

## General comment

The authors intend to publish this manuscript as a model description paper. However, the model description (Section 2) is incomplete impeding scrutiny and reproducibility of the results. Although additions for autoxidation is well described or referenced, the manuscript lacks specific numbers and formulas for the RO<sub>2</sub>-RO<sub>2</sub> reaction rate constants depending on the structure and size of the radicals. For general and specific numbers one is left to dig into the ADCHAM code uploaded on Zenodo. For instance, it is not obvious where to find the expressions of the relevant rate constants. A presentation, possibly with tables, of a systematic assignment of rate constants and dimers yields must be part of the model description.

Response: We sincerely thank the reviewer for pointing out this important issue and apologize for the insufficient clarity of the model description in the original manuscript. We agree that the description of the RO<sub>2</sub>-RO<sub>2</sub> chemistry was not sufficiently explicit, which made it difficult for readers to identify how the reaction rate constants and dimer formation processes are assigned.

In the revised manuscript, we have expanded Section 2 to provide a clearer description of how the RO<sub>2</sub>-RO<sub>2</sub> reaction rate constants are determined in the model, including the principles used to assign the rate constants based on the structure and type of the radicals. In addition, to ensure transparency and reproducibility, we now provide the complete list of RO<sub>2</sub>-RO<sub>2</sub> reactions together with other reactions and their corresponding rate constants in a dedicated reaction file "SIM\_HOM.def" available in the Zenodo repository.

With these additions, readers can now directly understand the parameterization strategy from the manuscript and access the full set of reactions and rate constants used in the simulations without the need to extract them from the source code. We thank the reviewer for this helpful suggestion, which has improved the clarity and reproducibility of the model description.

Line 321-328: RO<sub>2</sub> + RO<sub>2</sub> rate coefficients are assigned according to the overall

oxidation state and molecular size of the RO<sub>2</sub> radicals, using the number of oxygen atoms as a proxy for the degree of functionalization. This approach is consistent with the parameterization described above, where more highly oxygenated and generally larger RO<sub>2</sub> radicals are assumed to exhibit higher reactivity in RO<sub>2</sub> + RO<sub>2</sub> reactions. SIM-HOM uses RO<sub>2</sub> + RO<sub>2</sub> reaction rates leading to closed-shell monomer products in the range of  $1 \times 10^{-12}$  to  $1.5 \times 10^{-11}$  cm<sup>3</sup>s<sup>-1</sup> and RO<sub>2</sub> + RO<sub>2</sub> reactions leading to HOM dimers in the range of  $1 \times 10^{-14}$  to  $1.5 \times 10^{-12}$  cm<sup>3</sup>s<sup>-1</sup>.

## Major comments

### 1. Dimers from monoterpenes

Only for monoterpene chemistry (?) I could identify rate constants `kRO2_RO2_PRAM` and `kROOR_PRAM`. The former a pseudo-unimolecular one and the latter a bimolecular one. Maybe they are assigned the values `1D-12` and `1D-13*RO2` as could be guessed by looking at the Input file `input_PRAM01.txt`. In the list of reaction rates in `secondRates.f90` these are found in `RCONST` Array elements multiplied by some chosen integers. Maybe the rationale is described in a previous article describing PRAM but should also be described here. I could not identify rate constants for specific RO<sub>2</sub> categories from isoprene and sesquiterpene chemistry. I want to stress that I am very familiar with the MCM and other chemical mechanisms.

Response: We thank the reviewer for this careful reading of the code and for pointing out the lack of clarity in the manuscript. We apologize that the description of the RO<sub>2</sub> + RO<sub>2</sub> parameterization, especially for isoprene and sesquiterpene chemistry, was not sufficiently explicit in the current version, which may have caused confusion.

For monoterpenes, the rate constants labeled as `kRO2_RO2_PRAM` and `kROOR_PRAM` in the original code indeed correspond to a pseudo-unimolecular representation and a bimolecular representation (explicit ROOR formation), respectively. As correctly inferred from the input file, these parameters are assigned

base values on the order of  $10^{-12} \text{ cm}^3\text{s}^{-1}$  and  $10^{-13} \text{ cm}^3\text{s}^{-1}$ , and are implemented in `secondRates.f90` through `RCONST` array elements multiplied by category-specific integer factors. These integer factors are not arbitrary fitting parameters; rather, they are used to assign different  $\text{RO}_2$  classes to distinct reactivity tiers, thereby setting the appropriate order of magnitude for their effective rate coefficients while keeping the mechanism computationally tractable.

For isoprene- and sesquiterpene-derived  $\text{RO}_2$ , we apply the same structural treatment. That is,  $\text{RO}_2$  radicals are grouped into predefined categories according to carbon number, oxygen content, and each category is associated with the same base rate constants but scaled by selected integer coefficients. These coefficients are used to differentiate relative reactivities among  $\text{RO}_2$  classes and to reflect expected trends in dimerization propensity (e.g., enhanced reactivity for highly oxygenated  $\text{RO}_2$ ). We agree that this was not clearly stated in the manuscript and have now added a dedicated paragraph in Section 2 explicitly describing this generalized parameterization framework and its extension to isoprene and sesquiterpene systems.

To avoid possible misunderstanding that these rate constants are specific to a particular precursor or unique PRAM formalism, we have renamed `kRO2_RO2_PRAM` and `kROOR_PRAM` in the revised manuscript to `kRO2_RO2` and `kROOR`, respectively. The text now clearly explains that these are generic parameters applied consistently across precursor classes within the SIM-HOM framework.

Because the full SIM-HOM mechanism contains thousands of reactions, it is not feasible to list all  $\text{RO}_2 + \text{RO}_2$  reactions explicitly in the manuscript. For transparency and reproducibility, we now explicitly refer readers to the `SIM-HOM.def` file, where all individual reactions and their assigned rate constants can be inspected in detail. We hope that with these revisions, the rationale and implementation of the  $\text{RO}_2 + \text{RO}_2$  chemistry are now sufficiently clear.

## 2. Dimers from isoprene and sesquiterpens

For those two compounds is completely obscure (to me) which rate constants and why have they been assigned for the dimer formation. The description of the modifications

for autoxidation are described in the text. However, like for the monoterpenes the specifics like the relevant block of reaction list cannot be found anywhere for reference/scrutiny. KPP-generated files for the integration of the associated ODE systems cannot be used for such purpose. I could not even find the equation (.eqn) and species (.spc) files.

Response: We thank the reviewer for this follow-up comment and apologize for the lack of clarity regarding the accessibility of the isoprene and sesquiterpene dimer chemistry in the previous version.

We agree that the relevant reaction blocks were not sufficiently easy to identify in the original submission. In the revised version, we have clearly indicated in the manuscript which reaction classes correspond to isoprene- and sesquiterpene-derived RO<sub>2</sub> dimer formation, including the naming conventions used for these species and reactions.

Provided the original SIM-HOM.def file as supplementary material, so that the full reaction list and species definitions can be directly inspected in a human-readable format.

Added explicit pointers to the corresponding mechanism files in the SIM-HOM directory, where the complete set of reactions and associated rate constants is available. We fully understand that KPP-generated ODE solver files are not suitable for mechanism scrutiny. The revised submission now ensures that the mechanism definition files themselves are accessible for transparent evaluation and reproducibility. We hope these revisions adequately address the reviewer's concern regarding the visibility and traceability of the dimer chemistry for isoprene and sesquiterpenes.

### 3. RO<sub>2</sub> Permutation reactions

At lines 306-316 it is stated that only cross-reactions between autoxidizable and non-autoxidizable RO<sub>2</sub> significantly contribute to the accretion products. For those reactions which rate constants are used and how do they change with structure and size of the RO<sub>2</sub>? What is the yield of ROOR? Are autoxidizable RO<sub>2</sub> ever considered as part of the "RO<sub>2</sub> pool" defined by the MCM permutation reactions formalism?

Response: We thank the reviewer for this important question and apologize that the

previous description may have created ambiguity regarding the relationship between the RO<sub>2</sub> pool formalism and explicit ROOR formation.

In SIM-HOM, all RO<sub>2</sub> (independent of precursor type and independent of whether they are capable of autoxidation), are treated as part of a common RO<sub>2</sub> pool in the sense of the MCM permutation framework. Autoxidizable RO<sub>2</sub> are therefore fully included in the bulk RO<sub>2</sub> loss processes represented by permutation reactions, and they are not excluded or treated separately at that level. The distinction between autoxidizable and non-autoxidizable RO<sub>2</sub> is introduced only when parameterizing accretion (ROOR) formation. Specifically, RO<sub>2</sub> + RO<sub>2</sub> reactions are assigned a common base bimolecular rate coefficient on the order of 10<sup>-12</sup> cm<sup>3</sup>s<sup>-1</sup>, consistent with typical literature values for organic peroxy radical reactions. Structural dependence, such as carbon number and oxygen content, is represented through category-based scaling factors that modulate the effective branching toward stable ROOR formation. In this framework, cross-reactions between autoxidizable and non-autoxidizable RO<sub>2</sub> are assigned branching to ROOR, as these combinations are found to be the dominant pathway leading to low-volatility accretion products. The ROOR yield is therefore not prescribed as a single fixed value but emerges from the combination of the base RO<sub>2</sub> + RO<sub>2</sub> rate constant and the category-dependent branching ratio applied to specific RO<sub>2</sub> classes.

We have revised the manuscript to clarify that all RO<sub>2</sub> species remain members of the general RO<sub>2</sub> pool used in the permutation formalism, and that the autoxidizable versus non-autoxidizable distinction is applied solely for determining the branching to explicit ROOR formation, not for defining participation in the RO<sub>2</sub> pool itself. We hope this revised explanation makes the treatment logically transparent and resolves the reviewer's concern.

Line 311-332: Autoxidizable RO<sub>2</sub> radicals, due to their higher degree of functionalization, exhibit faster dimerization rates (Berndt et al., 2018). Non-autoxidizable RO<sub>2</sub> radicals, which are generally present at higher concentrations, can serve as reaction partners in these bimolecular reactions. Reactions between two autoxidizable RO<sub>2</sub> are not explicitly represented, due to their extremely low

concentrations, which makes their contribution to dimer formation negligible. Likewise, reactions between two non-autoxidizable RO<sub>2</sub> are not treated as explicit accretion product formation pathways due to their low propensity to form accretion products. Instead, these reactions remain represented within the generic RO<sub>2</sub> loss framework of the RO<sub>2</sub> pool, where they contribute to closed-shell monomer formation through the pseudo-unimolecular reaction scheme. In this way, the total RO<sub>2</sub>–RO<sub>2</sub> reaction flux among all RO<sub>2</sub> species is still accounted for, while only those combinations most relevant for HOM dimer formation are treated explicitly.

RO<sub>2</sub> + RO<sub>2</sub> rate coefficients are assigned according to the overall oxidation state and molecular size of the RO<sub>2</sub> radicals, using the number of oxygen atoms as a proxy for the degree of functionalization. This approach is consistent with the parameterization described above, where more highly oxygenated and generally larger RO<sub>2</sub> radicals are assumed to exhibit higher reactivity in RO<sub>2</sub> + RO<sub>2</sub> reactions. SIM-HOM uses RO<sub>2</sub> + RO<sub>2</sub> reaction rates leading to closed-shell monomer products in the range of  $1 \times 10^{-12}$  to  $1.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  and RO<sub>2</sub> + RO<sub>2</sub> reactions leading to HOM dimers in the range of  $1 \times 10^{-14}$  to  $1.5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ . This choice reflects the generally smaller branching fraction of the accretion channel relative to the formation of monomer products. As a result, the effective branching ratio toward accretion products in the model is typically on the order of ~10%, consistent with recent experimental and theoretical studies (Murphy et al., 2025; Berndt et al., 2018). Because these dimers arise from explicit bimolecular reactions, the identities of these products are determined by the specific pair of reacting RO<sub>2</sub> precursors.

Ref:

Berndt, T., Mender, B., Scholz, W., Fischer, L., Herrmann, H., Kulmala, M., and Hansel, A.: Accretion Product Formation from Ozonolysis and OH Radical Reaction of  $\alpha$ -Pinene: Mechanistic Insight and the Influence of Isoprene and Ethylene, *Environ. Sci. Technol.*, 52, 11069-11077, 10.1021/acs.est.8b02210, 2018.

Murphy, S. E., Crouse, J. D., Poulsen, A. S., Lipson, J. E., Kjaergaard, H. G., and Wennberg, P. O.: Accretion product formation in the self- and cross-reactions of small  $\beta$ -hydroxy peroxy radicals, *Environ. Sci. - Atmospheres*, 5, 1312-1325,

10.1039/d5ea00106d, 2025.

#### 4. Validity of the RO<sub>2</sub> Permutation formalism

This formalism has the fundamental assumption that CH<sub>3</sub>O<sub>2</sub> is the dominant RO<sub>2</sub> justifying the estimate of  $k$  as the geometric average of two self-reaction rate constants, one of CH<sub>3</sub>O<sub>2</sub> and one of the RO<sub>2</sub> at hand. The observations used for model Validation are from Experiments with apparently no nitrogen oxides and likely RO<sub>2</sub>-RO<sub>2</sub> and RO<sub>2</sub>-HO<sub>2</sub> reactions as the dominant RO<sub>2</sub> sinks. CH<sub>3</sub>O<sub>2</sub> is not to be expected the dominant RO<sub>2</sub>. Given that the self-reaction rate constant of CH<sub>3</sub>O<sub>2</sub> is among the lowest ones, how is this inconsistency going to affect the optimal values for the key rate constants affecting dimer formation? Could the authors elaborate on that and perform a sensitivity simulation?

Response: We thank the reviewer for raising this fundamental point concerning the validity of the RO<sub>2</sub> permutation formalism under our experimental conditions.

We agree that the classical permutation expression is formally derived under the assumption that CH<sub>3</sub>O<sub>2</sub> is the dominant RO<sub>2</sub> species and that the cross-reaction rate constant can be approximated as the geometric mean of the self-reaction rate constants of CH<sub>3</sub>O<sub>2</sub> and the RO<sub>2</sub> under consideration. In our simulations, however, we consider five different VOC systems (including monoterpenes, isoprene, and sesquiterpenes), and the dominant RO<sub>2</sub> species varies substantially among these systems depending on precursor structure and experimental conditions.

In SIM-HOM, the permutation formalism is therefore used primarily as a practical framework to represent bulk RO<sub>2</sub> reactivity. The RO<sub>2</sub> + RO<sub>2</sub> rate coefficients should be regarded as effective parameters describing the ensemble behavior of a dynamically evolving RO<sub>2</sub> distribution, rather than strict mechanistic values tied to CH<sub>3</sub>O<sub>2</sub> dominance. The parameters are selected to reproduce observed HOM concentrations across the five VOC systems. Therefore, it is important to note that SIM-HOM is coupled to the MCM chemical framework, which imposes additional constraints on the treatment of RO<sub>2</sub> chemistry. In MCM, the permutation approach implicitly assumes that CH<sub>3</sub>O<sub>2</sub> represents a major fraction of the RO<sub>2</sub> pool. If this assumption leads to an

underestimation of certain  $\text{RO}_2 + \text{RO}_2$  reaction rates, mechanisms coupled to MCM must still remain broadly consistent with that treatment. Assigning substantially higher  $\text{RO}_2 + \text{RO}_2$  rate coefficients within SIM-HOM alone could otherwise shift the balance of  $\text{RO}_2$  sinks and cause these reactions to dominate the  $\text{RO}_2$  fate relative to the rest of the MCM chemistry. A fully consistent solution would therefore require revisiting the representation of the  $\text{RO}_2$  pool and  $\text{RO}_2$  reaction rates in MCM itself, which is beyond the scope of the present study.

To evaluate the impact of this assumption, we performed sensitivity simulations in which the  $\text{RO}_2 + \text{RO}_2$  rate constant was uniformly scaled by factors of 0.5 and 2. The results show that total HOM concentrations respond noticeably to these perturbations, indicating that the model output is sensitive to this parameter under low-NO conditions where  $\text{RO}_2\text{-RO}_2$  reactions are a major sink. When the rate constant is reduced by a factor of 0.5, HOM concentrations change substantially, likely because the system is largely governed by the competition between  $\text{RO}_2$  autoxidation and  $\text{RO}_2\text{-RO}_2$  reactions, so altering the rate shifts the dominant  $\text{RO}_2$  fate. When the rate constant is increased by a factor of 2, enhanced  $\text{RO}_2$  termination slightly reduces the fraction of  $\text{RO}_2$  radicals that successfully undergo extended autoxidation and form HOM products, which is chemically consistent.

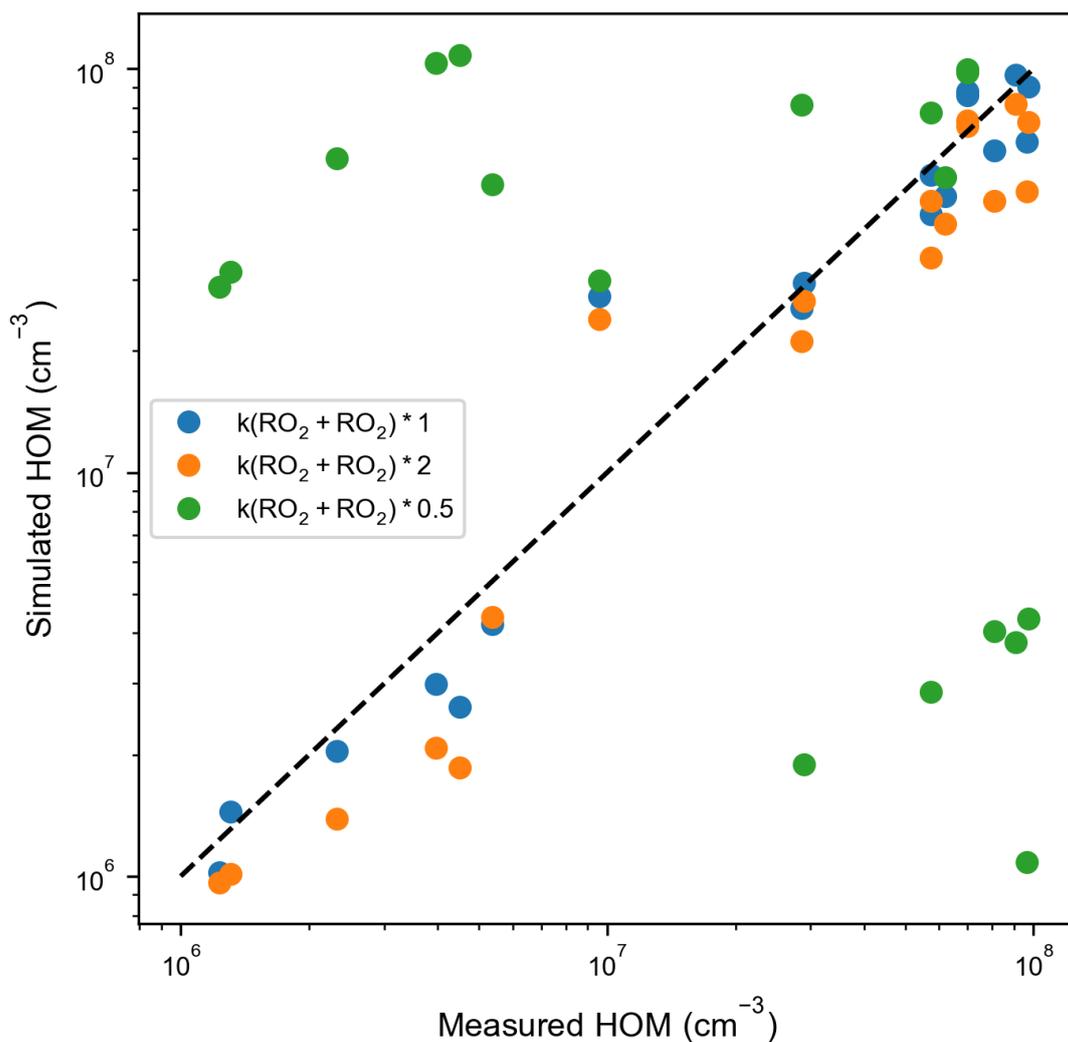


Fig.R3. Modelled and measured HOM concentrations. The different model results are from the SIM-HOM sensitivity tests where all  $\text{RO}_2 + \text{RO}_2$  reaction rates ( $k(\text{RO}_2 + \text{RO}_2)$ ) were scaled up or down with a factor of two compared to the default values..

#### Minor comments

- There are many instances with no blank space between end of sentence and reference.

Response: Thanks, these blank spaces have been added.

- line 198: where is ozone 10% of isoprene oxidation? Is it a global average? Provide a reference.

Response: Yes. The statement that ozone accounts for approximately 10% of isoprene

oxidation refers to a commonly cited estimate in the literature and is also consistent with results from many global chemical transport models under typical atmospheric conditions. We have added appropriate references to clarify this in the revised manuscript.

Table R1. Branching ratios (%) of isoprene oxidation pathways

Pathway	RCIM, global	v11-02c, global	Literature, global	RCIM, SE USA	RCIM, Amazon	RCIM, E China	
Isoprene +	OH	88	83	85 <sup>b</sup> , 84 <sup>c</sup> , 80 <sup>d</sup>	85	86	91
	O <sub>3</sub>	10	15	9 <sup>b</sup> , 11 <sup>c</sup> , 15 <sup>d</sup>	11	13	4.5
	NO <sub>3</sub>	1.7	2.3	5 <sup>c</sup> , 5 <sup>b</sup> , 5 <sup>d</sup> , 6-7 <sup>e,f</sup>	4.2	0.2	5.1
ISOPOO +	HO <sub>2</sub>	41	42	53.5 <sup>g</sup>	31	45	14
	NO	28	31	33.5 <sup>g</sup>	46	6.4	73
	RO <sub>2</sub>	8.8	13		5.1	15	1.4
	H shift	22	14	20 <sup>b</sup> , 9.6 <sup>g</sup> , 30 <sup>h</sup>	18	33	11
ISOPOO isomer <sup>i</sup>	<i>E/Z</i> -1-OH- $\delta$	6.5	2.4 <sup>j</sup>	16 <sup>k</sup>	5.5	10	4.1
	1-OH- $\beta$	59	51 <sup>j</sup>	44 <sup>k</sup>	59	55	61
	<i>E/Z</i> -4-OH- $\delta$	14	18 <sup>j</sup>	15 <sup>k</sup>	12	19	7.9
	4-OH- $\beta$	21	28 <sup>j</sup>	25 <sup>k</sup>	23	16	27

Line 199: O<sub>3</sub> oxidation accounts for approximately 10% of isoprene's global loss (Bates and Jacob, 2019).

Ref: Bates, K. H. and Jacob, D. J.: A new model mechanism for atmospheric oxidation of isoprene: global effects on oxidants, nitrogen oxides, organic products, and secondary organic aerosol, *Atmos. Chem. Phys.*, 19, 9613–9640, <https://doi.org/10.5194/acp-19-9613-2019>, 2019.