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 #4:

This study investigates how systematic changes in both the magnitude and composition of the bimolecular RO_2· reaction sink, through varying contributions from NO, HO_2·, and RO_2·, affect HOM composition and SOA formation while maintaining an approximately constant α pinene + OH turnover rate in the SAPHIR STAR chamber. The work builds directly on Baker et al. (2024), extending the previously explored HO_2·/RO_2· dimension to include NO containing and mixed NO/HO_2· chemical regimes.

Several aspects of the study are particularly noteworthy. First, the experimental design provides strong control over the entry flux into α pinene oxidation while systematically modifying the downstream RO_2· reaction environment, allowing chemical regime effects to be investigated more cleanly than in many conventional chamber experiments. Second, the analysis in Sect. 4.4 is particularly interesting. The inferred shift between the $C_{10}H_{15}O_x$· and $C_{10}H_{17}O_x$· precursor families is examined using three complementary molecular signatures, including non ON monomers, C_{20} accretion products, and organic nitrates. Together, these observations provide a persuasive mechanistic picture. Third, the authors are generally transparent about the limitations of their framework and appropriately report observations that cannot be fully explained by the proposed mechanisms, such as the persistence of the $C_{10}H_{14}O_z$ family.

Overall, the qualitative conclusions are well supported by multiple lines of evidence. In particular, the data consistently indicate substantial changes in HOM composition and a decrease in SOA formation potential as the system moves away from the RO_2· dominated regime. The seed addition experiments also support the conclusion that ON HOMs partition less efficiently to the particle phase than non ON products of similar molar mass under the experimental conditions employed here. However, several of the more quantitative and mechanistic conclusions require further refinement, because the central chemical regime parameters rely on modeled radical concentrations and generic reaction rate coefficients. Most of the concerns raised below appear addressable through additional analysis of existing data, clearer quantification of uncertainties, and expanded discussion rather than through new experiments.

Specific Comments

1. Sensitivity to generic rate coefficients

Please provide a table in the Supplementary Information showing how SRO_2 and the relative contributions of the reactions change when k(RO_2+RO_2) and k(RO_2+NO) are varied within a plausible range, and clarify whether the relative order of the regimes is maintained. In part, the framework relies on a single value: k(HOM-RO_2· + R'O_2·) = 5.0×10^{-12} cm^3 s^{-1}. Because the relative contributions

of RO_2·+RO_2·, RO_2·+NO, and RO_2·+HO_2· differ among conditions, uncertainty in this rate coefficient will not affect all conditions equally. Demonstrating that the regime ordering is robust to plausible variations in these rate coefficients would substantially strengthen the quantitative use of the framework.

- Thank you for this suggestion! A sensitivity analysis including the table you suggested (Table S9) has been included in the supplement and the results of the sensitivity analysis indicate that the regime ordering is robust. For details, please see the general discussion at the start of the document.

2. α-pinene ozonolysis

Lines 212–213: Authors mention that at least 75% of α-pinene turnover was driven by the reaction with OH radical. However, since the O_3 inflow was adjusted to maintain a nearly constant OH· concentration, it may be possible that the relative contribution of ozonolysis varied depending on the CO and NO perturbation conditions. If the ozonolysis fraction changes alongside the imposed chemical regime, it could be an additional variable rather than a constant background factor. Please provide further details on this point in the main text.

- Thank you for raising this important consideration. To show that the ozone inflow adjustment did not significantly or systematically influence the contribution of O_3 to the α-pinene turnover we added Tab. S8 in the supplement, which lists the OH concentration as well as α-pinene turnover with both OH and O_3 as well as their turnover to the total contribution. We introduced the table in the main text in L. 225 and added further detail on the effect of ozone adjustment in L.232.

3. Scope of conclusion

This experiment addresses only sub-ppbv NO conditions, with a maximum reported steady-state NO concentration ([NO] SS) of 0.5 ppbv. Therefore, the broad reference to "urban" conditions in lines 645–646 falls outside the scope of this study, and a qualifying statement or explanation regarding this should be added. Similarly, regarding the statement in lines 636–637 that similar effects are expected for "all monoterpenes," it must be specified that the quantitative significance of RO_2 isomerization, alkoxy chemistry, nitrate formation, and accretion reactions varies depending on the type of precursor.

- Thank you for your input, we agree that this statement was oversimplifying the transfer to other SOA precursors and have therefore replaced it as following (starting in L.709): *“This work focuses on the α-pinene+OH system as an exemplary case, but 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.”*

4. Minor details

- Abstract, line 20: “An important source ... are” should be corrected to ensure subject-verb agreement.
- Abstract, line 25: “Steady -state” should be corrected to “steady-state”.

- Introduction, lines 38–39: “One important source of SOA are” should be corrected to ensure subject-verb agreement.
- Table 1: The extra closing parenthesis after “Saunders et al., 2003))” should be removed.
- Line 250: “lesser oxidized products” should be corrected to “less oxidized products.”
- Line 375: “The good correlation ... show” should be corrected to “The good correlation ... shows”.
- Line 417: HOM-Acc is presented in Fig. 5e, not Fig. 5c.
- Fig. 6 caption: “$C_{20}H_{23}Oz$” appears to be a typo for “$C_{20}H_{32}Oz$,” which is used in the main text and the figure; verification is required.
- Line 612: “extend of formation” should be corrected to “extent of formation.”

- All mentioned passages have been reworked, thank you for your attention to detail!

References

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