Secondary and Regional Contributions to Organic PM

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With Contributions from:
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Objective

Conduct controlled laboratory experiments investigating secondary organic aerosol (SOA) formation through cloud processing

In the Process

• Consider whether experiments suggest “source tracers” or “process indicators” to aid field investigations of SOA

• Examine Pittsburgh Supersite data for evidence of SOA formation through cloud processing

• Provide kinetic/mechanistic data needed to refine SOA models
In-Cloud SOA Formation

- Organic gases are oxidized (e.g., in interstitial spaces of clouds) to water-soluble compounds.
- Water-soluble gases partition into cloud droplets and oxidize further (e.g., by ·OH formed photochemically).
- Low volatility products remain in the particle phase upon cloud evaporation, contributing secondary organic aerosol (SOA), especially in FT (Blando and Turpin, 2000; Geleneser and Varga, 2005)
Evidence for In-Cloud SOA

*Organic PM Concentrations Aloft*

- Heald et al., 2005 (ICART): Organic PM concentrations in FT exceed current model predictions (i.e., without in-cloud SOA).
- **Polidori et al., 2006 (Pittsburgh)**; Lim and Turpin, 2002 (Atlanta): Elevated ground level SOA with down-mixing of air from aloft.

*Oxalic Acid Concentration Dynamics*

- Heald et al., 2006; Chebbi and Carlier, 1996; Yu et al., 2005; Kawamura et al., 1993: Concentration dynamics link oxalic acid with potential aqueous precursor aldehydes or with sulfate (formed through cloud processing).
- Sorooshian et al. 2006 (ICART); 2007(MACE); Crahan et al., 2004: In-cloud organic acid measurements/simulations suggest oxalic acid is formed through cloud processing.

*Cloud Chemistry Modeling*

- Warneck, 2003; Ervens et al., 2004; **Lim et al., 2005**: predict in-cloud organic acids and SOA from emissions
Lim Cloud Chemistry Model (to guide experiments):

**Gas phase**

- **ISOPRENE** + oxidants (·OH, O₃, NO₃)
  - HOCH₂CHO (glycolaldehyde)
  - CHOCHO (glyoxal)
  - CH₃COCHO (methylglyoxal)

- **Phase transfers**
- **Rxs with ·OH**
  - HOCH₂CH(OH)₂
  - HOCH₂COOH (glycolic acid)
  - (OH)₂CHCH(OH)₂
  - (OH)₂CHCOOH (glyoxylic acid - hydrated)
  - HOOCOOH (oxalic acid)

- **Aqueous phase**
  - CO₂
  - HCOOH (formic acid)
  - CH₂(OH)₂ (formaldehyde - hydrated)
  - CH₃COOH (acetic acid)
  - CH₃COCOOH (pyruvic acid)

Lim et al., 2005
**Ervens Model:** aqueous methylglyoxal and pyruvic acid photo-oxidation does not form low volatility organic acids

\[
\begin{align*}
\text{CH}_3\text{COCHO} & \quad \text{(methylglyoxal)} \\
\text{CH}_3\text{COCH(OH)}_2 & \\
\text{CH}_3\text{COCOOH} & \rightarrow \text{CH}_3\text{COCOOH} \\
& \quad \text{(pyruvic acid)} \\
& \downarrow \\
\text{CH}_3\text{COH} & \leftrightarrow \text{CH}_3\text{COH} \\
& \quad \text{(acetaldehyde)}
\end{align*}
\]
Predicted In-Cloud SOA Concentrations:
(Ervens et al., 2004; Lim et al., 2005)

- 10 – 25% of measured oxalic acid formed from aqueous reactions with methylglyoxal, glyoxal and glycolaldehyde (clean – polluted continental)

- Oxalic acid remains mostly in the particle phase upon droplet evaporation, forming SOA.

- Additional precursors

- Additional low volatility organics

- Aqueous photooxidation pathways/products largely assumed

- Predicted products had not been verified experimentally
Objective:
Validate and refine aqueous-phase reaction pathways and improve kinetics

Approach:
Conduct aqueous-phase photooxidation experiments, measure products, model product formation

Organic + H₂O₂ + UV (plus controls)

To provide supply of ·OH
Results: Oxalic acid is formed from GLY, MG, PA

<table>
<thead>
<tr>
<th>Organic</th>
<th>Glyoxal</th>
<th>Methylglyoxal</th>
<th>Pyruvic Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc. (N)</td>
<td>2 mM (3)</td>
<td>2 mM (3)</td>
<td>10 mM (3)</td>
</tr>
<tr>
<td>H$_2$O$_2$</td>
<td>10 mM</td>
<td>10 mM</td>
<td>20 mM</td>
</tr>
<tr>
<td>pH*</td>
<td>4.1 - 4.8</td>
<td>4.2 – 4.5</td>
<td>2.7</td>
</tr>
</tbody>
</table>

Experiment: ORG+UV+$\text{H}_2\text{O}_2$

UV Control: ORG+ $\text{H}_2\text{O}_2$

$\text{H}_2\text{O}_2$ Control: ORG+UV

Organic Control: UV+$\text{H}_2\text{O}_2$

*Typical cloud/fog pH 2-5; Catalase to stop reactions; Samples frozen
Carlton et al., 2006; Altieri et al., 2006; Carlton et al (2007)
Pyruvic Acid Results:

**Gas phase**

**ISOPRENE + oxidants (·OH, O₃, NO₃)**

- HOCH₂CHO (glycolaldehyde)
- CHOCHO (glyoxal)
- CH₃COCHO (methylglyoxal)

**Aqueous phase**

- HOCH₂CH(OH)₂ (glycolic acid)
- (OH)₂CHCH(OH)₂
- CH₃COCH(OH)₂
- (glyoxylic acid - hydrated)
- (formaldehyde - hydrated)
- HOOCCOOH (oxalic acid)
- CH₂(OH)₂

**Phase transfers**

- Rxs with ·OH

Carlton et al., 2006
Electrospray Ionization Mass Spectrum (ESI-MS): Mixed Standard of Pyruvic Acid and Predicted Products

ESI: soft ionization, does not fragment

positive mode protonates cmpds with basic functional groups MW+1

negative deprotonates cmpds with acidic functional groups MW-1

- **Oxalic**: 89
- **Pyruvic**: 87
- **Glyoxylic**: 73
- **Pyruvic**: 175
ESI-MS Spectrum of Pyruvic Acid Experiment (t=202 min): Regular Distribution of Oligomer System

Lim mechanism is incomplete; oxalic acid and larger MWt (oligomers) form

Altieri et al., 2006
Oxalic acid and oligomers form.
Both are likely to contribute to SOA after droplet evaporation.
Glyoxal:

LIM MODEL: Glyoxal $\rightarrow$ Glyoxylic Acid $\rightarrow$ Oxalic Acid

Lim model reproduces $\text{H}_2\text{O}_2$ in reaction vessel but poor prediction of oxalic acid ($r^2 = 0.001$) meas. glyoxylic acid cannot explain oxalic acid formation
Glyoxal Results - ESI-MS:

Mixture standard containing the precursor and products that are predicted by initial model

The spectrum we would expect if the initial mechanism were complete
Glyoxal Results: ESI-MS

- Glyoxal rapidly destroyed
- Spectral “complexity” develops that cannot be explained by initial mechanism
- (large compounds with alcohol/aldehyde (pos) and acid (neg) functionalities)
- “Complexity” in positive and negative modes dissipates ~ 30-40 min
- oxalic acid formed (dominates 150 min spectrum)
Glyoxal Results: ESI-MS

Glyoxal $\rightarrow$ Glyoxylic Acid $\rightarrow$ Oxalic Acid

Retention Time (min)

Absorbance (mAU)

- Oxalic acid
- Glyoxylic acid
- Formic acid
- Unresolved carbon (large, multifunctional, alcohol or acid functionalities)
Expanded Glyoxal Photooxidation Mechanism

- (OH)$_2$CHCH(OH)$_2$ (glyoxal-hydrated)
- (OH)$_2$CHCOOH (glyoxylic acid-hydrated)
- HOOCCOOH (oxalic acid)
- HCOOH (formic acid)
- CO$_2$

Reactants:

- a: $k = 3 \times 10^7$
- b: $k = 1.1 \times 10^8$
- c: $k = 5 \times 10^3$

Large multifunctional compounds

\[ \cdot \text{OH} \]
**Glyoxal → Formic Acid**

- Not identified as an aqueous-phase glyoxal oxidation product in the atmospheric chemistry literature


\[
\begin{align*}
\text{glyoxal hydrated} & \quad \rightarrow \quad \text{glyoxylic acid} \\
\text{glyoxylic acid} & \quad \rightarrow \quad \text{formic acid}
\end{align*}
\]
Expanded Glyoxal Photooxidation Mechanism

\[
\begin{align*}
\text{(glyoxal-hydrated)} & \quad \text{(glyoxylic acid-hydrated)} & \quad \text{(oxalic acid)} & \quad \text{(formic acid)} & \quad \text{CO}_2 \\
\text{(H}_2\text{O}_2 \cdot \text{OH)} & \quad \text{(H}_2\text{O}_2 \cdot \text{OH)} & \quad \text{(H}_2\text{O}_2 \cdot \text{OH)} & \quad \text{(H}_2\text{O}_2 \cdot \text{OH)}
\end{align*}
\]

- \( a \): \( k = 3 \times 10^{10} \)
- \( b \): \( k = 1.1 \times 10^8 \)
- \( c \): \( k = 5 \times 10^3 \)
Measurements and Predictions Using Expanded Mechanism

Meas/Modeled glyoxylic acid <MDL. Only 1% of oxalic acid from glyoxal → glyoxylic acid → oxalic acid pathway. Large multifunctional products important to oxalic acid formation and contribute to SOA themselves.

Reaction Vessel Max:
- 0.02 g Oxalic / g Glyoxal (90 min)
- 0.3 g MF cmpd / g Glyoxal (30 min)

Carlton et al., 2007
Methylglyoxal Results:

• “haystacks” with regular pattern of mass differences; oligomer system

• Like pyruvic acid experiments (MG itself not involved)

• Structure not seen in mixed stds (not artifact)

• No oligomers in controls (·OH involved)
Methylglyoxal:

\[
\begin{align*}
H_3C-\text{C-C}-\text{C-H} + \cdot\text{OH} & \rightarrow H_3C-\text{C-}^{\ddagger}\text{-C-H} \\
\text{methylglyoxal hydrated} & \rightarrow H_3C-\text{C-OH} + H-C-OH
\end{align*}
\]

Formic and acetic acid form directly
Insufficient glyoxylic to explain oxalic
Oligomers involved in oxalic
Oligomers and oxalic → SOA
Expanded Methylglyoxal Mechanism

\[
\text{CH}_3\text{COCH(OH)}_2 \quad \text{(Methylglyoxal-hydrated)}
\]

\[
\text{(OH)}_2\text{CHCOOH} \quad \text{(glyoxylic acid-hydrated)}
\]

\[
\text{HOOC COOH} \quad \text{(oxalic acid)}
\]

\[
\text{CH}_2\text{(OH)} \quad \text{(formaldehyde-hydrated)}
\]

\[
\text{HCOOH} \quad \text{(formic acid)}
\]

\[
\text{CO}_2
\]

Initial - Lim

Expanded - experiments

Oligomers
Methylglyoxal Results: OM/OC = 1.0-2.5 (avg 1.9) for m/z >300

FT-ICR provides exact elemental comp. >300 m/z

OM/OC comparable to cloud water, regional aerosol. Lower than organic acids

OM/OC comparable to cloud water, regional aerosol. Lower than organic acids
Cloud parcel model: Isoprene with/without cloud chemistry. Barbara Ervens Collaboration (see poster)

Gas phase chemistry + uptake only

With cloud chemistry

- Cloud chemistry yields ~ 0.5 - 5%
- Approximately doubles SOA
CMAQ runs: Annmarie Carlton Collaboration (see poster)
With and without in-cloud SOA formation (using Yields of 4 to 30%)

SOA from cloud processing – Eastern United States
Experimental Findings:

Oxalic acid forms from glyoxal/methylglyoxal in aqueous-phase

Oligomers and other large multifunctional compounds also form

Thus, SOA will form through cloud processing

Large multifunctional compounds (including oligomers) appear to play a role in oxalic acid formation

Experiments used to validate and refine reaction pathways/kinetics

This work demonstrates a linkage between marine, biogenic and anthropogenic precursors of glyoxal, methylglyoxal and pyruvic acid (including isoprene) and in-cloud SOA formation
Future Directions

Use mass spectroscopic tools to better understand:

- The structure and properties of oligomers
- Oligomer formation and degradation

Pursue continued methylglyoxal model improvements:

- Through improved understanding of oligomers
- Through experiments with intermediates

Incorporate this process into atmospheric models:

- Chemical and Cloud parcel models: kinetics to atmospheric yields and parameterizations
- Air quality and climate models: Magnitude and implications
Acknowledgements

**Past/present Students, Postdocs**
- Annmarie Carlton
- Katie Altieri
- Yi Tan
- Mark Perri
- Ho-Jin Lim
- Adam Reff

**Collaborators**
- Sybil Seitzinger
- Barbara Ervens
- Jeehuin Lee
- John Reinfelder

**Support**
- U.S. EPA – STAR
- NSF

**Related Modeling Studies**
- CMAQ poster - Carlton
- Cloud parcel poster - Ervens