

Supporting Information

Stability of Monoterpene-Derived α -Hydroxyalkyl-Hydroperoxides in Aqueous Organic Media – Relevance to the Fate of Hydroperoxides in Aerosol Particle Phases

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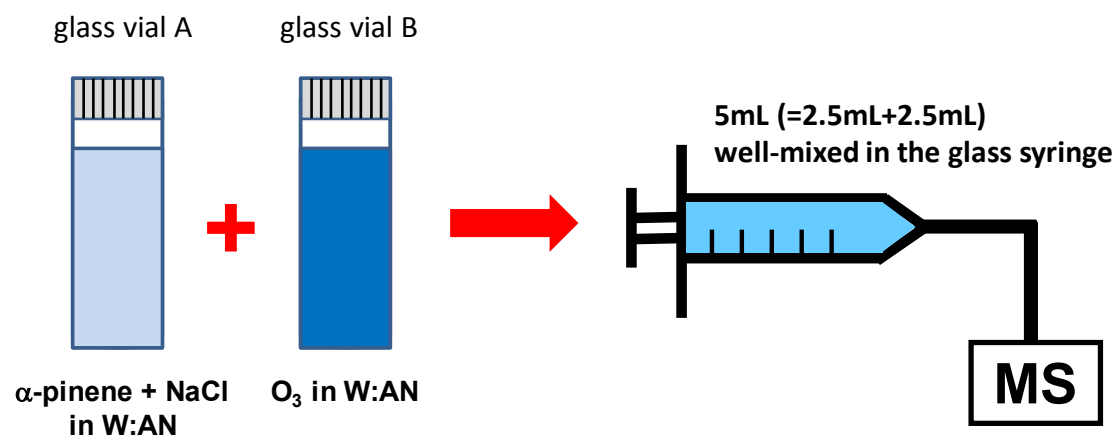


Figure S1 – Schematic setup and procedure of present methods.

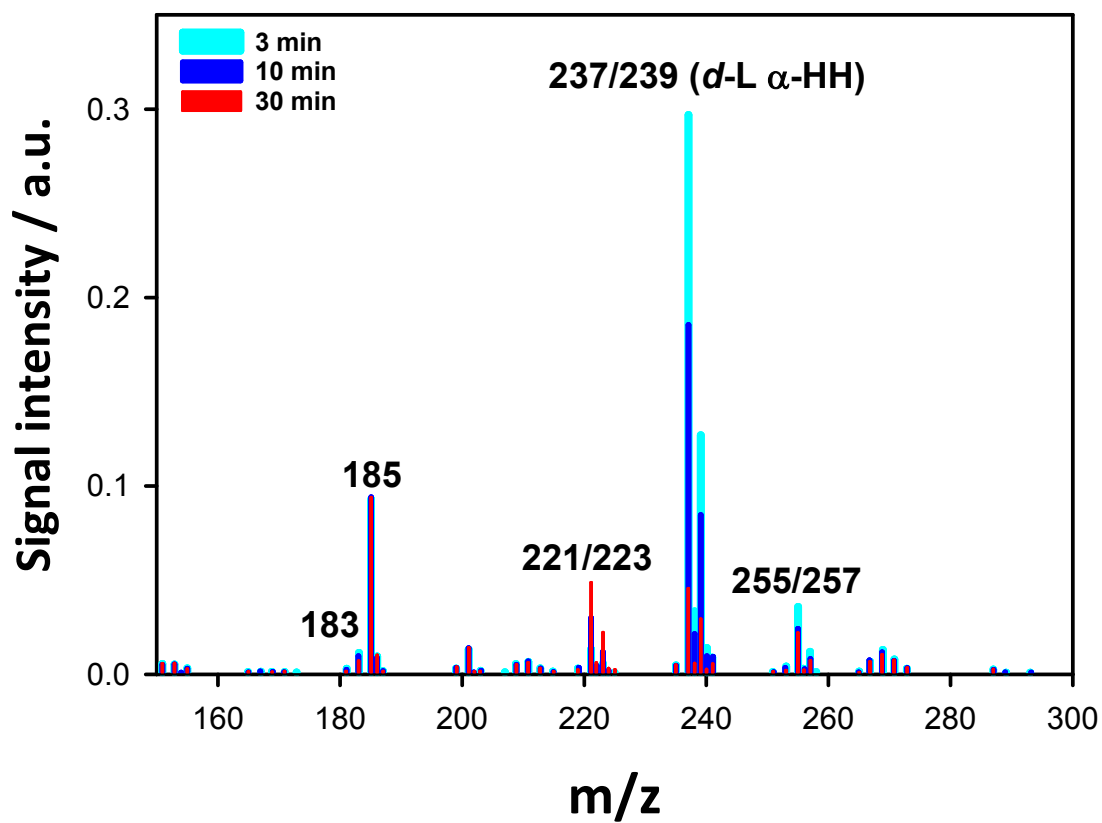


Figure S2 – Negative ion mass spectra of 1mM *d*-limonene (*d*-L) + 0.2 mM NaCl + [O₃]₀ = 0.08 mM in W:AN (50:50 = vol:vol) solution as a function of time.

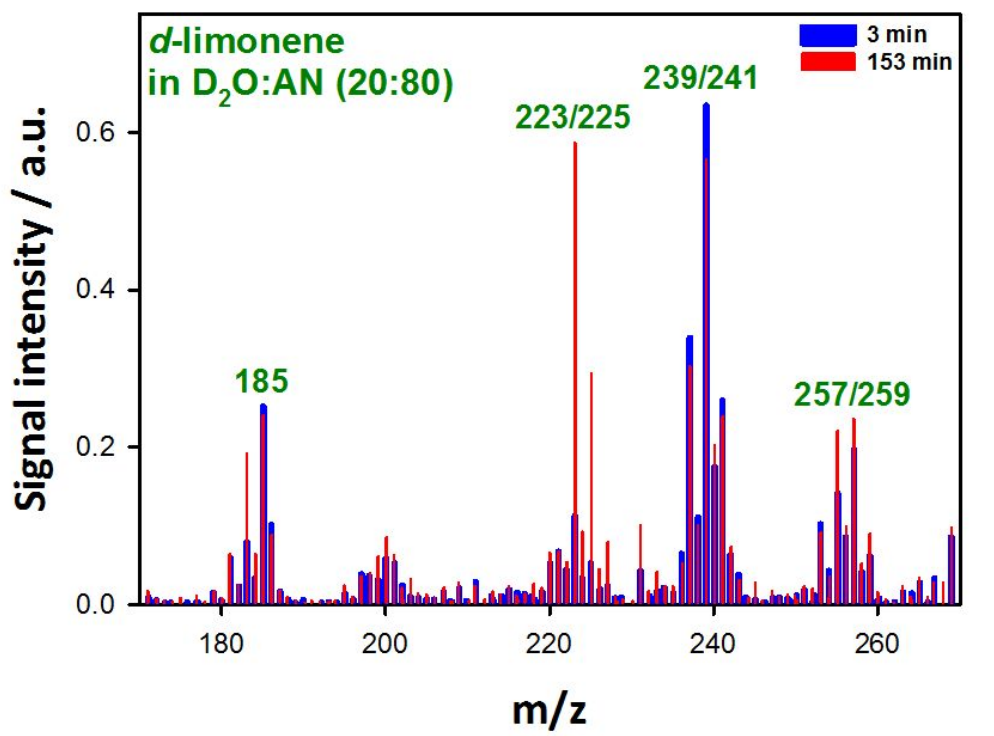


Figure S3 – Negative ion mass spectra of 10 mM *d*-limonene + 0.2 mM NaCl + $[O_3]_0 = 0.09$ mM in $D_2O:AN$ (20:80 = vol:vol) solution as a function of time.

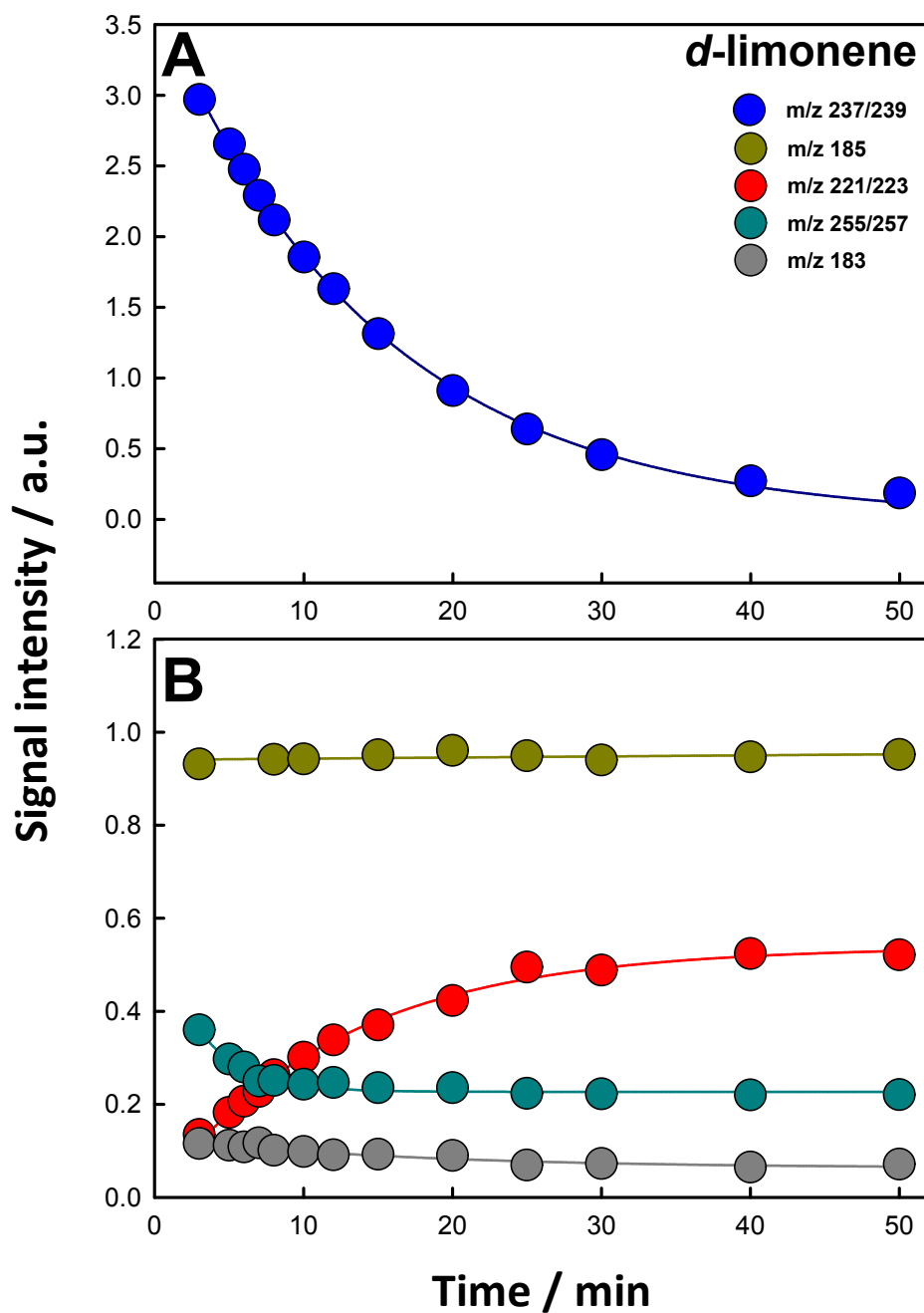


Figure S4 – Temporal profiles of chloride-adducts of *d*-limonene α -HHs and other products obtained from the liquid-phase reaction of 1mM *d*-limonene + 0.2 mM NaCl + $[O_3]_0 = 0.08$ mM in W:AN = 50:50 = vol:vol. The lines for m/z 237/239 and m/z 221/223 are exponential decay and rise function of signal intensity (S) = $S_{01} \exp(-k_1 t)$ and $S_{\max} [1 - \exp(-kt)]$, respectively. Other lines are guides to the eye.

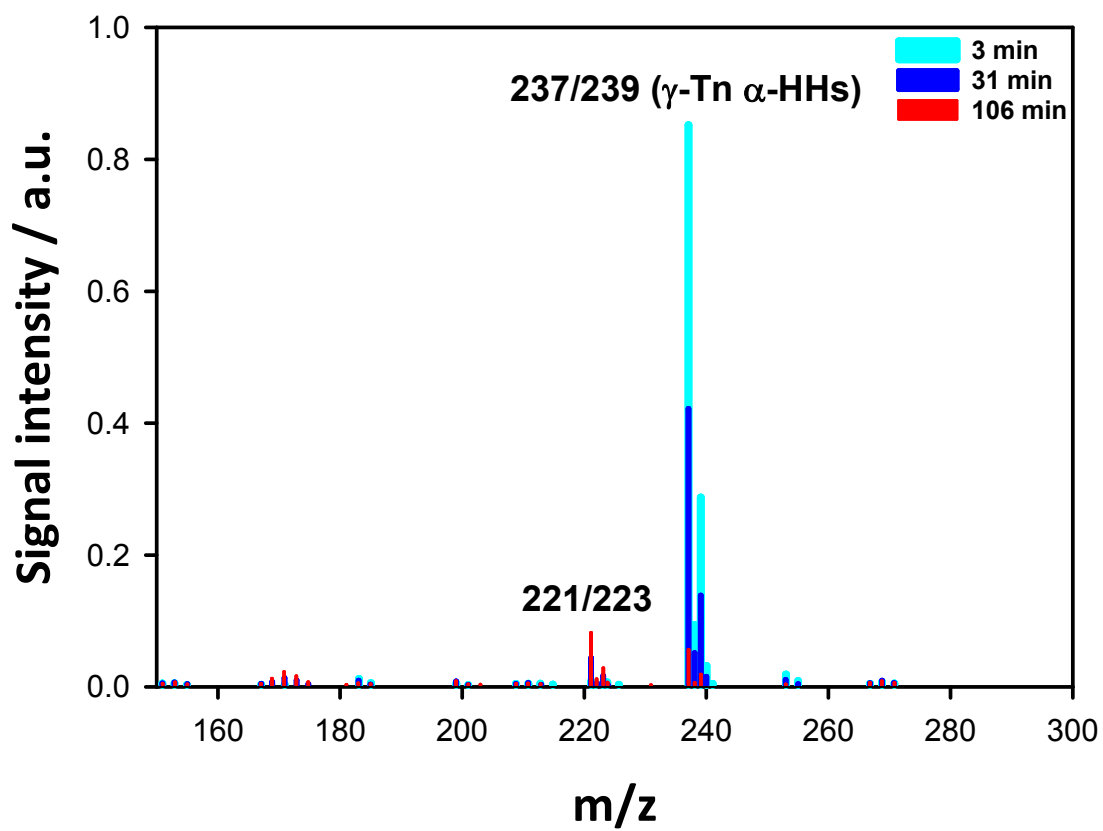


Figure S5 – Negative ion mass spectra of 1mM γ -terpinene (γ -Tn) + 0.2 mM NaCl + $[O_3]_0 = 0.05$ mM in W:AN (50:50 = vol:vol) solution as a function of time.

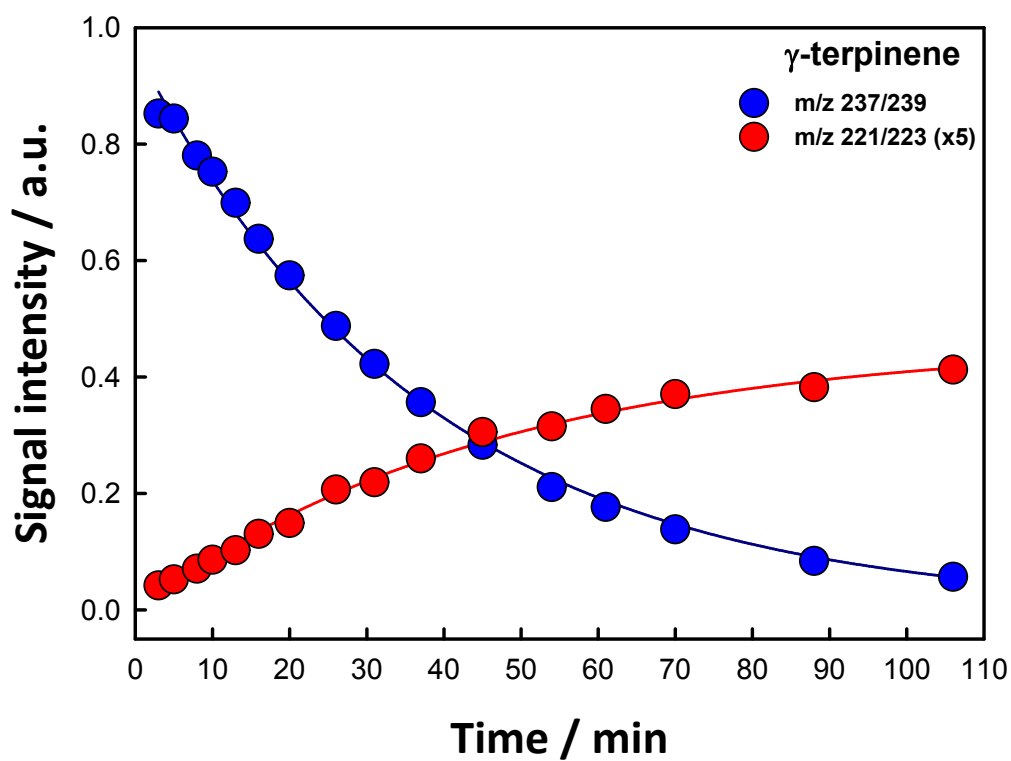


Figure S6 – Temporal profiles of chloride-adducts of γ -terpinene α -HHs (m/z 237/239) and *gem*-diol (m/z 221/223, signal intensity multiplied by 5) products obtained from the liquid-phase reaction of γ -terpinene + 0.2 mM NaCl + $[O_3]_0 = 0.05$ mM in W:AN = 50:50 = vol:vol. The lines for m/z 237/239 and m/z 221/223 are exponential decay and rise function of signal intensity (S) = $S_{01} \exp(-k_1 t)$ and $S_{max} [1 - \exp(-kt)]$, respectively.

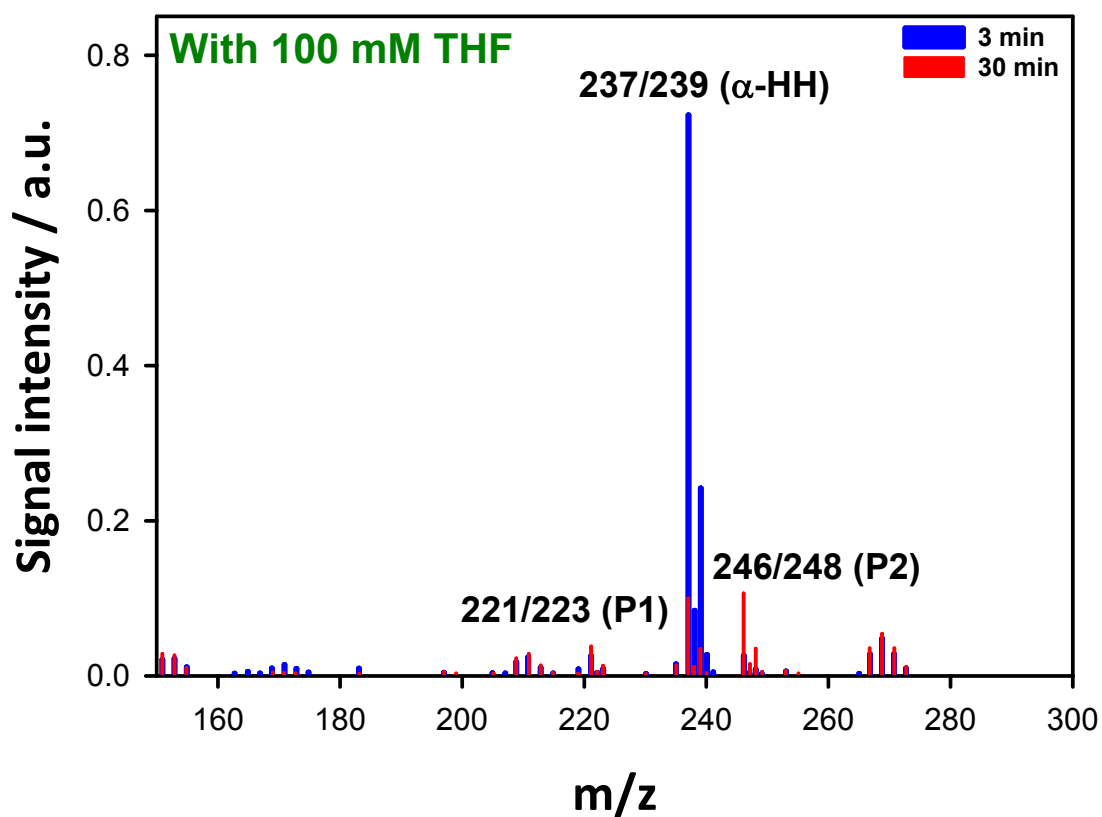


Figure S7 – Negative ion mass spectra of 1 mM α -pinene + 0.2 mM NaCl + 100 mM tetrahydrofuran (THF) + $[O_3]_0 = 0.02$ mM in W:AN (50:50 = vol:vol) solution as a function of time.

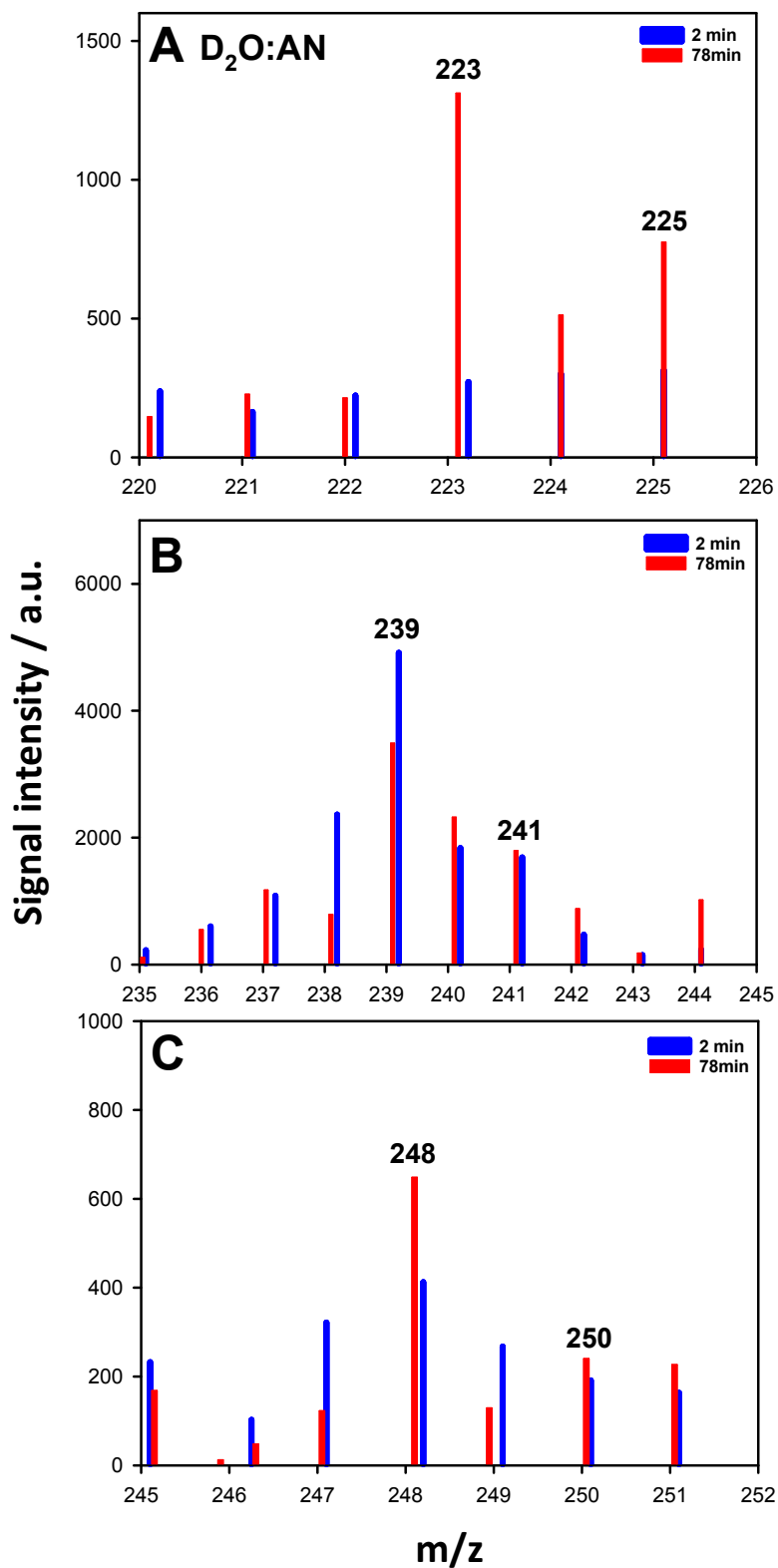


Figure S8 – Negative ion mass spectra of 10 mM α -pinene + 0.2 mM NaCl + $[O_3]_0 = 0.1$ mM in $D_2O:AN$ (20:80 = vol:vol) solution as a function of time.

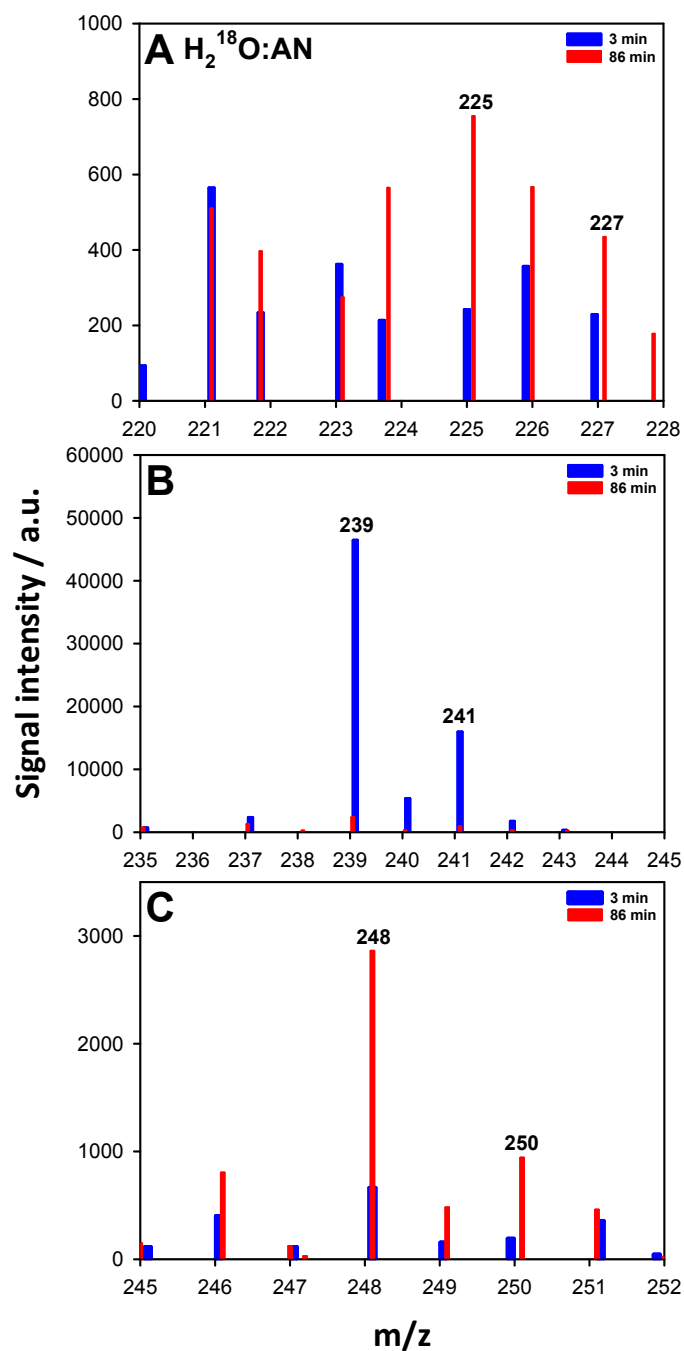


Figure S9 – Negative ion mass spectra of 10 mM α -pinene + 0.2 mM NaCl + $[\text{O}_3]_0 = 0.06$ mM in $\text{H}_2^{18}\text{O}:\text{AN}$ (20:80 = vol:vol) solution as a function of time.

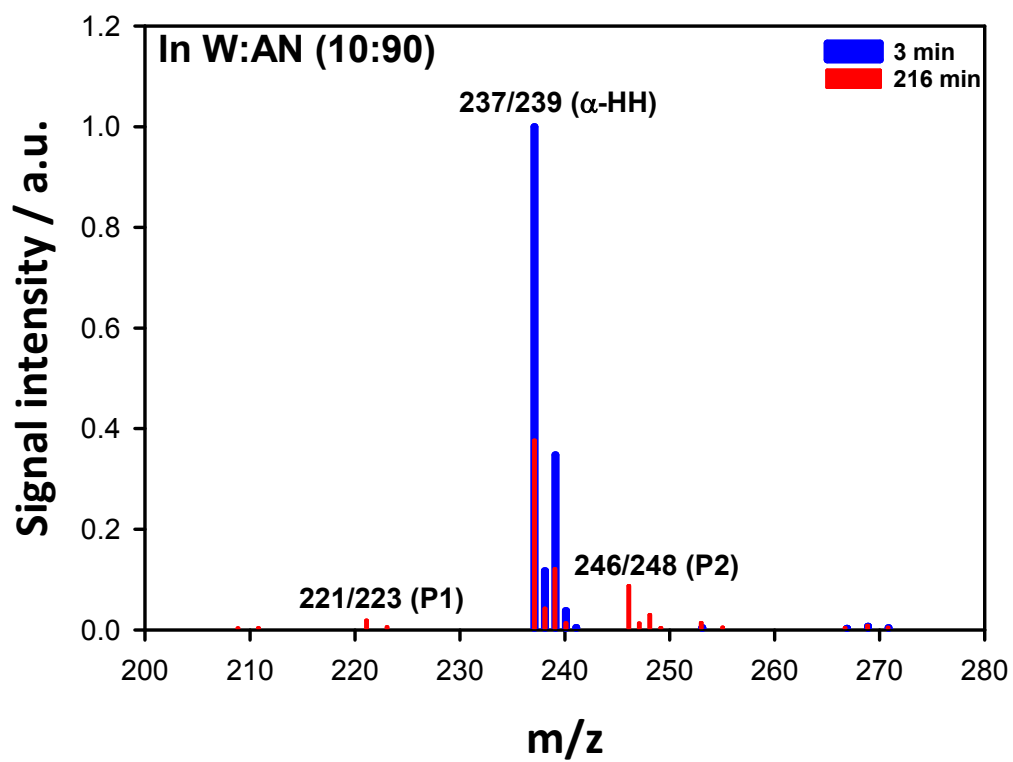


Figure S10 – Negative ion mass spectra of 1 mM α -pinene + 0.2 mM NaCl + $[\text{O}_3]_0 = 0.06$ mM in W:AN (10:90 = vol:vol) solution after 3 min and 216 min.

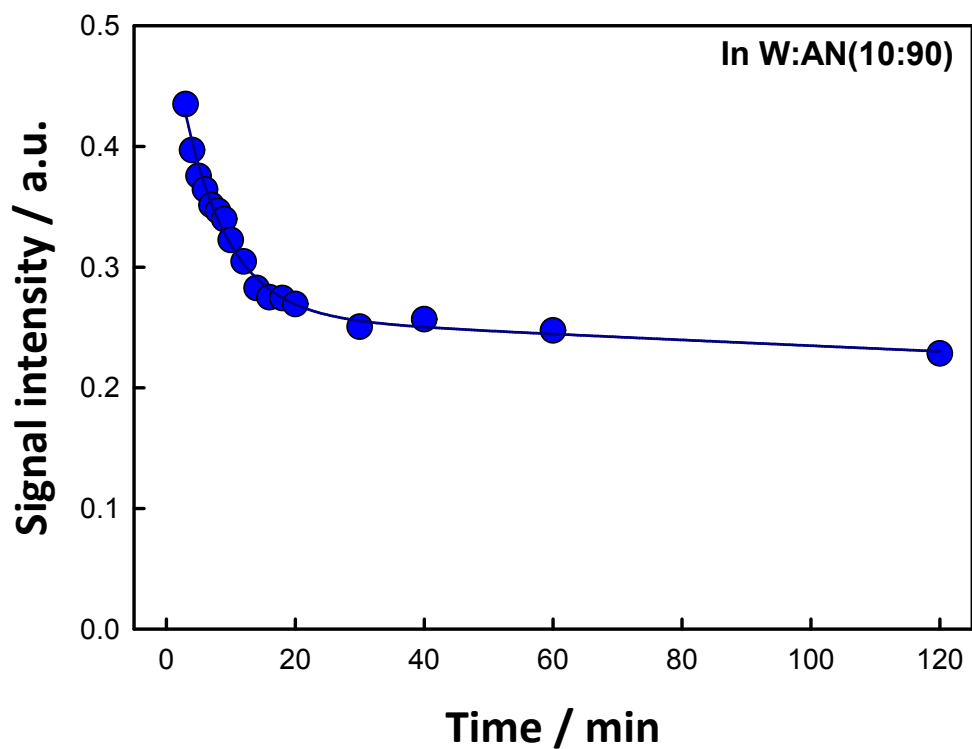


Figure S11 – Temporal profile of α -pinene α -HHs (m/z 237) obtained from the liquid-phase reaction of 1 mM α -pinene + 0.2 mM NaCl + $[O_3]_0 = 0.06$ mM in W:AN = 10:90 = vol:vol. The line is a bi-exponential decay fitted with a function of signal intensity (SI) = $S_{01} \exp(-k_1 t) + S_{02} \exp(-k_2 t)$. See main text for details.

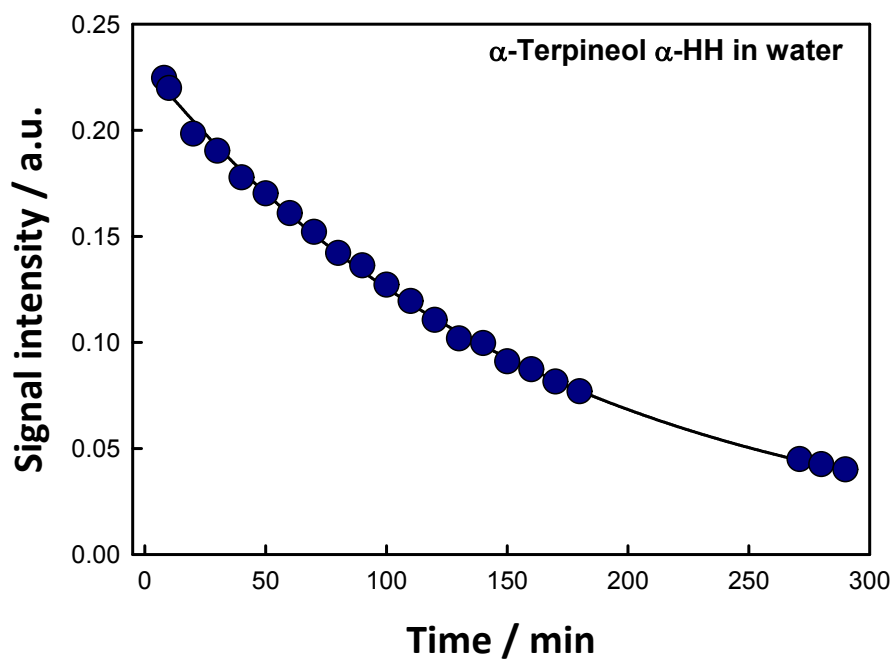


Figure S12 – Temporal profiles of chloride-adducts of α -terpineol α -HHs (m/z 255) obtained from the liquid-phase reaction of 1 mM α -terpineol + 0.2 mM NaCl + $[O_3]_0 = 0.05$ mM in neat water. The line is exponential decay fitted with a function of signal intensity (S) = $S_{01} \exp(-k_1 t)$. See main text for details.

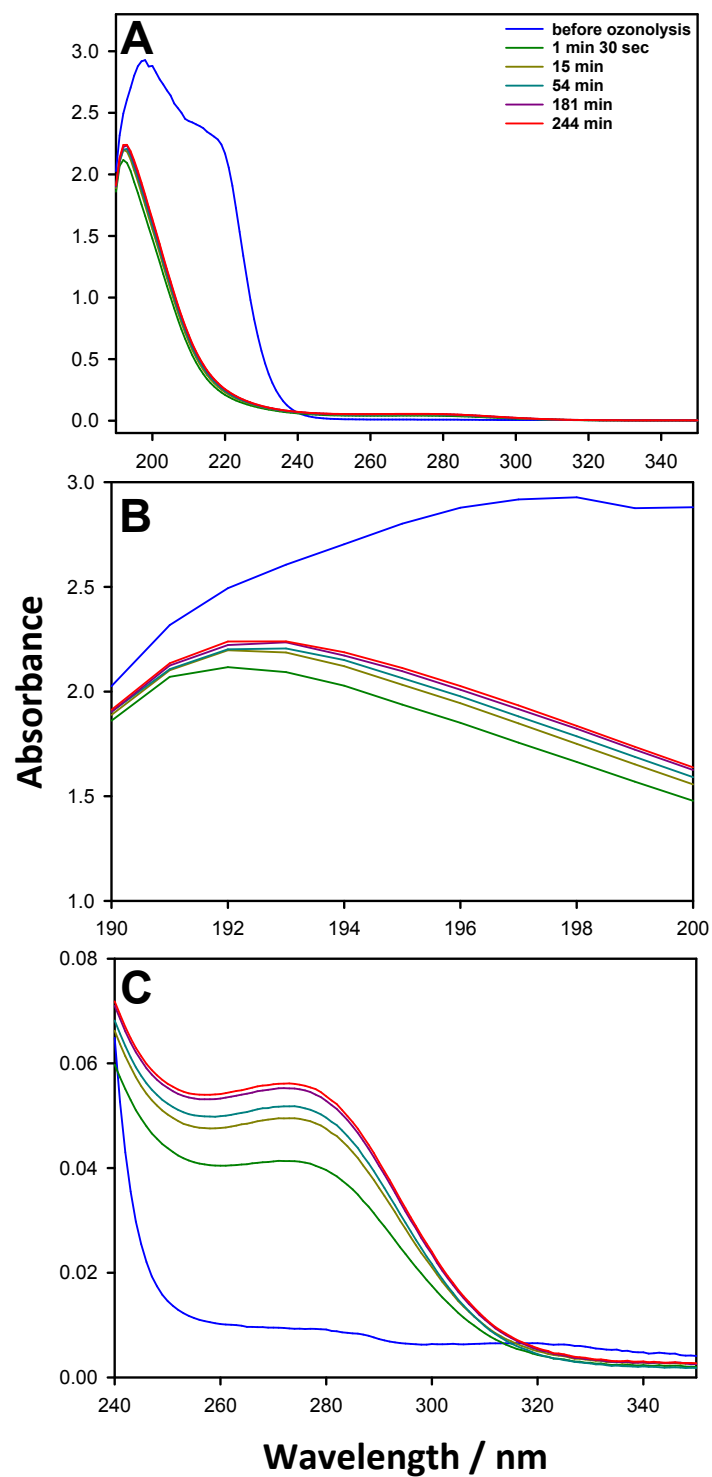
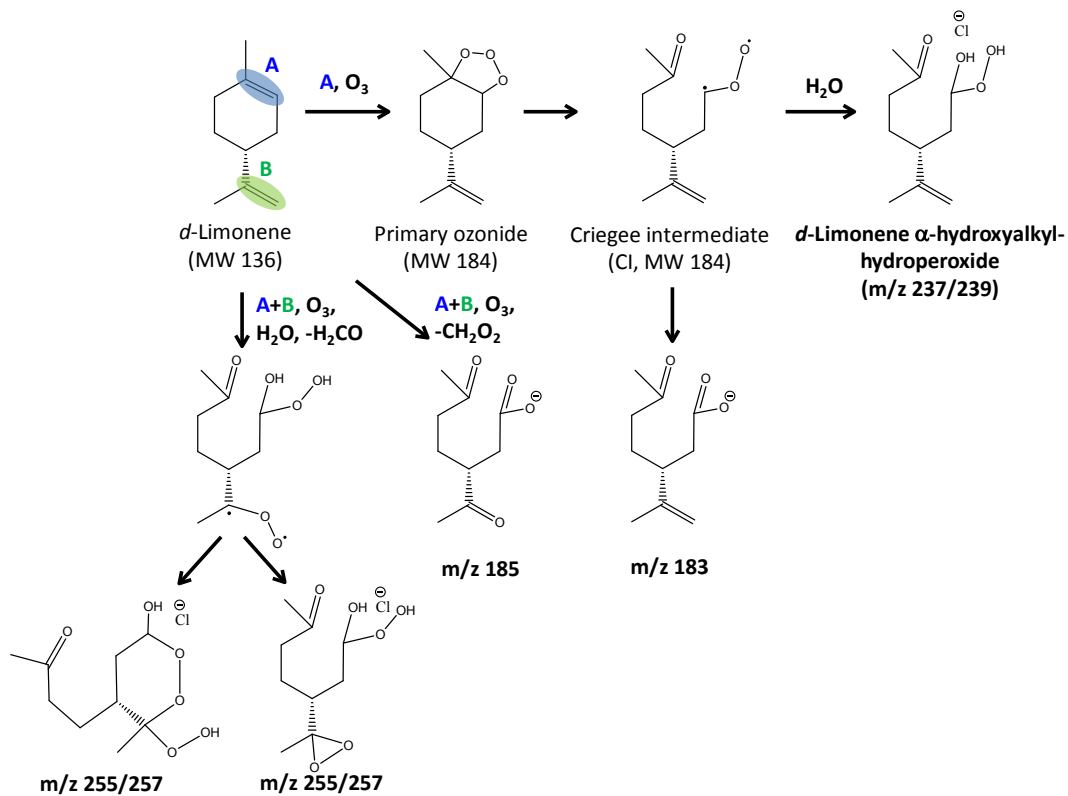
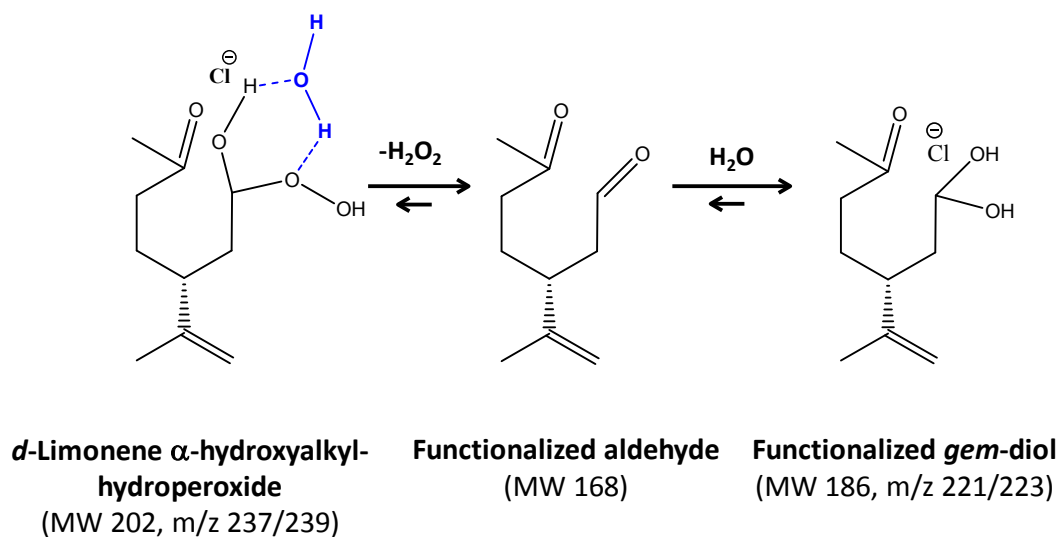


Figure S13 – A) UV-Vis spectra (measured by Agilent 8453) obtained from 1 mM β -caryophyllene + 0.2 mM NaCl in water:acetonitrile (50:50) solvent before/after ozonolysis ($[O_3]_0 = 0.05$ mM) as a function of time. B, C) Zooming-in spectra.

Scheme S1 – Mechanism of *d*-Limonene Ozonolysis in Aqueous Phases



Scheme S2 – Mechanism of Formation of *Gem*-diol from *d*-Limonene α -HHs



Scheme S3 – Mechanism of Formation of the m/z 246/248 Species (P2)

