Mechanisms and SOA Formation for the Atmospheric Degradation of Xylenes

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Ireland
Sources
• Automobile fuels, solvents
• Aromatics typically contribute 20-25% to anthropogenic VOC emissions

Transformation
• Reaction with hydroxyl radical (OH) in troposphere
• Formation of ozone, nitrates, secondary organic aerosol (SOA)

Impacts
• Air pollution and Health effects in urban areas

Information required
• Kinetics of reaction, identity & yields of oxidation products
• Reactivity of the oxidation products towards OH, NO₃, O₃, sunlight
• Produce a detailed atmospheric degradation mechanism for inclusion in models (e.g. MCM) used to predict pollution forming ability of VOCs
Dimethylphenols and Tolualdehydes

2,3-DMP

2,4-DMP

2,5-DMP

benzaldehyde

o-tolualdehyde

2,6-DMP

3,4-DMP

3,5-DMP

m-tolualdehyde

p-tolualdehyde
Atmospheric Simulation Chamber

- in situ FTIR spectroscopy
- NOx and O\textsubscript{3} analysers
- GC, GC-MS
- Particle Sizer and counter

- FEP foil (3910 litres)
- Dry purified air
- Atmospheric P and T
- Humidity control
Kinetic Studies

**Relative rate method**

\[ (1) \quad \text{OH} + \text{aromatic} \quad \xrightarrow{k_1} \quad \text{Products} \]

\[ (2) \quad \text{OH} + \text{reference} \quad \xrightarrow{k_2} \quad \text{Products} \]

\[
\frac{-\text{dln}[\text{aromatic}]}{\text{dt}} = k_1[\text{OH}] \\
\frac{-\text{dln}[\text{reference}]}{\text{dt}} = k_2[\text{OH}]
\]

\[
\frac{\ln [\text{aromatic}]_0}{[\text{aromatic}]_t} = \frac{k_1 \ln [\text{reference}]_0}{k_2 [\text{reference}]_t}
\]

<table>
<thead>
<tr>
<th>OH reactions</th>
<th>NO\textsubscript{3} reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Radical Source</strong></td>
<td>CH\textsubscript{3}ONO + hv → CH\textsubscript{3}O + NO</td>
</tr>
<tr>
<td></td>
<td>CH\textsubscript{3}O + O\textsubscript{2} → CH\textsubscript{2}O + HO\textsubscript{2}</td>
</tr>
<tr>
<td></td>
<td>HO\textsubscript{2} + NO → OH + NO\textsubscript{2}</td>
</tr>
<tr>
<td></td>
<td>NO\textsubscript{2} + O\textsubscript{3} → NO\textsubscript{3} + O\textsubscript{2}</td>
</tr>
<tr>
<td><strong>Reference Compound</strong></td>
<td>1,3,5-trimethylbenzene for DMPs</td>
</tr>
<tr>
<td></td>
<td>1,2,4-trimethylbenzene for aldehydes</td>
</tr>
<tr>
<td></td>
<td>NO\textsubscript{3} + NO\textsubscript{2} ↔ N\textsubscript{2}O\textsubscript{5}</td>
</tr>
<tr>
<td></td>
<td>o-cresol for DMPs</td>
</tr>
<tr>
<td></td>
<td>n-propyl ether for aldehydes</td>
</tr>
</tbody>
</table>
Kinetics data for dimethylphenols

\[
\ln\left(\frac{[\text{BMP}]_0}{[\text{BMP}]_t}\right) = k_4 t
\]

- 2,6-Dimethylphenol
- 3,4-Dimethylphenol
- 3,5-Dimethylphenol
## Kinetics results for dimethylphenols

<table>
<thead>
<tr>
<th>Compound</th>
<th>$k_{OH}^a$</th>
<th>$k_{NO3}^a$</th>
<th>$\tau_{OH}^b$ (s)</th>
<th>$\tau_{NO3}^c$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,3-Dimethylphenol</td>
<td>8.3 ± 1.1</td>
<td>8.0 ± 2.0</td>
<td>2.9 ± 0.3</td>
<td>7502</td>
</tr>
<tr>
<td>2,4-Dimethylphenol</td>
<td>7.4 ± 0.8</td>
<td>7.2 ± 1.8</td>
<td>3.1 ± 0.3</td>
<td>8468</td>
</tr>
<tr>
<td>2,5-Dimethylphenol</td>
<td>8.8 ± 1.2</td>
<td>8.0 ± 2.3</td>
<td>3.0 ± 0.4</td>
<td>7078</td>
</tr>
<tr>
<td>2,6-Dimethylphenol</td>
<td>6.7 ± 0.9</td>
<td>6.6 ± 1.7</td>
<td>4.9 ± 0.5</td>
<td>8635</td>
</tr>
<tr>
<td>3,4-Dimethylphenol</td>
<td>8.3 ± 0.9</td>
<td>8.1 ± 2.1</td>
<td>2.5 ± 0.2</td>
<td>7558</td>
</tr>
<tr>
<td>3,5-Dimethylphenol</td>
<td>11.4 ± 1.4</td>
<td>11.3 ± 3.0</td>
<td>1.1 ± 0.1</td>
<td>5482</td>
</tr>
</tbody>
</table>

$^a$ In units of $10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

$^b\tau_{OH} = 1/k_{OH}[OH]$, where 12 hour daily average [OH] = $1.6 \times 10^6$ molecule cm$^{-3}$

$^c\tau_{NO3} = 1/k_{NO3}[NO_3]$, where 12 hour daily average [NO$_3$] = $5 \times 10^8$ molecule cm$^{-3}$

- Both OH and NO$_3$ reactions important
- Opposite trends in reactivity for OH and NO$_3$
- Different reaction mechanisms
Sites activated for OH addition

2,3-dimethylphenol
2,4-dimethylphenol
2,5-dimethylphenol
2,6-dimethylphenol
3,4-dimethylphenol
3,5-dimethylphenol
Mode of NO$_3$ attack
Sites activated for NO$_3$ addition

- 2,3-dimethylphenol
- 2,4-dimethylphenol
- 2,5-dimethylphenol
- 2,6-dimethylphenol
- 3,4-dimethylphenol
- 3,5-dimethylphenol
## Kinetics results for tolualdehydes

<table>
<thead>
<tr>
<th>Compound</th>
<th>$k_{\text{OH}}^a$</th>
<th>$k_{\text{NO}_3}^b$</th>
<th>$\tau_{\text{OH}}^c$ (hr)</th>
<th>$\tau_{\text{NO}_3}^d$(hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzaldehyde</td>
<td>1.4 ± 0.1</td>
<td>1.2 ± 0.2</td>
<td>4.3 ± 1.3</td>
<td>19.8</td>
</tr>
<tr>
<td>o-tolualdehyde</td>
<td>2.1 ± 0.2</td>
<td>1.8 ± 0.2</td>
<td>9.8 ± 2.6</td>
<td>13.6</td>
</tr>
<tr>
<td>m-tolualdehyde</td>
<td>2.1 ± 0.2</td>
<td>1.7 ± 0.2</td>
<td>9.5 ± 2.6</td>
<td>13.4</td>
</tr>
<tr>
<td>p-tolualdehyde</td>
<td>2.1 ± 0.2</td>
<td>1.3 ± 0.2</td>
<td>9.5 ± 3.0</td>
<td>13.6</td>
</tr>
</tbody>
</table>

- $k_{\text{OH}}^a$ in units of $10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.
- $k_{\text{NO}_3}^b$ in units of $10^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.
- $\tau_{\text{OH}}^c = 1/k_{\text{OH}}[\text{OH}]$, where 12 hour daily average $[\text{OH}] = 1.6 \times 10^6$ molecule cm$^{-3}$.
- $\tau_{\text{NO}_3}^d = 1/k_{\text{NO}_3}[\text{NO}_3]$, where 12 hour daily average $[\text{NO}_3] = 5 \times 10^8$ molecule cm$^{-3}$.

- Only OH reaction is important
- Tolualdehyde isomers have the same reactivity
- Similar trend in reactivity for OH and NO$_3$
UV Absorption Spectra of Tolualdehydes
Sunlight Photolysis of Tolualdehydes
Sunlight Photolysis of Tolualdehydes

- photolysis lifetime for o-tolualdehyde = 1-2 hr

- m- and p-tolualdehyde are not photolyzed
1,2-benzenedicarboxaldehyde ~ 25% yield
Aromatic cyclic alcohol ~ 65% yield

FTIR Spectra of Products

(a) after 1hr 52m ins photolysis
(b) after subtraction of o-tolualdehyde
(c) reference spectrum 1-indanol
(d) reference spectrum of phthalic dicarboxaldehyde
(e) reference spectrum of phthalide
Proposed Mechanism

\[ \text{O} \quad \text{H} \quad \text{C} \quad \text{O} \quad \text{CH}_3 \quad \xrightarrow{h\nu} \quad \text{H} \quad \text{C} \quad \text{O} \quad \text{CH}_3 \]

\[ \xrightarrow{\text{isomerisation}} \]

\[ \text{H} \quad \text{C} \quad \text{OH} \quad \xrightarrow{\text{cyclicisation}} \]

\[ \xrightarrow{65\%} \quad \text{HO} \quad \xrightarrow{25\%} \quad \xrightarrow{\text{O}_2} \quad \text{C} \quad \text{O} \quad \text{C} \quad \text{C} \]
Secondary Organic Aerosol Formation
Secondary Organic Aerosol Formation

\[
\text{Aerosol Volume Concentration (μm}^3\text{/cm}^3) \\
\text{Aerosol Mass Concentration (μg/m}^3) \\
\]

\[
y = 1.0908x + 4.1554 \\
R^2 = 0.9978
\]

Open to sunlight
Secondary Organic Aerosol

- Not just formed in laboratory studies!!
- Secondary organic fraction represents up to 70% of the organic mass of fine aerosols (PM2.5)
- Composition of SOA?
- Formation mechanisms?
- Main species contributing to SOA?
Denuder-Filter Sampling

- Denuder tube coated with XAD-4 resin
- Filter
- Sorbent
- Particle phase
- Gas phase

Air Flow
Denuder-Filter Sampling at UCC

- 5-channel glass denuder
- Coated with XAD-4 resin
- Doped with pentafluorobenzyl hydroxyl amine (PFBHA)
Derivatization of oxygenated organics

![Diagram of derivatization reactions](image)

**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 fragments here

MW = 448

Fragment mass = 181

More than one isomer possible- (multiple peaks)
p-xylene photo-oxidation experiment

- Aerosol mass yield = 3.84%
p-xylene photo-oxidation
GC-MS Analysis of p-xylene extracts (filter)

- Glyoxal
- Methylglyoxal
- Methylobutenedial
- C4 dicarbonyl
- Hexenedione
- P-tolualdehyde
GC-MS Analysis of p-xylene extracts (filter)

- p-tolualdehyde 2.34%
- glyoxal 2.48%
- methylglyoxal 2.41%
- C4-dicarbonyl 0.25%
- hexenedione 1.10%
- dimethylbenzoquinone 0.03%
- methylbutenedial 2.10%
- Other 89.28%
Gas/Particle Partitioning

- Many organic compounds partition between gas and particle phase

$$K_p$$

Organic aerosol

Gas phase products

VOC

oxidized
Gas/Particle Partitioning Values

• Kp calculated both theoretically:
\[ K_{p_{theoretical}} = \frac{f_{om} \times 760 \times R \times T}{MW_{om} \times \gamma_{om} \times P^o_L \times 10^6} \]

• and experimentally:
\[ K_{p_{exp}} = \frac{C_{particle}}{C_{gas} \times [aerosol]} \]

(Pankow)
Gas/Particle Partitioning Values

<table>
<thead>
<tr>
<th>Product</th>
<th>p-tolualdehyde</th>
<th>Hexenedione</th>
<th>Glyoxal</th>
<th>Methylglyoxal</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_p$ theoretical</td>
<td>3.93x10^{-07}</td>
<td>2.04x10^{-06}</td>
<td>1.73x10^{-09}</td>
<td>3.69x10^{-09}</td>
</tr>
<tr>
<td>$K_p$ experimental</td>
<td>8.84x10^{-06}</td>
<td>4.58x10^{-06}</td>
<td>5.57x10^{-05}</td>
<td>3.28x10^{-05}</td>
</tr>
</tbody>
</table>

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

(vapor pressures from SPARC on line calculator- University of Georgia)
Acid-catalyzed Polymerization uptake of glyoxal to particles

Liggio et al.
Conclusions

• Advances in knowledge of the reactivity of xylene oxidation products – improved mechanisms

• Small dicarbonyl compounds partition to the particle phase much more than expected from vapor pressure calculations

• Suggests further processes occurring on/in particles (oligomerization)
  -eg. Kalberer et al. Science 2004
Future Directions

• On-tube derivatization of acids/phenols

• Further chamber experiments on aromatic aldehydes and phenols

• Mass balance for xylene photo-oxidation systems still poor (at best 45%). New experimental approaches using state-of-the-art analytical techniques are needed.
Acknowledgements

• Lars Thuener
• Brice Temime-Roussel
• Ger Rea
• Grainne Clifford
• Perla Bardini
• Robert Healy
• Wahid Mellouki (Orleans)
• Amalia Munoz (Valencia)