Supporting Information:

**In Situ** Mass Spectrometric Detection of Interfacial Intermediates in the Oxidation of RCOOH(aq) by Gas-Phase OH-Radicals

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Since mass spectrometers detect net charge, the first step is the separation of pre-existing anions from cations in the inflowing solutions.\(^1,2\)

1- We have demonstrated experimentally that the charges we detect are largely produced pneumatically by showing that ion signals (i) increase at higher gas velocities \(v_g\) and (ii) extrapolate to zero as \(v_g \to 0.\)\(^2\)

2- We have confirmed that the modest polarizations of the microjets do not affect the observed chemistries\(^3-8\) by showing that the kinetics of the reaction of dissolved \(\alpha\)-tocopherol with gaseous ozone determined on the basis of negative and positive ion detection were identical.\(^6\)

3- Since the nebulizer gas can fragment the first generation microdroplets but not the smaller charged droplets for hydrodynamic reasons,\(^9,10\) the creation of net charge is a one-time event.

4- Second generation microdroplets may lose mass via solvent evaporation in the dry \(N_2(g)\) atmosphere, but retain their excess charges. We have verified that the net charge carried by the ensemble of microdroplets is proportional to the concentrations of the reactant, intermediates and products formed on the surface of the jet during reactive gas-liquid collisions.

5- The concentration dependences observed in present and previous experiments strongly support our assumption that the detected species are indeed produced on the surface of the intact jet containing microdroplets \((D_0 > 1 \mu m)\) (whose composition is identical to that of the injected solution) rather than on the ensemble of daughter droplets (whose compositions span the broad distributions generated by random solvent evaporation).\(^3-5,11\) This finding corroborates previous reports showing
that the titration curves of carboxylic acids and trimethylamine obtained from the
dependence of the carboxylate and trimethylammonium mass spectrometric signals as
functions of pH in this setup are identical to those determined by standard titrations in
the injected solutions, both leading to the ionization constants reported in the
literature, i.e., pKa = 4.8 and 9.8, respectively. 3,4

6- A key feature of our instrument is that the jet issuing from the nozzle source is
orthogonal to the polarized inlet to the mass spectrometer. Therefore, the charged
droplets deflected toward the mass spectrometer preferentially originate from the
interfacial layers of the jet, while its core maintains its forward trajectory. The ejection
of dissolved ions to the gas-phase takes place from the smallest droplets at the end of
a sequence of events comprising extensive solvent evaporation, and net charge
crowding in shrinking droplets that become unstable and undergo a cascade of
Coulomb explosions. 12,13 Finally, gas-phase ions are sorted out and detected by the
online mass spectrometer.

7- The possibility that the species we monitor were produced in the reactions of
gases with the highly concentrated, high surface-to-volume small droplets undergoing
Coulomb explosions is excluded by experimental evidences. We had found that
product signal intensities decrease (rather than increase) by injecting the reactive
gases 5 mm and 10 mm downstream (relative to the standard position of the gas
injector) along the jet direction. 14 This is the expected outcome of a process in which
products are formed in collisions of the reactive gases with the intact jet. The fact that
product formation is not completely suppressed by shifting the gas injector
downstream is ascribed to the fact that the gas beams lose their collimation by
turbulent mixing with the nebulizer gas at the reaction zone.
Previous data analysis based on mass balances and the kinetic theory of gases suggested that the thickness of the interfacial layers sampled in these experiments is less than one nm. More compellingly, we recently showed that the depth of the interfacial layers sampled in our experiments is controllable as a function of nebulizer gas velocity $v_g$. Under the present high $v_g$ ($\sim 160$ m/s) condition, anions that reside at the topmost layers of the air–water interface are preferentially detected as mass signals.
Figure S1 Negative ion electrospray mass spectra of 0.01 mM (pH 5.6) (A, B) or 1.0 mM (pH 3.7) (C, D) octanoic acid microjets exposed to 570 or 600 ppmv O$_3$(g), respectively, in O$_2$(g)/H$_2$O(g)/N$_2$(g) mixtures at 1 atm and 298 K. Cyan: laser off. Red: under 40 mJ, ~8 ns pulses (at 10 Hz) of 266 nm radiation. 1 ppmv = 2.46 × 10$^{13}$ molecules cm$^{-3}$. 
Figure S2 Negative ion electrospray mass spectra of 2.5 mM octanoic acid in 50 vol% H$_2^{18}$O microjets exposed to 610 ppmv O$_3$(g)/O$_2$(g)/H$_2$O(g)/N$_2$(g) mixtures at 1 atm and 298 K. Cyan: laser off. Red: under 40 mJ, ~8 ns pulses (at 10 Hz) of 266 nm radiation ([· OH]$_0$ ~ 60 ppmv). 1 ppmv = 2.46 × 10$^{13}$ molecules cm$^{-3}$. 
Figure S3 Negative ion electrospray mass spectra of 1 mM octanoic acid, 1 mM hexanoic acid, and 10 mM acetic acid microjets in the absence (blue)/presence (cyan, red) of 266 nm laser beam irradiation under just N₂ atmosphere.
Figure S4 Electrospray mass spectral signal intensities from aqueous 1 mM (pH 3.7) acetic acid microjets exposed to \( \text{O}_3(\text{g})/\text{O}_2(\text{g})/\text{H}_2\text{O}(\text{g})/\text{N}_2(\text{g}) \) mixtures at \( [\text{O}_3(\text{g})] \) \( \sim 610 \text{ ppmv} \) irradiated by 266 nm laser beams for \( \sim 10-50 \mu\text{s} \) contact times as a function of laser energy mJ pulse\(^{-1}\). Laser energies (x-axis) at 1, 5, 10, 20, 30, and 40 mJ pulse\(^{-1}\) correspond to \( [\cdot \text{OH}]_0 \approx 2, 10, 18, 34, 47 \) and 58 ppmv, respectively. 1 ppmv = \( 2.46 \times 10^{13} \) molecules cm\(^{-3}\). The \( m/z = 59 \) (\( \text{CH}_3\text{COO}^- \)), 73 (\( \text{CH} (\text{COO}^-) = \text{O} \)), and 90 (\( \text{CH}_2(\text{COO}^-)\text{OO}^- \)).
Figure S5 Electrospray mass spectral signal intensities from aqueous 0.1 mM (pH 4.8) hexanoic acid microjets exposed to \(O_3(g)/O_2(g)/H_2O(g)/N_2(g)\) mixtures at \([O_3(g)] \sim 610\) ppmv irradiated by 266 nm laser beams for \(\sim 10-50\) μs contact times as a function of laser energy mJ pulse\(^{-1}\). Laser energies (x-axis) at 1, 5, 10, 20, 30, and 40 mJ pulse\(^{-1}\) correspond to \([\cdot OH]_0 = 2, 10, 18, 34, 47\) and 58 ppmv, respectively. 1 ppmv = \(2.46 \times 10^{13}\) molecules cm\(^{-3}\). The \(m/z = 115\) (C\(_5\)H\(_{11}\)COO\(^-\)), 129 (C\(_5\)H\(_9\) (COO\(^-\))=O), and 146 (C\(_5\)H\(_{10}\)(COO\(^-\))OO\(^-\)).
Figure S6 Total mass signal intensities of formed products, including the carbonyl, alcohol, peroxyl radical, and peroxide, were divided by the loss of octanoate, \([\text{[OA]}_{\text{without 266nm}} - \text{[OA]}_{\text{with 266nm}}] \) at [O_3(g)] = 570~640 ppmv. Laser energy was 40 mJ pulse\(^{-1}\) (\([\cdot \text{OH}]_0 = 54~61\) ppmv).
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