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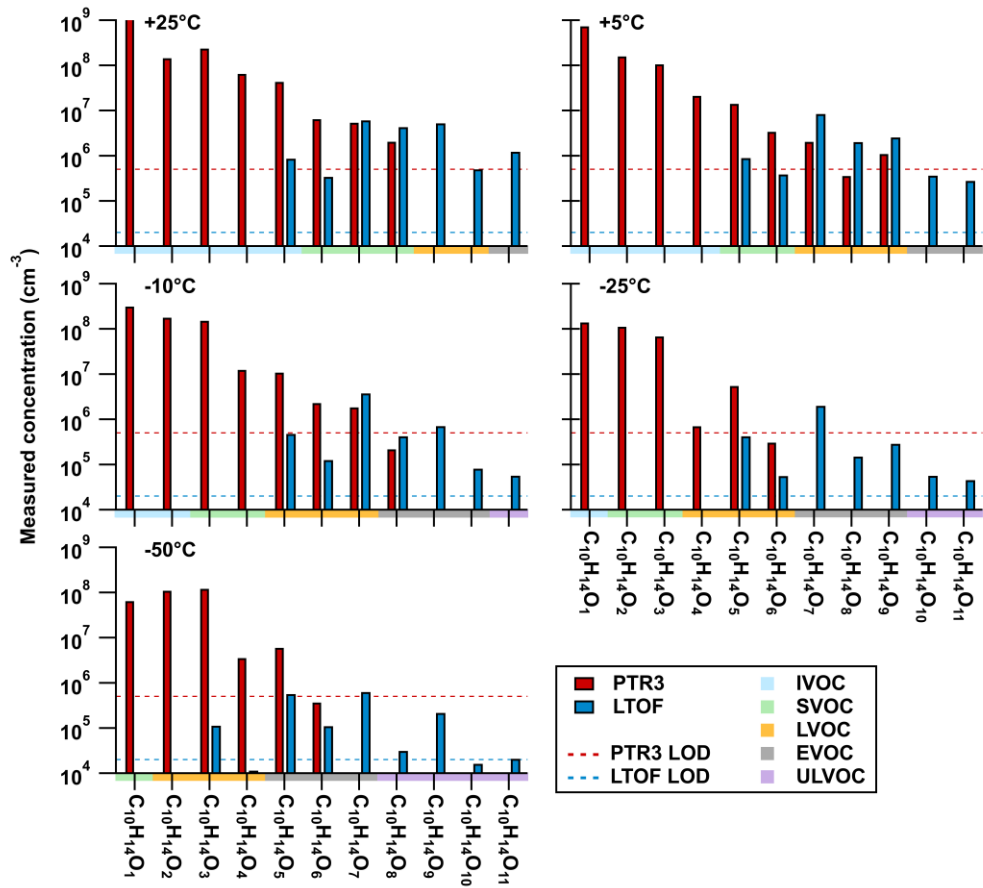
Supplement of

Molecular understanding of new-particle formation from α -pinene between -50 and $+25$ °C

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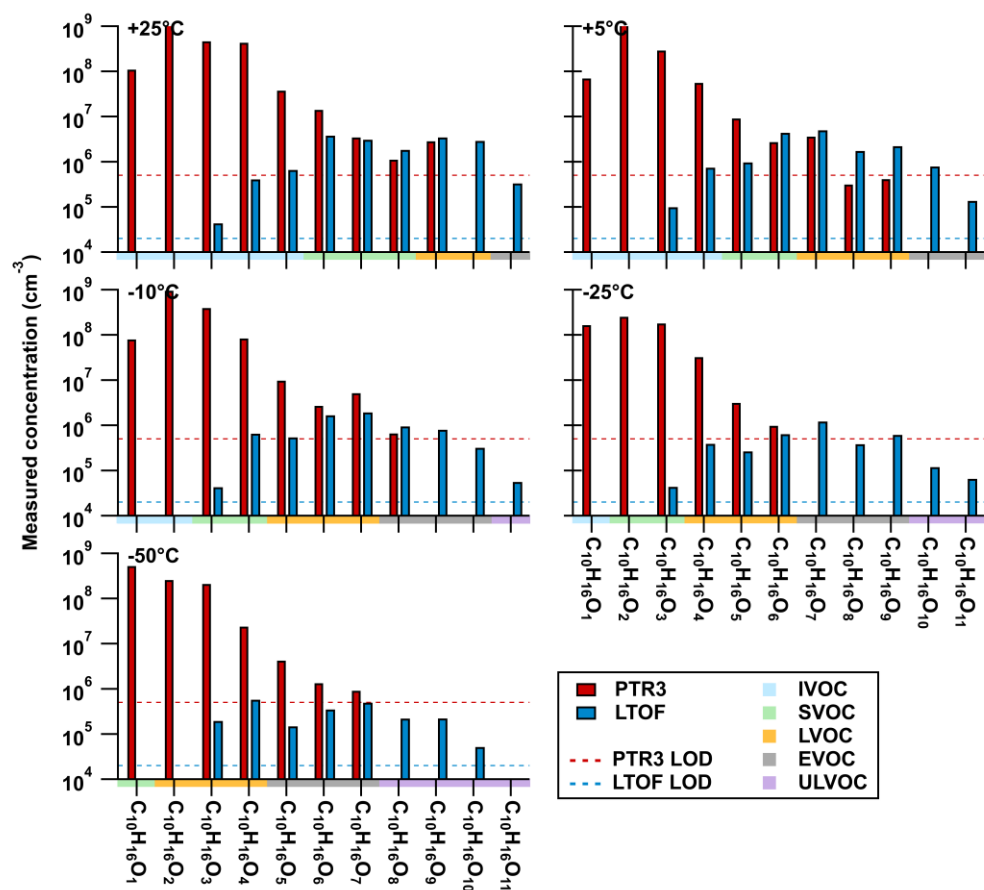


Figure S1: Distribution of α -pinene oxidation products at different temperatures.

Quantitative comparison of α -pinene oxidation products measured by the PTR3 instrument (red) and the nitrate CI-API-TOF (blue) at similar α -pinene oxidation rates. The dashed lines indicate the instrumental LOD for each instrument. The shading of the bottom axes illustrates the corresponding volatility class for each molecule at the given temperature. The PTR3 instrument is capable to measure the lower oxidation states of the oxidation products, while the nitrate CI-API-TOF is quantitative within the range of higher oxidation states. Both instruments show a good correlation in the O/C range of 0.6 to 0.7. Due to the intense drop in volatility with temperature even low oxidized products are able to nucleate and the PTR3 instrument needs to be included to represent a qualitative evaluation of the nucleating material.

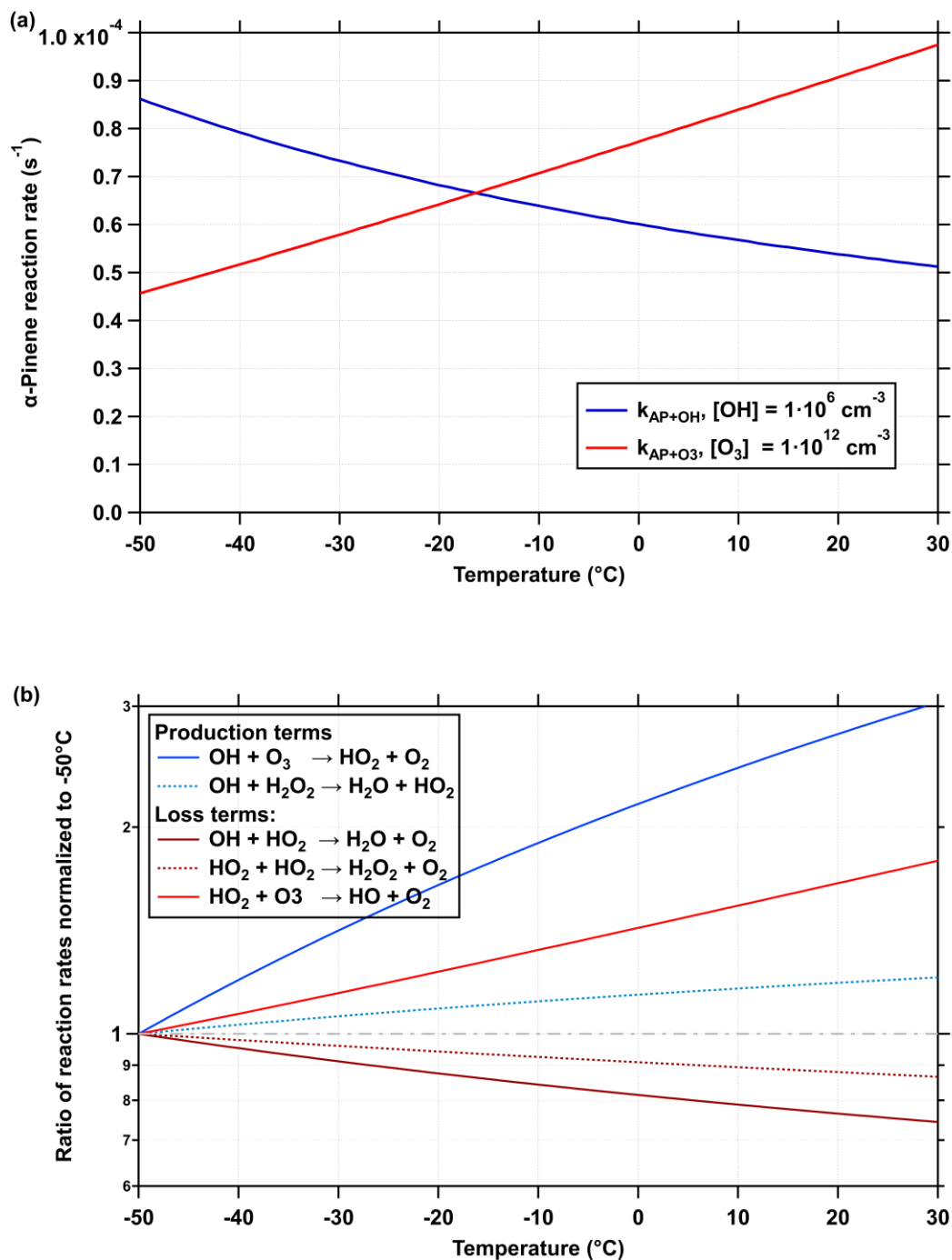


Figure S2: Reaction rate of the α -pinene ozonolysis and OH^{\bullet} oxidation and normalized reaction rates of HO_2^{\bullet} as function of different temperatures.

(a) The temperature dependence of the α -pinene ozonolysis rate (red curve) at typical O_3 mixing ratios of 40 ppb_v compared to the oxidation rate by OH^{\bullet} radicals (blue curve) at typical experimental $[OH^{\bullet}] \sim 1e6 \text{ cm}^{-3}$. The OH^{\bullet} oxidation rate is reciprocal with temperature and results in around twice the rate of the ozonolysis at -50 $^{\circ}C$ for the given experimental concentrations. This ratio is almost reversed for experiments at 25 $^{\circ}C$. (b) Temperature dependence of the main

production (green) and loss (red) terms of HO_2^\bullet reaction in the CLOUD chamber normalized to the reaction rate at -50°C . Both production terms show an increase with increasing in temperature, while only one loss term show a positive and the rest a negative temperature dependence. This will result in sum to a higher mean HO_2^\bullet concentration at higher temperatures.

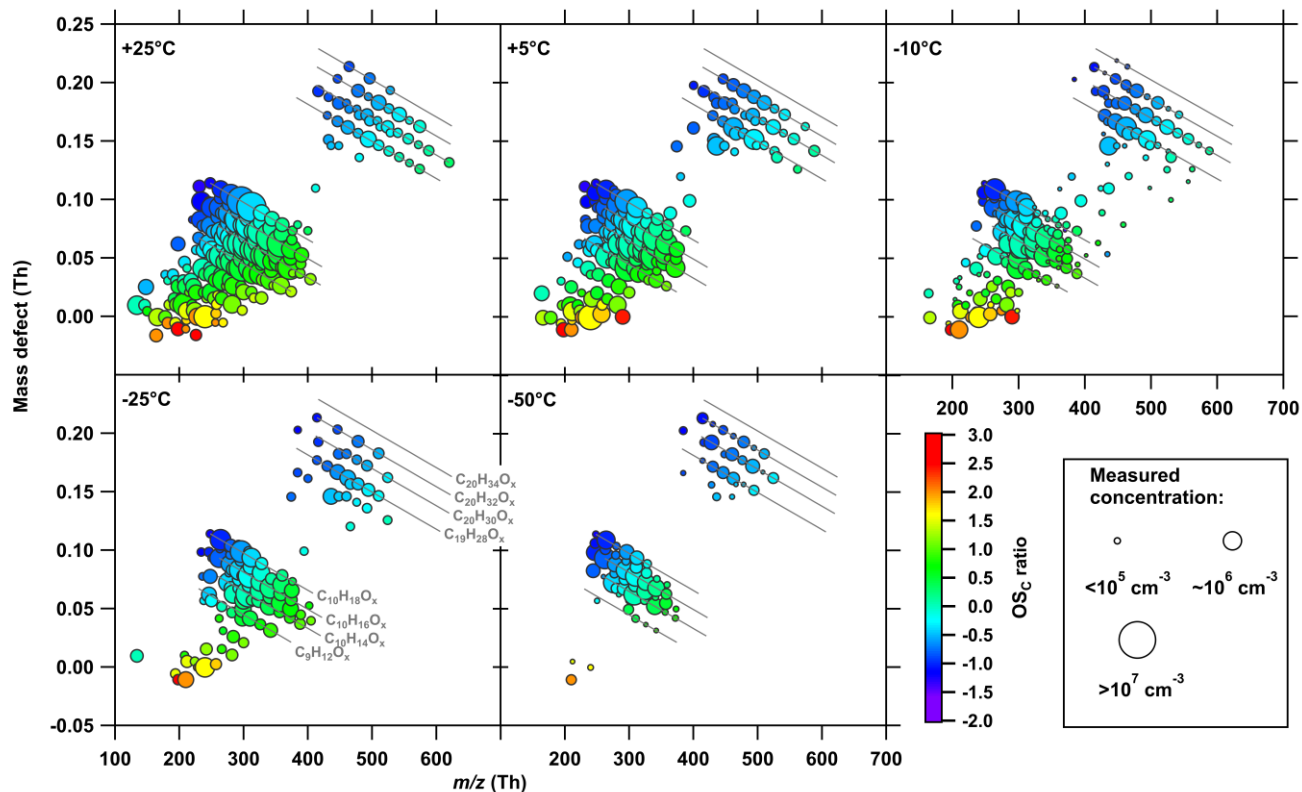


Figure S3: Illustration of the oxidation states of the HOMs based on their mass-defect at five different temperatures.

The experimental data is consistent to the Figures shown in the main text. For every temperature an approximately similar oxidation rates ($2 - 3 \cdot 10^6 \text{ molecule} \cdot \text{cm}^{-3} \cdot \text{s}^{-1}$) is used. The data represent an average of a constant steady-state concentration of about one hour. The color-coding shows the oxidation state of carbon (OS_C) of each individual detected molecule.

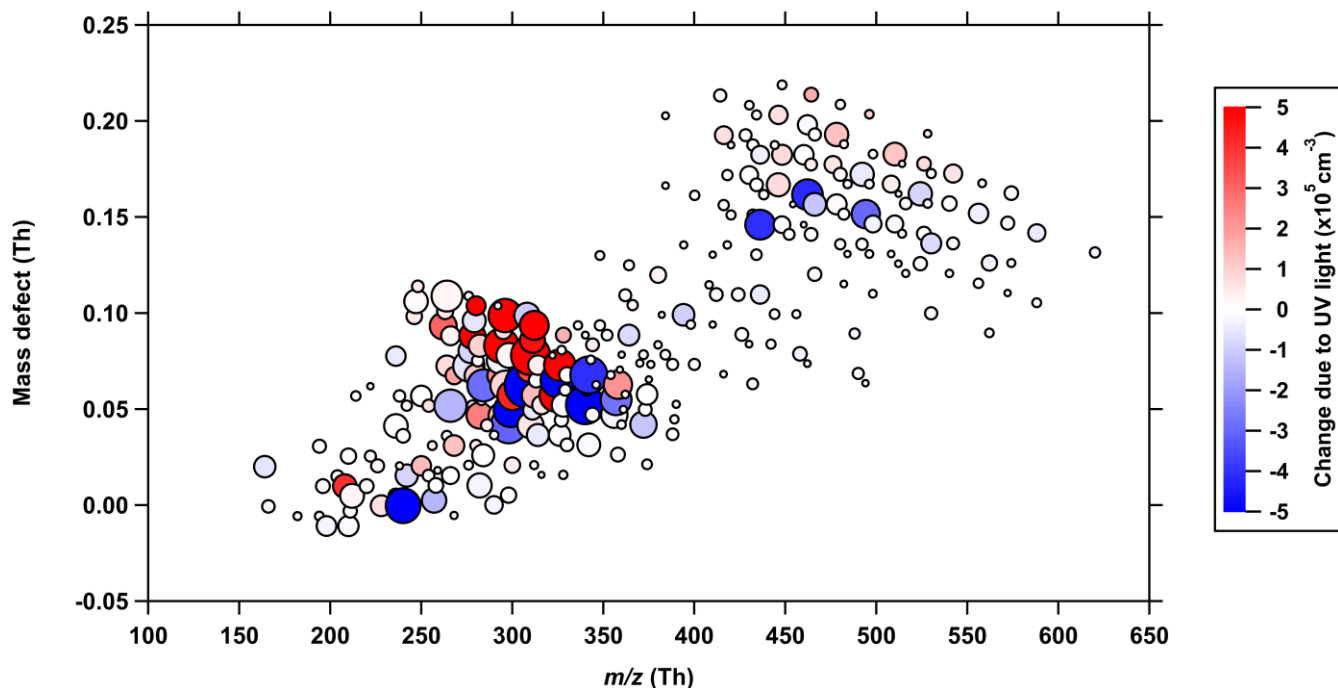


Figure S4: Mass-defect plot of the concentration change of the neutral highly-oxygenated molecules (HOMs) detected by the CI-APi-TOF between dark and UV-illuminated conditions.

The α -pinene and ozone flow into the chamber was kept constant during these runs to allow for a direct comparison. The measured concentration of α -pinene dropped from 618 to 504 pptv, respectively, due to the additional reaction with the elevated OH^{*} radical concentration produced by the UV light. The ozone concentration showed a slight increase from 46 to 48 ppbv. The area of the marker points is logarithmically scaled to their concentration at dark conditions. The color code indicates the change in the intensity of each individual molecule by switching to UV light conditions.

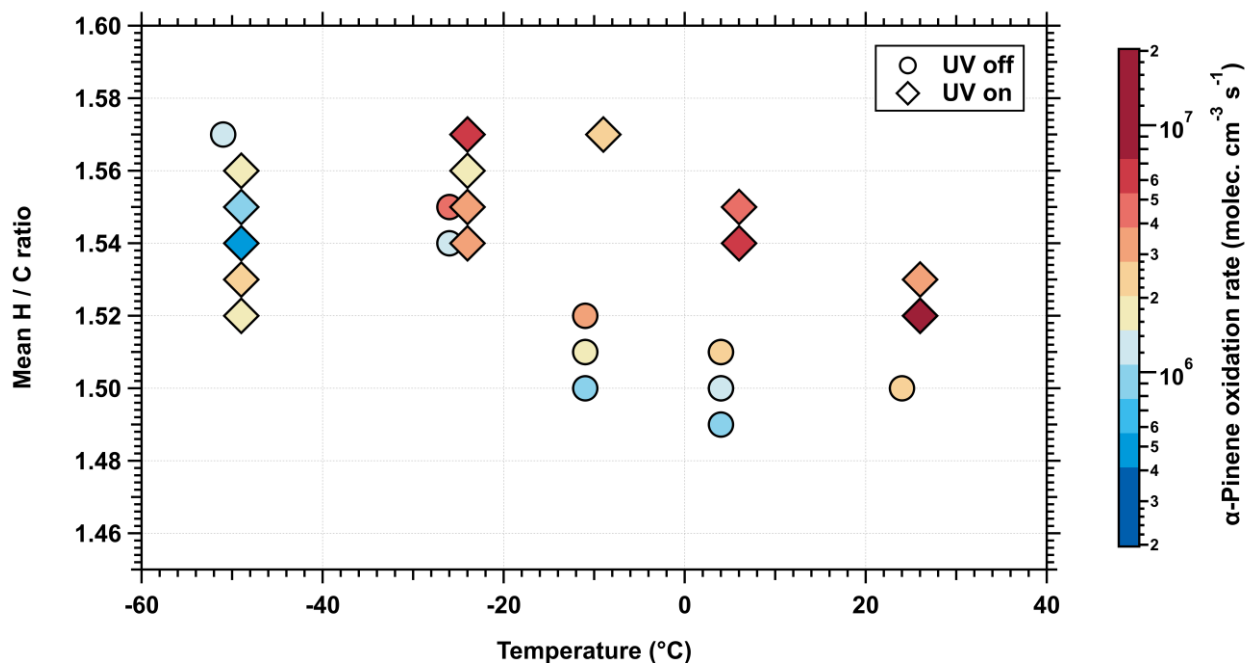


Figure S5: Mean hydrogen-to-carbon (H/C) atomic ratio observed with the CI-API-TOF for varying α -pinene reacted concentrations for dark (circle) and UV illuminated (diamond) conditions at different temperatures.

The mean H/C at UV illuminated conditions is elevated due to the increased reaction of α -pinene with OH^{*} radicals compared to dark conditions.

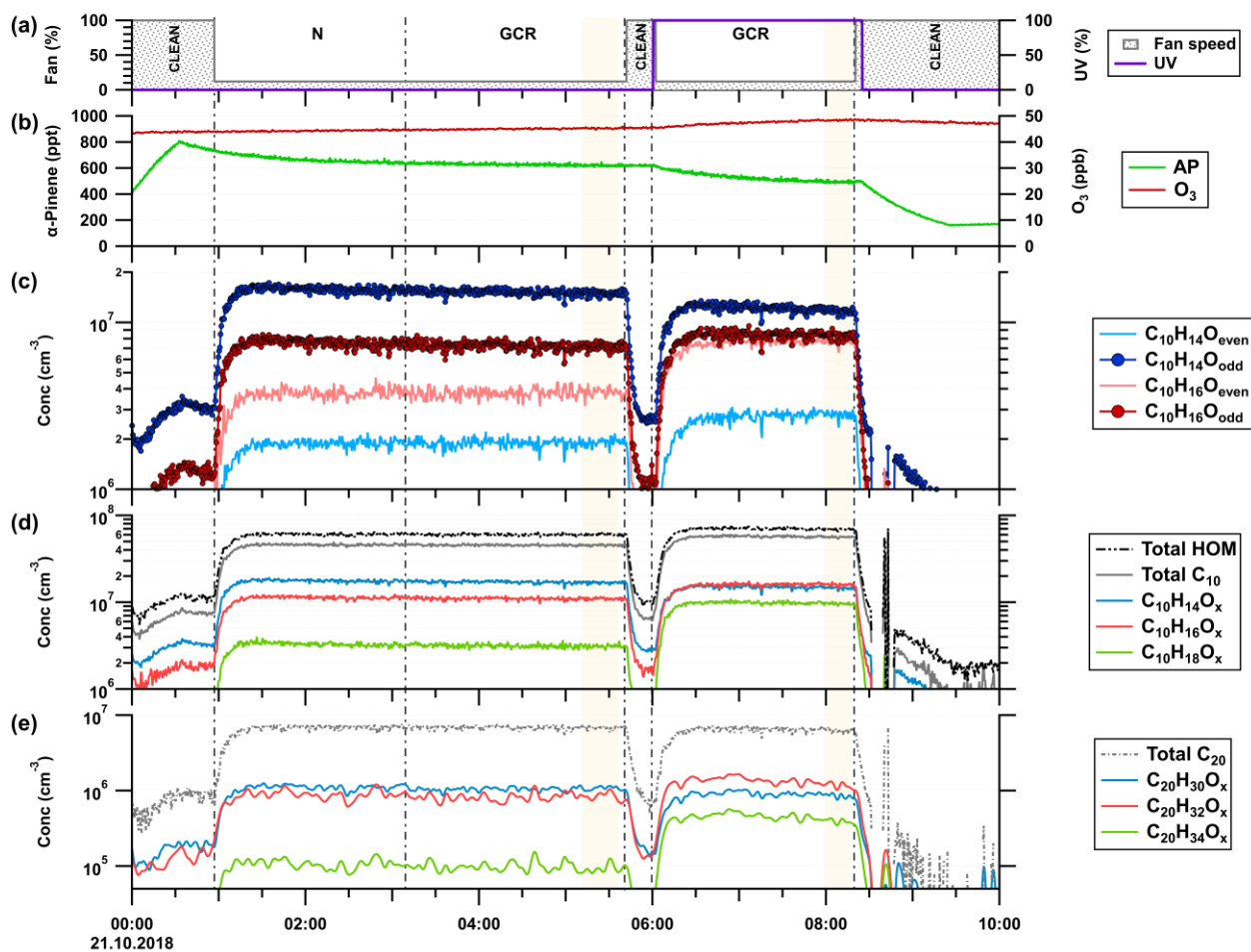


Figure S6: Change of HOM class distribution during an α -pinene oxidation experiment due to UV-illumination.

The α -pinene flow into the chamber was set to a constant level at 00:30 until 8:25am, while the ozone flow was kept constant all the time to ensure a direct comparison during dark and UV illuminated conditions. While there is no change in the HOM distribution when changing from neutral to GCR conditions there is a clear change when the UV light is switched on. The UV light elevates the OH^\bullet radical concentration inside the chamber by a factor of 2. Due to the additional oxidation reagents, the α -pinene level drops from 618 to 504 ppt, while the ozone level increases slightly. This also affects the oxidation chemistry. The termination of the RO_2^\bullet radicals by HO_x^\bullet radicals is increased which leads to more $\text{C}_{10}\text{H}_{14,16}\text{O}_{\text{even}}$ products. Also, the initial oxidation reaction by OH^\bullet radical addition will form more carbon-centered radicals with the formula $\text{C}_{10}\text{H}_{17}\text{O}_x^\bullet$. These radicals lead to closed-shell products with 16 and 18 hydrogen atoms in the monomer molecule as well as 32 and 34 hydrogen atoms in the dimer products (blue and green trace in the lower panels). The increase of the $\text{C}_{10}\text{H}_{18}\text{O}_x$ closed-shell products by a factor of 3.5 also concludes an increase of OH^\bullet radicals by a factor of 2 as the products are square root

dependent on the OH^\bullet radical concentration. The higher HO_x^\bullet radical concentration also change the RO_2^\bullet radical termination pathway. Due to the competition with the $\text{RO}_2^\bullet + \text{RO}_2^\bullet$ termination which forms the extremely low volatile C_{20} -dimers this additional pathway will end up in more C_{10} -monomer molecules while the total amount of HOMs are slightly elevated.