

The Synergistic Interplay between Catalysis and Organic Electrosynthesis

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To most chemists the term 'electrocatalysis' is known as the facilitation of a heterogeneous electron transfer via a chemical interaction between the electrode and a substrate [1]. The opposite case, the utilization of a heterogeneous electron exchange to catalyze a chemical reaction ("electrochemical catalysis"), is a much less known but yet a very powerful approach in electrosynthesis [2]. Here, the injection (or removal) of an electron into (or from) a substrate triggers a redox-neutral reaction (e. g. a molecular rearrangement) that may otherwise require harsh conditions and/or the use of reagents. Such processes involve the electrogeneration of an ionic or radical ionic species, which after a coupled chemical step either undergoes a backward electron exchange with the electrode (ECEb mechanism) or triggers a chain process in the bulk solution. Under these circumstances, sub-stoichiometric amounts of charge are sufficient to achieve a full conversion and conceptionally, the electrons and holes can be understood as being catalysts.

In this contribution, the concepts of electrocatalysis and electrochemical catalysis will be contrasted and discussed. Electrocatalysis will be presented from the perspective of organic electrochemistry, where molecular catalysts ("redox mediators") with well-defined active sites are typically used [1]. The underlying principles will be illustrated with recent examples from our group, including TEMPO-mediated anodic oxidations and transformations that are initiated by electro-generated hypervalent halogen compounds [3,4]. For the discussion of electrochemical catalysis, the Newman-Kwart rearrangement of O-aryl thiocarbamates to the corresponding S-aryl compounds will be used [5,6].

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