Aerosol Flow Tube Studies of Secondary Organic Aerosol Formation through Gaseous NOx and Aqueous Nitrate Ion Photochemistry

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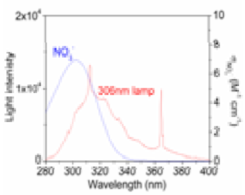
Introduction

- Particulate nitrate is a significant component of aged urban aerosol[1] and is expected to become more important in the future atmosphere due to expected increase in nitrate precursor emissions and the decline of ammonium sulfate aerosols in wide regions on the earth.[2]
- Nitrate ion has a rich photochemistry in the bulk aqueous phase, with a weak absorption centered at 300 nm, that leads to NO_2 formation along with oxidants such as O(^{3}P) and OH.[3]

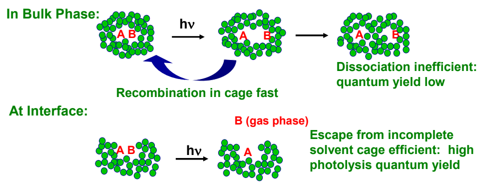
$$NO_3^- + h\nu \rightarrow [NO_3^-]^*$$

$$[NO_3^-]^* \rightarrow NO_2^- + O(^3P) \qquad \Phi^{O(^3P)}(305\,nm) = 0.0011$$

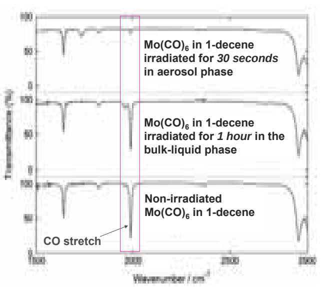
$$[NO_3^-]^* \rightarrow NO_2^\bullet + O^{\bullet -} \xrightarrow{H_2O} NO_2^\bullet + {}^\bullet OH + OH^- \qquad \Phi^{OH}(305 - 313\,nm) = 0.013$$



- Photochemistry at interfaces can be quite different than the bulk.

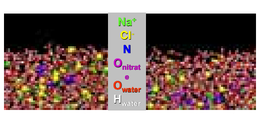


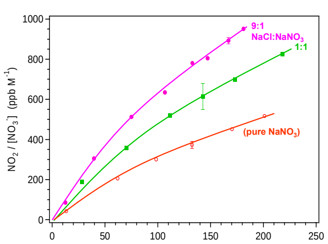
- For example, $Mo(CO)_6$ was photolyzed by UV radiation in both the aerosol and bulk phases.[4]



- Infrared absorption spectra on aerosolized and bulk solutions of $Mo(CO)_6$ in 1-decene. Note UV irradiation times.
- The nearly three orders of magnitude faster photolysis rate of aerosolized $Mo(CO)_6$, has been attributed to an incomplete solvent cage at the interface.[4]

- Additional interface effects have been observed in photolysis of thin films of deliquesced $NaNO_3$–NaCl mixtures.[5]
- Enhanced production of NO_2 relative to NO_3^- have been observed with increasing fraction of chloride ion.[5]

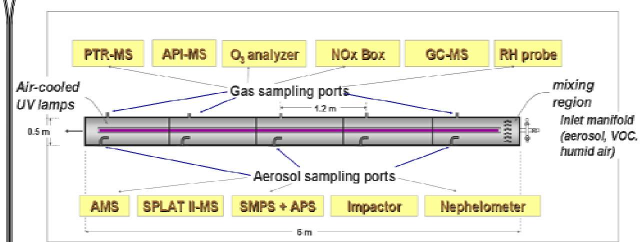




- Enhanced production of NO_2 correlates with MD simulations showing increased nitrate ion concentration near the surface at higher NaCl to $NaNO_3$ ratios.

- A high volume, low flow, stainless steel flow system was designed to investigate the interaction of photolyzed nitrate aerosol in the presence of volatile organic compounds.

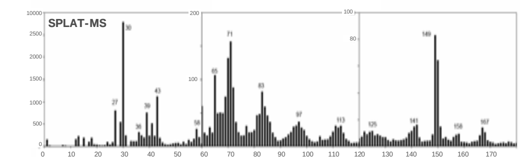
Experimental

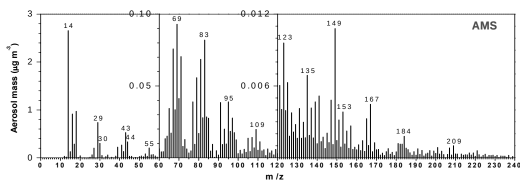


Results

1. NO_x – α-pinene photochemistry

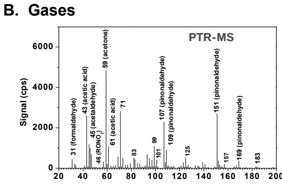
A. Particles





- α-pinene (500 ppb); NO_2 (2 ppm); ± C_6H_{12} (200 ppm); RH 68%; flow 20 L/min; temp. 22 ° C
- SOA was formed through NO_x – α-pinene photochemistry.
- No impact when cyclohexane was added as a OH free radical scavenger.
- Aerosol yield was dramatically decreased by addition of nitric oxide (separate experiment) showing that O_3 is the SOA generator.[6]
- SOA particle density = 1.25 ± 0.05 g/cm³.
- Particle composition was size independent.
- The largest peak (m/z =30) in SPLAT-MS is due to organic nitrate.

B. Gases



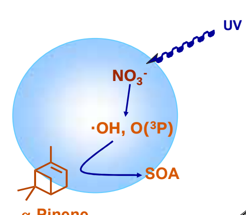
Compounds	PTR-MS peaks (m/z)	% Yield * [6]
Pinonaldehyde	169, 151, 123, 109, 107, 99	22 ± 6
Acetone	59	12 ± 3
Acetaldehyde	45	3.9 ± 1.7
Acetic acid	61, 43	8.6 ± 1.9
Organic Nitrate	46	~20 model estimated
Formaldehyde	31	5 ± 1
Formic acid	47	2.5 ± 1.4
Pinene oxide	153, 135, 109	0.9 ± 0.1

* from static chamber experiment

- Organic nitrates are major products of the photooxidation.
- Identification of individual organic nitrates will be critical in the future.

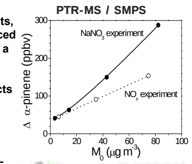
2. Nitrate ion – α-pinene photochemistry

- Do organics oxidize at the surface of irradiated sodium nitrate?

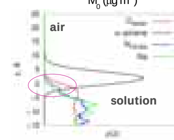


A. Gases

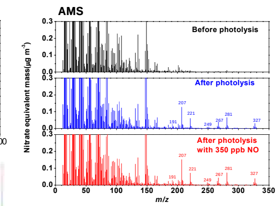
- Chamber experiments, with a thin deliquesced film of $NaNO_3$, show a smaller mass of *suspended* aerosol and gaseous products per ppb of pinene reacted.[7]



- MD simulations of α-pinene and aqueous $NaNO_3$ show overlap in probability density, ρ(z), of pinene and nitrate ion.[7]



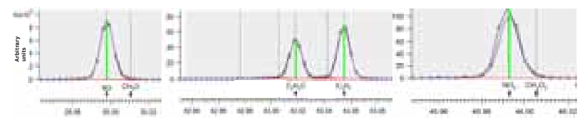
B. Particles



- New products, including high MW products, are formed by the photochemistry.
- The addition of NO has no effect on high MW products.

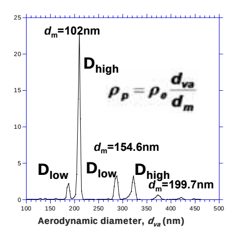
3. High resolution AMS spectra identify specific fragmentation products.

- $NaNO_3$ + α-pinene (500 ppb) + hν ; 350 ppb of nitric oxide added after 115 minutes of photolysis

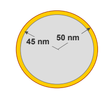


- AMS spectra for 2.5 hr photolysis of $NaNO_3$ aerosol and α-pinene in which NO was added after 1 hr. m/z 30 was primarily NO(+), m/z 43 was about 50:50 C_3H_7(+)/CH_3CO(+) and m/z 46 was NO_2(+).

4. SPLAT-MS and SMPS data



- Size selected aerosol of electrical mobility diameter, d_m was further analyzed by SPLAT-MS to measure the aerodynamic diameter, d_{va}.[8]
- This revealed aerosol particles with a lower density = 1.8333 g/cm³, and a higher density = 2.0588 g/cm³, which corresponds to $NaNO_3$.



Assuming an organic coating (density 1.25 g/cm³) over a spherical core of sodium nitrate (density 2.06 g/cm³), a 5 nm thick coating over a 45 nm core would have a net density corresponding to observed low density particles

Atmospheric Implications

- Inorganic nitrate is often a major component of particles in polluted urban air. Our laboratory results show that SOA formation results from the photolysis of nitrate in the presence of α-pinene.
- If nitrate photolysis occurs at or near the surface of the particles, the production of OH and O(^{3}P) may be particularly efficient due to the reduced solvent cage, and would increase oxidation of organics at the interface.
- This suggests that the photolysis of nitrate occurring in airborne particles and on surfaces in the boundary layer (e.g., buildings, roads, ground) may lead to oxidation of organics.
- Preliminary results suggest:
  - $NaNO_3$ particles become coated with organics during photooxidation
  - High MW products are also formed on sodium nitrate particles during photolysis

Acknowledgements

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