Testing the Speed of a 13,500-Reaction Chemical Mechanism with SMVGGEAR II and the Accuracy of the Mechanism Against Smog Chamber Data

International Conference on Atmospheric Chemical Mechanisms

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Outline

• Motivation
• Master Chemical Mechanism v3.1
• SMVGEAR II
• Model comparison
• Smog Chamber comparison
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Motivation

• Model organic chemistry explicitly
• Condensation and aerosol formation of organic species
  – Climate implications
• Local and global 3D simulations
  – Need fast and accurate model
Outline

- Motivation
- **Master Chemical Mechanism v3.1**
- SMVGEAR II
- Model comparison
- Smog Chamber comparison
Master Chemical Mechanism

• “...a near-explicit chemical mechanism describing the degradation of 135 volatile organic compounds (VOCs) in the troposphere” for the purpose of investigating ozone production

• University of LEEDS in the UK
Master Chemical Mechanism

• Based on available laboratory data
  – Not fully tested versus field/photochemical reactor data
• 13,500 reactions and 4,600 chemical species
Outline

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SMVGGEAR II

- Sparse-matrix ODE solver
  - Gear solution mechanism – accurate
  - Sparse-matrix - fast

<table>
<thead>
<tr>
<th>Number of Operations - MCM v. 3.1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<tr>
<td>------------------------------------</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Order of matrix</td>
</tr>
<tr>
<td>Decomp. 1</td>
</tr>
<tr>
<td>Decomp. 2</td>
</tr>
<tr>
<td>Backsub. 1</td>
</tr>
<tr>
<td>Backsub. 2</td>
</tr>
</tbody>
</table>
Sparse-Matrix Reductions

<table>
<thead>
<tr>
<th>Order of Matrix</th>
<th>Number of Multiplications Necessary for First Decomposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Initial</td>
</tr>
<tr>
<td>2</td>
<td>Day</td>
</tr>
<tr>
<td>3</td>
<td>Night</td>
</tr>
</tbody>
</table>

- Initial
- Day
- Night

- 1,000
- 2,000
- 3,000
- 4,000
- 5,000

Order of Matrix vs. Number of Multiplications Necessary for First Decomposition
Computer Timings

Intel Pentium 4 Extreme, 3.2 GHz

Without: time(4649 species):time(140 species) = 74 million
With: = 360
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ACBM vs MCM

- **CH₄** - treated explicitly
  - SMV: 1.80E+00
  - MCM: 1.80E+00

**Time of Day**

- 6:00 AM to 5:00 PM

**ppb**

- CH₄ (SMV)
- CH₄ (MCM)
- NO (SMV)
- NO (MCM)
- NO₂ (SMV)
- NO₂ (MCM)
- O₃ (SMV)
- O₃ (MCM)

**Graph**

- **O₃ (SMV)**
- **O₃ (MCM)**

**Time of Day**

- 6:00 AM to 5:00 PM

**ppb**

- O₃ (SMV)
- O₃ (MCM)
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MCM v. 2

• Previous work by Jinyou Liang, 2002
• Comparing MCM v. 2 with smog-chamber data
  – 7000 Reactions
  – Modified four reaction rates for toluene and m-xylene intermediates to more closely match CBIV rates
NO

**Observational Data**

**MCM v.2**

**MCM - Modified**
The graph shows the concentration of nitrogen dioxide (NO₂) over the course of a day. The y-axis represents parts per billion (ppb) of NO₂, while the x-axis represents the time of day. The data is presented as observational data points (diamonds), along with two modeled curves: MCM v.2 (purple line) and MCM - Modified (red line). The peaks and troughs of the curves indicate the variation of NO₂ levels throughout the day.
O₃

Observational Data
MCM v.2
MCM - Modified

Time of Day

ppb

6 8 10 12 14 16 18

6 8 10 12 14 16 18
MCM v.3.1 – What’s Next

- Verify with smog-chamber data
  - Improved aromatics reactions
- Compare with field data
- Add vapor pressures and model condensation
Acknowledgements

• NASA
• Jinyou Liang, CARB
• Mark Jacobson, Stanford University
Toluene

Observational Data
MCM1
MCM0

Time of Day
ppb

6 8 10 12 14 16 18
MCM v. 2 Modifications

1. \((C_6H_5O)CH_3 + OH \rightarrow HC(O)CH=CHCH=CHC(O)CH_3 + HO_2\)
   
   Original \(k = 1 \times 10^{-10}\)  \(\rightarrow\) Modified \(k = 3 \times 10^{-10}\)

2. \(HC(O)CH=CHCH=CHC(O)CH_3 \rightarrow HC(O)CH=CHC(O)CH_3 + 2 HO_2 + 2 CO\)
   
   Original \(J = 8.46 \times 10^{-6}\)  \(\rightarrow\) Modified \(J = 1 \times 10^{-3}\)

3. \((C_6H_4O)(CH_3)_2 + OH \rightarrow HC(O)CH=CHC(CH_3)=CHC(O)CH_3 + HO_2\)
   
   Original \(k = 1 \times 10^{-10}\)  \(\rightarrow\) Modified \(k = 3 \times 10^{-10}\)

4. \(HC(O)CH=CHC(CH_3)=CHC(O)CH_3 \rightarrow HC(O)C(CH_3)=CHC(O)CH_3 + 2 HO_2 + 2 CO\)
   
   Original \(J = 8.46 \times 10^{-6}\)  \(\rightarrow\) Modified \(J = 1 \times 10^{-3}\)
Observational Data

MCM1

MCM0

Time of Day

ppb
MCM Chemistry Summary

**VOC**

**initiation reactions**
- **photolysis**
  - carbonyls, ROOH, RC(O)OOH and RONO₂
- **OH reaction**
  - all VOC and oxygenated products
- **NO₃ reaction**
  - alkenes, dienes, aldehydes and ethers
- **O₃ reaction**
  - alkenes, dienes, and unsaturated oxygenated products

**reactions of intermediates**
- **oxy: RO**
  - O₂ reaction decomposition isomerisation
- **peroxy: RO₂**
  - reaction with NO, NO₂, NO₃, HO₂, R'O₂
- **excited Criegee [RC(OO)R']^+**
  - stabilisation decomposition

**products**
- **oxygenated products**
  - carbonyls, ROOH, ROH, RC(O)OOH, RC(O)OH, RONO₂, PANs, multifunctional and CO
Degradation of Butane

- Broken down into $\text{CO}_2$, CO, or organic chemicals
- 510 reactions, 186 Species, 20 primary emitted VOC
What do you do with it?

1. Validate MCM with data and by comparing to other mechanisms
2. Use in air pollution modeling
   • Ozone
What’s been done (recently)?

Evaluation of isoprene degradation in the detailed tropospheric chemical mechanism, MCM v3, using environmental chamber data

– P.G. Pinho, C.A. Pioa, M.E. Jenkinb,

• Both isoprene and butane generally performed well
• a number of parameter modifications were identified which resulted in an improved performance
  – Relate to the magnitude of sources of free radicals from organic chemical process and the yields of radicals from the reactions of O3 with unsaturated oxygenates
  – It was necessary to include a representation of the reactions of O(3P) with isoprene, MACR and MVK (which were not previously treated in MCM v3)
• MCM v3 was also compared with that of the SAPRC-99 mechanism
What’s been done (recently)?

Modelling of the photooxidation of toluene: conceptual ideas for validating detailed mechanisms (2002)

- V. Wagner1, M. E. Jenkin2, S.M. Saunders1*, J. Stanton1, K. Wirtz3, and M. J. Pilling1

• Model simulations for toluene-NOx experiment
• Two major shortcomings
  - OH production is too low by 80%
  - Ozone concentration at the end of the experiment is overpredicted by 55%
What’s been done (here)?

• Jinyou Liang and Mark Jacobson - 1999 Paper, MCM v1
  – Compared with 2 other mechanisms
  – Utilized SMVGGEAR II – reduced calculations by a factor of 15,000
  – Compared to smog-chamber data and L.A. field data

• Similar study done in 2002 with MCM v2
  – Version 3 came out
## Improvement in Computer Time using SVMGEAR II

<table>
<thead>
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<th>Initial</th>
<th>After Sparse Matrix Reductions</th>
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<tr>
<td></td>
<td>Day</td>
<td>% Reduction</td>
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<tr>
<td>No. operations backsub. 2</td>
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<td>10,215</td>
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</tbody>
</table>
Results for Toluene
What am I going to do?

• Similar to Jinyou Liang, with MCM v3.1

1. Update SVMGEARII code with latest mechanism
2. Compare data to smog chamber data, field measurements and other mechanisms
3. (Maybe) determine condensable species with vapor pressure data