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 (RO_2) formed from alpha-pinene ozonolysis. Acyl-RO_2s 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, NO_2 was used as an acyl-RO_2 scavenger, and the reduction in RO_2 signals was used to probe the fraction of acyl-RO_2s 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-RO_2 cross reactions also lead to ROH + R=O products, and if the inital peroxy radical group is on a primary carbon atom, the R=O can be a source of acyl-RO_2 following a secondary OH reaction. Alkyl RO_2s 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 RO_2 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 O_3, therefore the contribution of secondary OH oxidation to acyl RO_2 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 RO_2 formation is negligible even under the high O_3 condition (Exp 22, 500 ppb α-pinene + 180 ppb O_3). As shown in Figure S9, the acyl RO_2 $C_9H_{13}O_4$ (C89CO3 in Figure S9a) and $C_{10}H_{15}O_5$ (C920CO3 in Figure S9b) can be formed from both C-C cleavage/H-shift of $C_{10}H_{15}O_4$-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 RO_2 species during the whole reaction period under the high O_3 condition (Exp 22, 500 ppb α-pinene + 180 ppb O_3). In addition, the acyl RO_2 $C_{10}H_{15}O_4$ (C96CO3) that can be only formed from OH oxidation of pinonaldehyde contributes to only 0.01% and 0.2% of the total $C_{10}H_{15}O_4$-RO_2 and total acyl RO_2 concentration, respectively. Therefore, the contribution of secondary OH oxidation to acyl RO_2 in this study is minor and the majority of acyl RO_2 species measured here are formed from the ozonolysis channel.
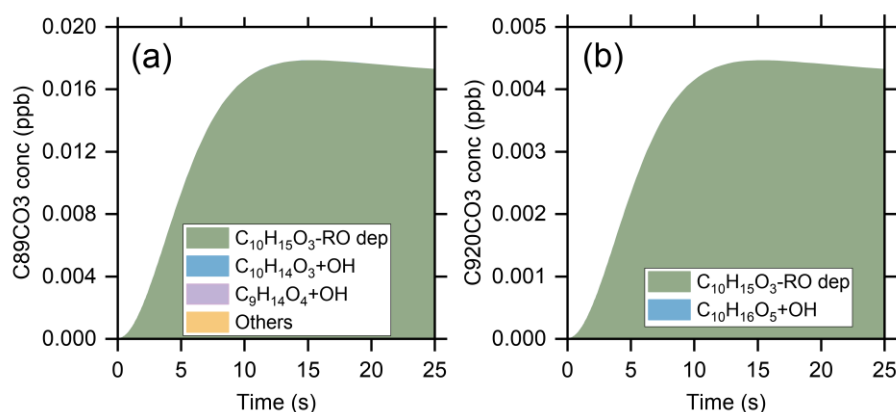

Figure S9 Simulated contribution of different processes to the formation of (a) $C_9H_{13}O_4$ (C89CO3) and (b) $C_{10}H_{15}O_5$ (C920CO3) acyl-RO_2 during ozonolysis of α-pinene (Exp 22, 500 ppb α-pinene + 180 ppb O_3).

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 RO_2 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 O_3. Indeed, kinetic model simulations incorporating the secondary OH chemistry show that the contribution of secondary OH oxidation to acyl RO_2 formation is negligible even under high O_3 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 RO_2 formation.

Considering that the secondary OH oxidation of aldehyde products can also contribute to the formation of acyl RO_2 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 RO_2 $C_9H_{13}O_4$ (C89CO3 in Figure S9a,) and $C_{10}H_{15}O_5$ (C920CO3 in Figure S9b) can be formed from both C-C cleavage/H-shift of $C_{10}H_{15}O_4$-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 RO_2 species during the whole reaction period. In addition, the acyl RO_2 $C_{10}H_{15}O_4$ (C96CO3) that can be only formed from OH oxidation of pinonaldehyde contributes to only 0.01% and 0.2% of the total $C_{10}H_{15}O_4$-RO_2 and total acyl RO_2 concentration, respectively (not shown). Therefore, the contribution of secondary OH oxidation to acyl RO_2 in this study is minor and the majority of acyl RO_2 species measured here are formed from the ozonolysis channel."

The more functionalized acyl-RO_2s with an -OOH group elsewhere in the molecule are known to undergo H-scrambling reactions to form peroxy acids (R-C(O)OOH) 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 $C_{10}H_{15}O_8$-RO_2 that they report has a 1,6 H-scramble available that leads to a peroxy acid and an alkyl RO_2. 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 $C_{10}H_{15}O_8$ acyl-RO_2 above, this could to an extent explain the low reduction in signal upon NO_2 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 $C_{10}H_{15}O_8$-RO_2 to NO_2 addition. As shown in Figure S14, when a 1,6 H-shift rate of 1×10^5 s^{-1} is considered, the extent of the reduction in $C_{10}H_{15}O_8$-RO_2 with NO_2 addition indeed becomes smaller, especially when the yield of ring-opened $C_{10}H_{15}O_4$-RO_2 in the model is at a higher limit (89%). Therefore, the H-scrambling reactions of the ring-opened acyl $C_{10}H_{15}O_8$-RO_2 could to certain extent explain the low reduction in its signal upon NO_2 addition.
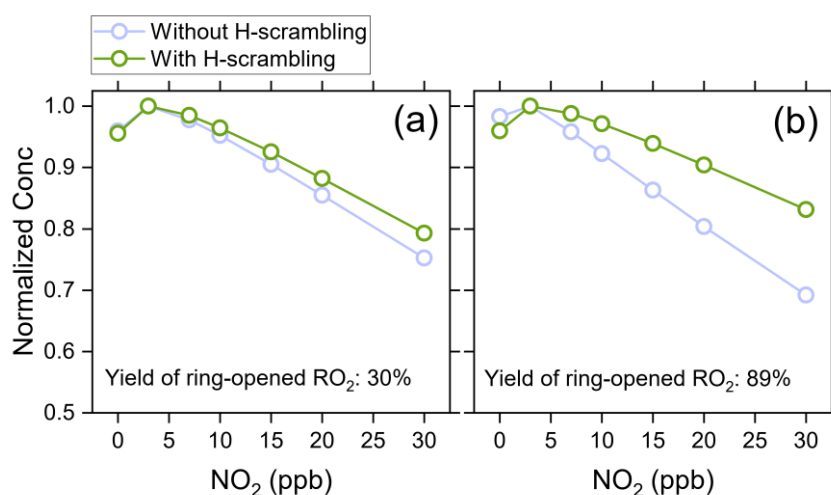

Figure S14 Simulated influence of H-scrambling reaction on the behavior of the ring-opened acyl $C_{10}H_{15}O_8$-RO_2 as a function of added NO_2 concentration (Exps 8-14). A 1,6 H-scrambling rate of 1×10^5 s^{-1} and an alkyl RO_2+NO_2 rate coefficient of 5×10^{-12} cm^3 $molecule^{-1}$ s^{-1} were used in the model.

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

"Thirdly, the ring-opened $C_{10}H_{15}O_8$-RO_2, a highly functionalized acyl RO_2 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 NO_2 reaction and result in a lower reduction in its signal upon NO_2 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 $C_{10}H_{15}O_8$ acyl-RO_2

It has been suggested that the functionalized acyl RO_2 radicals with an -OOH group could undergo H-scrambling reactions to form peroxy acids at rates of 1×10^3-1×10^5 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 $C_{10}H_{15}O_8$-RO_2 to NO_2 addition. As shown in Figure S14, considering a 1,6 H-shift rate of 1×10^5 s^{-1}, the simulated reduction in total $C_{10}H_{15}O_8$-RO_2 concentration with the addition of 30 ppb NO_2 decreases from 25% to 21% for a $C_{10}H_{15}O_4$-RO_2 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 $C_{10}H_{15}O_8$-RO_2 could to certain extent explain the low reduction in its signal upon NO_2 addition."

Line 468: Regarding the speculation of the formation of alkyl $C_9H_{15}O_3$-RO_2 to explain the discrepancy between experiments and simulations, this would compete with the formation of the ring-opened and ring-retaining $C_{10}H_{15}O_4$-RO_2. How did the sensitivity analysis of including the $C_9H_{15}O_3$-RO_2 in the model affect the yield of the $C_{10}H_{15}O_4$-RO_2s and the subsequent acyl-RO_2s derived from them?

Response: We have evaluated the influence of the sensitivity analysis of $C_9H_{15}O_3$-RO_2 yield on other $C_{10}H_{15}O_4$-RO_2 as well as on the contribution of acyl RO_2 to total C_{7-10} HOMs. As shown in Figure S16, as the $C_9H_{15}O_3$-RO_2 yield increases from 0% to 3%, the simulated concentration of a ring-retaining $C_{10}H_{15}O_4$-RO_2 radical (C10H15O4KB) decreases by only ~5% and other $C_{10}H_{15}O_4$-RO_2 species are basically unchanged. As the $C_9H_{15}O_3$-RO_2 is considered to only produce highly oxygenated alkyl RO_2 in the model, the increase in its yield results in a decrease in the contribution of acyl RO_2 to the total C_9 HOMs. However, the contributions of acyl RO_2 to total C_7, C_8, and C_{10} HOMs are almost unchanged. These results indicate that the relatively small production of $C_9H_{15}O_3$-RO_2 has no significant influence on the yield of $C_{10}H_{15}O_4$-RO_2 and the subsequent acyl RO_2.

We have added the above results and discussion to Section 3.3 in the main text and Figure S16 to the SI.
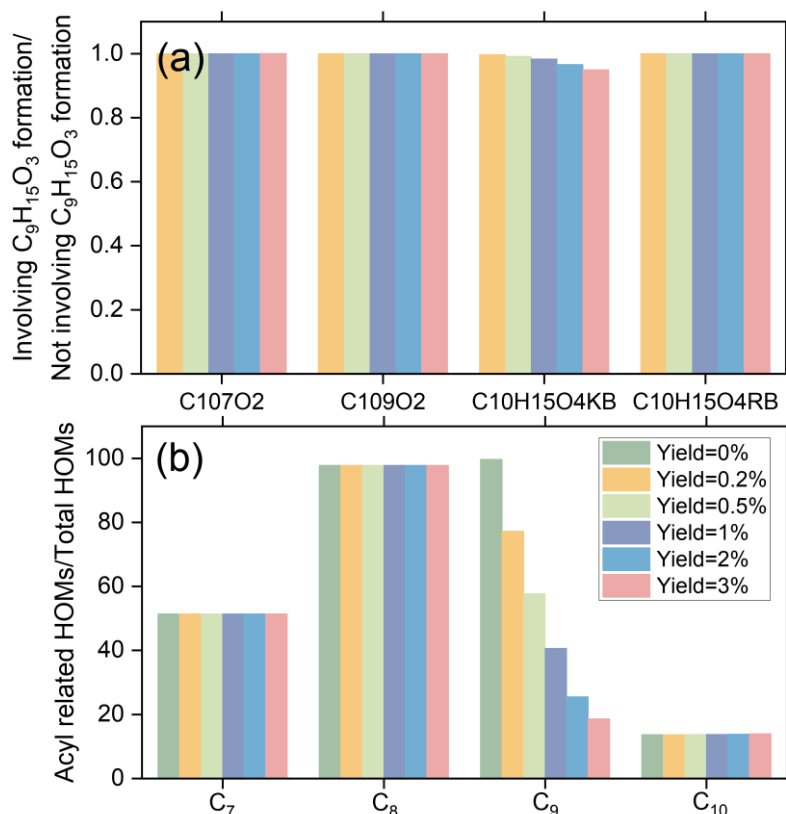
Figure S16 Influences of $C_9H_{15}O_3$-RO_2 production on (a) the yield of $C_{10}H_{15}O_4$-RO_2 and (b) the

contribution of acyl RO_2 to total C_{7-10} HOMs (Taking Exp 8 as an example). The C10H15O4KB and C10H15O4RB denote a ring-retaining and a ring-opened $C_{10}H_{15}O_4$-RO_2, respectively (see Table S3 and the main text).

Are any of the acyl peroxy nitrates detected by the NO_3-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 NO_3. Do the decrease in e.g. C_7 and C_8 RO_2 signals when NO_2 is added show an increase in the corresponding APN signals? I think a spectrum figure maybe in the supplementary showing the acyl-RO_2 and acyl-$ROONO_2$ peaks would be useful.

Response: We have added a spectrum figure in SI showing the signal changes of acyl RO_2 and their corresponding $RC(O)OONO_2$ (Figure S3). It can be seen that the signals of acyl RO_2 decrease remarkably with the addition of NO_2. Accordingly, the signals of highly oxygenated $RC(O)OONO_2$ such as $C_9H_{13}O_9NO_2$, $C_9H_{17}O_7NO_2$, and $C_{10}H_{15}O_7NO_2$ increase significantly. We note that some of $RC(O)OONO_2$ have very similar m/z values with some alkyl RO_2. For example, the m/z values of $C_8H_{13}O_6NO_2$ (251.0641) and $C_8H_{13}O_8NO_2$ (283.0539) are very close to those of $C_9H_{15}O_8$-RO_2 (251.0767) and $C_9H_{15}O_{10}$-RO_2 (283.0665), respectively, which always have high ion signals. As a result, although some $RC(O)OONO_2$ are expected to be formed with NO_2 addition, they could not be unambiguously detected by nitrate-CIMS due to their overlapping with strong alkyl RO_2 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 RO_2 signals, the production of highly oxygenated $RC(O)OONO_2$ species such as $C_9H_{13}O_9NO_2$, $C_9H_{17}O_7NO_2$, and $C_{10}H_{15}O_7NO_2$ with the addition of NO_2 were observed (see the spectra in Figure S3). However, we note that although some $RC(O)OONO_2$ such as $C_8H_{13}O_6NO_2$ and $C_8H_{13}O_8NO_2$ are expected to be formed with NO_2 addition, they could not be unambiguously detected by nitrate-CIMS due to the overlapping of their peaks with strong alkyl RO_2 peaks ($C_9H_{15}O_8$-RO_2 and $C_9H_{15}O_{10}$-RO_2) in this study."
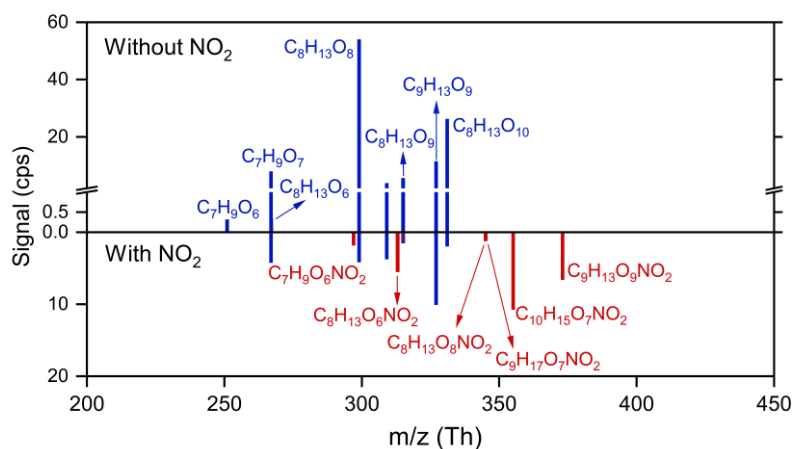

Figure S3 Signals of measured acyl RO_2 and the related $RC(O)OONO_2$ with and without the addition of NO_2 (Exps 8 and 14).

Figure 4. In pathway 3, the final H-shift of the acyl-oxy is unlikely to compete with CO_2 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 $C_{10}H_{15}O_3$ alkoxy radical that can undergo H-shift to form an acyl RO_2.

Pathway 3

Primary $C_{10}H_{15}O_4$ $C_{10}H_{15}O_5$
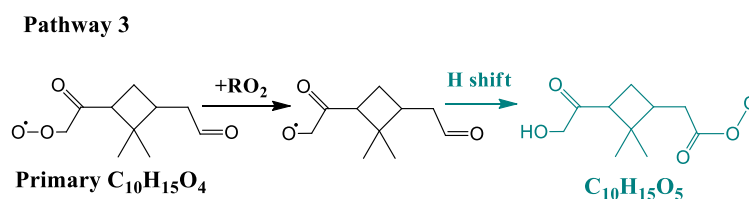
References:

Knap, H. C. and Jørgensen, S.: Rapid Hydrogen Shift Reactions in Acyl Peroxy Radicals, J. Phys. Chem. A, 121, 1470-1479, 10.1021/acs.jpca.6b12787, 2017.