Supporting Information:

Reactivity of Monoterpene Criegee Intermediates at Gas-Liquid Interfaces

Junting Qiu[a], Shinnosuke Ishizuka[b], Kenichi Tonokura[a], Agustín J. Colussi[c], Shinichi Enami*[b]

[a]Graduate School of Frontier Sciences, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa 277-8563, Japan.

[b]National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba 305-8506, Japan

[c]Ronald and Maxine Linde Center for Global Environmental Science, California Institute of Technology, Pasadena, California, 91125, U.S.A.

*Author to whom correspondence should be addressed:

S.E. enami.shinichi@nies.go.jp, phone: +81-29-850-2770

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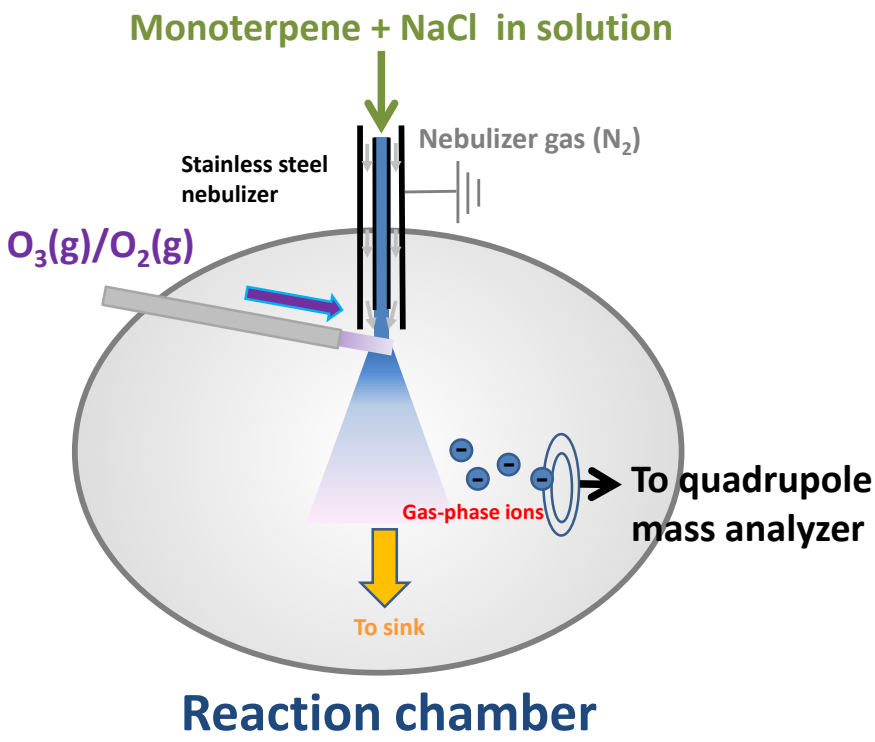


Figure S1 – Schematic diagram of the experimental setup.

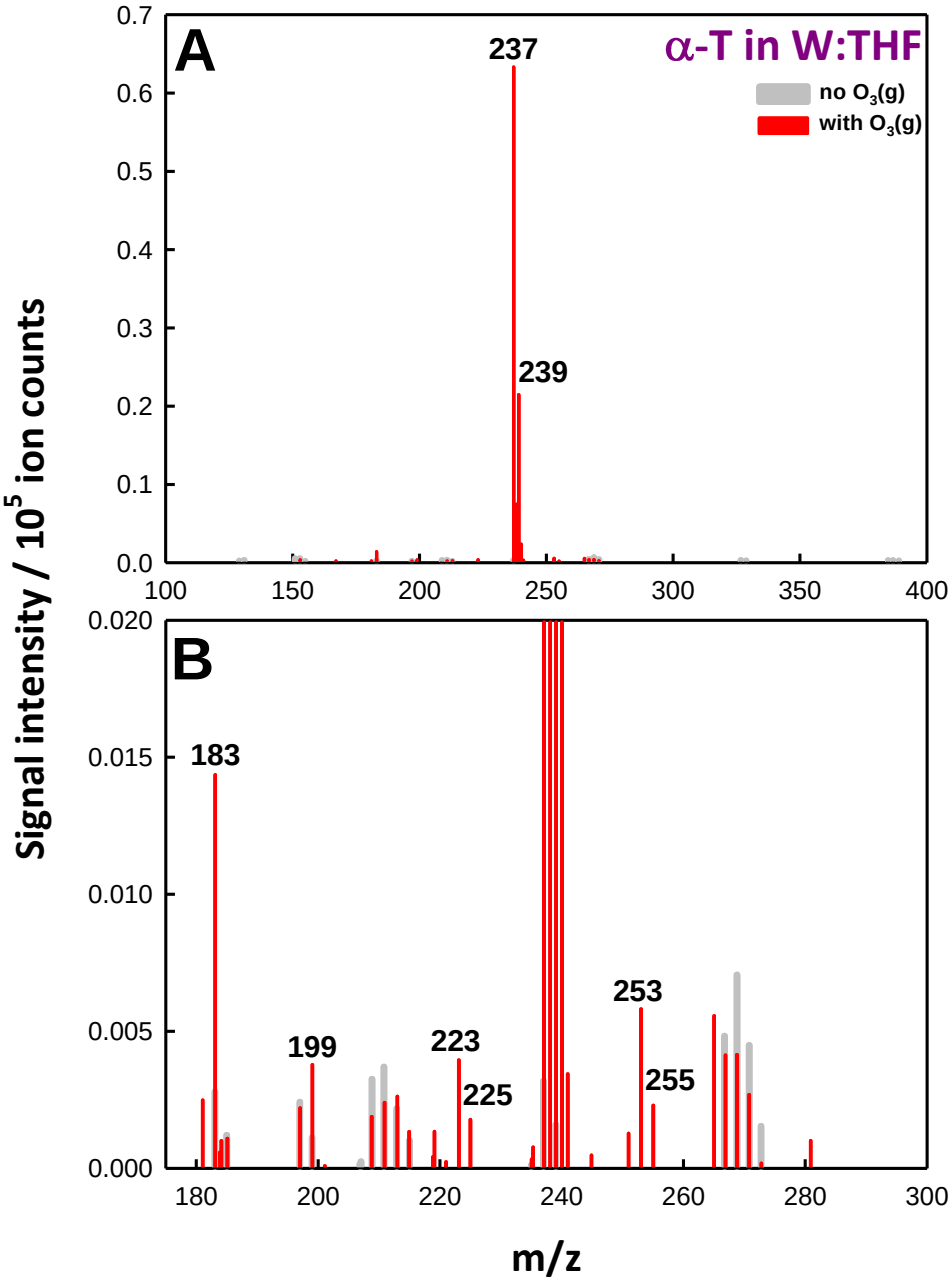


Figure S2 –A) Negative ion mass spectrum of 1 mM α-terpinene + 0.2 mM NaCl in W:THF (1:4 = vol:vol) solution microjets before (gray), and during exposure to O_3(g) (red, E = 3.1 x 10^{11} molecules cm^{-3} s) at 1 atm and 298 K. The m/z 237;239 signals correspond to chloride-adducts of α-hydroxy-hydroperoxides. B) Zooming-in on the minor products.

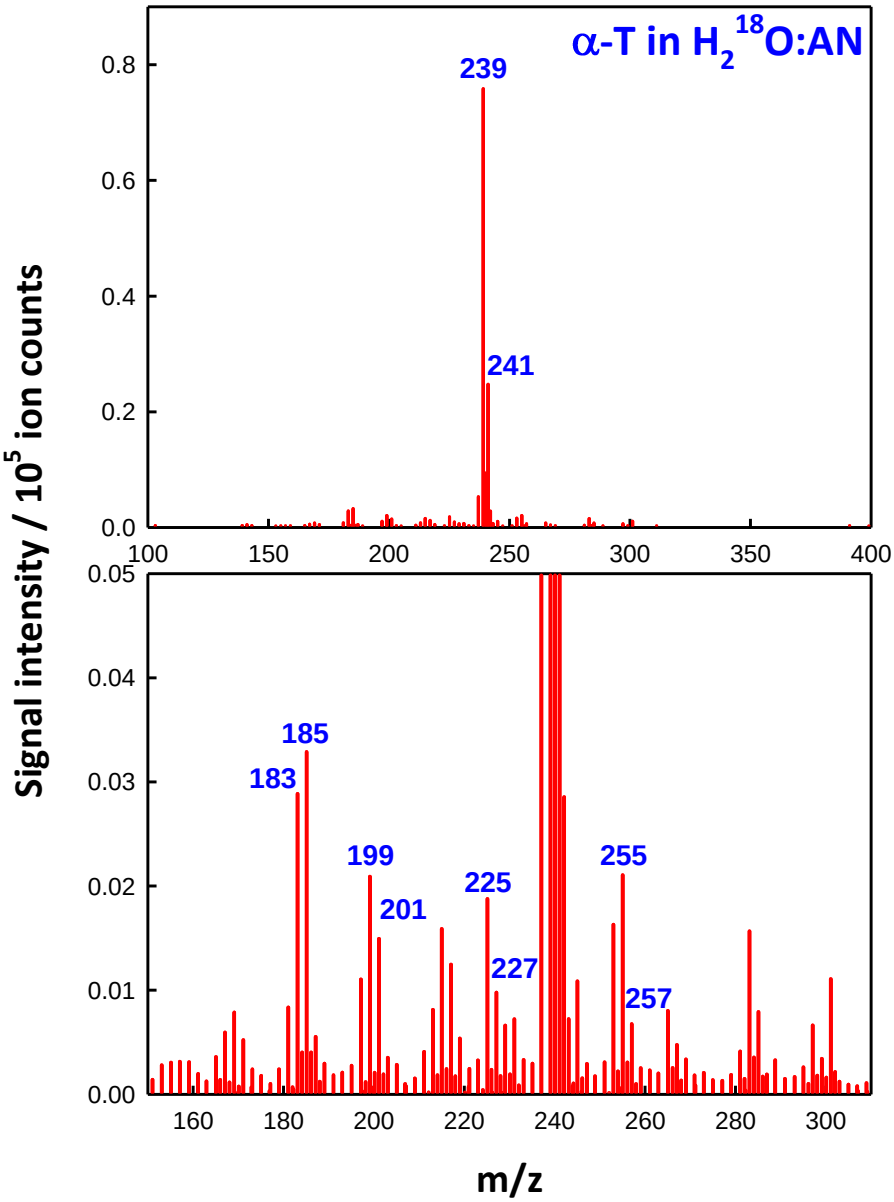


Figure S3 –A) Negative ion mass spectrum of 1 mM α-terpinene + 0.2 mM NaCl in $H_2{}^{18}O$:AN (1:4 = vol:vol) solution microjets exposed to O_3(g) (E = 5.1 x 10^{11} molecules cm^{-3} s) at 1 atm and 298 K. The m/z 239;241 signals correspond to chloride-adducts of α-hydroxy-hydroperoxides from the reaction of CIs with $(H_2{}^{18}O)_n$. B) Zooming-in on the minor products.

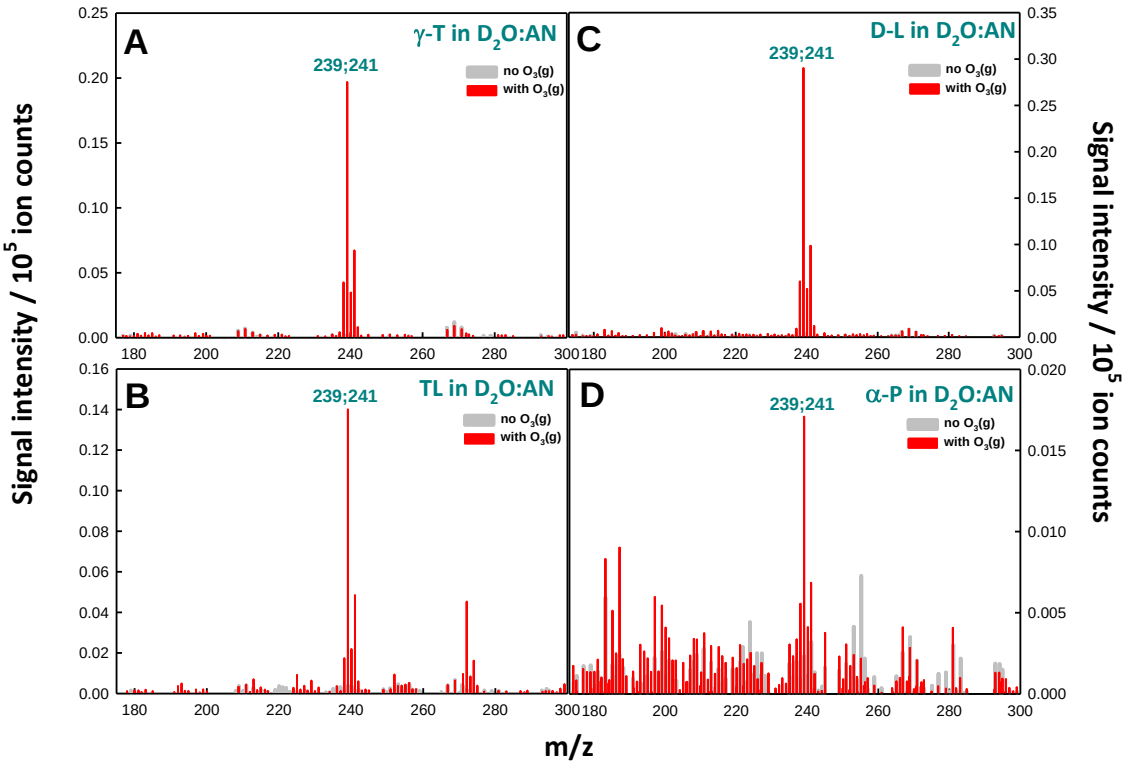


Figure S4 – Negative ion mass spectra of 1 mM γ-terpinene (A), terpinolene (B), d-limonene (C) or α-pinene (D) + 0.2 mM NaCl in D_2O:AN (1:4 = vol:vol) solution microjets before (gray), and during exposure to O_3(g) (red, $E \approx 5.2 \times 10^{11}$ molecules cm^{-3} s) at 1 atm and 298 K. The m/z 239;241 signals correspond to chloride-adducts of α-hydroxy-hydroperoxides from the reaction of CIs with $(D_2O)_n$.

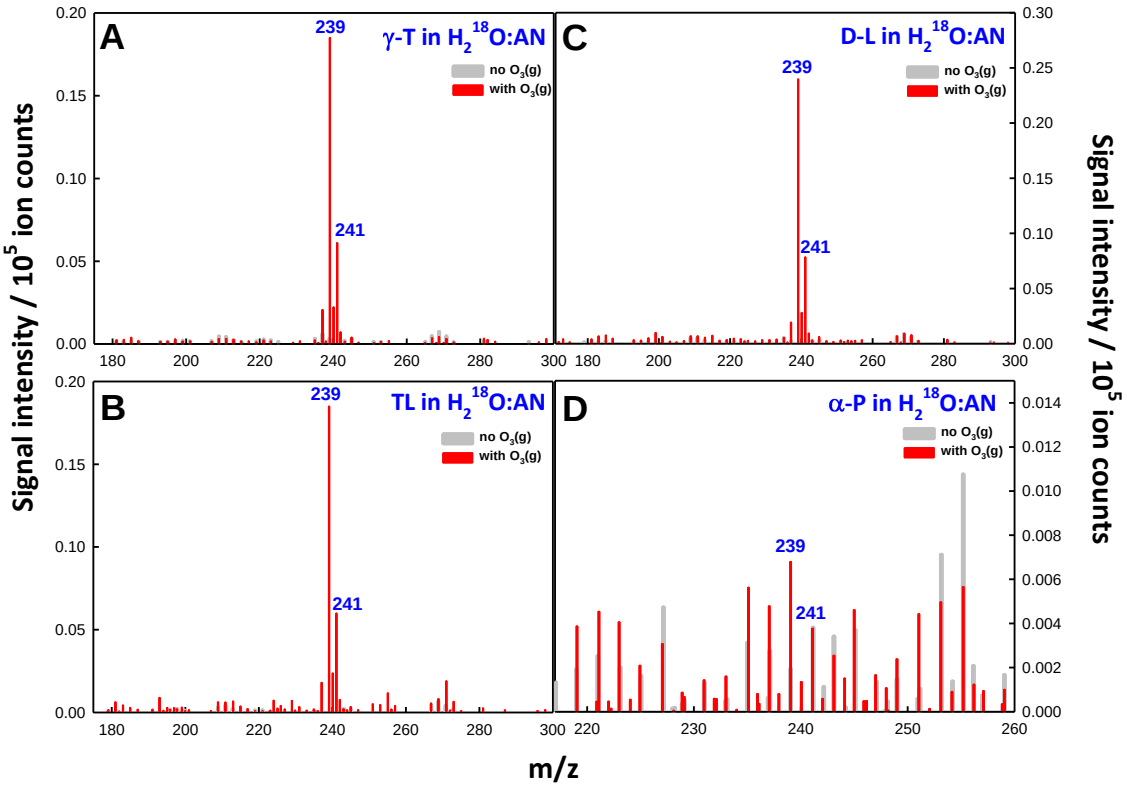


Figure S5 – Negative ion mass spectra of 1 mM γ-terpinene (A), terpinolene (B), d-limonene (C) or α-pinene (D) + 0.2 mM NaCl in $H_2{}^{18}O$:AN (1:4 = vol:vol) solution microjets before (gray), and during exposure to O_3(g) (red, $E \approx 5.2 \times 10^{11}$ molecules cm^{-3} s) at 1 atm and 298 K. The m/z 239;241 signals correspond to chloride-adducts of α-hydroxy-hydroperoxides from the reaction of CIs with $(H_2{}^{18}O)_n$.

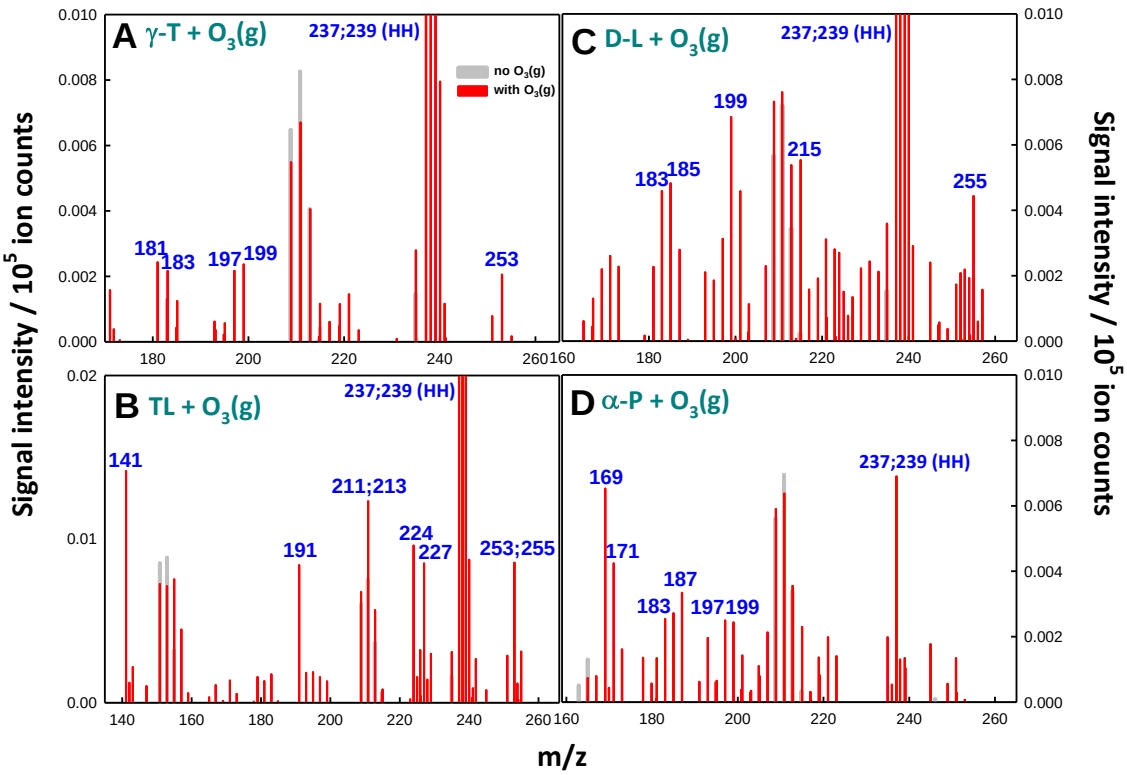


Figure S6 – Zooming-in mass spectra of 1 mM γ-terpinene (A), terpinolene (B), d-limonene (C) or α-pinene (D) + 0.2 mM NaCl in W:AN (1:4 = vol:vol) solution microjets before (gray), and during exposure to O_3(g) (red, $E \approx 5.2 \times 10^{11}$ molecules cm^{-3} s) at 1 atm and 298 K.

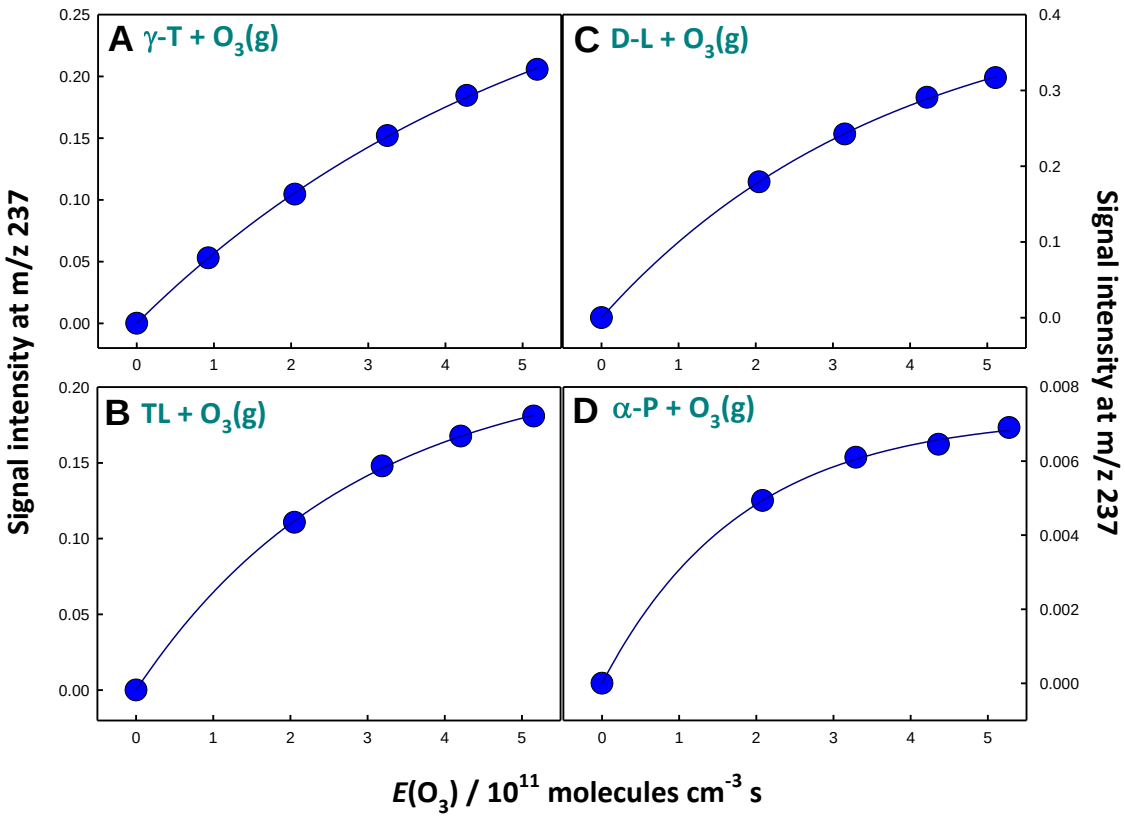


Figure S7 – Mass spectral signal intensities of hydroxy-hydroperoxide product (m/z 237) from 1 mM γ-terpinene (A), terpinolene (B), d-limonene (C), or α-pinene (D) + 0.2 mM NaCl in W:AN (1:4 = vol:vol) solution microjets exposed to O_3(g) as a function of O_3(g) exposure (in 10^{11} molecules cm^{-3} s). Connecting lines are guides to the eye.

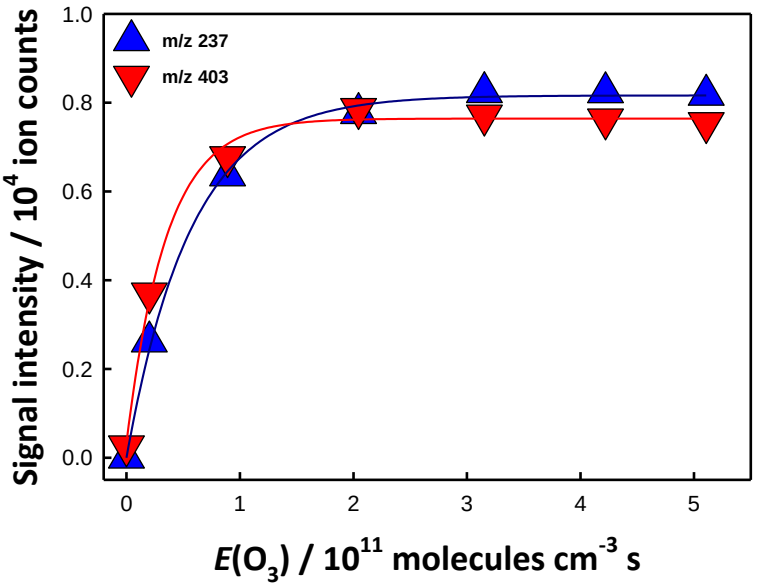


Figure S8 – Product mass spectral signal intensities for m/z 237 (hydroxy-hydroperoxides) and m/z 403 (C_{20} ester hydroperoxides) from 1 mM α-terpinene + 0.2 mM NaCl + 10 mM *cis*-pinonic acid in W:AN (1:4 = vol:vol) solution microjets exposed to O_3(g) as a function of O_3(g) exposure (in 10^{11} molecules cm^{-3} s). Connecting lines are guides to the eye.

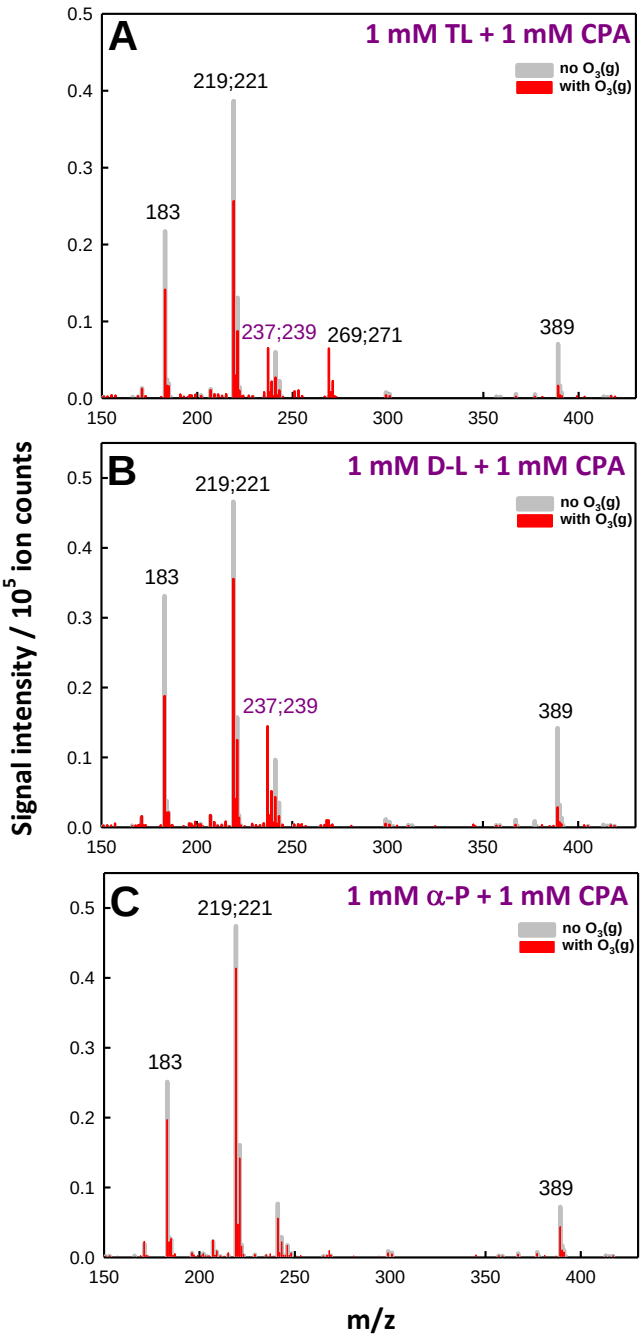


Figure S9 – Negative ion mass spectra of 1 mM terpinolene (A), d-limonene (B) or α-pinene (C) + 0.2 mM NaCl + 1 mM *cis*-pinonic acid in W:AN (1:4 = vol:vol) solution microjets before (gray), and during exposure to O_3(g) (red, $E \approx 5.1 \times 10^{11}$ molecules cm^{-3} s) at 1 atm and 298 K. Note the absence of mass signals at m/z 403;405 (from CIs + CPA) in the presence of O_3(g).

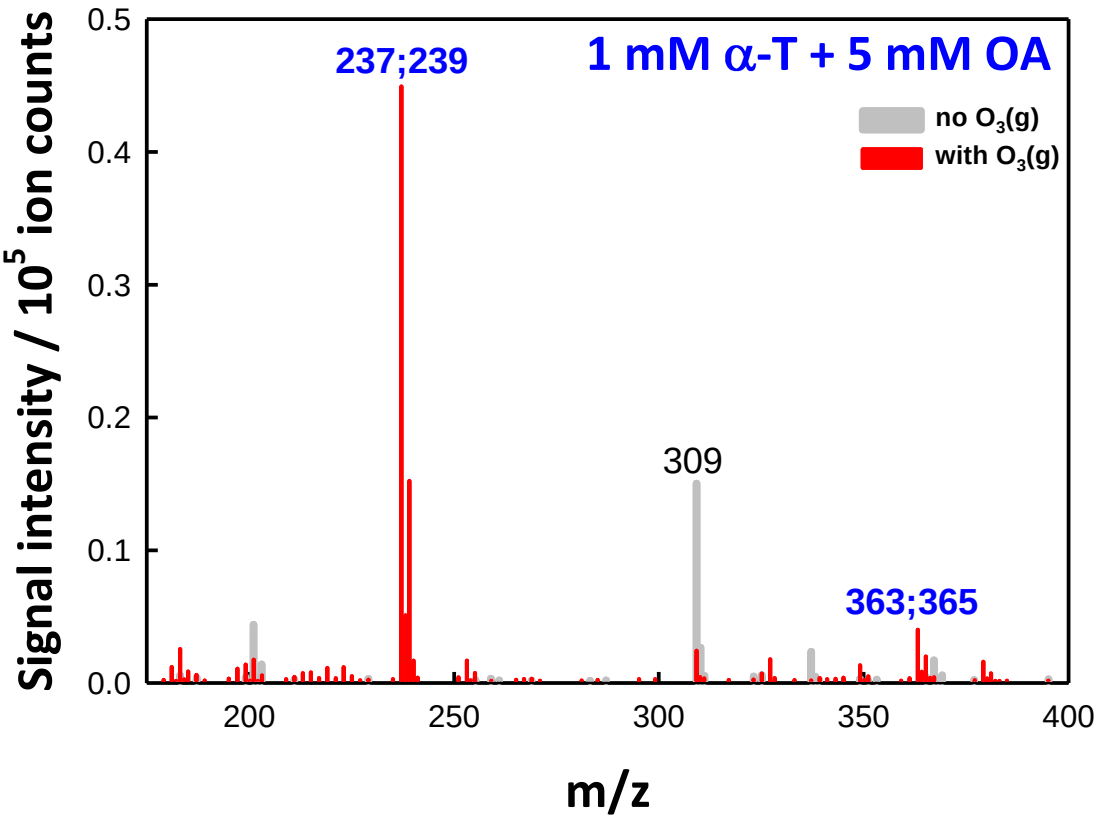


Figure S10 – Negative ion mass spectra of 1 mM α-terpinene + 0.2 mM NaCl + 5 mM octanoic acid (OA) in W:AN (1:4 = vol:vol) solution microjets (gray), or those exposed to O_3(g) (red, E = 5.4 x 10^{11} molecules cm^{-3} s) at 1 atm and 298 K. The signals at m/z 309 appearing without O_3(g) exposure is assigned to $Na(OA)_2^-$. In the presence of O_3(g), new mass signals at m/z 363;365 (from CIs + OA) in addition to those at m/z 237;239 (from CIs + $(H_2O)_n$) appear.

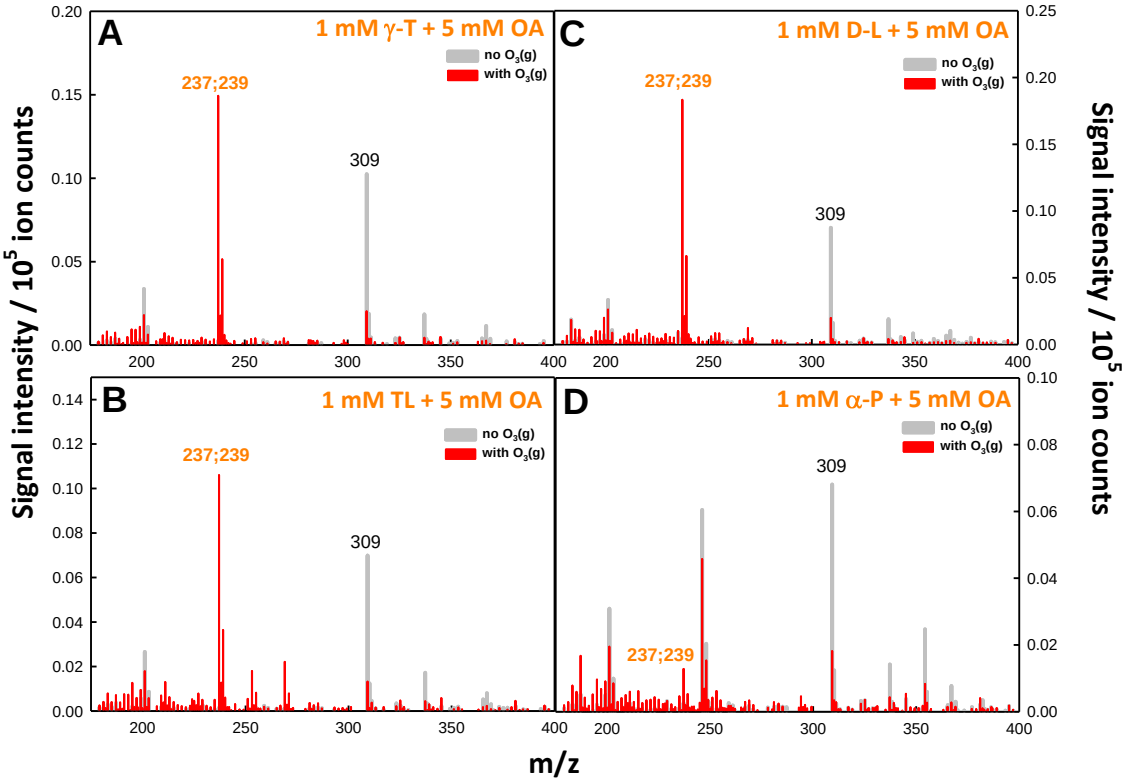
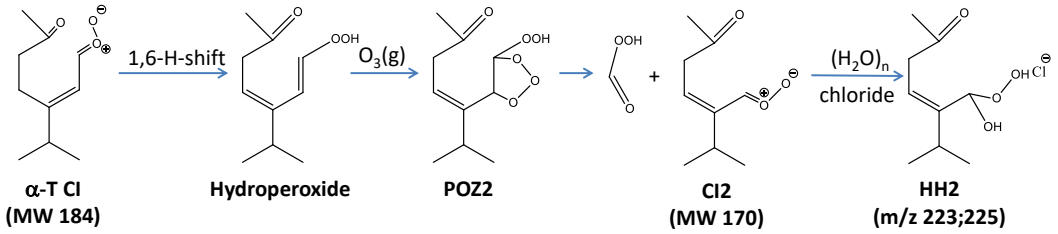
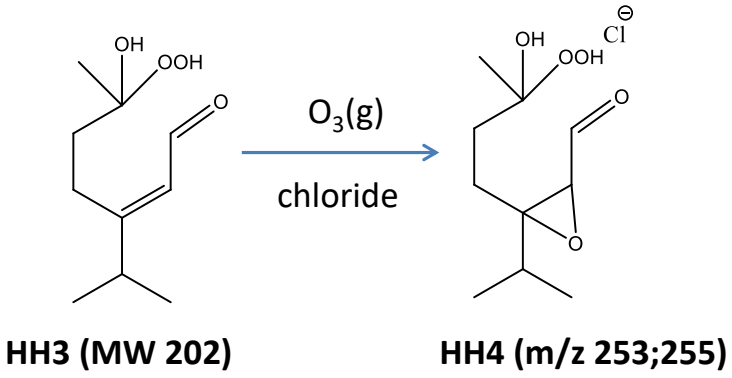


Figure S11 – Negative ion mass spectra of 1 mM γ-terpinene (A), terpinolene (B), d-limonene (C) or α-pinene (D) + 0.2 mM NaCl + 5 mM octanoic acid (OA) in W:AN (1:4 = vol:vol) solution microjets before (gray), and during exposure to O_3(g) (red, $E \approx 5.3 \times 10^{11}$ molecules cm^{-3} s) at 1 atm and 298 K. Note the absence of mass signals at m/z 363;365 (from CIs + OA) in the presence of O_3(g).

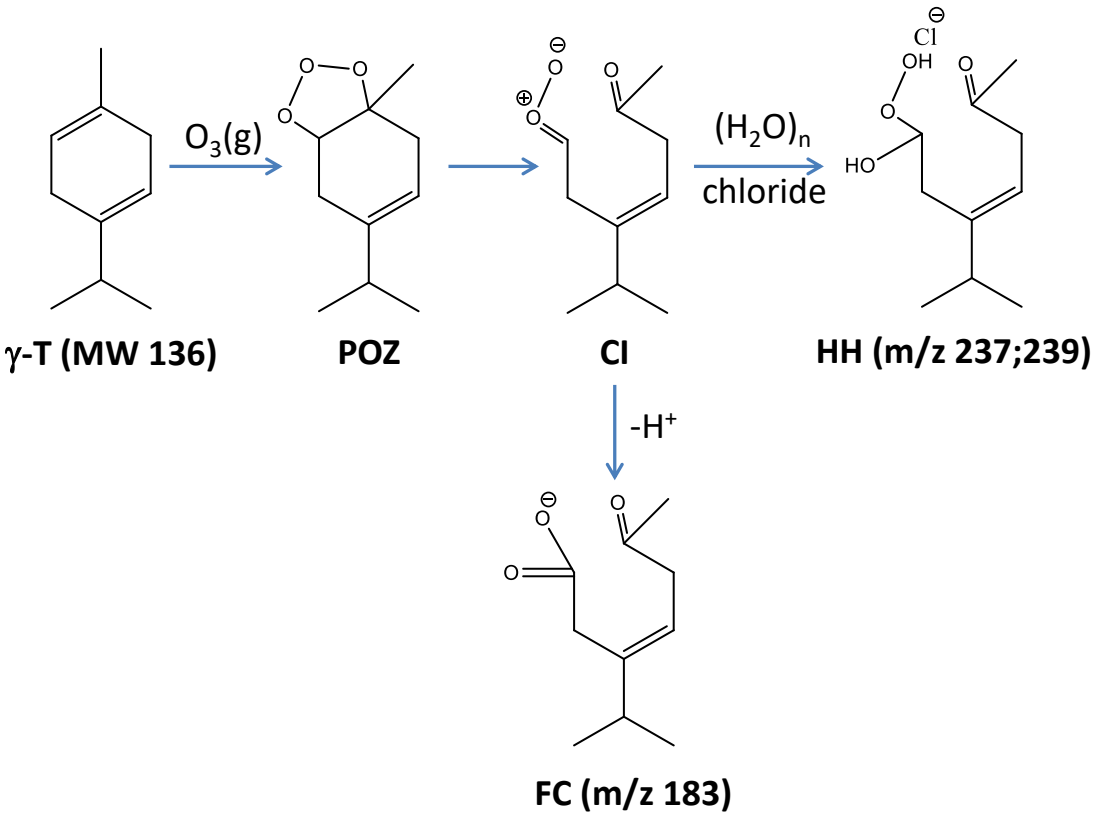
Scheme S1. Scheme for generation of the m/z 223;225 product during ozonolysis of α-terpinene at the gas–liquid interface. The proposed 1,6-hydrogen-shift is in accordance with previous reports.[1-2] Representative structures are shown among isomers.



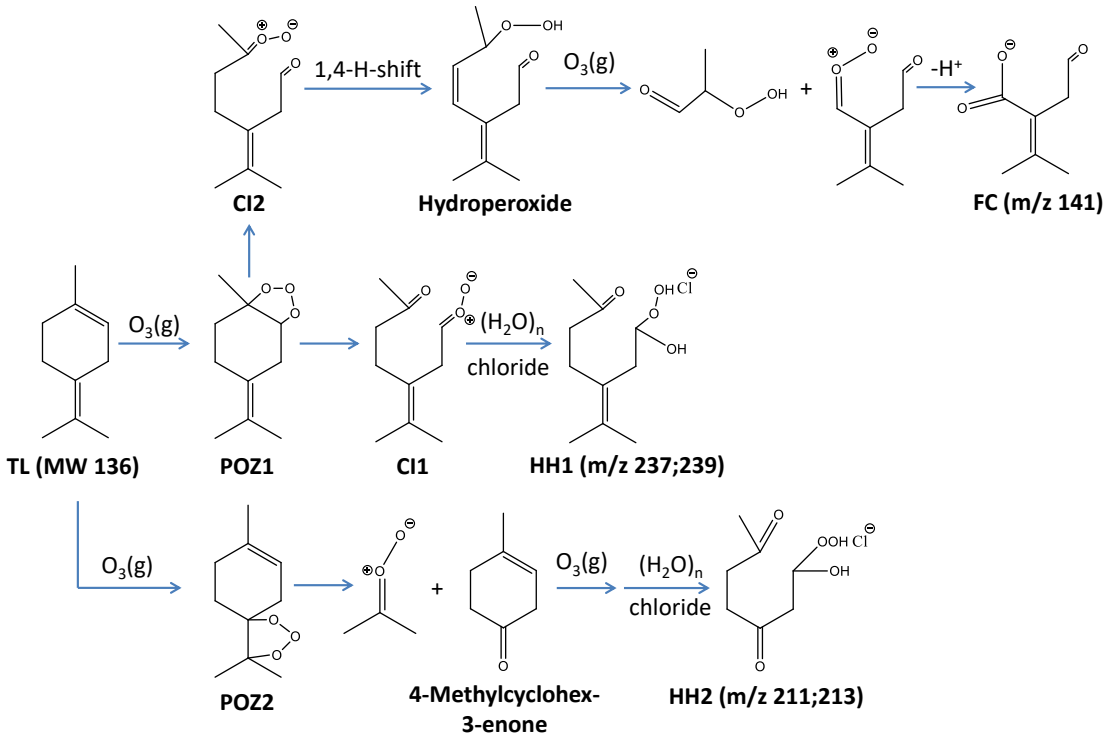
Scheme S2. Scheme for generation of the m/z 253;255 product during ozonolysis of α-terpinene at the gas–liquid interface. The proposed epoxidation reaction is in accordance with previous reports.[3-4] Representative structures are shown among isomers.



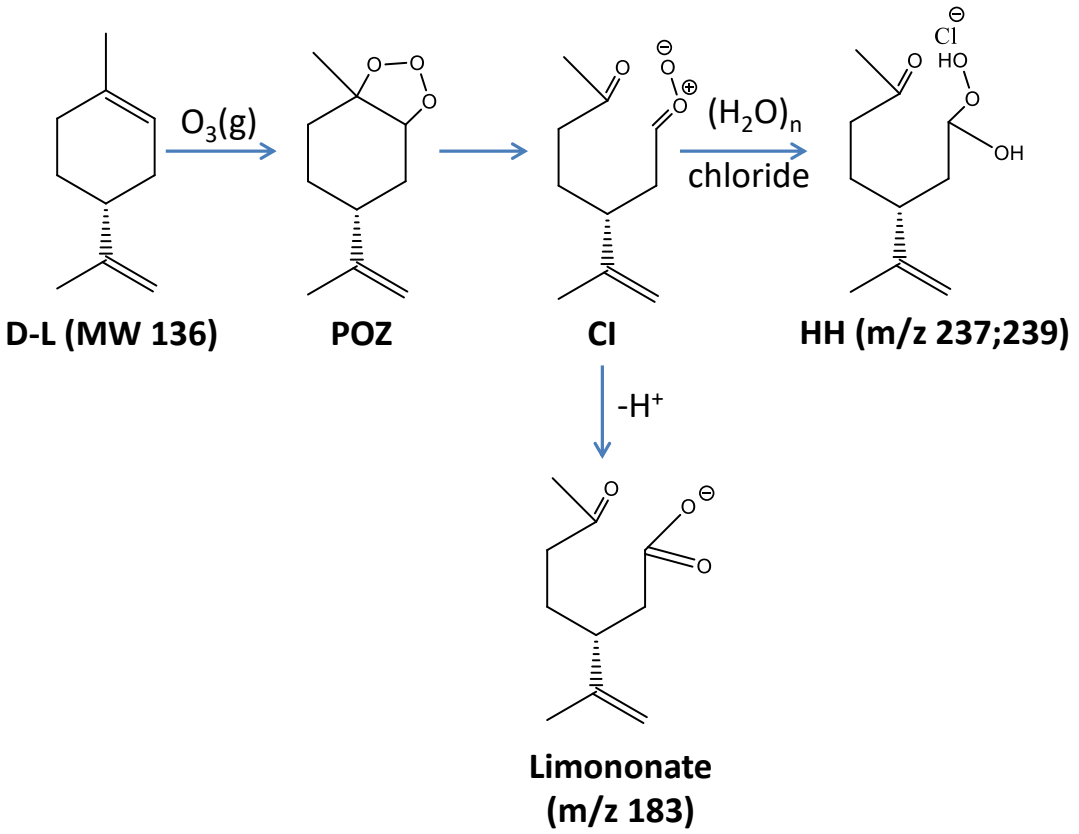
Scheme S3. Scheme of ozonolysis of γ-terpinene at the gas–liquid interface. Here we show representative structures among isomers.



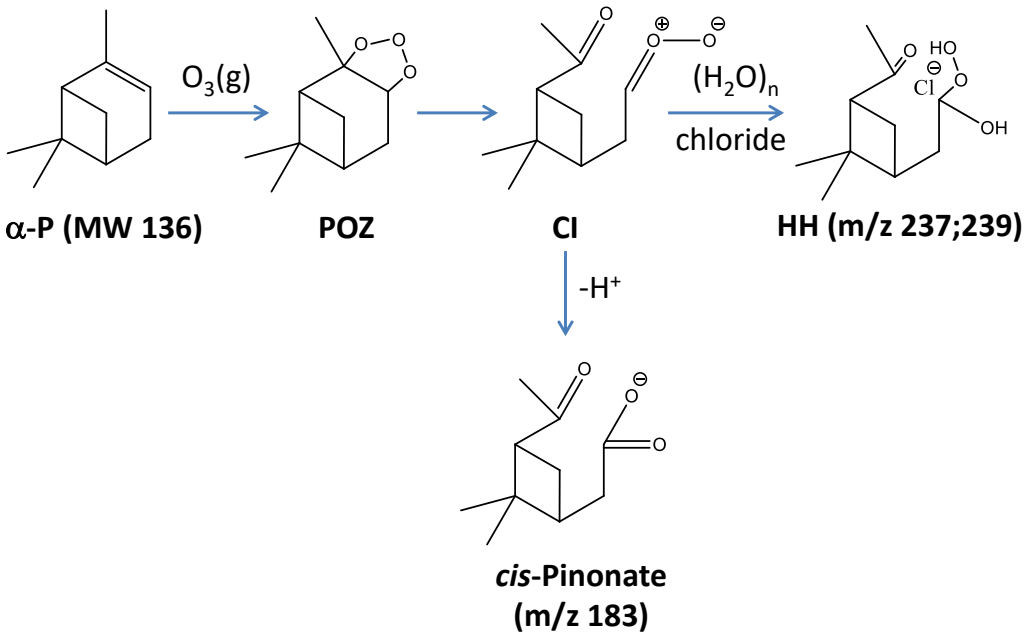
Scheme S4. Scheme of ozonolysis of terpinolene at the gas–liquid interface. The proposed 1,4-hydrogen-shift is in accordance with previous reports.[2, 5] Here we show representative structures among isomers.



Scheme S5. Scheme of ozonolysis of d-limonene at the gas–liquid interface. Here we show representative structures among isomers.



Scheme S6. Scheme of ozonolysis of α-pinene at the gas–liquid interface. Here we show representative structures among isomers.



SI REFERENCES

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