CB6
Version 6 of the Carbon Bond Mechanism

Greg Yarwood, ENVIRON
Gookyoung Heo, UT Austin
Gary Whitten, SmogReyes
Presented by Mark Estes, TCEQ
October 14, 2010
Outline

- CB6 Objectives
- Project Team
- Mechanism Design
- Preparing Emissions for CB6
- Evaluation with Chamber Data
- CAMx Implementation and Testing
- Conclusions and Recommendations
CB6 Objectives

• TCEQ-sponsored research suggests mechanism differences (i.e. uncertainties) may influence response to emission reductions

• Carbon Bond mechanism last updated in 2005
  – New data and interpretations emerge
  – Faster computers permit more detailed mechanisms
  – Several updates ready from TCEQ projects in FY08/09
    ▪ Toluene, isoprene, nitryl chloride, NO2*

• CB6 objectives
  – Update mechanism core to 2010
  – Expand mechanism to address emerging needs
  – Combine and integrate available updates from recent TCEQ work
  – Perform complete mechanism evaluation
  – Implement and test in CAMx
Project Team

• Gary Whitten
  • Consultant in Point Reyes, California
  • Inventor of Carbon Bond approach (CB2, CB4/CBM-X, CB05/CB05-TU)
  • Project Role: Mechanism updates for isoprene, aromatics, alkenes

• Gookyoung Heo
  • Post-doc at UT Austin and soon moving to UC Riverside
  • Project Role: Mechanism evaluation; Critical review of mechanism updates and implementation

• Greg Yarwood
  − Principal at ENVIRON in Novato, California
  − Role: Overall mechanism design/implementation; CAMx
CB6 Mechanism Design

• Constraints
  – Maintain backwards compatibility with existing databases
    ▪ Can use CB05 (or even CB4) emission with CB6
  – Computational efficiency
    ▪ Limit simulation time increases

• Emerging needs
  – Lower ozone standard emphasizes regional problems
    ▪ Improve long-lived, abundant VOCs such as propane
    ▪ Fate of NOz (e.g., organic nitrates) — recycled back to NOx?
  – Secondary organic aerosol (SOA) often important for fine PM
    ▪ Gas-phase chemistry should support SOA requirements
    ▪ Volatility basis set (VBS) being used for gas/aerosol partitioning
    ▪ Aqueous reactions form SOA from dicarbonyls (e.g., glyoxal)
CB6 Updates for Oxidants

• Oxidant updates
  – Inorganic reactions to IUPAC 2010
  – Recent photolysis data (IUPAC, NASA/JPL, other)
  – New aromatics chemistry
  – New isoprene chemistry
  – New ketone species (acetone and higher ketones)
  – Explicit propane, benzene, ethyne (acetylene)

• Optional oxidant updates
  – Optional means available and can chose whether/when to use
  – Nitryl chloride (CINO2) formation and chlorine atom reactions (based upon TexAQS 2000 and TexAQS II results)
  – Photo-excited NO2 (NO2*) which remains controversial – real or artifact?
CB6 Updates that Support Aerosol Modeling

• Additional SOA precursors
  Added new VOCs that are SOA precursors
  – Benzene
  – Ethyne (acetylene)

• Explicit alpha-dicarbonyls: –C(O)CH(O) also –C(O)CH₂OH
  Aqueous reactions form SOA by polymerizing these compounds
  – Glyoxal (GLY), methylglyoxal (MGLY), glycolaldehyde (GLYD)
  – Precursors are isoprene, aromatics, ethene, propene (etc.), ethyne
  – GLY and GLYD are newly explicit in CB6

• Improved hydrogen peroxide
  Hydrogen peroxide converts SO₂ to sulfate aerosol in clouds
  – Improve how some peroxy radical reactions (RO₂ + HO₂) are handled
Preparing Emissions for CB6

- **Propane: PRPA**
  - In CB05 was 1.5 PAR + 1.5 NR

- **Benzene: BENZ**
  - In CB05 was 1 PAR + 6 NR

- **Ethyne (acetylene): ETHY**
  - In CB05 was ALDX

- **Acetone: ACET**
  - In CB05 was 3 PAR

- **Higher ketones: KET**
  - Methyl ethyl ketone ($\text{CH}_3\text{C(O)CH}_2\text{CH}_3$) is the prototypical example
  - MEK was 4 PAR in CB05, is 3 PAR + KET in CB6

- **Other new CB6 species** (e.g., GLY, GLYD) have negligible emissions
## Summary of CB6 and CB05

<table>
<thead>
<tr>
<th></th>
<th>CB05</th>
<th>CB6</th>
<th>Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas-phase reactions</td>
<td>156</td>
<td>218</td>
<td>+ 40%</td>
</tr>
<tr>
<td>Photolysis reactions</td>
<td>23</td>
<td>28</td>
<td>+ 22%</td>
</tr>
<tr>
<td>Gas-phase species</td>
<td>51</td>
<td>77</td>
<td>+ 50%</td>
</tr>
<tr>
<td>Emissions species for ozone</td>
<td>16</td>
<td>21</td>
<td>+ 31%</td>
</tr>
</tbody>
</table>

Some notable reaction rate changes from CB05 to CB6:

- \( \text{OH} + \text{NO}_2 = \text{HNO}_3 \) increased by 5% => greater radical sink
- \( \text{HCHO} + \text{hv} = 2 \text{HO}_2 + \text{CO} \) increased by 23% => greater radical source
- \( \text{HO}_2 + \text{NO} = \text{OH} + \text{NO}_2 \) increased by 5% => more efficient ozone formation
- \( \text{NO}_2 + \text{hv} = \text{NO} + \text{O} \) increased by 7% => more ozone
- \( \text{N}_2\text{O}_5 + \text{H}_2\text{O} = 2 \text{HNO}_3 \) decreased by ~80%
  - Less NOx removal at night
  - Very important to include \( \text{N}_2\text{O}_5 \) reaction on aerosol surfaces
Evaluation with Chamber Data

- Evaluated CB6 using environmental chamber simulations
- Evaluated CB6 using a hierarchical approach (e.g., from CO – NOx system to complex VOCs – NOx system)
- Used ~340 chamber experiments of 8 different smog chambers (7 indoor and 1 outdoor)
  - First, screened available chamber experimental data to select useful data for mechanism evaluation
- Used 3 performance metrics to evaluate CB6:
  - Max(O₃): Maximum O₃ concentration
  - Max(D(O₃-NO)): Maximum \{([O₃] – [NO])_{t=t} - ([O₃] – [NO])_{t=0}\}
  - NOx crossover time: Time when NO₂ becomes equal to NO
- Compared CB05, CB05-TU and CB6
  - Also produced chamber simulation results for CB05 and CB05-TU
Hierarchical Approach

- Test each component of CB6, and systematically evaluate the entire CB6 mechanism while minimizing compensating errors.
Chamber Data

• UC Riverside chamber database
  – UC Riverside database contains experimental data for thousands of experiments produced at UC Riverside and TVA (Tennessee Valley Authority)
  – Note: UNC chamber data were not used due to the light model issue

• Selecting chamber data useful for CB6 evaluation
  – Excluded blacklight-used experiments whenever possible
  – For most cases, 10 ppb < [NOx]o < 300 ppb

• Evaluating each components of CB6
  – Used ~195 chamber experiments of single test compounds (or special mixtures) (e.g., CO - NOx)
  – For MEOH (methanol), ETOH (ethanol), ETHA (ethane) and PRPA (propane), only blacklight/mixture experiments were available

• Evaluating interactions of CB6 components and CB6 as a whole
  – Used 145 surrogate mixture experiments (e.g., 8-compnent VOC mixture – NOx)
Chamber Simulation Results: Time series plots

- Example: experiment TVA080 (toluene – NOx experiment in the TVA chamber)
- As NO and toluene are oxidized, $O_3$ increases
Chamber Simulation Results: Results for TOL

- 20 TOL – NOx experiments (18 with toluene and 2 with ethyl benzene)
- Performance metrics were used to quantify mechanism performance.

Summary of mechanism performance using model errors of metrics

<table>
<thead>
<tr>
<th></th>
<th>CB05</th>
<th>CB05-TU</th>
<th>CB6</th>
<th>CB05</th>
<th>CB05-TU</th>
<th>CB6</th>
<th>CB05</th>
<th>CB05-TU</th>
<th>CB6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max(O₃) [%]</td>
<td>-49</td>
<td>-17</td>
<td>-11</td>
<td>-40</td>
<td>-14</td>
<td>-10</td>
<td>79</td>
<td>-29</td>
<td>22</td>
</tr>
<tr>
<td>Max(D(O₃-NO)) [%]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NOx crossover time [min]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average model error</td>
<td>28</td>
<td>16</td>
<td>15</td>
<td>26</td>
<td>14</td>
<td>12</td>
<td>63</td>
<td>19</td>
<td>20</td>
</tr>
<tr>
<td>Standard deviation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Performance of CB6: $\text{Max}(O_3)$

Model errors [units: %]:

\[
\frac{\text{model} - \text{measured}}{\text{measured}}
\]

**Surg-Full** experiments: full surrogate VOC mixtures

**Surg-NA** experiments: no aromatics

CB6 generally improved and within +/- 20% bias

Note: Only blacklight/mixture experiments were available for MEOH (methanol), ETOH (ethanol), ETHA (ethane).
New Species in CB6: Max(O$_3$)

Model errors [units: %]:

\[
\frac{\text{model} - \text{measured}}{\text{measured}}
\]

CB6 much improved and within +/- 20% bias

Ethyne (ETHY) could be improved

Note: Only blacklight/mixture experiments were available for PRPA (propane)
Performance of CB6: NOx crossover time

Model Error for NOx Crossover Time [min]

- ISOP
- TERP
- Surg-Full
- Surg-NA
- Surg-Inc
- XYL
- TOL
- ETOH
- MEOH
- IOLE
- OLE
- ETH
- ALD2
- PAR
- ETHA
- FORM
- CO

CB6 comparable to CB05 and mostly within +/- 20 min

Note: Only blacklight/mixture experiments were available for MEOH (methanol), ETOH (ethanol), ETHA (ethane).

Delayed crossover time for isoprene with CB6:
- Need for further work?
- Only 6 experiments

Model errors [units: minute]:
(model – measured)
Ne Species in CB6: NOx crossover time

Model errors [units: minute]:
(model – measured)

CB6 much improved and within +/- 20 min except for ethyne (ETHY)

Note: Only blacklight/mixture experiments were available for PRPA (propane)
Summary of CB6 Performance

• **Overall summary:** CB6 performed better in simulating $O_3$ than CB05 and CB05-TU

• **CB6 Performance for major components** existing both in CB05 and CB6
  – Inorganics (CO and other inorganics): similar
  – Aldehydes (FORM, ALD2, ADLX): similar or better
  – Alcohols (MEOH, ETOH): not clear due to experiment uncertainties
  – Alkanes (ETHA, PAR): not clear due to experiment uncertainties
  – Olefins (ETH, OLE, IOLE): similar
  – Aromatics (TOL, XYL): far better than CB05 especially for TOL
  – Isoprene (ISOP): worse performance in simulating NOx crossover times
  – Terpenes (TERP): similar

• **Performance for newly added explicit species**
  – CB05 performed better than CB05 for ACET (acetone), KET (higher ketones), PRPA (propane), BENZ (benzene) and ETHY (ethyne)

• **Performance for surrogate VOCs-NOx mixtures:** Similar or better

• **Further studies:** (1) GLY (glyoxal), TOL and XYL, ISOP and ETHY; (2) using experimental data of blacklight-used experiments and UNC chamber experiments.
Use HDDM to Assess VOC Reactivity

- Use HDDM with Los Angeles episode
- Use $dO_3/dVOC$ and $dO_3/dNOx$ to identify VOC limited grid cells
- Calculate $dO_3/dVOC$ for individual VOC species
  - Assume each has same spatial/temporal emissions distribution as total VOC
- Relative reactivity for each VOC is like an MIR factor
VOC Reactivity Analysis for Los Angeles modeling evaluation

CB6 and CB05 reactivity factors calculated from an LA simulation using HDDDM and calibrated to CB05 MIRs.
### VOC Reactivity Analysis

<table>
<thead>
<tr>
<th>CB6 Species</th>
<th>CB05</th>
<th>CB6</th>
<th>Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>ETHA</td>
<td>0.135 (a)</td>
<td>0.135 (a)</td>
<td>0%</td>
</tr>
<tr>
<td>PRPA</td>
<td>0.504 (b)</td>
<td>0.541</td>
<td>7%</td>
</tr>
<tr>
<td>PAR</td>
<td>0.336</td>
<td>0.509</td>
<td>51%</td>
</tr>
<tr>
<td>ACET</td>
<td>1.01 (b)</td>
<td>0.564</td>
<td>-44%</td>
</tr>
<tr>
<td>KET</td>
<td>0.336 (b)</td>
<td>1.39</td>
<td>314%</td>
</tr>
<tr>
<td>ETHY</td>
<td>7.22</td>
<td>0.487</td>
<td>-93%</td>
</tr>
<tr>
<td>ETH</td>
<td>4.26</td>
<td>4.95</td>
<td>16%</td>
</tr>
<tr>
<td>OLE</td>
<td>8.02</td>
<td>9.66</td>
<td>20%</td>
</tr>
<tr>
<td>IOLE</td>
<td>13.7</td>
<td>16</td>
<td>17%</td>
</tr>
<tr>
<td>ISOP</td>
<td>12.1</td>
<td>12.7</td>
<td>5%</td>
</tr>
<tr>
<td>TERP</td>
<td>8.5</td>
<td>9.91</td>
<td>17%</td>
</tr>
<tr>
<td>BENZ</td>
<td>0.336 (b)</td>
<td>1.39</td>
<td>314%</td>
</tr>
<tr>
<td>TOL</td>
<td>2.15</td>
<td>7.39</td>
<td>244%</td>
</tr>
<tr>
<td>XYL</td>
<td>14.2</td>
<td>20.5</td>
<td>44%</td>
</tr>
<tr>
<td>FORM</td>
<td>4.32</td>
<td>4.87</td>
<td>13%</td>
</tr>
<tr>
<td>ALD2</td>
<td>4.68</td>
<td>5.8</td>
<td>24%</td>
</tr>
<tr>
<td>ALDX</td>
<td>7.22</td>
<td>8.35</td>
<td>16%</td>
</tr>
<tr>
<td>MEOH</td>
<td>0.354</td>
<td>0.48</td>
<td>36%</td>
</tr>
<tr>
<td>ETOH</td>
<td>1.11</td>
<td>1.53</td>
<td>38%</td>
</tr>
</tbody>
</table>

- CB6 and CB05 reactivity factors calculated relative to ethane using CAMx-HDDM for Los Angeles

- Increased reactivity with CB6 for many species, especially aromatics, C4+ alkanes (PAR), alcohols

- Changes expected for species that are newly added in CB6 (see note b)

(a) The reactivity of ethane (ETHA) was held constant at 0.135

(b) PRPA, ACET, KET, ETHY and BENZ are not model species in CB05 and therefore are represented by surrogate species
8-hr Ozone: Eastern US episodes

Episode Daily
Max 8-Hr Ozone

Ozone increases
Hydroxyl radical (OH) at 1 pm

Episode
Average 1-Hr OH at 1 pm
Hydrogen Peroxide (H₂O₂)

CB05

CB6

Episode Daily Max 8-Hr H₂O₂

Lower H₂O₂ in areas with high biogenic VOC
Summary of CB6 and CB05

<table>
<thead>
<tr>
<th></th>
<th>CB05</th>
<th>CB6</th>
<th>Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas-phase reactions</td>
<td>156</td>
<td>218</td>
<td>+ 40%</td>
</tr>
<tr>
<td>Photolysis reactions</td>
<td>23</td>
<td>28</td>
<td>+ 22%</td>
</tr>
<tr>
<td>Gas-phase species</td>
<td>51</td>
<td>77</td>
<td>+ 50%</td>
</tr>
<tr>
<td>Emissions species for ozone</td>
<td>16</td>
<td>21</td>
<td>+ 31%</td>
</tr>
</tbody>
</table>

Some notable reaction rate changes from CB05 to CB6:

- OH + NO₂ = HNO₃ increased by 5% => greater radical sink
- HCHO + hν = 2 HO₂ + CO increased by 23% => greater radical source
- HO₂ + NO = OH + NO₂ increased by 5% => more efficient ozone formation
- NO₂ + hν = NO + O increased by 7% => more ozone
- N₂O₅ + H₂O = 2 HNO₃ decreased by ~80%
  - Less NOx removal at night
  - Very important to include N₂O₅ reaction on aerosol surfaces
Conclusions and Recommendations

• CB6 mechanism agrees better with chamber data than CB05

• Mechanism issues remain, including
  – Aromatics
    ▪ Nature and magnitude of the NOx sinks
      – Experiments proposed to the AQRP
    ▪ Uncertainties for dicarbonyl products
      – Acetylene experiments suggest glyoxal is uncertain
      – Obtain and analyze European data (EUPHORE chamber)
  – Isoprene
    ▪ Performance could be improved
    ▪ Only 6 experiments, none from the UCR EPA chamber
  – NOx recycling from organic nitrates
    – Experiments proposed to the AQRP
  – Relationship between pure compound and mixture experiments
Conclusions and Recommendations

• CAMx implementation complete, but more testing recommended
  – Simulation times greater than expected
    ▪ Mechanism sensitivity tests
  – Los Angeles results for VOC-limited conditions as expected
  – TCEQ domain results for NOx-limited conditions need to be explained
    ▪ Mechanism sensitivity tests
    ▪ Make use of HDDM, including sensitivity output for radicals
  – Compare CB6 and CB05 emissions sensitivity

• Test OSAT/PSAT implementation

• Implement chemical process analysis (CPA)