Supporting Information

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SI Methods

Experimental Procedures. An electrospray ionization mass spectrometer (Hewlett-Packard-1100 MSD) consisting of an atmospheric pressure spraying chamber of orthogonal ion-sampling geometry was used in this study (1). The orthogonal orientation of the liquid jet relative to the inlet to the mass spectrometer ensures that only a small fraction of analyte, sheared from the jet periphery by a nebulizer gas, is analyzed. Gas–liquid interfacial reactions were investigated in experiments in which pH-adjusted aqueous solutions were pumped (at 50 μL·min⁻¹ using a Harvard Apparatus syringe pump) into the electrospray chamber through an electrically grounded stainless steel capillary injector (150 μm external diameter, 100 μm bore). This capillary was surrounded by a coaxial sheath (250 μm internal diameter) issuing N₂ nebulizer gas at 0.5 L·min⁻¹. RCOOH vapor beams were produced by sparging N₂ gas through liquid acids or their aqueous solutions maintained at constant temperature. This arrangement guarantees that RCOOH molecules hit the surface of the microjet before being incorporated into the bulk liquid. A fraction of gas–liquid collisions results in proton transfers from RCOOH to the surface of the jet, followed by online mass-spectrometric detection of the RCOO⁻ ion produced therein. Because mass spectrometers only detect charged species, our technique requires the separation of anions from cations present in the electroneutral aqueous jet. Charge separation is achieved during jet nebulization in which part of the kinetic energy of the high-speed nebulizer gas is converted into surface and electrostatic energy of the droplets sheared off the outermost layers of the aqueous jets (2–4). As a result, some of the resulting droplets have excess positive or negative charges (5) proportional to ion concentrations at the interfacial layers. We have confirmed the surface sensitivity of our experiments by showing that (i) sampled anions are fractionated following a normal Hofmeister series during the nebulization of equimolar salt solutions (6–10), (ii) mass spectra are specifically affected by added cationic or anionic surfactants (11–13), (iii) we are able to detect the products of gas–liquid reactive collisions, including the protonation of gas–phase bases (12), weak carboxylic acids (12), isoprene (14), and the dissociation of the strong nitric acid at air–water interface (15). Typical experimental conditions are as follows: drying gas 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%; Sigma-Aldrich) and acetic acid (99%; Sigma-Aldrich) were used as received. All solutions were prepared in deionized water (resistivity 18.2 MΩ cm) from a Millipore Milli-Q gradient system. Solution pH was adjusted by adding concentrated HCl or NaOH solutions and measured with a calibrated pH meter (VWR). Fig. 1 shows a schematic of how charge separation is accomplished via pneumatic shearing of a slow-moving (~0.1 m·s⁻¹) analytic jet by the fast annular nebulizer gas (~250 m·s⁻¹).

As the smaller charged drops progress toward mass-spectrometer inlet, rapid solvent evaporation is promoted by the drying gas. Within ~100 μs, drops’ radii shrink to the Rayleigh limit, given by

\[ q = 8 \pi \varepsilon \varepsilon_0 \gamma R^1/2 \]

at which the Coulombic repulsions between excess charges in the drop overwhelm surface tension, whereby the charged drops fission into smaller charged drops (2). Here \( q \) is the charge on the droplet, \( \varepsilon \) is the dielectric permittivity, \( \gamma \) is the surface tension of the solvent, and \( R \) is the drop radius. Notice that these electrostatic (Coulomb) explosions do not separate negative from positive charges, but only the excess charges of the same sign acquired during the jet breakup by the nebulizer. Also notice that anions may recombine with remaining counterions (or associate with neutrals) in shrinking charged droplets, but the net ions drawn per unit time from the initial jet, \( j(RCOO\cdot_\text{H}_2\text{O}_n \cdot \text{H}_3\text{O}^+) \) [ions × time⁻¹], is conserved in sprays of noninteracting droplets. As the smaller droplets undergo further evaporation, eventually the excess ions are ejected into the gas phase and become amenable for mass-spectrometric detection. The electrokinetic phenomena observed by Saykally and coworkers in a similar setup (16) occur at liquid jet speeds ~500 times higher than in our experiments.

Computational Details. Energy-optimized water clusters with 10 and 20 molecules, \( W_{10} \) and \( W_{20} \) respectively, were used to gain insight into the proton transfer process at molecular level. In the chosen configurations each water-molecule hydrogen bonds with three neighboring water molecules. Insertion of an OH⁻ into \( W_{10} \) and \( W_{20} \), representative of air–water interfaces of bulk systems with high and low basicity, respectively, leads to a relaxed (OH⁻ \( W_{10} \) ) structures with OH⁻ emerging to the surface of the cluster and hydrogen bonded to five water molecules. Anions exhibiting propensity for air–water interface have been reported by experiments and theoretical calculations (17–19). Incoherent RCOOH(g) molecule binds to the pure water cluster into optimized adducts (\( W_p \cdot \text{RCOOH} \)) via two hydrogen bonds with the release of \( \Delta H^f = −8.3 \text{ kcal/mol} \) and \( \Delta G^f = 2.9 \text{ kcal/mol} \) (due to loss in translational entropy). The counterion to OH⁻ in other experiments, Na⁺, was not included in the calculations with small water clusters because they are expected to be separated by distances much larger than our small-sized model. Due to electrostatic bias, water molecules surrounding OH⁻ become better proton acceptors. We recently reported that proton transfer from gas-phase molecules of a strong acid, HNO₃(g), alighting aqueous surfaces could be catalyzed by interfacial anions, Cl⁻. In absence of interfacial Cl⁻, the proton transfer to the surface of water was minimal due to a large kinetic barrier. In case of weak acids, RCOOH(g), we observe that

i) Proton transfers from interfacial RCOOH to pure water is hindered by a large kinetic barrier. All calculations with pure water clusters (\( W_{10} \) and \( W_{20} \)) optimizing geometries with RCOO⁻ and H3O⁺ separated by one to four layers of water molecules relaxed back to undissociated RCOOH and \( W_n \).

ii) Unlike the case of HNO₃(g) on aqueous surface, wherein proton transfer to water was catalyzed by interfacial Cl⁻, in case of RCOOH(g) there are kinetic and thermodynamic barriers for analogous proton transfer with interfacial Cl⁻ (Fig. S3). In other words, the electrostatic bias and concomitant solvent rearrangements by interfacial Cl⁻ are inadequate to catalyze proton transfer from a weak acid.

iii) \( W_{10} \cdot \text{OH}^- \) clusters were chosen to represent the surface of water with bulk pH ~12. On this cluster, the dissociation of interfacial RCOOH was spontaneous (Fig. 3B).

iv) \( W_{20} \cdot \text{OH}^- \) clusters were chosen to represent the surface of mildly acidic water (pH ~4). We found stable dissociation products with proton transferred to OH⁻ and RCOO⁻ located outside water cluster (Fig. 3A). Reactants and products were separated by a transition state, searched by optimizing structures in which the two O–H bonds connecting RCOOH with hydronium were constrained, until the chosen set of constraints led to an imaginary frequency vibration. The path
of steepest ascent is then followed by tracking the eigenvector of the motion associated with the imaginary frequency, until an energy maximum is found. Full Hessian harmonic calculations were then performed for the transition state (TS) structures.

### S1 Discussion

The OH$_{IF}$ surface density, $\sigma_{OH-IF}$, sensed by RCOOH(g) molecules on the aerial side of water could be estimated from the frequency of RCOOH(g) collisions with the surface of the jet given by the kinetic theory of gases: $f_{coll} = 1/4 \gamma c n$. Here $\gamma \sim 0.05$ is the reactive uptake coefficient of RCOOH(g) on 4 $< \text{pH} < 8$ water [i.e., we adopt the value measured by Hu et al., for CH$_2$COOH(g) on neutral water at 293 K (20), $c = 2.4 \times 10^4 \text{cm}^{-1}$ is the mean thermal molecular speed of RCOOH(g) at 300 K, and $n$ its number density in molecules cm$^{-3}$ (21). For estimated gas–liquid contact times of $\tau \sim 10$–50 $\mu$s (14, 22), at $n \sim K_{1/2} = 1.0 \times 10^{12}$ molecules cm$^{-3}$ (at pH 5.1 and 10.1) we obtain: $\sigma_{OH-IF} = f \times \tau \sim (3–15) \times 10^3 \text{OH}^{-} \text{cm}^{-2}$, or a surface-charge density of $\sigma_{OH} \sim (0.5–2.5) \text{nC cm}^{-2} < 10 \text{nCoulomb (nC) cm}^{-2}$.

The evaluation of pH$_{IF}$ from pH$_{BG}$ measurements requires assumptions about (i) the charge distribution and dielectric properties of water in the interfacial double layer, (ii) whether they should be treated as continuous and monotonic functions of depth, and (iii) whether surface polarization is due to the unmatched distributions of the intrinsic H$^+$/OH$^-$ ions at the interface and/or the preferential orientation of water dipoles therein (23–26). All of the above issues remain outstanding at present (23–29).

Fig. S1.  Schematic diagram of the experimental setup. Aqueous solutions are injected in the spraying chamber (shown in blue) of an electrospray mass spectrometer by through an electrically grounded stainless steel nebulizer (100 μm internal diameter) and briefly exposed to RCOOH(g) (shown in green). Concentric flow of nebulizer gas (shown in red) shears aqueous jet into smaller droplets within ~10 μs, some of which carry excess charge. After subsequent solvent evaporation those charged drops become increasingly unstable due electrostatic repulsion and excess ion(s) are ultimately ejected to the gas phase via field desorption, and detected by mass spectrometry in < 1 ms. The spray chamber is at 1 atm of N₂, 293 K throughout.
**Fig. S2.** Dissociation of gaseous hexanoic acid vapors at the air–water interface as a function of the pH of bulk water in the absence and presence of inert electrolytes. Unlike the case of the strong HNO₃, interanions are unable to catalyze the dissociation of a weak carboxylic acid. All experiments in 1 atm of N₂ at 293 K.

**Fig. S3.** Lack of chloride (green atom) effects on proton transfer from gaseous CH₃COOH to the surface of water. Unlike the case of HNO₃ (15), chloride is unable to catalyze CH₃COOH dissociation.