

Supporting Information

Superacid Chemistry on Mildly Acidic Water

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EXPERIMENTAL METHODS

Our experiments involve the nebulization of aqueous solutions of various compositions into the spraying chamber of an electrospray ionization mass spectrometer¹⁻⁴ (ESI-MS, Agilent 1100 MSD Series, modified with a injection system for gaseous reactants) continuously flushed with gaseous hexanoic acid (PCOOH)/N₂ mixtures at 1 atm, 293 K (Fig. S1).⁵⁻⁹ PCO(OH)₂⁺ ions generated *in situ* via gas/liquid reactions,^{10,11} on the surface of the injected liquid microjet, 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 ($v_l = 11$ 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)^{-1/2}] expected in 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 PCOOH(g) molecules mostly collide with the liquid microjet and first-generation microdroplets. Note that PCO(OH)₂⁺ excesses carried by charged microdroplets should be conserved in subsequent collisions with neutral PCOOH(g). Furthermore, 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 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.

Nitrogen carrier gas saturated with hexanoic acid vapor from a temperature-controlled PCOOH(*l*) reservoir, is introduced into the spraying chamber via an injector orthogonal to liquid microjet (Fig. S1). The [PCOOH(g)] values given in the text and figure captions were calculated from the N₂(g) flow rate (typically $f = 100$ sccm), the vapor pressure PCOOH(*l*) at $T = 291$ K, $p = 1.0 \times 10^{-5}$ bar, and the dilution factor (f/F) introduced by the drying N₂(g) (flow rate = F). Gas flow rates were measured with calibrated mass flow controllers (MKS). Conditions in typical experiments were: drying gas flow rate: 10 L min⁻¹; drying gas temperature: 340 °C; inlet voltage: - 3.5 kV relative to ground; fragmentor voltage: 26 V. Hexanoic acid (> 99.9 %, Sigma-Aldrich) was used as received. All solutions were prepared in purified water (Resistivity = 18.2 MΩ cm) from a Millipore Milli-Q gradient water purification system. Solution pH_{BLK} was adjusted by adding HCl/NaOH and measured with a calibrated pH meter (VWR).

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Table S1 Experimental data for Fig.1 (main text). PCOOH_2^+ ESI-MS $m/z = 117$ signal intensities as functions of pH. **A:** Signals from PCOOH_2^+ produced on aqueous microjets exposed to 77 ppbv $\text{PCOOH}(\text{g})$ for 10 μs . **B:** PCOOH_2^+ signals from 1 mM $\text{PCOOH}(\text{aq})$ microjets. All experiments in 1 atm $\text{N}_2(\text{g})$ at 293 K.

A		B	
pH	$m/z = 117$ signal intensity	pH	$m/z = 117$ signal intensity
1.0	0.831	1.7	0.057
1.4	1.000	2.5	0.075
2.0	0.900	2.9	0.086
2.2	0.815	3.7	0.049
2.2	0.450	4.0	0.006
2.5	0.538	4.1	0.006
2.5	0.460	4.2	0.001
3.1	0.186		
3.1	0.037		
3.4	0.020		
3.4	0.001		
3.4	0.024		
4.0	0.053		
4.5	0.027		
5.1	0.017		
5.9	0.007		

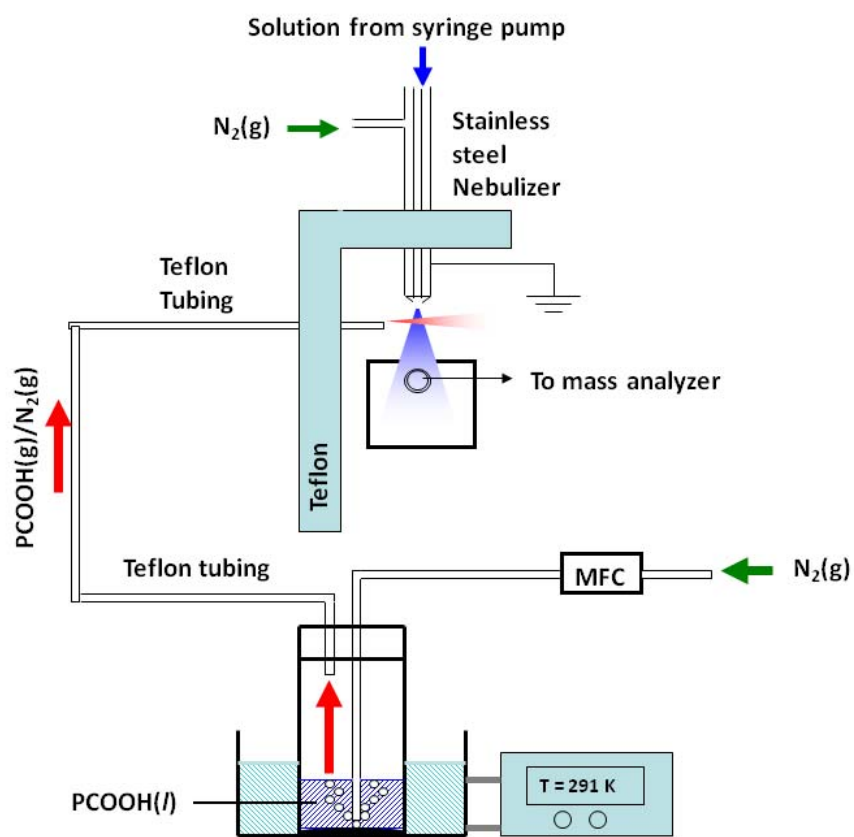


FIGURE S1