-developed Ti-CIMS, determine the mechanism by which H2O2 affects the formation of NPF precursors. Experiments were performed at room temperature and 0–90% RH.

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 RO2+RO2 reactions. Clearly, no Ti-CIMS is not able to observe the reaction steps that are affected by H2O2.

Discussion. SCIaccretion 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?

<table>
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<tr>
<th>Observations</th>
<th>Monoterpenes oxidation experiments show that:</th>
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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 the 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.

Conclusions

Monoterpenene oxidation experiments show:

- High RH suppresses NPF from monoterpenes oxidation, but not by decreasing RO2 autoxidation products.
- Cannot rule out the contribution of SCIaccretion products, which are not visible using NO2-Ti-CIMS.
- Also possible that HOM clusters may react with water vapor in such a way as to suppress further growth.

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.


Results. For all systems, number-size distributions and TDCIMS-derived acid-base ratios are shown to the right.

- NH4+ + H2SO4: The enhancing effect of H2O2 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 + H2SO4: No enhanced nucleation and significantly increased acid-base in sub-12 nm particles.
- DMA + HNO3: H2O2 enhanced growth somewhat, but number concentration was not affected. Unlike the H2SO4 system, acid-base was constant at 1.1 over all sizes measured.

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Reference

Smith (2019) for the base + sulfuric acid experiments.

Discussion. Cluster stability calculations were performed on the HNO3 system using ACDC cluster dynamics code. The addition of one H2O to the cluster increased evaporation rates by a factor of 10^2. Water doesn’t stabilize clusters.

References


Smith, Nanna McLaughlin, Bryan M. Wong, and James N. Smith (2018) An Experimental and Modeling Study of Nanoparticle Formation and Growth From Dimethylamine and Nitric Acid, The Journal of Physical Chemistry A. Accepted Manuscript. DOI: 10.1021/acs.jpca.8b07614

Exploring the Impacts of Water Vapor on New Particle Formation Mechanisms

James N. Smith1, Sabrina Chee2, Nanna Myllly3, Xiaoxiao Li2, Jingkun Jiang2, Jeffrey Pierce3

1Department of Chemistry, Univ. of California, Irvine, CA; 2School of Environment, Tsinghua University, Beijing, China; 3Department of Atmospheric Science, Colorado State Univ., Ft. Collins, CO