Influence of photooxidation and oligomerisation on the hygroscopicity and volatility of 1,3,5-TMB SOA

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Definitions

• Primary Organic Aerosol (POA)
  – Aerosol particles which are directly emitted into the atmosphere.

• Secondary Organic Aerosol (SOA)
  – Aerosol particles which are formed in the atmosphere from gas phase by chemical reaction.
Partitioning theory

Case 1: Low aerosol mass

Saturation vapor pressure = Volatility

Low | Medium | High

Saturation vapor pressure
Partitioning theory

Case 2: High aerosol mass

Saturation vapor pressure = Volatility

- Low
- Medium
- High
Partitioning theory

Low aerosol mass

High aerosol mass

Partitioning changes with the mass loading
• Evaporation of POA with increasing the dilution (i.e. decreasing the mass loading)
• At ambient condition only 25% of POA exist

Robinson et al. 2007 Science
More volatile compounds stay in the gas phase, and then this could form SOA after oxidation / oligomerisation (chemistry transformation) in the gas phase.
• Experimental setup description

• Hygroscopicity and volatility of SOA produced using low (60 ppb) and high (1200 ppb) initial precursor (TMB) concentrations.
Smog Chamber facility

- Temperature Control
- RH = 50%
- Gas input facilities $\text{NO}_x, \text{VOC}$
- 4 xenon lamps
Typical experiment at the Smog Chamber
Instruments

- VT DMA \(\rightarrow\) measures the Volatility properties

\[
\text{VFR}(T, \text{Time}) = \frac{\text{Volume after heating}}{\text{Volume at 25}^\circ\text{C dry}}
\]

\[
\text{VFR}(T) = \text{Volume Fraction Remaining (expressed in \%)}
\]
Instruments

- HTDMA \rightarrow \text{measures Hygroscopic properties}

\[
GF(RH) = \frac{\text{Diameter humid (RH)}}{\text{Diameter dry}}
\]
• **VHTDMA** measures the **Hygroscopic properties of the residual aerosol remaining after the oven**

\[
VH_{\text{GF}}(\text{RH}, T) = \frac{\text{Diameter humid (RH)}}{\text{Diameter after heating}}
\]
SOA from 1,3,5-Trimethylbenzene (TMB)

• Low precursor concentration experiment
  • 60 ppb TMB
  • 30 ppb NO\textsubscript{x}
  • 400 ppt SO\textsubscript{2}

• High precursor concentration experiment
  • 1200 ppb TMB
  • 600 ppb NO\textsubscript{x}
  • 400 ppt SO\textsubscript{2}
Low initial precursor concentration
•At a specific temperature, the VFR increases with time i.e. the particles become less and less volatile: This can be explained either by oligomerisation or oxidation or both.
At higher temperature, the VFR is lower. More compounds evaporate at higher temperature.

At 120°C and at 140°C the VFR increases with time. This can be explained either by oligomerisation or oxidation or both.
Increase of the hygroscopic property with time: 
Oxidation has a stronger effect on hygroscopicity than oligomerisation
• At 120 °C the remaining particle have the same GF of the non-heated particle.
• The GF of the remaining particle increases with time.
High initial precursor concentration

New partitioning

Mass produced during low precursor concentration
At higher temperature, the VFR is lower.

VFR increases with time (Oxidation or oligomerisation or both).

Compared to low concentration, we have the same trend and value of the VFR.
Partitioning ...

Low aerosol mass  
High aerosol mass

Partitioning changes with the mass loading
For high precursor concentration, we expect partitioning of more volatile species (less oxidized) into the particle phase which should decrease the hygroscopicity.

The GF stays more or less stable with time.
The hygroscopicity of the remaining particle (120 and 140 °C) is higher than the non-heated particle.

The partitioning of more volatile species (less oxidized) into the particle phase decreases the hygroscopicity. By removing this volatile species (which lower the hygroscopicity), the remaining particles gains a higher hygroscopic property. **The concentration of the precursor does have an important impact on the hygroscopic property of SOA.**
Conclusions

• Due to partitioning, precursor concentration has an effect on the particle physical properties (hygroscopicity).
• The particle chemistry changes with time (becomes more oxidized and more oligomerised) which leads to a change of the hygroscopic and volatile properties.
• The VHTDMA technique is well suited to the investigation of such phenomena
Thanks for your attention
Oligomerisation seen from the LDI-MS

- 2.5 hrs: mainly peaks < m/z 400
- 3.5 hrs: Kalberer et al. 2004 Science
- 6.5 hrs: grown oligomer

David, 2002 (not my child)
Evidence of Oxidation from the W-TOF AMS

Duplissy et al. in preparation

Time after light on [hours]

O to C ratio
Mass Concentration (µg m$^{-3}$)

Date and Time

- 05:30
- 10:05:2007
- 15:30
- 16:00
- 16:30
- 17:00
- 17:30

SOA
Organic Nitrates

- No heating
- 120 °C at high flow rate
- 140 °C at high flow rate

120 °C
120 °C
140 °C
This results supports our understanding that more volatile material partition into SOA at high mass concentrations.
My talk will be about SOA: How does it look like?
• Residence time effect: At the same temperature a higher residence time allows further volatilisation (Woo et al., 2007): Oven of my VTDMA not well suited to study volatility of a specific compound.

• At a specific temperature, the VFR increase with time i.e. the particles become less and less volatile: This can be explained either by oligomerisation or oxidation or both.
At 140 ºC, the hygroscopicity of the remaining particle is a bit lower, within the error bar.
Need to show size and correct for Kelvin effect....
With 90 nm particle
Is it due to Kelvin effect?
Error Plot

- **VFR [%]**
- **Bulk GF at 95 %**

**Temperature Experienced**
- $T = 25^\circ C$
- $T = 100^\circ C$
- $T = 2 \times 100^\circ C$
- $T = 120^\circ C$
- $T = 140^\circ C$

**Time after lights on [hours]**

![Error Plot](image_url)
HTDMA Principle

GF(RH) = \frac{\text{Size at a certain RH}}{\text{Size when it is dry}}

Allowed accurate measurement up to 95% RH
Critical Supersaturation?  

GF, size influence
Continual increase of the growth factor with time during 20 hours,
Oxidation processing
Typical Experiment

Gas phase

Particle phase
• Continuous increase of the growth factor during 20 hours (Oxidation)

• No size dependence of hygroscopic growth
  (also observed for α-pinene and isoprene)
• Why do not you use longer residence time?
  – We would like to study the oligomere, not the monomers out of the oligomere destroyed by the Oven (Woo Jin An paper)
  – We would like to avoid polymerisation artifact which could also occurs in the oven. For example Methyl glioxide in an oven for polymers. (Ref???)

• Are the VFR measured absolute value?
  – No because not enough residence time. But can be use as a relative value.

• Oven change properties of aerosol??
• Sulfate influence the hygroscopicity??
Remaining Question and informations

• Does Oligomeres hydrolyse at 95% RH
• Polygomeres are made from assembling monomereres. During this assembling, monomereres loss Oxygen (H2O is released).
Remember list

- Talk about Woo Jin An residence time studies (read the paper...)
- Show one graph with VFR and GF vs temperature
POA emission factor decreases with increasing dilution i.e. the AMF decreases

POA EF are determined at low dilution → if dilution takes place a new volatility distribution is formed.

Red: POA as measured
Hatched: one assumes that there are IVOCs between the non-volatiles (POA) and the highly volatile species (e.g. toluene)