Response to Reviewer #2

We are grateful to the reviewer for the thoughtful comments on the manuscript. Our point-to-point responses to each comment are as follows (reviewer’s comments are in black font and our responses are in blue font).

General Comments

In this study, the authors investigated the fraction of acyl peroxy radicals (RO₂) formed from alpha-pinene ozonolysis. Acyl-RO₂'s are of crucial atmospheric importance due to their higher reactivity and their role in the formation of aerosol precursors. In flow reactor alpha-pinene ozonolysis experiments, NO₂ was used as an acyl-RO₂ scavenger, and the reduction in RO₂ signals was used to probe the fraction of acyl-RO₂s produced. The paper is well written and makes a significant contribution towards the better understanding of a key aerosol forming system in the atmosphere. I recommend the publication of the manuscript in ACP after the authors address my minor comments below:

In addition to dimer formation and producing RO, alkyl-RO₂ cross reactions also lead to ROH + R=O products, and if the initial peroxy radical group is on a primary carbon atom, the R=O can be a source of acyl-RO₂ following a secondary OH reaction. Alkyl RO₂s can have significant yields for this reaction. Was this accounted for in the model and in the analysis of the experiments?

Response: Thanks for the reviewer’s comment. During the OH oxidation of α-pinene, acyl RO₂ can be formed from the secondary OH oxidation of aldehydes such as pinonaldehyde. However, in the present study, the secondary OH oxidation is significantly inhibited due to an excess of α-pinene compared to O₃, therefore the contribution of secondary OH oxidation to acyl RO₂ formation is expected to be relatively small. We considered the secondary OH oxidation in the model simulations, and found that the contribution of secondary OH oxidation to acyl RO₂ formation is negligible even under the high O₃ condition (Exp 22, 500 ppb α-pinene + 180 ppb O₃). As shown in Figure S9, the acyl RO₂ C₉H₁₀O₄ (C89CO3 in Figure S9a) and C₁₀H₁₅O₅ (C920CO3 in Figure S9b) can be formed from both C-C cleavage/H-shift of C₁₀H₁₅O₅-RO (Figure 4) and OH oxidation of the first-generation aldehyde products. However, the contributions from secondary OH oxidation are negligible for the two acyl RO₂ species during the whole reaction period under the high O₃ condition (Exp 22, 500 ppb α-pinene + 180 ppb O₃). In addition, the acyl RO₂ C₁₀H₁₅O₄ (C96CO3) that can be only formed from OH oxidation of pinonaldehyde contributes to only 0.01% and 0.2% of the total C₁₀H₁₅O₅-RO₂ and total acyl RO₂ concentration, respectively. Therefore, the contribution of secondary OH oxidation to acyl RO₂ in this study is minor and the majority of acyl RO₂ species measured here are formed from the ozonolysis channel.

Figure S9 Simulated contribution of different processes to the formation of (a) C₉H₁₀O₄ (C89CO3) and (b) C₁₀H₁₅O₅ (C920CO3) acyl-RO₂ during ozonolysis of α-pinene (Exp 22, 500 ppb α-pinene + 180 ppb O₃).

We have added the following discussions to Section 3.2 of the main text.

“In addition, the secondary OH oxidation of aldehyde products can also produce acyl RO₂ radicals during ozonolysis of α-pinene. However, in the present study, the secondary OH oxidation is expected to be
insignificant due to an excess of α-pinene compared to O₃. Indeed, kinetic model simulations incorporating the secondary OH chemistry show that the contribution of secondary OH oxidation to acyl RO₂ formation is negligible even under high O₃ conditions (see details in Section S2 and Figure S9)”.

We have also added the following content and Figure S10 to the SI.

“S2. Contribution of secondary OH oxidation to acyl RO₂ formation.

Considering that the secondary OH oxidation of aldehyde products can also contribute to the formation of acyl RO₂ during ozonolysis of α-pinene, kinetic model simulations incorporating secondary OH chemistry were also performed under typical experimental conditions. As shown in Figure S9, the acyl RO₂ C₉H₇O₄ (C99CO3 in Figure S9a) and C₁₀H₁₅O₂ (C920CO3 in Figure S9b) can be formed from both C-C cleavage/H-shift of C₁₀H₁۵O₂-RO (Figure 4) and OH oxidation of the first-generation aldehyde products. However, the contributions from secondary OH oxidation are negligible for the two acyl RO₂ species during the whole reaction period. In addition, the acyl RO₂ C₁₀H₁₅O₂ (C96CO3) that can be only formed from OH oxidation of pinonaldehyde contributes to only 0.01% and 0.2% of the total C₁₀H₁₅O₂ - RO₂ and total acyl RO₂ concentration, respectively (not shown). Therefore, the contribution of secondary OH oxidation to acyl RO₂ in this study is minor and the majority of acyl RO₂ species measured here are formed from the ozonolysis channel.”

The more functionalized acyl-RO₂5 with an -OOH group elsewhere in the molecule are known to undergo H-scrambling reactions to form peroxy acids (R-C(Ο)(ΟOH)) at rates of 1E3 – 1E5 s⁻¹ (Knap et al. 2017, J. Phys. Chem. A, 121(7), pp.1470-1479). Can the authors comment on the possible role of this reaction in their experiments? For example, the ring-opened acyl C₁₀H₁₅O₂-RO₂ that they report has a 1,6 H-scramble available that leads to a peroxy acid and an alkyl RO₂. For their model system, Knap et al. estimate a rate coefficient for the 1,6 H-shift of 1.5E5 s⁻¹. If the rate coefficient is comparable for the alpha-pinene derived C₁₀H₁₅O₂ acyl-RO₂ above, this could to an extent explain the low reduction in signal upon NO₂ addition.

Response: We appreciate the reviewer’s point. We have performed a model simulation to evaluate the influence of H-scrambling reactions on the response of ring-opened acyl C₁₀H₁₅O₂-RO₂ to NO₂ addition. As shown in Figure S14, when a 1,6 H-shift rate of 1×10⁵ s⁻¹ is considered, the extent of the reduction in C₁₀H₁₅O₂-RO₂ with NO₂ addition indeed becomes smaller, especially when the yield of ring-opened C₁₀H₁₅O₂-RO₂ in the model is at a higher limit (89%). Therefore, the H-scrambling reactions of the ring-opened acyl C₁₀H₁₅O₂-RO₂ could to certain extent explain the low reduction in its signal upon NO₂ addition.

![Figure S14 Simulated influence of H-scrambling reaction on the behavior of the ring-opened acyl C₁₀H₁₅O₂-RO₂ as a function of added NO₂ concentration (Exps 8-14). A 1,6 H-scrambling rate of 1×10⁵ s⁻¹ and an alkyl RO₂+NO₂ rate coefficient of 5×10⁻¹² cm³ molecule⁻¹ s⁻¹ were used in the model.](image)

We have added the following discussions to Section 3.3 in the main text.

“Thirdly, the ring-opened C₁₀H₁₅O₂-RO₂, a highly functionalized acyl RO₂ radical with an –OOH group, may be able to undergo very fast intramolecular H-scrambling reactions to form a peroxy acid as
suggested by Knap and Jørgensen (2017), which would compete with the NO₂ reaction and result in a lower reduction in its signal upon NO₂ addition (see details in Section S3).”

We have also added the following content and Figure S14 to the SI.

“S3 Possible influence of H-scrambling reactions on the behavior of C₁₀H₁₅O₄ acyl-RO₂

It has been suggested that the functionalized acyl RO₂ radicals with an -OOH group could undergo H-scrambling reactions to form peroxy acids at rates of 1×10⁻¹⁰⁻¹×10⁻⁹ s⁻¹ (Knap and Jørgensen, 2017). Here, we performed a model simulation to evaluate the influence of this reaction on the response of the ring-opened acyl C₁₀H₁₅O₄-RO₂ to NO₂ addition. As shown in Figure S14, considering a 1,6 H-shift rate of 1×10⁻⁹ s⁻¹, the simulated reduction in total C₁₀H₁₅O₄-RO₂ concentration with the addition of 30 ppb NO₂ decreases from 25% to 21% for a C₁₀H₁₅O₂-RO₂ yield of 30% (lower limit) and from 31% to 17% for a yield of 89% (higher limit). These results suggest that the H-scrambling reactions of the ring-opened acyl C₁₀H₁₅O₂-RO₂ could to certain extent explain the low reduction in its signal upon NO₂ addition.”

Line 468: Regarding the speculation of the formation of alkyl C₆H₉O₁-RO₂ to explain the discrepancy between experiments and simulations, this would compete with the formation of the ring-opened and ring-retaining C₁₀H₁₅O₂-RO₂. How did the sensitivity analysis of including the C₆H₉O₁-RO₂ in the model affect the yield of the C₁₀H₁₅O₂-RO₂s and the subsequent acyl-RO₂s derived from them?

Response: We have evaluated the influence of the sensitivity analysis of C₆H₉O₁-RO₂ yield on other C₁₀H₁₅O₂-RO₂ as well as on the contribution of acyl RO₂ to total C₇-₁₀ HOMs. As shown in Figure S16, as the C₆H₉O₁-RO₂ yield increases from 0% to 3%, the simulated concentration of a ring-retaining C₁₀H₁₅O₂-RO₂ radical (C₁₀H₁₅O₂4KB) decreases by only ~5% and other C₁₀H₁₅O₂-RO₂ species are basically unchanged. As the C₆H₉O₁-RO₂ is considered to only produce highly oxygenated alkyl RO₂ in the model, the increase in its yield results in a decrease in the contribution of acyl RO₂ to the total C₉ HOMs. However, the contributions of acyl RO₂ to total C₇, C₈, and C₁₀ HOMs are almost unchanged. These results indicate that the relatively small production of C₆H₉O₁-RO₂ has no significant influence on the yield of C₁₀H₁₅O₂-RO₂ and the subsequent acyl RO₂.

We have added the above results and discussion to Section 3.3 in the main text and Figure S16 to the SI.

![Figure S16](image-url)

Figure S16 Influences of C₆H₉O₁-RO₂ production on (a) the yield of C₁₀H₁₅O₂-RO₂ and (b) the
contribution of acyl RO₂ to total C₇-10 HOMs (Taking Exp 8 as an example). The C10H15O4KB and C10H15O4RB denote a ring-retaining and a ring-opened C₁₀H₁₅O₂-RO₂, respectively (see Table S3 and the main text).

Are any of the acyl peroxy nitrates detected by the NO₃-CIMS? Alpha-pinene derived APNs with 8 oxygen atoms or more should have at least 2 -OOH functional groups and will presumably cluster well with NO₃. Do the decrease in e.g. C₇ and C₈ RO₂ signals when NO₂ is added show an increase in the corresponding APN signals? I think a spectrum figure maybe in the supplementary showing the acyl-RO₂ and acyl-ROONO₂ peaks would be useful.

Response: We have added a spectrum figure in SI showing the signal changes of acyl RO₂ and their corresponding RC(O)OONO₂ (Figure S3). It can be seen that the signals of acyl RO₂ decrease remarkably with the addition of NO₂. Accordingly, the signals of highly oxygenated RC(O)OONO₂ such as C₉H₁₃O₆NO₂, C₉H₁₅O₇NO₂, and C₁₀H₁₅O₇NO₂ increase significantly. We note that some RC(O)OONO₂ have very similar m/z values with some alkyl RO₂. For example, the m/z values of C₉H₁₃O₆NO₂ (251.0641) and C₉H₁₅O₇NO₂ (283.0539) are very close to those of C₁₀H₁₅O₈-RO₂ (251.0766) and C₁₀H₁₇O₁₀-RO₂ (283.0665), respectively, which always have high ion signals. As a result, although some RC(O)OONO₂ are expected to be formed with NO₂ addition, they could not be unambiguously detected by nitrate-CIMS due to the overlapping with strong alkyl RO₂ peaks in this study.

We have added the following discussions to Section 3.1 in the main text.

“Along with the marked reduction in acyl RO₂ signals, the production of highly oxygenated RC(O)OONO₂ species such as C₉H₁₃O₆NO₂, C₉H₁₅O₇NO₂, and C₁₀H₁₅O₇NO₂ with the addition of NO₂ were observed (see the spectra in Figure S3). However, we note that although some RC(O)OONO₂ such as C₈H₁₃O₆NO₂ and C₈H₁₅O₇NO₂ are expected to be formed with NO₂ addition, they could not be unambiguously detected by nitrate-CIMS due to their overlapping with strong alkyl RO₂ peaks in this study.”

![Figure S3 Signals of measured acyl RO₂ and the related RC(O)OONO₂ with and without the addition of NO₂ (Exps 8 and 14).](image)

Figure 4. In pathway 3, the final H-shift of the acyl-oxy is unlikely to compete with CO₂ See reaction r12 and description therein in Vereecken et al. 2009, Phys. Chem. Chem. Phys. 11(40), pp.9062-9074.

Response: Thanks for the reviewer’s comment. We have updated pathway 3 with a C₁₀H₁₅O₃ alkoxy radical that can undergo H-shift to form an acyl RO₂.

Pathway 3

![Pathway 3 Diagram](image)
References: