Kinetic modelling of secondary organic aerosol (SOA) formation: connecting the data points
Fundamental Secondary Organic Aerosol (SOA) Properties

**Volvatility & Partitioning**

- **High mass loading**
  - Low T → High T
  - Low loading → High loading

- **Viscosity**
  - Low RH → High RH
  - Low T → High T
  - Solid → Semi-solid → Liquid

Koop et al. PCCP (2011)
Consequences of SOA Properties

Equilibrium Partitioning

Case: Outside Sink

Non-Equilibrium Partitioning
(viscous particle)

Equilibrium Partitioning + Oligomerization

= semi-volatile molecule
Feedback & Interaction Between SOA Properties

Volatility & Partitioning

Viscosity

Oligomerization
Interactions of Physical-Chemical Properties of SOA

Inverse Modelling

Kinetic Model
microscopic properties

Chamber Experiments
macroscopic observables
Aerosol Particle:
Multiphase Chemical System

Complications for treatment of SOA formation:

- Particle growth leads to imbalance in layer sizes.
- Evolving concentration gradients require high initial layer count.
- Low computational efficiency.

KM-GAP (Shiraiwa ACP 2012)
Aerosol Particle: Multiphase Chemical System

**New:** Adaptive Layer Splitting and Merging Scheme *(size and gradient)*
Modelling Strategy for SOA Chamber Experiments

**Kinetic Model**

- $[Z]_{g}$ \rightarrow $[Z]_{g}$
- $[Z]_{gs}$
- $[Z]_{b1}$ \rightarrow $[Z]_{b1}$
- $[Z]_{b2}$ \rightarrow $[Z]_{b2}$
- $[Z]_{b3}$ \rightarrow $[Z]_{b3}$
- $[Z]_{b4}$ \rightarrow $[Z]_{b4}$
- $[Z]_{bk}$ \rightarrow $[Z]_{bk}$
- $[Z]_{bn}$ \rightarrow $[Z]_{bn}$

**Chemical Mechanism** (semi-explicit)

- $[Z]_{g}$
- $[Z]_{gs}$
- $[Z]_{b1}$
- $[Z]_{b2}$
- $[Z]_{b3}$
- $[Z]_{b4}$
- $[Z]_{bk}$
- $[Z]_{bn}$

**Volatility**

- bin1
- bin2
- bin3
- bin4
- bin5
- bin6

**KM-GAP 2.0**

- dimers (0-2 nitrate groups)
- oligomers
Key Model Parameters and Global Optimization Algorithm

Model Parameters

- Volatility basis set
- Gas-phase wall loss rate: $k_{\text{wall}} \sim 0.25 \text{ h}^{-1}$
- Enthalpy of vaporization
- Oligomerization rate
- Viscosity

MCGA - Global Optimization Algorithm (Inverse Modelling Approach)

Monte Carlo sampling

- Randomly sampled parameter sets

Genetic Algorithm

- Parameter sets: Parameter set 1, Parameter set 2, ..., Parameter set N
- Survival
- Recombination
- Mutation

Goodness of fit

Environmental Chamber Experiments

Georgia Tech Environmental Chamber

12 m³ Teflon bag

Reaction System

NO$_3$ oxidation via injection of N$_2$O$_5$

(+)-α-pinene

limonene

Conditions

< 5 % RH

(NH$_4$)$_2$SO$_4$ seed

Instruments

HR-ToF-AMS

HR-FIGAERO-CIMS

SMPS

Sally Ng
Environmental Chamber Experiments

<table>
<thead>
<tr>
<th>Formation</th>
<th>Evaporation</th>
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<tbody>
<tr>
<td>1. limonene $\rightarrow$ NO$_3$</td>
<td></td>
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<tr>
<td>2. $\alpha$-pinene $\rightarrow$ NO$_3$</td>
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<tr>
<td>3. $\alpha$-pinene + limonene $\rightarrow$ NO$_3$</td>
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<tr>
<td>4. $\alpha$-pinene $\rightarrow$ NO$_3$ $+$ limonene $\rightarrow$ NO$_3$</td>
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Temperature Profile

Temperature (°C) vs. Time

1. α-pinene
2. Limonene
Model simulations with well-mixed particle phase:

**Reversible oligomerization** can explain differences.

Limonene SOA more oligomerized than α-pinene SOA.
Mixed Precursor Experiments – Well-mixed Particle Phase

3 SIMULTANEOUS OXIDATION

4 SEQUENTIAL OXIDATION

Evaporation rate is not reproduced in mixed precursor simulations

Is limonene SOA slowing down α-pinene SOA evaporation?
(A) SOA formation is not strongly affected by viscous phase state.

(B) Semi-volatile molecules take longer to evaporate / are trapped inside.

(C) Diffusion barrier could increase over time due to crust formation.
Elevated viscosity can explain slow evaporation of SOA.

Application of Stokes Einstein equation yields viscosity of $10^8 \text{ Pa s}$, typical for $\alpha$-pinene SOA.
SEQUENTIAL EXPERIMENT: Core-Shell Morphology?

Constant Diffusivity

Oligomerization-Dependent

Scenarios are indistinguishable with the current set of input data.
Secondary Organic Aerosol (SOA) formation from monoterpene precursor mixtures can be described using kinetic multi-layer models, but the gas-phase chemical mechanism has to be simplified.

**SOA partitioning** can occur as non-equilibrium process, either due to formation of oligomers or viscous phase state.

**SOA yields** were mostly unaffected by mixing precursors in this study, but evaporation behavior was strongly affected.

Oligomerization and diffusion effects are difficult to separate from looking at SMPS data. There is a need to combine different experimental techniques to solve this puzzle.
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