Reassessing Hydrogen Evolution Reaction Pathways Using Turnover Frequency: From Stepwise to Concerted Mechanisms.

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The hydrogen evolution reaction (HER) is one of the most extensively studied processes of electrochemistry. The reaction was mainly studied and reported as a stepwise pathway, known as: a Volmer step (proton adsorption onto the surface forming the H* adsorbed species), followed by either a Heyrovský step (electrochemical reduction of H* to form a hydride that subsequently reacts with a proton to produce H_2) or a Tafel step (chemical coupling of two H* species to form H_2). However, with the growing demand for renewable fuels like green hydrogen, a more detailed analysis of HER has become essential. In our studies we observed a uncommon pathway to HER, a Concerted one, where proton and electron transfer occur simultaneously. This is remarkable not only as rarely mechanisms occur in one step, but also due to generally the more steps, the greater the energy loss between the processes. Thus, a reaction with fewer steps generally is more efficient. In sum, this work aims to investigate the HER mechanism using a cobalt porphyrazine catalyst, demonstrating that different mechanisms can guide an optimization process. This evaluation is based on the turnover frequency (TOF)[1] of HER in various media, using simulations adapted from the OER model proposed by Cyrille[2].

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References:

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