Supplementary Material

NOx emissions, isoprene oxidation pathways, vertical mixing, and implications for surface ozone in the Southeast United States

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Table S1 – Species Added to GEOS-Chem

<table>
<thead>
<tr>
<th>Species</th>
<th>Note</th>
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<tbody>
<tr>
<td>HPALD</td>
<td>Hydroperoxyaldehydes (C₅H₈O₃)</td>
</tr>
<tr>
<td>HC187</td>
<td>Epoxide oxidation product m/z 187-189</td>
</tr>
<tr>
<td>DHDN</td>
<td>C₅ dihydroxydinitrate</td>
</tr>
</tbody>
</table>

Table S2 – Reaction Rates and Productions Updated in GEOS-Chem

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reference</th>
<th>Rate Constant</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>RIO₂ + HO₂ → 0.937RIP + 0.063OH + 0.025MACR + 0.038MVK + 0.063HO₂ + 0.063CH₂O</td>
<td>(Liu et al., 2013)</td>
<td>2.06E-13*exp(1300/T)</td>
<td>(Saunders et al., 2003)</td>
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<tr>
<td>RIO₂ + NO → 0.91NO₂ + 0.82HO₂ + 0.82CH₂O + 0.476MVK + 0.344MACR + 0.058HC₅ + 0.03DIBOO + 0.009ISOPND + 0.081ISOPNB</td>
<td>(Liu et al., 2013; Fisher et al., 2016)</td>
<td>2.7E-12*exp(350/T)</td>
<td>(Paulot et al., 2009a)</td>
</tr>
<tr>
<td>RIO₂ → HO₂ + HPALD</td>
<td>(Peeters et al., 2009; Peeters and Muller, 2010; Crounse et al., 2011)</td>
<td>4.07E8*exp(-7694/T)</td>
<td>Rate adjusted by Crounse et al. (2011)</td>
</tr>
<tr>
<td>RIO₂ + RIO₂ → 0.91HO₂ + 0.75CH₂O + 0.455MVK + 0.29MACR + 0.09DIBOO + 1.11HC₅ + 0.29CO</td>
<td>(Xie et al., 2013)</td>
<td>2.3E-12</td>
<td>(Xie et al., 2013)</td>
</tr>
<tr>
<td>HPALD + OH → MGLY + CO + CH₂O + OH</td>
<td>(Squire et al., 2015)</td>
<td>5.1E-11</td>
<td>(Wolfe et al., 2012)</td>
</tr>
<tr>
<td>HPALD + hυ → OH + HO₂ + 0.5GLYC +</td>
<td>(Stavrakou et al., 2010)</td>
<td>Rate is equivalent to</td>
<td>(Peeters and Muller,</td>
</tr>
</tbody>
</table>
The yields are not identical to the Lee et al. (2014) values and there is artificial recycling of ISOPNDO$_2$ to account for non-unity reactants (i.e. in Lee et al. (2014) one ISOPNDO$_2$ reacts with 1.06ISOPNDO$_2$).

In Lee et al. (2014), a C5 hydroperoxide is formed (ROOH). In order to close the nitrogen budget this would have to be ISNP – a peroxide species with a nitrate group.

Replace C4NACID in Lee et al. (2014) with PROPNN.

HNO$_3$ added to this reaction to close the nitrogen budget, as we replace ethyl nitrate with its oxidation product, peroxyacetyl nitrate.

Update pre-exponential factor of this reaction in globchem.dat from Bates et al. (2014).

Other organic products were identified by Bates et al. (2014). These structural isomers are replaced with CO for the epoxide product (m/z 201) and a new species (also added as a tracer) is added to GEOS-Chem to account for the m/z 187 and 189 isomers.
References


Stavrou, T., Peeters, J., and Müller, J. F.: Improved global modelling of HO<sub>x</sub> recycling in isoprene oxidation: evaluation against the GABRIEL and INTEX-A aircraft campaign measurements, Atmospheric Chemistry and Physics, 10, 9863-9878, 10.5194/acp-10-9863-2010, 2010.
