New Particle Formation and Growth From the Reaction of Methanesulfonic Acid with Amines and the Ozonolysis of Terpenes

Véronique Perraud, Matthew L. Dawson, Carla Waring-Kidd, Michael J. Eilts, Mychel E. Varner, R. Benny Gerber, Andrew S. Martinez, Donald Dabdub and Barbara J. Finlayson-Pitts

1Department of Chemistry, University of California, Irvine, CA, United States; 2Department of Mechanical and Aerospace Engineering, University of California, Irvine, CA, United States

Introduction / Previous Work on MSA + Amines + H2O

- Atmospheric aerosols negatively impact human health, reduce visibility and affect the climate by scattering and absorbing solar radiation and changing cloud properties.1-4
- Models typically consider sulfuric acid (H2SO4) nucleation as the major source of new particles in the atmosphere. However, these methods consistently underpredict particle formation, indicating other sources and/or co-nucleating species may play a role.5-11
- Ammonia and amines have recently been identified as important co-nucleating species in particle formation from sulfuric acid.12-13 Also, recent research at ARUC using a flow tube reactor (Fig. 2) has identified methanesulfonic acid (MSA, CH3SO3H) and ammonia as a potentially important source of particles.14

References:

Figure 2: Complex dependence of particle formation on precursor concentration in the MSA-amine-water system, for trimethylamine (TMA) and dimethylamine (DMA).15

Results

- MDA
- DMA
- TMA

Figure 3: Calculated energy diagram and proposed kinetically-based nucleation mechanism16

References:

New Particle Formation and Growth from the Ozonolysis of Terpenes

Goal: Study the formation and growth mechanism/kinetics of SOA from MSA + Amines + H2O at shorter reaction time.

Table 2: Residence time in the flow tube

<table>
<thead>
<tr>
<th>Residence time (h)</th>
<th>Flow tube test</th>
<th>Flow tube test</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>0.05</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Figure 12: Design of the mini-flow tube experiment6

Step 1: Residence time measurements

- Low mass concentration
- Flow rate
- Nucleation and growth rates

Results

- Very little evaporation, less than 20% loss in 20 hrs
- Good agreement with results from Vaden et al., 2012 for high-generated and ambient SOA particles
- Evaporation behavior is consistent with that predicted based on in-canister equilibrium partitioning of known ozonolysis products

Figure 13: Isoprene/O3 SOA Experiments

- 18B uptake and box slower in SOA than liquid PEG model system
- SOA has a higher velocity (PDI 0.1 vs 0.2)
- Loss of SOA from 18B is very slow considering the high vapor pressure of 18B (10 Torr)
- SOA behaving like a semi-solid and herring diffusion
- Aim to extend method to other organic/nitrile/PEG/MSA model systems

2 - A New Approach for SOA analysis: Atmospheric Solid Analysis Probe Mass Spectrometry (ASAP-MS)17-22

Results

- The new sampling analysis method no more transfer of the sample to
- The new analysis increases for MOI analysis
- Able to compare different conditions, such as those presented in this study, with much higher accuracy
- Gas analysis is simultaneously available

Figure 15: Sampling/Analysis scheme

- Thermal desorption of the SOA products using a temperature ramp from 200°C to 400°C
- Soft ionization forming (MSH) ions
- Detection using a time-of-flight mass spectrometer allowing accurate mass determination

Figure 16: Thermogram

References:

New Mini Flow tube Experiments

- Recent studies show that aerosols are semi-solid or glassy, which will affect the way SOA penetrates into SOA
- The uptake of SVOCs may be better represented by a condensation mechanism

Goal: Investigate SOA phase and uptake of VOCs

1 - ATR-FTIR Experiments

- IR spectrum of SOA coating
- IR signal monitored as a function of temperature
- Evaporation rate and IR spectrum of evaporated material

Figure 14: Organic nitrate uptake on n-alkane/PEG, SOA and Pentane

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