



Supplement of

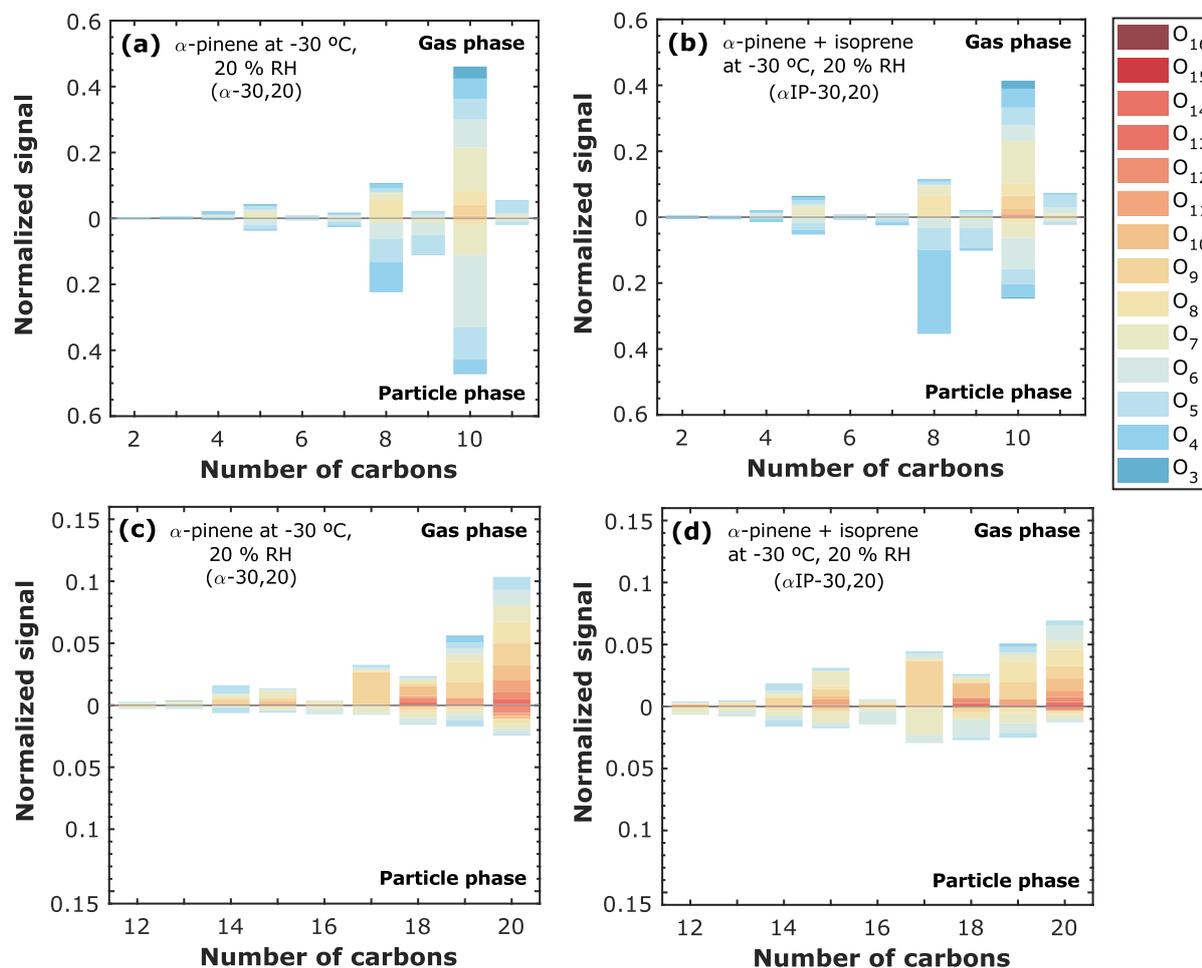
Chemical composition of nanoparticles from α -pinene nucleation and the influence of isoprene and relative humidity at low temperature

Lucía Caudillo et al.

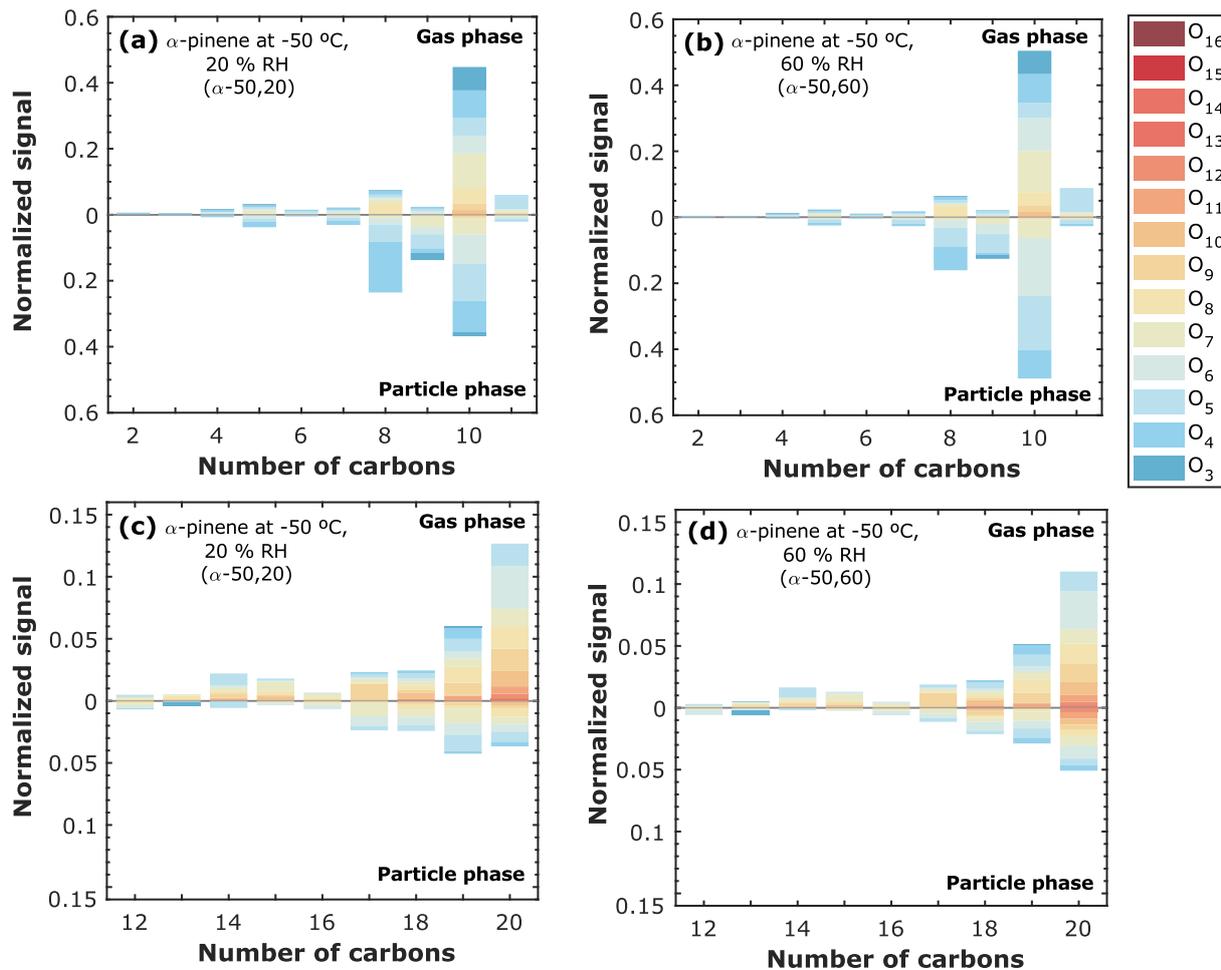
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Supplementary Material



5 **Figure S1. Carbon atom distribution C₂₋₁₁ and C₁₂₋₂₀ and oxygen atom content in gas and particle phase molecules. Both phases are measured with a Nitrate CI-API-TOF mass spectrometer, while the TD-DMA is coupled to it for particle phase measurements. (a) and (c) α -pinene oxidation products at $-30\text{ }^{\circ}\text{C}$ and 20 % RH (α -30,20), (b) and (d) α -pinene + isoprene oxidation products at $-30\text{ }^{\circ}\text{C}$ and 20 % RH (α IP-30,20). The level of α -pinene was between 1 and 8 ppbv in (a) (b) (c) and (d), while isoprene level reached up to 30 ppbv in (b) and (d). Ozone level was stable at ~ 100 ppbv for all the experiments. The intensities are normalized by the total signal in each system and phase. Each color represents a specific number of oxygen atoms in the range of 3 to 16.**

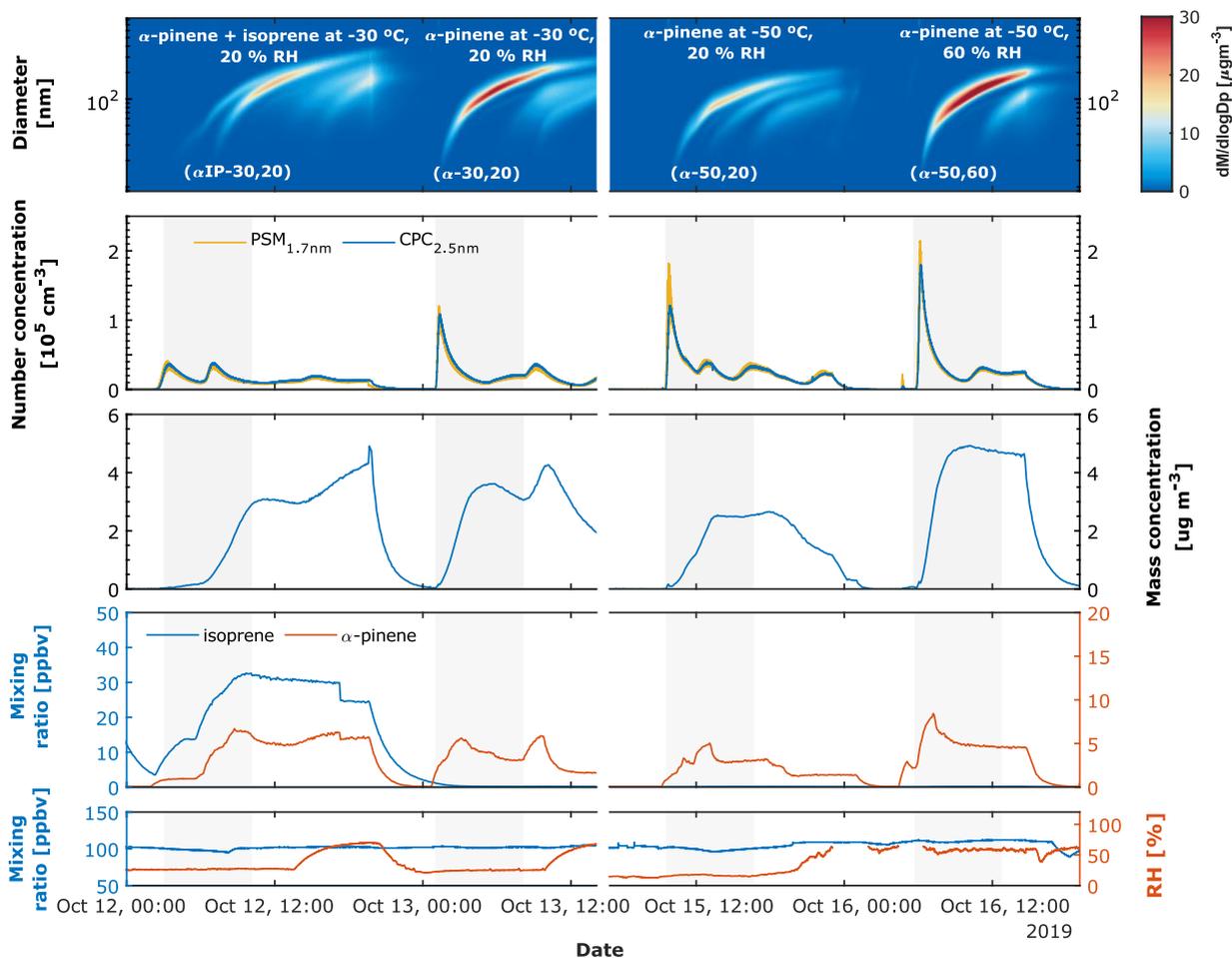


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Figure S2. Carbon atom distribution C₂₋₁₁ and C₁₂₋₂₀ and oxygen atom content in gas and particle phase molecules. Both phases are measured with a Nitrate CI-API-TOF mass spectrometer, while the TD-DMA is coupled to it for particle phase measurements. (a) and (c) α -pinene oxidation products at -50 °C and 20 % RH (α -50,20), (b) and (d) α -pinene oxidation products at -50 °C and 60 % RH (α -50,60). The level of α -pinene was between 1 and 8 ppbv and Ozone level was stable at ~ 100 ppbv for all the experiments. The intensities are normalized by the total signal in each system and phase. Each color represents a specific number of oxygen atoms in the range of 3 to 16.

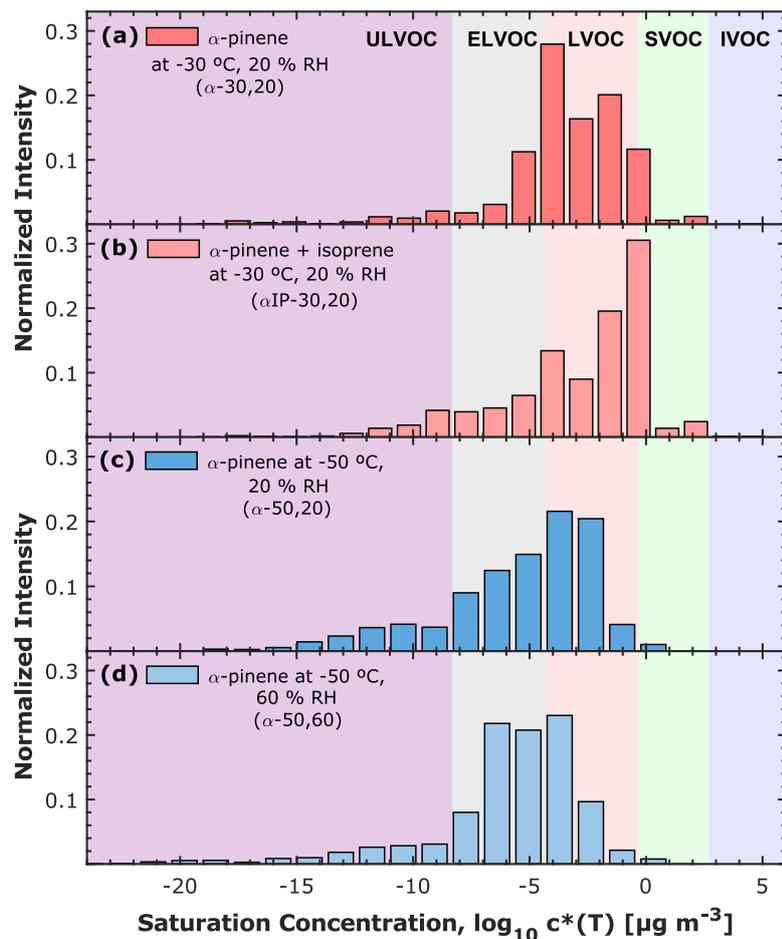
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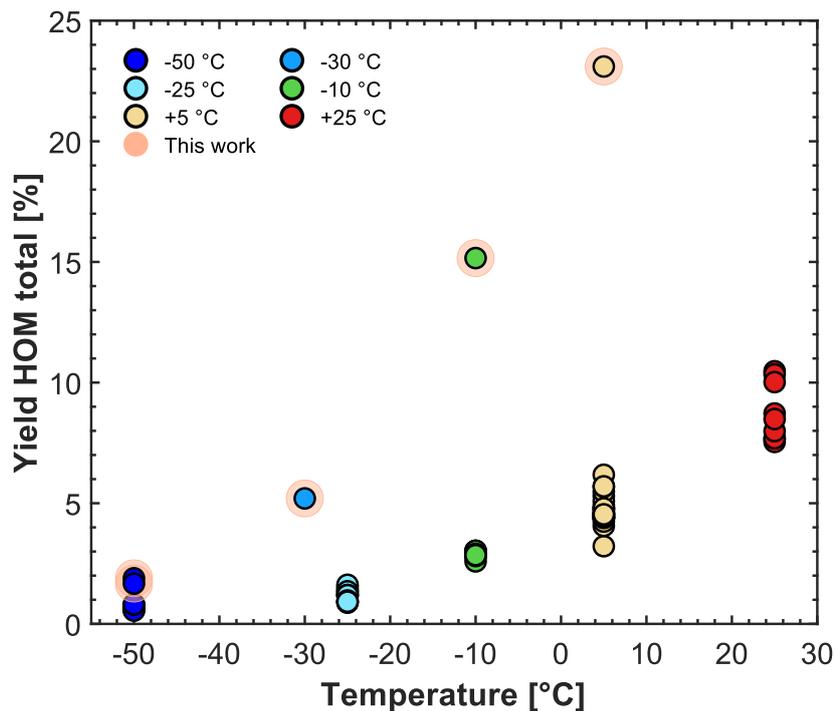


25 Figure S3. Experimental overview for pure biogenic new particle formation. First panel: particle size distribution for four different experiments: α -pinene + isoprene at $-30\text{ }^{\circ}\text{C}$ and $20\text{ }\%$ RH (α IP-30,20); α -pinene at $-30\text{ }^{\circ}\text{C}$ and $20\text{ }\%$ RH (α -30,20); α -pinene at $-50\text{ }^{\circ}\text{C}$ and $20\text{ }\%$ RH (α -50,20) and α -pinene at $-50\text{ }^{\circ}\text{C}$ and $60\text{ }\%$ RH (α -50,60). The color scale represents the normalized mass concentration in $\mu\text{g m}^{-3}$. Second panel: Particle number concentration in cm^{-3} measured by the PSM with a cut-off diameter of 1.7 nm and CPC with a cut-off diameter of 2.5 nm . Third panel: Mass concentration in $\mu\text{g m}^{-3}$ (obtained by integrating the normalized mass concentration from the SMPS). Fourth panel: Mixing ratio in ppbv for the biogenic precursor gases, isoprene and α -pinene. Fifth panel: Ozone mixing ratio in ppbv and relative humidity in $\%$. The shaded areas refer to the time where the particles were collected using the TD-DMA.

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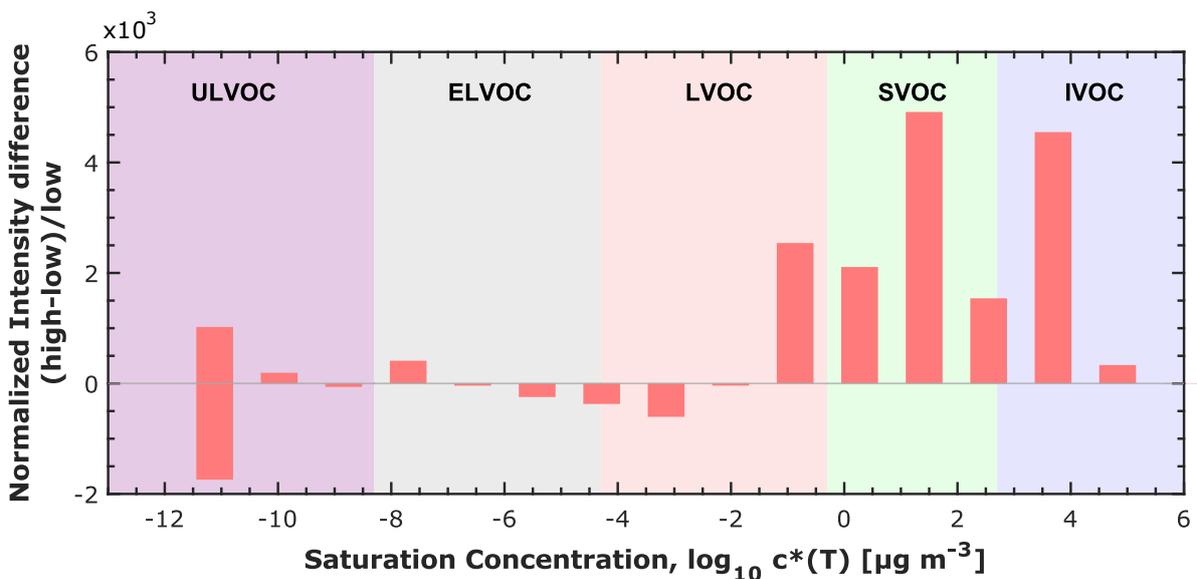


35 **Figure S4. TD-DMA Volatility distribution of the measured oxidation products in the particle phase for four different experiments (Figure 5 in linear scale): (a) α -pinene at $-30\text{ }^{\circ}\text{C}$ and $20\text{ }\%$ RH (α -30,20); (b) α -pinene + isoprene at $-30\text{ }^{\circ}\text{C}$ and $20\text{ }\%$ RH (α IP-30,20);**
 40 **(c) α -pinene at $-50\text{ }^{\circ}\text{C}$ and $20\text{ }\%$ RH (α -50,20) and (d) α -pinene at $-50\text{ }^{\circ}\text{C}$ and $60\text{ }\%$ RH (α -50,60). Every individual volatility bin includes the sum of the intensity for the oxidation products normalized by the total signal in each system. Every individual volatility bin is defined at 300 K , shifted, and widened according to their corresponding temperature. The color bands in the background indicate the volatility regimes as in Donahue et al. (2012) and in Schervish and Donahue (2020). The normalized intensity is dimensionless. Nevertheless, it should be noted that the particle phase signal is given in normalized counts per second integrated over the evaporation time [ncps. s].**

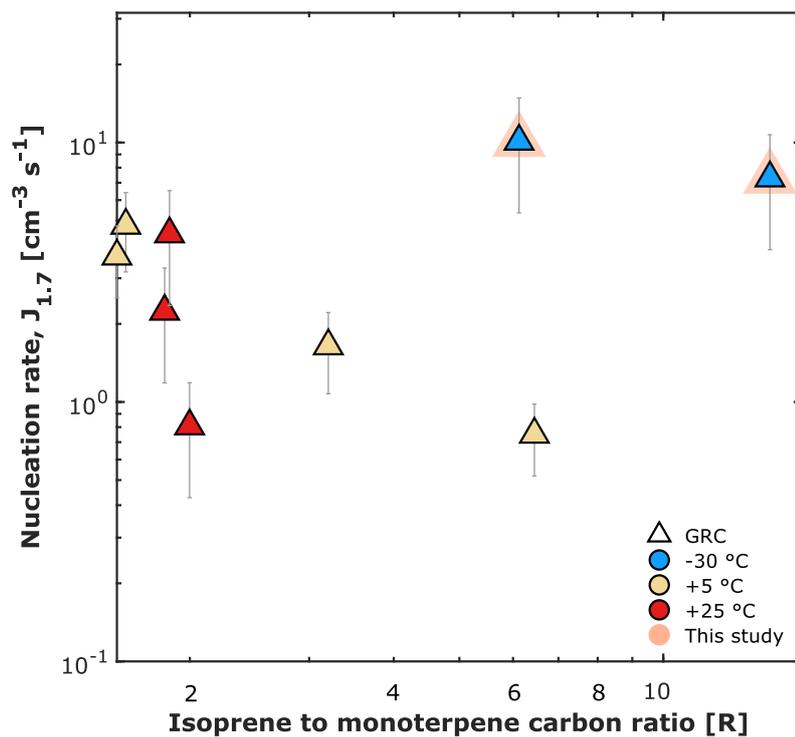


45 **Figure S5.** Yield of total HOM as a function of temperature for pure α -pinene systems. Data points at -50 °C, -25 °C, -10 °C, +5 °C and +25 °C are from Simon et al. (2020) and the data points with the orange shadows are the contribution of this study (α -30,20, α -50,20 and α -50,60 and complementary pure α -pinene experiments at +5 °C and at -10 °C). The level of precursor gases from Simon et al., (2020) were 0.2 to 0.8 ppbv for α -pinene and 40 to 50 ppbv for ozone, while for experiments reported here (shown with orange shadows), the mixing ratios were 1 to 8 ppbv for α -pinene and 100 ppbv for ozone.

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55 Figure S6. Volatility distribution of gas phase for two different systems and the normalized difference between them. Gas phase is measured with a Nitrate CI-API-TOF mass spectrometer. Every individual volatility bin includes the normalized intensity difference (high-low)/low, which is calculated based on intensity of the system at high level of precursor gases (α -pinene was 2 - 3 ppbv and Ozone ~ 100 ppbv) and on the system at low level of precursor gases (α -pinene was 0.2 - 0.8 ppbv and Ozone ~ 40 - 50 ppbv). Every individual volatility bin is defined at 300 K, shifted, and widened according to their corresponding temperature. The lowest bin is an overflow bin (which contains the volatility bins with saturation concentration < -11 $\mu\text{g m}^{-3}$). The color bands in the background indicate the volatility regimes as in Donahue et al. (2012) and in Schervish and Donahue (2020).



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Figure S7. Pure biogenic nucleation rates at 1.7 nm diameter against isoprene-to-monoterpene carbon ratio (R) at different temperatures. Triangles represent Galactic Cosmic Rays (GCR) conditions. Data points at +5 °C and +25 °C are from Heinritzi et al., (2020). The points with the orange shadows are the experiments reported in this study for α -pinene + isoprene oxidation products at -30 °C and 20 % RH (α IP-30,20).

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