Automating The Search for New Pathways in Atmospheric Oxidation Chemistry

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Why search for new (gas-phase) organic oxidation chemistry?

• In recent years, novel gas-phase mechanisms have been shown to play an important role in the formation of SOA

Autoxidation

IEPOX

Crounse et al., JPCL, 2013

Paulot et al., Science, 2009
Systematizing the Search for Novel Oxidation Chemistry

• Are there other non-canonical oxidation mechanisms that we have missed or overlooked?
• How do we look for these mechanisms in a way that is not prohibitively expensive?
Systematizing the Search for Novel Oxidation Chemistry
The Reaction Mechanism Generator

- Thermodynamics: Group Additivity
- Kinetics:
  - Extensive database of QM data
  - Hierarchical rate rule “families”
  - estimation protocol

Generating Reaction Networks

- 200 “chemically reasonable” mono- and bifunctionally substituted pentanes

\[ \text{Alcohol} \quad \text{Hydroperoxide} \quad \text{Carbonyl} \quad \text{Alkoxy} \quad \text{Ether} \quad \text{Alkene} \]

(incorporated in carbon skeleton)
Example: Carbonyl Alcohol 2,1
Filtering the RMG Output

<table>
<thead>
<tr>
<th>R•</th>
<th>RO•</th>
<th>RO2•</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fast</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(competes with known atmospheric removal process)</td>
<td>Competes with O₂ reaction</td>
<td>Within cutoff factor of fastest unimolecular rate</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Interesting</td>
<td></td>
<td></td>
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<tr>
<td>(non-canonical reaction)</td>
<td>NOT: R + O₂ → RO₂•</td>
<td>NOT: RO• + O₂ → R=O + HO₂•</td>
</tr>
<tr>
<td></td>
<td>ROOH → •OH + R=O</td>
<td>RO• → •R’ + R”=O</td>
</tr>
<tr>
<td></td>
<td>R + O₂ → HO₂• + Alkene</td>
<td>RO₂• → •QOOH</td>
</tr>
</tbody>
</table>
RMG and RO$_2$ isomerizations

- RMG finds 1334 unique RO$_2$ isomerization reactions that meet the cutoff criteria.
- Majority of these have rates far below 0.01 s$^{-1}$, but a sizable tail ($\sim$15%) above this cutoff.

Bianchi et al., Chem. Rev., 2019
RMG and RO$_2$ isomerizations

- Compare RMG estimated rates with SAR rates for mono and bifunctionally substituted RO$_2$ isomerizations
- RMG captures general behavior fairly well, with exception of the “Scrambling” reaction

Vereecken and Nozière, Atmos. Chem. Phys., 2020
RMG and RO$_2$ isomerizations

- On average, most of the categories are actually captured fairly well by RMG.
- Scrambling reaction is systematically underestimated; suggests need for better data in RMG.
Looking for Novel Chemistry

- RO₂/C=O cyclization
- RO/C=O cyclization
- Cyclic ether
- RO₂/OOH ozonide
- R/C=O cyclization
- RO ring open
- R ring open
Looking for Novel Chemistry

• Categorize the filtered RMG reactions into 13 groups, the 9 that show up most frequently are shown here with their distribution of rates from RMG

• This is not particularly useful
Looking for Novel Chemistry

- The ratio of the rate of interest to the total removal rate is a better metric for how much the reaction may matter in the atmosphere.
Carbonyl Cyclization: a possible novel reaction pathway?

Sebbar et al., Int. J. Chem. Kin., 2019
Possible Atmospheric Implications of the \( \text{RO}_2/\text{Carbonyl Ring Closure} \)

- O-O bond break?
- \( \text{O}_2 \) addition?
- Further oxidation?
- Photolysis?

Sebbar et al., Int. J. Chem. Kin., 2019
Possible Atmospheric Implications of the RO$_2$/Carbonyl Ring Closure

\[ \text{VOC} \xrightarrow{\text{OH}} \text{R}^\cdot \xrightarrow{\text{O}_2} \text{R}'(=\text{O})\text{RO}_2^\cdot \]

- ROOH
- RC(O)OH
- RC(O)OOH
- ROON$_2$
- NO$_2^\cdot$
- HO$_2^\cdot$
- NO$^\cdot$
- RO$_2^\cdot$
- ROH
- RC(O)R'

- \text{RO}^\cdot$
- \cdot\text{QOH}$
- \text{Isomerization}
- ??
- \text{Fragmentation? Functionalization?}

Ring Closure (no NO needed!)
Conclusions

• RMG finds fast RO$_2$ radical isomerizations, demonstrating it’s utility as a tool in the search for novel oxidation chemistry

• We find several novel classes of organic radical transformations, including an RO$_2$/C=O cyclization reaction

• Further investigation is needed!
  • Validation of new pathways (via theory or experiment)
  • Fates of new products
  • Implications for SOA potentials