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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 #1

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Pullinen et al. described an atmospheric simulation chamber work in the JPAC chamber on the photooxidation of α-pinene and β-pinene at low and high NOx conditions at quite high humidity (relative humidity$\sim$63%). The main focus of the study is to investigate mechanism that NOX might suppress SOA formation in the respective experiments. The authors distinguished highly oxygenated multifunctional molecules (HOM), that can contribute to SOA yields, at low NOX levels as HOM-PP products (such as ketones, alcohols or hydroperoxides) and HOM accretion product with C>10 and C<20 (HOM-ACC). They attributed the NOX effect on suppression of the SOA mass to the

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Discussion paper

significant decrease of HOM-ACC as NOx increasing. When NOX was added to the reaction system HOM-PP was also decreased but HOM-organic nitrates (HOM-ON) concentrations increased on the cost of HOM-PP. and they find there was no systematic difference in effective uptake coefficients γeff for HOM-ON at high NOx levels and HOM-PP at low NOx levels when they have the same number of O-atoms in the moiety. At the presence of ammonium sulfate seed particles, γeff of HOM with more than 6 O-atoms determined to be > 0.5 in average and for HOM containing more than 8 O-atoms, γeff $\sim$ 1. The finding makes a nice contribution to the literature in this area those have to simplify to estimate the uptake coefficients for particle organic nitrates (e.g. (Fisher et al., 2016; Marais et al., 2016)). I think it is an important and informative piece of work, providing experimental information to help current understanding of SOA formation under relevant atmospheric conditions. The subject of the paper is therefore directly within the ACP remit, and the manuscript is well written and the technical aspects and interpretations are reasonable. I recommend it be published in ACP after the following minor comments are addressed.

General points.

1. The paper concluded with increasing NOX HOM-ACC strongly decreases and consequently suppress SOA formation. While the experiments and analysis appear robust and in agreement with some literature, it is important to point out that some other literature such as Pye et al., (2015) and Marais et al. (2016), with specific representation of particulate organic nitrate predict the reduction in NOx emissions causes a considerable reduction in organic aerosol. Could authors comment on this discrepancy? In this regard, in Figure 2 authors showed HOM spectra with and without NOX addition. It might be worthwhile to mention total SOA or HOM mass for these two cases for easier comparison.

2. Page 11, Line 2 a) The authors estimated a molar yield of $\sim$36% for the ON formed from β –pinene which is higher than the largest previously reported values (26 ± 7% Rindelaub et al., (2016), while for similar condition of this study (acidic seed aerosol

and RH∼ 60%), they even estimated less (∼6%). b) The authors mentioned at the Figure 9's caption "The effect of hydrolysis of 80% of the organic bound nitrate has no substantial effect on the SOA mass." However, Boyd et al. (2015) estimated particle-phase hydrolysis of organic nitrates compose 45–74% of the organic aerosol.

These discrepancies might be attributed to estimation of a slower aerosol hydrolysis in this study? and subsequently underestimation of importance of hydrolysis for explaining the SOA mass suppression with increasing NOX in the system?

3) Page 18, Line 11-24 The authors discussed higher humidity in their chamber and hydrolysis as the key for less estimation of OrgNO3 fraction in the particulate-phase than as determined by AMS and also finding (∼11%) by Zhao et al. (2018). It is important to point out not only Zhao et al. but also many recent measurements (e.g., Romer et al., 2016) and modeling studies (e.g., Pye et al., 2015; Fisher et al., 2016; Zare et al., 2019) estimated a higher fraction of organic nitrates in the particle phase (∼10%-20%). As they also considered a rather fast hydrolysis for organic nitrate aerosols it might be worthwhile to compare the result here to their results as well. However, it might be useful to mention Zare et al. show that at a more humid condition (similar to this study with higher RH) heterogeneous uptake to particle water tends to form less particulate organic nitrates against uptake to dry organic aerosols. Considering the impact of humidity at the aerosol formation together with the impact on the loss process of hydrolysis for particulate organic nitrates could help reconcile the discrepancy?

Minor comments

Page 3, for less confusion and similar to the other relevant papers, it is better to give a same reaction number for reactions with similar reactants, e.g. (R4) and (R4a) should be "(R4a)" and "(R4b)", and also for R5 and R7 should change as "(R5a)" and "(R5b)".

Page 6, Line 1-4, multiplication sign for reaction rates are missed.

Page 6, Line 2, References should be lined up in the proper sequence.

Page 13, Line 13, remove spare space before parentheses.

Page 15, Line 1-4, remove redundant parentheses.

Page 15, Line 21, remove extra “was”

Page 15, line 24, “estimated to be”

Page 32, Figure1, for better readability write axis label on the right-hand side from down to up, similar to the left-hand side of the figure.

Page 37, Line4, the brown bars look like more “orangeish” than brown in my eyes.

Page 40, Line 5-6 used different font.

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