ToF-AMS characterisation of SOA from NO3 oxidation of $\beta$-Pinene

AMS Users Meeting 2008  | Astrid Kiendler-Scharr
Secondary Organic Particles

• Current estimates of global biogenic SOA sources: 12 – 910 TgC/yr
• Comparisons field observation – model show large discrepancies
• C14 measurements in OA show large contribution of „modern“ C
• NO3 as anthropogenic oxidant
• SOA and organic nitrate yields from NO3 + monoterpane
• Measurements during the international NO3/N2O5 Intercomparison at SAPHIR summer 2007
cylindrical shape 280 m$^3$
diameter 5 m, length 18 m

double wall FEP film,
light transmission 85%

high purity liquid N$_2$ and O$_2$
gas replacement flux: 0 – 400 m$^3$/h
• Two experiments $\beta$-Pinene+NO3 under dry/wet conditions
• Measured Parameters:
  - RH, T, O3, NOx
  - VOCs, NO3, N2O5
  - organic nitrates (NO2-TD-LIF)
  - SOA number density (CPC) and size distribution (SMPS)
  - SOA composition (AMS)

Submitted to ACP:
Organic nitrate and secondary organic aerosol yield from NO3 oxidation of $\beta$-pinene evaluated using a gas-phase kinetics/aerosol partitioning model
Comparison SMPS and AMS: $\beta$-Pinene + NO$_3$, dry

![Graph showing SMPS and AMS data comparison for $\beta$-Pinene + NO$_3$ SOA over a period from 20.6.2007 to 21.6.2007. The graph plots concentration in µg/m$^3$ against time, with lines for SMPS mass, AMS total, organic (Org) with RIE = 1.4, and nitrate (NO$_3$) with RIE = 1.1. The vaporizer temperature is also shown.]
Comparison SMPS and AMS: $\beta$-Pinene + NO3, dry

![Graph showing comparison between SMPS and AMS for $\beta$-Pinene + NO3, dry](graph.png)
Nitrate Diagnostics

AMS Users Meeting, 5.9.2008
$\text{NO}_2^+ = 0.05 + 0.1 \times \text{NO}^+$
Nitrate Diagnostics

\[
\text{NO}_3 = a + b \times \text{NO}_3 \text{ at m/z 30} \\
a = 0.013 \pm 0.02 \\
b = 0.1 \pm 0.007 \\
V_{Pr} = 0.93
\]

\[
\text{Frag}_{org}[30] = 0.893 \times \text{frag}_{organic}[58], 0.893 \times \text{frag}_{organic}[83]
\]
Organics Composition AMS

SAPHIR 20.6.2007
β-Pinene + NO₃ SOA

- SMPS mass
- AMS total
- Org
- NO₃
Organics Composition AMS

- **Estimated molar mass of organic nitrates**

  Organic/Nitrate ratio $R$ at $T = 145^\circ$C
  assuming all signal at this temperature from organic nitrates
  $\rightarrow R = 2.7 \pm 0.2$ results in $MW = 229 \pm 12$ g/mole

- **Fraction of SOA consisting of organic nitrates**

  Two approaches:
  Organic/Nitrate ratio $R = 9 \pm 1$ throughout the experiment
  With $MW$ of organic nitrate = 215-231 g/mole this corresponds to 32-41% of total aerosol mass is organic nitrate

  At $T = 145 ^\circ$C the ratio of AMS mass (4.5 $\mu$g/m$^3$) to SMPS mass (11.6 $\mu$g/m$^3$) corresponds to 39% of total aerosol mass is organic nitrate.
Organics Composition AMS

Nitrate equivalent mass (µg m\(^{-3}\))

- MSSD NO\(_3\) 3.43233
- MSSD Org 29.4062
Organics Composition AMS
Organics Composition AMS

- Ratio $\text{NO}_2^+ / \text{NO}^+$
- Ratio $\text{NO}_2^+ / \text{NO}^+$ from $\text{NH}_4\text{NO}_3$

Vaporizer Temperature (°C)

- Ratio organics/NO3

- Organic / NO3
Comparison dry/humid experiment

SOA from β-pinene + NO$_3$

- dry Experiment
  RH ~ 60%

Vaporizer Temperature (°C)
Summary

SOA yield ~50% under both dry and humid conditions

SOA density 1.6 g/cm3

Organic to Nitrate ratio is ~ 9

Organic nitrates decompose in NO⁺, NO₂⁺ mostly

NO₂⁺/NO⁺ ratio ~ 0.1 for SOA studied < than from inorganic nitrate

Higher masses containing C, H, N, and O difficult to identify but Peaks found at e.g. m/z 76, 153
Thank you!