

Supporting information for

**Prompt formation of organic acids in pulse
ozonation of terpenes on aqueous surfaces**

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EXPERIMENTAL METHODS

Our experiments involve the injection of solutions of various compositions into the spraying chamber of an electrospray ionization mass spectrometer¹⁻⁴ (ESI-MS, Agilent 1100 MSD Series, modified with an orthogonal inlet port for gaseous reactants) continuously flushed with gaseous O₃/O₂/N₂ mixtures at 1 atm, 295 K (Fig. S1).⁵⁻⁹ Anionic and cationic products generated *in situ* via gas/liquid reactions,^{10,11} on the surface of the injected liquid, are monitored and quantified by online ESI-MS within 1 millisecond. Solutions are pumped (50 μL min⁻¹) into the spraying chamber through a *grounded* stainless steel needle (100 μm bore) coaxial with a sheath issuing nebulizer N₂(g) at high flow rates.⁴ The fast nebulizer gas (typically at $v_g = 2.5 \times 10^4$ cm s⁻¹) shreds the interfacial layers of the much slower liquid microjet ($v_j = 11$ cm s⁻¹) into microdroplets that may carry excess anions or cations. The production of charged microdroplets from a neutral liquid is the normal outcome of the charge fluctuations of magnitude proportional to (droplet mass)^{-½} expected from a statistical breakup process, i.e., droplet charging *does not* require the application of an external electric field.¹¹⁻¹³ Charged microdroplets subsequently evaporate solvent in the chamber while being drawn to the electrically polarized inlet of the mass spectrometer with increasing acceleration: $a = (ze/m) E$. The latter statement follows from the fact that the converging electric field E becomes more intense near the inlet while droplets lose mass m but retain excess charge ze . The resulting strong direct correlation between droplet size and residence time ensures that O₃(g) molecules mostly collide with the liquid microjet and first-generation microdroplets. Because the microjet direction is orthogonal to the axis of the mass analyzer, the ions ultimately detected by ESI-MS largely issue from microdroplets moving along the periphery rather than the axis of the spray cone (Fig. S1). Since these microdroplets are the progeny of nascent droplets shred from the surface of the microjet, they are naturally enriched with surface-active species.¹⁴ The ESI mass spectra acquired in

these experiments therefore report the composition of the outermost layers of the microjet.

Ozone is generated by flowing UHP O₂(g) (> 99.998 %, Matheson) through a commercial ozonizer (Ozone Solutions), diluted tenfold with ultrapure N₂(g), and quantified by UV absorption spectrophotometry (HP 8452) at 250 and 300 nm prior to entering the spraying chamber, where it immediately intersects β-caryophyllene solution microjets. An effective contact time $\tau_E \sim 10 \mu\text{s}$ between reactive gases with solutes present on the surface of the liquid microjets was previously determined in similar experiments on the protonation of trimethylamine (TMA).¹⁵

Reported [O₃(g)] values correspond to the concentrations sensed by solutes on the microjet. They are estimated from [O₃(g)] in the inflow gas multiplied by a 1/10 dilution factor due to the simultaneous flow of N₂ drying gas into the spraying chamber. Gas flows were regulated by calibrated mass flow controllers (MKS) and a needle valve. Typical instrumental parameters were as follows: drying gas temperature, 340 °C; Nebulizer pressure, 2 atm; collector capillary voltage, +3.5 kV; fragmentor voltage, 17 V. All solutions were prepared in purified water (Resistivity = 18.2 MΩ cm) from a Millipore Milli-Q gradient water purification system. β-caryophyllene (> 98.5 %, Sigma-Aldrich) was repeatedly washed with Milli-Q water to remove water-soluble impurities. NaI (> 99 %, EM Science), methanol (> 99.9 %, Fisher), and acetonitrile (> 99.9 %, Fisher) were used without further purification.

Captions to Figures

Fig. S1 Schematic diagram of the experimental setup and O₃(g) injection system. MFC stands for mass flow controller.

Fig. S2 Negative ion MS of β-caryophyllene microjets doped with 0.01 (A), 0.03 (B), 0.2 (C), and 2 mM (D) NaI with/without O₃(g).

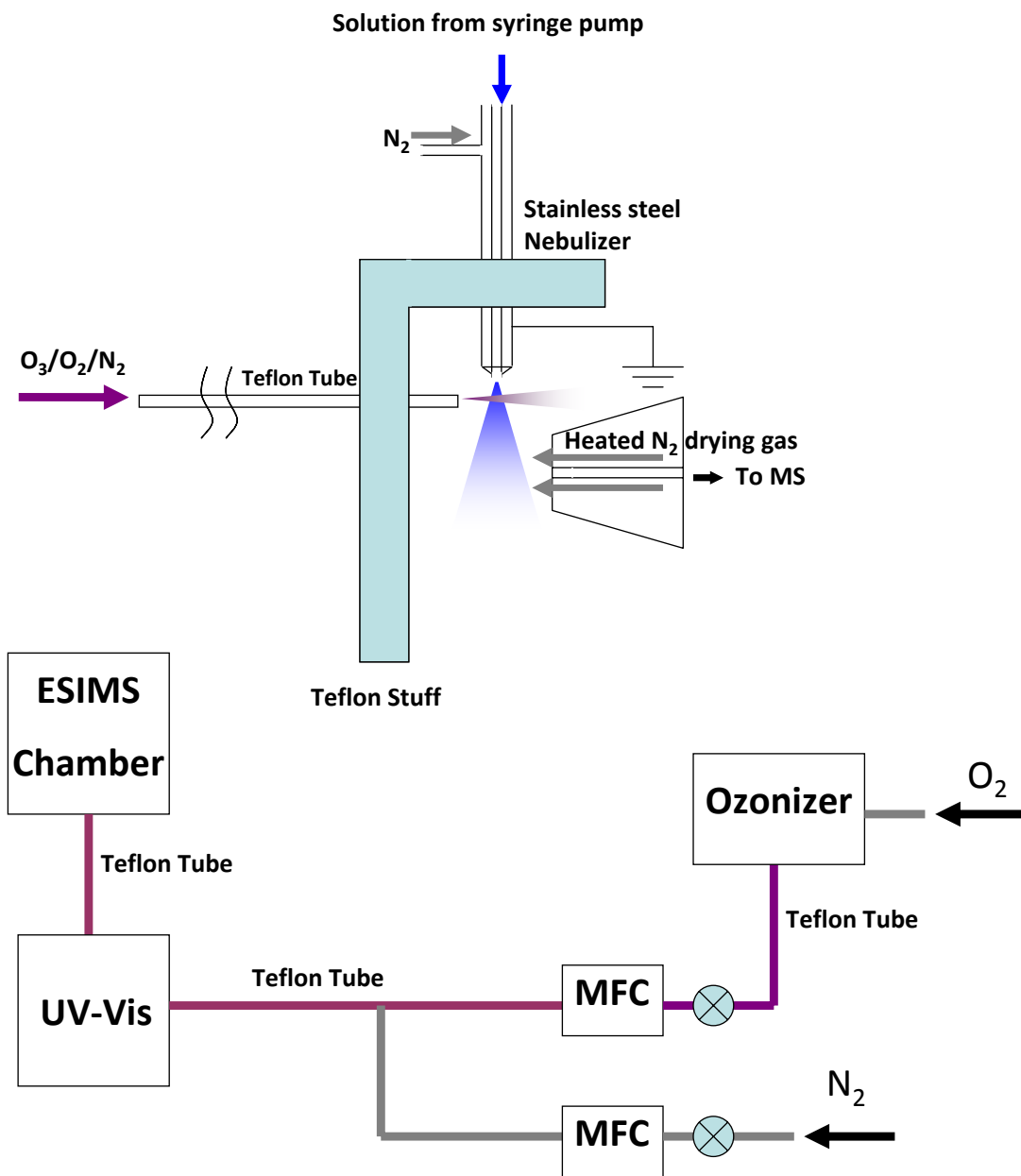


Fig. S1

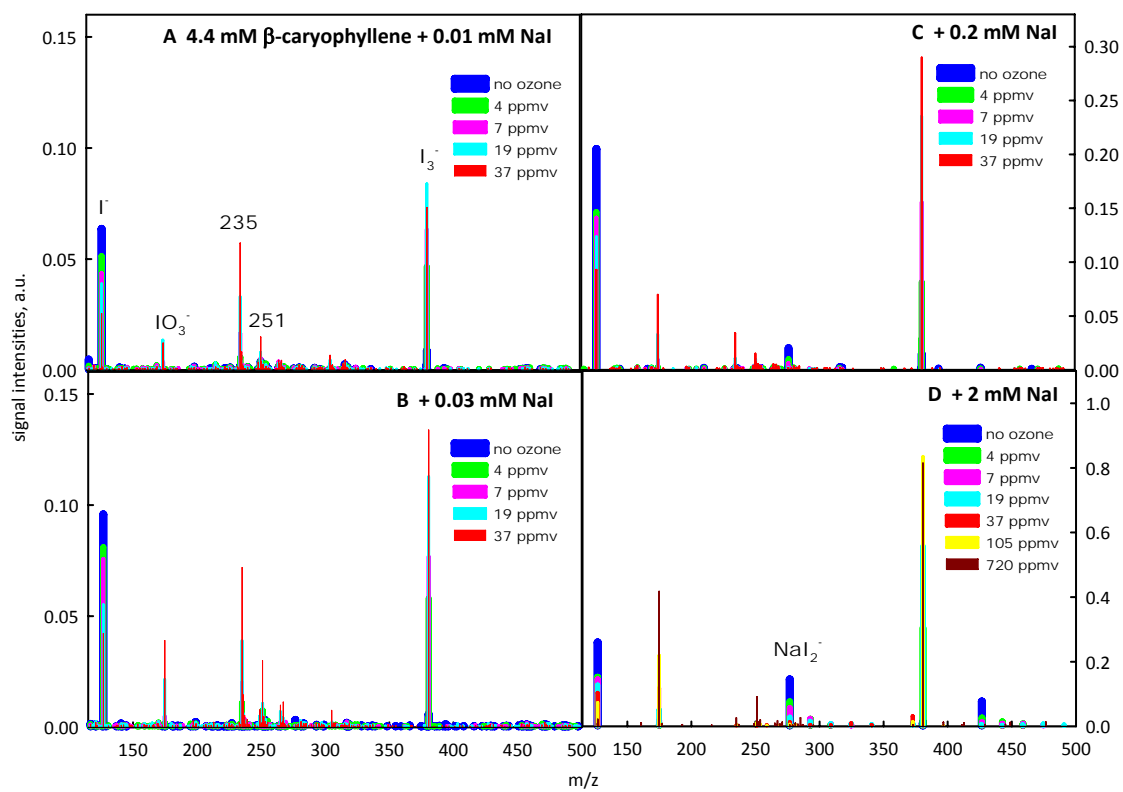


Fig. S2

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