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 manuscript the authors report a combined experimental and modelling study of the formation and fate of acylperoxy radicals formed from the reaction of a-pinene with ozone in a flow reactor. The alkyl and acyl RO_2 radicals and highly oxidized molecules (HOMs) were monitored using a chemical ionization mass spectrometer with nitrate ion ionization. RO_2 radicals and HOMS were assigned based on elemental formulas and acyl RO_2 radicals were distinguished from alkyl RO_2 radicals by addition of NO_2, which forms $RC(O)OONO_2$ (acyl peroxy nitrates) that are relatively stable under the conditions of the experiments, thus removing acyl RO_2 signal. Because the changes in acyl RO_2 concentrations can also impact other aspects of the chemistry, a detailed F0AM model employing a modified Master Chemical Mechanism was employed to interpret the results.

Overall, the experiments and modelling were well done and the approach seems to have yielded quite useful and interesting results. The authors provide a very thorough and thoughtful discussion of the results, which is clearly written and easy to follow. Considering the high technical quality of the study and the importance of these reactions to the formation of HOMs and ROOR dimers, both of which are currently of much interest because of their potential role in secondary organic aerosol (SOA) formation, I think the paper is well suited for ACP. I have only a few minor comments.

Specific Comments

1. Line 137: I don't understand the point of converting signals to "concentrations" using sulfuric acid since the actual concentrations will be highly sensitive to the structure of the RO_2 radical and HOM. Presenting the results this way is misleading. Since the "concentrations" are only used to calculate contributions of various species relative to each other, normalized signals will give the same results and be a more honest presentation of the data.

Response: Thanks for the reviewer's comment. We have changed the normalized concentrations of various species to their normalized signals in the revised manuscript.

2. Line 149: Have the authors considered partitioning of RO_2 radicals to particles and what influence that could have on the results? The vapor pressures of the radicals should be similar to those of HOMs, so I don't see any reason that they would not form SOA, and they likely undergo different reactions in the particles since isomerization would be restricted.

Response: We appreciate the reviewer's point. We used a scanning mobility particle sizer (SMPS, TSI) employing both long and nano differential mobility analyzers (model 3081 and 3085 for different particle sizes) to clarify whether there is SOA formation in the experiments. We did not observe SOA formation by SMPS in Exps 1-28. Only in Exp 31 where the reacted α-pinene reaches 36.8 ppb, we observed SOA formation with very low particle mass concentrations ($5.0×10^{-4}$-$5.7×10^{-3}$ μg m^{-3}) and number concentrations (63-395 # cm^{-3}). Therefore, we suggest that the negligible to low formation of SOA under these experimental conditions has no significant influence on the RO_2 fates.

We have added the results to Section 2.1 of the revised manuscript.

"To clarify whether there is SOA formation in the experiments, a scanning mobility particle sizer (SMPS, TSI), which consists of an electrostatic classifier (model 3080), a long or nano differential mobility analyzer (model 3081 and 3085 for different particle sizes), and a condensation particle counter (model 3087), was used to monitor the formation of SOA particles. Except in Exp 31 where the reacted α-pinene reached 36.8 ppb and there was low SOA formation with particle mass concentrations of $5.0×10^{-4}$-$5.7×10^{-3}$ μg m^{-3} and number concentrations of 63-395 # cm^{-3}, no particle formation was observed by SMPS. Therefore, the RO_2 radicals and closed-shell products would be primarily distributed in the gas phase, with their fates negligibly influenced by the low SOA formation under these experimental conditions."

3. Line 342: In this section it is not clear to me what conclusions are based on measurements, modelling, or a combination of the two. Please make that more clear.

Response: To be more precise, we have clarified the relevant descriptions using "measured signals" and

"simulated contributions" in this section.

4. Line 530: Considering that $RO_2 + NO_2$ rate constants have been measured for a variety of alkyl and acyl RO_2 radicals and are pretty consistently ~1E–11 (Orlando & Tyndall 2012), it seems unlikely that the value is as low as suggested here. Any explanation based on RO_2 structure would imply that the same effects apply to the $RO_2 + NO$ rate constant, which is essentially identical to the NO_2 value (Orlando & Tyndall 2012). This would have significant consequences for predictions of conditions under which autoxidation reactions are important in the atmosphere, since this usually depends on the competition between RO_2 isomerization and the $RO_2 + NO$ reaction. What are other possible explanations for the apparent discrepancy?

Response: We appreciate the reviewer's point. Orlando and Tyndall (2012) have summarized that the rate coefficients of functionalized $RO_2 + NO_2$ are in the range of $(5\text{-}10) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. However, these coefficients are mainly for the RO_2 species with small molecular sizes. A recent study by Berndt et al. (2015) determined a $RO_2 + NO_2$ rate coefficient of $(1.6 \pm 0.5) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} for a highly oxidized acyl RO_2 radical $O,O-C_6H_7(OOH)_2O_2$ arising from the gas-phase ozonolysis of cycloalkanes, which is several times smaller the rates reported for the relatively simple RO_2 (Orlando and Tyndall, 2012). Therefore, it is possible that some of the α-pinene-derived RO_2 radicals react with NO_2 less efficiently than the smaller RO_2 radicals do. Such differences in the $RO_2 + NO_2$ rate coefficient may partially explain the observed increase in $C_{20}H_{34}O_x$ dimer formation as a function of added NO_2.

References:

Berndt, T., Richters, S., Kaethner, R., Voigtländer, J., Stratmann, F., Sipilä, M., Kulmala, M., and Herrmann, H.: Gas-Phase Ozonolysis of Cycloalkenes: Formation of Highly Oxidized RO_2 Radicals and Their Reactions with NO, NO_2, SO_2, and Other RO_2 Radicals, J. Phys. Chem. A, 119, 10336-10348, 10.1021/acs.jpca.5b07295, 2015.

Orlando, J. J. and Tyndall, G. S.: Laboratory studies of organic peroxy radical chemistry: an overview with emphasis on recent issues of atmospheric significance, Chem. Soc. Rev., 41, 6294-6317, https://doi.org/10.1039/C2CS35166H, 2012.