Gas Phase Hydration of Methylglyoxal to Form the Geminal Diol

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Organic Aerosols

• Two major types of organic aerosols
  – Primary (POA)

Direct Particle Emissions to Atmosphere (Natural or Anthropogenic)
Organic Aerosols

- Two major types of organic aerosols
  - Primary (POA) and Secondary (SOA)
Organic Aerosols

- Two major types of organic aerosols
  - Primary (POA) or Secondary (SOA)
- Incredibly complex interaction with climate

http://earthobservatory.nasa.gov/Features/Aerosols/
Adapted from Chung et al. J. Geophys Res. (2005) 110, D24207
Organic Aerosols

- Two major types of organic aerosols
  - Primary (POA) or Secondary (SOA)
- Incredibly complex interaction with climate
- Need for fundamental understanding of molecular processes that lead to organic aerosol formation

Atmospheric Heating

Surface Cooling

http://earthobservatory.nasa.gov/Features/Aerosols/
Adapted from Chung et al. J. Geophys Res. (2005) 110, D24207
Methylglyoxal

- Produced from atmospheric processing of biogenic and anthropogenic volatile organic compounds (VOCs).
- One of the most abundant $\alpha$-dicarbonyl compounds present in the atmosphere.
- Proposed as a major source of SOA

Carlton et al., Atmos. Chem. Phys., (2009), 9, 4987–5005.
Methylglyoxal is Ubiquitous

Methylglyoxal is found in aerosol throughout the atmosphere.

Urban

Rural

Remote

Aqueous Phase Hydration

• Exists primarily as the diol and tetrol in the aqueous phase

\[
\begin{align*}
\text{H}_2\text{O} & \quad \text{60% diol} \\
\text{H}_2\text{O} & \quad \text{40% tetrol}
\end{align*}
\]

Can Methylglyoxal undergo hydration to form the gem-diol in the gas phase?

- Theory suggests it is energetically unfavorable to form the methylglyoxal diol species in the gas phase.

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Experimental work done in our lab suggests this is incorrect and that the diol does form in the gas phase.

Sample Purification

• In order to prepare pure methylglyoxal for gas phase experiments it must first be dehydrated and then distilled.
  – Sample is attached to a vacuum line and gently heated for 12-15 hours

Sample Purification

• Add equimolar amount of P$_2$O$_5$ as drying agent

• Distill under vacuum using two cold water condensers

• Collect pure methylglyoxal using liquid nitrogen trap

• Pure sample is a bright green color

Spectra collected from 1000-8000 cm$^{-1}$ at 0.5 cm$^{-1}$ resolution.

FTIR Results

Upon addition of water to methylglyoxal there is a clear change in the IR spectrum.

Spectra of methylglyoxal and a mixture of methylglyoxal and methylglyoxal diol

FTIR Results

\( \nu_8 = \text{carbonyl stretch} \)

\( \nu_9 = \text{aldehyde stretch} \)

FTIR Results

\(v_8 = \text{carbonyl stretch}\)

\(v_9 = \text{aldehyde stretch}\)

Methylglyoxal diol OH fundamental stretching region

FTIR Results

- Using the partial pressures of the methylglyoxal, diol, and water we can calculate an equilibrium rate constant
- The diol concentration was determined using the OH stretch and the theoretically determined cross section

\[ K_P = \frac{P_{\text{dil}}}{P_{\text{Mgly}}P_{\text{H2O}}} \]

\[ \Delta G^0 = -RT(lnK_P) \]

### FTIR Results

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$P_{\text{diol}}$ (atm)</th>
<th>$P_{\text{water}}$ (atm)</th>
<th>$P_{\text{mgly}}$ (atm)</th>
<th>KP</th>
<th>$\Delta G^\circ$ kcal mol$^{-1}$</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>$1.08 \times 10^{-5}$</td>
<td>$1.25 \times 10^{-3}$</td>
<td>$5.40 \times 10^{-5}$</td>
<td>159</td>
<td>$-3.13$</td>
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<tr>
<td>2</td>
<td>$1.06 \times 10^{-5}$</td>
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<td>157</td>
<td>$-3.12$</td>
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<td>3</td>
<td>$1.07 \times 10^{-5}$</td>
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<td>$5.40 \times 10^{-5}$</td>
<td>161</td>
<td>$-3.13$</td>
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<tr>
<td>4</td>
<td>$3.16 \times 10^{-5}$</td>
<td>$1.59 \times 10^{-3}$</td>
<td>$1.29 \times 10^{-4}$</td>
<td>154</td>
<td>$-2.98$</td>
</tr>
</tbody>
</table>

- The experimentally determined values for the Gibbs free energy of the reaction to form the diol show the reaction to be favorable.
- The values determined would suggest it is significantly more favorable than theoretical calculations predict, even when compared to calculations for hydration in aqueous solutions.

Gas phase vs. solution phase methlyglyoxal UV cross section

In solution, methylglyoxal is primarily present as the diol (60%)

Incoherent Broadband Cavity Enhanced Absorption Spectroscopy (IBBCEAS)

455 nm UV LED

99.993% Reflective Mirrors

Optical Fiber 450 ±20nm BPF

Metgly

Dry Air

H₂O

RH Probe

“static” cell

Grating Spectrometer with CCD Detector

440 - 470 nm

Jessica Axon Thesis
IBBCEAS Results

A small change is seen in the absorption cross section when relative humidity is increased.
UV Direct Absorption Spectrometer

Horriba iHR 550 UV Spectrometer with blue sensitized CCD detector

Pressure Gauge
To Vacuum Line

Energetiq Laser Driven Xe Arc Lamp

200-400 nm
UV Direct Absorption Spectrometer

- 1 mtorr to >1 Atm
- $\lambda > 200$ nm
  - Current typical experiments 200-400 nm
- Can go to visible wavelengths 400-700 nm
- 0.01 nm resolution
Implications for Atmospheric Chemistry

Radical Products

Water clusters

Products

Water clusters

H₂O(n)

UV-vis hv

IR or UV-vis hv

H₂O(n)

H₂O

H₂O
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