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

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Abstract. OH reactivity (OHR) is an important control on the oxidative capacity in the atmosphere but remains poorly constrained. For an improved understanding of OHR, its evolution during oxidation of volatile organic compounds (VOCs) is a major aspect requiring better quantification. We use the fully explicit Generator of Explicit Chemistry and Kinetics of Organics in the Atmosphere (GECKO-A) model to study the OHR evolution in the low-NO photooxidation of several VOCs, including decane (an alkane), m-xylene (an aromatic), and isoprene (an alkene). Oxidation progressively produces more saturated and functionalized species. Total organic OHR (including precursor and products, OHR\textsubscript{VOC}) first increases for decane (as functionalization increases OH rate coefficients), and m-xylene (as much more reactive oxygenated alkenes are formed). For isoprene, C=\ C bond consumption leads to a rapid drop in OHR\textsubscript{VOC} before significant production of the first main saturated multifunctional product, i.e., isoprene epoxydiol. The saturated multifunctional species in the oxidation of different precursors have similar average OHR\textsubscript{VOC} per C atom. The latter oxidation follows a similar course for different precursors, involving fragmentation of multifunctional species to eventual oxidation of C1 and C2 fragments to CO\textsubscript{2}, leading to a similar evolution of OHR\textsubscript{VOC} per C atom. An upper limit of the total OH consumption during complete oxidation to CO\textsubscript{2} is roughly 3 per C atom. We also explore the trends in radical recycling ratios. We show that differences in the evolution of OHR\textsubscript{VOC} between the atmosphere and an environmental chamber, and between the atmosphere and an oxidation flow reactor (OFR) can be substantial, with the former being even larger, but these differences are often smaller than between precursors. The Teflon wall losses of oxygenated VOCs in chambers result in substantial deviations of OHR\textsubscript{VOC} from atmospheric conditions, especially for the oxidation of larger precursors, where multifunctional species may suffer near-complete wall losses, resulting in significant underestimation of OHR\textsubscript{VOC}. For OFR, the deviations of OHR\textsubscript{VOC} evolution from the atmospheric case are mainly due to significant OHR contribution from RO\textsubscript{2} and lack of efficient organic photolysis. The former can be avoided by lowering the UV lamp setting in OFR, while the latter is shown to be very difficult to avoid. However, the former may significantly offset the slowdown in fragmentation of multifunctional species due to lack of efficient organic photolysis.
1 Introduction

Photooxidation is a key process altering the concentrations of trace gases in the atmosphere (Levy II, 1971; Atkinson and Arey, 2003). It is also the main contributor to the formation of O₃ and secondary aerosols (Haagen-Smit, 1952; Chameides et al., 1988; Hallquist et al., 2009). Both products are major tropospheric pollutants (Nel, 2005; Cohen et al., 2017) and the latter have large climate impacts (Stocker et al., 2014).

Hydroxyl radical (OH) is the primary oxidizing agent in atmospheric photooxidation (Levy II, 1971). Its atmospheric fate is governed by the species that it reacts with, i.e., OH reactants. The first-order rate constant of OH consumption by an OH reactant is often called its OH reactivity (OHR), equal to the product of the reactant concentration and second-order rate constant with OH. Total OHR ($OHR_{\text{tot}}$), i.e., the sum of OHR across all OH reactants ($OHR_{\text{tot}} = \sum (k_i \times c_i)$, where $k_i$ and $c_i$ are the second-order rate constant with OH and concentration of the $i$th OH reactant), is the real first-order loss rate constant of OH.

OHR has been measured for over 20 years (Kovacs and Brune, 2001) in various settings, e.g., urban areas (Lu et al., 2013; Whalley et al., 2016), forested areas (Nölscher et al., 2016; Zannoni et al., 2016), and environmental chambers (Nehr et al., 2014; Nölscher et al., 2014). Despite numerous measurements and remarkable technical developments (Yang et al., 2016; Fuchs et al., 2017), a sizable fraction of total OHR in most measurements has not been chemically speciated, leading to so-called “missing reactivity” (Williams and Brune, 2015; Yang et al., 2016). Multiple studies (Nölscher et al., 2016; Whalley et al., 2016; Sato et al., 2017) have attributed missing reactivity to the highly complex mixture of intermediates and products of volatile organic compound (VOC) oxidation, most of which are oxygenated VOCs (OVOCs). Primary VOCs themselves have been found to be the largest contributor of the speciated OHR in many studies (Yang et al., 2016). In order to well understand ambient OHR, the evolution of OHR (including that from OVOCs) during primary VOC photooxidation thus needs to be investigated.

Experimentally, this can be done in environmental chambers. However, only a few such experiments have been published (Nakashima et al., 2012; Nehr et al., 2014; Nölscher et al., 2014; Sato et al., 2017), all under high-NO conditions, where the key organic radical intermediate in VOC oxidation, i.e., organic peroxy radical ($RO_2$), mainly reacts with NO. To our knowledge, no experiment of this type at low NO, where $RO_2$ can substantially react with hydroperoxy radical ($HO_2$), has been published so far, probably due to the high difficulty in achieving low-NO conditions in chambers. Also, many OVOCs, which may account for missing reactivity, have sufficiently low volatility to significantly partition to chamber walls (Matsunaga and Ziemann, 2010; Krechmer et al., 2016), further complicating these experiments. The OVOC wall losses also often limit operation times of chamber experiments to a few hours, after which the wall losses are so large that meaningful interpretation of experimental results would be difficult. Therefore, the highest equivalent photochemical age that can be reached in chamber experiments is also typically hours and far shorter than would be needed to explore the OHR evolution in later stages of VOC oxidation.

Oxidation flow reactors (OFR) are an alternative to chambers with much smaller volume, shorter residence time (and thus smaller wall losses of trace gases), and stronger oxidative capacity (Kang et al., 2007; Brune, 2019; Peng and Jimenez, 2020). The most common version of OFR is equipped with low-
pressure Hg lamps emitting UV at 185 and 254 nm, which photolyzes water vapor, O₃, and O₂, and generates a large amount of OH both directly and through subsequent radical reactions. High OH concentration in OFR often leads to equivalent photochemical age of days to weeks (Li et al., 2015; Peng et al., 2015). In principle, OFR can also be employed to explore OHR evolution in VOC oxidation. However, OHR from VOC (OHRVOC, from both precursor and oxidation intermediates/products, in which we include CO as an “organic” product of VOC oxidation) can have strong impacts on oxidative capacity (particularly OH concentration) and hence radical chemistry in OFR at both low (Li et al., 2015; Peng et al., 2015) and high NO (Peng and Jimenez, 2017; Peng et al., 2018). Peng and Jimenez (2020) have called for highly chemically detailed modeling of gas-phase organic chemistry in OFR to assess the impacts of organic OH reactants on OH in a more quantitative manner.

In this study, we explore for the first time the OHR evolution in entire low-NO VOC photooxidation processes by modeling. Since chemical mechanism incompleteness causes other models to unsatisfactorily simulate measured OHRt (Williams and Brune, 2015), we use the fully chemically explicit model GECKO-A (Generator of Explicit Chemistry and Kinetics of Organics in the Atmosphere) (Aumont et al., 2005). We simulate the photooxidation of different types of VOCs in the atmosphere, in chamber, and in OFR, to find out general trends of OHR evolution in VOC oxidation and whether VOC oxidation chemistries in chamber and OFR are representative of that in the atmosphere in terms of OHR evolution.

2 Methods

Here we first discuss the VOC precursor types and conditions selected for the model cases in this study. Then we describe the GECKO-A model and present our additional mechanism, model, and software development required for this study.

2.1 Model cases

The photooxidation of an alkane (decane), an alkene (isoprene), and an aromatic (m-xylene) is investigated under a variety of conditions without any NO. In pristine regions such as open oceans, NO has typical concentrations on the order of 1 ppt (Wofsy et al., 2021) and hence contribute only a few percent to RO₂ loss (Peng et al., 2019). For simplicity, we choose not to maintain such a low NO level in the simulations, but to model zero-NO cases instead. The model cases are listed in Table 1: i) two cases under ambient conditions, one with constant sunlight at solar zenith angle of 45° and the other with diurnally-varying solar radiation and a noontime solar zenith angle of 0°; ii) four cases under typical chamber conditions, i.e., low (10 s⁻¹) / high (100 s⁻¹) precursor OHR with / without gas-particle-wall partitioning; and iii) five cases under OFR conditions, of which two conditions resulting in significant non-tropospheric organic photolysis (Peng et al., 2016) and one leading to remarkable deviations of RO₂ fate from that in the troposphere are not recommended in practice, but are still included for completeness since they are similar to conditions in some literature studies (Table 1). For the UV source in chamber cases, we adopt the spectrum of the blacklight and fluorescence light array in the University of Colorado Environmental Chamber Facility (CU Chamber; Krechmer et al., 2017). The parameterization for the reversible gas-wall partitioning is taken from Krechmer et al. (2016) with updates of Liu et al. (2019). The cases under ambient conditions, and chamber conditions with low / high precursor OHR are simulated for 10, and 6 / 30 d, respectively, to encompass an equivalent photochemical age of >10 d in
each case (given a typical average ambient OH concentration of 1.5x10^6 molecules cm^{-3} in the real atmosphere (Mao et al., 2009); see Fig. 1 for the correspondence between equivalent photochemical age and OH exposure (OH_{exp}, i.e., the integral of OH concentration over time)). The simulated OFR in the present work employs the light source parametrization obtained by Li et al. (2015) and Peng et al. (2015). UV at both 185 and 254 nm is used to generate OH, i.e., the “OFR185” mode of operation. The residence time in the OFR is always 3 min.

In addition, we simulate illustrative cases of methane oxidation, under ambient and OFR conditions (Table 1 and Section 3.1). Note that these two simulations are performed using the GECKO-A generated mechanism (see Section 2.2) in another chemical-kinetics solver, KinSim (Peng and Jimenez, 2019), to avoid possible numerical issues, as methane oxidation by OH is very slow (Atkinson and Arey, 2003) and very long runs are needed. To characterize trends of OHR evolution (see Section 3.5), the ambient cases with constant sunlight are simulated for two more alkanes, i.e., butane and heptane (Table 1). To explore the effects of UV sources in OFR (see Section 3.4), two simulations under a typical OFR condition with an additional broad-spectrum UV source (5 and 10000 times the chamber UV source in this study, respectively) are performed for isoprene (Table 1).

2.2 The GECKO-A model

GECKO-A (Aumont et al., 2005; Camredon et al., 2007; Valorso et al., 2011), is an explicit chemical model which uses known mechanisms and rates supplemented with experimentally-based structure-activity relationships to generate comprehensive atmospheric oxidation mechanisms for organic species. The mechanisms are implemented within a box model with a two-step solver (Verwer, 1994; Verwer et al., 1996). In mechanism generation, isomer lumping for mechanism reduction purposes is applied to certain products with branching ratios < 1% (here typically N-containing products, which are not relevant for our simulations). It has a negligible impact on the results.

The core isoprene scheme in GECKO-A is adopted from Master Chemical Mechanism v3.3.1 (Jenkin et al., 2015), while the meta-xylene oxidation mechanism follows MCM v3.2 (Jenkin et al, 2003, Bloss et al, 2005) until ring-breaking occurs, whereupon the GECKO-A mechanism generator implements the standard SAR protocols.

We tested the effect of solver integration timestep length on output precision. The output species concentrations in all simulations but for isoprene OFR (Table 1) converge well as integration timestep decreases (Fig. S1). In the isoprene OFR test cases, the output values oscillate over a small range (<~5%) for integration timesteps ≤ 0.01 s (Fig. S1). Since this numerical error is smaller than typical rate constant measurement uncertainties (from ~10% to a factor of 2–3; Burkholder et al., 2015), let alone the uncertainties related to the SARs used in GECKO-A, it is deemed acceptable for the relevant simulations in this study. The integration timestep for each simulation in the present work is reported in Table 1.

We allow mechanism generation to proceed through to CO₂ production in most cases in this study. The only exception is for extremely low-volatility species (saturation vapor pressure < 10^{-11} atm) which are considered to be completely and irreversibly partitioned to the particle phase. Particle- and wall-phase species are no longer considered in the OHR budget, since heterogeneous oxidation is much slower than gas-phase oxidation (e.g., George and Abbatt, 2010). Gas-particle-wall partitioning is activated only for the chamber cases where wall effects are considered. For the ambient cases and the chamber cases
without gas-wall partitioning, gas-particle partitioning is also disabled to avoid artificial condensation of gases into the particle phase. In environments with very low NO (e.g., remote atmosphere), organic aerosol concentration is typically 0.2 μg m\(^{-3}\) (Hodzic et al., 2020) while most major intermediates/products have higher saturation concentrations (C*) and hence largely stay in the gas phase. C* is calculated using the parameterization of Nannoolal et al. (2008) (default option of GECKO-A). Although SIMPOL (Pankow and Asher, 2008) was recommended by Krechmer et al. (2016) to estimate C* for the chamber wall partitioning treatment using their parameterization, the C* estimates by the Nannoolal and SIMPOL parameterizations are close (generally within a factor of 2) for the species that can reversibly partition between the gas and wall phases (C* ~ 0.1–1000 μg m\(^{-3}\)) in this study. This difference is smaller than the uncertainties of the Krechmer et al. (2016) parameterization. Therefore, the use of the parameterization of Nannoolal et al. (2008) for C* estimation is acceptable.

Concerns have previously been expressed about non-conservation of carbon in GECKO-A (Mouchel-Vallon et al., 2020). This has proven in the current simulations to be almost entirely due to lack of accounting for product CO\(_2\) in some handwritten reactions. We edited the handwritten isoprene and m-xylene schemes (see above and Section 2.2.3) for carbon balance, which reduced simulation-end carbon losses in the m-xylene and isoprene ambient cases with constant UV from 4% and 9%, respectively, to negligible levels (<0.4%; Fig. S2).

For the current study, we have made several updates to GECKO-A, i.e., i) inclusion of key OFR-specific radical reactions, ii) extension of the UV range considered to cover 185 and 254 nm, and iii) updates to the low-NO m-xylene oxidation mechanism, so that GECKO-A is able to simulate OFR chemistry and the entire process of low-NO m-xylene photooxidation (until CO/CO\(_2\)). We will describe these three updates below.

### 2.2.1 Key radical reactions in oxidation flow reactor

We have added several reactions that are unimportant in the troposphere, but that are required to fully represent the radical chemistry within the OFR (Li et al., 2015). The most important inorganic reactions are H\(_2\)O + h\(\nu\) (185 nm) → H + OH, O\(_2\) + h\(\nu\) (185 nm) → 2O(\(^{3}\)P), and O(\(^{3}\)P) + O\(_2\) → O(\(^{1}\)D) + O\(_2\). These three reactions, together with O(\(^{3}\)P) + O\(_2\) + M → O\(_3\) + M and O(\(^{1}\)D) + H\(_2\)O → 2OH, which are already in the GECKO-A inorganic radical chemistry scheme, are responsible for the OH generation in OFR. The OFR radical chemistry has previously been modeled in detail using KinSim (Peng and Jimenez, 2019), which was validated against experimental observations (Li et al., 2015; Peng et al., 2015). A comparison between KinSim and GECKO-A for a range of OFR conditions shows typical agreement between the two models within 2% for key outputs.

Due to high OH in OFR, reaction of RO\(_2\) with OH is also included in mechanism generation, with an assumed rate constant of 1x10\(^{-10}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) (Peng et al., 2019). The products of this type of reaction are assumed to be RO (alkoxy radical) + HO\(_2\) for alkyl RO\(_2\) and R (alkyl radical) + CO\(_2\) + HO\(_2\) for acyl RO\(_2\). Although these reactions for certain RO\(_2\) may have reaction intermediates, the reactions of the intermediates are believed to be very fast in OFR (Peng and Jimenez, 2020) and hence only the probable final products (no intermediates) of these reactions are included in mechanism generation. The reaction of RO\(_2\) with OH is not included in the mechanisms for the ambient and chamber simulations due to low contribution of this pathway to the RO\(_2\) fate in those cases.
2.2.2 Organic photolysis at 185 and 254 nm

Organic photolysis is assessed in GECKO-A via a lookup table of j-values for reference chromophores pre-calculated at different solar zenith angles with the TUV 1-D radiative transfer model (Madronich and Flocke, 1999). The reference cross-sections used in the model generally do not cover the UV wavelengths at which OFR operates (with narrow peaks at 185 nm and 254 nm) since they are not tropospherically relevant. Thus it was necessary to extend to 185 nm the relevant reference absorption cross-sections. We have done this using literature values via the Mainz UV-Vis spectral atlas (Keller-Rudek et al., 2020) or by extrapolating the available cross-section data, using other similar chromophores as references. Details of all cross-section extensions are given in Table S1. Where quantum yield information was not available, we assume values of unity since photons at 185 and 254 nm are usually sufficiently energetic to make photolysis occur (Ausloos and Lias, 1971). In case of multiple product channels for a photolyzed molecule, the branching ratios of those channels at 185 and 254 nm are estimated through extrapolation of branching ratio data from available ranges followed by a renormalization. Finally, we apply the OFR UV spectrum within TUV to calculate OFR-relevant j-value lookup tables.

2.2.3 Mechanism of low-NO m-xylene oxidation

The meta-xylene oxidation mechanism in GECKO-A follows MCM v3.2 until all aromatic, epoxy, or bridged-peroxy rings are broken (See Scheme S1). Since the MCM was designed for typical urban environments with abundant NOx, it omits some reaction pathways for other oxidants, assuming them to be of negligible importance. The relevant photolysis loss pathways are slow under ambient conditions and inactive in the OFR case. This leads to persistence and accumulation of certain hydroperoxides and their interconverting peroxy radicals under low-NO conditions. We added two low-NO oxidation reactions to the xyleneol branch of the meta-xylene oxidation scheme, Scheme S1. In the 51% branch, we allow the unsaturated bicyclic peroxy “MXYLOOH” to react with, sequentially, OH (estimating $k_{OH} \sim 3 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) and HO$_2$ (estimating $k_{RO_2+HO_2} \sim 1 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$), to produce a saturated bicyclic peroxy (denoted “TT8001” in Scheme S1). In the 42% branch, we add a competing O$_3$ reaction with the alkoxy radical “MXCATEC1O”, producing an unsaturated carbonyl alkoxy radical “1T8000” which eliminates CH$_3$ to form the unsaturated cyclic hydroxy dicarbonyl “TU7000”. Both products are then further oxidised via the standard GECKO SARs.

2.3 GECKO Loader and Plotter

To allow GECKO-A outputs, which are usually highly complex and voluminous, to be explored and visualized in detail on standard (non-UNIX) personal computers, we have developed the GECKO Loader and Plotter based in the data-analyzing and graphic-making package Igor Pro 8.0 (WaveMetrics, Lake Oswego, Oregon, USA). This tool assists on the rapid and detailed analysis of model-chamber/OFR comparison studies.

Specifically, the GECKO Loader and Plotter facilitates: i) filtering the (sometimes extremely large and finely-resolved) model results time series to examine specific characteristics, ii) identifying the most abundant and/or influential species in each phase (gas, particle, and wall), iii) selecting species by specific chemical identity (molecular formula, specific formula, and/or functional group identity), iv) plotting time series of individual species and their formation/destruction rates, v) assessing and
displaying aggregated properties (volatility distribution, mass spectrum, Henry’s law constant
distribution) of the product mixture and subsets thereof, and vi) calculating bulk characteristics of the
simulation (OH\textsubscript{exp}, OHR\textsubscript{VOC}, light intensity, elemental ratios etc.) and relating species abundances to
them.

3 Results and discussions

In this section, we will show the evolution of OHR\textsubscript{VOC} in the photooxidation of different precursors
under various conditions. To aid the presentation of this evolution for larger precursors, whose oxidation
is more complex, the oxidation of the simplest VOC, i.e., methane, will be first discussed. After
presenting the results of individual precursors, we will compare the results between conditions and
between precursors to illustrate the general trends. Along with the OHR evolution, OH recycling ratio
(β\textsubscript{1}, defined as number of OH molecules generated from organic reactions per OH consumed by organics)
and HO\textsubscript{x} (= OH + HO\textsubscript{2}) recycling ratio (β\textsubscript{2}, defined as number of OH and HO\textsubscript{2} molecules generated from
organic reactions per OH consumed by organics) will also be discussed, as they are important parameters
that may considerably affect the budget of atmospheric oxidizing agents (Stone et al., 2012) and the HO\textsubscript{2}-
to-OH ratio and RO\textsubscript{2} chemistry in OFR (Peng et al., 2015, 2019).

3.1 Methane

To explain one of the main features in the OHR evolution in VOC photooxidation, i.e., OHR\textsubscript{VOC}
peaking at a certain OH\textsubscript{exp}, the oxidation of CH\textsubscript{4} is employed as an example because of its simpler
mechanism (Scheme S2). The results of this oxidation under the ambient condition show that OHR\textsubscript{VOC}
peaks at an OH\textsubscript{exp} of about 1x10\textsuperscript{13} molecules cm\textsuperscript{-3} s\textsuperscript{-1} (Fig. S3). As the OHR of the precursor always
decreases during its oxidation, the appearance of such a peak of OHR\textsubscript{VOC} before all VOCs are finally
oxidized to CO\textsubscript{2} indicates that the OHR increase from intermediates and products is faster than the OHR
decrease of the precursor. This is obviously the case for CH\textsubscript{4} oxidation, as there is no significant CH\textsubscript{4}
loss before OH\textsubscript{exp} \approx 10\textsuperscript{13} molecules cm\textsuperscript{-3} s\textsuperscript{-1}, by its very slow reaction with OH (rate constant on the order
of 10\textsuperscript{-13} cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1}; Atkinson and Arey, 2003) and all the non-CO\textsubscript{2} intermediates/products of the
oxidation (CH\textsubscript{3}OOH, CH\textsubscript{2}OH, HCHO, and CO) are orders of magnitude more reactive toward OH than
is CH\textsubscript{4} (Atkinson and Arey, 2003). This large difference in precursor and intermediate/product oxidation
timescales allows the oxidations of intermediates/products (including CO, whose reaction rate constant
with OH is \approx 2x10\textsuperscript{-13} cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1}; Burkholder et al., 2015) to establish a steady state, whereby the
OHR of the intermediates/products is proportional to the concentration/OHR of CH\textsubscript{4}. After OH\textsubscript{exp} \approx 10\textsuperscript{13}
molecules cm\textsuperscript{-3} s, CH\textsubscript{4} concentration decay, and consequently that of all intermediates/products, become
significant, giving the OHR\textsubscript{VOC} peak around 1x10\textsuperscript{13} molecules cm\textsuperscript{-3} s.

We also performed a simulation under a typical OFR condition. The OHR\textsubscript{VOC} peak also appears
around 1x10\textsuperscript{13} molecules cm\textsuperscript{-3} s in this case for the same reasons discussed above, but its height is almost
twice that of the ambient case (Fig. S3). The OHR of CO in both cases is similar, while that of CH\textsubscript{3}OH
is higher in the ambient case but those of CH\textsubscript{3}OOH and HCHO are significantly higher in the OFR case.
This is because the relative importance of the various reactions involved in CH\textsubscript{4} oxidation (Scheme S2)
depends on the conditions in each reactor.

In the OFR case, OH and HO\textsubscript{2} concentrations are \approx 4 and \approx 3 orders of magnitude higher than
typical ambient values, respectively (Peng et al., 2015). The reactions of two intermediates, CH\textsubscript{3}OOH
and HCHO, with OH and the reaction of the only major RO₂ involved, CH₃OO, with HO₂ are much faster than their photolysis or the self-reaction of CH₃OO (Scheme S2). Neglecting organic photolysis and CH₃OO self-reaction (and thus CH₃OH as a product of the latter), the mechanism of CH₄ oxidation can be simplified to an OH-driven chain (CH₄ → CH₂OOH → HCHO → CO → CO₂) with a fast steady-state branch on CH₂OOH (CH₂OOH ↔ CH₃OO). For a simple chain, as we show in Appendix A, the OHR of precursor and that of each intermediate are equal. At the OHR_VOCS peak, the OHR of HCHO and CO are very close to that of CH₄, while that of CH₂OOH is larger, because the branch reaction CH₂OOH + OH → CH₃OO + H₂O also contributes to OHR, but does not affect the chain (and hence the OHR of the downstream species). With such an idealized chain mechanism, the OHR_VOCS peak height equals the precursor OHR multiplied by the number of steps needed to produce CO₂.

In contrast, the OHR_VOCS peak height (and its composition) in the ambient case cannot be explained by the simple chain. Both HCHO photolysis and CH₃OO self-reaction play a major role in the oxidation in this case, and are significantly faster than the reactions in the simple chain (HCHO + OH and CH₃OO + HO₂). In terms of the relationship of these two reactions with the chain, HCHO photolysis bypasses HCHO + OH in converting HCHO to CO, while CH₃OO self-reaction bypasses CH₂OOH, in effect short-circuiting the involvement of OH in the oxidation and hence lowering OHR_VOCS (Appendix A). Since the only reaction of CO is CO + OH, its OHR at the OHR_VOCS peak is essentially unaltered.

3.2 Decane

3.2.1 Ambient and OFR cases

The evolution of OHR_VOCS during the oxidation of another alkane, decane, under ambient and OFR conditions exhibit a smaller difference and smaller peak enhancements than those in the methane cases (Fig. 1), although the chain lengths of the decane oxidation to CO₂ should be much longer than that of methane. The ambient cases with constant and diurnal solar radiation have almost the same OHR_VOCS evolution as a function of OH_exp (Figs. 1 and 2). Contrary to the methane cases, OHR_VOCS in all five decane simulations for OFR conditions is lower than that for ambient conditions.

These differences from the methane cases arise because a key assumption of the simple reaction chain model, i.e., slow precursor decay allowing intermediates/products to build up and reach a steady state, no longer holds in decane oxidation. The main first-generation products, i.e., secondary decyl hydroperoxides, react with OH only < x₃ more rapidly than does decane, as the significant activation effect of the –OOH group only applies to the α-H, and all other H atoms in this long chain alkyl can, though less reactive, be abstracted by OH (Kwok and Atkinson, 1995; Aumont et al., 2005). When decyl hydroperoxides are present in significant amounts (OH_exp ~ 5 × 10¹⁰ molecules cm⁻³ s⁻¹), decane loss is also significant (Fig. 3). Also, oxidation of monohydroperoxides to ketones, their most likely fate (due to the activated α-H), lowers OHR_VOCS, as the oxidation removes the most activated H (Kwok and Atkinson, 1995). The multifunctional products of further oxidation in the mid OH_exp range (before ~2 × 10¹¹ molecules cm⁻³ s⁻¹), mainly have -OOH and -CO- (Fig. 4), which do not further increase OHR substantially with respect to monohydroperoxides, for similar reasons as the comparison of monohydroperoxides with decane. After the OHR_VOCS peak, the precursor is largely consumed and -CH(OOH)- groups become increasingly oxidized to -CO- in both monohydroperoxides and multifunctional hydroperoxides (Figs. 3 and 4), which rapidly decreases OHR_VOCS. Since the decane oxidation chain does not reach a steady state,
it results in only limited OHR\textsubscript{VOC} enhancement at peak.

The differences between the ambient and OFR cases for decane oxidation are for different reasons
than in the case of CH\textsubscript{4}. In the absence of steady state for the nodes (stable species) in the decane
oxidation chains (nodes far downstream insufficiently populated), organic photolysis and RO\textsubscript{2} self- and
cross-reactions only help move OHR contributors to downstream nodes, but do not significantly change
their total concentrations. This is shown by the relatively small differences in the composition of stable
OHR contributors between the ambient and OFR cases (Fig. 3). The remarkable difference between these
cases is the contribution of RO\textsubscript{2} to OHR, which is as high as ~3 s\textsuperscript{-1} in the OFR case shown in Fig. 3,
while estimated to be only up to ~0.1 s\textsuperscript{-1} in the ambient case, given the RO\textsubscript{2} concentration in the
simulation.

It is known that RO\textsubscript{2} + OH can be a significant RO\textsubscript{2} loss pathway in OFR, especially when OH
and HO\textsubscript{2} production is relatively strong (higher relative humidity (RH) and UV). We have previously
advised to avoid such conditions in low-NO chemistry based on simplified modeling, because of its high-
NO-like organic product (Peng et al., 2019). Here our chemically explicit modeling results show that the
limitation for OFR chemistry caused by RO\textsubscript{2} + OH may not be as serious as suggested by Peng et al.
(2019), at least in terms of OHR\textsubscript{VOC} and, to some extent, of organic composition (Fig. 3). The condition
of the OFR case shown in Fig. 3 (30% RH, medium UV, and 10 s\textsuperscript{-1} initial OHR) is a compromise between
the goals of reaching an equivalent photochemical age of ~10 d, avoiding significant non-tropospheric
organic photolysis, and keeping a more atmospherically relevant RO\textsubscript{2} chemistry (Peng et al., 2016; Peng
et al., 2019; Peng and Jimenez, 2020). In this case, the fractional contribution of RO\textsubscript{2} + OH to RO\textsubscript{2} fate
is still sizable (>30%). However, the evolution of the composition of monofunctional species in this OFR
case before the OHR\textsubscript{VOC} peak equivalent age is similar to that in the ambient case (Fig. 3), as
hydroperoxide production through RO\textsubscript{2} + HO\textsubscript{2} is still the main loss pathway of the first-generation RO\textsubscript{2}
and RO produced from RO\textsubscript{2} + OH can also form ketones, i.e., the main second-generation products. The
other main fate of RO, i.e., isomerization, leads to slightly faster production of multifunctional species,
since the product of the recombination of the immediate product of this isomerization, i.e., an alkyl
radical, with O\textsubscript{2} is already a bifunctional RO\textsubscript{2}. This isomerization also creates a hydroxyl group on the C
backbone, resulting in a relatively high share of hydroxyl in the functional groups of the multifunctional
species (Fig. 4).

Before the OHR\textsubscript{VOC} peak, as OH\textsubscript{exp} increases, carbonyls accumulate. They are prone to Norrish-
type photochemistry (Turro et al., 2009) which plays a major role in the OHR evolution after the OHR\textsubscript{VOC}
peak in the ambient cases by breaking C10 species into smaller molecules (Fig. 3). Alkenes, which can
only be produced via Norrish Type II reaction in this case (Turro et al., 2009), are non-negligible OHR
contributors around 3x10\textsuperscript{11} molecules cm\textsuperscript{-3} s. A set of oxygenated C1 and C2 species are also largely
produced through organic photolysis followed by reactions with (O\textsubscript{2} and) HO\textsubscript{2}. Organic photolysis, along
with OH reaction pathways, can also produce RO\textsubscript{2}. Self- and cross-reactions of acylperoxy radicals,
which are formed in significant amounts in this OH\textsubscript{exp} range, can rapidly generate alkoxy radicals
(Orlando and Tyndall, 2012), which may decompose subsequently (Ziemann and Atkinson, 2012). At
~1x10\textsuperscript{12} molecules cm\textsuperscript{-3} s, the small species produced account for about half of OHR\textsubscript{VOC} in the ambient
cases (Fig. 3). In the OFR cases, organic photolysis is usually much weaker than in the atmosphere (Peng
et al., 2016; Peng and Jimenez, 2020), as the negligible OHR of alkenes in the OFR case in Fig. 3 also indicates. However, fragmentation of multifunctional species does not appear to be significantly weaker in the OFR case than in the ambient case shown in Fig. 3. This is largely due to fast RO2 + OH. The reactions of acylperoxys with OH lead to direct fragmentation (Orlando and Tyndall, 2012). Highly functionalized RO can also form from the reactions of multifunctional RO2 with OH, and then often rapidly decompose. RO2 + OH also results in a major difference of the OFR case from the ambient case at high equivalent ages (Fig. 3), i.e., lower (higher) OHR contribution from CH3OOH (HCHO) in OFR than in the atmosphere. Most CH3OO reacts with OH to produce CH3O then HCHO in the OFR case, leaving a minor fraction of CH3OO reacting with HO2 to form CH3OOH.

3.2.2 Chamber cases

Two types of chamber simulations, with and without wall partitioning, are considered in this study. The latter have almost the same results as the ambient cases in terms of the evolution of OHRVOC and its composition as a function of OH\textsubscript{exp} (Fig. 1). Despite different spectra, sunlight and chamber lights cover the same wavelength range and usually generate oxidizing agent radicals (e.g., OH and HO2) in similar amounts. Therefore, all key parameters are very similar between the ambient case with constant solar radiation and the chamber case (with 10 s\textsuperscript{-1} initial OHR) and without gas-wall partitioning. This explains the high similarities between the results of the ambient cases and the chamber cases without wall partitioning. Unfortunately, the lack of wall partitioning is not realistic.

The chamber cases with gas-wall partitioning, which are realistic, show very large deviations from the ambient cases (Figs. 1 and 3). These deviations are remarkably larger than those of the OFR cases, and are obviously due to wall partitioning of OVOCs. The wall removes more than half of the OHR of decane oxidation intermediates/products (Figs. 1 and 2) and hence also removes the OHR\textsubscript{VOC} peak in the relevant chamber cases (Fig. 1). In detail, about half of decyl hydroperoxides partition to the wall in the chamber case shown in Fig. 3, as decyl is a relatively large alkyl and leads to hydroperoxides of sufficiently low volatility to promote wall partitioning. The C10 ketones, usually of higher volatility than the corresponding hydroperoxides, do not show significant wall partitioning (Fig. 3), while the multifunctional C10 species, of even lower volatility than the corresponding hydroperoxides, are almost completely partitioned to the wall. The multifunctional species that survive the wall partitioning at high OH\textsubscript{exp} (~1x10\textsuperscript{12} molecules cm\textsuperscript{-3} s) are formed via C10 fragmentation and are thus of higher volatility (Fig. 3). The heavy wall partitioning of multifunctional species also significantly slows down their oxidative evolution in both the wall phase and the gas phase relative to the ambient cases (Fig. 4).

As OH\textsubscript{exp} increases and large multifunctional species are formed in increasing amounts from oxidation, their near-complete partitioning to the wall decreases the OHR of decane oxidation intermediates/products by a factor up to 8 around 1x10\textsuperscript{12} molecules cm\textsuperscript{-3} s compared to the chamber cases without gas-wall partitioning (Fig. 2). At higher OH\textsubscript{exp} (long oxidation times) gas-phase concentrations of partitioning species decline, allowing reverse partitioning back from the wall which then serves as a source rather than a sink. As a result, the ratio of the OHR of oxidation intermediates/products in the chamber case with wall partitioning to that without wall partitioning decreases (Fig. 2).

3.2.3 OH and HO\textsubscript{2} recycling ratios

As discussed above, we also compute OH (β\textsubscript{1}) and HO\textsubscript{2} (β\textsubscript{2}) recycling ratios in decane oxidation.
Note that these quantities also include OH and HO\(_2\) generated as a result of organic photolysis. The differences in these recycling ratios between the simulated cases are relatively small. \(\beta_1\) is close to 0 at \(\text{OH}_{\text{exp}} < \sim1 \times 10^{16} \text{ molecules cm}^{-3} \text{ s}\) (Fig. 1), as the initial reaction of decane with OH only produces an RO\(_2\) and subsequently C10 hydroperoxides, and no HO\(_2\). Then, \(\beta_1\) undergoes a fast increase between \(\sim1 \times 10^{10}\) and \(1 \times 10^{11}\) molecules cm\(^{-3}\) s (Fig. 1), as the further oxidation of C10 hydroperoxides to ketones fully recycles OH (\(R_1\text{-CH(OOH)}\text{-R}_2 + \text{OH} \rightarrow R_1\text{-CO-R}_2 + \text{H}_2\text{O} + \text{OH}\)) in the ambient and chamber cases. Nevertheless, \(\beta_1\) only increases up to ~0.4 at this stage in the ambient and chamber cases, as oxidation of C10 hydroperoxides to dihydroperoxy species and precursor oxidation also account for a substantial fraction of OH loss but do not recycle it. In the OFR cases, \(\beta_1\) only increases up to ~0.2-0.3 at this stage, since RO\(_2\) + OH starts to be active but does not recycle OH. Then, \(\beta_1\) roughly plateaus up to \(\sim1 \times 10^{12}\) molecules cm\(^{-3}\) s, as the overall effect of the decrease in hydroperoxy concentration, reducing OH recycling, and the increase in the concentration of acyloxy, enhancing OH recycling through its reaction with HO\(_2\) (Orlando and Tyndall, 2012), is relatively small. Finally, \(\beta_1\) gradually decreases to 0 (Fig. 1), as all OVOCs degrade to highly oxidized C1 species, i.e., HCHO, HCOOH, CO, which only have HO\(_2\) recycling but no OH recycling, and the unreactive CO\(_2\).

The HO\(_2\) recycling ratio (\(\beta_2\)) in decane oxidation is similar to \(\beta_1\) before \(\sim1 \times 10^{11}\) molecules cm\(^{-3}\) s for the ambient and chamber cases, as only OH (but not HO\(_2\)) is recycled at this stage. \(\beta_2\) is a little higher in the OFR cases than in the other cases at this stage because of the HO\(_2\) recycling by RO\(_2\) + OH. However, at higher OH\(_{\text{exp}}\), \(\beta_2\) continues to increase with OH\(_{\text{exp}}\) to a final value of 1 (Fig. 1). This difference between \(\beta_1\) and \(\beta_2\) is by definition due to HO\(_2\) recycling. Its significance rises in parallel with that of organic photolysis, which can often produce HCO radicals and acyloxy radicals. The former extremely rapidly undergoes HCO + O\(_2\) → CO + HO\(_2\); the latter can rapidly convert peroxy radicals to alkloxy radicals (Orlando and Tyndall, 2012), which may then react with O\(_2\) to generate HO\(_2\) (Ziemann and Atkinson, 2012). At very high OH\(_{\text{exp}}\) (\(10^{12} – 10^{13}\) molecules cm\(^{-3}\) s), reactive highly oxidized small VOCs are the dominant OHR contributors and many of them recycle HO\(_2\) during their oxidation by OH (Fig. 3). Finally, once CO becomes the only remaining OHR contributor, \(\beta_2\) is 1.

3.3 m-Xylene

Most features in m-xylene oxidation can be explained based on similar discussions as for decane oxidation in Section 3.2. OHR\text{VOC} has also a maximum during the oxidation (Figs. 1 and S4), as most of the direct products of m-xylene oxidation by OH, i.e., the unsaturated carbonyl (MXYEPOXMUC in MCM v 3.2 notation, see Scheme S1), the unsaturated endo-cyclic peroxy (MXYBIPERO2), and xylanols, are more reactive toward OH than m-xylene. The OHR of these initial products is enhanced much more during the oxidation of m-xylene than of decane, owing to the creation of C=C bonds in many post-aromatic (ring-opening) products, hence the OHR\text{VOC} peak enhancement in m-xylene oxidation is larger than in decane oxidation. Because the reaction rate constant of m-xylene with OH slightly exceeds that of decane, the OHR\text{VOC} peak in m-xylene oxidation occurs at slightly lower OH\(_{\text{exp}}\) than in decane oxidation (Fig. 1). In the OFR case under the same condition as the decane case shown in Fig. 3, the evolution of OHR of the stable organic species is again similar to that in the ambient case. And OHR\text{VOC} is higher in the OFR case again mainly due to OHR from RO\(_2\) (Fig. 1 and S4). Several main first- and second-generation products are already highly functionalized through fast O\(_2\) addition.
(Scheme S1) and they are also often unsaturated and prone to further functionalization. Therefore, the degree of functionalization in saturated aliphatic multifunctional species is much higher in m-xylene than in decane oxidation (Fig. 4). Also, as several aromatic-scheme-specific reaction types occur in the early stages of m-xylene oxidation, e.g., endo O₂ addition (creating -OO- etc.) and ring-opening (creating -CO-, -CHO etc.), multifunctional species functionality is more diverse than in decane oxidation (Fig. 4).

Photolysis again plays a role in species fragmentation and the production of highly oxidized C1 and C2 species after the OHR_VOC peak (Fig. S4).

Wall partitioning also substantially reduces the OHR_VOC in the relevant chamber cases of m-xylene oxidation (Figs. 1, 2 and S4). The precursor (m-xylene) is a C₈ species and even many first-generation products of its oxidation are highly oxygenated (Scheme S1) lower-volatility species. The relative reduction of OHR of the intermediates/products also increases with OH_exp up to ~1x10⁷ m⁺ s⁻¹ molecules cm⁻³ s⁻¹, as volatile species are oxidized and become more prone to wall partitioning (Fig. 2). At higher OH_exp, the wall again serves as an OVOC source (Fig. 2).

The evolution of β₁ and β₂ in m-xylene oxidation is somewhat different than in decane oxidation (Fig. 1). In the ambient cases, they are non-negligible even at OH_exp as low as 1x10⁶ molecules cm⁻³ s⁻¹ (~0.05 and ~0.45, respectively). OH is mainly recycled from one of endo-cyclic peroxy routes (m-xylene + OH + 2O₂ → MXYBIPERO₂; MXYBIPERO₂ + HO₂ → MXYBIPEROOH + O₂; MXYBIPEROOH + OH → MXYOBIPEROH + H₂O + OH (Scheme S1)), which involve various functional groups and open the possibility of radical recycling. The third step of this route is very fast (with a rate constant on the order of 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹). Once the second step takes place, the third step contributes to OH recycling. However, in the OFR cases with strong water vapor photolysis (not in the other OFR cases) and the chamber cases with gas-wall partitioning, the third step does not play a significant role and β₂ is ~0 at very low OH_exp (Fig. 1). In the former cases, this is due to the relatively slow second step (RO₂ + HO₂), while in the latter cases, the highly oxygenated compounds partition to the wall even more rapidly (in hundreds of s; Krechmer et al., 2016) than their reactions with HO₂. Strong HO₂ recycling occurs in all simulated cases from the beginning of the oxidation (Fig. 1), since two of the three major channels of m-xylene + OH (i.e., those forming MXYEPOXMUC and xylenol, respectively) produce HO₂ as well.

As more multifunctional species are formed (particularly through ring-opening) near the OH_exp of the peak OHR_VOC, HO₂ recycling is also active, with β₁ increasing and β₂ remaining high (Fig. 1). There are a few peaks in β₁ and β₂ for certain chamber cases. The peak in β₂ for the chamber case with high initial OHR (10⁶ s⁻¹) and no walls results from RO₂ cross-reactions, many of which produce alkoxy radicals that subsequently yield carbonyls and HO₂ through reactions with O₂ (Orlando and Tyndall, 2012). RO₂ cross-reactions are significant in that OH_exp range also because i) high precursor concentration translates into higher RO₂ concentration and ii) acylperoxy radicals, whose reactions with other RO₂ are fast (Orlando and Tyndall, 2012), are rapidly formed from the oxidation of -CHO groups in the ring-opening products (Scheme S1). The peaks in the chamber cases with wall partitioning are caused by a small number of species (in particular methylglyoxal) sufficiently volatile to stay in the gas phase and thus have disproportionate influence on β₁ and β₂. Methylglyoxal photolysis and the reaction of HO₂ with CH₃COCO(OO), i.e., the acylperoxy formed through methylglyoxal + OH, are largely
responsible for the HO$_2$ and OH recycling at the OH$_{exp}$ of the peaks. At higher OH$_{exp}$, calculated $\beta_1$ and $\beta_2$ become less reliable, since remaining apparent OHR contributors may in fact be persistent artifacts of the incompleteness of the (hand-written) m-xylene oxidation mechanism which may substantially bias $\beta_1$ and $\beta_2$ when the concentrations of remaining OHR contributors should be generally low. Therefore, we do not try to interpret the features in $\beta_1$ and $\beta_2$ at high OH$_{exp}$ for m-xylene oxidation.

3.4 Isoprene

The most salient difference of the OHR$_{VOC}$ evolution in the photooxidation of isoprene from that of the other precursors in this study is the lack of OHR$_{VOC}$ peak in the isoprene cases (Figs. 1 and S5). The decrease in OHR$_{VOC}$ all along this photooxidation is expected since the reaction of isoprene with OH is very fast (at 1x10$^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$; Atkinson and Arey, 2003) and all intermediates/products of this photooxidation react with OH more slowly than isoprene. The OHR$_{VOC}$ of the intermediates/products peaks slightly after an OH$_{exp}$ of 1x10$^{10}$ molecules cm$^{-3}$ s (Fig. 1). At this OH$_{exp}$, the main type of the first-generation products, oxygenated unsaturated species (e.g., isoprene-derived unsaturated hydroxyl hydroperoxides (ISOPOOH)), are largely produced from isoprene + OH and their loss rates (with rate constant with OH slightly lower than that of isoprene) reach the maxima (Fig. S5). Further oxidation leads to the loss of all C=C bonds in the isoprene C backbone and thus a substantial drop of the OHR of the molecule.

Before OH$_{exp}$=5x10$^{10}$ molecules cm$^{-3}$ s in isoprene photooxidation, the main deviations from the ambient cases shown by the chamber cases with wall partitioning are again caused by wall partitioning of multifunctional species, but their relative magnitudes are different than in the photooxidations of decane and m-xylene, with the impacts of wall partitioning being smaller (Fig. S5). Oxygenated species derived from isoprene, a C5 species, should be generally more volatile and less prone to wall partitioning than those derived from decane and m-xylene. On the other hand, isoprene reacts with OH much more rapidly than do decane or m-xylene, creating a larger deviation from the steady state for RO$_2$ directly derived from isoprene and a more remarkable decrease in the OHR of the first-generation products (Fig. S5). In the OFR case shown in Fig. S5, RO$_2$ contributes negligibly to OHR$_{VOC}$, since many first-generation isoprene-derived RO$_2$ have other very fast loss pathways and the very fast decay of isoprene cannot sustain RO$_2$ production at OH$_{exp}$>1x10$^{10}$ molecules cm$^{-3}$ s.

After OH$_{exp}$=5x10$^{10}$ molecules cm$^{-3}$ s, the deviation caused by chamber wall partitioning becomes more significant as highly oxidized and lower-volatility multifunctional species (Fig. 4) are formed in significant amounts (Figs. 2 and S5). At very high OH$_{exp}$, the wall again acts as a source of OVOCs in isoprene oxidation, as in those of the other precursors (Fig. 2). The deviations of OFR cases from the ambient cases are mainly caused by RO$_2$ + OH and lack of organic photolysis. These two effects lead to too much HCHO produced and inefficient production of other C1 and C2 species (Fig. S5).

To test whether one of the issues, i.e., lack of organic photolysis in OFR, can be mitigated by adding tropospherically-relevant UV sources, we perform two additional simulations. Adding the emissions corresponding to high Hg lamp setting with five times the UV of the CU Chamber (a rough upper limit for experimental implementation) has negligible effect (Fig. S6). To reach a ratio between tropospherically-relevant UV (UVA+UVB) intensity and OH concentration similar to that in the ambient case with constant sunlight requires addition of a chamber light ~10000 times stronger than the CU.
Chamber light. Such a strong UV source is obviously not realistic, and, while it does increase both early 
organic photolysis and the relative contribution of C1 and C2 photoproducts to OHR$_{VOC}$ around 2x10$^{11}$ 
molecules cm$^{-3}$ s (Fig. S6), it increases the deviation of this OFR case from the ambient cases at very 
high OH$_{exp}$, where oxidation of C1 and C2 species to CO proceeds much more rapidly than in the 
atmosphere.

Product functionality in isoprene oxidation is more diverse than in decane oxidation (Fig. 4). This 
is due to both the propensity of the isoprene C=C bonds to addition of various groups, and the active 
isomerization of isoprene oxidation intermediates (Wennberg et al., 2018). Notably, epoxy groups in 
species such as isoprene-derived epoxydiol (IEPOX) account for a large fraction of saturated product 
functionality (Fig. 4), particularly at OH$_{exp}$ on the order of 10$^{10}$ molecules cm$^{-3}$ s. In the gas phase of the 
chamber cases with wall partitioning, the overwhelming majority of saturated multifunctional organic 
molecules are IEPOX up to 1x10$^{11}$ molecules cm$^{-3}$ s (Fig. 4), as more highly-oxidized species mostly 
partition to the wall.

IEPOX formation from isoprene-derived hydroperoxide (ISOPOOH) oxidation by OH 
(ISOPOOH + OH → IEPOX + OH) leads to the peak of OH recycling around 3x10$^{10}$ molecules cm$^{-3}$ s 
(Fig. 1). OH recycling is active even at very low OH$_{exp}$ (1x10$^9$ molecules cm$^{-3}$ s) because a significant 
amount of ISOPOOH forms early and can recycle OH through its oxidation, except in the OFR cases 
with strong water vapor photolysis, where ISOPOOH cannot be efficiently formed from first-generation 
RO$_2$, HO$_2$ recycling is also active in the entire course of the photooxidation (Fig. 1), because of a number 
of isomerization and photolysis pathways that form alkoxy radicals and highly oxidized C1 species such 
as HCOOH, HCHO, and CO at very high OH$_{exp}$ (Fig. S5).

3.5 Trends in OHR per C atom

To explore some general trends of OHR evolution in VOC photooxidation, simulations are 
performed for the ambient cases with constant UV for two additional alkanes between methane and 
decane, i.e., butane and heptane. The results of these simulations are compared to the existing analogous 
cases in Fig. 5. For all cases, the OHR$_{VOC}$ peak height decreases and the OH$_{exp}$ of the OHR$_{VOC}$ peak shifts 
towards lower OH$_{exp}$, as the C number of the precursor alkane increases. This can be explained by the 
fact that the OH rate constants of these alkanes increase with C number, and suggests a possible general 
trend between OHR peak location and C number.

To explore these trends further, we calculate the OHR per unit starting concentration of C atom 
(in the precursor) in all ambient cases with constant UV in this study (Fig. 5b). In this study, CO$_2$ is not 
included initially but produced during the oxidation. Therefore, C atoms in the produced CO$_2$ are taken 
into account in the calculation of OHR per C atom. For real atmospheric cases, initial CO$_2$ is present but 
should not be considered in this calculation. Note that OHR per C atom has a unit of cm$^3$ atom$^{-1}$ s$^{-1}$ and 
represents the average contribution to the rate constant with OH of all considered C atoms. Despite large 
differences among the reactivities of these precursors, the OHR per C atom in the simulations of all 
precursors but methane converges near an OH$_{exp}$ of 3x10$^{11}$ molecules cm$^{-3}$ s, and then follows a very 
similar downward trend (Fig. 5b). This OH$_{exp}$ value is roughly where saturated multifunctional species 
have their maximal relative contribution to the OHR$_{VOC}$ (Figs. 3 and S5). Even in the ambient cases of 
m-xylene oxidation, saturated multifunctional species also account for about half of OHR$_{VOC}$ when the
contribution of aromatics, some of which may artificially persist due to mechanism incompleteness, is
excluded (Fig. S4). Also, At OH$_{exp} > \sim$5x10$^{11}$ molecules cm$^{-3}$ s$^{-1}$, a C atom in saturated multifunctional
species on average has at least 0.3 functional groups in the ambient cases (Fig. 4), and the functional
group composition is relatively diverse at this OH$_{exp}$. Therefore, the convergence value of OHR per C
atom of $\sim$2x10$^{-12}$ cm$^{-3}$ atom$^{-1}$ s$^{-1}$ at $\sim$3x10$^{11}$ molecules cm$^{-3}$ s$^{-1}$ can be largely regarded as a relatively
invariant average of those of secondary H and $\alpha$-H of various O-containing functional groups. Note that
this average is for low-NO conditions and can be lower at high NO due to deactivating effects of N-
containing groups formed during oxidation (Isaacman-VanWertz and Aumont, 2020).

Before the convergence, isoprene has the highest OHR per C atom (on the order of 10$^{-11}$ cm$^{-3}$ atom$^{-1}$ s$^{-1}$) among the precursors and intermediates/products (Fig. 5b), because of its conjugated C=C bonds.

The OHR per C atom of its first-generation oxidation products is slightly lower and close to that of the
oxidation intermediates/products of m-xylene, as the main contributors in both cases are oxygenated
monoalkenes. The average OHR per C atom of the studied alkanes increases with C number (Fig. 5b),
with the upper limit around 1x10$^{-12}$ cm$^{-3}$ atom$^{-1}$ s$^{-1}$ consistent with Kwok and Atkinson (1995), since the
less-reactive -CH$_2$ groups (with OHR per C atom of $\sim$1x10$^{-11}$ cm$^{-3}$ atom$^{-1}$ s$^{-1}$) contribute proportionally
less to molecular OHR as C number increases. Conversely, the early-stage products of alkane oxidation
(mainly alkyl monohydroperoxides) show higher average OHR per C atom for shorter molecules (Fig.
5b), owing to the activating (increasing OHR) contribution of the -OOH group.

Following the convergence of OHR per C atom, this quantity in all non-methane ambient cases
in this study sees a similar decay (Fig. 5b). This coincides with multifunctional species broken into small
highly oxidized C1 and C2 compounds. Although among them there are species with OHR per C atom $>\sim$
5x10$^{-12}$ cm$^{-3}$ atom$^{-1}$ s$^{-1}$ (e.g., CH$_3$OOH, CH$_3$CHO, and HCHO), the average OHR per C atom of these C1
and C2 species are mainly governed by those reacting more slowly (e.g., HCOOH and particularly CO)
and hence reaching higher concentrations amid the fast decay of multifunctional species. The similar fast
drop of OHR per C atom after OH$_{exp}$ $\sim$1x10$^{12}$ molecules cm$^{-3}$ s$^{-1}$ for various precursors implies a transition
from OHR from saturated multifunctional molecules to OHR from CO before the final oxidation to CO$_2$
(which has zero OHR).

3.6 Total OH consumption for each precursor

Integrating OHR per C atom over OH$_{exp}$ allows us to assess the average number of OH molecules
consumed by each C atom during the entire course of oxidation. This quantity can also be apportioned
to the contributions of different OH reactants (Fig. 6). Due to incomplete oxidation of several species,
especially CO, the value of this quantity for an oxidation with all C atoms ending up with CO$_2$ should be
higher than those at simulation end (OH$_{exp}$ $\sim$4x10$^{12}$ molecules cm$^{-3}$ s$^{-1}$). We correct this in Fig. 6 by
including additional contribution of CO to make its total contribution 1, since CO, the typical penultimate
product, consumes one OH molecule in its final oxidation, but is still present in significant quantities at
the end of our simulations. Thus, each C atom reacts with OH $\sim$3 times in the course of the oxidation of
isoprene and decane to CO$_2$ (Fig. 6). A simplistic and chemically intuitive explanation for this number
is that the average oxidation state ($\overline{O}_C$) of both isoprene and decane C atoms is $\sim$2, and needs to increase
to the value of +4 in CO$_2$ at the end of the oxidation. A C1 unit reacting once with OH likely increases
its $\overline{O}_C$ by $\sim$2. This increase is usually realized by an abstraction of H atom by OH or an addition of OH
(\(\text{OS}_C + 1\)), followed by an abstraction of H atom by O\(_2\) or an addition of O\(_2\) (\(\text{OS}_C + 1\)). Note that ~3 OH consumed per C atom oxidized to CO\(_2\) is likely an upper limit, since the mechanisms in this study do not include RO\(_2\) autoxidation (Crounse et al., 2013; Ehn et al., 2014), which reduces the number of OH needed for complete VOC oxidation. Also, in a real low-NO environment, NO is still present in low concentrations and converts RO\(_2\) to RO. RO may undergo H abstraction through isomerization or reaction with O\(_2\), which also lowers the number of OH needed, although the effect is usually small.

The surprisingly large contribution of hydroperoxy xylenol (C\(_9\)H\(_{10}\)O\(_3\)) to OH consumed per C atom in m-xylene oxidation (Fig. 6) is an artifact of mechanism incompleteness. This species may undergo an abstraction of the H atom in its -OH group by OH. The resulting RO may be converted back to it through a reaction with HO\(_2\). The lack of efficient exit channels from this interconversion artificially sustains it for an extended period, leading to inflated OH consumption.

4 Summary and conclusions

Using the fully explicit GECKO-A model, we simulated OHR evolution in the photooxidation of several types of VOCs (i.e., alkane, alkene, and aromatic) without NO until very high equivalent photochemical ages (>10 d) under a variety of conditions (in the atmosphere, chamber, and OFR). We analyzed the simulations in detail and found a number of common features as well as some differences resulting from certain precursors. They are summarized below:

- All simulated non-methane cases very roughly follow this general oxidation chain pattern: precursor \(\rightarrow\) first-generation products \(\rightarrow\) (second-generation products \(\rightarrow\)) multifunctional species \(\rightarrow\) highly oxidized C1 and C2 species \(\rightarrow\) CO (or HCOOH) \(\rightarrow\) CO\(_2\). These species are generally not at steady state and gain significance/predominance one after another in the entire course of oxidation. Simulation results suggest that fragmentation products are not formed in significant amounts until the late stage of the oxidation, which would be a key difference from studies of OHR evolution in high-NO VOC oxidation (Nakashima et al., 2012; Sato et al., 2017).

- In methane oxidation, the intermediates do not gain dominance in sequence. Instead, they simultaneously increase as the oxidation proceeds, then simultaneously decrease when the methane decay becomes significant. The OHR evolution in methane oxidation is close to the idealized steady-state chain model, as the reaction of methane with OH is orders of magnitude slower than those of its oxidation intermediates, which allows the intermediates to reach their steady state.

The following discussion refers to the non-methane cases.

- Where different types of species dominate OHR\(_{\text{VOC}}\) in sequence, OHR\(_{\text{VOC}}\) increases after the current dominant type converts to one with a higher average OHR per C atom, and vice versa. Photooxidations of alkanes and aromatics follow the increasing trend from precursor to saturated multifunctional species (via alkyl monohydroperoxides) and from precursor to unsaturated oxygenated species, respectively. The increase in aromatic oxidation is likely to be more significant, since unsaturated oxygenated species are more reactive than saturated multifunctional species. The conversions from multifunctional species to CO\(_2\) lead to a decay of OHR\(_{\text{VOC}}\) in both alkane and aromatic photooxidations. OHR\(_{\text{VOC}}\) in alkene photooxidation is likely to always drop rapidly during C=C bond oxidation and more slowly afterwards.

- C atoms in >C=C<, -CH\(_2\)-, and -CH\(_3\) have OHR per C atom on the order of \(10^{-11}\), \(10^{-12}\), and \(10^{-13}\) cm\(^3\)
atom\(^{-1}\) s\(^{-1}\), respectively. Together with these values, a relatively weak enhancement of OHR per C atom of a C atom with -OH substitution can explain the large range spanned by the precursors and their intermediates/products in this study at low OH\(_{\text{exp}}\). Around an OH\(_{\text{exp}}\) of \(3 \times 10^{11}\) molecules cm\(^{-3}\) s\(^{-1}\), precursors are largely converted to saturated multifunctional species (e.g., by addition to C=C bonds in unsaturated precursors and abstraction of H atoms in saturated precursors), and the reactive mixtures of those precursors thus have similar OHR per C atom. They then all follow the course: multifunctional species \(\rightarrow\) highly oxidized C1 and C2 species \(\rightarrow\) CO (or HCOOH) \(\rightarrow\) CO\(_2\) and show similar decays of OHR per C atom.

- In decane and isoprene oxidation, our simulations show that each C atom consumes at most \(~3\) OH molecules in the course of its oxidation to CO\(_2\). This can be simplistically explained as 3 occurrences of oxidation by OH that increase, by 2 each time, the \(\overline{O_S C}\) of decane and isoprene (\(~2\)) to that of CO\(_2\) (\(+4\)). The total number of OH consumed by each C atom is likely to be lower when RO\(_2\) autoxidation can be included in the mechanism generation.

In general, the OHR evolution differences resulting from different precursors are larger than those due to different conditions. The difference in OHR\(_{\text{VOC}}\) between the ambient cases with constant and diurnal sunlight is small. Nevertheless, physical conditions may still lead to significant differences, which are summarized below:

- In chambers, gas-wall partitioning can be a prominent issue that causes substantial wall partitioning of certain OVOCs of lower volatility. The clearest example in this study is the near-complete removal of C10 multifunctional species from the gas phase in decane oxidation, and hence the disappearance of the OHR\(_{\text{VOC}}\) peak. The wall also preferentially absorbs more oxidized (and thus lower-volatility) species, which alters the functional composition of gas-phase multifunctional species. The wall can even serve as a source of multifunctional species at very high OH\(_{\text{exp}}\), when the gas-phase concentrations of those species are very low. The magnitude of the effects of wall partitioning also depends on the size of the precursor, with the oxidation of larger precursors in chambers suffering larger impacts of wall partitioning.

- The strong wall losses have important implications, as they can change our modeling results substantially. Systematic OVOC wall partitioning corrections must be made for low-NO oxidation chamber experiments that study OHR\(_{\text{VOC}}\). In case of large precursors, highly chemically explicit modeling will likely be necessary to infer the OHR of multifunctional species, which may account for a large fraction of missing reactivity but suffer near-complete wall losses. Although the few existing chamber studies on OHR\(_{\text{VOC}}\) evolution were all under high-NO conditions, which may result in more fragmentation and higher-volatility products, the magnitude of wall partitioning of large multifunctional species in this study is so substantial that we believe this magnitude would also be important at high NO. Schwantes et al. (2017) considered wall partitioning in their modeling of o-cresol oxidation based on MCM v3.3.1 but still could not achieve good agreement with the measurements for a number of products. Considering this, one should not assume that it is appropriate to neglect wall partitioning in high-NO chamber experiments, just based on agreement between the high-NO chamber experiments and the modeling with MCM-based schemes and without gas-wall partitioning corrections in some literature OHR\(_{\text{VOC}}\) evolution studies.
- OFR has two issues under certain conditions that can cause deviations from the ambient cases in terms of OHR\textsubscript{VOC}. Strong RO\textsubscript{2} + OH may significantly contribute to OHR\textsubscript{VOC}. Interestingly, this type of reactions does not seem to be able to substantially alter the composition of OHR\textsubscript{VOC} before the OHR\textsubscript{VOC} peak. Besides, the conditions resulting in strong water vapor photolysis have already been identified as those leading to atmospherically irrelevant RO\textsubscript{2} chemistry in low-NO OFR in previous studies (Peng et al., 2019; Peng and Jimenez, 2020). As long as OFR users follow the guidelines for experimental planning provided in those studies (and use a much lower UV lamp setting), strong RO\textsubscript{2} + OH can be avoided, as shown in Fig. 1.

- The other main issue of OFR is lack of efficient organic photolysis, particularly at high OH\textsubscript{exp}, when multifunctional species break into highly oxidized C1 and C2 compounds. This problem has been highlighted in previous studies (Peng et al., 2016; Peng and Jimenez, 2020) and been shown again in the present work to be extremely difficult to avoid if a high OH\textsubscript{exp} is desired. However, the conversion of multifunctional species into highly oxidized C1 and C2 species may not be much slower in OFR than in the atmosphere, since RO\textsubscript{2} + OH, leading to RO formation and subsequently its decomposition, may also play a major role in this conversion. This also results in significantly higher (lower) production of HCHO (CH\textsubscript{3}OOH) in OFR than in the atmosphere at high equivalent ages.

With all the key findings in this study presented above, we believe that we have, to some extent, addressed all the three issues for OHR studies raised by Williams and Brune (2015). We largely speculated the likely source of the “missing reactivity”, i.e., multifunctional species, by the fully explicit GECKO-A model. A contrast between the technical issues in some isoprene and m-xylene simulations and the high consistency in the other cases highlights the importance of the completeness of the mechanism (even beyond the MCM level) in OHR-related modeling studies. Finally, this study may have opened up the possibility of parameterizing the OHR evolution in (at least low-NO) VOC photooxidation as a function of OH\textsubscript{exp} only with the often-available knowledge on the first- and second-generation products and the relevant SARs such as Kwok and Atkinson (1995), as the OHR evolution beyond multifunctional species has been shown to be similar for most VOC oxidations. This parametrization may be utilized in regional and global models to better constrain OHR at high equivalent photochemical ages, e.g., in remote regions.

Appendix A: The effect on OH reactivity of non-OH reactions in an OH-driven reaction chain

1) Consider the following reaction chain, where OH is the only oxidant:

\[
\begin{align*}
A_1 + OH &\rightarrow A_2, \quad k_1 \\
A_2 + OH &\rightarrow A_3, \quad k_2 \\
A_3 + OH &\rightarrow A_4, \quad k_3 \\
\text{...}(\text{etc.})
\end{align*}
\]

At steady state, \(k_1[A_1][OH] = k_2[A_2][OH] = k_3[A_3][OH] = \ldots = C\) (\(C\) is a constant).

Then OHR due to individual species, OHR\textsubscript{i}, is equal to \(C/[OH]\) and is identical for all species.

2) Consider a parallel conversion of \(A_1\) to \(A_2\) by a means other than reaction with OH:

\[
\begin{align*}
A_1 + OH &\rightarrow A_2, \quad k_1 \\
A_1 + B &\rightarrow A_2, \quad k_1', \quad B \neq OH
\end{align*}
\]

At steady state, \(k_1[A_1][OH] + k_1'[A_1][B] = C\).
Therefore, OHR$_{A1}$ = $k_1[A_1] < C/[OH]$.  

3) Now consider a reaction converting $A_1$ directly to $A_3$ occurring in parallel to reaction chain 1),  

$A_1 + D \rightarrow A_3$, \quad $k_3^\prime$, \quad D ≠ OH

$A_1 + OH \rightarrow A_2$, \quad $k_1$

$A_2 + OH \rightarrow A_3$, \quad $k_2$

At steady state, $k_1'[A_1][D] + k_3[A_2][OH] = C$

And OHR$_{A1}$ < C/[OH], since $k_3[A_1][OH] = k_2[A_2][OH]$.  

**Code/Data availability**  
The chemical mechanisms generated and the outputs of the GECKO-A simulations in this study are available upon request.  

**Author contribution**  
ZP and JLJ conceived the study. ZP designed the study. JL-T and ZP performed the simulations. HS, JL-T, ZP, and JLJ developed the GECKO Loader and Plotter. ZP, JL-T, JJO, and BA made updates and developments for GECKO-A. ZP, JL-T, JJO, BA, and JLJ analyzed the results. ZP led the manuscript writing with inputs from all authors.  

**Competing interests**  
There are no competing interests to declare.  

**Acknowledgements**  
This work was partially supported by NSF AGS-1822664 and AGS-1740610. We thank Sasha Madronich and Alma Hodzic for useful discussions. We would like to acknowledge high-performance computing support from Cheyenne (doi:10.5065/D6RX99HX) provided by NCAR’s Computational and Information Systems Laboratory, sponsored by the National Science Foundation.
References


Peng, Z., Lee-Taylor, J., Orlando, J. J., Tyndall, G. S. and Jimenez, J. L.: Organic peroxy radical chemistry in oxidation flow reactors and environmental chambers and their atmospheric relevance,


Figure 1. Total organic OH reactivity (OHR) with and without the contribution of the precursor, OH recycling ratio ($\beta_1$), and HO$_x$ recycling ratio ($\beta_2$) as a function of OH exposure (or equivalent photochemical age; second x-axis) in the photooxidations of decane, isoprene, and m-xylene under different conditions in the atmosphere, oxidation flow reactor (OFR), and chamber.
Figure 2. Ratios of OHR of the products between the chamber cases without and with wall partitioning at initial OHR of 10 and 100 s⁻¹, and between the ambient cases with constant and diurnal sunlight for the photooxidations of decane, m-xylene, and isoprene as a function of OH exposure.
Figure 3. Absolute and fractional contributions to the organic OHR during decane photooxidation of the main species and types of species as a function of OH exposure in the ambient case with constant sunlight; the OFR case with relative humidity of 30%, medium UV lamp setting, and initial OHR of 10 s⁻¹; and the chamber case with initial OHR of 10 s⁻¹ and gas-wall partitioning. The types of species shown in this figure exclude the C1 and C2 species listed separately. The OHR of the wall-phase species are the values as if those species are gas-phase OHR contributors, although they actually do not react with OH in the simulations.
Figure 4. Average number of functional group per C atom as a function of OH exposure in the saturated multifunctional species in the ambient case with constant sunlight, the OFR case with relative humidity of 70%, high UV lamp setting, and initial OHR of 10 s⁻¹, and the gas and wall phases in the chamber case with initial OHR of 10 s⁻¹ and gas-wall partitioning of the photooxidations of decane, m-xylene, and isoprene. Note that the functional group “-O-” represents ether, ester, and epoxy groups in the GECKO-A model.
Figure 5. (a) OHR and (b) OHR per initial C atom concentration of the organics (including and excluding the precursor) as a function of OH exposure in the ambient cases with constant sunlight of the photooxidation of methane, butane, heptane, decane, isoprene, and m-xylene.
Figure 6. Average numbers of OH molecules consumed per C atom in the ambient cases with constant sunlight during photooxidation of isoprene, decane, and m-xylene. The contribution from CO that is not yet oxidized by OH at the end of simulation is also added to ensure that each CO molecule consumed one OH radical. ISOPOOH, IEPOX, C_{10}H_{22}O_{2}, C_{10}H_{22}O_{3}, C_{8}H_{10}O_{2}, and C_{8}H_{10}O_{3} are isoprene hydroxyl hydroperoxides, isoprene epoxydiols, decyl hydroperoxides, hydroxydecyl hydroperoxides, m-xylene hydroperoxide, and hydroperoxy m-xyleneol, respectively.
Table 1. Conditions and integration timesteps of the simulations in the present work.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Environment</th>
<th>Relative humidity (%)</th>
<th>UV</th>
<th>Initial OH reactivity (s⁻¹)</th>
<th>Integration timestep (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>Ambient</td>
<td>30</td>
<td>Constant sunlight&lt;sup&gt;a&lt;/sup&gt;</td>
<td>10</td>
<td>KinSim-determined&lt;sup&gt;b&lt;/sup&gt;</td>
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<td></td>
<td>Oxidation flow reactor</td>
<td>70</td>
<td>High lamp setting&lt;sup&gt;c&lt;/sup&gt;</td>
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<td></td>
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<td>Diurnal sunlight</td>
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<tr>
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<td>30</td>
<td>Constant sunlight&lt;sup&gt;a&lt;/sup&gt;</td>
<td>10</td>
<td>0.0025</td>
</tr>
<tr>
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<td>Oxidation flow reactor</td>
<td>70</td>
<td>High lamp setting&lt;sup&gt;c&lt;/sup&gt;</td>
<td>10</td>
<td>Min: 0.1; Max: 120 (1 d), 300 (2–10 d)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Low lamp setting&lt;sup&gt;c&lt;/sup&gt;</td>
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<td>0.0025</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Medium lamp setting&lt;sup&gt;f&lt;/sup&gt;</td>
<td>10</td>
<td>0.0025</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>High lamp setting&lt;sup&gt;g&lt;/sup&gt;</td>
<td>10</td>
<td>0.0025</td>
</tr>
<tr>
<td></td>
<td>Chamber (without wall)</td>
<td>30</td>
<td>CU Chamber spectrum&lt;sup&gt;g&lt;/sup&gt;</td>
<td>10</td>
<td>Min: 0.1; Max: 120 (6 d), 300 (7–30 d if needed)</td>
</tr>
<tr>
<td></td>
<td>Chamber (with wall)</td>
<td>30</td>
<td>CU Chamber spectrum&lt;sup&gt;g&lt;/sup&gt;</td>
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<td>Min: 0.1; Max: 120 (6 d), 300 (7–30 d if needed)</td>
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<tr>
<td>m-Xylene</td>
<td>Ambient</td>
<td>30</td>
<td>Constant sunlight&lt;sup&gt;a&lt;/sup&gt;</td>
<td>10</td>
<td>0.001</td>
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<tr>
<td></td>
<td>Oxidation flow reactor</td>
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<td>High lamp setting&lt;sup&gt;c&lt;/sup&gt;</td>
<td>10</td>
<td>0.001</td>
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<td></td>
<td>Oxidation flow reactor</td>
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<td>High lamp setting&lt;sup&gt;c&lt;/sup&gt;</td>
<td>10</td>
<td>0.001</td>
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<td>Low lamp setting&lt;sup&gt;c&lt;/sup&gt;</td>
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<td>0.001</td>
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<td></td>
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<td>Medium lamp setting&lt;sup&gt;f&lt;/sup&gt;</td>
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<td>0.001</td>
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<td></td>
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<td>High lamp setting&lt;sup&gt;g&lt;/sup&gt;</td>
<td>10</td>
<td>0.001</td>
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<td></td>
<td>Chamber (without wall)</td>
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<td>CU Chamber spectrum&lt;sup&gt;g&lt;/sup&gt;</td>
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<td>Min: 0.1; Max: 120 (6 d), 120 (7–30 d if needed)</td>
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<td>Chamber (with wall)</td>
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<td>CU Chamber spectrum&lt;sup&gt;g&lt;/sup&gt;</td>
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<td>Min: 0.1; Max: 120 (6 d), 120 (7–30 d if needed)</td>
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<td>Constant sunlight&lt;sup&gt;a&lt;/sup&gt;</td>
<td>10</td>
<td>Min: 0.1; Max: 120 (1 d), 300 (2–10 d)</td>
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</tbody>
</table>

<sup>a</sup> At solar zenith angle of 45°.<br>
<sup>b</sup> Simulation performed in the solver KinSim, which fully controls its integration timestep selection.<br>
<sup>c</sup> Diurnal variation between solar zenith angles of 0 and 90°.<br>
<sup>d</sup> UV at 185 nm = 1 x 10<sup>14</sup> photons cm<sup>2</sup> s<sup>−1</sup>; UV at 254 nm = 8.5 x 10<sup>15</sup> photons cm<sup>2</sup> s<sup>−1</sup>.<br>
<sup>e</sup> UV at 185 nm = 1 x 10<sup>14</sup> photons cm<sup>2</sup> s<sup>−1</sup>; UV at 254 nm = 4.2 x 10<sup>13</sup> photons cm<sup>2</sup> s<sup>−1</sup>.<br>
<sup>f</sup> UV at 185 nm = 1 x 10<sup>13</sup> photons cm<sup>2</sup> s<sup>−1</sup>; UV at 254 nm = 1.4 x 10<sup>15</sup> photons cm<sup>2</sup> s<sup>−1</sup>.<br>
<sup>g</sup> UV source spectrum of the University of Colorado Environmental Chamber Facility (Krechmer et al., https://doi.org/10.5194/acp-2021-118 Preprint. Discussion started: 24 February 2021 © Author(s) 2021. CC BY 4.0 License.
2017).