A Predictive Kinetic Model for Aerosol Formation from Toluene

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gas phase chemistry

oxygenated products

partition to the particle phase

particle phase reactions
NO $\rightarrow$ NO$_2$ $\rightarrow$ O$_2$

$\cdot$CH$_2$ $\rightarrow$ OH $\rightarrow$ OH $\rightarrow$ toluene

O$_2$ $\rightarrow$ C$\,$7 diene-dial

rearrangement

ring cleavage radical

butenedial, pentenedial

methylglyoxal, glyoxal
Gas and particle phases are linked via G/P partitioning

\[ iC_{\text{gas}} + \sum \text{OM} \rightarrow iC_{\text{part}} \]

\[ K_p = \frac{iC_{\text{part}}}{iC_{\text{gas}} \sum \text{OM}} \]

Gas phase reactions

Methyl glyoxal

CH\text{\textsubscript{3}}-C-C=O

Particle
\[ K_p = \frac{760 \, RT \, f_{om}}{p_{iL}^* \, \gamma \, MW \, 10^6} \]

- \[ K_p = \frac{k_{on}}{k_{off}} \]

- \([i_{\text{gas}}] + [i_{\text{om}}] \quad \leftrightarrow \quad [i_{\text{part}}] \]
- \(k_{on} \quad \leftrightarrow \quad k_{off}\)
Glyoxal in the gas and particle phase

Vapor pressures ~ 40-50 torr

\( K_p = \frac{760 \, RT \, f_{om}}{p_i^* \, \gamma \, M_w \times 10^6} \)

\( K_p = \frac{i \, C_{part}}{i \, C_{gas} \, \Sigma OM} \)
Glyoxal in the gas and particle phase (PFBHA)
GLY_{gas} + \sum \text{OM} \rightarrow \text{GLY}_{\text{part}}

500 \times k_{on}
Glyoxal in water strongly favors hydration

The hydration equilibrium constant for

glyoxal$\leftrightarrow$ dihydrate; $K_h = 7 \times 10^4$
Liggio, Li, McLaren suggest uptake coefficients ($\gamma_{\text{accom}}$) of $8 \times 10^{-4}$ to $7.3 \times 10^{-3}$.
\[ k_{on} = \frac{6.0 \times 10^{-10} \gamma_{accom} \langle c \rangle} {4 \rho_p D_p} \]
Particle Off-gassing Experiments

\[ \ln \left( \frac{C_{out}^i}{C_{in}^i} \right) = -k_{off}^i \times t_{off}^i \]

\[ k_{off}^i = \frac{k_b T}{h} \exp \left( -\frac{\Delta \phi_a}{k_b T} \right) \]
\[ k_{\text{off}}^i = \frac{k_b T}{h} \exp\left(-\frac{\Delta \phi_a}{k_b T}\right) \]

\[ \ln\left(\frac{C_{\text{out}}^i}{C_{\text{in}}^i}\right) = -k_{\text{off}}^i \times t_{\text{off}}^i \]

\[ p_{L, 298 K}^0 (\text{torr}) \]

\[ E_a (kJmol^{-1}) = -3.7 \times \log\left(\frac{p_{L, 298 K}^0}{\text{torr}}\right) + 64.8 \]
Evaporation energy barriers and vapor pressures

\[ y = -0.807x + 74.2 \]

\[ R^2 = 0.9452 \]
Volatile “Hot” DMA system
Kalberer, et al, Offenberg et al.

Smog chamber

$DMA_1$
Volatile “Hot” DMA system

- Smog chamber
- DMA$_1$
- heat
- DMA$_2$
Current Mechanism has:

- 98 gas phase reactions
- 67 gas to particle phase species
- 16 “particle phase” reactions

CB4 (2002) chemistry
Model Simulations of UNC outdoor Toluene/NOx Experiments
## Products

<table>
<thead>
<tr>
<th>Product</th>
<th>$250 \mu g/m^3$</th>
<th>$13 \mu g/m^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GLYPOLY</td>
<td>60</td>
<td>17</td>
</tr>
<tr>
<td>MGLYPOLY</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>SEED1</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>Organic nitrates</td>
<td>7</td>
<td>26</td>
</tr>
<tr>
<td>CH3N02phenols</td>
<td>11</td>
<td>13</td>
</tr>
<tr>
<td>organic peroxides</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>C6OHNO2ACID</td>
<td>1</td>
<td>13</td>
</tr>
<tr>
<td>others</td>
<td>2</td>
<td>5</td>
</tr>
</tbody>
</table>
0.54 ppmV TOL + 0.37 ppm NOx
0.54 ppmV TOL + 0.37 ppm NOx
0.5 ppm V TOL + 0.2 ppm NOx
1 ppmV TOL + 0.3 ppm NOx
0.1 ppmV TOL + 0.13 ppm NOx

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Particle massconc (µg/m³)

Toluene, NOx-O3 conc (ppm)

LDT (hours)
Model Simulations of the EUPHORE Chamber Data
0.5ppmv TOL + 0.05 ppm NOx

![Graph showing concentrations of Toluene, O₃, NO, NO₂, and Particle mass conc (µg/m³) over time (LDT hours)].
0.5 ppmV TOL + 0.13 ppm NOX

[Graph showing concentrations of Toluene, O3, NO, NO2, and TSP over time (LDT hours)]
0.5 ppmv TOL + 0.13 ppmv NOx
Model Simulations of the Caltech Chamber Data
Predicted aerosol mass conc. vs. Caltech reported mass conc.
Toluene SOA behavior with in an atmospheric HC mixture
SOA from 0.1 ppmV toluene+0.1 ppm NOx
w/wo 3 ppmC HC mixture

Without HC mix

µg/m³
8:00 10:24 12:48 15:12 17:36
SOA from terpene mixtures

0.05 ppmV $\alpha$-pinene
0.02 ppmV d-limonene
0.05 ppm NO$_x$
SOA from terpene mixtures

EDT (Hour)

NO/NO₂ Conc (ppm)

0.00 0.05 0.10 0.15 0.20 0.25 0.30

O₃ Conc (ppm)

0.00 0.05 0.10 0.15 0.20 0.25 0.30

-0.05 0.00 0.05 0.10 0.15 0.20 0.25

EDT (Hour)

6.0 7.5 9.0 10.5 12.0 13.5 15.0

042006S

NO data
NO₂ data
NO sim
NO₂ sim
O₃ data
O₃ sim
SOA from terpene mixtures

![Graph showing SOA formation from terpene mixtures with various terpenes and their concentrations over time.](042006S)
Summary statements

- Did not used any acidity reactions
- tends to simulate toluene
- many products
- concentration levels
- Nucleation
- Thanks to the EPA STAR program
- And to Harvey Jeffries for providing the Morpho kinetics solver