A New Explicit Model of Isoprene Oxidation

Effects on NOx, Oxidant, and VOC Budgets

Kelvin H. Bates* & the Caltech isoprene team: John Crounse, Leah Dodson, Renee McVay, Laura Mertens, Tran Nguyen, Eric Praske, Becky Schwantes, Matt Smarte, Jason St Clair, Alex Teng, Paul Wennberg, John Seinfeld

Abstract

A nearly complete gas-phase oxidation mechanism of isoprene and its major products is developed, incorporating results from recent laboratory studies as well as insights from theoretical approaches. The **explicit mechanism**, made available in KPP format for easy use in box modeling, is compiled with the aim of providing accurate atmospheric simulations of the impact of isoprene emissions on HO_x, NO_x, and products known to be involved in condensed phase processes. A reliable representation of the role of isoprene photochemistry in these chemical processes is crucial to quantifying its influence on ozone formation and regional climate. Additionally, we offer a **simplified mechanism** appropriate for implementation in chemical transport models that retains the essential chemistry required to accurately simulate this chemistry under the typical conditions where isoprene is emitted and oxidized in the atmosphere. Here, we show preliminary results from the incorporation of this simplified mechanism into GEOS-Chem, a global chemical transport model.

Look for our upcoming paper, "The Gas-Phase Reactions of Isoprene and its Major Oxidation Products", in *Chem. Rev.*

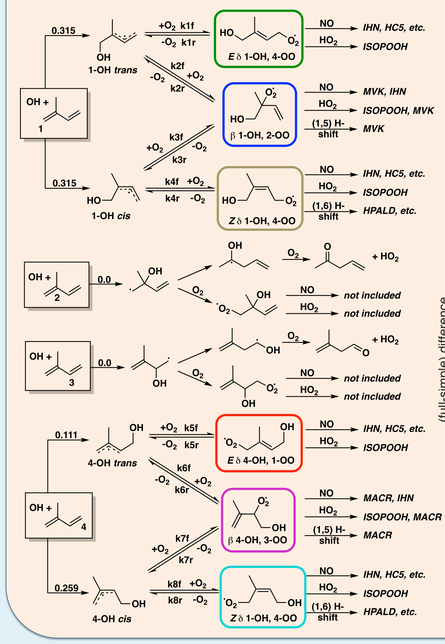
Outline

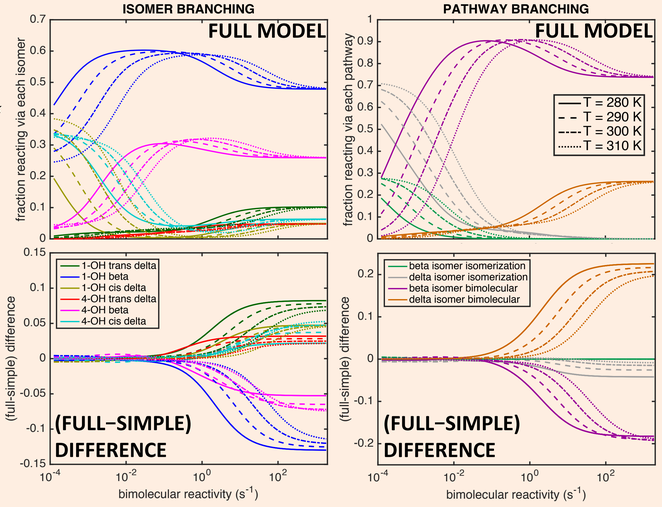
The following is a list of topics covered in our review, and the major sections of our explicit isoprene mechanism. Topics in **bold** (the "greatest hits") are described on this poster, but feel free to ask about any of the others!

1. Mechanism Development
   - **RO_2 + NO reactions**
   - **RO_2 + HO_2 reactions**
   - Hydrogen shifts (isomerization)
2. Isoprene + OH
   - Location of OH addition
   - **O_2 addition to allylic radicals - peroxy radical dynamics**
   - **Reactions of ISOPOO (NO, HO_2, RO_2, & isomerization)**
3. Isoprene + O_3
4. Isoprene + NO_3
5. Isoprene + Cl
6. Photochemistry of major oxidation products
   - Methyl vinyl ketone (MVK)
   - Methacrolein (MACR)
   - Hydroxy hydroperoxides (ISOPOOH)
   - Epoxydiols (IEPOX)
   - Nitrates (hydroxy-, carbonyl-, and hydroperoxynitrates)
   - Methacryloyl peroxynitrate (MPAN)
   - Hydroperoxy aldehydes (HPALD)
   - Hydroxymethyl hydroperoxide (HMHP)
7. **Preliminary modeling**
8. Remaining Challenges

Peroxy Radical Dynamics

- We use a scheme modified from Teng *et al.*, "Isoprene Peroxy Radical Dynamics," *J. Am. Chem. Soc.*, 2017.
- It is crucial to represent the allylic and peroxy radicals derived from isoprene as a dynamic system, as their isomer (and product) distribution can vary with pressure, temperature, and bimolecular lifetime.
- The explicit mechanism individually represents all 10 allylic and peroxy radicals that follow OH addition at C1 and C4; the simplified mechanism reduces this to two species, representing the steady-state peroxy radical distributions. These simplifications provide isomer and reaction pathway branching ratios within 5% of the explicit model for atmospheric conditions (P = 0.5-1 atm, T > 280 K, $k_{bimolecular} < 1\ s^{-1}$).





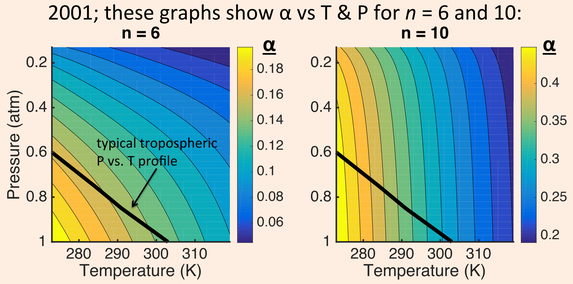
Left: isoprene peroxy radical dynamics following the addition of OH.
Above: dependence of peroxy radical isomer (left) and reactive pathway (right) branching ratios on bimolecular lifetime (x axis) and temperature (line style) in the new explicit mechanism (top), and the difference between the explicit and simplified models (bottom).

RO_2 + NO

- We implement a new parameterization for the branching ratios of nitrate formation (α) from RO_2 + NO reactions.
- Dependence of α on molecular size is derived from Teng, *et al.*, 2015, where *n* = # of non-H atoms (for *n* > 4):

$$\alpha_0 = [0.045 \times n] - 0.2$$

- Dependence of α on T and P is derived from Arey, *et al.*, 2001; these graphs show α vs T & P for *n* = 6 and 10:



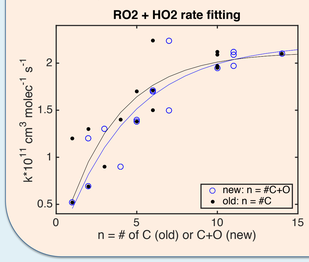
- α is scaled ×1.25/×0.75 for tertiary/primary peroxy radicals.
- α is further adjusted for functionalization (β-/γ-carbonyl, nitrate, hydroxy, and hydroperoxy groups).

RO_2 + HO_2

- We formulate RO_2 + HO_2 rate coefficients based on Orlando, *et al.*, 2012, after adding data and refitting for *n* = # of non-H atoms (excluding the peroxy moiety):

$$k_{RO_2+HO_2} = 2.82 \times 10^{-13} \times e^{(1300/T)} \times [1 - e^{(-0.231 \times n)}]\ cm^3\ molec^{-1}\ s^{-1}$$

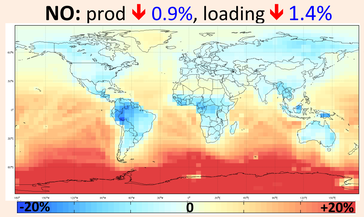
- We parameterize the radical propagating branching ratio (RO_2 + HO_2 → RO + OH + O_2) similarly to the RO_2 + NO → nitrate branching ratio, based on functionalization: tertiary > secondary > primary, with increased radical propagation for β-/γ-carbonyl, nitrate, hydroxy, and hydroperoxy groups.



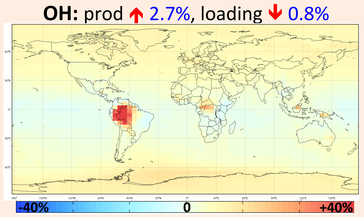
Preliminary Modeling

- A preliminary version of the simplified mechanism (~150 reactions and 50 species) was incorporated into GEOS-Chem, a chemical transport model.
- Comparisons shown below are between our simplified mechanism and the basic chemical mechanism that comes with v.10-01 of GEOS-Chem.
- Simulations were run for the year 2014 following an 18-month spinup, using GEOS-FP meteorology on a 4˚ x 5˚ grid with 72 vertical levels.
- Maps show annual averages over the bottom 1 km of the troposphere.

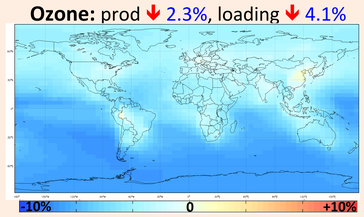
NO: prod ↓ 0.9%, loading ↓ 1.4%



OH: prod ↑ 2.7%, loading ↓ 0.8%



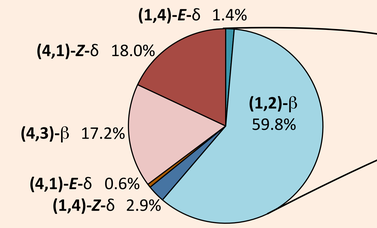
Ozone: prod ↓ 2.3%, loading ↓ 4.1%



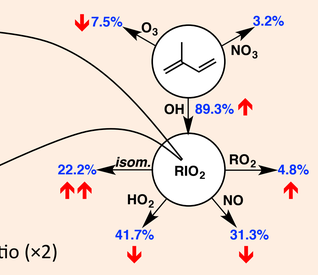
The new mechanism results in:

- Increased NO_x transport from higher nitrate yields
- Increased OH recycling from isomerization pathways
- Lower overall O_3 production

Globally averaged peroxy radical isomer pathway branching

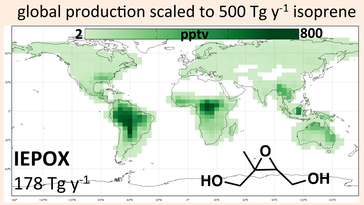


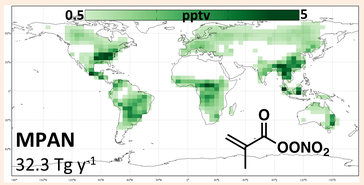
Globally averaged reactive pathway branching

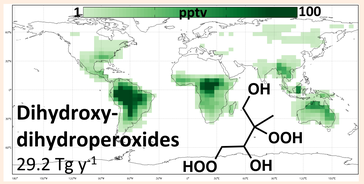


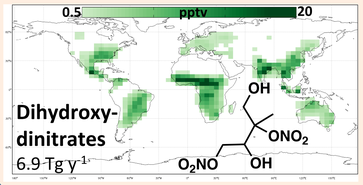
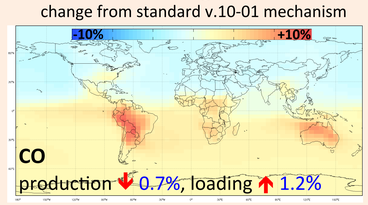
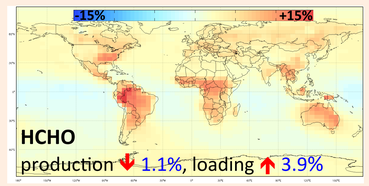
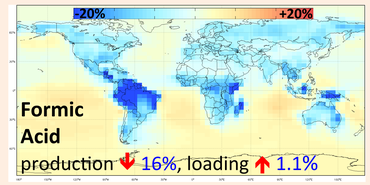
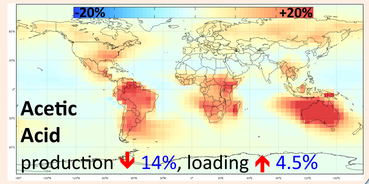
↑ (1,2):(4,3)-β ratio → ↑ MVK:MACR ratio (×2)

SOA precursors:
global production scaled to 500 Tg y^{-1} isoprene









Small organics:
change from standard v.10-01 mechanism