

Liwen Yang et al. “SIM-HOM (version 1.0): A Mechanistic Module for the formation of highly oxygenated organic molecules from Isoprene, Monoterpene and Sesquiterpene evaluated with ADCHAM (version 1.0)”

Paul Wennberg

This is a very welcome effort to build a mechanistically informed module that can capture the formation of highly oxygenated molecules in the oxidation of biogenic alkenes initiated by OH and ozone. The authors have used MCM and other compiled mechanisms that provide detailed gas phase oxidation insights and added pathways that describe HOM formation from autoxidation and RO<sub>2</sub>+RO<sub>2</sub> chemistry. They use a set of simulations from CLOUD to benchmark the compiled mechanism both with single and mixed alkene starting mixtures. The mechanism has significant skill and will substantially advance our ability to simulate the production of HOMs and the associated aerosol in many regions of the world.

Response: We thank the reviewer for positive and constructive evaluation of our work. We appreciate the concise and accurate summary of our study, as well as the recognition of these key improvements we have made in developing a mechanistically detailed module for simulating HOM formation during the oxidation of biogenic alkenes. We address the reviewer’s specific comments in detail below.

In our response, original comments from reviewers are in black, our response is in blue and revised texts in the manuscript are in green.

I recommend publication in close to the current version. I ask the authors, however, to consider providing a more complete description of what chemistry drives the HOM formation – I suspect that perhaps the ‘top ten’ pathways provide most of the HOM production in each system and it would be helpful for future investigations to have this quantified here.

Response: We thank the reviewer for this constructive suggestion. We agree that identifying the dominant processes leading to HOM formation would be valuable for future studies. However, we find it difficult to implement this analysis in a clear and mechanistically meaningful way within the framework of the current model. In our

simulations, HOM formation does not arise from a small number of isolated pathways, but rather from a highly coupled sequence of reactions. Many reactions, such as the initial oxidation steps or early autoxidation processes, do not directly produce HOM but strongly influence the composition of the radical pool and the probability of subsequent HOM-forming reactions. Their contribution to HOM formation is therefore indirect but still essential, which makes it challenging to rigorously define and rank discrete “pathways” that drive HOM production.

To illustrate this complexity, we performed a simple sensitivity test in which key autoxidation steps prior to HOM formation in the monoterpene- and sesquiterpene-dominated O<sub>3</sub> oxidation systems were selectively suppressed. Specifically, we set the rate coefficients of three RO<sub>2</sub> autoxidation steps to zero individually and examined the resulting change in simulated HOM concentrations. When the autoxidation steps leading to RO<sub>2</sub> species with O = 4 and O = 6 were suppressed, the simulated HOM concentrations decreased substantially. In contrast, suppressing the autoxidation step leading to RO<sub>2</sub> with O = 5 resulted in an increase in HOM concentrations. In the mechanism, the RO<sub>2</sub> species with 5 O atoms originate from the autoxidation of alkoxy radicals (RO) formed in earlier RO<sub>2</sub> reactions. When this autoxidation channel is removed, the system may appear to shift the radical budget toward alternative RO<sub>2</sub> + RO<sub>2</sub> reactions that produce RO radicals, which can subsequently undergo further oxidation and contribute to HOM formation. Due to the limited availability of experimental constraints for pure isoprene systems, we did not perform the same sensitivity test for the isoprene mechanism.

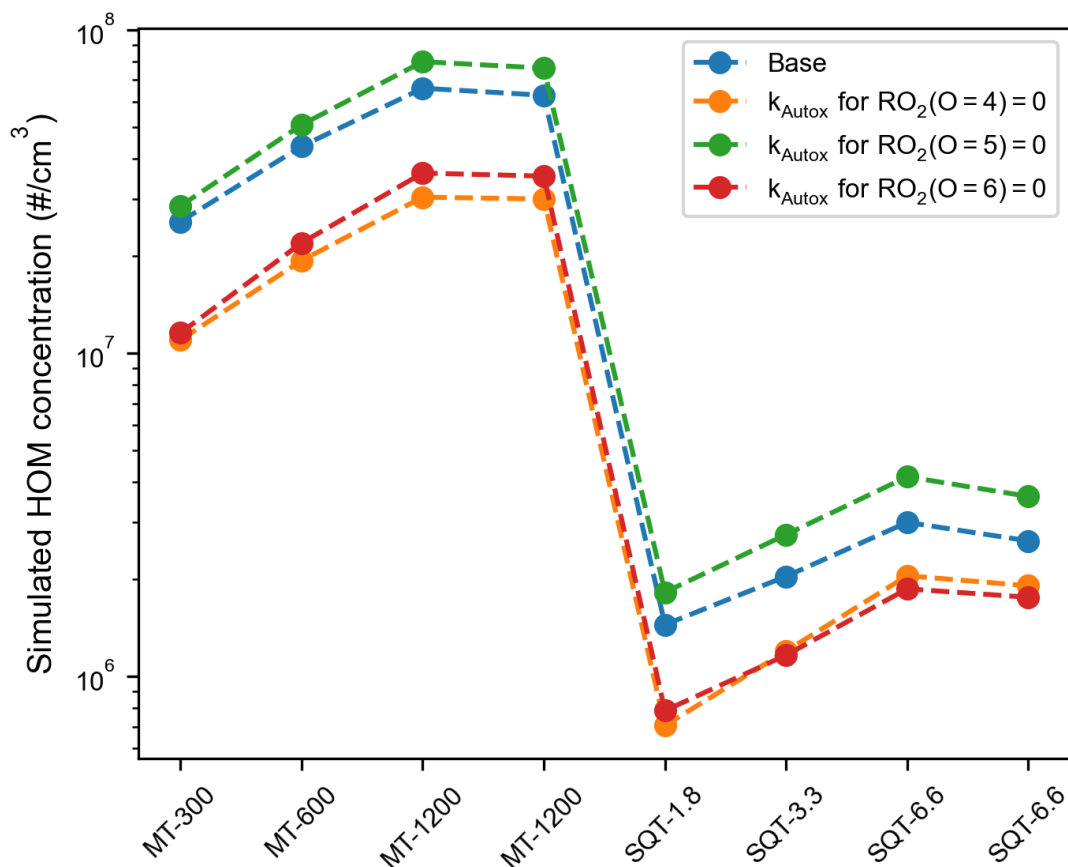


Fig R1. Modelled HOM concentrations during monoterpene and sesquiterpene ozonolysis experiment. The different model results are from the model sensitivity tests with different autoxidation settings.

This example illustrates that even reactions occurring prior to HOM formation can influence HOM yields in non-linear ways by altering the balance between  $\text{RO}_2$ ,  $\text{RO}$ , and subsequent autoxidation processes. As a result, the contribution of individual reactions cannot always be interpreted independently, and the concept of a small set of dominant linear pathways may not fully capture the behavior of the coupled radical system.

In addition, the relative importance of individual reactions is strongly condition-dependent, for example with respect to  $\text{NO}$  concentration, precursor type, and oxidant regime. A ranking derived under a specific set of conditions may therefore not be generally applicable. Conducting individual sensitivity analyses for the very large

number of reactions included in the mechanism would also be computationally demanding and may not necessarily lead to a physically interpretable ranking of pathways. For these reasons, we believe that providing a robust and generally meaningful “top pathway” analysis is difficult within the scope of the present study. Nevertheless, we appreciate the reviewer’s suggestion and consider that the development of systematic pathway analysis tools for complex HOM chemistry would be a valuable direction for future work.

For the RO<sub>2</sub> + RO<sub>2</sub> chemistry my sense, based on Murphy et al., 2025 (<https://pubs.rsc.org/zh-tw/content/articlepdf/2025/ea/d5ea00106d>), is that the dimer formation branching ratio is generally ~10%. Even for simple alkanes (e.g. ethane RO<sub>2</sub>), this seems the case. To the extent that this is true, the major question is just the rate coefficients for these RO<sub>2</sub>+RO<sub>2</sub> reactions. Given that addition of a functional group (e.g. HOCH<sub>2</sub>CH<sub>2</sub>OO vs CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OO) has such a rate enhancement, I am curious whether such enhancements are additive in your mechanism (e.g. does adding a carbonyl and an alcohol or acid yield 100x rate – see for example Ziola and Ziemann - J Phys Chem A. 2025 Feb 13; 129(6):1688-1703). I would also ask the authors to provide evidence for the statement (ln314) “Likewise, reactions between two non-oxidizable RO<sub>2</sub> are not included due to their low propensity to form accretion products”. Finally, in the monoterpene RO<sub>2</sub> section, please add a reference to Kenseth, 2023 where you cite Peräkylä et al., 2023. [<https://www.science.org/doi/10.1126/science.adi0857> ]

**Response: (1) On additivity of functional group effects (carbonyl, alcohol, acid, etc.)**

We thank the reviewer for raising this important mechanistic question and for pointing to Ziola and Ziemann (2025). **In the current version of SIM-HOM, we do not assume additive rate enhancements based on the number or type of functional groups (e.g., carbonyl + alcohol leading to 100× enhancement). Instead, we parameterize RO<sub>2</sub> + RO<sub>2</sub> rate coefficients according to overall oxidation state and molecular size (i.e., number of carbon and oxygen atoms), without explicitly resolving individual functional group.**

In practice, this representation is conceptually similar to a functional-group-based description but expressed in a simplified form: the number of oxygen atoms ( $nO$ ) is used as a proxy for the degree of functionalization rather than explicitly tracking specific functional groups. This choice reflects the current limitations in available structure–reactivity relationships for  $RO_2$  radicals, resulting in the substantial increasing uncertainty from explicit group-based scaling, and the significant computational cost such a treatment would impose in large chemical mechanisms.

Accordingly, more highly oxygenated (i.e., more autoxidized and generally larger)  $RO_2$  radicals are assigned higher  $RO_2 + RO_2$  rate coefficients, whereas less oxygenated radicals are assigned lower values. Specifically, for isoprene-derived  $RO_2$ ,  $k_{(RO_2 + RO_2)}$  is set in the range of  $1 \times 10^{-12}$ – $8 \times 10^{-12}$   $cm^3 s^{-1}$ ; for monoterpene-derived  $RO_2$  radicals,  $1 \times 10^{-12}$ – $1.5 \times 10^{-11}$   $cm^3 s^{-1}$ ; and for sesquiterpene-derived  $RO_2$  radicals,  $5 \times 10^{-12}$ – $1.5 \times 10^{-11}$   $cm^3 s^{-1}$ . We have clarified this assumption explicitly in the revised manuscript to avoid any misunderstanding that a functional-group additivity framework is applied.

## **(2) On the assumed dimer branching ratio for dimer formation**

We agree that recent literature, including Murphy et al. (2025), suggests that the effective branching ratio toward accretion (ROOR-type) products is often on the order of ~10%, even for relatively simple alkyl peroxy radicals. In SIM-HOM, however, we do not prescribe a fixed dimer branching ratio. In the model configuration, considering computational limitations,  $RO_2 + RO_2$  accretion reactions are treated independently from other reaction channels. Accretion reactions are implemented explicitly, representing reactions between autoxidizable  $RO_2$  and several major non-autoxidizable  $RO_2$  species in each system. All other  $RO_2 + RO_2$  pathways are treated as permutation reactions. Consequently, the effective branching ratio for ROOR formation is not prescribed as a constant value in the model.

In our implementation,  $RO_2 + RO_2$  reactions leading to closed-shell monomers are assigned rate coefficients in the range of  $1 \times 10^{-12}$  to  $1.5 \times 10^{-11}$   $cm^3 s^{-1}$ , whereas  $RO_2 + RO_2$  reactions leading to HOM dimers are assigned rate coefficients in the range of  $1 \times 10^{-14}$  to  $1.5 \times 10^{-12}$   $cm^3 s^{-1}$ . As a result, the effective branching ratio toward ROOR

formation in the model is typically on the order of ~10%. Because these ROOR products arise from bimolecular  $\text{RO}_2 + \text{RO}_2$  reactions, the specific ROOR species formed depend on the identities of the reacting  $\text{RO}_2$  precursors.

### **(3) On the exclusion of reactions between two non-oxidizable $\text{RO}_2$**

In SIM-HOM, dimer formation is restricted to reactions involving at least one highly oxygenated (HOM-type)  $\text{RO}_2$  radical. Reactions between two non-oxidizable (i.e., low-oxygen, non-HOM-forming)  $\text{RO}_2$  radicals are therefore not treated as explicit accretion product formation pathways. Instead, they are represented within a pseudo-unimolecular loss framework against the total  $\text{RO}_2$  pool, leading to closed-shell monomer products.

This treatment does not imply that reactions between two non-oxidizable  $\text{RO}_2$  radicals are incapable of forming ROOR accretion products. Rather, they are not explicitly considered because the primary purpose of SIM-HOM is to represent the HOM formation. This simplification is motivated by several considerations. First, experimental evidence indicates relatively low formation rates of ROOR products from low-oxygen  $\text{RO}_2$  radicals under atmospheric conditions (Berndt et al., 2018). Second, from a mechanistic perspective, the formation of HOM accretion products containing at least six oxygen atoms typically requires the two precursor  $\text{RO}_2$  radicals to collectively contain at least eight oxygen atoms. Consequently, ROOR formation relevant for HOM chemistry is expected to preferentially occur between highly oxygenated, oxidizable  $\text{RO}_2$  radicals and more abundant  $\text{RO}_2$  radicals that do not undergo autoxidation.

In the revised manuscript, we have clarified that reactions between two non-oxidizable  $\text{RO}_2$  radicals are represented within the generic  $\text{RO}_2$  loss scheme rather than being fully excluded. We also explicitly state that accretion product formation is limited to reactions involving HOM-type  $\text{RO}_2$  radicals and have added literature support for the reduced accretion efficiency of non-oxidizable  $\text{RO}_2$  radicals.

### **(4) Additional reference request (monoterpene $\text{RO}_2$ section)**

We thank the reviewer for this suggestion and have added a citation to Kenseth et al., 2023, alongside Peräkylä et al., 2023, to appropriately acknowledge recent advances in monoterpene RO<sub>2</sub> chemistry and accretion product formation.

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 products are probably not HOM. 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., Crounse, 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.

To my knowledge, however, there is no evidence that acyl peroxy radicals yield such ROOR and I would like to understand what this mechanism suggests as CH<sub>3</sub>C(O)OO is both one of the most ubiquitous (PAN decomposition) and reacts at 1/10 the collision rate. This is especially important during nighttime with NO<sub>3</sub> addition to biogenic alkenes will produce RO<sub>2</sub> in a low radical environment.

Response: We thank the reviewer for raising this important question regarding the potential role of acyl peroxy radicals in ROOR formation. While experimental evidence remains limited for small acyl peroxy radicals such as CH<sub>3</sub>C(O)OO, previous mechanistic studies have suggested that acyl-containing RO<sub>2</sub> radicals formed in the oxidation of biogenic VOCs can participate in RO<sub>2</sub> + RO<sub>2</sub> reactions leading to peroxide dimers. For example, Zhang et al. (Zhang et al., 2015@PNAS) proposed reaction pathways in which acyl peroxy radicals produced during monoterpene oxidation can form ROOR-type dimers through RO<sub>2</sub> + RO<sub>2</sub> reactions.

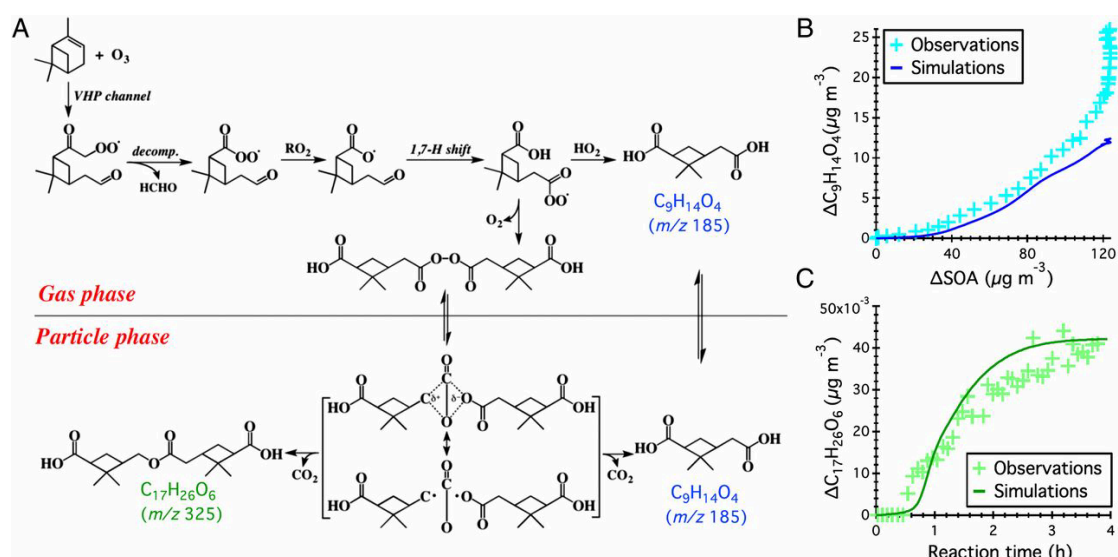


Figure R2. (A) Proposed gas- and particle-phase mechanism for the formation of the dimer C<sub>17</sub>H<sub>26</sub>O<sub>6</sub> and pinic acid (C<sub>9</sub>H<sub>14</sub>O<sub>4</sub>). Model simulations (solid line) and experimental observations (plus sign) of the growth dynamics of (B) C<sub>9</sub>H<sub>14</sub>O<sub>4</sub> and (C) C<sub>17</sub>H<sub>26</sub>O<sub>6</sub>. (Zhang et al., 2015)

In the present model, we do not introduce a specific or separate parameterization for acyl peroxy radicals. Instead, they are treated within the general RO<sub>2</sub> + RO<sub>2</sub> reaction framework applied to all organic peroxy radicals. In other words, the mechanism does not assume any enhanced or distinct ROOR-forming behavior for acyl peroxy radicals compared with other RO<sub>2</sub> species. As a result, their contribution to ROOR formation in the model is determined solely by their abundance and the generic RO<sub>2</sub> + RO<sub>2</sub> reaction parameterization.

We agree with the reviewer that small acyl peroxy radicals such as CH<sub>3</sub>C(O)OO, which can be produced from processes such as PAN decomposition, are expected to have different kinetic characteristics and may not efficiently form ROOR. In the present mechanism, accretion product formation is mainly associated with large multifunctional RO<sub>2</sub> radicals produced during VOC oxidation and autoxidation. These RO<sub>2</sub> radicals contain substantially more carbon atoms and functional groups and are therefore considered the dominant precursors of ROOR-type dimers. Small RO<sub>2</sub> radicals, including simple acyl peroxy radicals, are not expected to contribute significantly to ROOR formation in the model. We have clarified this point in the

revised manuscript to avoid the impression that such small RO<sub>2</sub> species are treated as efficient ROOR precursors.

Ref:

X. Zhang, R.C. McVay, D.D. Huang, N.F. Dalleska, B. Aumont, R.C. Flagan, & J.H. Seinfeld, Formation and evolution of molecular products in  $\alpha$ -pinene secondary organic aerosol, *Proc. Natl. Acad. Sci. U.S.A.* 112 (46) 14168-14173, <https://doi.org/10.1073/pnas.1517742112> (2015).

Finally, I would suggest that although NO<sub>x</sub> is not considered in the current model it would be helpful to include in the “future work” some commentary on whether NO<sub>3</sub> chemistry with biogenics is likely to be important source of HOMs and which alkenes you would recommend be studied in more detail. For example, I think one of the first demonstrations the ROOR formation from NO<sub>3</sub> addition is important for SOA was Sally Ng’s study in 2008 that illustrated that this pathway was likely responsible for all the SOA formed in an isoprene chamber study - <https://acp.copernicus.org/articles/8/4117/2008/acp-8-4117-2008.html>. I’d recommend citing this study in the introduction as well

Response: We thank the reviewer for this constructive suggestion. We agree that discussing the potential importance of NO<sub>3</sub> chemistry with BVOCs for HOM formation would significantly strengthen the “Future Work” section, and we will add a dedicated paragraph addressing this aspect. We also cited the chamber study by Sally Ng and co-workers (Ng et al., 2008) in the introduction.

Regarding the potential of NO<sub>3</sub> reactions to serve as an important source of HOMs, current literature suggests that the answer is compound-dependent. For isoprene, NO<sub>3</sub> oxidation appears to be substantially more efficient in forming HOMs than O<sub>3</sub> or OH oxidation. Reported HOM molar yields from isoprene + NO<sub>3</sub> are ~1.2% (Zhao et al., 2021), whereas corresponding yields from isoprene + O<sub>3</sub> and isoprene + OH are much lower, ~0.01% and ~0.03%, respectively (Jokinen et al., 2015). These comparisons suggest that, under nighttime or high-NO<sub>3</sub> conditions, isoprene + NO<sub>3</sub> chemistry could

represent a disproportionately important source of HOMs relative to other oxidants. We will therefore explicitly identify isoprene as a high-priority candidate for future NO<sub>3</sub>-BVOC mechanistic development within SIM-HOM.

For sesquiterpenes, available laboratory data indicate HOM yields of ~1.7–1.8% (e.g., Jokinen et al., 2016, *Boreal Env. Res.*; Richters et al., 2016, *ES&T*), supporting the view that large, highly substituted alkenes are efficient precursors of HOMs. Although most existing yield data are derived from O<sub>3</sub> or OH oxidation, multiple double bonds suggest that NO<sub>3</sub> addition could also promote rapid autoxidation and potentially efficient dimer formation. We will therefore highlight sesquiterpenes as another important class warranting detailed NO<sub>3</sub>-focused investigation.

For monoterpenes, however, existing studies indicate that HOM formation from O<sub>3</sub> oxidation (2.9–7%, Ehn et al., 2014; Kirkby et al., 2016) and OH oxidation (~1.2%, Kirkby et al., 2016) is already substantial. This indicates that, unlike isoprene, NO<sub>3</sub> chemistry is less likely to represent a uniquely dominant HOM source for monoterpenes, although it may still contribute under specific nocturnal conditions. Nevertheless, it is important to note that NO can exert nonlinear effects on HOM formation (Nie et al., 2023). Such nonlinear NO influences on RO<sub>2</sub> chemistry and HOM production have already been discussed in previous mechanistic studies, including the PRAM framework. We will therefore clarify in the revised manuscript that, while NO<sub>3</sub> chemistry may not dominate monoterpene oxidation, its interaction with RO<sub>2</sub> chemistry could still influence HOM formation under certain atmospheric conditions. We will clarify this compound-dependent perspective in the revised manuscript.

Overall, we agree with the reviewer that inclusion of NO<sub>3</sub>-BVOC chemistry is an important next step. In the revised manuscript, we will cite Ng et al. (2008) to contextualize the role of NO<sub>3</sub>-initiated ROOR formation, and (ii) expand the “Future Work” section to discuss, in a structured manner, the relative importance of NO<sub>3</sub> oxidation for isoprene, sesquiterpenes, and monoterpenes, and to prioritize specific alkenes (particularly isoprene and selected sesquiterpenes) for future mechanistic development and model integration.

Line 72-76: Additionally, RO<sub>2</sub>-RO<sub>2</sub> can result in the formation of HOM monomers, where two RO<sub>2</sub> react to produce two new molecules, often with one less oxygen atom than their precursors. RO<sub>2</sub>-RO<sub>2</sub> reactions can also form HOM dimers (Heinritzi et al., 2020; Berndt et al., 2018; Ng et al., 2008), which are less volatile than HOM monomers and play a pivotal role in NPF and SOA formation.

.....

Line 611-621: In particular, the potential contribution of NO<sub>3</sub>-initiated oxidation to HOM formation is not yet represented in the current version of the model. Recent studies suggest that the importance of NO<sub>3</sub> chemistry is strongly compound-dependent. For example, laboratory measurements indicate that HOM yields from isoprene + NO<sub>3</sub> reactions (~1.2%) (Zhao et al., 2021) are substantially higher than those from isoprene oxidation by O<sub>3</sub> or OH (Jokinen et al., 2015), implying that NO<sub>3</sub> chemistry may represent an important nighttime source of HOMs from isoprene. For larger BVOCs such as sesquiterpenes, their multiple double bonds and high reactivity may also favor rapid autoxidation following NO<sub>3</sub> addition, potentially leading to efficient HOM formation. In contrast, monoterpenes already exhibit substantial HOM production through O<sub>3</sub> and OH oxidation (Ehn et al., 2014; Kirkby et al., 2016), suggesting that NO<sub>3</sub> chemistry may play a less dominant role, although it could still contribute under certain nocturnal conditions.

Ref:

Berndt, T., Hoffmann, E. H., Tilgner, A., and Herrmann, H.: Highly oxidized products from the atmospheric reaction of hydroxyl radicals with isoprene, *Nat. Commun.*, 16, 12, 10.1038/s41467-025-57336-1, 2025.

Ehn, M., Thornton, J. A., Kleist, E., Sipila, M., Junninen, H., Pullinen, I., Springer, M., Rubach, F., Tillmann, R., Lee, B., Lopez-Hilfiker, F., Andres, S., Acir, I. H., Rissanen, M., Jokinen, T., Schobesberger, S., Kangasluoma, J., Kontkanen, J., Nieminen, T., Kurten, T., Nielsen, L. B., Jorgensen, S., Kjaergaard, H. G., Canagaratna, M., Dal Maso, M., Berndt, T., Petaja, T., Wahner, A., Kerminen, V. M., Kulmala, M., Worsnop, D. R., Wildt, J., and Mentel, T. F.: A large source of low-volatility secondary organic aerosol,

Nature, 506, 476-479, 10.1038/nature13032, 2014.

Heinritzi, M., Dada, L., Simon, M., Stolzenburg, D., Wagner, A. C., Fischer, L., Ahonen, L. R., Amanatidis, S., Baalbaki, R., Baccarini, A., Bauer, P. S., Baumgartner, B., Bianchi, F., Brilke, S., Chen, D. X., Chiu, R., Dias, A., Dommen, J., Duplissy, J., Finkenzeller, H., Frege, C., Fuchs, C., Garmash, O., Gordon, H., Granzin, M., El Haddad, I., He, X. C., Helm, J., Hofbauer, V., Hoyle, C. R., Kangasluoma, J., Keber, T., Kim, C., Kürten, A., Lamkaddam, H., Laurila, T. M., Lampilahti, J., Lee, C. P., Lehtipalo, K., Leiminger, M., Mai, H. J., Makhmutov, V., Manninen, H. E., Marten, R., Mathot, S., Mauldin, R. L., Mentler, B., Molteni, U., Müller, T., Nie, W., Nieminen, T., Onnela, A., Partoll, E., Passananti, M., Petäjä, T., Pfeifer, J., Pospisilova, V., Quéléver, L. L. J., Rissanen, M. P., Rose, C., Schobesberger, S., Scholz, W., Scholze, K., Sipilä, M., Steiner, G., Stozhkov, Y., Tauber, C., Tham, Y. J., Vazquez-Pufleau, M., Virtanen, A., Vogel, A. L., Volkamer, R., Wagner, R., Wang, M. Y., Weitz, L., Wimmer, D., Xiao, M., Yan, C., Ye, P. L., Zha, Q. Z., Zhou, X. Q., Amorim, A., Baltensperger, U., Hansel, A., Kulmala, M., Tomé, A., Winkler, P. M., Worsnop, D. R., Donahue, N. M., Kirkby, J., and Curtius, J.: Molecular understanding of the suppression of new-particle formation by isoprene, *Atmospheric Chemistry and Physics*, 20, 11809-11821, 10.5194/acp-20-11809-2020, 2020.

Kirkby, J., Duplissy, J., Sengupta, K., Frege, C., Gordon, H., Williamson, C., Heinritzi, M., Simon, M., Yan, C., Almeida, J., Trostl, J., Nieminen, T., Ortega, I. K., Wagner, R., Adamov, A., Amorim, A., Bernhammer, A. K., Bianchi, F., Breitenlechner, M., Brilke, S., Chen, X. M., Craven, J., Dias, A., Ehrhart, S., Flagan, R. C., Franchin, A., Fuchs, C., Guida, R., Hakala, J., Hoyle, C. R., Jokinen, T., Junninen, H., Kangasluoma, J., Kim, J., Krapf, M., Kurten, A., Laaksonen, A., Lehtipalo, K., Makhmutov, V., Mathot, S., Molteni, U., Onnela, A., Perakyla, O., Piel, F., Petaja, T., Praplan, A. P., Pringle, K., Rap, A., Richards, N. A. D., Riipinen, I., Rissanen, M. P., Rondo, L., Sarnela, N., Schobesberger, S., Scott, C. E., Seinfeld, J. H., Sipilä, M., Steiner, G., Stozhkov, Y., Stratmann, F., Tome, A., Virtanen, A., Vogel, A. L., Wagner, A. C., Wagner, P. E., Weingartner, E., Wimmer, D., Winkler, P. M., Ye, P. L., Zhang, X., Hansel, A., Dommen, J., Donahue, N. M., Worsnop, D. R., Baltensperger, U., Kulmala, M., Carslaw, K. S.,

and Curtius, J.: Ion-induced nucleation of pure biogenic particles, *Nature*, 533, 521-526, 10.1038/nature17953, 2016.

Jokinen, T., Kausiala, O., Garmash, O., Peräkylä, O., Junninen, H., Schobesberger, S., Yan, C., Sipilä, M., and Rissanen, M. P.: Production of highly oxidized organic compounds from ozonolysis of  $\beta$ -caryophyllene: laboratory and field measurements, *Boreal Environment Research*, 21, 262-273, 2016.

Jokinen, T., Berndt, T., Makkonen, R., Kerminen, V. M., Junninen, H., Paasonen, P., Stratmann, F., Herrmann, H., Guenther, A. B., Worsnop, D. R., Kulmala, M., Ehn, M., and Sipilä, M.: Production of extremely low volatile organic compounds from biogenic emissions: Measured yields and atmospheric implications, *Proc. Natl. Acad. Sci. U. S. A.*, 112, 7123-7128, 10.1073/pnas.1423977112, 2015.

Ng, N. L., Kwan, A. J., Surratt, J. D., Chan, A. W. H., Chhabra, P. S., Sorooshian, A., Pye, H. O. T., Crouse, J. D., Wennberg, P. O., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol (SOA) formation from reaction of isoprene with nitrate radicals ( $\text{NO}_3$ ), *Atmos. Chem. Phys.*, 8, 4117-4140, 10.5194/acp-8-4117-2008, 2008.

Nie, W., Yan, C., Yang, L., Roldin, P., Liu, Y., Vogel, A. L., Molteni, U., Stolzenburg, D., Finkenzeller, H., Amorim, A., Bianchi, F., Curtius, J., Dada, L., Draper, D. C., Duplissy, J., Hansel, A., He, X.-C., Hofbauer, V., Jokinen, T., Kim, C., Lehtipalo, K., Nichman, L., Mauldin, R. L., Makhmutov, V., Mentler, B., Mizelli-Ojdanic, A., Petäjä, T., Quéléver, L. L. J., Schallhart, S., Simon, M., Tauber, C., Tomé, A., Volkamer, R., Wagner, A. C., Wagner, R., Wang, M., Ye, P., Li, H., Huang, W., Qi, X., Lou, S., Liu, T., Chi, X., Dommen, J., Baltensperger, U., El Haddad, I., Kirkby, J., Worsnop, D., Kulmala, M., Donahue, N. M., Ehn, M., and Ding, A.: NO at low concentration can enhance the formation of highly oxygenated biogenic molecules in the atmosphere, *Nat. Commun.*, 14, 3347, 10.1038/s41467-023-39066-4, 2023.

Richters, S., Herrmann, H., and Berndt, T.: Different pathways of the formation of highly oxidized multifunctional organic compounds (HOMs) from the gas-phase ozonolysis of  $\beta$ -caryophyllene, *Atmospheric Chemistry and Physics*, 16, 9831-9845, 10.5194/acp-16-9831-2016, 2016

Zhao, D. F., Pullinen, I., Fuchs, H., Schrade, S., Wu, R. R., Acir, I. H., Tillmann, R.,

Rohrer, F., Wildt, J., Guo, Y. D., Kiendler-Scharr, A., Wahner, A., Kang, S., Vereecken, L., and Mentel, T. F.: Highly oxygenated organic molecule (HOM) formation in the isoprene oxidation by NO<sub>3</sub> radical, *Atmospheric Chemistry and Physics*, 21, 9681-9704, 10.5194/acp-21-9681-2021, 2021.

## 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 1×10<sup>-12</sup> to 1.5×10<sup>-11</sup> 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 1×10<sup>-14</sup> to 1.5×10<sup>-12</sup> cm<sup>3</sup>s<sup>-1</sup>. 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.

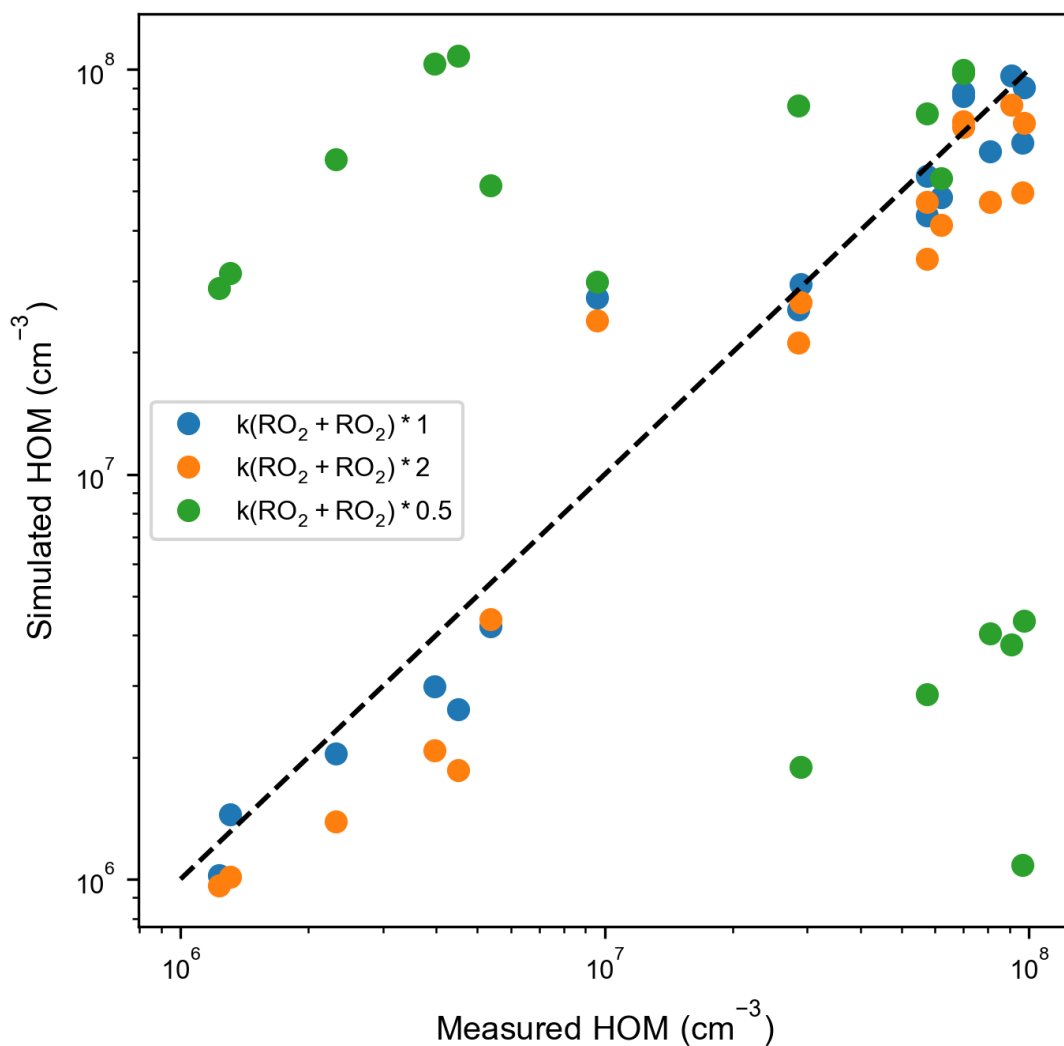


Fig.R3. Modelled and measured HOM concentrations. The different model results are from the SIM-HOM sensitivity tests where all  $\text{RO}_2 + \text{RO}_2$  reaction rates ( $k(\text{RO}_2 + \text{RO}_2)$ ) were scaled up or down with a factor of two compared to the default values..

#### 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.