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Nitrate radical oxidation of γ-terpinene: hydroxy nitrate, total organic nitrate, and secondary organic aerosol yields

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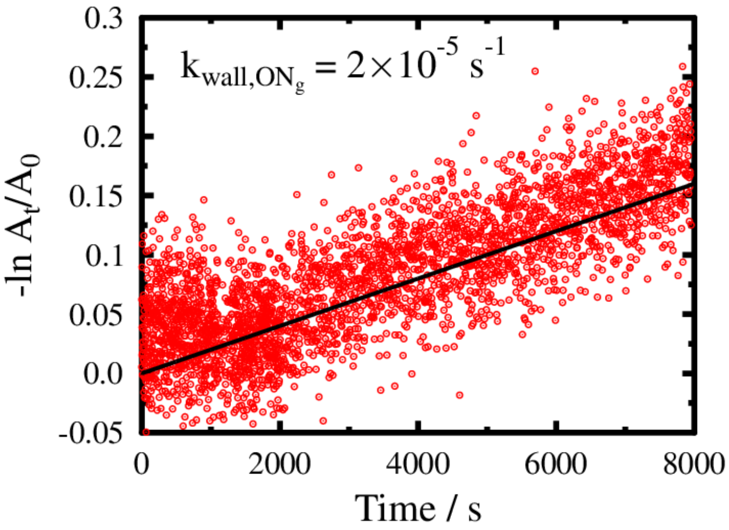

Figure S1. Wall loss rate of m/z 342 as measured by CIMS, corresponding to the monoterpene hydroxy nitrate–I^- adduct.

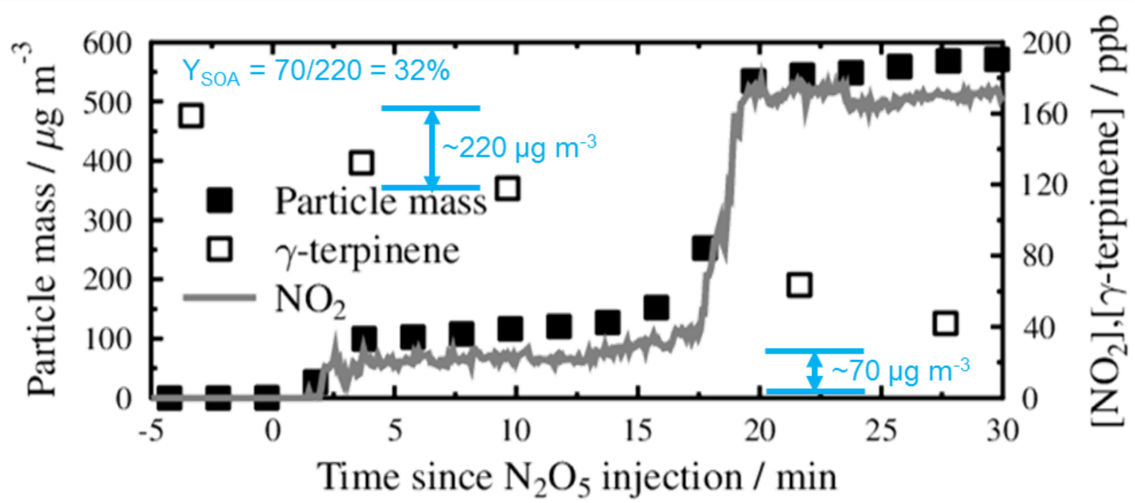

Figure S2. Example experimental time series and calculation of SOA yield.

Identification of ON in filter extracts

Figure S3 shows the extracted ion chromatograms (EIC) of the synthetic α-pinene-derived hydroxy nitrate (red), and potential particle-phase organic nitrates, including the first-generation hydroperoxy nitrate (green) and di-hydroxy di-nitrate (blue). For each EIC, there is a corresponding MSMS (MS^2) spectrum, which shows the fragment ions of the parent [M+AcO^-] adduct ion species. The synthesized α-pinene-derived hydroxy nitrate adduct with AcO^- (*m/z* = 274.1291) MS^2 spectrum indicates there are two primary fragment ions that correspond to AcO^- and NO_3^-. These ions were then used as signatures to identify organic nitrate species in the filter sample extracts. Detected masses and their corresponding mass spectra and tandem mass spectra were further analyzed and matched according to the chemical formula: $C_aH_bN_cO_d$. Of the two samples analyzed, the most abundant species with the NO_3^- fragment ion have an *m/z* = 353.1197, corresponding to a molecule with chemical formula $C_{10}H_{18}N_2O_8$ + AcO^- , and *m/z* = 290.1241 ($C_{10}H_{17}NO_5$ + AcO^-).

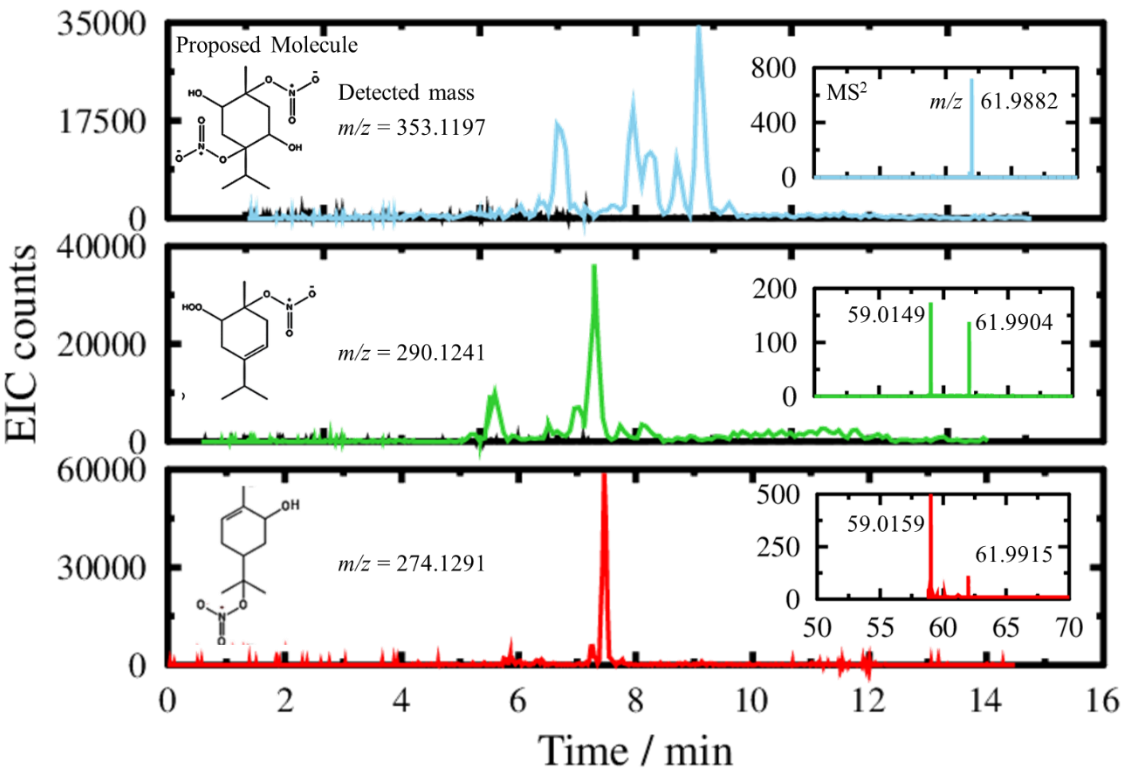

Figure S3. UPLC-ESI(-)-ToF-MS/MS extracted ion chromatograms (EIC) for the synthetic α-pinene-derived hydroxy nitrate (red), hydroperoxy nitrates present in the filter extracts (green), and di-hydroxy–di-nitrates present in the filter extracts (blue). For reference, the background EICs

(HPLC-grade methanol) for each mass are also plotted (black). The insets show the MS^2 spectra and the listed *m/z* values in the MS^2 spectra correspond to the most intense peak. Potential molecular structures are shown for reference.

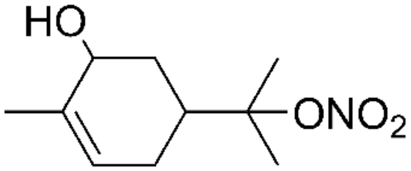

Figure S4. Molecular structure of the synthetic α-pinene-derived hydroxy nitrate used for calibration of the CIMS.

Box model inputs

The box model applied to simulate the reaction and products from the NO_3 oxidation of γ-terpinene was performed in Matlab v7.7.0 using the ordinary differential equations (ODE23s) solver in Matlab. Table S1 lists the various reactions and rate constants applied in the model. The majority of the rate constants were abstracted from those applied in the Master Chemical Mechanism version, with the exception of NO_3 + γ-terpinene since the MCM does not explicitly include γ-terpinene. Wall loss rate constants were included in the model for NO_3, N_2O_5, and the hydroxy-, hydroperoxy-, and keto-nitrates as described in the footnotes of Table S1.

Table S1. Box model parameters for simulating the NO_3+γ-terpinene reaction in the chamber.

Reaction	**Rate constant**
$N_2O_5 \rightarrow NO_3 + NO_2$	$\frac{1\times10^{-12}}{2.13\times10^{-27}e^{\frac{11025}{T}}}$ cm^3 $molecule^{-1}$ s^{-1}
$NO_3 + NO_2 \rightarrow N_2O_5$	1×10^{-12} cm^3 $molecule^{-1}$ s^{-1}
[a]NO_3 + wall → loss	6×10^{-4} s^{-1}
[b]N_2O_5 + wall → loss	5×10^{-6} s^{-1}
[c]γ-terpinene + NO_3 → α-nitrooxy peroxy radical	24×10^{-12} cm^3 $molecule^{-1}$ s^{-1} *0.35

α-nitrooxy peroxy radical + NO_3 → α-nitrooxy alkoxy radical + NO_2	2.3×10^{-12} cm^{3} molecule^{-1} s^{-1}
α-nitrooxy peroxy radical + HO_2 → β-hydroperoxy nitrate	$2.91 \times 10^{-13} e^{\frac{1300}{T}}$ cm^{3} molecule^{-1} s^{-1} *0.914
α-nitrooxy peroxy radical + RO_2 → β-hydroxy nitrate	2.5×10^{-13} cm^{3} molecule^{-1} s^{-1} *0.1
α-nitrooxy peroxy radical + RO_2 → α-nitrooxy alkoxy radical	2.5×10^{-13} cm^{3} molecule^{-1} s^{-1} *0.8
α-nitrooxy peroxy radical + RO_2 → β-keto nitrate	2.5×10^{-13} cm^{3} molecule^{-1} s^{-1} *0.1
α-nitrooxy alkoxy radical + O_2 → β-keto nitrate + HO_2	$2.5 \times 10^{-14} e^{\frac{-300}{T}}$ cm^{3} molecule^{-1} s^{-1}
α-nitrooxy-β-alkoxy radical → keto-aldehyde + NO_2	4×10^{5} s^{-1}
[c]γ-terpinene + NO_3 → β-nitrooxy peroxy radical	24×10^{-12} cm^{3} molecule^{-1} s^{-1} *0.65
β-nitrooxy peroxy radical + NO_3 → β-nitrooxy alkoxy radical + NO_2	2.3×10^{-12} cm^{3} molecule^{-1} s^{-1}
β-nitrooxy peroxy radical + HO_2 → α-hydroperoxy nitrate	$2.91 \times 10^{-13} e^{\frac{1300}{T}}$ cm^{3} molecule^{-1} s^{-1} *0.914
β-nitrooxy peroxy radical + RO_2 → α-hydroxy nitrate	6.7×10^{-15} cm^{3} molecule^{-1} s^{-1} *0.1
β-nitrooxy peroxy radical + RO_2 → β-nitrooxy alkoxy radical	6.7×10^{-15} cm^{3} molecule^{-1} s^{-1} *0.9
β-nitrooxy alkoxy radical → keto-aldehyde + NO_2	1×10^{6} s^{-1}
[d]Wall loss rate of hydroxy nitrate, keto nitrate, and hydroperoxy nitrate	2×10^{-5} s^{-1}

[a]Wall loss rate from Fry et al. (2009). [b]Wall loss rate from Perring et al. (2009). [c]Reaction rate constant from Martinez et al. (1999). [d]Wall loss rates derived from the measurement of hydroxy nitrate wall loss.