Comparing GECKO-A and MechGen as a starting point for mechanism simplification

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The starting point: Explicit and Semi-Explicit Models

**GECKO-A**
Developed at LISA (ISPL, Paris) with collaborations from NCAR
- Mechanisms can run to **millions** of reactions & species
- Generates reactions based on SARs
- Includes gas-phase chemistry and partitioning to aerosols

**MechGen**
Developed at UCR, with CARB funding:
- Underlies the SAPRC-18 mechanism
- Mechanisms can run to **many thousands***

* MechGen is usually run for 1 generation but is applied here to several generations, iteratively, to approximate completion

We are attempting to use these models to inform the development of reduced mechanisms
Mechanism Generation Flow Diagram

**MechGen**
- uses a similar decision flow
- usually for only 1 generation
- iterates for several generations for current project

**MechGen • uses a similar decision flow • usually for only 1 generation • iterates for several generations for current project**
### MechGen vs GECKO-A: mechanism size comparison

<table>
<thead>
<tr>
<th>precursor</th>
<th>GECKO-A (to completion)</th>
<th>MechGen (several generations)*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>#species</td>
<td>#reactions</td>
</tr>
<tr>
<td>Propane</td>
<td>800</td>
<td>3K</td>
</tr>
<tr>
<td>Butane</td>
<td>1.7K</td>
<td>11K</td>
</tr>
<tr>
<td>2-methylfuran</td>
<td>4K</td>
<td>24K</td>
</tr>
<tr>
<td>Isoprene</td>
<td>3K</td>
<td>18K</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>8K</td>
<td>90K</td>
</tr>
<tr>
<td>Octane</td>
<td>26K</td>
<td>170K</td>
</tr>
<tr>
<td>A-pinene</td>
<td>400K</td>
<td>2M</td>
</tr>
</tbody>
</table>

**Assumptions**

- Reactivity cutoff: 5% branching ratio
- Volatility cutoff: 1e-13 atm
- Lumping?: similar isomers (large Cn)

*MechGen is usually run for 1 generation but is applied here to several generations, iteratively, to approximate completion.*
Translation of MechGen/SAPRC mechanisms into GECKO-A format

We have built a **MechGen -> GECKO-A** mechanism translator, which will be made available to the community.

=> MechGen/SAPRC and GECKO-A mechanisms can run in the SAME box model.

### Example precursors:
- propane, 2-methyl furan, isoprene, α-pinene

<table>
<thead>
<tr>
<th>GECKO-A</th>
<th>MechGen</th>
</tr>
</thead>
<tbody>
<tr>
<td>C03000</td>
<td>CH₃CH₂CH₃</td>
</tr>
<tr>
<td>FU0002</td>
<td>-O₁-CdH=CdH=Cd₁CH₃</td>
</tr>
<tr>
<td>ISOPRE</td>
<td>CH₃Cd(=CdH₂)CdH=CdH₂</td>
</tr>
<tr>
<td>APINEN</td>
<td>C₁₂H₇CH₂CH(C₁(CH₃)CH₃)CH₂CdH =Cd₂CH₃</td>
</tr>
</tbody>
</table>

### Example reactions: propane + OH => RO₂ product

<table>
<thead>
<tr>
<th>GECKO-A</th>
<th>MechGen (lumped RO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC03000 + GHO =&gt; G203000</td>
<td>R) 1.11e-12 ;PROPANE + OH = RO2-0001 + SumRO2</td>
</tr>
<tr>
<td>GC03000 + GHO =&gt; G203001</td>
<td>... Followed by RO2+RO2 reactions in up to 7 lumped classes</td>
</tr>
<tr>
<td>... Followed by RO2+RO2 reactions in up to 7 lumped classes</td>
<td>... Followed by RO2+RO2 reactions in 2 lumped classes</td>
</tr>
</tbody>
</table>

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5.527E-12</td>
<td>836.</td>
</tr>
<tr>
<td></td>
<td>4.717E-12</td>
<td>555.</td>
</tr>
</tbody>
</table>
Approach

• Put both mechanisms into a common format, to allow comparison in a single box model
• Find bulk properties of the resulting mixture relevant to reactivity and aerosol formation
• Use comparisons to find any systematic differences between the mechanism generators
• Where we intend to go: Test increasingly simplified/lumped mechanisms to assess how well they reproduce the explicit results
Model comparisons: total OH reactivity, s\(^{-1}\)

**Run conditions**
- Constant light
- Fixed oxidant concentrations:
  - \([\text{OH}]\) 1.4e+7 molec/cc
  - \([\text{O}_3]\) 0.12 ppm
  - \([\text{NO}_2]\) 3 ppb
  - \([\text{NO}]\) 0.4 ppb
  - \([\text{NO}_3]\) 0.6 ppt
  - \([\text{HO}_2]\) 37 ppt
  - \([\text{RO}_2]\) 30 ppt
  - \([\text{RCO}_3]\) 5 ppt

**Graphs**

- **Propane**
  - Upper lines: include precursor
  - Lower lines: products only

- **2m-furan**
  - Upper lines: include precursor
  - Lower lines: products only

- **Cyclohexane**
  - Upper lines: include precursor
  - Lower lines: products only

- **Octane**
  - Upper lines: include precursor
  - Lower lines: products only

- **Isoprene**
  - Upper lines: include precursor
  - Lower lines: products only

- **α-pinene**
  - Upper lines: include precursor
  - Lower lines: products only

**Models**
- **GECKO-A**
- **MechGen**
- **MechGen w/o RO2 isom**

Solid lines = include precursor
Dashed lines = products only
Cyclohexane OHR differences arise from different products…

Major difference:
- MechGen => R-O-R
- GECKO-A => -CO(OH)

Where do these different species come from?
Simplified scheme with selected example pathways arising from different chemical assumptions.
Multifunctional acids (GECKO) react faster than R-O-R MechGen with OH and NO₃.

### GECKO-A: top 6 acids

<table>
<thead>
<tr>
<th>name</th>
<th>formula</th>
<th>$k_{OH}$</th>
<th>$k_{NO₃}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A02000</td>
<td>CH₃CO(OH)</td>
<td>8.0e-13</td>
<td>6.43e-19</td>
</tr>
<tr>
<td>AO3000</td>
<td>CH₂(OH)CH₂CO(OH)</td>
<td>5.9e-12</td>
<td>5.0e-16</td>
</tr>
<tr>
<td>AO4000</td>
<td>CH₂(OH)CH₂CH₂CO(OH)</td>
<td>8.4e-12</td>
<td>5.2e-16</td>
</tr>
<tr>
<td>AD3000</td>
<td>CO(OH)CH₂CHO</td>
<td>2.2e-11</td>
<td>4.8e-15</td>
</tr>
<tr>
<td>AO2000</td>
<td>CH₂(OH)CO(OH)</td>
<td>2.2e-12</td>
<td>3.1e-16</td>
</tr>
<tr>
<td>AD4000</td>
<td>CO(OH)CH₂CH₂CHO</td>
<td>2.2e-11</td>
<td>1.1e-14</td>
</tr>
</tbody>
</table>

**Mean:** 1.0e-11 3.4e-15

### MechGen: top 6 R-O-R

<table>
<thead>
<tr>
<th>name</th>
<th>formula</th>
<th>$k_{OH}$</th>
<th>$k_{NO₃}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ORG-0337</td>
<td>C₁H₂CO-O-COC₁H₂</td>
<td>4.1e-13</td>
<td>1.5e-17</td>
</tr>
<tr>
<td>GBUTYACT</td>
<td>C₁H₂CH₂-O-COC₁H₂</td>
<td>2.0e-12</td>
<td>4.0e-17</td>
</tr>
<tr>
<td>ORG-0572</td>
<td>C₁H₂CH(OH)-O-COC₁H₂</td>
<td>3.0e-12</td>
<td>6.8e-16</td>
</tr>
<tr>
<td>ORG-0667</td>
<td>C₁H₂CO-O-CH₂C₁O</td>
<td>4.4e-13</td>
<td>8.5e-18</td>
</tr>
<tr>
<td>VOC-0309</td>
<td>C₁H₂CH₂CO-O-C₁(OH)C₁H₂CO(OONO₂)</td>
<td>1.8e-12</td>
<td>4.0e-17</td>
</tr>
<tr>
<td>VOC-0369</td>
<td>CO(OONO₂)CH₂CO-O-C₁HO</td>
<td>1.3e-13</td>
<td>2.1e-18</td>
</tr>
</tbody>
</table>

**Mean:** 1.3e-12 1.3e-16

⇒ For OHR and NO₃R in cyclohexane, GECKO-A >> MechGen
Model comparisons: total NO$_3$ reactivity, s$^{-1}$

**Run conditions**
Constant light

Fixed oxidant concentrations:
- [OH] 1.4e+7 molec/cc
- [O3] 0.12 ppm
- [NO2] 3 ppb
- [NO] 0.4 ppb
- [NO3] 0.6 ppt
- [HO2] 37 ppt
- [RO2] 30 ppt
- [RCO3] 5 ppt

**GECKO-A**
MechGen
MechGen w/o RO2 isom

Solid lines = include precursor
Dashed lines = products only
Model comparisons: vapor pressure (log10 atm) @ 2 x precursor lifetime

Octane, 2 lifetimes
2-methyl furan, 2 lifetimes
Isoprene, 2 lifetimes
Cyclohexane, 2 lifetimes

Y-axis: concentration (ppbC)

GECKO-A
MechGen
MechGen w/o RO2 isom

Estimations by method of Nannoolal et al. (2008)
Model comparisons: Henry's law coefficient (log10 M/atm) @ 2 x precursor lifetime

Y-axis: concentration (ppbC)

X-axis: vapor pressure (log10 M/atm)

- octane, 2 lifetimes
- a-pinene, 2 lifetimes
- isoprene, 2 lifetimes
- cyclohexane, 2 lifetimes

2-methyl furan, 1τ
2τ
3τ
4τ
5τ

GECKO-A
MechGen
MechGen w/o RO2 isom
Conclusions

• GECKO-A and MechGen compare well for OHR, NO3R, vapor pressure, Henry’s Law coefficient.
  • Biggest differences are in cyclohexane: MechGen includes additional cyclization-decomposition reactions
• Autooxidation / RO2 isomerization does not make a significant difference in most cases here

Next steps:
  • Assess chemistry differences under a range of conditions.
  • Progressively increase the degree of lumping in MechGen & repeat the comparisons

ALSO:
  • We have funding to hire a postdoc for the mechanism reduction project – let us know if you’re interested!

AND:
  • Both models & their SARs are recently updated: look for the public release of GECKO-A and of MechGen documentation in 2023!
<table>
<thead>
<tr>
<th></th>
<th>GECKO-A</th>
<th>MechGen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Funding &amp; Effort</td>
<td>EU Magnify project based at IPSL</td>
<td>CARB: Developed at UCR</td>
</tr>
<tr>
<td>Objective: Generate...</td>
<td>...explicit &amp; complete <strong>multi-generation multi-species</strong> chemical schemes for use as-is in box model studies</td>
<td>...near-explicit <strong>single-generation single-species</strong> VOC mechanisms for use in deriving &amp; updating lumped SAPRC mechanisms</td>
</tr>
<tr>
<td>Box model</td>
<td><strong>Purpose-built</strong> accompanying model</td>
<td>No dedicated model: mechanisms inform SAPRC studies</td>
</tr>
<tr>
<td>Web interface</td>
<td>geckoa.lisa.u-pec.fr (single-species, a few generations)</td>
<td>mechgen.cert.ucr.edu (single-species, single-generation)</td>
</tr>
<tr>
<td>Peer-reviewed publications</td>
<td><strong>Original version</strong>: Aumont et al. (2005) + incremental development papers; numerous studies of chem. complexity</td>
<td><strong>Updated version</strong>: Model description manuscript is ready for peer review.</td>
</tr>
<tr>
<td>Documentation</td>
<td><strong>Updated version</strong> has full referencing. User guide in development.</td>
<td>In development: summary at <a href="http://www.cert.ucr.edu/~carter/SAPRC">www.cert.ucr.edu/~carter/SAPRC</a></td>
</tr>
<tr>
<td>Status</td>
<td><strong>Updated version</strong>: Public release and manuscript planned for 2023</td>
<td><strong>Updated version</strong> supports SAPRC-22, which is nearly complete.</td>
</tr>
</tbody>
</table>

The documentation / SAR update efforts are nearly complete (as of late 2022).
OH reaction
Jenkin M. et al., 2018a, 2018b

O₃ reaction
Jenkin et al., 2020
Newland et al., 2022

NO₃ reaction
Kerdouci J., et al., 2014

Photolysis
RCHO + hν → R + HCO
RONO₂ + hν → RO + NO₂
ROOH + hν → RO + OH

Thermal decomposition
Jenkin et al., 2019

Peroxy alkyl chemistry
Jenkin et al., 2019

Peroxy acyl chemistry
Jenkin et al., 2019

Alkoxy chemistry
Vereecken L. and Peeters J., 2009
Vereecken L. and Peeters J., 2010