

Supporting Information of

Water Dramatically Accelerates the Decomposition of

α -Hydroxyalkyl-Hydroperoxides in Aerosol Particles

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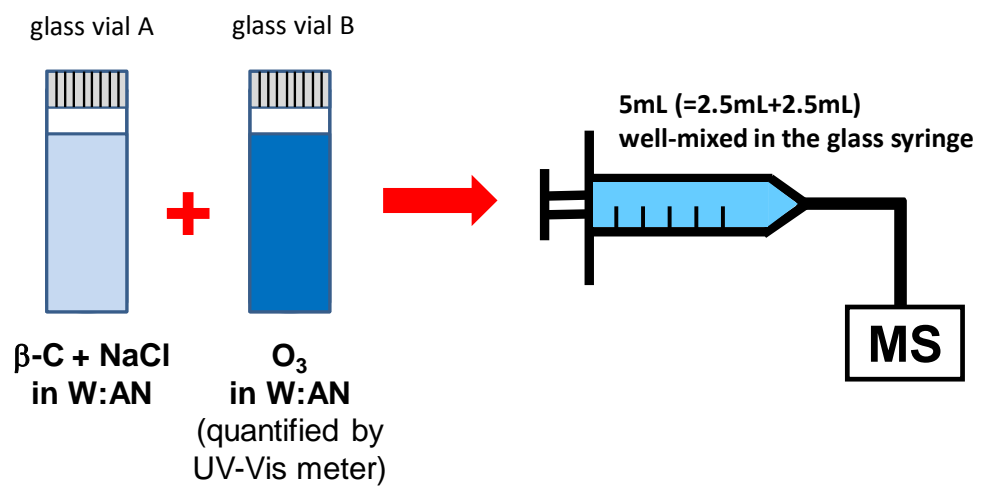


Figure S1 – Schematic setup and procedure of present methods.

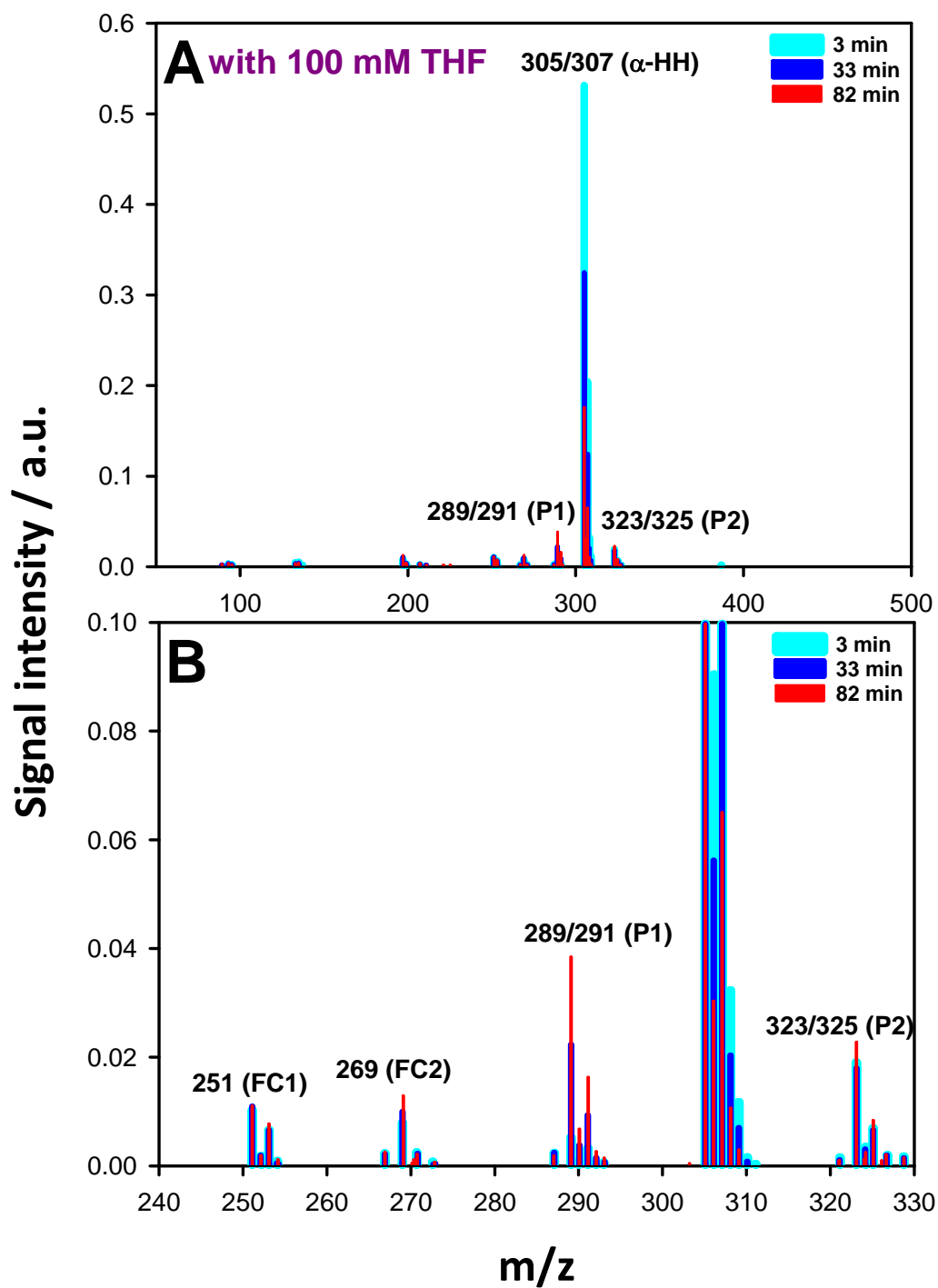


Figure S2 – Negative ion mass spectra of 1 mM β -caryophyllene + 0.2 mM NaCl + 100 mM tetrahydrofuran (THF) + 0.03 mM $O_3(aq)$ in W:AN (50:50 = vol:vol) solution.

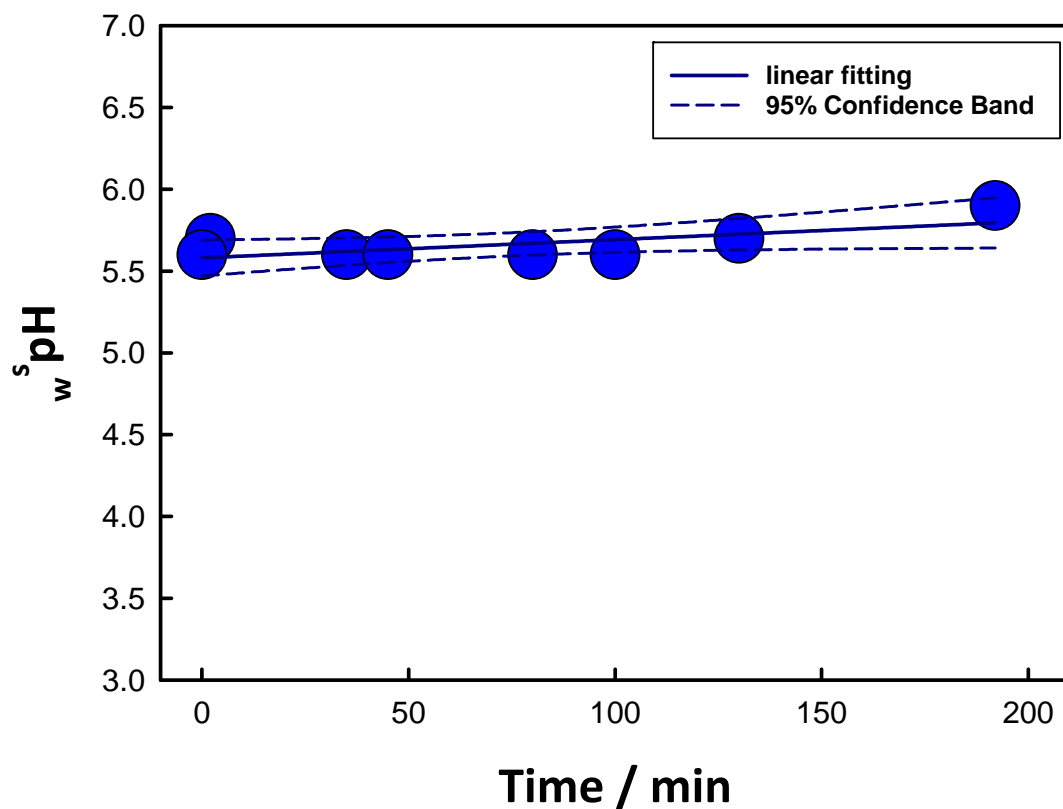


Figure S3 – Temporal profile of pH value from the solution of 1 mM β -caryophyllene + 0.2 mM NaCl in W:AN (50:50 = vol:vol) after bulk ozonolysis at $[\text{O}_3(\text{aq})]_0 = 0.04 \text{ mM O}_3(\text{aq})$. The pH values were measured with a calibrated pH meter (LAQUA F-74, Horiba). See Subirats et al. (Sep. Purif. Rev. 2007, 36, 231-255) for the definition of $s_w \text{pH}$.

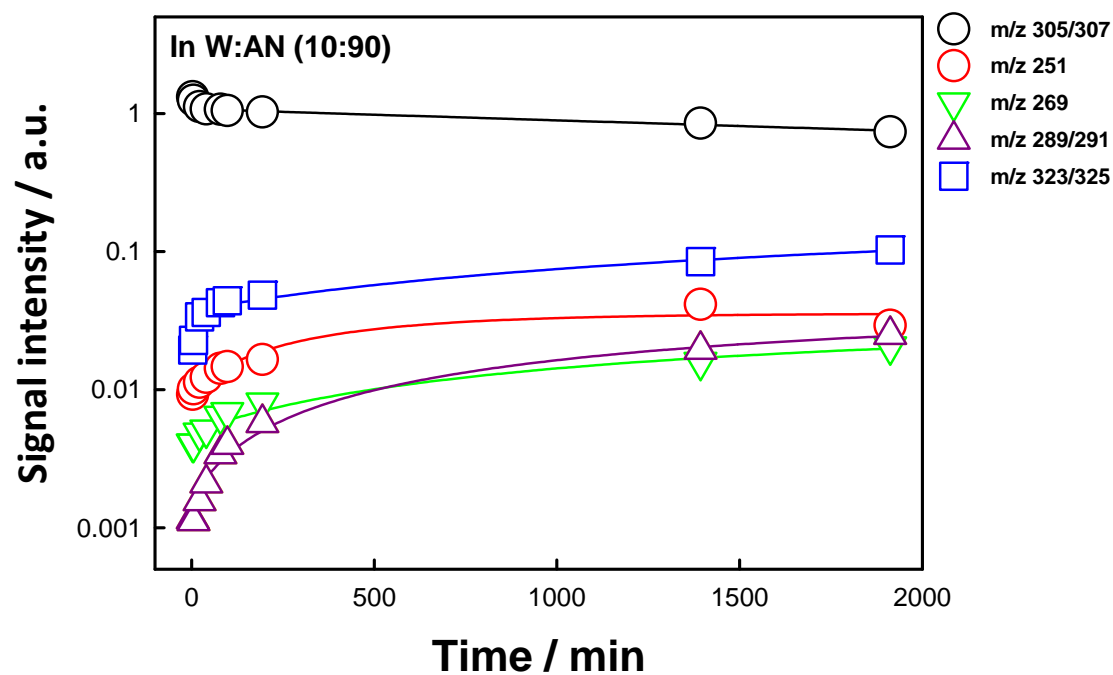


Figure S4 – Semi-log plot of mass spectral signal intensities of products (m/z 305/307, 251, 269, 289/291, 323/325) from (1 mM β -caryophyllene + 0.2 mM NaCl + 0.06 mM O_3) in water:acetonitrile (W:AN = 10:90 = vol:vol, [W] = 5.6 M) mixtures as a function of time. A black line for m/z 305/307 is a fitting curve of $S = S_0 \exp(-k_0t) + S_0' \exp(-k_1t)$. Other lines are guides to the eye. See text for details.

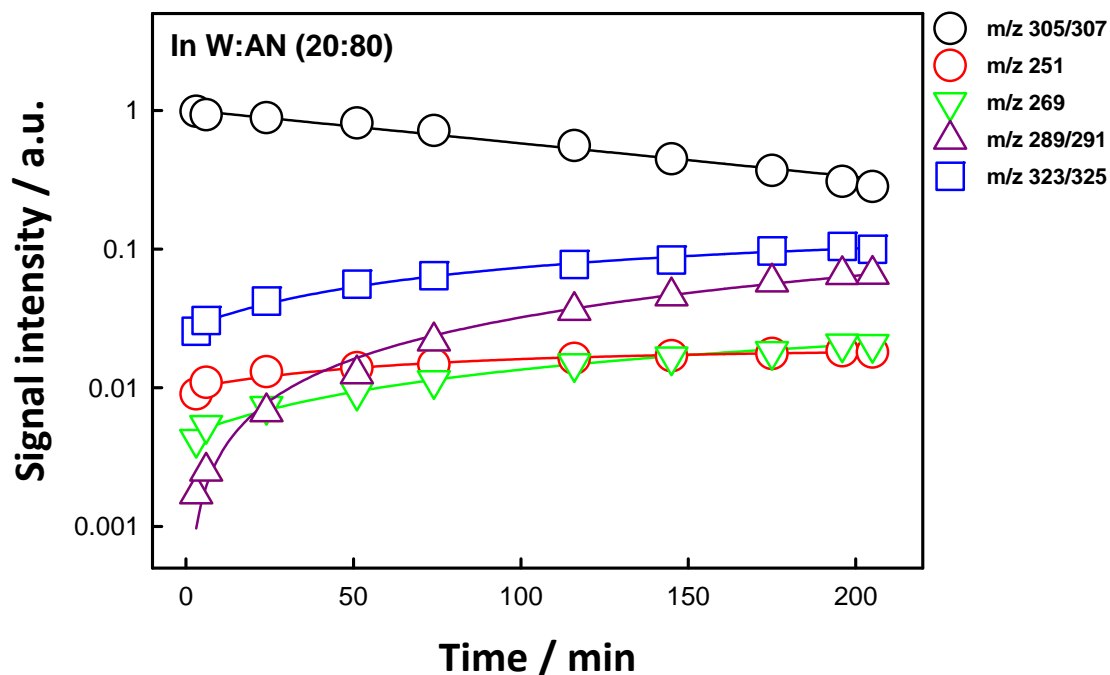


Figure S5 – Semi-log plot of mass spectral signal intensities of products (m/z 305/307, 251, 269, 289/291, 323/325) from (1 mM β -caryophyllene + 0.2 mM NaCl + 0.04 mM O_3) in water:acetonitrile (W:AN = 20:80 = vol:vol, [W] = 11.1 M) mixtures as a function of time. Lines are exponential decay for m/z 305/307 and rise for m/z 289/291 fitted with signal intensity $S = S_0 \exp(-k_1 t)$ and $S_\infty [1 - \exp(-kt)]$, respectively. Other products are fitted with signal intensity $S = S_0 + S_\infty [1 - \exp(-kt)]$. See text for details.

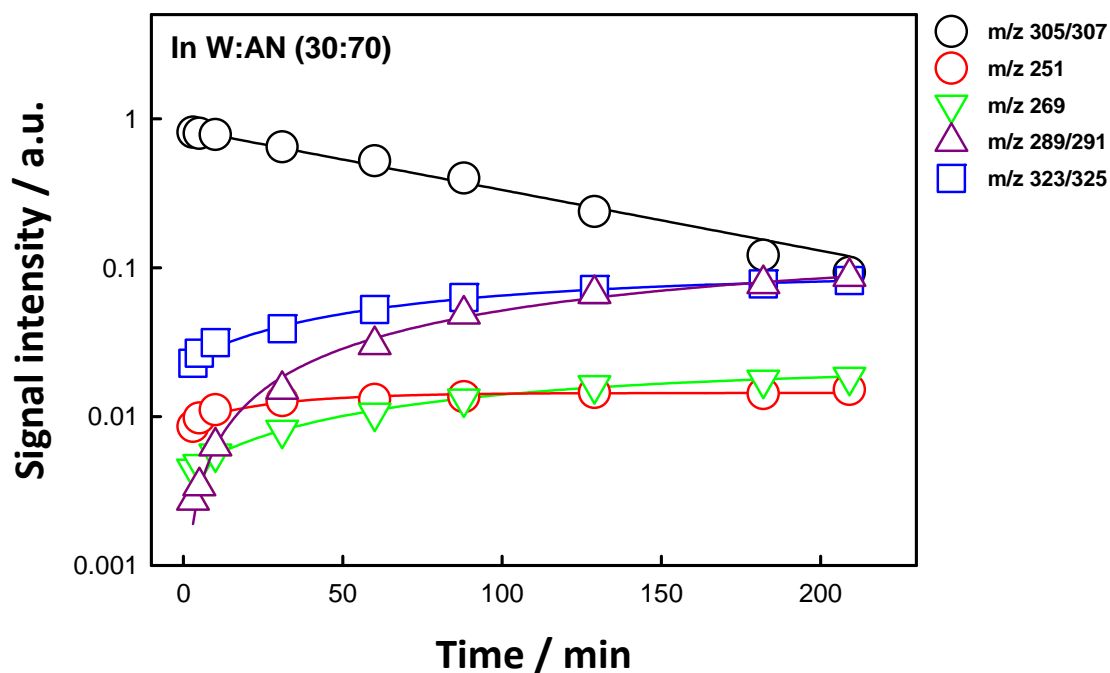


Figure S6 – Semi-log plot of mass spectral signal intensities of products (m/z 305/307, 251, 269, 289/291, 323/325) from (1 mM β -caryophyllene + 0.2 mM NaCl + 0.05 mM O_3) in water:acetonitrile (W:AN = 30:70 = vol:vol, [W] = 16.7 M) mixtures as a function of time. Lines are exponential decay for m/z 305/307 and rise for m/z 289/291 fitted with signal intensity $S = S_0 \exp(-k_1 t)$ and $S_\infty [1 - \exp(-kt)]$, respectively. Other products are fitted with signal intensity $S = S_0 + S_\infty [1 - \exp(-kt)]$. See text for details.

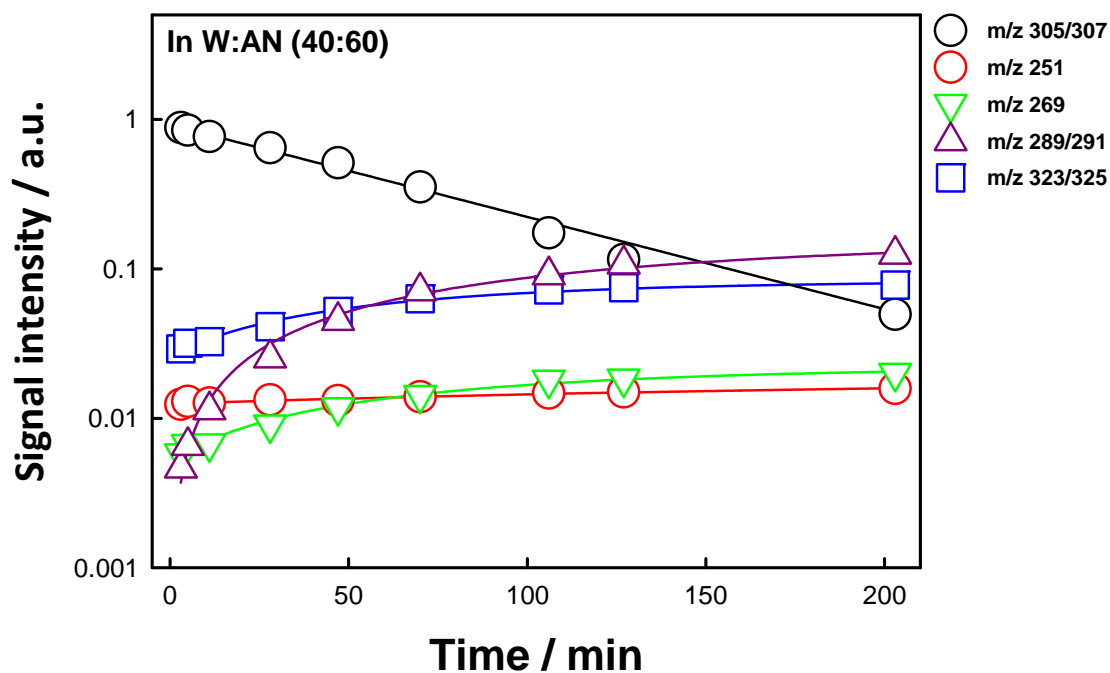


Figure S7 – Semi-log plot of mass spectral signal intensities of products (m/z 305/307, 251, 269, 289/291, 323/325) from (1 mM β -caryophyllene + 0.2 mM NaCl + 0.04 mM O_3) in water:acetonitrile (W:AN = 40:60 = vol:vol, [W] = 22.2 M) mixtures as a function of time. Lines are exponential decay for m/z 305/307 and rise for m/z 289/291 fitted with signal intensity $S = S_0 \exp(-k_1 t)$ and $S_\infty [1 - \exp(-kt)]$, respectively. Other products are fitted with signal intensity $S = S_0 + S_\infty [1 - \exp(-kt)]$. See text for details.

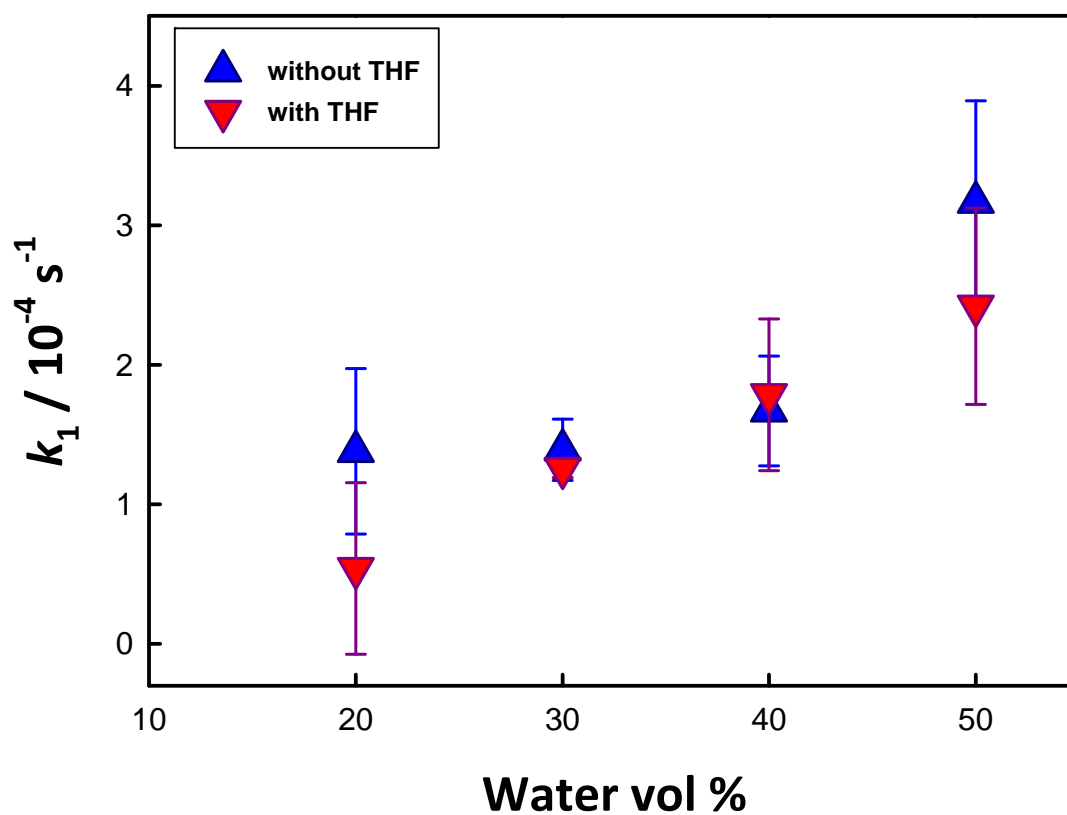


Figure S8 – The first-order rate constant k_1 derived from temporal profiles of α -HHs (m/z 305/307) in 1 mM β -caryophyllene + 0.2 mM NaCl + ~ 0.04 mM $\text{O}_3(\text{aq})$ in the absence (blue) or presence (red) of 100 mM tetrahydrofuran (THF) at 298 ± 3 K as a function of water vol % in W:AN solution. Error bars are derived from 3-5 independent measurements.

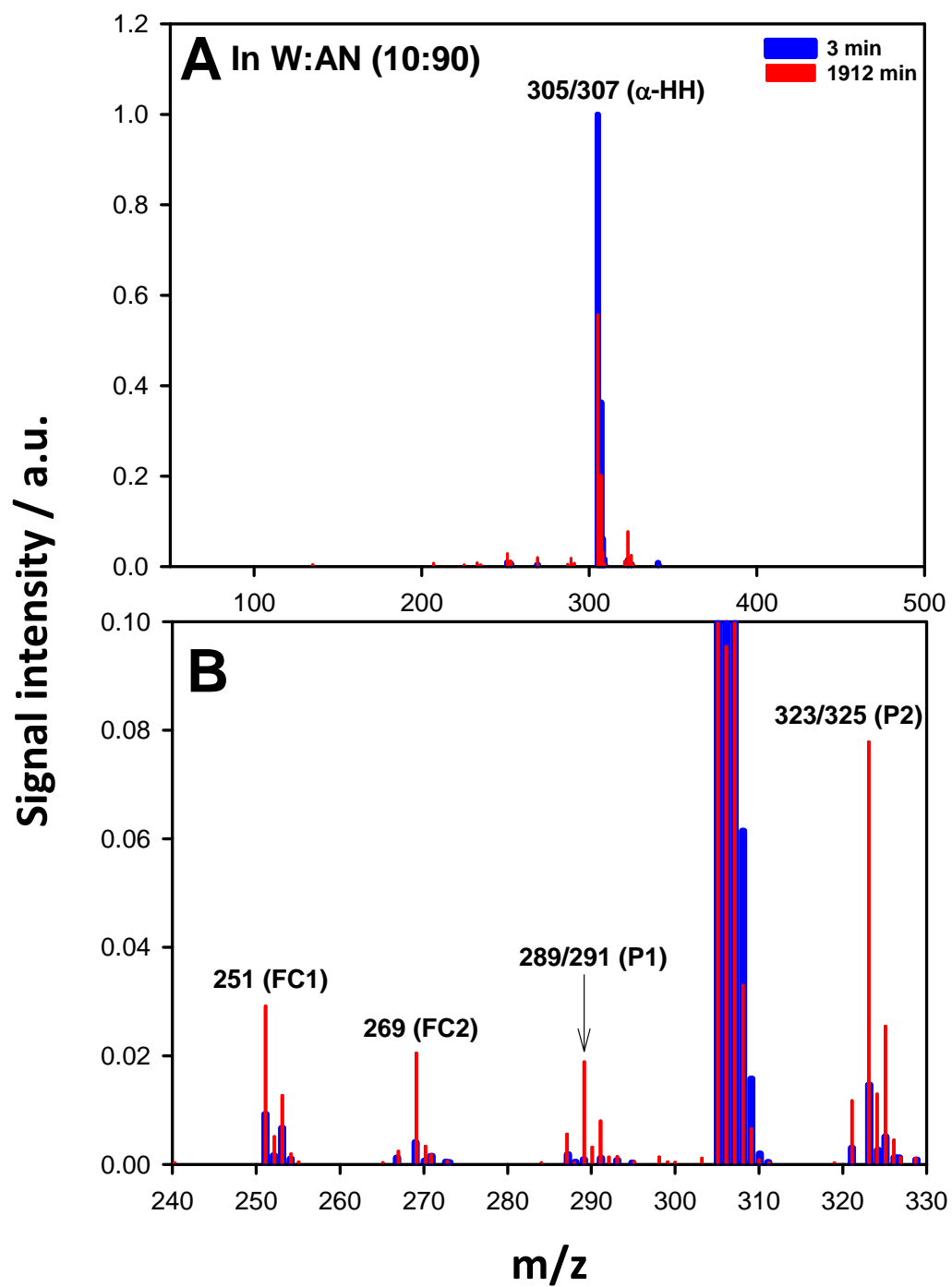


Figure S9 – Negative ion mass spectra of 1 mM β -caryophyllene + 0.2 mM NaCl + 0.06 mM $O_3(aq)$ in W:AN (10:90 = vol:vol) solution after 3 min and 1912 min (\sim 32 hours).