Evolution of OH reactivity in low-NO volatile organic compound photooxidation investigated by the fully explicit GECKO-A model

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OH reactivity governs OH lifetime

• OH reactivity (OHR) is
  – the sum of the products of the reactant concentrations ($c_i$) and their OH reaction rate coefficients ($k_i$).
    – $OHR = \sum_i k_i c_i$

• OHR provides constraints on OH lifetime and budget

Adapted from OH Reactivity Wiki
(https://sites.google.com/site/reactivitywiki/home)
OHR is not well constrained

- Significant missing reactivity
  - Likely unspeciated intermediates and products

- Underestimation by Master Chemical Mechanism
  - Mechanism incompleteness

- OHR in clean remote regions
  - Low NO, high photochemical age

Williams and Brune. *A roadmap for OH reactivity research.* Atmos. Environ. 2015

Sato et al. AE 2017

Whalley et al. ACP 2016
We use the fully explicit GECKO-A model

• To model the OHR evolution in the low-NO photooxidation of
  – Alkanes (including decane)
  – A typical aromatic, m-xylene
  – A typical alkene, isoprene

• In different environments
  – Atmosphere
  – Large Teflon chamber
  – Oxidation flow reactor (OFR)

• Until very high (>10 d) photochemical ages
GECKO-A Generator Principles

**Precursors**

**GECKO-A**

*Computer program:*
Automatically generates oxidation scheme (reactions, mass transfer between phases, …)

**Protocol:**
Identify oxidation pathways
Estimates missing data

**Explicit chemical schemes + properties (Psat, H, …)**

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Beginning:

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_3 & \quad + \text{OH} \\
\text{CH}_3\text{CH}_2\text{CH}_3 & \quad + \text{OH} \\
\text{CH}_3\text{CH(OO.)CH}_3 & \quad + \text{NO} \\
\text{CH}_3\text{CH}_2\text{CH}_2(\text{OO.}) & \quad + \text{NO} \\
\text{…} & \quad \text{…} \\
\text{…} & \quad \text{…} \\
\text{…} & \quad \text{…} \\
\text{…} & \quad \text{…} \\
\text{…} & \quad \text{…} \\
\text{CO}_2 + \text{H}_2\text{O} & \quad \text{end}
\end{align*}
\]

Slide courtesy of Julia Lee-Taylor
Decane oxidation: ambient case

- Diurnal vs. constant sunlight makes little difference

Decane $\rightarrow$ C10 hydroperoxides ($\rightarrow$ C10 ketones)

$\rightarrow$ Multifunctional species

$\rightarrow$ Fragments (mainly C1 and C2, some larger ones)

$\rightarrow$ CO (or HCOOH) $\rightarrow$ CO$_2$
A common oxidation chain

- **Precursor** $\rightarrow$ first-generation products ($\rightarrow$ second-generation products) $\rightarrow$ saturated multifunctional species $\rightarrow$ fragmentation products $\rightarrow$ CO (HCOOH) $\rightarrow$ CO$_2$

- **Decane** $\rightarrow$ C10 hydroperoxides ($\rightarrow$ C10 ketones) $\rightarrow$ saturated multifunctional species $\rightarrow$ fragmentation products $\rightarrow$ CO (HCOOH) $\rightarrow$ CO$_2$

- **m-Xylene** $\rightarrow$ oxygenated alkenes ($\rightarrow$ oxygenated alkenes) $\rightarrow$ saturated multifunctional species $\rightarrow$ fragmentation products $\rightarrow$ CO (HCOOH) $\rightarrow$ CO$_2$

- **Isoprene** $\rightarrow$ ISOPOOH ($\rightarrow$ IEPOX) $\rightarrow$ saturated multifunctional species $\rightarrow$ fragmentation products $\rightarrow$ CO (HCOOH) $\rightarrow$ CO$_2$
OHR per C atom

- OHR per C atom converges when saturated multifunctional species are formed
  \[ k_{\text{per C}} = 1-2 \times 10^{-12} \text{ cm}^3 \text{ atom}^{-1} \text{ s}^{-1} \]

- Similar decay afterwards

- Can be parameterized for lumped model
OH consumed per C atom

- OH oxidation once $\rightarrow$ C oxidation state (OSc) $+\sim 2$
  - $\sim 3$ OH oxidations for OSc from $\sim -2$ to $+4$
Chamber w/o wall is similar to the atmosphere

- Similar UV range
- Similar OH concentration
- No other perturbation

Decane oxidation
Substantial OVOC wall losses in Teflon chamber

- Near-complete wall loss of C10 multifunctional species
- No OHR peak
- Significant hindrance of gas-phase chemistry at higher ages
Decane oxidation:
OFR with strong water vapor photolysis

In the OFR case
• Suppression of products at low ages
  – OH:HO₂ → 1:1 due to strong H₂O+hν(185 nm) → OH+HO₂
• Less fragmentation products at high ages
  – Insufficient organic photolysis
Summary

• Common oxidation chain
  – Precursor $\rightarrow$ first-generation products $\rightarrow$ second-generation products $\rightarrow$ saturated multifunctional species $\rightarrow$ fragmentation products $\rightarrow$ CO (HCOOH) $\rightarrow$ CO$_2$
  – Similar OHR per C evolution since saturated multifunctional species

• Substantial OVOC chamber wall losses for medium-size precursors
  – May lead to qualitatively different results

• OFR deviations
  – RO$_2$ accumulation at lower ages at high RH and lamp setting
  – Lack of efficient organic photolysis at higher ages