Reply to reviewer #3

We thank the reviewer #3 for the helpful comments. We addressed all points raised.

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.

Reply:

1) In contrast to the opinion of referee #3 we are convinced that literature data is in support of our explanations. We would like to note that hydrolysis of ON and particulate ON is not the focus of our paper and our data at one RH are not suited to reconcile possibly inconclusive findings in the literature:

a) Our methodology is sound: because the effective uptake coefficients for both, HOM-PP and HOM-ON are close to unity, we can predict the mass fraction of ON and also organic bound nitrate ($OrgNO_3$) in particles. $OrgNO_3$ expected by uptake of HOM was compared to the amount of $OrgNO_3$ found in the particles by direct measurement. We found a strong discrepancy. A likely explanation for this difference is hydrolysis of organic nitrates in the condensed phase, as this is discussed extensively in the literature (e.g.). The experiments here were performed at 60% RH. Considering the strong dependence of hydrolysis on relative humidity we could also explain the differences of the $OrgNO_3$ content in particles found by us in different experiments at lower relative humidity of 30% (here and Zhao et al., 2018).

b) The production of ON depends on the VOC/NOX ratio and only a fraction of the ON will be transferred to the particulate phase and contribute to SOA. Hydrolyzing of the particulate phase ON depends on their structure (Boyd et al. 2015, Browne et al. 2013, Hu et al.2011), relative humidity, and the acidity of the particles (Rindelaub et. al. 2015). Hence, the fraction of particulate $OrgNO_3$ in particles can be variable in lab studies at different conditions and a same content of $OrgNO_3$ cannot be expected a priori. This makes comparison between experiments difficult.

c) ON hydrolysis depends on the character of the ON and only tertiary ON are supposed to hydrolyse fast (Hu et al. 2011). The fraction of tertiary ON depends on the formation process. E.g. oxidation of β-pinene with NO_3 led to only a small fraction of tert. ON, so hydrolysis is not so important in case of VOC oxidation by NO_3 (Boyd et al. 2015), whereas photochemical production can lead to large fractions of tert. ON and strong hydrolysis (Browne et al. 2013, Takeuchi and Ng, 2019).

Taking a) - c) into account we come to different conclusions as Referee 3. In contrast to the opinion of referee #3 we assess our results as being well within the range of findings reported in the literature (e.g. Day et al., 2010; Liu et al., 2012; Browne et al., 2013; Jacobs et al., 2014; Rindelaub et al., 2016, 2015; Boyd et al., 2015; Bean and Hildebrandt Ruiz, 2016, Takeuchi and Ng, 2019). All found fast and substantial hydrolysis for photochemically formed particulate ON.

2) We agree with referee #3 that our descriptions of the determination of effective uptake coefficients (Section 2.4) needed some more details on the experiments. This is described in our response to the specific comment 3.b and we accordingly modified section 2.4.

3) We went through the manuscript and removed grammatical errors and tried to improve the language.

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.

We modified and extended 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.

The particles were dried and this is now described in the experimental section (p.6, line 26, in the revised manuscript)

3. Page 8 section 2.4

a. Line 25. What does "finite vapor pressure" mean?

We reformulated that sentence and skipped the notation finite pressure (p.9, line 17 and line 20, in the revised manuscript).

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.

Reply:
No, the uptake experiments were done in one run, starting with the non-seeded chamber. When steady state was reached i.e. stable HOM production, seed particles were added over a few hours to the chamber. Since the chemical production was not affected by adding seed particles, the surface of seed particles provided an increasing sink for the HOM, leading to lower concentrations compared to the non-seeded start. To achieve a sufficient dynamic range of HOM concentrations, a certain level of β-pinene was needed, that caused some NPF in the non-seeded begin of the experiment. The NPF required extrapolation to zero surface in order to calculate c^0(HOM). c^0(HOM) is the concentration in absence of particles which is only determined by (same) production and wall loss. The wall loss coefficients of HOM were determined in independent experiments at lower concentration levels.
We reformulated section 2.4 to better describe how the experiments were conducted. A short paragraph was put in front of Section 2.4 where the experimental procedure is shortly described (p. 9, line 1-8, in the revised manuscript).

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 mixing 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.

Reply:
Yes, the referee is correct, seed particles were added only in experiment series 3. Regarding the effects of NPF in determining γ_{eff}: uptake of HOM by pure organic particles was certainly considered. The surface concentration (S_P) of purely organic particles was $0.2x10^{-3}$ m^2/m^3 while S_P increased up to $1.2x10^{-3}$ m^2/m^3 after adding seeds. Plots 1/c(HOM) vs. S_P where linear over the whole range. Or in other words, the pure organic particles matched the behavior of the coated ones. To make this clearer we modified section 2.4 and added a short paragraph in Section 2.4 (p 9, line 1-8, p.10, line 24 - 31 and p.11, line 1-2, in the revised manuscript).
We discussed the procedure of determining γ_{eff} also section 3.5 (p.14, line17-22, in the revised manuscript)

Particle formation by NPF was desired in experiment series 4 in order to determine $OrgNO_3$ by AMS. The experiments were started at low NO_X to get nucleation and then NO_X was stepwise increased. This seemed easier to us in organic aerosols than in aerosols with seeds. Since HOM form SOA by solely condensation, the organic matrix is the same in SOA formed in NPF and on neutral ammonium sulfate seeds. As stated, the resulting SOA yields shown in Figure 7 were about the same as yields observed in seeded experiments in Sarrafzadeh et al. 2016. In experiment 1 NPF wouldn’t affect the results, but in presence of NO_X NPF is strongly suppressed anyhow (Wildt et al., 2014, Sarrafzadeh et al., 2016). So, NPF is only unwanted in experiment series 2, where one would like to have the HOM totally in the gas-phase in order to determine the expected composition of the SOA by HOM-PP, HOM-ON, HOM-ACC. In the low NO_X cases some NPF took place in series 2, but again with increasing NO_X NPF was suppressed. In cases where NPF took place, loss to particles was corrected as described in supplement section S3.

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?

As described in manuscript, these compounds had a different composition and showed a different time behavior (increased with time independent on the photochemistry). They cannot affect the uptake coefficients, because the uptake coefficients were determined at $[NOX]_{SS}$ = 4 ppb (β-pinene) or less (α-pinene). As stated in the manuscript and can be seen in Figure S5 (supplement) at these NO_X levels such compounds were unimportant. They could have some effect on the SOA yields at the highest NO_X, but that effect is at maximum their contribution to the total HOM. The chamber was flushed for at least on day between experiments until the compounds were below detection limit.
We believe that we gave the phenomenon sufficient attention and showed that it does not much affect our results.
We further weakened the statement that they are formed at the wall (p.14, line 6-8, in the revised manuscript).

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.

We don't understand this comment. The paragraph at page 13 around line 16 deals with uptake coefficients and Figure 5. We are of course aware that SOA yields depend on OA mass, but this not our question here. Experiments in Figure 7 where all performed at the same conditions but changing NO_X. The average SOA load was 16±5 $\mu g/m^3$, ranging from 11 $\mu g/m^3$ to 23 $\mu g/m^3$ and this information was added to the caption of Figure 7, in the revised manuscript.

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

Reply:
We obviously did not specify sufficiently what we meant. We modified the text (p.15, line 9-11, in the revised manuscript).
Equilibrium partitioning of HNO_3 is difficult to predict for SOA at 60%RH. There is some water in the particles and the system will be highly non-ideal. In any case at 24 ug/m^3 HNO_3 (<8 ppb) the amount in the particulate phase will be orders of magnitude smaller than the gas-phase concentration and an upper limit of 0.1 ug/m^3 is well within expectations by thermodynamics. (HNO_3 has a vapor pressure at RT of about 5000 Pa.) However, for our considerations it is only important that we determined the $OrgNO_3$ mass correctly and do not falsely count OrgNO3 as inorganic nitrate.

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.

We added more references including Ng et al., 2017, as well as Claflin and Ziemann, 2018,

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

We added Takeuchi and Ng, 2019 to the reference list.

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.".

We modified that passage and added references. (p.17, line 5-16, in the revised manuscript)

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.

We specified more clearly what we are going to compare (p.18, line 25-26, in the revised manuscript).

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.

Reply
We think there is a misunderstanding. $OrgNO_3$ is not the same as particulate ON. It is the nitrate carried by ON. We clarified that throughout the manuscript. We added a note to section 2.3 (p.8, line 16-17, in the revised manuscript), reformulated section 4.1. in large parts (p.18 line 2-15, in the revised manuscript) and modified the first paragraph of section 4.2 (p.18, line 22-23, in the revised manuscript).
We basically show that HOM will dominate the composition of particulate phase in our experiment, because of their large γ_{eff}. Therefore we can predict from the HOM composition, i.e. HOM-PP, HOM-ON and HOM-ACC, the ON and therewith $OrgNO_3$ that should be expected in the particulate phase. We modified the text at several instances showing and discussing now mass concentrations of HOM-ON and all other HOM in new Figure 3 and

new Figure 4. From new Figures 3 and 4 it should now become clear that we got ON mass fractions up to several 10% in the particulate phase. This is in agreement with many other studies, including Takeuchi and Ng, 2019. The discrepancy we discussed was in $OrgNO_3$ expected from HOM and directly measured by AMS, where we find 60-80% loss of the nitrate function. This is somewhat higher than observations of Takeuchi and Ng, 2019, but in agreement with expectations discussed in Boyd et al., 2015, Browne et al. 2013, Fisher et al., 2016.

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