We thank the editor and reviewers for their effort and the reviewers for their feedback and insightful comments. A detailed answer to each individual comment can be found below.

We would like to start with a response to a key point brought up in multiple comments regarding the applied framework to estimate the importance of bimolecular reactions of RO_2 with NO, HO_2, and RO_2. The reviewers have pointed out the large uncertainties in the presented approach due to the utilization of box-modeled concentrations of the reaction partners and the generic rate coefficients. We fully agree that these are key concerns and a known limitation.

Regarding the uncertainty in the modeled reaction partner concentration, we included a reference in L. 296 to Baker et al. (2024), who showed that in the HO_2/RO_2 system the model correctly reproduces the HO_2 trend in comparison to measurements by bromide CIMS. Furthermore, as asked for by reviewers #1, #3 and #4, we performed a sensitivity analysis based on a variation of the pseudo-first order rate coefficients of RO_2, HO_2, and NO by ±30 %. This value is based on previous publications comparing box model results utilizing MCM chemistry to measurements in monoterpene photooxidation experiments (Rolletter et al., 2019; Kaminski et al., 2017). The results of the sensitivity analysis show that a change of the pseudo-first reaction order of this magnitude would, while it changes the specific reaction partner contributions and total bimolecular reaction rate, not impact the classification of the chemical regime or the ordering of the regimes. The results of the sensitivity analysis are described and discussed in Supplement **Sec. S9** and introduced in the main text in L. 301.

In general, we want to underline that we see the development of the framework and shown methodology as an important result to provide a tool for analysis. This is of more meaning than the derived values for rate coefficients in detail. When better inputs become available, they can be "plugged in" to get better constraint results. This is now better clarified in the main text (L.315):

"In general, the framework is intended as an analysis tool, so the reported bimolecular reaction rates and contributions by the reaction partners should not be seen as final quantitative results but rather as trend indicators in the process of better understanding the observed changes in HOM and SOA formation."

The framework uses bulk reaction rate coefficients as the goal is to plausibly describe the bulk chemistry and not the reactions of a singular RO_2. For the application of the framework to bulk trends, we utilized the generic information available and believe the applied rate coefficients are state-of-the-art. We have added an explanation in L.346 to clarify the purpose of the framework:

"The purpose of the chemical regime categorization is to plausibly describe the bulk chemistry to understand shifts in the HOM product distribution. In contrast, individual RO_2· may have very different reaction rate coefficients compared to the utilized generic values, so that the reaction pathways of a specific RO_2· may not be correctly captured."

In the absence of further constraints, it is difficult to provide a systematic sensitivity analysis of the applied reaction rates, as for a singular RO_2 basically any combination of slower or faster rate coefficients is imaginable (e.g. a much faster NO reaction and a much slower HO_2 reaction would of course significantly change the contributions to the bimolecular reaction rate). However, we want to highlight that Section 4.1 *"Termination product contributions as proof of utility for the chemical regime framework"* specifically shows that the trends described by the generic rate coefficients and modeled concentrations capture the trends observed in the measured HOM product distribution and

that using the generic/bulk reaction rate coefficients therefor seems to capture the bulk trends in the product distribution, making the approach a valuable analysis tool.

As mentioned above, depending on use case and availability the same method could be applied with more specific rate coefficients. Here, we see great prospects in combination with automated mechanism generation models like GECKO (Aumont et al., 2026).

Please find the detailed reviewer comments with our answers and applied changes below (reviewer comments in blue, answers in black).

Reviewer #1:

This manuscript investigates how changes in the RO_2 reaction regime affect HOM composition and SOA formation from α-pinene photooxidation. The experimental design is valuable, particularly the attempt to maintain a nearly constant α-pinene–OH turnover while systematically varying the relative importance of RO_2 reactions with NO, HO_2 and RO_2. The study therefore addresses an important issue in interpreting chamber experiments, where RO_2+RO_2 chemistry can be more important than under many atmospheric conditions. The results are interesting and the manuscript contains a substantial amount of useful experimental information. I think the study is potentially suitable for publication in ACP. However, several aspects of the framework and its interpretation would benefit from further clarification. I therefore recommend that the following points be addressed before publication.

Specific comments

1. The framework relies on modeled HO_2 and total RO_2 concentrations, for which no direct absolute measurements are available. Could the authors provide a simple sensitivity analysis showing how plausible changes in these concentrations affect S_{RO2} and the inferred reaction-partner fractions?

    - Thank you for this suggestion, such a sensitivity analysis has been included in Supplement Sec. S9, for details please see the general response to all reviewers above.

2. The calculated reaction-partner fractions depend directly on the generic rate coefficients adopted for RO_2+NO, RO_2+HO_2 and RO_2+RO_2. Given the uncertainty associated with applying single representative rate coefficients to a chemically diverse RO_2 population, it would be useful to show how sensitive the derived partner fractions and S_{RO2} are to reasonable variation in these coefficients. This is particularly relevant for mixed regimes such as the ~50% HO_2/45% NO case, where the distinction between the two contributions may not be robust within the uncertainty of the framework.

    - Thank you for this thoughtful comment and please see the general discussion above. A general sensitivity analysis is difficult due to the lack of constraints in the possible reaction rate coefficients. However, while we cannot confirm the circa 50:50 contribution in the mixed regimes, our results (Sec. 4.1) show that the regime was successfully shifted from dominated by one reaction partner to the other.

3. The manuscript frequently refers to the total bimolecular RO_2 reaction rate as a "termination" rate, although it also notes that part of the RO_2+NO and RO_2+RO_2 chemistry can proceed

through RO formation and regenerate RO_2. I therefore suggest using terms such as "bimolecular RO_2 reaction rate" or "RO_2 loss frequency" for the total pool, and reserving "termination" for pathways that actually end the autoxidation chain.

- Thank you for pointing this out! We agree and have modified the following text sections:
  L.167: Replaced "bimolecular termination" by "bimolecular reactions"
  L.192: Replaced "bimolecular termination" by "bimolecular reaction rate"
  L.198: Replaced "termination reaction rate" by "bimolecular reaction rate"
  L.326: Replaced "termination reactions" by "bimolecular reactions"
  L.343: Replaced "termination" with "bimolecular reaction rate"
  L.372: Replaced "termination reactions" with "bimolecular reactions"
  L.388: Replaced "termination" with "bimolecular reactions"
  L.405: Replaced "where termination by RO_2·+RO_2· is negligible" by "where the contribution of RO_2·+RO_2· is negligible"
  L.411: Replaced "bimolecular termination sink" by "bimolecular reaction pool", changed "Contribution of RO_2·+RO_2· to the termination sink ≤5 % " to "Contribution of RO_2·+RO_2· ≤5 %"
  L.412: Replaced "termination partner" by "reaction partner".
  L.421: Replaced "termination reactions" by "reactions" and replaced "termination pathways" by "reaction pathways"
  L.442: Replaced "comparable termination sink rates" by "comparable bimolecular reaction rates"
  L.530: Replaced "termination" by "reactions"

4. In Sect. 4.6, the fraction remaining in the gas phase after seed addition is used as a proxy for product volatility, but the observed fraction may also depend on uptake kinetics, equilibration timescale, solubility and particle properties. In addition, adding a condensation sink could affect the lifetime of condensable intermediates and hence subsequent oxidation chemistry. The assumptions behind this interpretation should be stated more explicitly.

   - Thank you for this input, we agree that the assumption of unchanged precursor chemistry was missing and have added the following statement in L. 598:
     "The comparison is based upon the assumption that the precursor chemistry is not significantly disturbed by the seed addition."
     The discussion of other factors besides volatility impacting partitioning to the particle was raised starting from L. 623 and has been extended not only due to this comment but also comments by reviewer #3.

5. Some of the mechanistic and broader atmospheric conclusions appear stronger than can be directly established from the present experiments. The proposed importance of alkoxy–peroxy chemistry is plausible and consistent with the observed product distributions, but RO radicals or specific alkoxy–peroxy steps were not directly measured, and the authors acknowledge that persistent HOM formation may also involve fast RO_2 intramolecular H-shifts. In addition, the experiments are limited to the α-pinene+OH system, whereas the Conclusions suggest that the observed factor-of-two SOA reduction could serve as an

estimate of the bias when RO_2-dominated laboratory results are extrapolated to atmospheric conditions, and that similar effects may apply to all monoterpenes. I suggest distinguishing more clearly between conclusions directly supported by the measurements and broader mechanistic or atmospheric implications.

- We thank the reviewer for raising this concern! In accordance with this comment and point 3) of reviewer #4 we have reworked parts of the conclusion, specifically changing the statement regarding the transfer to other monoterpenes as follows (L. 708 and following):
  "This work focuses on the α-pinene+OH system as an exemplary case, but ~~similar effects can be expected for all monoterpens.~~ the presented underlying shifts in the generic RO_2· chemistry are transferrable to other monoterpenes and in general SOA precursors, when considering differences in autoxidation rates, bimolecular reaction pathways and alkoxy chemistry. "
  Furthermore, we removed the statement in L. 698:
  "*This may also be an estimator for the bias of SOA yields if results from RO_2· dominated laboratory systems are directly transferred to atmospheric situations, where HO_2· and NO dominate*"
  Instead, we now provide an implication for future work:
  "Even for increases in the RO_2· bimolecular reaction rate by up to a factor of six the decrease in SOA yield stabilized at a maximum factor of circa two. Whilst these reductions only provide snapshots of influence of changing chemical regime on SOA yield, they are sufficiently great to motivate future work investigating the effect of changing chemical regime on SOA for experiments that are transferable to ambient atmosphere simulations, such as those quantifying volatility basis sets.

Minor and technical comments:

1. The authors may consider using "highly oxygenated organic molecules" for HOM, consistent with the terminology recommended by Bianchi et al. (2019).

   - Thank you for the suggestion, we changed this in the introduction of the abbreviation in L.20 and L.38.

2. All experiments were conducted at 50% RH. Could the authors briefly explain the rationale for this choice? Since RH can affect aerosol water content, particle phase state and gas–particle partitioning, particularly in the ammonium-sulfate-seeded experiments, it would also be useful to comment on whether the observed HOM/SOA trends are expected to remain similar under substantially drier or more humid conditions.

   - Thank you for the question! A relative humidity of 50 % was chosen to make sure the ammonium sulfate seed particles are in a metastable state with a low aerosol liquid water content: The particles were generated by spraying a solution and the efflorescence point of ammonium sulfate is 39 % (Wei et al., 2025), thus 50 % RH ensures that no crystallization takes place. A brief expanation of this reasoning was included in L. 218.
     Regarding the HOM and SOA formation trends: We do not expect large effects of changes in humidity (within a range typical to the lower troposphere) on the

described gas-phase HOM chemistry. For the particulate phase we expect formation of an organic phase as shown by Anttila et al. (2007) and Folkers et al. (2003). Water content in the particles is low (derivable from gowth factors at 50% RH of ca. 1.23 for ammonium sulfate (Choczynski et al., 2021) and ca. 1.02 in the a-pinene organic phase (Varutbangkul et al., 2006). However, at high humidities and therefore high aerosol liquid water content the water solubility of products would play a larger role and reactions in the aqueous-phase could become important.

3. A simplified overview scheme showing the competing RO_2 reactions with NO, HO_2 and RO_2, the alkoxy–peroxy pathway, and the resulting HOM-Mon, HOM-Frag, HOM-Acc and ON-HOM classes would make the manuscript easier to follow. The authors could consider expanding Fig. 1 into such an overview rather than showing only the alkoxy–peroxy step.

    - Thank you for the helpful suggestion, we included an overview figure showing the different HOM-RO_2 reaction pathways in Fig. 1 moving the before shown alkoxy-peroxy step to the supplement as Fig. S1 and refer to it in the main manuscript in L.90. We further included a figure showing the formation pathways of the different HOM-Mon families (Fig. 1b)), as well as a table (Tab. S1) summarizing the termination reactions leading to each non-ON HOM-Mon at the suggestion of reviewer #3. We hope providing these additional visualizations will make it easier to follow the connections between reaction partners and product classes and families.

4. Figure 2a: The repeated radical dots in the axis labels make the labels visually rather cluttered.

    - Thank you for pointing this out, we fixed the axis labels.

5. The authors include several O_4 and O_5 compounds in the HOM classes, although HOMs are conventionally defined here as compounds containing at least six O atoms. Please make this extended definition explicit in the relevant figures/captions and sums (e.g., $HOM_{O\geq4}$, or another suitable notation to avoid ambiguity).

    - Thank you for the suggestion, we did introduce this deviation from the HOM definition by Bianchi, et al (2017) in L. 276 and following, but have further added a mention of this in the figure captions of Fig. 3, Fig. 5, Fig. 6, Fig. 8.

6. The agreement between the calculated partner fractions and measured product distributions is encouraging. However, the linear fit in Fig. 3 is forced through zero, while the fit in Fig. 4 is constrained through the hypothetical 1:1 point. It would be useful to also report the corresponding unconstrained fits, or briefly discuss how sensitive the apparent relationships are to these constraints.

    - The unconstrained fits are now included in the supplement as Fig. S6 and Fig. S7 to show that there are not meaningfully different from the constrained versions. A short discussion was added as well. The supplementary information is referred to in the main text in L. 386 and L. 419.

7. Line 417: “HOM-Acc sum (Fig. 5c)” should be corrected to “HOM-Acc sum Fig. 5e”.

    - Fixed, thank you!

8. In SI Line 141: the reference to Eq. (S3)? appears to be missing. Please also report the k_{wall} and k_{cond} values actually used for the correction.

    - Thank you for catching this, the reference was added (now SI L. 231). Furthermore the k_{wall} value and k_{cond} were added and can be found in the SI starting from L.234.

9. The reported steady-state NO concentrations appear inconsistent between Tables S4 and S5 and the main text.

    - Thank you for the attention to detail, after a careful check we could not find an inconsistency between the values: Table S4 and S5 (now S6 and S7) differ since S6 reports the modeled NO concentration and S7 reports the measured concentration. The main text refers to the measured concentration also shown in S7 (previously S5).

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