

The effect of NO_x on formation of Highly Oxidized Multifunctional Molecules and SOA in photochemical systems of α-pinene and β-pinene

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Pullinen et al., ACP, 2020, under revision,
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Overview

1. Motivation
2. Experiment
3. Result
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5. Summary
6. Figure captions for complex plots

1. Motivation

Sarrafzadeh et al., 2016:

SOA yield of β -pinene depend only moderately on $[\text{NO}_x]$,
if performed at otherwise same conditions

- OH concentration
- no nucleation
- seed surface

e.g. Ehn et al., 2014, Tröstl et al., 2016, Peräkylä et al., 2019

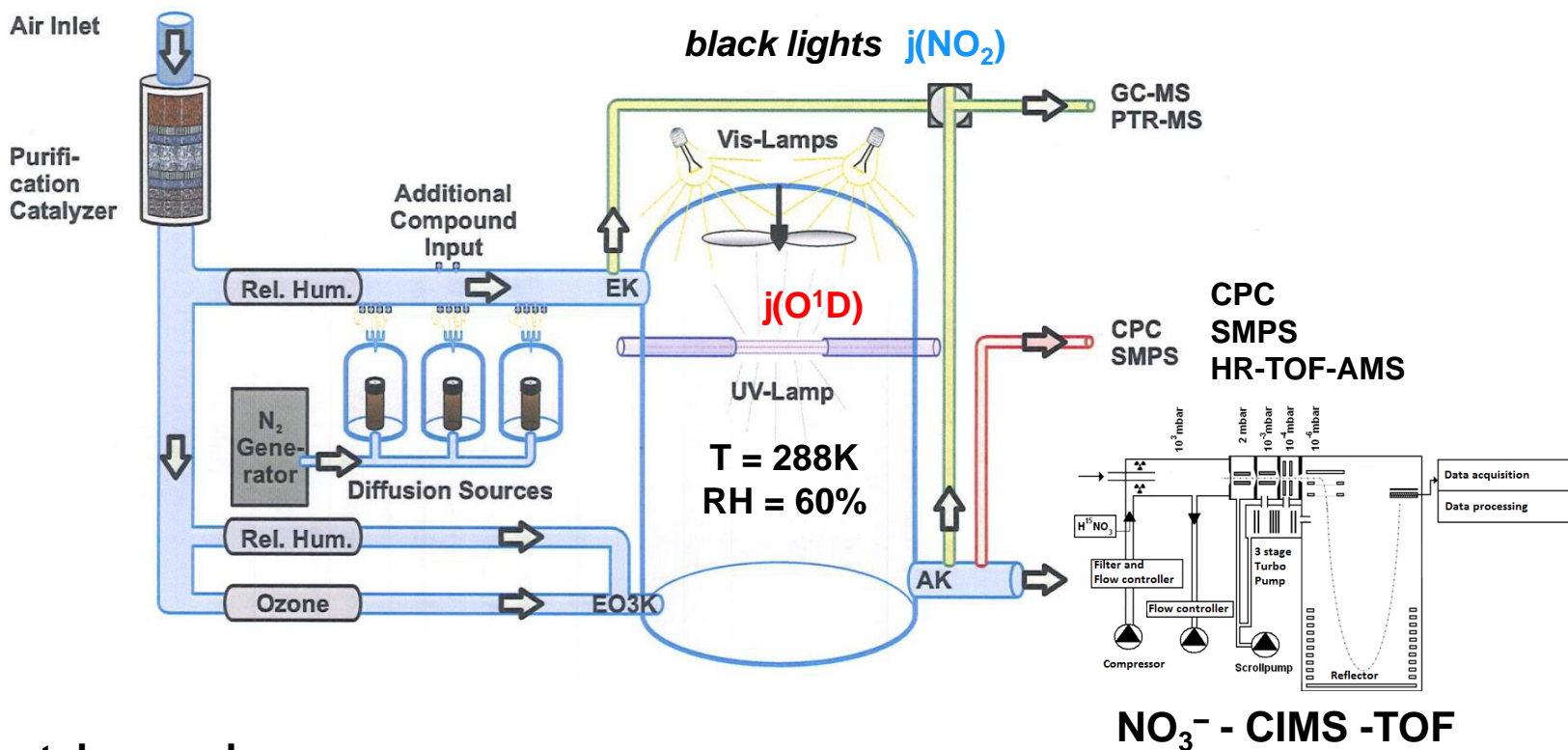
Highly oxynated organic molecules (HOM) are LVOC, ELVOC
HOM should make up a significant portion of SOA

e.g. Takeuchi et al., 2019

Organic nitrates contribute several 10% mass to SOA

Question: HOM organic nitrates (HOM-ON) ?

2. Experiment: Jülich Plant Atmosphere Chamber



Experimental procedure

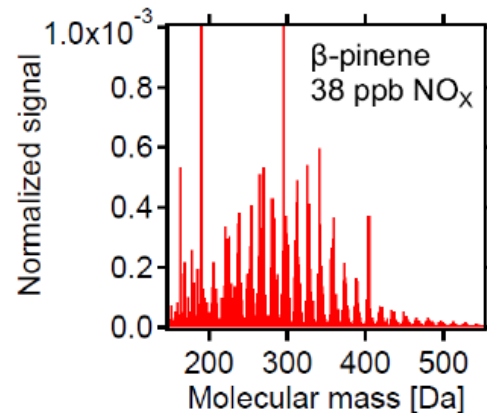
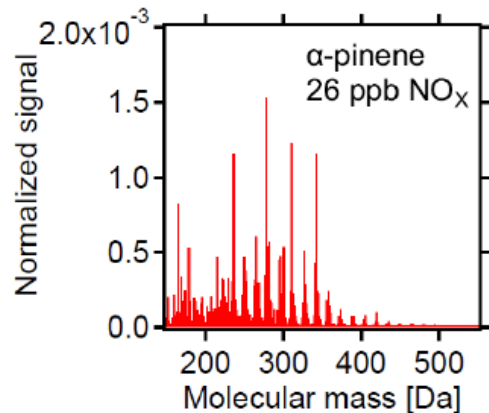
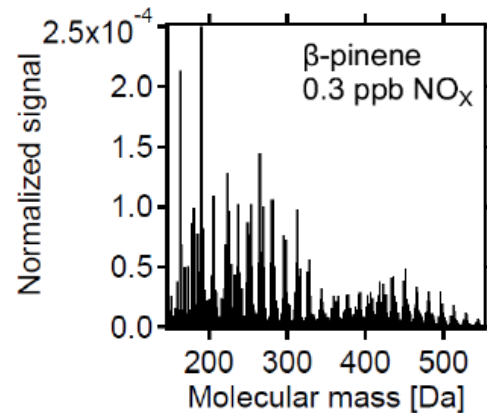
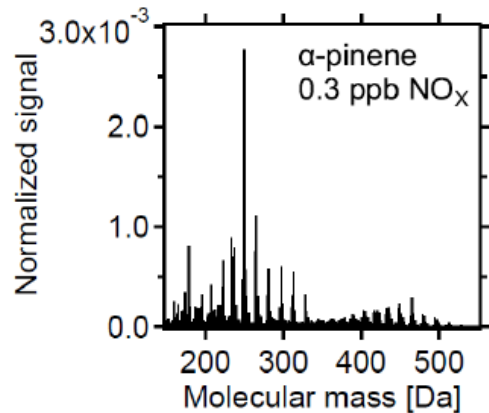
- Continuously stirred tank reactor (1450 L)
- Bring system into steady state
- **UV on**: photolyze O₃ and produce OH, range 0.1 - 8·10⁷ cm⁻³
- add NO_x
- black lights on: photolyze NO₂ → NO (0.3-100 ppb)

Chemical ionization mass spectrometry

- reagent ion: **NO₃⁻**
- Ionization source: Am 241
- Detection limit: sub-ppt level

Selective for Highly oxidized molecule

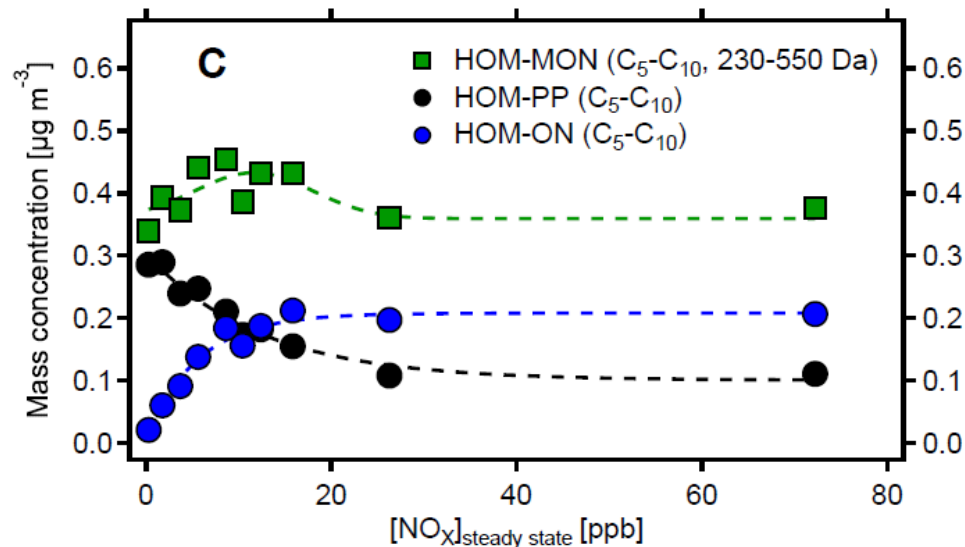
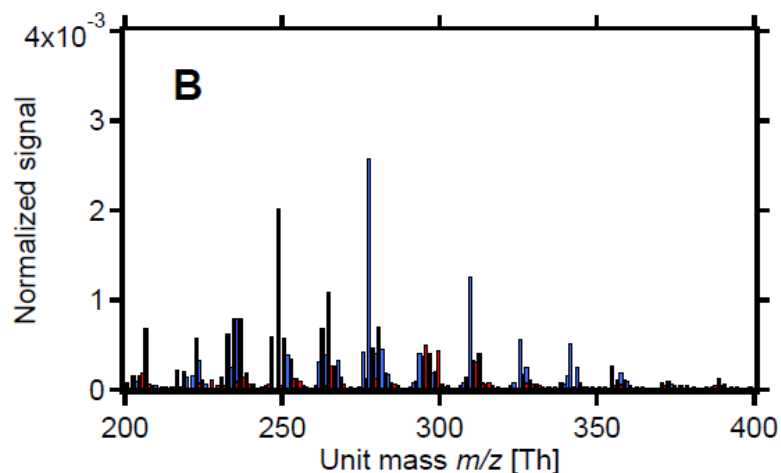
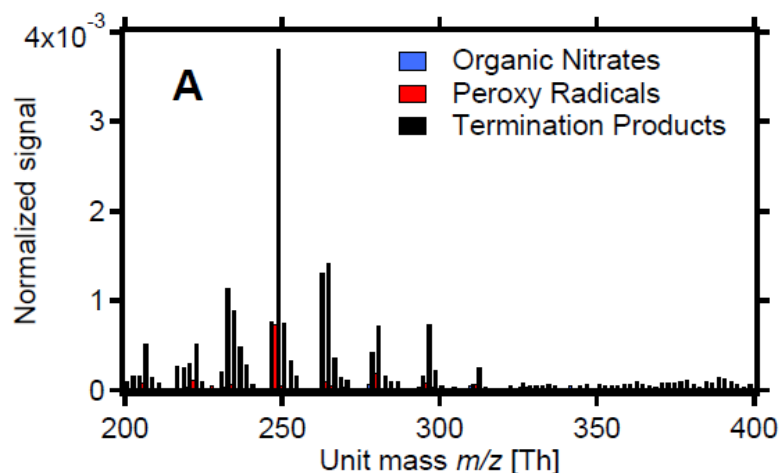
3.1 Result CIMS: HOM monomers & HOM accretion products



1. $\text{RO}_2 + \text{RO}_2 \rightarrow \text{HOM-PP}$
peroxy-peroxy products
2. $\text{RO}_2 + \text{RO}_2 \rightarrow \text{HOM-ACC}$
accretion products
3. $\text{RO}_2 + \text{NO/NO}_2 \rightarrow \text{HOM-ON}$
organic nitrates

- Accretion product intensity in range 420-550 Da decreased strongly
- Less and smaller accretion products ($\text{C}_{<20}$)
- Monomers shifted to higher molecular mass

3.2 Result CIMS: HOM-ON increase with $[\text{NO}_x]_{\text{ss}}$



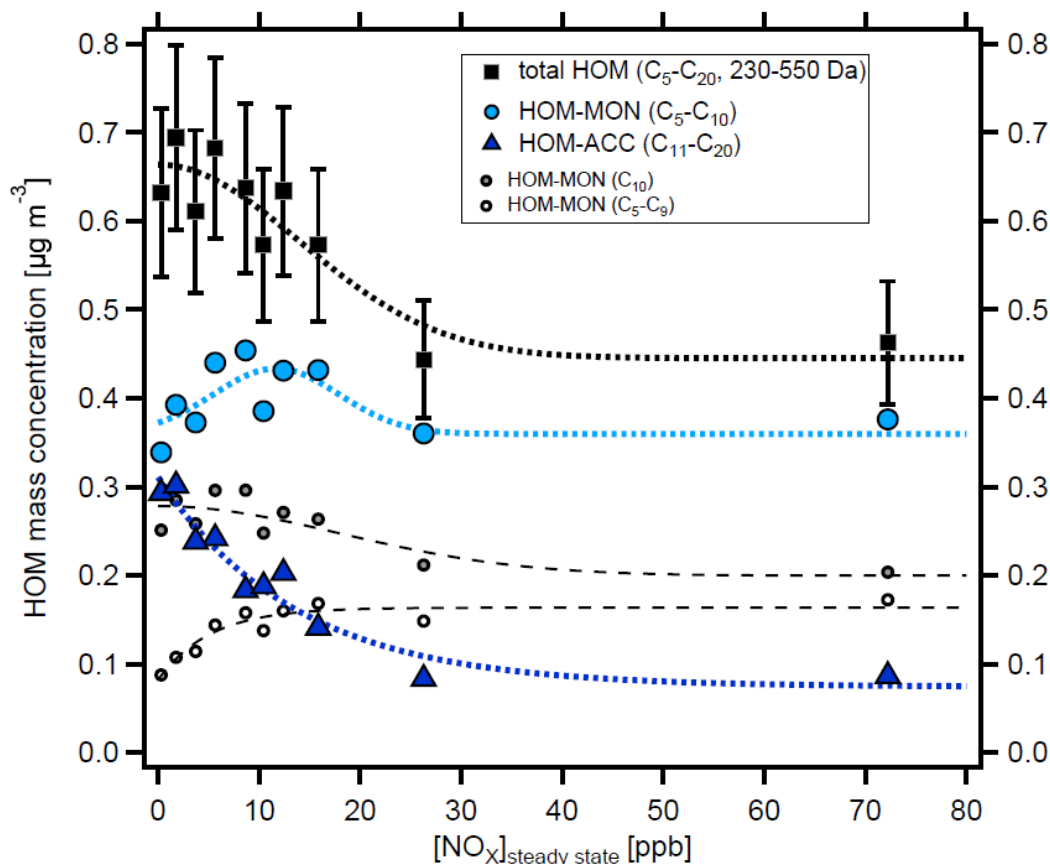
Reactions:

$\text{RO}_2 + \text{HO}_2$, $\text{RO}_2 + \text{RO}_2 \rightarrow \text{HOM-PP}$
(Peroxy-Peroxy termination products)



$\text{RO}_2 + \text{NO}$, $\text{RO}_2 + \text{NO}_2 \rightarrow \text{HOM-ON}$
(Organic Nitrates)

3.3 Result CIMS: HOM-ACC decrease with $[\text{NOX}]_{\text{ss}}$



Analysis in range 230-550 Da:

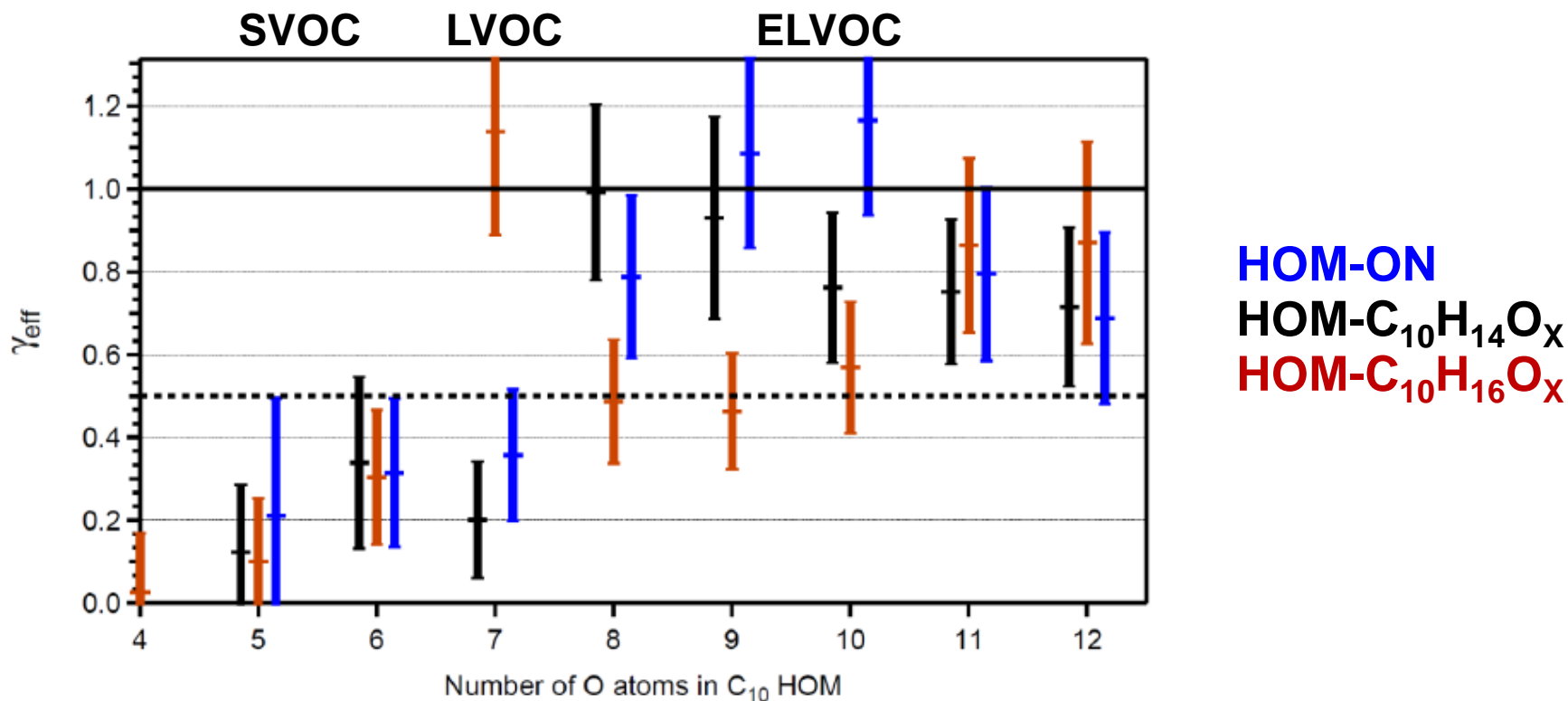
- accretion products (HOM-ACC, C_{11-20}) decrease with $[\text{NOX}]_{\text{ss}}$
- HOM-monomers remain about the same
- HOM with C_{10} decrease, while HOM with $\text{C}_{<10}$ increase with $[\text{NOX}]_{\text{ss}}$
- HOM with $\text{C}_{<10}$ are still highly functionalized as molecular mass $230 \text{ Da} \equiv \text{C}_{10}\text{H}_{14}\text{O}_6$

⇒ fragmentation via alkoxy radicals

⇒ suppression of HOM-ACC, reduction of total HOM mass

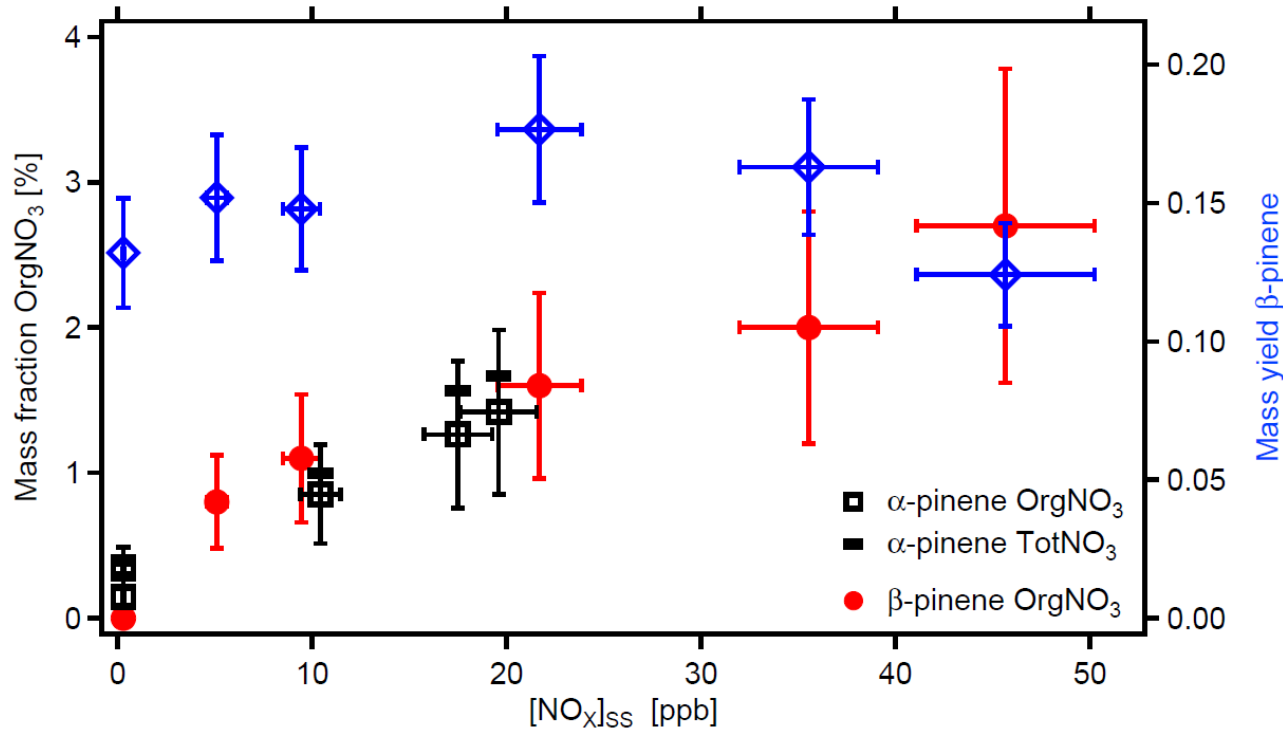
Effect on SOA formation ???

3.4 Result: HOM with $O_{>6}$ are LVOC or ELVOC



- Here: effective uptake coefficient γ_{eff} of 1 \Rightarrow no re-evaporation
 - HOM arising from same HOM-RO₂ have „similar“ vapor pressures
- \Rightarrow termination group in highly functionalized HOM doesn't matter so much
- \Rightarrow HOM with molecular mass >230 Da contribute „fully“ to SOA

4.1 Discussion: SOA yield and organic bound nitrate OrgNO₃

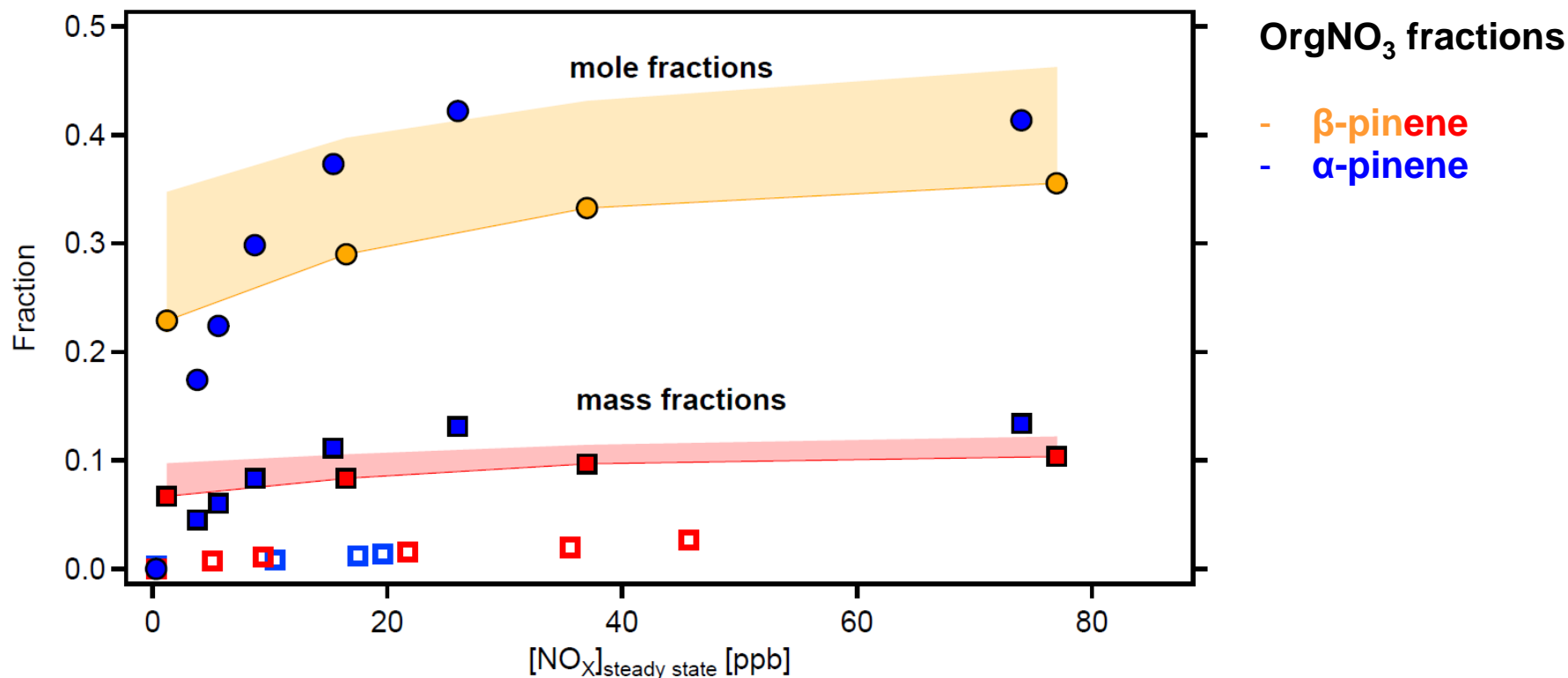


Diagnostic particles:

- OrgNO₃ determined by Aerosol Mass spectr. (HR-AMS)
- β -pinene SOA yield only moderately dependent on $[\text{NO}_x]_{\text{ss}}$

- mass fractions of OrgNO₃: a few %
- inorganic NO₃⁻ not important

4.2 Discussion: OrgNO₃ in HOM-ON(g) and particles



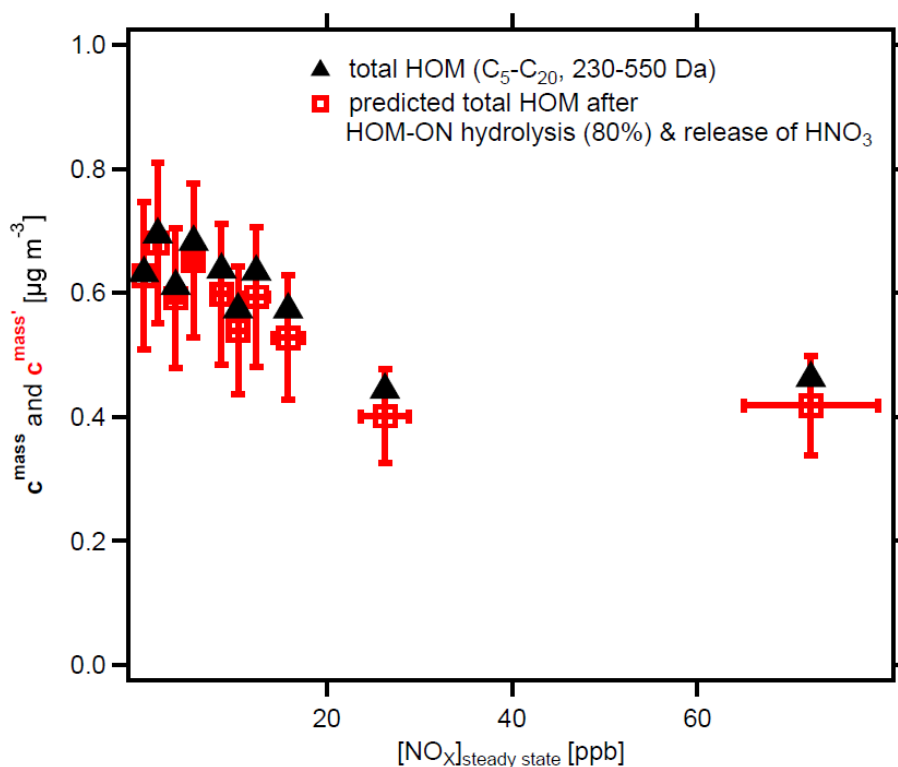
circles: expected molec. fractions of ON = gas-phase HOM-ON with $\gamma_{\text{eff}} \approx 1$

filled squares: expected OrgNO₃ from gas-phase HOM-ON with $\gamma_{\text{eff}} \approx 1$

open squares: measured OrgNO₃

discrepancy by a factor of 3 \Rightarrow hydrolysis of HOM-ON ?

4.3 Discussion: hydrolysis OrgNO₃ and SOA yield



Missing OrgNO₃ in particles:

If HOM-ON hydrolyse and evaporate

⇒ low OrgNO₃



⇒ strong decrease of SOA yield



If HOM-ON hydrolyse and only HNO₃ evaporates

⇒ low OrgNO₃



⇒ small effect on SOA yield



⇒ since HOM-ON are highly functionalized, likely only HNO₃ escapes the particulate phase; organic moiety remains, probably with –OH group formed (compare, Browne et al. 2013, Boyd et al. 2015, Takeuchi et al. 2019)

5. Summary: Effect of increasing $[\text{NO}_x]$

- a. Monomer HOM pattern change; carbonyls, hydroperoxide, alcohols etc.
→ organic nitrates (HOM-ON), HOM-ON are LVOC and ELVOC ($\gamma_{\text{eff}} \approx 1$)
=> *not much effect on SOA yield*
- b. Hydrolysis may reduce organic bound nitrate (OrgNO_3), but HOM organic moiety likely stays in the particulate phase
=> *not much effect on SOA yield*
- c. Fragmentation via alkoxy radicals increases, resulting in increase of $\text{C}_{<10}$ compounds
=> *minor effect on SOA, since $\text{C}_{<10}$ are still highly functionalized*
- d. Suppression of accretion products HOM-ACC.
 - Reduced chance for SVOC to form accretion products and to contribute to SOA formation.
 - Smaller accretion products, due to influence of alkoxy-induced fragmentation
→ higher vapor pressures
=> *major effect on reduction of SOA yield at highest $[\text{NO}_x]$*

6. Figure captions for complex plots

Slide 4: HOM spectra from photo-oxidation of α -pinene (left panels) and β -pinene (right panels) without NO_x addition (upper panels) and with NO_x addition (lower panels). NO_x concentrations in the α -pinene and β -pinene experiment were 26 ppb and 38 ppb, respectively. Background NO_x was 0.3ppb.

Slide 5: Figure 4: HOM pattern from α -pinene photo-oxidation at two NO_x levels in the monomer range. Panel A: low NO_x conditions ($[\alpha\text{-pinene}]_{\text{SS}} = 1.7$ ppb, $[\text{NO}_x]_{\text{SS}} = 0.3$ ppb), Panel B: high NO_x conditions ($[\alpha\text{-pinene}]_{\text{SS}} = 1.0$ ppb, $[\text{NO}_x]_{\text{SS}} = 8.7$ ppb). Black bars: HOM-PP termination products of reactions R3 and R4a. Blue bars: HOM-ON (organic nitrates). Red bars = HOM-RO₂ (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 $[\text{NO}_x]_{\text{SS}}$, HOM-PP (black) are decreasing, while the sum of all HOM-monomers remains about the same. At about 10 ppb $[\text{NO}_x]_{\text{SS}}$ HOM-ON make up half of the HOM monomers and at 26 ppb $[\text{NO}_x]_{\text{SS}}$ they make up about 50% of the total HOM (shown in slide 5).

Slide 6: Mass concentration of HOM products, C₅-C₂₀, with molecular masses from 230 to 550 Da (black squares), HOM monomers (light blue circles) and HOM accretion products (blue triangles) in dependence on $[\text{NO}_x]$ in an α -pinene photo-oxidation experiment). We were able to assign molecular formulas to more than 90% of the signal and the analysis is based on the assigned peaks (supplement, Table S1) applying the sensitivity of 3.7×10^{10} molecules cm⁻³ nc⁻¹. HOM accretion products decrease with increasing $[\text{NO}_x]$: 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 whereas HOM monomers remained about constant. The increasing importance of alkoxy radicals in the same molecular mass range (230 to 550 Da) with increasing $[\text{NO}_x]$ is indicated by the small circles: C₅₋₉ compounds (small open circles), which arise in large parts from fragmentation of alkoxy radicals, double from ≈ 0.9 to ≈ 1.8 $\mu\text{g m}^{-3}$ at the highest $[\text{NO}_x]_{\text{SS}}$, whereas the C₁₀ compounds (grey circles) drop by only about 30%. C₅₋₉ compounds must carry at least 7 O-atoms since the lower limit of the chosen mass range of 230 Da is the molecular mass of a C₁₀H₁₄O₆ compound. Assuming that compounds in the given mass range will contribute to SOA formation, the expected major contribution to lower SOA yields arises from the suppression of accretion products and not so much from increasing fragmentation via the alkoxy path. Dashed and dotted lines serve to guide the eye and have no further meaning. Concentrations were corrected due to turnover and particle surface. Turnover ranged from 8.7×10^7 cm⁻³s⁻¹ and 1.04×10^8 cm⁻³s⁻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 $\sim 10^{-6}$ m²m⁻³ to 6×10^{-5} m²m⁻³ resulting in correction factors between 1.0 and 1.45 with the highest correction factors at lower NO_x where new particle formation could not be suppressed.

6. Figure captions for complex plots (ctd.)

Slide 7: Effective uptake coefficients γ_{eff} for HOM-PP ($\text{C}_{10}\text{H}_{14}\text{O}_x$ black bars, $\text{C}_{10}\text{H}_{16}\text{O}_x$, brown bars) and HOM-ON ($\text{C}_{10}\text{H}_{15}\text{O}_x\text{NO}_2$, blue bars) in dependence of the number of O atoms in the respective HOM. HOM with different numbers of C, H, and O atoms, e.g. $\text{C}_{10}\text{H}_y\text{O}_x$ and $\text{C}_9\text{H}_{y-4}\text{O}_{x+1}$ HOM-PP, are treated together and the number of O-atoms is given for the C_{10} -HOM-PP. The second component, C_9 -HOM-PP, has one O atom more. Data were taken from β -pinene photo-oxidation experiment with $[\beta\text{-pinene}]_{\text{SS}} \sim 10$ ppb, $[\text{NO}_x]_{\text{SS}} \sim 4$ ppb. The signal intensity for the $\text{C}_{10}\text{H}_{14}\text{O}_4$ and HOM-ON with 4 O-atoms was too low to allow reliable determination of γ_{eff} and the respective data is left out. Uncertainties in γ_{eff} arise from the determination procedure as shown in slide 6. The black line indicates $\gamma_{\text{eff}} = 1$ and 0.5. An average Fuchs-Sutugin correction factor of 0.70 ($d_p = 175\text{nm}$) was applied to calculate γ_{eff} .

Slide 8: Mass fraction of organic bound nitrate (OrgNO_3) in SOA in dependence of $[\text{NO}_x]_{\text{SS}}$ (left y-axis). Black squares and red circles show data measured from α -pinene and β -pinene, respectively. Yields of SOA mass formation during the respective experiment are shown at the example of β -pinene (blue diamonds). The data are corrected for wall losses of HOM. In absence of OH, $[\alpha\text{-pinene}]_0$ was around 46 ppb, $[\beta\text{-pinene}]_0$ was around 37 ppb. NO_x was added at different amounts with $[\text{NO}_x]_0$ up to 103 ppb. Due to losses in reactions with OH and formation of organic nitrates, $[\text{NO}_x]$ decreased to the $[\text{NO}_x]_{\text{SS}}$ levels shown here. Uncertainties in NO_x data are estimated to $\pm 10\%$, uncertainties in SOA masses to $\pm 10\%$, and uncertainties in the content of OrgNO_3 are estimated to $\pm 40\%$. The black bars indicate the fraction of total nitrate (TotNO_3 , left scale) for the example of α -pinene, which is dominated by organic nitrate.

Slide 9: Molecular fractions of organic bound nitrate (OrgNO_3 , filled spheres) and mass fractions of OrgNO_3 (squares) as a function of $[\text{NO}_x]_{\text{SS}}$. Data from α -pinene (blue symbols) and β -pinene (orange and red symbols and areas). *Molecular fraction* of OrgNO_3 and HOM-ON are the same by definition. The mass fraction of OrgNO_3 in the gas-phase HOM is significantly higher than in the particulate phase as determined by AMS (open blue and red squares). The areas in orange and red give the potential error for β -pinene due to unresolved progressions and overlap of organic nitrates with peroxy radicals

Slide 10: Mass concentrations of total HOM ($\text{C}_5\text{-C}_{20}$) with molar masses between 230 to 550 Da. Black triangles show mass concentrations c^{mass} as determined. Red squares show $c^{\text{mass'}}$ i.e. the resulting SOA mass after considering OrgNO_3 loss by hydrolysis. $[\alpha\text{-pinene}]_{\text{SS}} = 0.9$ to 2.2 ppb, $[\text{NO}_x]_0$ up to 125 ppb, $[\text{NO}_x]_{\text{SS}} = 0.3$ to 74 ppb. The effect of hydrolysis of 80% of the organic bound nitrate has no substantial effect on the SOA mass. Analysis is based on assigned molecular formulas ($>90\%$ of the total signal) applying the sensitivity of 3.7×10^{10} molecules $\text{cm}^{-3} \text{nc}^{-1}$.