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Direct simulation of proton-coupled electron transfer reaction dynamics and mechanisms JOSHUA S. KRETCHMER, THOMAS F. MILLER III, Cal Inst of Tech (Caltech) — Proton-coupled electron transfer (PCET) reactions, in which both an electron and an associated proton undergo reactive transfer, play an important role in many chemical and biological systems. Due to the complexity of this class of reactions, a variety of different mechanisms fall under the umbrella of PCET. However, the physical driving forces that determine the preferred mechanism in a given system still remain poorly understood. Towards this end, we extend ring polymer molecular dynamics (RPMD), a path-integral quantum dynamics method, to enable the direct simulation and characterization of PCET reaction dynamics in both fully atomistic and system-bath models of organometallic catalysts. In addition to providing validation for the simulation method via extensive comparison with existing PCET rate theories, we analyze the RPMD trajectories to investigate the competition between the concerted and sequential reaction mechanisms for PCET, elucidating the large role of the solvent in controlling the preferred mechanism. We further employ RPMD to determine the kinetics and mechanistic features of concerted PCET reactions across different regimes of electronic and vibrational coupling, providing evidence for a new and distinct PCET reaction mechanism.

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