

Supporting Information of:

# **Criegee Intermediates React with Levoglucosan on Water**

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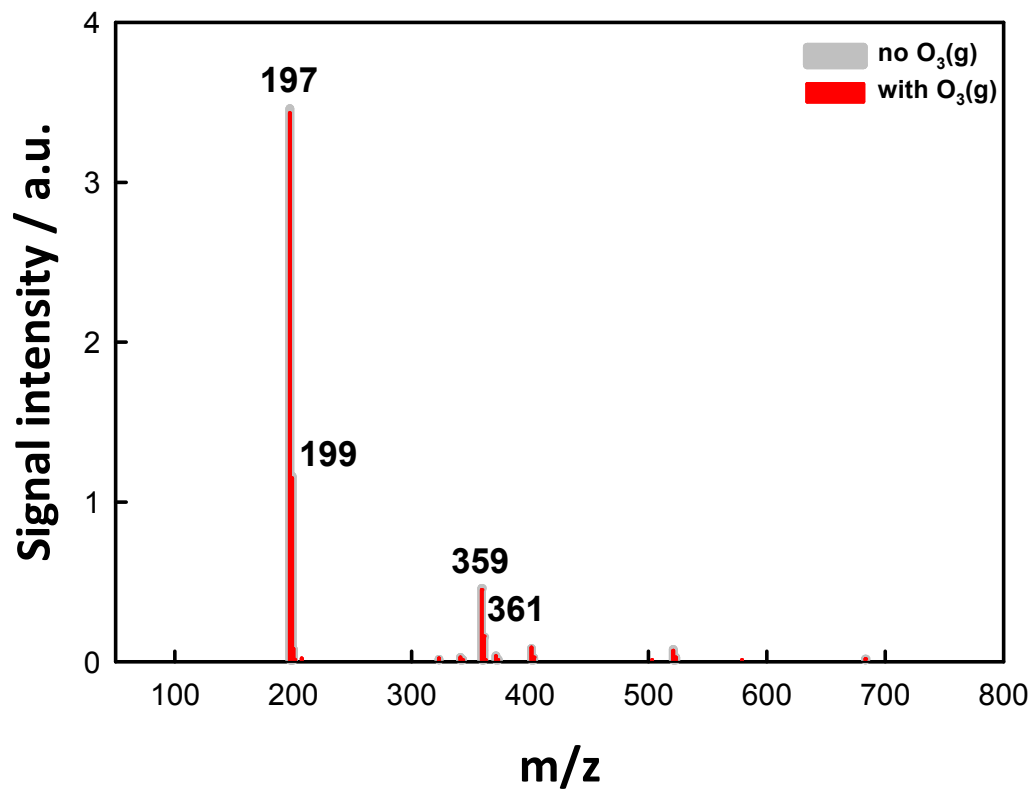
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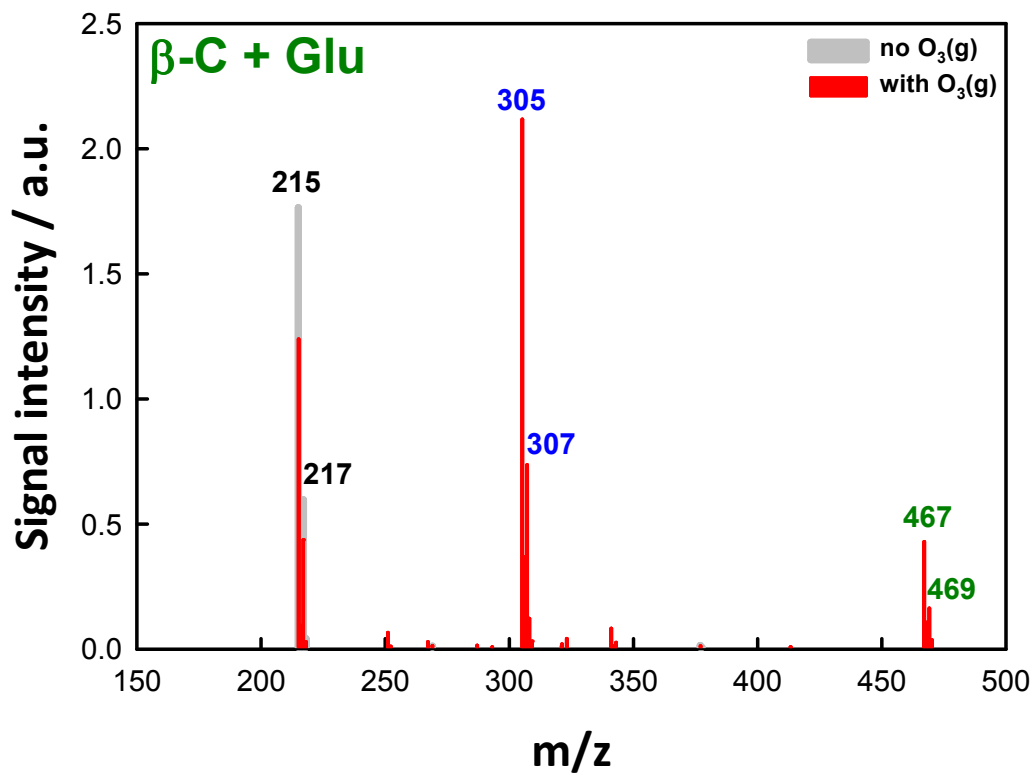
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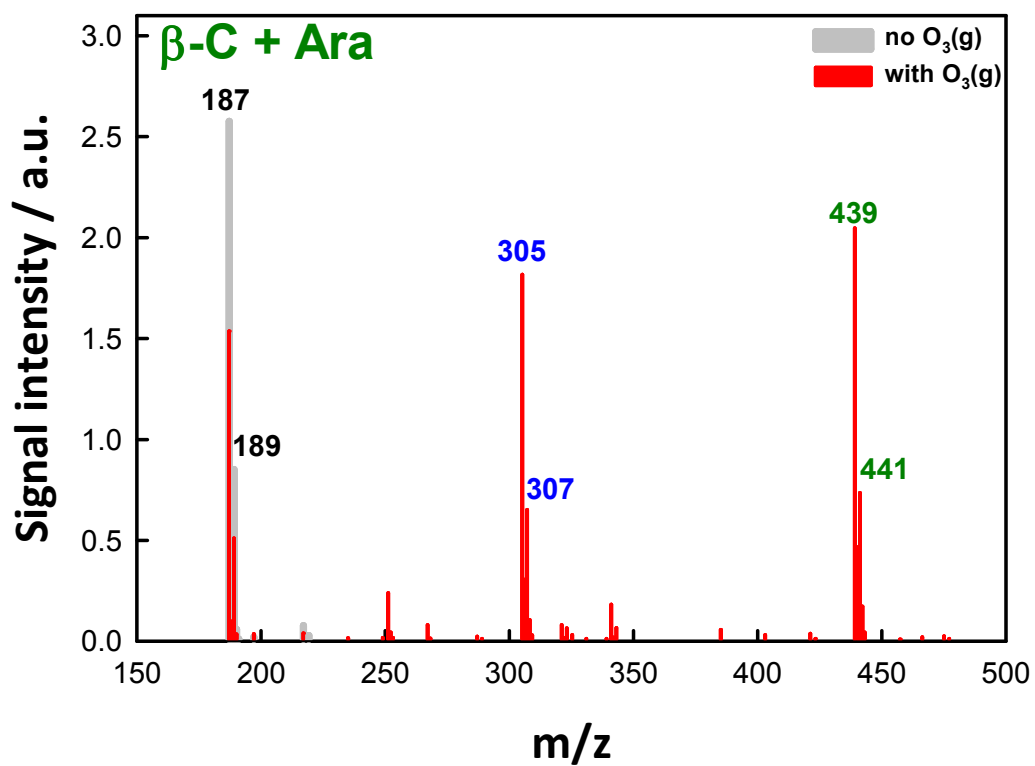
**FIGURE S1:** Negative ion mass spectra from 100 mM levoglucosan + 0.2 mM NaCl in AN:W (4:1 = vol:vol) solution microjets in the absence (gray) and presence of O<sub>3</sub>(g) (red,  $E = 2.4 \times 10^{11}$  molecules cm<sup>-3</sup> s). The m/z 197;199 and 359;361 correspond to chloride-Levo, and chloride-(Levo)<sub>2</sub> adducts, respectively. Note that no decrease of reactants and no product peaks are observed even with the largest O<sub>3</sub>(g) exposure.



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**Figure S2** – Negative ion electrospray mass spectra of 1 mM β-C + 0.2 mM NaCl + 10 mM glucose in AN:W (4:1=vol:vol) solution microjets (gray), or those exposed to O<sub>3</sub>(g) (red,  $E = 2.3 \times 10^{11}$  molecules cm<sup>-3</sup> s) at 1 atm and 298 K. The m/z 215;217 and 467;469 signals correspond to chloride-adducts of glucose and alkoxy-hydroperoxides (C<sub>21</sub> ether species) from the β-C's Cls + glucose reaction, respectively.

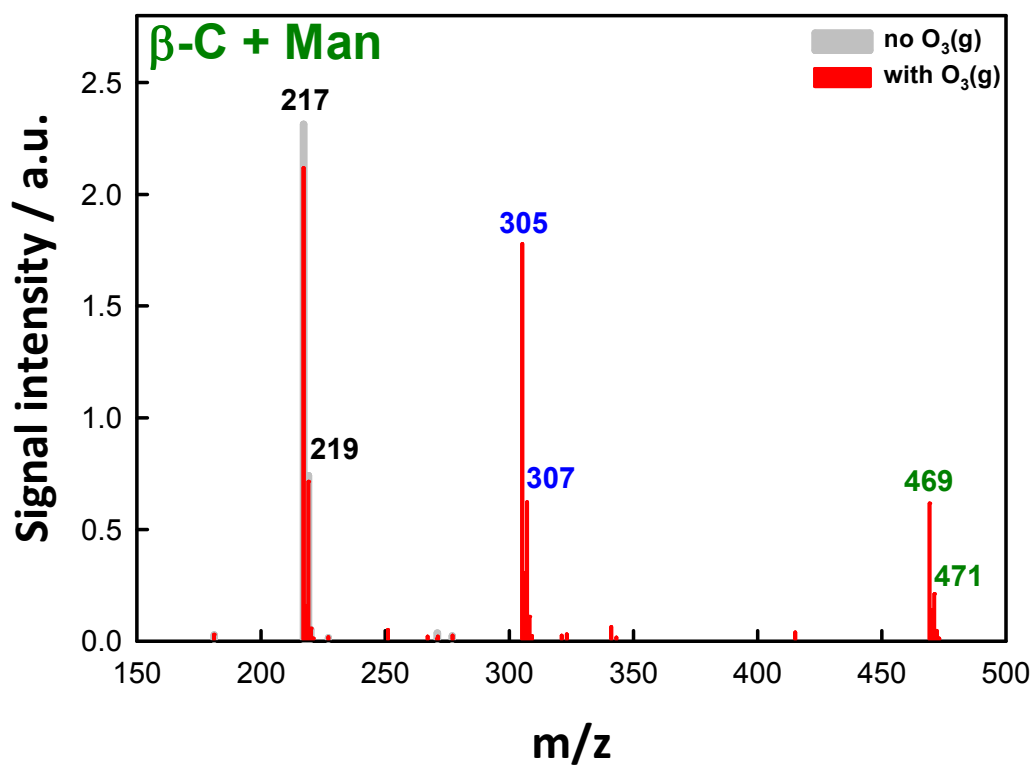
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**Figure S3** – Negative ion electrospray mass spectra of 1 mM β-C + 0.2 mM NaCl + 10 mM arabitol in AN:W (4:1=vol:vol) solution microjets (gray), or those exposed to O<sub>3</sub>(g) (red,  $E = 2.4 \times 10^{11}$  molecules cm<sup>-3</sup> s) at 1 atm and 298 K. The m/z 187;189 and 439;441 signals correspond to chloride-adducts of arabitol and alkoxy-hydroperoxides (C<sub>20</sub> ether species) from the β-C's Cls + arabitol reaction, respectively.

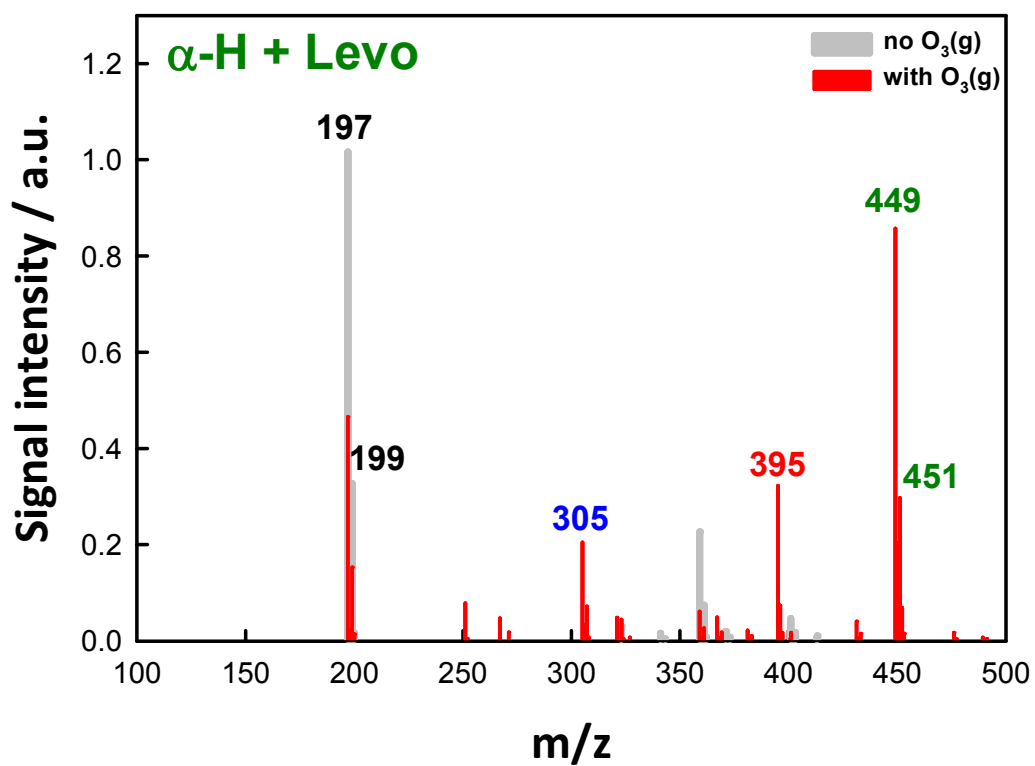
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**Figure S4** – Negative ion electrospray mass spectra of 1 mM β-C + 0.2 mM NaCl + 10 mM mannitol in AN:W (4:1=vol:vol) solution microjets (gray), or those exposed to O<sub>3</sub>(g) (red,  $E = 2.4 \times 10^{11}$  molecules cm<sup>-3</sup> s) at 1 atm and 298 K. The m/z 217;219 and 469;471 signals correspond to chloride-adducts of mannitol and alkoxy-hydroperoxides (C<sub>21</sub> ether species) from the β-C's Cls + mannitol reaction, respectively.

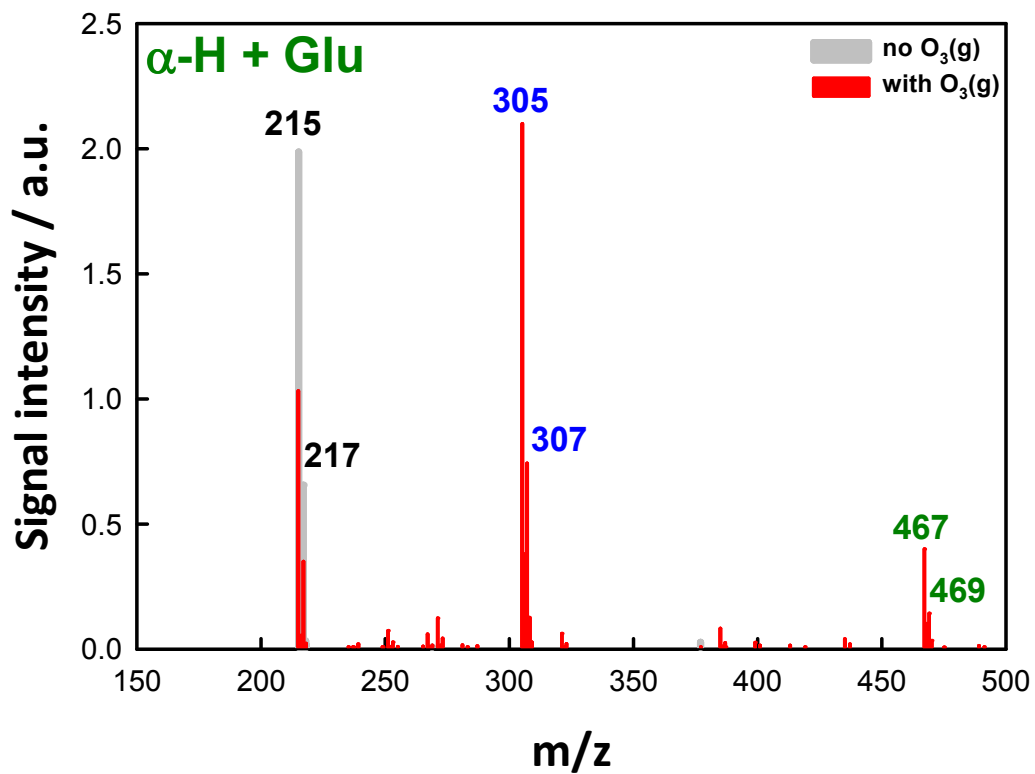
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**Figure S5** – Negative ion electrospray mass spectra of 1 mM  $\alpha$ -H + 0.2 mM NaCl + 100 mM levoglucosan in AN:W (4:1=vol:vol) solution microjets (gray), or those exposed to O<sub>3</sub>(g) (red,  $E = 2.4 \times 10^{11}$  molecules cm<sup>-3</sup> s) at 1 atm and 298 K. The m/z 449;451 signals correspond to chloride-adducts of alkoxy-hydroperoxides (C<sub>21</sub> ether species) from the  $\alpha$ -H's Cls + levoglucosan reaction.

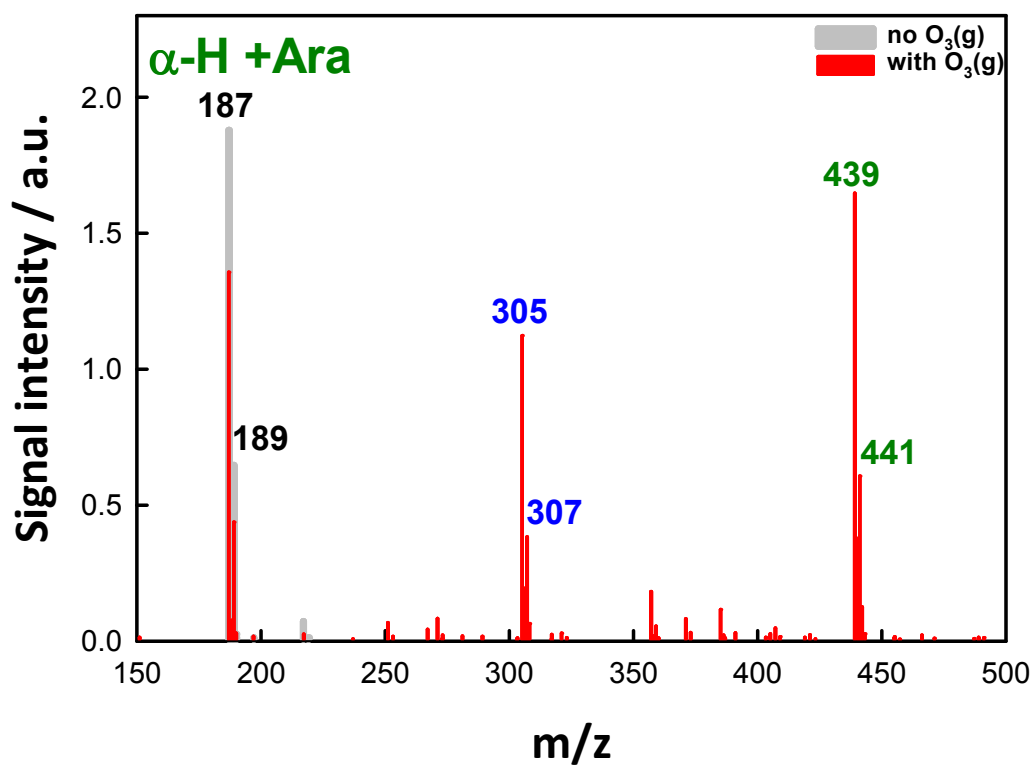
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**Figure S6** – Negative ion electrospray mass spectra of 1 mM  $\alpha\text{-H}$  + 0.2 mM NaCl + 10 mM glucose in AN:W (4:1=vol:vol) solution microjets (gray), or those exposed to  $\text{O}_3(\text{g})$  (red,  $E = 2.4 \times 10^{11}$  molecules  $\text{cm}^{-3}$  s) at 1 atm and 298 K. The m/z 467;469 signals correspond to chloride-adducts of alkoxy-hydroperoxides ( $\text{C}_{21}$  ether species) from the  $\alpha\text{-H}$ 's Cls + glucose reaction.

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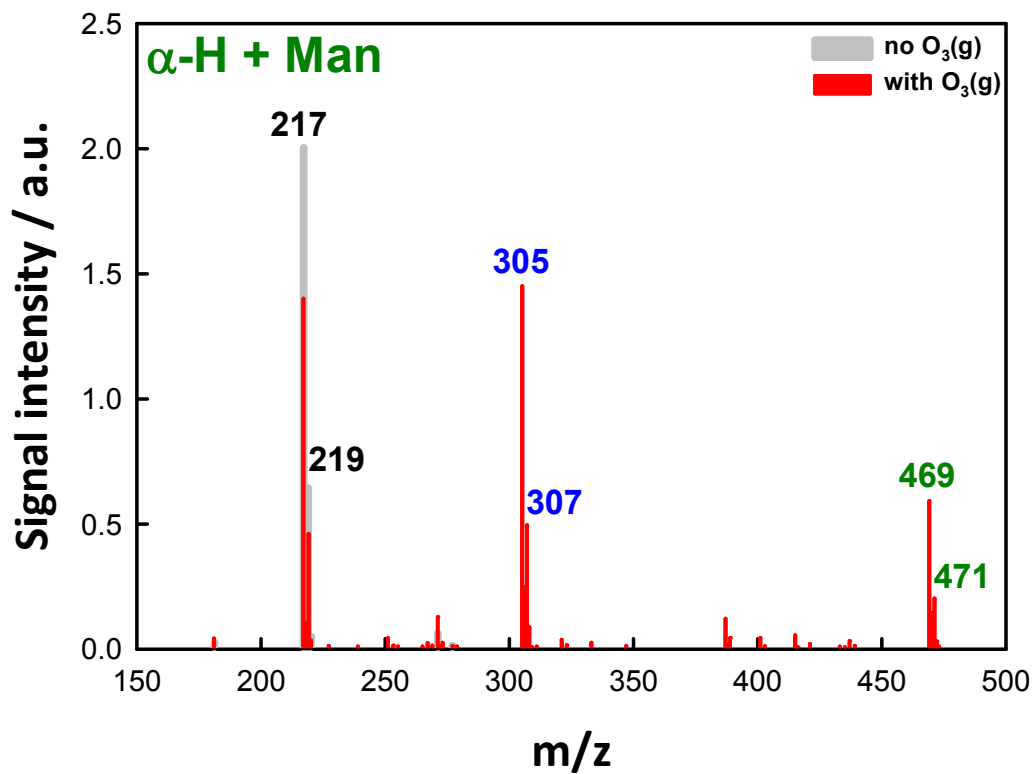


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**Figure S7** – Negative ion electrospray mass spectra of 1 mM  $\alpha\text{-H}$  + 0.2 mM NaCl + 10 mM arabitol in AN:W (4:1=vol:vol) solution microjets (gray), or those exposed to  $\text{O}_3(\text{g})$  (red,  $E = 2.4 \times 10^{11}$  molecules  $\text{cm}^{-3}$  s) at 1 atm and 298 K. The  $m/z$  439;441 signals correspond to chloride-adducts of alkoxy-hydroperoxides ( $\text{C}_{20}$  ether species) from the  $\alpha\text{-H}$ 's Cls + arabitol reaction.

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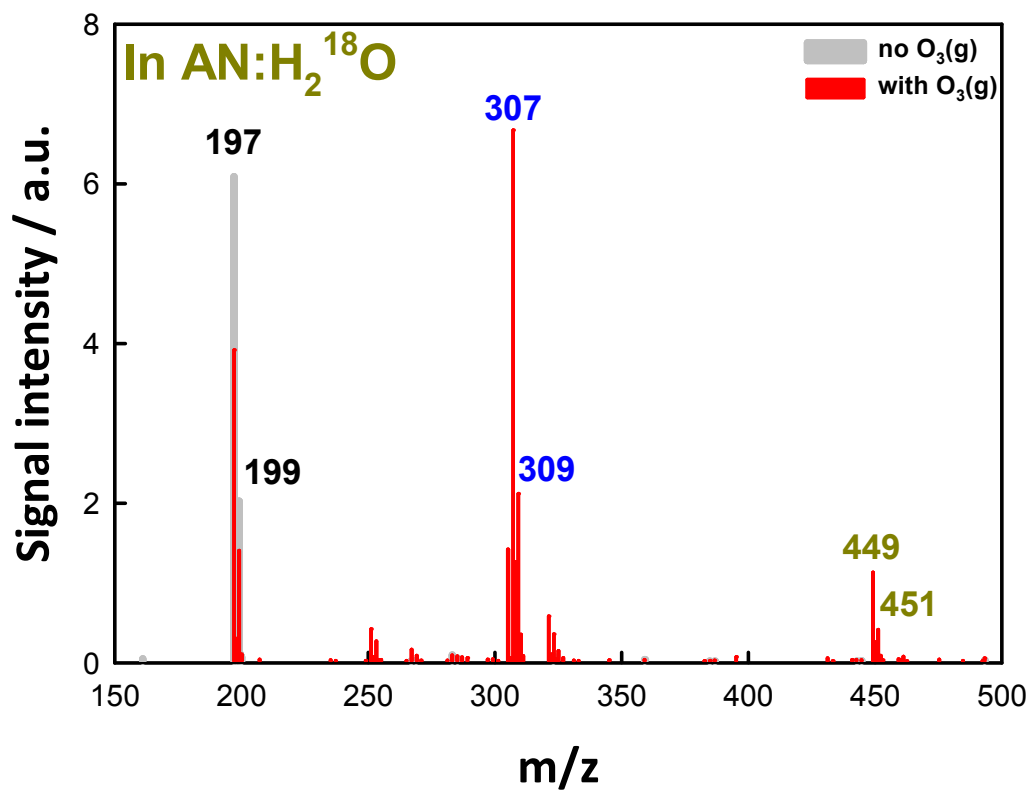




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**Figure S8** – Negative ion electrospray mass spectra of 1 mM  $\alpha\text{-H}$  + 0.2 mM NaCl + 10 mM mannitol in AN:W (4:1=vol:vol) solution microjets (gray), or those exposed to  $\text{O}_3(\text{g})$  (red,  $E = 2.3 \times 10^{11}$  molecules  $\text{cm}^{-3}$  s) at 1 atm and 298 K. The m/z 469;471 signals correspond to chloride-adducts of alkoxy-hydroperoxides ( $\text{C}_{21}$  ether species) from the  $\alpha\text{-H}$ 's Cls + mannitol reaction.

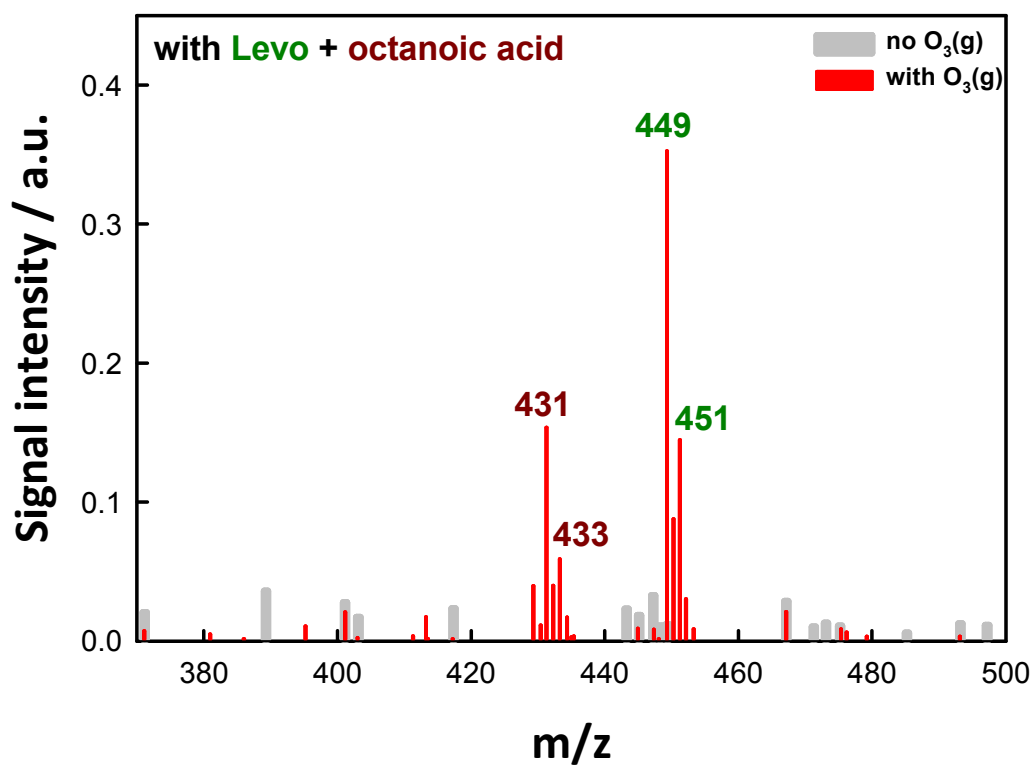
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**Figure S9** – Negative ion electrospray mass spectra of 1 mM  $\beta$ -C + 3 mM NaCl + 10 mM levoglucosan in AN:H<sub>2</sub><sup>18</sup>O (4:1=vol:vol) solution microjets (gray), or those exposed to O<sub>3</sub>(g) (red,  $E = 2.4 \times 10^{11}$  molecules cm<sup>-3</sup> s).

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**Figure S10** – Negative ion electrospray mass spectra of 1 mM  $\beta$ -C + 0.2 mM NaCl + 100 mM levoglucosan + 100 mM octanoic acid in AN:W (4:1=vol:vol) solution microjets (gray), or those exposed to O<sub>3</sub>(g) (red,  $E = 2.4 \times 10^{11}$  molecules cm<sup>-3</sup> s) at 1 atm and 298 K. The m/z 431;433 signals correspond to  $\alpha$ -acyloxy-hydroperoxides from the Cls + octanoic acid reaction.

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