Chemical Nucleation of Sulfuric Acid and Amines: Reaction Chamber Studies and Atmospheric Observations to Inform Our Understanding of Nucleation Processes

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Outline

• Atmospheric Nucleation

• Recent Field Measurements
  2009 Atlanta, Georgia

• Photochemical Reaction Chamber
  Preliminary Findings
Atmospheric Nucleation

- Nucleation is a significant source of global Cloud Condensation Nuclei (CCN)
- Standard Aerosol Instrumentation
  - neutral particle detection
  - detection limits
- Uncertainties in cluster composition, physical environment at time of nucleation, species responsible for cluster growth
• Nucleation is a significant source of global Cloud Condensation Nuclei (CCN)
Sulfuric Acid Correlation

- $\text{SO}_2 + \text{OH} \rightarrow \text{H}_2\text{SO}_4$
- Clustering of Hydrated $\text{H}_2\text{SO}_4$ occurs under atmospherically relevant conditions
- Observations show similar diurnal patterns for “detectable” particles, $\text{H}_2\text{SO}_4$ and larger sulfuric clusters
- Sulfuric acid and water vapor (binary system) CANNOT account for nucleation/growth

Zhao, Eisele, Titcombe, et al., JGR–Atmospheres, 2010, 115
Atmospheric Measurements

Jiang et al. 2010 (in preparation)

Experimental data

\[ y = 5.1 \times 10^{-6} x - 0.0013, \quad R = 0.75 \]
Nucleation Reaction System

Cluster Chemical Ionization Mass Spectrometer (cluster-CIMS)
Photochemical Reaction Chamber

aka
“The Machine”
Photochemical Reaction Chamber

Schematic of Photochemical Reaction System:
Reaction Chamber, Cluster-CIMS, and Particle Size Distribution (PSD) Instrumentation

**Reaction Chamber**
- Heat exchanger
- 50:50 Water/Ethylene Glycol
- Ultra-violet light
- Air circulation fan
- Teflon bag 1000 L
- Teflon window
- Sampling ports
- Gate valve
- Fume hood
- O3 monitor

**PSD**
- Po199 charger
- Sheath: 5 lpm
- Nano-DMA
- CPC
- UCPC
- Sheath: 14.5 lpm
- Vacuum (vented to roof)

**Cluster-CIMS**
- Ion source
- Critical orifice 2.88 lpm
- 300 L/s turbomolecular pump
- 600 L/m Scroll pump
- Exhaust to hood
- Pinhole N2
- Nitric vapor
- Additional ion source N2
- N2 backfill

**Symbol & Color Key**
- Mass flow controller
- SO2
- O3
- Regulator
- Rotometer
- Coolant fluid
- N2
- HNO3 in N2
- Sheath flow (temperature air)
Amine Nucleation

PSD 100727 (dN/dlogDp (#/cm³))

SO₂ “Commas”  SO₂ + Amine “Tongues”
Cluster-CIMS Chemical Information

7/27/10 Experiment 2: SO2 9 ppb, 24% RH

Peaks:
62, 80, 97*, 108*, 110*, 113*, 115*
125/127, 138, 142*, 147, 150, 152,
154, 158*, 160*, 162*, 164, 168, 171,
176*, 178, 180, 182, 188, 190, 192,
195*, 197*, 201, 204, 206, 208, 211*,
213*, 217*, 221*, 227*, 239, 241, 246,
258, 264, 277/278*, 289/290*, 293*,
296*, 308, (300, 305, 308, 312, 319,
322, 325 higher background?) 328, 340*,
347*, 351-353*, 358, 363*, 369/370, 373,
378, 383*, (390-398*), 408*

*Signal intensity increases
during nucleation event: note 1 scan during
H$_2$SO$_4$ and Amine Nucleation

“Commas”

Time averaged signal
7/27/10 Experiment 2: 9 ppb SO$_2$, 24% RH

“Tongues”

Time Averaged Signal
7/27/10 Experiment 3: SO$_2$ 7ppb, 100 µL Dimethyl Amine vapor, 24% RH
H$_2$SO$_4$ + Amine Nucleation

$$OH + SO_2 \rightarrow HSO_3$$

$$HSO_3 + O_2 \rightarrow SO_3 + HO_2 \text{ (fast)}$$

$$SO_3 + 2H_2O \rightarrow H_2SO_4 + H_2O$$
H$_2$SO$_4$ + Amine Nucleation

\[
OH + SO_2 \rightarrow HSO_3
\]

\[
HSO_3 + O_2 \rightarrow SO_3 + HO_2 \text{ (fast)}
\]

\[
SO_3 + 2H_2O \rightarrow H_2SO_4 + H_2O
\]

\[
HSO_3 + O_2 + M \rightarrow HSO_5 + M
\]
Other SO$_2$ Oxidation Products

7/29/10 Experiment 2: 11ppb SO$_2$, 19% RH

First proposed: Friend et al. 1980, J. Physical Chemistry


Based on:
1.) physical data (nucleation rate)
2.) computational studies

7/29/10 Experiment 3: 8ppb SO$_2$, 15% RH, 10 µL DMA vapor

HSO$_5$
Summary

• “First” atmospheric and experimental measurements of amines in new particle formation events

• Photochemical reaction chamber particle formation events at atmospherically relevant conditions

• Evidence of additional SO$_2$ oxidation products for the production of new particles: HSO$_5$,$_n$ (SO$_3$)

• [Relative humidity affect on sulfuric acid cluster stability]
Future Work

Computational Fluid Dynamics: Ion Processes in Inlet

Pathlines Colored by Surface ID

Particle Traces Colored by Particle Residence Time (s)

Credit: Derek Oberriet
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