Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2019-1168-AC4, 2020

Atmospheric Chemistry and Physics Discussions

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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Received and published: 15 May 2020

We thank referee#1 for the helpful comments. Please, find our responses in the pdf-file attached. Please, see new Figures 3 & 4 below.

Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2019-1168/acp-2019-1168-AC4-supplement.pdf

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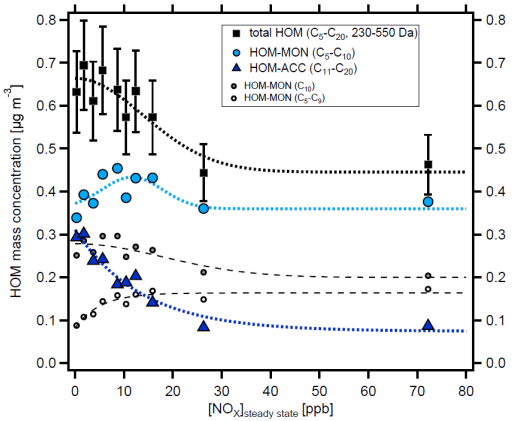

Figure 3. Mass concentration of HOM products in dependence on $[NO_X]_{SS}$ in α-pinene photo-oxidation experiments. C_5-C_{20} compounds with molecular masses 230-550 Da were added up for total HOM (black squares) and divided into HOM monomers (light blue circles) and HOM accretion products (blue triangles). The analysis is based on the assigned peaks (>90% of the total signal) and the sensitivity of 3.7×10^{10} molecules cm^{-3} nc^{-1} (suppl. section 1.2). 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 µg m^{-3} and 0.09 µg m^{-3}, respectively, to total HOM, whereas HOM monomers contribute about 0.4 µg m^{-3} over the whole range. More than 70% of HOM-ACC were suppressed at the highest $[NO_X]$ while HOM monomers remained about constant. The increasing importance of alkoxy radicals with increasing $[NO_X]_{SS}$ is indicated by the small circles: $C_{5\text{-}9}$ compounds (small open circles) arise in large parts from fragmentation of alkoxy radicals. They double from ≈0.9 to ≈1.8 µg m^{-3} at the highest $[NO_X]_{SS}$, whereas the C_{10} compounds (grey circles) drop by only about 30%. $C_{5\text{-}9}$ 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 $C_{10}H_{14}O_6$. Assuming that compounds in the selected mass range will contribute to SOA formation, the lower SOA yields at high $[NO_X]$ 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 S1.2. Turnover ranged from 8.7×10^{7} $cm^{-3}s^{-1}$ and 1.04×10^{8} $cm^{-3}s^{-1}$ 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 ~10^{-4} m^2m^{-3} to 6×10^{-5} m^2 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.

Fig. 1.

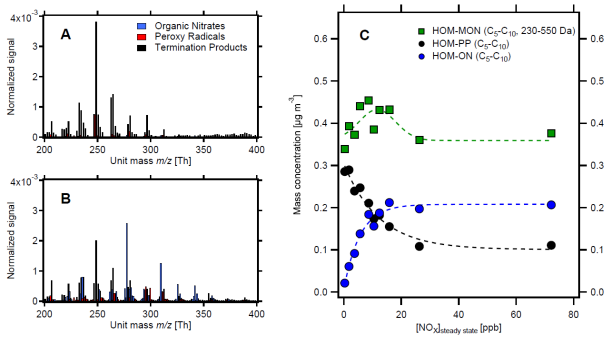

Figure 4: HOM pattern from α-pinene photo-oxidation at two NO_X levels in the monomer range. Panel A: low NO_X conditions ($[\alpha\text{-pinene}]_{SS}$ = 1.7 ppb, $[NOX]_{SS}$ = 0.3 ppb), Panel B: high NO_X conditions ($[\alpha\text{-pinene}]_{SS}$ = 1.0 ppb, $[NOX]_{SS}$ = 8.7 ppb). Black bars: HOM-PP termination products of reactions R3 and R4a. Blue bars: HOM-ON (organic nitrates). Red bars = HOM-RO_2 (peroxy radicals). The signals were normalized to the sum over all detected ions. Panel C: Mass concentrations of HOM monomers (green) in the molecular mass range 230-550 Da. HOM-ON (blue) are increasing with increasing $[NO_X]_{SS}$, HOM-PP (black) are decreasing, while the sum of all HOM-monomers remains about the same. At about 10 ppb $[NO_X]_{SS}$ HOM-ON make up half of the HOM monomers and at 26 ppb $[NO_X]_{SS}$ they make up about 50% of the total HOM (shown in Figure 3).

Fig. 2.

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