Secondary and Regional Contributions to Organic PM

Barbara J. Turpin
Rutgers University

With Contributions from:
Anmari Carlton, Katy Altieri, Sybil Seitzinger, Barbara Ervens, Ho-Jin Lim, Yi Tan, Mark Perri
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
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; Gelencser 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**

- **HOCH₂CH(OH)₂** → **(OH)₂CHCH(OH)₂** (67%)
- **HOCH₂COOH** (glycolic acid)

**Rxs with ·OH**

- **(OH)₂CHCOOH** (glyoxylic acid - hydrated)
- **CH₃COOH** (acetic acid)
- **CH₂(OH)₂** (formaldehyde - hydrated)
- **HCOOH** (formic acid)

Aqueous phase:

- **HOOC-COOH** (oxalic acid)
- **CO₂**

Lim et al., 2005
**Ervens Model**: aqueous methylglyoxal and pyruvic acid photo-oxidation does not form low volatility organic acids
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>H2O2</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+H2O2**
- **ORG+ H2O2**
- **ORG+UV**
- **UV+H2O2**

*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**

- Phase transfers
- Rxs with ·OH

**Reactions:**

- HOCH₂CH(OH)₂ → (OH)₂CHCH(OH)₂ (67%)
- HOCH₂COOH → (OH)₂CHCOOH (8%)
- CH₃COCH(OH)₂ → CH₃COCH(OH)₂ (92%)
- HOOCCOOH → CH₂(OH)₂ (15%)
- CO₂ → HCOOH (formic acid)

**Products:**

- (glycolaldehyde)
- (glyoxal)
- (methylglyoxal)
- (glycolic acid)
- (glyoxylic acid - hydrated)
- (acetic acid)
- (oxalic acid)
- (formaldehyde - hydrated)

**References:**

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
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

- Oxalic acid
- Glyoxylic acid
- Formic acid
- Unresolved carbon (large, multifunctional, alcohol or acid functionalities)

Retention Time (min):
- $t = 0$ mins.
- $t = 2$ mins.
- $t = 32$ mins.
- $t = 61$ mins.
- $t = 146$ mins.
Expanded Glyoxal Photooxidation Mechanism

\[
\begin{align*}
\text{(glyoxal-hydrated)} & \quad \text{(glyoxylic acid-hydrated)} & \quad \text{(formic acid)} \\
\text{(oxalic acid)} & \quad \text{CO}_2
\end{align*}
\]
Glyoxal $\rightarrow$ Formic Acid

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

Expanded Glyoxal Photooxidation Mechanism

- \((\text{glyoxal-hydrated})\): \((\text{OH})_2\text{CHCH(OH)}_2\)
- \((\text{glyoxylic acid-hydrated})\): \((\text{OH})_2\text{CHCOOH}\)
- \((\text{oxalic acid})\): \(\text{HOOCCOOH}\)
- \((\text{formic acid})\): \(\text{HCOOH}\)
- \((\text{carbon dioxide})\): \(\text{CO}_2\)

Reactions:

- Reaction a: \(\cdot\text{OH} \rightarrow \text{large multifunctional compounds}\)
  - Rate constant: \(k = 3\times10^3\)

- Reaction b: \((\text{OH})_2\text{CHCH(OH)}_2 + \cdot\text{OH} \rightarrow (\text{OH})_2\text{CHCOOH}\)
  - Rate constant: \(k = 1.1\times10^8\)

- Reaction c: \((\text{OH})_2\text{CHCOOH} + \cdot\text{OH} \rightarrow \text{HCOOH}\)
  - Rate constant: \(k = 5\times10^3\)
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:**

\[
\begin{align*}
\text{H}_3\text{C}-\text{C}=&\text{C}-\text{H} \quad \cdot\text{OH} \\
\quad \text{OH} &
\end{align*}
\]

methylglyoxal hydrated

\[
\begin{align*}
\text{H}_3\text{C}-\text{C}=&\text{C}-\text{H} \quad \rightarrow \\
\quad \text{OH} &
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{C}=&\text{C}-\text{H} \quad \rightarrow \\
\quad \text{OH} &
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{C}=&\text{C}-\text{OH} + \text{H}-\text{C}-\text{OH} \\
\quad &
\end{align*}
\]

acetic acid  formic acid

Formic and acetic acid form directly

Insufficient glyoxylic to explain oxalic

Oligomers involved in oxalic

Oligomers and oxalic → SOA
Expanded Methylglyoxal Mechanism

\[
\begin{align*}
\text{CH}_3\text{COCH(OH)}_2 \quad &\quad \text{(Methylglyoxal-hydrated)} \\
\cdot\text{OH} \quad &\quad \rightarrow \\
\text{(OH)}_2\text{CHCOOH} \quad &\quad \text{(glyoxylic acid-hydrated)} \\
\\cdot\text{OH} \quad &\quad \rightarrow \\
\text{HOOC}\text{COOH} \quad &\quad \text{(oxalic acid)} \\
\\cdot\text{OH} \quad &\quad \rightarrow \\
\text{CO}_2 \\
\h_{\nu}/\cdot\text{OH} \quad &\quad \rightarrow \\
\text{CH}_3\text{COOH} \quad &\quad \text{(acetic acid)} \\
\h_{\nu}/\cdot\text{OH} \quad &\quad \rightarrow \\
\text{CH}_2(\text{OH}) \quad &\quad \text{(formaldehyde-hydrated)} \\
\h_{\nu}/\cdot\text{OH} \quad &\quad \rightarrow \\
\text{HCOOH} \quad &\quad \text{(formic acid)}
\end{align*}
\]

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
Cloud parcel model: Isoprene with/without cloud chemistry. Barbara Ervens Collaboration (see poster)

Gas phase chemistry + uptake only

- 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