The role of nitrate radicals (NO$_3$) in aerosol life cycle: Secondary organic aerosol formation and aging of atmospheric organic aerosols

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EPA STAR Review
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Nitrate radicals (NO$_3$) are a major nighttime oxidant

- Reacts with approximately 20% of all biogenic volatile organic carbons (Pye et al., 2010)

- Monoterpene+NO$_3$ reaction has high organic nitrate and SOA yields (e.g., Griffin et al., 1999; Fry et al., 2009)

- NO$_3$ is created by the reaction of anthropogenic NO$_2$ with O$_3$

  \[
  \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2
  \]

Nitrate radical oxidation of BVOCs represent a direct way for linking anthropogenic emissions and biogenic SOA formation
Synergetic Approach of Studying Organic Aerosols

**Research Goal:** determine the extent to which \( \text{NO}_3 \) radicals oxidation of BVOC affect organic aerosol loading and composition over its atmospheric lifetime.

Foundation for predicting aerosol formation

- Laboratory studies

Evolution of ambient aerosols (sources, processes, fates)

- Field measurements

Instrumentation

Advanced mass spectrometry
Field Measurements: SOAS and SCAPE

- Southern Oxidant and Aerosol Study (SOAS)
  - 2013 June - July
  - Centreville (rural Alabama)

- Southeastern Center of Air Pollution and Epidemiology study (SCAPE)
  - 2012 May - 2013 Feb
  - Greater Atlanta Area (urban and rural)

Xu et al., PNAS, 2015
Xu et al, ACP, 2015
OA Source Apportionment in the SE US

- OA sources vary spatially and seasonally
- Less-Oxidized Oxygenated Organic Aerosol (LO-OOA) is an important factor across all seasons and sites
- LO-OOA can account for 19-34% of total OA in SE US

Xu et al., PNAS, 2015
Diurnal trends are similar for all sites and all seasons (diurnal trends are normalized by the highest LO-OOA concentration of each dataset).

- A diurnal maximum at night and a minimum in the afternoon.

Xu et al., PNAS, 2015
LO-OOA Nighttime Increase
-- boundary layer height change or production?

Nighttime increase still exists after adjusting by the boundary layer height
→ nighttime aerosol production

Xu et al., PNAS, 2015
LO-OOA at SOAS

- LO-OOA peaks at night and has same diurnal as monoterpenes.
- LO-OOA is identified in all seasons → monoterpenes seasonal variation
- LO-OOA is strongly correlated with “nitrate groups (-ONO2) in organic nitrates”
- Estimated based on AMS-IC method

**Contribution of monoterpenes + NO$_3^-$ chemistry to LO-OOA**

Xu et al., PNAS, 2015
Estimation of Particulate Organic Nitrates

Three independent methods to estimate particulate organic nitrates

1. AMS-IC method: AMS total nitrate - PILS inorganic nitrate

2. AMS NO\(^+\)/NO\(_2\)\(^+\) ratio method: (Farmer et al., 2010)

\[
\begin{align*}
\frac{\text{NO}_2,\text{org}}{\text{NO}_2,\text{meas} \times \left( \frac{R_{\text{meas}}}{R_{\text{ON}}} - \frac{R_{\text{AN}}}{R_{\text{ON}}} \right)} & \quad \text{NO}^+$/NO\(_2\)^+ for ammonium nitrate \ (~ 2) \\
\frac{\text{NO}_\text{org}}{\text{NO}_\text{AN}} & \quad \text{NO}^+$/NO\(_2\)^+ for organic nitrate \ (depends on VOC, instrument, etc, \ ~ 5 - 10 )
\end{align*}
\]

3. PMF method: include NO\(^+\) and NO\(_2\)^+ in PMF analysis

Xu et al., ACP, 2015
NO$_3_{\text{org}}$ and NO$_3_{\text{inorg}}$ in the SE US

- Concentration of “nitrate groups” (-ONO$_2$)
- **Organic origin**: similar amount year round, is $\sim 0.2$ ug/m$^3$
- **Inorganic origin**: higher in winter months, $\sim 0.8 - 1.4$ ug/m$^3$

Xu et al., ACP, 2015
Ubiquitous Presence of Particulate Organic Nitrate

**Organic origin:** 63-100% of total “nitrate groups” conc. in summer

**Organic nitrates are 5-12% of total OA in summer**
(assume MW = 200 -300 g/mole)  

Xu et al., ACP, 2015
Fundamental Lab Studies: Monoterpenes + NO$_3$

1. Laboratory studies of SOA formation from monoterpenes + NO$_3$
   SOA (SOA yields, formation mechanisms, organic nitrates)
   - Effect of RH
   - Seed Acidity (highly acidic seed, Guo et al., 2015)
   - Peroxy radical fate: Mostly likely “Low-NOx” chemistry (RO$_2$+HO$_2$)
   - Loadings ~ 10 μg/m$^3$
   - α-pinene, β-pinene, limonene

2. Changes in SOA and organic nitrates with continued processing
   - Hydrolysis
   - Dilution
   - Temperature Change
   - Dark/photochemical aging
Fate of Peroxy Radicals (RO$_2$)

Figure 1. General schematic of gas-phase peroxy radical chemistry in SOA formation.
Continued Processing of OA and ON

- Different Perturbations
- Changes with hydrolysis, atmospheric dilution, temperature change, photochemical (OH) and dark (NO$_3$) aging,
Georgia Tech Environmental Chamber Facility

Dual chamber facility, 300 lights, temperature range 4-40 °C.

Boyd et al., ACP, 2015
Georgia Tech Environmental Chamber Facility

Gas-phase measurements
- Q-CIMS
- HR-ToF-CIMS
- GC-FID
- O₃ monitor
- Chemiluminescence NO/NO₂/NOₓ analyzer
- CAPS NO₂ monitor

Particle-phase measurements
- HR-ToF-AMS
- FIGAERO-HR-ToF-CIMS
- SMPS
- CPC
- Offline filter characterization
SOA Formation from $\alpha$-pinene + NO$_3$ and $\beta$-pinene + NO$_3$

- Temperature = 25 °C
- RH = 50 – 54%
- Highly acidic MgSO$_4$/H$_2$SO$_4$ seed
- RO$_2$+HO$_2$ and RO$_2$+NO$_3$ pathways

Nah et al., ES&T, 2016
• Humidity and RO$_2$ fate does not have a strong effect on aerosol mass yield
• Aerosol mass yields: 27.0-104.1% for mass loadings ranging from 5.1-216.1 µg/m$^3$
• β-pinene+NO$_3$ can potentially contribute to a large fraction of ambient aerosol

Boyd et al., ACP, 2015
β-pinene+NO$_3$ : Gas-phase Products

- Aerosol and gas phase species appear almost immediately
- Organic nitrate species identified by Q-CIMS
- Fast reaction with immediate condensation of products

Boyd et al., ACP, 2015
**β-pinene+NO$_3$: Aerosol Composition and Dark Aging**

- Large fraction of nitrate species at NO$^+$ (m/z 30) and NO$_2^+$ (m/z 46), 11%
- NO$^+$ / NO$_2^+$ ratio = 4.8 – 10.2
- Relatively large signal at m/z 67 (C$_5$H$_7^+$) and m/z 91 (C$_7$H$_7^+$)
- Increase in O/C with dark aging: 18% (dry), 6% (humid)  
  Boyd et al., ACP, 2015

**45-74% of aerosol is organic nitrates**
Relevance of $\beta$-pinene+NO$_3$ to SOAS

Spectrum of LO-OOA at SOAS has similar features to laboratory $\beta$-pinene+NO$_3$ SOA at $m/z > 60$

Using results from chamber experiments →

$\beta$-pinene+NO$_3$ can potentially make up as much as 50% of nighttime OA production at SOAS

Xu et al., PNAS, 2015
Boyd et al., ACP, 2015
Highly-Oxygenated ON in Chamber Studies (β-pinene + NO₃)

- Highly-oxygenated ON observed in FIGAERO-CIMS with 4 – 9 oxygen atoms
- Rapid formation, likely occurs through auto-oxidation (Crounse et al., 2013; Ehn et al., 2014)

Nah et al., ES&T, 2016
ON Observed with FIGAERO-HR-ToF-CIMS

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- 41 ON observed for β-pinene+NO$_3$ (32 observed at SOAS, Lee et al., 2016)
- 5 ON for α-pinene+NO$_3$ (4 observed at SOAS, Lee et al., 2016)

NO$_3$ chemistry forms atmospherically relevant highly oxygenated ON

Nah et al., ES&T, 2016
Aerosol ON that is not removed by deposition can either form nitric acid through hydrolysis or be released as NO\textsubscript{x} through photolysis or OH oxidation.
1. β-pinene+NO$_3$: Organic Nitrate Hydrolysis

- Likely that majority (~90%) of ON is primary (which do not hydrolyze at appreciable rates)
- ~10% of ON hydrolyzes with a lifetime of 3-4.5 hr
  - Much higher than primary/tertiary ON ratio predicted by SOA formed from photooxidation under high NOx conditions (Browne et al., 2013)
- What happens to ON that do not hydrolyze? (do they get photolyzed /OH reaction?)

Nitrate/Org in wet expt

Nitrate/Org in dry expt

Boyd et al., ACP, 2015
2. Photochemical Aging of Nighttime Aerosol

β-pinene + NO₃

α-pinene + NO₃

- Photochemically aging, OH + hν
- β-pinene+NO₃ SOA: photochemical aging has little effect
- α-pinene+NO₃: a large fraction of reactive nitrogen is released from the α-pinene SOA back to the gas phase during photooxidation.

Nah et al., ES&T, 2016
Conclusions

- LO-OOA (19-34%): likely originates from monoterpenes, and its formation could be controlled by nighttime NO$_3$ chemistry (NO$_x$ effect)

- ON contributes up to 12% of ambient OA in SE US in summer

- $\beta$-pinene+NO$_3$ reaction
  - FIGAERO-HR-ToF-CIMS: Formation of highly oxygenated ON species in both gas- and particle-phase, many of which observed at SOAS
  - This reaction likely contributes substantially to ambient LO-OOA and ON
  - Peroxy radical fate and RH does not have a strong effect on SOA yield

- Hydrolysis: ~90% of the ON formed from the $\beta$-pinene+NO$_3$ reaction are primary nitrates, do not hydrolyze at appreciable rates

- Atmospheric perturbations
  - Particulate ON from $\beta$-pinene+NO$_3$: NOx sinks
  - Particulate ON from $\alpha$-pinene+NO$_3$: photochemical oxidation may be an important atmospheric NOx source in the day

Laboratory studies should be an integrated part of field studies
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