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Interactive comment on “Impact of NO_x on secondary organic aerosol (SOA) formation from α-pinene and β-pinene photo-oxidation: the role of highly oxygenated organic nitrates” *by* Iida Pullinen et al.

Anonymous Referee #3

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This manuscript reported HOM organic nitrates, permutation products, and accretion products formation from the oxidation (mostly OH oxidation) of a-pinene and b-pinene. Effective uptake coefficients of HOM on particles was also investigated and reported. Experiments were conducted in CSTR under high RH conditions without seed particles (except for the uptake experiments). It was found that increasing NOx affects the fraction of each type of HOM products formed. The fraction of organic bound nitrate (OrgNO3) stored in gas-phase HOM-ON was found to be substantially higher than the fraction of particulate OrgNO3 and was attributed to particle-phase hydrolysis of OrgNO3. Lastly, SOA yields were also reported and discussed. The suppression of SOA yields with increasing NOx was attributed to suppression of gas-phase HOM accretion products.

This is an interesting study and falls within the scope of ACP. It contributes to our further understanding of monoterpene oxidation in the presence of NOx and the resulting organic nitrate formation and chemistry. There are three main comments that should be addressed prior to publication 1) more analysis needs to be conducted to reconcile the discrepancy between the fraction of particulate OrgNO3 reported in this study and other prior studies in literature. The authors attributed this to hydrolysis but this is not supported by data in literature, 2) more details need to be provided regarding the evaluation of the effective uptake coefficients, and 3) the manuscript should be edited for language. More detailed comments are provided below.

Specific comments

1. Page 5 line 12. It would be useful to include the amount of ozone added and the steady state ozone concentration in Table 1.

2. Page 6 line 16. Were the seed particles dried before being injected into the chamber? I would assume not but it is not clear from the manuscript. Please specify.

3. Page 8 section 2.4 a. Line 25. What does “finite vapor pressure” mean?

b. I do not fully understand how these experiments were conducted. From this section, it appears that experiments without seeds (and no organic aerosol formation via nucleation) were compared with experiments with seeds (ammonium sulfate particles injected) to determine the effective uptake coefficient. My understanding from the experimental section is that seed particles were only added in “experiment series 3” (i.e., experiments to determine effective uptake coefficient), and no seed particles were added in all other experiments. Presumably, organic aerosol formation via nucleation took place in all other experiments. However, according to Table 1, the b-pinene mix-

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Discussion paper

ing ratio used in “experiment series 3” was the same as other all experiments. If so, shouldn’t nucleation also took place in ““experiment series 3”, and that particles (organic particles) would be present in the system even though no ammonium sulfate particles were added (see page 13 line 12)? If this is the case, one needs to consider uptake onto pure organic particles? Please describe and discuss these clearly in the revised manuscript.

4. Page 12, line 12. The authors noted that the highly-oxidized C<10 nitrates were observed with increasing NOx and that “supposedly, they did not arise from gas-phase chemistry but were formed at the walls”. Please elaborate. What mechanisms at the walls? If there is chemistry on the walls, how would this affect section 2.4 (determination of uptake coefficient) if there is also some sort of wall memory?

5. Page 13, line 16, please also indicate (e.g., in Figure 7) the organic mass concentration, as SOA yield is also highly dependent on organic mass.

6. Page 14, lines 1-2. Are these mass concentrations in the gas and particle phases consistent with equilibrium partitioning of HNO3?

7. Page 16, line 9. There are many more studies. For example, see review and references in Ng et al. (ACP, 2017). Some more recent studies, for example, Claflin and Ziemann (J. Phys. Chem. A, 2018), are also relevant.

8. Page 16 line 16. A recent study by Takeuchi and Ng (ACP, 2019) also reported on the ON formed by photooxidation of monoterpenes.

9. Page 16 line 23. Please provide citations for this statement “We found contributions between 0 % and 2.7 % by AMS, which is within the range of most other data reported in the literature but at the lower end.”.

10. Page 17 line 9. It was stated that “Our findings are in agreement with observations by Lee et al. (2016b) in a field study.” My understanding is that the study by Lee et al. was conducted in a rural environment, presumably with very low level of NOx.

The ambient conditions were quite different from laboratory conditions employed in this study. Please justify why an agreement would be expected between results in Lee et al. and this study.

11. Page 18-19, section 4.3. The fraction of OrgNO3 is much lower in this study than Zhao et al. and other studies in literature. The authors attributed this to potential hydrolysis of organic nitrates in the particle phase as experiments in Zhao et al. were conducted at much lower RH. However, a recent study by Takeuchi and Ng (ACP, 2019), conducted at similar RH to this study, showed that the fraction of organic nitrates in the particles is also much higher than that reported in this study, and the fraction or organic nitrates undergoing hydrolysis was constrained. More analysis should be conducted here to evaluate why the value reported in this study is much lower than prior literature.

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