Electrochemical oxidations through hypervalent iodine redox catalysis

Chemical synthesis is a crucial branch of industry, providing multiple indispensable products that range from simple ones, such as fertilizers, dyes, fuels, to the most sophisticated – advanced materials and pharmaceuticals. However, in the 21st century, chemical synthesis faces considerable challenges related to its environmental impact, in particular, in the terms of greenhouse gas emissions, energy efficiency, and the generation of toxic waste. Therefore, improving the level of sustainability of chemical synthesis is one of the principal tasks of chemical research nowadays, so that the synthesis can be carried out in a possibly efficient and environmentally benign manner.

Chemical reactions, that is the transformations of matter, are always associated with a concurrent flow of energy. Some of them, such as combustion, release the energy contained in starting materials, converting them into lower-energy species. Other, conversely, require the supply of energy to progress. In general terms, the reactions that create complexity, for instance, assembling a larger and more complicated molecule out of simpler ones, will usually need the energy to be provided. Most of the synthetic reactions fall into this category. A traditional approach to carry out such reactions is to couple them with other, sacrificial, chemical transformations that are downhill in energy. In other words, the general scheme of many synthetic reactions is following: substrates + high-energy compound → product + low-energy compound. This is far from optimal, since, first, the 'high energy compound' has to be produced, which costs energy and resources, and, second, the 'low-energy compound' constitutes a waste by-product, often a toxic chemical, which has to be disposed of.

This research project at its core addresses the issue of the sustainability of chemical synthesis, by employing electric power to drive energetically uphill chemical reactions, instead of using auxiliary high-energy chemicals. This way, it will allow for the elimination of both the need for extra reagents and the generation of attendant waste streams. Moreover, electrosynthesis is highly compatible with the current intensive expansion of renewable electric energy sources.

The electricity has been for long time used for stimulating simple chemical processes, for instance, the splitting of water into hydrogen and oxygen. However, its application in more complex reactions, in particular these involving organic compounds, has been challenged by the sluggish electron transfer rates for many organic molecules and the need to couple the single-electron events that are typical of electrochemistry with the two-electron events required for bond-breaking and -making in organic reactions. In recent years, so-called electrocatalysis has emerged as an effective mean to solve above problems. It employs special compounds, electrocatalysts, added in small quantity, which convey applied potential from the electrode to the reaction medium, intermediating the energy transfer. In this project, it is envisioned to employ so-called hypervalent iodine compounds as the electrocatalysts. These species have been used in many valuable synthetic reactions, however, up to now requiring a full equivalent of terminal oxidant (i.e., the 'high-energy compound'). Due to the related economic and environmental concerns, it has effectively prevented the widespread application of such reactions, especially on a large scale. The application of electrochemical stimulus to activate hypervalent iodine species will radically, yet elegantly, tackle above issues, removing the burden to translate this chemistry into industrial and semi-industrial setups. Additionally, the compounds of iodine that are to be used are generally non-toxic and environmentally benign, which constitutes a huge advantage, especially in the context of the synthesis of therapeutics.