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 #3:

The authors present a systematic laboratory study of α-pinene photooxidation in the SAPHIR-STAR chamber, focusing on how the chemical regime affects HOM and SOA formation. The experiments vary NO and HO2 separately and simultaneously while keeping the α-pinene + OH turnover approximately constant. The authors introduce a generic framework based on two parameters: the total pseudo-first-order bimolecular RO2 reaction rate and the fractional contributions of NO, HO2, and RO2 to that sink. They analyze changes in HOM product families, organic nitrates (ON), accretion products (HOM-Acc), monomers (HOM-Mon), and fragments (HOM-Frag). This is a well-designed and timely study that addresses an important gap in understanding how NOx and HO2 availability control HOM and SOA formation. The manuscript is generally clear and the mechanistic discussion is thoughtful. However, several conclusions rest on modeled radical concentrations, generic rate coefficients, and product-class assignments that require additional validation and uncertainty analysis. The atmospheric implications are interesting but need to be more carefully reconciled with the observed reductions in SOA yield.

Major Comments

The central framework depends on box-modeled steady-state concentrations of HO2 and the sum of RO2 radicals. The authors acknowledge that no direct HO2 or RO2 measurements were available. Given that the key parameters are derived from these modeled concentrations, the robustness of the entire regime classification should be quantified. I recommend a sensitivity analysis in which the modeled HO2 and RO2 concentrations are perturbed within reasonable uncertainties and the resulting changes in the regime parameters and conclusions are reported.

- Thank you for this suggestion, such a sensitivity analysis has been included (Supplement Sec. S9), for details please see the general discussion at the start of the document.

The framework uses generic rate coefficients for HOM-RO2 + NO, HOM-RO2 + HO2, and HOM-RO2 + RO2, and assumes an average autoxidation rate of 0.1 s-1. Real HOM-RO2 chemistry involves a wide distribution of H-shift rates, and the fate of a given RO2 depends on its specific structure. The conclusion that a bimolecular rate exceeding 0.1 s-1 implies earlier termination is therefore an oversimplification. The authors should either (a) provide a sensitivity study using a range of autoxidation rates (e.g., 0.01–1 s-1), or (b) more clearly frame the framework as a qualitative/tendency indicator rather than a quantitative predictor.

- Thank you for the comment, we agree that our reasoning to compare the bimolecular RO_2 reaction rate to a specific autoxidation rate could have been clearer and have

therefore taken two measures to clarify the comparison:
1) We added an explanatory passage starting from L. 307 to explain the choice of 0.1 s^{-1} as the autoxidation rate to compare to and how the comparison should be interpreted, which reads:
"The RO_2· bimolecular reaction rate is utilized as a qualitative indicator if atmospherically relevant autoxidation reactions are interrupted by bimolecular reactions of RO_2·. To this end, we compare the RO_2· bimolecular reaction rate with an autoxidation rate of 0.1 s^{-1}. This value is chosen as representative since autoxidation rates of 0.1 s^{-1} and faster, are fast enough to compete with the expected RO_2· bimolecular reaction rate in pristine and rural conditions in which autoxidation and HOM formation have been previously reported. See for example Yan et al. (2016) who reported HOM formation in a boreal forest at NO concentrations of up to 0.4 ppbv (resulting in a k_{NO+RO2}·[NO] of 0.09 s^{-1}).
Autoxidation rate coefficients vary widely, and the value of 0.1 s^{-1} is intended to serve only as a threshold for analysis."
2) We changed the terminology in L. 329, L.331, L.337 and L.354 to not refer to 0.1 s^{-1} as an average autoxidation rate but rather as a representative autoxidation rate for atmospherically relevant autoxidation steps.

The attribution of HOM families to specific termination pathways is central to the interpretation. Some assignments are convincing, but others are ambiguous. For example, C10H18O2 can arise from HO2 termination or from RO2 + RO2 alcohol formation; C10H14O2 can be formed by multiple pathways, including internal termination and alkoxy radical chemistry. The authors acknowledge some of these issues, but the manuscript would benefit from a more systematic uncertainty table for each key family. In particular, the claim that ON-HOM are uniquely from RO2 + NO is supported by the UV-A-off experiment, but PAN-like formation from acyl peroxy + NO2 cannot be fully excluded.

- Thank you for the suggestion! A table with the potential formation pathways for the utilized non-ON HOM-Mon families has been added to the Supplement as Tab. S1 and is introduced in the main manuscript in L.101 and further referenced to help the reader's understanding in L. 402 and L.505.
  The potential contribution of acyl-peroxy RO2+NO2 is introduced in Sec. 2.1 and discussed in Sec. 4.1, so that we believe the possibility of ON formation from NO2 is – given the here presented material, sufficiently covered.

The interference of ON-HOM with HOM-RO2 detection in the CIMS is also acknowledged, but its impact on the trends in Fig. 5b and 5e is not quantified. How much of the apparent decrease in C10-HOM-RO2 or HOM-Acc could be due to overlapping ON peaks or reduced sensitivity? This needs a more detailed error analysis.

- Thank you for your question, a reduction in HOM-Acc due to overlap with ON-HOM peaks leading to missing or misassignment of HOM-Acc is not expected since HOM-Acc are detected on even mass-to-charge ratios in the nitrate CIMS, while ON-HOM are detected on odd mass-to-charge ratios. Only HOM-Acc containing nitrogen would be detected on odd mass-to-charge ratios, but no such species were found in our analysis.
  Regarding the decrease of C10-HOM-RO2 we agree that the decrease could be

strongly influenced by the overlapping ON-HOM peaks. A detailed error analysis for the sum of the detected C10-HOM-RO2 is difficult since each individual C10-HOM-RO2 is impacted differently depending on three factors:
1) The signal of the HOM-RO2 itself (smaller signals are impacted stronger).
2) The number of ON-HOM found at the same mass-to-charge ratio, as well as the number of C13-isotope peaks of significant non-ON C9 products.
3) The signal of those ON-HOM and isotope peaks.
Cases with high HOM-RO2 signal and comparatively low ON-HOM and isotope contribution at the same mass-to-charge will be of course much less impacted than small HOM-RO2 signals as shoulders of much larger ON-HOM signals, an example of such a "worst case scenario" is also what is shown in Supplement Fig. S4. Due to C10-HOM-RO_2 potentially falling below the detection limit and since we did not assign HOM-RO_2 peaks that have too high uncertainties the C10-HOM-RO2 sum will rather underestimate the present C10-HOM-RO2 and this is how we formulated it in the manuscript now (L.467):
*"The detection of small C_{10}-HOM-RO_2· signals maybe influenced by the presence of high ON-HOM signals (see Supplement **Sec. S6**), therefore, the C_{10}-HOM-RO_2· sum (**Fig. 5b**)) has some bias in cases of high NO and HOM-ON. This especially is the case at short HOM-RO_2· lifetimes due to high bimolecular reaction rates, which lower the concentrations of HOM-RO_2· in general. Thus, the values shown in **Fig. 5b)** represent a lower limit for two reasons. Firstly, steady-state concentrations of the HOM-RO_2· decrease, potentially to close or below the detection limit of the instrument. And secondly, at the same time, the detection may be additionally biased by larger ON-HOM peaks at the same mass-to-charge ratio."*

The conclusion that ON-HOM have higher volatility than non-ON termination products relies on the fraction-remaining approach with ammonium sulfate seed. This method is useful but sensitive to seed surface area, particle mass loading, equilibration time, wall losses, and condensed-phase diffusion. The authors should report the seed surface area and mass concentrations, the time to reach steady state, and whether gas-phase wall losses differ between ON and non-ON compounds.

- Thank you for bringing up this concern, the seed surface area and particle mass loadings are reported in the Supplement Sec. S17 (previously Sec. S13) and we added a reference to this information in L.589. Typical HOM molecule lifetimes towards particle uptake calculated for our experiments were 30-40 seconds and the corresponding k_{cond} values have been added in the Supplement in L. 221 and following.
  Experiments determining the wall loss of HOM have been performed and are referred to in the Supplement in Sec. S20. For the correction of the SOA yield only one wall-loss rate is utilized, with the underlying assumption that the contributing species are so low in volatility, that their wall-loss is only diffusion controlled and every collision with the wall leads to a loss.
  When we take into account different volatilities we of course also expect that higher volatile compounds have a slower wall loss rate/higher lifetime towards the wall. And since the fraction remaining indicates that ON-products have higher volatility, a slower wall loss rate is also expected. In an exemplary comparison of one ON-HOM to

a non ON product of similar mass this expectation is met. The comparison was added to the Supplement Sec. S21 and is referred to in the main text in L. 607.

Subtracting the nitrate group mass is an interesting approach, but it assumes that the volatility difference is mainly due to molar mass and not to functional-group-specific interactions such as hydrogen bonding or solubility. The discussion of Sagawa and Shikata (2014) and Suda et al. (2014) is helpful, but additional support—e.g., comparison with literature volatility estimates or a thermodynamic model—would strengthen the conclusion.

- Here we do not agree with the reviewer. In contrast, the nitrate group was subtracted in order to take out the molecular weight effect on the vapor pressure, caused by adding NO to a HOM-$RO_2\cdot$ radical (+30 g mol^{-1}) in comparison to carbonyl formation (-16 g mol^{-1}), alcohol formation (-15 g mol^{-1}), (or adding an H-atom (+1 g mol^{-1}). After this rough weight correction, remaining changes in vapor pressures (gas-phase fraction remaining) should reflect the different functionality.
- However, we agree with the reviewer that additional support from a thermodynamic model would assist the paper and the reader in interpreting the effect of the relatively low hydrogen bond strength in nitro groups. Therefore, we revised this paragraph (L.623) to read :
  "The smaller than expected decrease in volatility compared to non-ON termination products could potentially be connected to missing hydrogen bonds from the organic nitrate group (compared to OH and OOH termination groups). To compare the expected behavior of an ON to a non-ON product the pure component saturation vapor pressure of two early generation α-pinene+·OH autoxidation products of similar mass (circa 250 g mol^{-1}) was estimated using the online calculator (Rbisa, 2026) for the EVAPORATION method (Compernolle et al., 2011). Details on the molecules can be found in the Supplement Sec. S18. The comparison yielded a circa 10^4 Pa factor higher vapor pressure for the ON product with a saturation vapor pressure of $7\cdot10^{-6}$ Pa vs. $2\cdot10^{-11}$ Pa for the ON compared to the non-ON product, indicating a higher volatility of the ON product. Applying the definition used by Li et al. (2023) for a low volatility organic compound (saturation vapor pressure between 10^{-6} Pa and 10^{-8} Pa), the ON product would be considered just not yet a LVOC, while the non-ON product would be considered as extremely low in volatility."

The wall-loss-corrected SOA yields show a maximum reduction of about a factor of two when moving away from RO2-dominated conditions. The authors argue that this is due to both lower HOM production and higher HOM volatility. However, SOA yield also depends on the absorptive partitioning of semivolatile products, which in turn depends on the total organic mass concentration. Since the experiments were designed to have similar α-pinene + OH turnover but different HOM concentrations, the organic mass loading may differ between regimes. The authors should either (a) show that the organic mass concentrations were sufficiently similar, or (b) use a partitioning model to separate changes in production from changes in partitioning. Without this, the statement that the observed yield reduction is an estimator of the bias of RO2-dominated laboratory systems may be premature.

- We would like to first answer in a general fashion. The concept of the experiments is to hold the a-pinene turnover constant, which is by definition one determinant of the SOA yield, besides the observed SOA mass. This means if the SOA mass and thus the SOA yield changes, this must be due to changes in the (HOM-) chemistry following the primary a-pinene oxidation. This is what we discuss. The effect of lower SOA yield because less condensable material is available adds naturally to the lower SOA yield.
- However, we agree with the reviewer that differences in partitioning due to different mass loadings are a factor to consider. The OA mass loadings and total particle surface areas can be found in the Supplement (previously Sec. S13, now Sec. S17). The effect of OA mass loading was introduced in L.587 and we extended the statement as follows: *"The organic mass concentration of each investigated steady state can be found in Supplement **Sec. S17** and span a range of 1.7 µg m^{-3} to 3.4 µg m^{-3}. Due to the overall low organic loading and the moderate changes, we do not expect large changes in partitioning due to changes in available organic matter. Additionally, we would like to note that missing HOM sources reducing the available organic particle mass would also intensify decreases in SOA formation in the atmosphere."*

The conclusion states that "more 'urban' atmospheric conditions with higher availability of NO might be more efficient in SOA formation than previously assumed." This appears to conflict with the observed decrease in SOA yield with increasing NO. The authors seem to mean that HOM-RO2 + NO can continue autoxidation and open new formation pathways, partially offsetting termination. This nuance should be stated more carefully.

- Thank you for your comment, we have reworked the statement to clarify that there are multiple considerations at play here: a) The SOA formation decreases in comparison to the "unrealistic" laboratory case dominated by RO2+RO2. b) Higher bimolecular reaction rates can interrupt the autoxidation chain and decrease SOA formation rates. c) When an interruption of the autoxidation chain takes place HOM-RO2+NO can continue the chain through alkoxy-peroxy steps and indeed even open new pathways. To include this considerations we changed L. 720 to:
  "Though, both the higher availability of NO and HO_2· decrease the SOA formation in comparison to the biased laboratory case dominated by RO_2·+ RO_2· our results indicate that more "urban" atmospheric conditions with higher availability of NO might be more efficient in SOA formation than previously assumed, while the current understanding of more "pristine" environments with high importance of HO_2· could lack critical pathways into HOM formation."

In addition, the experiments use j(NO2) ≈ 1.0 × 10-3 s-1, which is lower than typical summertime atmospheric values (~4 × 10-3 s-1), and NO steady states are generally <1 ppbv. Real urban environments can have much higher NO and different HO2/NO ratios. The authors should discuss how the framework could be extrapolated to higher NOx conditions and what additional experiments would be needed to test the "urban" implication.

- It is correct that the j(NO2) achieved in the experiments is significantly lower than typical summertime values, which is clearly stated in the manuscript (L. 240). This affects the distribution of NO_x species between NO and NO_2 leading to a higher importance of NO_2 compared to the atmosphere. The HO_2 level can then be affected due to

HO_2+NO→OH+NO_2. However, regarding the NO concentration we classified the regimes not based on total concentrations but by the contribution to the RO_2 bimolecular reaction rate. Within this definition we could test the implications of more "urban" conditions with higher importance of NO as well as cover the range of HO_2/NO (conditions from 80 % of the bimolecular reaction rate by HO_2 to circa 50 % by both NO and HO_2 up to 80 % and 95 % by NO). We see no need here to modify the manuscript.

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