Proton transfer reaction at the air-water interface

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Proton transfer (PT) through and across aqueous interfaces is a fundamental process in chemistry and biology. Unveiling the mechanism will help to understand the ubiquitous nature of PT at other interfaces, such as vacuum-ice interfaces. Notwithstanding its importance, it is not generally realized that interfacial PT is quite different from conventional PT in bulk water. Here the mechanism of PT across air-water boundaries is investigated in experiments in which the protonation/deprotonation of gaseous trimethylamine (TMA), n-hexanoic acid (PCOOH), nitric acid (HNO₃) and isoprene (ISO) upon collision with liquid water microjets is monitored by online electrospray mass spectrometry as a function of bulk pH.

We found, although PCOOH(aq) is a very weak base (pKₐ< 3), PCOOH(g) is converted to PC(OH)₂⁺ on pH < 4 water via a process that ostensibly retains some of the exoergicity of its gas-phase counterpart, PCOOH + H₃O⁺ = PC(OH)₂⁺ + H₂O, ΔG < -22 kcal mol⁻¹. We infer that H₃O⁺ emerges at the surface of pH < 4 water and behaves as a superacid (Fig. 1). The extremely large kinetic isotope effects (KIE) observed on H₂O/D₂O microjets and their inverse dependences on pH indicate that protonation of PCOOH(g) on water (1) involves tunneling, (2) is faster than H-isotope exchange, and (3) is progressively confined to the outermost layers as water becomes more acidic (Fig. 2). PT across steep water density gradients appear to be promoted by both dynamic and thermodynamic factors.

【References】