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 ($k_i$).
  - $\text{OHR} = \sum_i k_i c_i$

- 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

Peng and Jimenez, CSR 2020
GECKO-A Generator Principles

Precursors

Explicit chemical schemes + properties (Psat, H, ...)

Experimental data & structure activity relationships (SAR)

GECKO-A

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

Protocol:
Identify oxidation pathways
Estimates missing data

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 → first-generation products (→ second-generation products) → saturated multifunctional species → fragmentation products → CO (HCOOH) → CO₂

  - Decane → C10 hydroperoxides (→ C10 ketones) → saturated multifunctional species → fragmentation products → CO (HCOOH) → CO₂
  
  - m-Xylene → oxygenated alkenes (→ oxygenated alkenes) → saturated multifunctional species → fragmentation products → CO (HCOOH) → CO₂

  - Isoprene → ISOPOOH (→ IEPOX) → saturated multifunctional species → fragmentation products → CO (HCOOH) → CO₂
OHR per C atom

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

- 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 $-2$ 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
  - $\text{OH} : \text{HO}_2 \to 1:1$ due to strong $\text{H}_2\text{O} + \text{hv}(185 \text{ nm}) \to \text{OH} + \text{HO}_2$

- 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