Gas-Particle Partitioning of Carbonyls in Simulation Chamber Studies of Secondary Organic Aerosol Formation

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Gas/Particle Partitioning

• Many organic compounds partition between gas and particle phase

\[ K_p = \frac{[\text{particle phase}]}{[\text{gas phase}][\text{aerosol}]} \]

• \( K_p = [\text{particle phase}]/[\text{gas phase}][\text{aerosol}] \)
Denuder-Filter Sampling

- Denuder tube coated with XAD-4 resin
- Filter
- Sorbent

**Particle phase**

**Gas phase**

Typically used for non-polar organic compounds

Air Flow
Secondary Organic Aerosol (SOA)

- Aim: to apply denuder-filter sampling to studies of SOA formation
- Secondary organic fraction represents up to 70% of the organic fraction of fine aerosols
- Composition of SOA?
- Formation mechanisms?
- Main species contributing to SOA?
Biogenic Precursors of SOA

Acyclic Triolefins
- Myroene
- Ocimene

Oxygenated Terpenes
- Linalool
- Terpinene-4-ol

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

Cyclic Diolactone
- Limonene
- α-Terpinene
- γ-Terpinene
- Terpinolene

Sesquiterpenes
- β-Caryophyllene
- α-Humulene

Anthropogenic Precursors of SOA

SOA Formation

Emission of Volatile Organic Compounds

- Alkanes (>C7)
- Aromatics
- Alkenes (>C6)
- ~100 compounds

SOA Precursors

Reaction with OH, O₃, NO₃

Low volatility products
- Multifunctional oxygenates

Gas-particle Partitioning

High volatility products
- Carbonyls
Derivatization of oxygenated organics

FIGURE 1. Derivatization reactions. (Top) PFBHA derivatizes a carbonyl group. (Bottom) BSTFA derivatizes an $-\text{OH}$ group in acids and alcohols.

Yu et al. ES&T 1998, 32, 2357-2370
Glyoxal derivatized

MW = 448

Fragment mass = 181

More than one isomer possible- (multiple peaks)
### Example: OH + Limonene SOA

<table>
<thead>
<tr>
<th>ID</th>
<th>Nomenclature</th>
<th>Structure</th>
<th>MW (g mol⁻¹)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>Lactic acid</td>
<td><img src="image1" alt="Structure" /></td>
<td>116</td>
<td>0.14</td>
</tr>
<tr>
<td>10</td>
<td>2-hexanollic acid</td>
<td><img src="image2" alt="Structure" /></td>
<td>116</td>
<td>0.24</td>
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<tr>
<td>21</td>
<td>Malic acid</td>
<td><img src="image3" alt="Structure" /></td>
<td>116</td>
<td>2.85</td>
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<tr>
<td>23</td>
<td>Fumaric acid</td>
<td><img src="image4" alt="Structure" /></td>
<td>112</td>
<td>0.01</td>
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<tr>
<td>26</td>
<td>3,6-Dioxohexanoic acid</td>
<td><img src="image5" alt="Structure" /></td>
<td>158</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>Hexanoic acid</td>
<td><img src="image6" alt="Structure" /></td>
<td>146</td>
<td>0.01</td>
</tr>
<tr>
<td>30</td>
<td>Ketolimonone acid</td>
<td><img src="image7" alt="Structure" /></td>
<td>180</td>
<td>0.23</td>
</tr>
<tr>
<td>31</td>
<td>7-Hydroxylimonononic acid</td>
<td><img src="image8" alt="Structure" /></td>
<td>184</td>
<td>0.07</td>
</tr>
<tr>
<td>32</td>
<td>Norlimonene acid</td>
<td><img src="image9" alt="Structure" /></td>
<td>172</td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>3-Isopropyl-1,3-dihydroxybutanol</td>
<td><img src="image10" alt="Structure" /></td>
<td>148</td>
<td>0.24</td>
</tr>
<tr>
<td>37</td>
<td>4-Isopropyl-1-methyl-1,5-dihydroxy-2-oxocyclohexene</td>
<td><img src="image11" alt="Structure" /></td>
<td>186</td>
<td>2.25</td>
</tr>
<tr>
<td>38</td>
<td>Ketonolimonene acid</td>
<td><img src="image12" alt="Structure" /></td>
<td>174</td>
<td>0.40</td>
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<tr>
<td>42</td>
<td>Limonic acid</td>
<td><img src="image13" alt="Structure" /></td>
<td>188</td>
<td>0.14</td>
</tr>
<tr>
<td>47</td>
<td>2-Isopropylpentanedioic acid</td>
<td><img src="image14" alt="Structure" /></td>
<td>174</td>
<td>0.20</td>
</tr>
<tr>
<td>53</td>
<td>Ketolimonone acid</td>
<td><img src="image15" alt="Structure" /></td>
<td>168</td>
<td>0.29</td>
</tr>
<tr>
<td>57</td>
<td>5-Hydroxylimononic acid</td>
<td><img src="image16" alt="Structure" /></td>
<td>200</td>
<td>0.06</td>
</tr>
<tr>
<td>65</td>
<td>7-Hydroxylimononic acid</td>
<td><img src="image17" alt="Structure" /></td>
<td>200</td>
<td>0.16</td>
</tr>
</tbody>
</table>

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Jaoui et al., ES&T, 2006, 40, 3819-3828
Denuder-Filter Sampling at UCC

- 5-channel glass denuder
- Coated with XAD-4 resin
- Denuder and filter doped with pentafluorobenzyl hydroxyl amine (PFBHA) to convert polar carbonyls to oximes
Trapping Efficiency Tests

- Range of carbonyls introduced to chamber (10 - 200 ppbv)

Trapping efficiency = \(100 \times \left(1 - \frac{C_{\text{out}}}{C_{\text{in}}}\right)\)
XAD-4 vs XAD-4/PFBHA

Benzaldehyde

Trapping Efficiency (%)

Time (min)

XAD-4
XAD-4 + PFBHA

\[ \text{Benzaldehyde} \]
XAD-4 vs XAD-4/PFBHA

Methylglyoxal

Trapping Efficiency (%)

Time (min)

Temime et al., ES&T, 2007, 41, 6514-6520
Atmospheric Simulation Chamber at UCC

- on-line GC
- NOx and O₃ analysers
- denuder – filter, GC-MS
- Particle Sizer and counter

- FEP foil (6000 litres)
- Dry purified air
- Atmospheric P and T
- Humidity control
p-xylene photo-oxidation experiment

- Aerosol mass yield = 3.84%
p-xylene photo-oxidation

H-abstraction

OH addition

OH addition

ring cleavage

Reactions:

1. H-abstraction
2. OH addition
3. OH addition
4. Ring cleavage
GC-MS Analysis of p-xylene extracts (filter)

Reconstructed ion chromatogram (m/z 181) of a filter extract from XYL_NOx_1
1: glyoxal 2: methylglyoxal 3: oxopropanedial 4: 2,3-dioxobutanal 5: 3-hexene-2,5-dione
6: 2-hydroxy-3-oxobutanal 7: 2,3-dioxobutanal 8: oxopropanedial.
Denuder-Filter vs Filter Alone

- Glyoxal
- Methylglyoxal
- Hexenedione
- P-tolualdehyde

GC-MS response

- Denuder Filter
- Filter alone
## GC-MS Analysis of p-xylene extracts (filter)

<table>
<thead>
<tr>
<th>Relative humidity (%)</th>
<th>XYL_NOx_1</th>
<th>XYL_NOx_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;5</td>
<td>3.88 ± 0.26</td>
<td>4.37 ± 0.70</td>
</tr>
<tr>
<td>24</td>
<td>3.72 ± 0.12</td>
<td>3.47 ± 0.74</td>
</tr>
<tr>
<td>2-hydroxy-3-oxobutanal</td>
<td>0.66 ± 0.06</td>
<td>0.79 ± 0.14</td>
</tr>
<tr>
<td>2,3-dioxobutanal</td>
<td>5.22 ± 0.11</td>
<td>6.19 ± 0.57</td>
</tr>
<tr>
<td>3-hexene-2,5-dione</td>
<td>0.38 ± 0.04</td>
<td>0.31 ± 0.03</td>
</tr>
<tr>
<td>p-tolualdehyde</td>
<td>not observed</td>
<td>0.84</td>
</tr>
<tr>
<td>Total identified</td>
<td>15.92 ± 0.87</td>
<td>18.41 ± 2.52</td>
</tr>
</tbody>
</table>

% Contribution to SOA mass
Gas/Particle Partitioning Values

- $K_p$ calculated both theoretically:

\[
K_{p \text{theoretical}} = \frac{f_{om} \times 760 \times R \times T}{MW_{om} \times \gamma_{om} \times P^o_L \times 10^6}
\]

- $MW_{om}$ = Average molecular weight of organic species in particles (=120)
- $f_{om}$ = fraction of particle that is organic (= 1)
- $\gamma_{om}$ = Activity coefficient (assumed =1)
- $P^o_L$ = sub-cooled vapour pressure

*Pankow, Atmos Environ, 1994*
Gas/Particle Partitioning Values

- $K_p$ calculated both theoretically:

\[ K_{p_{\text{theoretical}}} = \frac{f_{om} \times 760 \times R \times T}{MW_{om} \times \gamma_{om} \times P_{L}^\circ \times 10^6} \]

*Pankow, Atmos Environ, 1994*

- and experimentally:

\[ K_{p_{\text{exp}}} = \frac{C_{\text{particle}}}{C_{\text{gas}} \times [\text{aerosol}]} \]
Gas/Particle Partitioning Values

<table>
<thead>
<tr>
<th></th>
<th>p-tolualdehyde</th>
<th>Hexenedione</th>
<th>Glyoxal</th>
<th>Methylglyoxal</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_p$ theoretical</td>
<td>3.2x10^{-07}</td>
<td>1.3x10^{-06}</td>
<td>9.8x10^{-10}</td>
<td>2.0x10^{-09}</td>
</tr>
<tr>
<td>$K_p$ experimental</td>
<td>4.3x10^{-06}</td>
<td>3.8x10^{-05}</td>
<td>4.2x10^{-05}</td>
<td>3.3x10^{-05}</td>
</tr>
<tr>
<td>$K_p_{exp/theory}$</td>
<td>13</td>
<td>29</td>
<td>43238</td>
<td>16963</td>
</tr>
</tbody>
</table>

• Glyoxal and methylglyoxal $K_p$ several orders of magnitude higher than expected

(vapour pressures from SPARC on line calculator- University of Georgia)
Experiments at PSI Chamber

Healy et al., ACP, 2008, 8, 3215-3230
Denuder-Filter Configurations

- Setup 2 allows for the trapping efficiency of the tube to be tested for each experiment.
Denuder vs Filter Extracts

Gas phase breakthrough

Glyoxal
Methylglyoxal

Gas phase

Particle phase
Photooxidation of Isoprene

![Graph showing the photooxidation of isoprene](image-url)

- Isoprene
- Methacrolein + MVK

**Axes:**
- Y-axis: Isoprene (ppbV) and Carbonyls (ppbV)
- X-axis: Time (min)
Photooxidation products

glycolaldehyde
methacrolein
methyl vinyl ketone
hydroxyacetone
methylglyoxal
glyoxal
C5 carbonyl
C4 hydroxycarbonyl
Gas/Particle Partitioning Values

<table>
<thead>
<tr>
<th></th>
<th>glycolaldehyde</th>
<th>Hydroxyacetone</th>
<th>Glyoxal</th>
<th>Methylglyoxal</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_p_{\text{theoretical}}$</td>
<td>$3.6 \times 10^{-07}$</td>
<td>$7.2 \times 10^{-07}$</td>
<td>$9.8 \times 10^{-10}$</td>
<td>$2.0 \times 10^{-09}$</td>
</tr>
<tr>
<td>$K_p_{\text{experimental}}$</td>
<td>$2.2 \times 10^{-05}$</td>
<td>$1.5 \times 10^{-05}$</td>
<td>$4.4 \times 10^{-05}$</td>
<td>$6.7 \times 10^{-06}$</td>
</tr>
<tr>
<td>$K_p_{\text{exp/theory}}$</td>
<td>59</td>
<td>20</td>
<td>45538</td>
<td>3476</td>
</tr>
</tbody>
</table>

- methacrolein, methylvinylketone not detected in particle phase
- Glyoxal and methylglyoxal $K_p$ several orders of magnitude higher than expected
Photooxidation of 1,3,5-TMB
Gas/Particle Partitioning Values

<table>
<thead>
<tr>
<th></th>
<th>2-methyl-4-oxo-2-pentenal</th>
<th>Methylglyoxal</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_p_{\text{theoretical}}$</td>
<td>9.3x10^{-07}</td>
<td>2.0x10^{-09}</td>
</tr>
<tr>
<td>$K_p_{\text{experimental}}$</td>
<td>1.8x10^{-04}</td>
<td>1.2x10^{-05}</td>
</tr>
<tr>
<td></td>
<td>*1.3x10^{-04}</td>
<td>*2.0x10^{-05}</td>
</tr>
<tr>
<td>$K_p_{\text{exp/theory}}$</td>
<td>190</td>
<td>6256</td>
</tr>
</tbody>
</table>

*Obtained using PTR-MS with denuder and heated inlet to vapourize SOA; Hellen et al, ES&T, (2008), 42, 7347-7353.*
SOA Formation mechanisms

1. Emission of Volatile Organic Compounds
   - Alkanes (>C7)
   - Aromatics
   - Alkenes (>C6)
   - ~100 compounds

2. SOA Precursors
   - Reaction with OH, O₃, NO₃
   - Low volatility products
     - Multifunctional oxygenates

3. High volatility products
   - Carbonyls

4. Partitioning
   - Gas-particle

5. Heterogeneous Reactions*

K_p exp ≈ K_p calc

K_p exp >> K_p calc
Acid-catalyzed Oligomerization-uptake of glyoxal to particles

Liggio et al.,
ES&T, 2005,
39, 1532-1541
Conclusions

• Small dicarbonyls (glyoxal and methyl glyoxal) partition to the particle phase much more than expected from vapour pressure calculations. Consistent with oligomerization hypothesis (in chambers at least!).

• Monofunctional carbonyl compounds much less likely to undergo reactive uptake

• Models that incorporate Kp for oxidation products should use compound-specific values (Johnson et al., 2005, 2006; Jenkin et al., 2004).
Future Directions

• On-tube derivatization of acids/phenols

• Further chamber experiments on oxygenated aromatics, PAHs and BVOCs

• What happens in the real atmosphere?
Sampling site
Denuder-filter sampling

Quartz fibre filters (2)
(PFBHA-treated)

Annular denuder
(XAD-4 coated & PFBHA-treated)

(KI-coated denuder)

Cyclone
(PM$_{2.5}$ fraction)

Inlet

To pump
GC-MS data (denuder & filter extracts) after sampling for 24 hr
23-24th September 2008

* Impurities or column peaks
## Carbonyls at Tivoli Docks

<table>
<thead>
<tr>
<th></th>
<th>Gas phase conc.</th>
<th>Particle phase conc.</th>
<th>Detection limit for standard</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ng/m³ (ppbv)</td>
<td>ng/m³</td>
<td>ng</td>
</tr>
<tr>
<td>MVK</td>
<td>1087 (0.38)</td>
<td>*</td>
<td>3.5</td>
</tr>
<tr>
<td>Methacrolein</td>
<td>380 (0.13)</td>
<td>*</td>
<td>1.0</td>
</tr>
<tr>
<td>Glycolaldehyde</td>
<td>1006 (0.48)</td>
<td>*</td>
<td>4.0</td>
</tr>
<tr>
<td>Hexanal</td>
<td>409 (0.10)</td>
<td></td>
<td>2.0</td>
</tr>
<tr>
<td>Heptanal</td>
<td>144 (0.03)</td>
<td></td>
<td>2.0</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>263 (0.06)</td>
<td></td>
<td>2.0</td>
</tr>
<tr>
<td>p-Tolualdehyde</td>
<td>55 (0.01)</td>
<td></td>
<td>0.6</td>
</tr>
<tr>
<td>Nonanal</td>
<td>404 (0.07)</td>
<td></td>
<td>5.0</td>
</tr>
<tr>
<td>Decanal</td>
<td>343 (0.05)</td>
<td></td>
<td>5.0</td>
</tr>
<tr>
<td>Glyoxal</td>
<td>77 (0.03)</td>
<td>?</td>
<td>0.6</td>
</tr>
<tr>
<td>Methylglyoxal</td>
<td>69 (0.02)</td>
<td>?</td>
<td>0.3</td>
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<tr>
<td>Dimethylglyoxal</td>
<td>102 (0.03)</td>
<td>?</td>
<td>0.6</td>
</tr>
<tr>
<td>3,5-dimethylbenzaldehyde</td>
<td>73 (0.01)</td>
<td></td>
<td>0.6</td>
</tr>
</tbody>
</table>

Sampling for 24 hours at 16.7 L/min. Weather conditions dry, mainly cloudy, light wind from SW.
First studies on SOA formation from naphthalene
Odum yield curves

\[ Y = \sum_{i=1}^{n} Y_i = M_0 \sum_{i=1}^{n} \left( \frac{a_i \times K_i}{1 + M_0 \times K_i} \right) \]
### Aerosol yield parameters

<table>
<thead>
<tr>
<th></th>
<th>One compound model</th>
<th>Two compounds model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \alpha )</td>
<td>( K )</td>
</tr>
<tr>
<td>( \text{RH}=0, )</td>
<td>0.1636</td>
<td>0.0113</td>
</tr>
<tr>
<td>( \text{HC/NOx}=1.0-1.8 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{RH}=0, )</td>
<td>0.2198</td>
<td>0.0125</td>
</tr>
<tr>
<td>( \text{HC/NOx}=3.0-4.4 )</td>
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<tr>
<td>( \text{RH}=25, )</td>
<td>0.2324</td>
<td>0.0081</td>
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<tr>
<td>( \text{HC/NOx}=1.0-1.8 )</td>
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<tr>
<td>( \text{RH}=50, )</td>
<td>0.2548</td>
<td>0.0095</td>
</tr>
<tr>
<td>( \text{HC/NOx}=1.0-1.8 )</td>
<td></td>
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</tr>
</tbody>
</table>
Acknowledgements

• Robert Healy, Shouming Zhou
• Kristina Kuprovskyte, Ashley Allshire
• Brice Temime (now in Marseille)
• Josef Dommen, Axel Metzger et al. (PSI)
XAD-4 vs XAD-4/PFBHA

2,6-dimethylbenzoquinone

Trapping Efficiency (%)

Time (min)
Glyoxal trimer dissolved in solvent mix vs dissolved in methanol
Kp calculations

\[ Kp_{\text{theoretical}} = \frac{f_{om} \times 760 \times R \times T}{MW_{om} \times \gamma_{om} \times P^o_L \times 10^6} \]

- \( MW_{om} \) = Average molecular weight of organic species in particles (=120)
- \( f_{om} \) = fraction of particle that is organic (=1)
- \( \gamma_{om} \) = Activity coefficient (assumed =1)
- \( P^o_L \) = sub-cooled vapour pressure
- Adsorption to particle surface not considered for Kp values
Polymerization reactions in aromatics-SOA polymer—”backbone”
Gas-phase Carbonyl yields for p-xylene

methylglyoxal 35%
methylbutenedial 3%

Glyoxal 30%
Hexenedione 5%

P-tolualdehyde 10%
Minimize Artefacts

- Direct filter sampling is prone to artefacts
- Adsorption of gases to filter - Positive artefact
- Desorption of semi-volatiles – Negative artefact
- Denuder-filter sampling minimizes artefacts
- Mainly used for non-polar organic compounds that partition between both gas and particle phases, e.g. PAHs