

The Effect of Nitric Acid on Cloud Processing of Glyoxal

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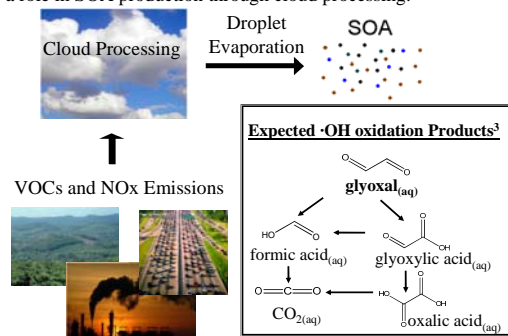
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Introduction

Volatile Organic Compounds (VOCs) such as isoprene are emitted into the atmosphere and oxidized in the gas phase to form water-soluble compounds (e.g., glyoxal). These compounds partition into cloud droplets, become further oxidized (e.g., by ·OH) and form low volatility products such as organic acids and oligomers. Low volatility products partition into the particle phase upon cloud droplet evaporation, forming **secondary organic aerosol (SOA)**. Nitric acid in the atmosphere may play a role in SOA production through cloud processing.



Motivation

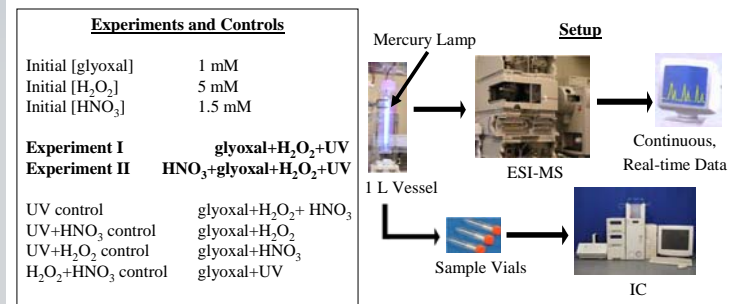
- SOA contributes to particulate matter (PM), which is linked to human health issues such as asthma, heart disease, and lung cancer.
- PM scatters and absorbs light, affecting the Earth's albedo, visibility, and climate.
- Current models under-predict organic PM in the atmosphere.
- There is increasing evidence that SOA is formed through cloud processing¹.
- Cloud processing is a potential source of SOA and will contribute to terrestrial and open-ocean deposition of organic compounds, including organic nitrogen compounds.

Objectives

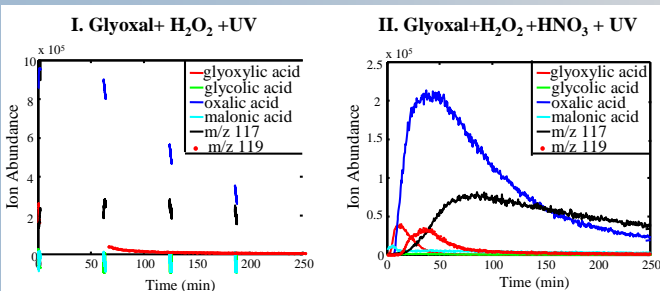
- 1) Conduct aqueous photochemical experiments with glyoxal and ·OH ± HNO₃ to simulate cloud processing
- 2) Identify unexpected products formed (e.g. organic acids, high molecular weight compounds, organonitrates)
- 3) Determine the effects of HNO₃ on cloud processing of glyoxal

Methods

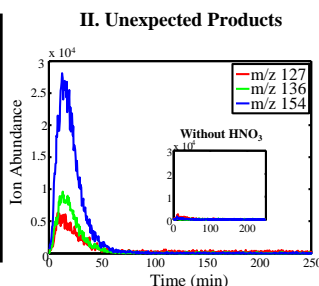
- Reactions conducted in 1 L borosilicate vessel
 - Cloud relevant pH
 - UV light from 254 nm mercury lamp generates ·OH radical from H₂O₂
- Continuous sampling with Electrospray Ionization Mass Spectrometer (ESI-MS) in positive and negative modes
- Additional samples taken and analyzed by Ion Chromatography (IC). Remaining samples immediately frozen



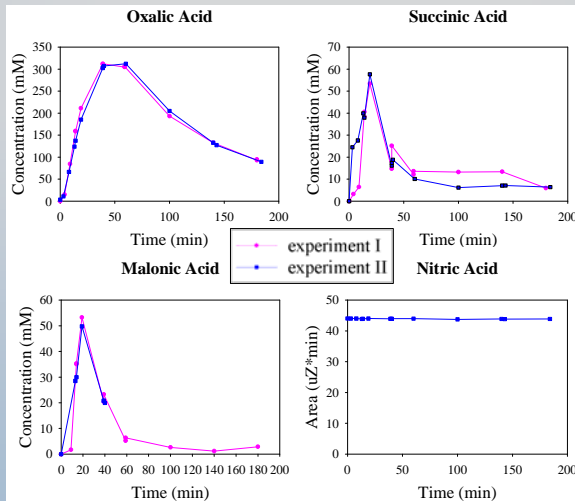
Results: ESI-Mass Spectrometry-Negative Mode



- Similar formation times for expected products
- Even-numbered *m/z* suggest presence of nitrogen compound
- Unexpected products form in I and II, in addition to those unique to II
- Unexpected products detected in experiment I not in II (not shown)
- Expected products not formed in control experiments (not shown)



Results: Ion Chromatography-Negative Mode



- Concentration dynamics of organic products (oxalic, succinic, and malonic acid) exhibited no change with addition of nitric acid
- Nitric acid concentration decreased <1%

Conclusions

- Aqueous reactions of glyoxal and ·OH (±HNO₃) form low volatility products that will contribute to SOA.
- No changes seen in concentration dynamics of most products with the addition of nitric acid.
- Even-numbered *m/z* products found in experiment II may be organonitrates.
- Organonitrates formed from cloud processing will be a small fraction (<1%) of total nitrogen compounds.

Future Work

- Identify organic nitrogen products from experiments.
- Determine formation pathways for organonitrate production in cloud water.
- Expand kinetic and mechanistic data for air quality and climate models.

References

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2. Blando, J.D., Turpin, B.J., 2000. Secondary organic aerosol formation in cloud and fog droplets: a literature evaluation of plausibility. *Atmospheric Environment* 34 (10), 1623-1632.
3. Carlton, A.G., Turpin, B.J., Altieri, K.E., Seitzinger, S.P., Reff, A., Lim, H.J., Ervens, B., 2007. Atmospheric oxalic acid and SOA production from glyoxal: Results of aqueous photooxidation experiments. *Atmospheric Environment* 41 (35), 7588-7602.

Acknowledgements

Special Thanks To: Yi Tan, The Institute of Marine and Coastal Sciences at Rutgers University, Research Internships in Ocean Sciences, and The National Science Foundation.