Electrified Addition and Subtraction of H₂ to Simplify Synthesis

Methodologies that rely on the addition and removal of molecular hydrogen from organic compounds are one of the most oft-employed transformations in modern organic chemistry, representing a highly relevant tactic in synthesis. Despite their overall simplicity, organic chemists are still pursuing sustainable and scalable processes for such transformations.

In this regard, electrochemical techniques have long been heralded for their innate sustainability as efficient methods to perform redox reactions. In our first report, we discovered a new oxidative electrochemical process for the α,β -desaturation of carbonyl functionalities. The described desaturation method introduces a direct pathway to desaturated ketones, esters, lactams and aldehydes simply from the corresponding enol silanes/phosphates, and electricity as the primary reagent. This electrochemically driven desaturation exhibits high functional group tolerance, is easily scalable (1–100 g), and can be predictably implemented into synthetic pathways using experimentally or computationally derived NMR shifts.

Our second report demonstrated the reductive electrochemical cobalt-hydride generation for synthetic organic applications inspired by the well-established cobalt-catalyzed hydrogen evolution chemistry. We have developed a silane- and peroxide-free electrochemical cobalt-hydride generation for formal hydrogen atom transfer reactions reliant on the combination of a simple proton source and electricity as the hydride surrogate. Thus, a versatile range of tunable reactivities involving alkenes and alkynes can be realized with unmatched efficiency and chemoselectivity, such as isomerization, selective E/Z alkyne reduction, hydroarylation, hydropyridination, strained ring expansion, and hydro-Giese.