Atmospheric Organic Aerosols

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Measurements downwind of urban sources of aerosol particles and precursor gases have shown that the mass concentration of secondary organic aerosol (SOA) can be several-fold greater than can be explained on the basis of current model calculations using observed precursor concentrations. ASR will continue conducting laboratory experiments on both gas-phase and aqueous-phase SOA formation to characterize the particle formation and the organic gases that react to form new organic aerosol material on aerosol seeds. ASR will use these experiments to guide the development of comprehensive chemical mechanisms... to guide the development of parameterizations that are simple enough to be applied to aerosol life cycle models.
Organic Mass
Sulfate Mass
Ammonium Mass
Nitrate Mass
Chloride Mass

Organics Contribute Significantly to Mass of Fine Aerosol

Organic Sources = Primary + SECONDARY

~ 70–90%

Zhang et al., GRL [2007]
Global Organic Aerosol Mass

Total Flux of Non-Methane Hydrocarbons to the atmosphere $\sim 1350$ Tg/y

Percent that condenses into particles directly $\sim 1$

Percent of the global NMHC flux to organic aerosol $\sim 10$

Conclusion: $\sim 90\%$ of organic aerosol comes from oxidation of NMHC (Secondary Organic Aerosol)

Of total global aerosol mass $\sim 50\%$ is organic

Goldstein and Galbally, ES&T (2007); Donahue et al., AE (2009)
Secondary Organic Aerosol (SOA) Formation

**VOC Examples:**
- Aromatics (e.g., Toluene)
- Monterpenes ($C_{10}H_{16}$)
  - $\alpha$-pinene
- Sesquiterpenes ($C_{15}H_{24}$)
  - $\beta$-caryophyllene

This Process is Studied in Laboratory Chambers

SOA Yield = $\Delta M_o / \Delta VOC$

$\Delta M_o$ = organic mass produced ($\mu g/m^3$)

$\Delta VOC$ = mass of reacted VOC ($\mu g/m^3$)
Primary vs. Secondary Organic Aerosol

- **Primary (POA):**
  - Directly emitted
  - Traditionally considered non-volatile and
  - Non-reactive

- **Secondary (SOA)**

  ![Chemical structures](image)

  \[\text{atmospheric oxidation}\]

  condensable products
Semivolatile Emissions

Shrivastava et al., *JGR* [2008]

Robinson et al., *Science* [2007]
Low-Volatility Organics

There is a large potential for low-volatility organics (\( C^* < 10^6 \mu g/m^3 \)) to form organic aerosol.

- **SVOCs**: Semivolatile Organic Compounds (\( C^* < 10^4 \))
- **IVOCs**: Intermediate Volatility Organic Compounds (\( 10^4 < C^* < 10^6 \mu g/m^3 \))
- **SVOCs**: Semivolatile Organic Compounds (\( C^* < 10^4 \))

Station fire from Roof Lab, Caltech 2009
SVOC and IVOC Emissions

- SVOC Emissions: 66% (Biomass Burning), 25% (Biofuel Burning), 9% (Anthropogenic (fossil fuel) burning)
- IVOC Emissions: 39%, 22%, 39%

Color scale: 0 to >10.0 x10^10 atomsC/cm²/s
Isoprene \((\text{C}_5\text{H}_8)\)

- Highest emissions among all non-methane hydrocarbons \((\sim 600 \text{ Tg/year})\) [Guenther et al., 2006]

- Photooxidation of isoprene leads to SOA formation, with complex behavior depending on the \(\text{NO}_x\) level and \(\text{NO}_2/\text{NO}\) ratio
Biogenic Hydrocarbons

Acyclic Triolefins
- Myrcene
- Ocimene

Oxygenated Terpenes
- Linalool
- Terpinene-4-ol

Bicyclic Olefins
- Δ^3-Carene
- α-Pinene
- β-Pinene
- Sabinene

Cyclic Diolefins
- Limonene
- α-Terpinene
- γ-Terpinene
- Terpinolene

Sesquiterpenes
- β-Caryophyllene
- α-Humulene
Aromatic Hydrocarbons

- m-xylene
- o-xylene
- p-xylene
- toluene
- ethylbenzene
- 1,2,4-trimethylbenzene
- 1,3,5-trimethylbenzene
- n-propylbenzene
- 1-methyl-3-n-propylbenzene
- 1,2-dimethyl-4-ethylbenzene
- 1,4-dimethyl-2-ethylbenzene
- 1,2,4,5-tetramethylbenzene
- p-dimethylbenzene
- m-ethyltoluene
- o-ethyltoluene
- p-ethyltoluene
- 1,2,3,5-tetramethylbenzene
General Mechanism of SOA Formation and Evolution

$S_{i}^{g}$: $i^{th}$-generation semi-volatile products in the gas phase
$S_{i}^{p}$: $i^{th}$-generation semi-volatile products in the particle phase
$N_{i}^{p}$: $i^{th}$-generation non-volatile products in the particle phase (e.g. semi-solid)
Peroxy radical chemistry

VOC

RO/ROH/R'=O

RO\textsubscript{2}

RO\textsubscript{2} \rightarrow OH/O_3/NO_3

Low-NO_x

ROOH + O_2

High-NO_x

Fragments/Carbonyls

RO + NO\textsubscript{2}

RONO\textsubscript{2}

RO

Reverse NO_x effect:

• Small alkoxy radical easily fragmented
• Organic nitrates relatively volatile
• Peroxides: important SOA components
Photooxidation of $C_{12}$ Alkanes

- Compounds studied:

  - Cyclododecane: $C_{12}H_{24}$
  - Hexylclohexane: $C_{12}H_{24}$
  - Dodecane: $C_{12}H_{26}$
  - 2-Methylundecane: $C_{12}H_{26}$

- Experimental conditions:

  - Ammonium sulfate seed; $T \sim 25^\circ C$, RH<5%
  - Low-NO$_x$ experiments: $H_2O_2 + h\nu \rightarrow 2OH$
  - High-NO$_x$ experiments: HONO + $h\nu \rightarrow OH + NO$
SOA Formation from C\textsubscript{12} Alkanes as an Illustration of the Nature of Multi-generation Oxidation

1st-generation products [Functional groups from Master Chemical Mechanism (MCM) University of Leeds]

The upper limit of $n_c$ should be the same as parent VOC.

The lower limit of $n_c$ lies in the domain of semi-volatile compounds.

The possible carbon number after multi-generation oxidation lies in the range between upper and lower limits.

3 products in 1st generation ($10 \leq n_c \leq 12$)
C\textsubscript{12} Alkanes – 2\textsuperscript{nd} Generation

The upper limit of \( n_c \) should be the same as parent VOC.

The lower limit of \( n_c \) lies in the domain of semi-volatile compounds.

The possible carbon number after multi-generation oxidation lies in the range between upper and lower limits.

7 products in 2nd generation
\( (8 \leq n_c \leq 12) \)
C_{12} Alkanes – 3^{rd} Generation

The upper limit of n_c should be the same as parent VOC.

The lower limit of n_c lies in the domain of semi-volatile compounds.

The possible carbon number after multi-generation oxidation lies in the range between upper and lower limits.

9 products in 3rd generation (6 \leq n_c \leq 12)
Carbon Number Range

\[ M_0(0) = 1 \mu g/m^3 \]
2-D mapping of SOA: Oxidation state vs. volatility

“volatility class” | ELVOC | LVOC | SVOC | IVOC | VOC

Donahue et al., ACP, 2011
Caltech Laboratory Chambers

- 2 Teflon chambers, 28 m³ each
- Scanning differential mobility analyzer (DMA): particle size distribution, volume
- GC-FID: hydrocarbon and NOₓ, O₃, RH, T
- CIMS and GC-TOFMS: gas-phase organics
- Aerodyne Aerosol Mass Spectrometer (AMS): on-line particle mass, composition
- Particle into Liquid Sampler coupled to IC (PILS/IC): organic and inorganic ions
- Teflon filters: off-line chemical analysis
  - UPLC/ESI-high resolution-TOFMS:
    - mass resolution ~ 12 000
    - accurate mass measurements (elemental compositions)
  - HPLC/ESI-Linear Ion Trap MS:
    - tandem MS measurements
    - structural elucidation & confirmation
  - GC/Ion Trap MS with prior derivatization
Dodecane Low-NO\textsubscript{x} Oxidation

Channel 1

\[ \text{Dodecane} \xrightarrow{\text{OH, O}_2} \text{OOH} \]

\[ \xrightarrow{\text{OH}} \text{OOH} \]

\[ \xrightarrow{\text{OH, O}_2, \text{HO}_2} \text{OOH} \]

\[ \text{decomposition} \]

\[ \xrightarrow{\text{O}_2} \text{O}_2 \]

\[ \xrightarrow{\text{O}_2, \text{HO}_2} \text{OOH} \]

Channel 2a

\[ \text{OOH} \xrightarrow{\text{OH, O}_2, \text{HO}_2} \text{OOH} \]

\[ \text{decomposition} \]

\[ \xrightarrow{\text{O}_2, \text{HO}_2} \text{OOH} \]

\[ \text{rev. isom} \]

\[ \xrightarrow{\text{OH}} \text{HOO} \]

\[ \xrightarrow{\text{OH}} \text{products} \]

Channel 2b

\[ \text{OOH} \xrightarrow{\text{hv}} \text{OOH} \]

\[ \text{isomerization} \]

\[ \xrightarrow{\text{OH}} \text{OH} \]

\[ \xrightarrow{\text{O}_2, \text{HO}_2} \text{OOH} \]

\[ \text{rev. isomerization} \]

\[ \xrightarrow{\text{OH}} \text{products} \]

Channel 3

\[ \text{OOH} \xrightarrow{\text{hv}} \xrightarrow{\text{O}_2, \text{HO}_2} \text{OOH} \]

\[ \xrightarrow{\text{OH}} \text{OH} \]

\[ \xrightarrow{\text{O}_2, \text{HO}_2} \text{OOH} \]

\[ \text{cyclization} \]
Mechanism and CIMS measurement: Carbonyl formation

[Graph showing the relationship between hours from lights on and concentration (ppb) of CARB, C_{12}H_{24}O, and CIMS (+) m/z = 223. The graph includes a line representing CARB, C_{12}H_{24}O, and a scatter plot of CIMS (+) m/z = 223 with a chi-squared value of 12.61. OH Exposure (molec cm^{-3} hr) is on the x-axis, and Concentration (ppb) and CIMS Signal (a.u.) are on the y-axes.]
Mechanism and CIMS measurement: Carbonyl hydroperoxide
Mechanism and CIMS measurement:
Acid formation
Carbon Balance

Majority of initial carbon ends up as $\geq 4^{th}$ generation compounds.
Van Krevelen Diagram - H:C vs. O:C for Organic Aerosol

- **Heald et al., GRL, 2010** showed a slope of -1 for ambient and laboratory data.
- **Ng et al., ACP 2011** showed a slope of -0.5 for ambient aerosol.
- **Chhabra et al., ACP 2011** showed how atmospherically relevant SOA chamber studies, when averaged, show similar slope on VK diagram as ambient aerosol.
- **Lambe et al., ACP 2011** present how PAM flow tube data has slope that is consistent with chamber and ambient data, and then extends the range for very high H:C/lowO:C to lower H:C/highO:C.
Low-NO$_x$ Alkane SOA

- Cumulative OH exposure for Low NO$_x$: 70-100 x10$^6$ molec. cm$^{-3}$ min
• SV-OOA has larger variability in $f_{43}$; Increasing photochemical age collapses variability, OOA components become increasingly similar to each other
• $f_{44}$ of the LV-OOA components similar to those from HULIS collected in filter samples
• Increasing photochemical age: increasing O/C, 44/43 ratio

Ng et al., ACP (2010)
Degree of oxidation obtained in chamber studies

Aromatic hydrocarbons

Photooxidation/heterogeneous oxidation of POA

Ng et al., ACP (2010)
This degree of chemical specificity is not possible in atmospheric models (even if all the reactions were known)
Cappa and Wilson Statistical Oxidation Model

- Oxidation kinetics in a multi-dimensional space defined by $n_C$ and $n_O$
- Tunable parameters:
  1. Avg # of O atoms added/reaction
  2. Decrease in volatility/O added
  3. Probability that a given product fragments

$$P_{\text{frag}} \text{ (per reaction)} = c_{\text{frag}} N_O$$

or

$$P_{\text{frag}} \text{ (per reaction)} = (N_O/N_C)^m$$

Random probability for location of C-C bond scission or only C1 species

Cappa and Wilson, ACPD (2012)
Statistical Oxidation Model

\[ C_nH_m + OH \rightarrow \text{products} + OH \rightarrow \text{more products} \]

“Lump” products by atomic composition (C & O atoms)

Three tunable parameters:
1. # of oxygen atoms added per reaction: \{1O, 2O, 3O, 4O\}
2. Mean decrease in \( \log C^* \) per oxygen added
3. Probability of fragmentation (w/ random fragments)

Cappa and Wilson, ACPD (2012)
Equilibrium Partitioning Theory

Cappa and Wilson, Submitted to ACP
Increasing Oxidation

Statistical Oxidation Model: With Fragmentation

2-D distributions of “molecules” in particle phase

Actual distribution depends on tunable parameters
Model vs. Measurement: $C_{OA}$ and O:C

Dodecane + OH

![Graphs showing COA and O:C atomic ratio over time for Low NOx and High NOx conditions.](image-url)

- $C_{OA}$ (observed)
- O:C (observed)
- Model #1
- Model #2

COA (µg m$^{-3}$)

O:C Atomic Ratio

[HC]/[HC]$_0$

Time (minutes)

Low NOx

High NOx
Model Results: Volatility and Fragmentation

\[ P_{\text{frag}} = c_{\text{frag}} \times N_{\text{oxygens}} \]
High NO$_x$ adds more oxygens per reaction than low NO$_x$.
Secondary Organic Aerosol (SOA) Formation: Phase State of Particles

Recent evidence for semi-solid behavior of SOA

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<th>Authors</th>
<th>SOA Type</th>
<th>Phenomena</th>
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<td>Vaden et al., <em>PNAS</em> (2010, 2011)</td>
<td>α-pinene SOA, ambient SOA</td>
<td>Delayed evaporation upon dilution → coated SOA, non-liquid like behavior</td>
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<tr>
<td>Shiraiwa et al., <em>PNAS</em> (2011)</td>
<td>O$_3$ uptake by amorphous protein and oxidative aging in flow tube</td>
<td>Kinetically limited by bulk diffusion</td>
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Secondary Organic Aerosol Formation and Aging

• SOA formation is characterized by multi-generational chemistry that involves both functionalization and fragmentation reactions, leading to higher oxidation state and lower volatility. NOx level is key.

• The relative importance of gas-phase oxidation vs. particle-phase reactions is not well established for most SOA-forming organic compounds.

• Laboratory chamber experiments remain the “gold standard” for studying SOA formation; both gas and particle phase mass spectrometry is crucial. Chamber SOA tends not to be as oxidized as ambient (loading effect, OH exposure?).

• A new frontier in SOA research involves understanding the importance of the particle phase state, e.g. multiple liquid phases in equilibrium, liquid-solid equilibrium, and the formation of semi-solid phases.

• Apply the new generation of SOA models to chamber data and implement into atmospheric models.
Alkane Photooxidation Chemistry
Semi-Explicit Chemical Modeling

Lumped Chemical Mechanism (e.g. SAPRC-07 and CBM-05)

NO\textsubscript{x}, NO\textsubscript{y}, HO\textsubscript{x}, O\textsubscript{3}, OVOC

SOA Parent Dynamics

Kinetic Model of SOA Formation, tuned to chamber data, volatility and aging chemistry

SOA mass concentration $n_{C}$, oxidation state O:C H:C