Development of a new mechanism for Isoprene oxidation.

Paul Wennberg, California Institute of Technology
his past and current group members
and many other friends

The 8th GEOS-Chem meeting (IGC8)

- - - For your consideration - - -
(GEOS-CHEM VI I -3?)
The gas-phase oxidation of isoprene and its first-generation degradation products

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Abstract. The gas-phase oxidation of isoprene and its first-generation oxidation products are described in detail. The mechanism is developed with the aim of both providing accurate simulations of the impact of isoprene chemistry on HOx and NOx free radical concentrations and to produce accurate representation of the yields of products known to be involved in condensed phase processes. The schemes presented represent a substantial advancement in computational chemistry over the schemes that have come before, affording new insight into the mechanisms at play. Insight from new theoretical approaches are also incorporated. Finally, we present a reduced 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.

1 Introduction

Volatile organic compounds (VOCs) emitted from vegetation significantly impact atmospheric photochemistry. This biogenic carbon flux is dominated by a single compound, isoprene (C5H8, 2-methyl-1,3-butadiene). The global budget of isoprene has been estimated by several approaches (Müller et al., 2008; Wang and Shallcross, 2000), typically constrained using surface flux measurements (Guenther and Hills, 1998; Wiedinmyer et al., 2004) and/or satellite observations (Shim et al., 2005). Estimates do not significantly vary between different approaches. The most up-to-date modeling framework suggests that, at roughly 500 Tg yr⁻¹, the emissions of isoprene alone comprise about half the total emissions of non-methane VOCs worldwide from nature (Guenther et al., 2012). This emission originates from the tropical distribution of forest (e.g., tropical Asia).

The majority of isoprene’s massive flux originates from a light-dependent de novo synthesis in plants using carbon from the Calvin cycle; dark production from microorganisms, plants, and animals is only a minor contribution (Sharkey, 1996). The question of why leaves emit isoprene is more complex. A recent unified hypothesis suggests that isoprene is synthesized in plant tissue to mitigate the compounded effects from several environmental stress factors that produce reactive oxygen species in vivo (Vickers et al., 2009), e.g., extreme temperatures, high light, water deficiency, soil salinity, air pollution, and mechanical damage.

Following biosynthesis, isoprene is lost to the atmosphere through stomata and does not significantly accumulate in the leaves (Fall and Monson, 1992). As a result, nearly the entire flux of isoprene occurs during daytime (Monson and Fall, 1989; Loreto and Sharkey, 1990). Further information on the biogenesis of isoprene and historical context of studies is provided by a number of reviews, including: Sharkey and
Isoprene + OH + NO
Impact of the isoprene photochemical cascade on tropical ozone

F. Paulot¹,², D. K. Henze², and P. O. Wennberg¹,³

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Figure S12: Relative change (in %) in the tropospheric ozone column as NOx emissions are set to North America mean NOx emission per capita (see text).
Isoprene Peroxy Radical Dynamics

Alexander P. Teng,† John D. Crounse,† and Paul O. Wennberg*†

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Table 7. Chronological estimates for α of ISOPO₂ + NO to form HN at 298 K and 1 atm (unless otherwise noted).

<table>
<thead>
<tr>
<th>α</th>
<th>T (K)</th>
<th>P (Torr)</th>
<th>technique</th>
<th>citation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.08 (+0.02)</td>
<td>298</td>
<td>740</td>
<td>chamber, FTIR</td>
<td>Tuazon and Atkinson (1990)</td>
</tr>
<tr>
<td>0.044 (+ 0.008)</td>
<td>298</td>
<td>743</td>
<td>chamber, GC-Pyrolysis-NO₂ detection</td>
<td>Chen et al. (1998)</td>
</tr>
<tr>
<td>0.12 (+ 0.07)</td>
<td>297</td>
<td>750</td>
<td>flowtube, FTIR</td>
<td>Sprengnether et al. (2002)</td>
</tr>
<tr>
<td>0.08 (+ 0.06)</td>
<td>297</td>
<td>445</td>
<td>flowtube, FTIR</td>
<td>Sprengnether et al. (2002)</td>
</tr>
<tr>
<td>0.15 (+ 0.10)</td>
<td>300</td>
<td>150</td>
<td>flowtube, LIF-NO₂ radical cycling</td>
<td>Chuang and Stevens (2002)</td>
</tr>
<tr>
<td>0.086</td>
<td>298</td>
<td>~760</td>
<td>Structure Activity Relationship</td>
<td>Giacopelli et al. (2005)</td>
</tr>
<tr>
<td>0.07</td>
<td>298</td>
<td>100</td>
<td>flowtube, FTIR</td>
<td>Pathen et al. (2007)</td>
</tr>
<tr>
<td>0.117 (+ 0.03)</td>
<td>296.5</td>
<td>~750</td>
<td>chamber, CIMS and modeling</td>
<td>Parler et al. (2006a)</td>
</tr>
<tr>
<td>0.07 (+0.02)</td>
<td>295</td>
<td>~760</td>
<td>chamber, GC-ECD with standards</td>
<td>Lockwood et al. (2010)</td>
</tr>
<tr>
<td>0.1 (+ 0.05)</td>
<td>298</td>
<td>760</td>
<td>-</td>
<td>IUPAC recommendation</td>
</tr>
<tr>
<td>0.09 (+0.04)</td>
<td>297</td>
<td>~760</td>
<td>chamber, INMS-CIMS</td>
<td>Xiong et al. (2005)</td>
</tr>
<tr>
<td>0.13 (+ 0.02)</td>
<td>297</td>
<td>745</td>
<td>chamber, CF₄O⁻ CIMS</td>
<td>Teng (2017)</td>
</tr>
</tbody>
</table>

DOI: 10.1021/jacs.6b12838

On Rates and Mechanisms of OH and O₃ Reactions with Isoprene-Derived Hydroxy Nitrates

Lance Lee, Alex P. Teng, Paul O. Wennberg, John D. Crounse, and Ronald C. Cohen

dx.doi.org/10.1021/jp4107603


Isoprene NO₃ Oxidation Products from the RO₂ + HO₂ Pathway

Rebecca H. Schwantes, Alexander P. Teng, Tran B. Nguyen, Matthew M. Coggon, John D. Crounse, Jason M. St. Clair, Xuan Zhang, Katherine A. Schilling, John H. Seinfeld, and Paul O. Wennberg

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Unexpected Epoxide Formation in the Gas-Phase Photooxidation of Isoprene

Fabien Paulot, John D. Crounse, Henrik G. Kjaergaard, Andreas Kürten, Jason M. St. Clair, John H. Seinfeld, Paul O. Wennberg

30 March 2009; accepted 25 June 2009
10.1126/science.1174251
Gas Phase Production and Loss of Isoprene Epoxidiols


dx.doi.org/10.1021/jp4107958
Kinetics and Products of the Reaction of the First-Generation Isoprene Hydroxy Hydroperoxide (ISOPOOH) with OH


DOI: 10.1021/acs.jpca.5b06532

Gas Phase Production and Loss of Isoprene Epoxidiols

Kelvin H. Bates,§ John D. Crounse,§ Jason M. St. Clair,§ Nathan B. Bennett,§|| Tran B. Nguyen,§ John H. Seinfeld,§‡ Brian M. Stoltz,§ and Paul O. Wennberg§

*Corresponding author.

1. No battleships were present.

2. The number of apples was not specified.

3. The temperature was not recorded.

4. The experiment was conducted indoors.
Isoprene Peroxy Radical Dynamics

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†Division of Geological and Planetary Sciences and ‡Division of Engineering and Applied Science, California Institute of Technology, Pasadena, California 91125, United States

DOI: 10.1021/jacs.6b12838
Atmospheric Fate of Methacrolein. 1. Peroxy Radical Isomerization Following Addition of OH and O₂

John D. Crounse,²,⁵ Hasse C. Knap,⁵ Kristian B. Olesen,⁵ Solveig Jørgensen,⁶ Fabien Paulot,⁶,⁸ Henrik G. Kjaergaard,⁵ and Paul O. Wennberg⁵,⁶,⁸

dx.doi.org/10.1021/jp211560u


Mechanism of the hydroxyl radical oxidation of methacryloyl peroxynitrate (MPAN) and its pathway toward secondary organic aerosol formation in the atmosphere

Tran B. Nguyen,⁶,⁹ Kelvin H. Bates,⁵ John D. Crounse,⁵ Rebecca H. Schwantes,⁵ Xuan Zhang,⁵ Henrik G. Kjaergaard,⁵ Jason D. Surratt,⁵ Peng Lin,⁵ Alexander Laskin,⁵ John H. Seinfeld⁵ and Paul O. Wennberg⁵

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Figure 6. Annual-averaged OH mixing ratio difference for 2012 resulting from the revised MVK mechanism (MVK + RCO_2). Results are reported for 0–1 km above the surface.

Atmospheric Fate of Methyl Vinyl Ketone: Peroxy Radical Reactions with NO and HO_2

Eric Praske, John D. Crouse, Kelvin H. Bates, Theo Kurtén, Henrik G. Kjærgaard, and Paul O. Wennberg

DOI: 10.1021/jp5107058

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Remaining questions & uncertainties

• What are the products and fates of the 1,6 H-shift chemistry?
• What are the rules for the OH-recycling reactions of OVOC?
• What are the rules for nitrate formation of OVOC?
• What are the fates of these nitrates? Heterogeneous chemistry?