2005 UPDATES TO THE CARBON BOND MECHANISM: CB05

Gary Z. Whitten, Smog Reyes
Greg Yarwood, ENVIRON

smogreyes@yahoo.com

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Ackowledgements

• EPA: Deborah Lueckeen and Sarwar Golam
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• ENVIRON: Sunja Rao and Abby Hoats
• Mark Yocke
• Mary Ligocki
Outline

• CB4/CB05 History
• CB05 Objectives
• Mechanism Updates
• Evaluation
• CB05/CB4 Comparison
CB4 (or CB-IV) History

1989  CB4 published (Gery et al. JGR paper, 1989)
1990  **UAM-IV version** of CB4 with updated to PAN reaction rates and explicit methanol/ethanol
1994  updated radical reactions for XO2/XO2N
1996  **OTAG version** with revised isoprene chemistry (Carter “1-product” mechanism). This version is in widespread use (e.g., CAMx M3 and CMAQ)
1999  CB99 developed: OH + NO₂ needed correcting
2002  CB2002 developed: not widely used
2005  CB4+ developed by extending the inorganic reactions in the OTAG version of CB4
CB05 Development Objectives

- Update the Carbon Bond Mechanism for use in EPA modeling studies
  - Ozone
  - PM/visibility
  - Air toxics and mercury
- Update science
  - extend range of atmospheric conditions
  - improve linkages from gas-phase chemistry linkage to aqueous and aerosol chemistry
- Understand changes relative to CB4
- Not “change for the sake of change”
CB05 Core Updates (1 of 3)

• Updated rate constants

• Extended inorganic reaction set (CB4+)
  – urban to remote tropospheric conditions
    • odd-H reactions, hydrogen (H₂), NO₃ reactions

• NOx recycling reactions
  – represent the fate of NOx over multiple days
    • photolysis and OH-reactions for both nitric acid (HNO₃) and organic nitrates (RNO₃)
CB05 Core Updates (2 of 3)

- Explicit chemistry for methane and ethane
  - clean background atmospheres
- Explicit methylperoxy radical, methyl hydroperoxide and formic acid
  - improved hydrogen peroxide (SO$_2$ $\rightarrow$ sulfate)
- Lumped higher organic peroxides, organic acids and peracids
  - improved organic peroxides (SO$_2$ $\rightarrow$ sulfate)
CB05 Core Updates (3 of 3)

- Internal olefin (RHC=CHR) species IOLE
  - higher reactivity at low VOC/NOx
- Higher aldehyde species ALDX
  - higher reactivity at low VOC/NOx
  - acetaldehyde (ALD2) now explicit (air toxics)
- Higher peroxyacyl nitrate species from ALDX called PANX
  - improved nitrogen cycling and transport
- Lumped terpene species TERP
  - biogenic contributions to oxidant and SOA
# Summary of CB4 and CB05

<table>
<thead>
<tr>
<th></th>
<th>CB4</th>
<th>CB05</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reactions</strong></td>
<td>96</td>
<td>156</td>
</tr>
<tr>
<td><strong>Species</strong></td>
<td>37</td>
<td>51</td>
</tr>
<tr>
<td>Alkanes</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Alkenes</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>Aromatics</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Aldehydes</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Alcohols</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Peroxides</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>PANs</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

- **Alkanes**: PAR, CH4 + ETHA
- **Alkenes**: ETH, OLE, ISOP + IOLE, TERP
- **Aromatics**: TOL, XYL, CRES
- **Aldehydes**: FORM, ALD2, MGLY + ALDX
- **Alcohols**: MEOH, ETOH
- **Peroxides**: H2O2 + MEPX, ROOH, PACD
- **PANs**: PAN + PANX
New Organic Precursors in CB05

<table>
<thead>
<tr>
<th>CB05</th>
<th>Representative Structure</th>
<th>C #</th>
<th>CB4 Equivalent</th>
</tr>
</thead>
<tbody>
<tr>
<td>ETHA</td>
<td>CH\textsubscript{3}-CH\textsubscript{3} (explicit species)</td>
<td>2</td>
<td>0.6 PAR + 1.4 NR</td>
</tr>
<tr>
<td>IOLE</td>
<td>-CH\textsubscript{2}CH=CH-CH\textsubscript{2} -</td>
<td>4</td>
<td>2 ALD2</td>
</tr>
<tr>
<td>ALDX</td>
<td>-CH\textsubscript{2}-CHO</td>
<td>2</td>
<td>ALD2</td>
</tr>
<tr>
<td>TERP</td>
<td>α-pinene and β-pinene</td>
<td>10</td>
<td>x PAR + y ALD2 + z OLE</td>
</tr>
</tbody>
</table>
The next few slides show some of the main expansions of the carbon bond mechanism from CB4 to CB05
  – First show CB4
  – Then show changes for CB05
Methane/Formaldehyde in CB4

CH4

OH

FORM

OH, NO3, hv

CO

OH

(CO2)
Methane/Formaldehyde in CB05

- Methylperoxy radical is the simplest RO2 and has many sources in CB05 in addition to CH4
- Better representation of high/low NOx conditions
- Methyl hydroperoxide and formic acid link to aqueous phase chemistry
Higher Aldehydes in CB4

ALD2 (higher acetaldehydes)

\[ \text{OH, NO3, hv} \]

C2O3 \[ \leftrightarrow \] PAN

\[ +/- \text{ NO2} \]

\[ \text{NO} \]

FORM (+ CO2)
Higher Aldehydes in CB05

(higher aldehydes) → ALDX

PANX ↔ CXO3

ALD2 (acetaldehyde) → PAN

AACD + PACD

MEO2 (+ CO2)

OH, NO3, hv

OH, NO3, hv

HO2, RO2

HO2, RO2

Better representation of high/low NOx conditions
More extensive aldehyde and PAN chemistry
Alkanes (PAR) in CB4

PAR (alkanes and paraffinic carbon)

OH

ALD2 + ROR (aldehydes)

ALD2 + PAR (ketones)
Alkanes (PAR) in CB05

Paraffinic chains with 3+ carbons can produce ALDX

ALDX photolyzes faster than ALD2

Similar change for terminal olefins (OLE)
CB05 Development and Evaluation

- Developed first, evaluated second: No mechanism tuning refinement stage

- UNC chamber data
  - Implemented CB05 in “Morpho”
  - Updated chamber mechanism
  - Compared to CB2002 – similar to CB4

- UCR chamber data
  - CB05 implemented and tested by Bill Carter
  - Chamber mechanism re-adjusted for CB05 by Carter
  - Evaluated both CB05 and fixed-parameter SAPRC99 used in CMAQ
UNC Experiments

• Show results related to CB05 mechanism updates
  – Chamber mechanism: CO
  – Higher aldehydes: ALDX
  – Terminal olefins: OLE (benefit of ALDX)
  – Internal olefins: IOLE

• Other species
  – Aromatics: TOL and XYL
UNC Chamber: CO

Updated chamber mechanism improves NO → NO₂ conversion and O₃ yield in characterization experiments with CO.

Measured = Solid Line
Simulated = Dashed Line
UNC Chamber: ALDX

ALDX photolysis improves NO → NO₂ conversion and O₃ timing in experiments with trimethylacetaldehyde and propionaldehyde.

Measured = Solid Line
Simulated = Dashed Line
UNC Chamber: OLE

ALDX product improves NO → NO₂ conversion and O₃ timing in experiments with propene, 1-butene and 1-pentene

Measured = Solid Line
Simulated = Dashed Line
UNC Chamber: IOLE

IOLE reactions and ALDX product improve NO, NO₂ and O₃ timing and peaks in experiments with equimolar mixture of 1-butene, cis-2-butene, trans-2-butene, and isobutene.

Measured = Solid Line
Simulated = Dashed Line

(VERTICAL SCALES DIFFER)
UNC Chamber: Aromatics

**TOL**

CB05 tends to be slow, but have correct final ozone

**XYL**

CB05 has mix of ozone under and over-prediction
UCR Experiments

- Over 350 experiments
  - Several chambers
  - Individual compounds
  - Mixtures of compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Number of Experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon monoxide</td>
<td>18</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>24</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>12</td>
</tr>
<tr>
<td>Ethene</td>
<td>39</td>
</tr>
<tr>
<td>Propene</td>
<td>89</td>
</tr>
<tr>
<td>t-2-Butene</td>
<td>12</td>
</tr>
<tr>
<td>Isoprene</td>
<td>18</td>
</tr>
<tr>
<td>Butane</td>
<td>10</td>
</tr>
<tr>
<td>Octane</td>
<td>5</td>
</tr>
<tr>
<td>Toluene</td>
<td>28</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>27</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>13</td>
</tr>
<tr>
<td>123-trimethylbenzene</td>
<td>9</td>
</tr>
<tr>
<td>Alpha-Pinene</td>
<td>11</td>
</tr>
<tr>
<td>Beta-Pinene</td>
<td>9</td>
</tr>
<tr>
<td>EPA surrogate mixture</td>
<td>25</td>
</tr>
<tr>
<td>Full surrogate mixture</td>
<td>18</td>
</tr>
</tbody>
</table>

- Charts to summarize many experiments
- Ozone bias by hour
  - Lines show 6 hours
  - Bias binned and counted

零偏差
UCR: CO/FORM

CO

Chamber mechanism better calibrated for SAPRC99 than CB05

Formaldehyde

HCHO photolysis the same: why is the performance different?

The CB05 and SAPRC99 inorganic mechanisms differ slightly, e.g., \( \text{OH} + \text{NO}_2 \)
UCR: Olefins

propene

SAPRC99 under-predicts ozone

trans-2-butene
UCR: Aromatics

**toluene**

CB05 forms ozone too slowly

**m-xylene**

CB05 ozone scattered and too low
UCR: XYL/TERP

1,2,4-trimethylbenzene

CB05 low
SAPRC99 high

α-pinene

CB05 translation of SAPRC99 TERP works well for α-pinene
Comparing CB05 and CB4 - Ozone

- Urban scenario
  VOC/NOx = 10

- CB05 has faster ozone production
  - radical production from IOLE and ALDX

- CB05 has same final ozone
  - nitrogen sinks (PANX and PAN) curtail ozone
CB05 and CB4 EKMA Diagrams

CB05

Ozone (ppb)

CB4

NOx (ppb)

VOC (ppbC)
Ozone Difference: CB05 minus CB4

- CB05 has higher ozone in VOC-limited conditions
  - radicals from IOLE and ALDX

- CB05 has slightly lower ozone in NOx-limited conditions
  - PANX formation
  - this scenario does not see opposing impact of NOx-recycling reactions
Recommendations

• There should be a comparative study of UCR and UNC chamber experiments, especially for aromatics, to understand apparent chamber differences

• Aromatics mechanism should be updated using new data – after evaluating chamber differences

• Experimental studies of NOx recycling from organic nitrates
Questions?