

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.

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We thank referee#2 for the helpful comments. Please, find our responses in the pdf-file attached. Please, see new Table 1 and new Figures 3 below.

Please also note the supplement to this comment:

<https://www.atmos-chem-phys-discuss.net/acp-2019-1168/acp-2019-1168-AC5-supplement.pdf>

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Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2019-1168>, 2020.

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Tables

Table 1: Overview of α -pinene and β -pinene experiments

| Experiment Description | [VOC] ₀ ^a [ppb] | [NO _x] ₀ ^a & ([NO _x] _{ss}) ^b [ppb] | [O ₃] _{ss} ^c [ppb] | [OH] _{ss} ^d [10 ⁻⁶ cm ³ s ⁻¹] |
|---|---|--|---|--|
| 1. Gas-phase yield of ON and gas-phase OrgNO ₂ (Section 3.1) | β -pinene 39→0 m-xylene 3.7 | 50 (20→30) | 19→30 | 2.3±20% |
| 2. Formation of HOM-ON (Section 3.3) | α -pinene 16.5 β -pinene 37 | 0.3 / 7.5 / 15.3 ^e / 26.7 / 39.7 / 45.5 (0.3 / 1.8 / 3.7 ^f / 5.7 / 8.7 / 10.4) / 52.9 / 59.1 / 83.3 / 137.8 (/ 12.4 / 15.8 / 26.8 / 72.2) | 62-152 | 4.5-7.5 Not determined Not determined |
| 3. Effective uptake coefficients* (Section 3.4) | α -pinene 12.5 β -pinene 37 | 0.3 (0.3) 30 (4) | 29 49 | 9.2±20% 8.8±20% |
| 4. OrgNO ₂ in SOA (Section 3.5) | α -pinene 46 β -pinene 38 | 0.3 / 32.0 / 51.0 / 60.0 (0.3 / 10.4 / 17.5 / 19.5) 0.3 / 6.7 / 13.4 / 32.9 / 54.8 / 103 (0.3 / 5.1 / 9.5 / 21.7 / 35.5 / 45.7) | 37-62 44-53 | 4.7-7.7 0.9-3.7 |

^a subscript 0 refers to mixing ratio in the inlet
^b subscript ss refers to mixing ratio in steady state
^c average of two experiments at [NO_x]₀ of 15 and 15.5 ppb ([NO_x]_{ss} of 3.6 and 3.75 ppb)
^d in presence of ammonium sulfate seed aerosols

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Fig. 1.

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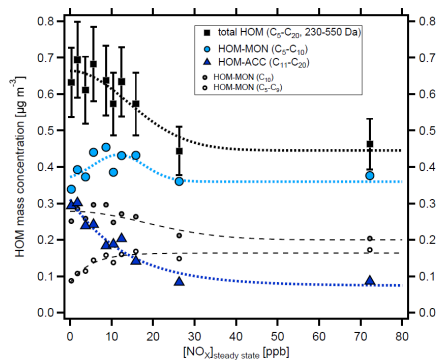


Figure 3. Mass concentration of HOM products in dependence on [NO_x]_{ss} in α -pinene photo-oxidation experiments. C₇-C₂₀ compounds with molecular masses 230-550 Da were added up for total HOM (black squares) and divided into HOM monomers (light blue circles) and HOM accretion products (blue triangles). The analysis is based on the assigned peaks (>90% of the total signal) and the sensitivity of $3.7 \cdot 10^{10}$ molecules cm⁻³ m³ (suppl. section I.2). HOM accretion products decrease with increasing [NO_x]_{ss} at the lowest and highest NO_x levels of 0.3 ppb and 72 ppb. HOM-ACC contribute 0.3 $\mu\text{g m}^{-3}$ and 0.09 $\mu\text{g m}^{-3}$, respectively, to total HOM, whereas HOM monomers contribute about 0.4 $\mu\text{g m}^{-3}$ over the whole range. More than 70% of HOM-ACC were suppressed at the highest [NO_x]_{ss} while HOM monomers remained about constant. The increasing importance of alkoxy radicals with increasing [NO_x]_{ss} is indicated by the small circles: C₇₋₈ compounds (small open circles) arise in large parts from fragmentation of alkoxy radicals. They double from ≈ 0.9 to $\approx 1.8 \mu\text{g m}^{-3}$ at the highest [NO_x]_{ss}, whereas the C₁₀ compounds (grey circles) drop by only about 30%. C₇₋₈ compounds must carry at least 7 O-atoms because the lower end of the mass range is set to 230 Da which is the molecular mass of C₇H₁₄O₄. Assuming that compounds in the selected mass range will contribute to SOA formation, the lower SOA yields at high [NO_x]_{ss} was due to the suppression of accretion products and increasing fragmentation via the alkoxy path played a minor role. Dashed and dotted lines save to guide the eye and have no further meaning. Concentrations were corrected as described in supplement section SI.2. Turnover ranged from $8.7 \cdot 10^5 \text{ cm}^{-3} \text{ s}^{-1}$ and $1.04 \cdot 10^6 \text{ cm}^{-3} \text{ s}^{-1}$ leading to correction factors in a range of 1.1 - 0.8. The correction factors were close to one thus did not add much uncertainty. Observed particle surface ranged from $\sim 10^6 \text{ m}^2 \text{ m}^{-3}$ to $6 \cdot 10^7 \text{ m}^2 \text{ m}^{-3}$ resulting in correction factors between 1.0 and 1.45 with the highest correction factors at lower [NO_x]_{ss} where new particle formation could not be suppressed.

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Fig. 2.

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