A new green route for high added-value products through epoxidation: design and optimization of a sono-electrochemical reactor

Job offer: ***PhD Thesis***, beginning ***September 1, 2024***

Chemical Engineering Laboratory (LGC, Université de Toulouse, CNRS, INPT, UPS) ***Toulouse, France***
Edytem (Université Savoie Mont Blanc et du CNRS) ***Le Bourget du Lac, France***

Description

This PhD thesis is part of the **PEPR project ECOCHEM** (**Eco-friendly and intensified chemical reactions**), involving 11 laboratories and funded by the National Research Agency (**ANR**). The project proposes a sustainable, scalable and efficient route to epoxidize olefins using water as the oxygen source, bio-inspired catalysts and ionic liquids as conducting solvents under sono-electrochemistry.

The direct transfer of an oxygen atom into a target molecule is a fundamental reaction in organic chemistry. For several decades, oxidation reactions have been investigated to produce various chemicals including epoxides. Epoxides are important oxygenated intermediates giving access to a large variety of daily products [1,2]. Yet, the synthesis of epoxides usually involves non-environmentally-friendly oxidants [3,4] displaying a low atom economy. Hence, despite their high oxidizing potential these species are converted into undesirable by-products such as that must be treated. For this reason, the development of clean and efficient processes for the manufacture of epoxides is a great challenge. To solve this problem, some processes use catalysts, including bio-inspired-homogeneous complexes [5], that generate hydrogen peroxide in situ by either reducing oxygen or oxidizing water in both chemical or electrochemical ways [6]. Electrosynthesis processes that aim at transforming organic molecules into products with higher added value via electron(s) transfer in association with water as an abundant, sustainable and safe oxygen atom source, present a recognized great potential [7]. Despite the advantages offered by organic electrosynthesis (safety, greenness, low price, energy efficiency, etc. [8]) and a significant renewed interest from chemists [9], its widespread application in synthetic organic chemistry is still limited [10] because of some issues to overcome. Among those, (i) aqueous and organic electrolytes present limited electrochemical stability [11] (ii) reactants can have a low solubility in these electrolytes; and (iii) electrochemical reactions may be slower than homogeneous chemical ones [12].

This thesis proposes a sustainable and efficient process combining electrochemistry, ultrasound (US) and ionic liquids (ILs) for the synthesis of epoxides from olefins using water as the oxidant and a bio-inspired catalyst. Indeed, (US) in electrochemistry is known to enhance the outcomes of heterogeneous reactions mainly through extremely facilitated mass-transfer that can lead to increased yield [13] and selectivity [14], electrode de-passivation and thermal effects [13]. Homogeneous chemical reactions can be also affected through the intense emulsification induced by the US and the generation of highly reactive radical species such as H• and OH• produced by sonolysis of the medium under the intense sound field [13,15].

The first part of the study will be devoted to **the synthesis, the characterization and the modification of the bio-inspired catalysts** based on earth-abundant first-row transition metal such as manganese, iron, cobalt. Based on the literature, easily scalable, as green as possible, synthesis procedures will be used and improved in a green perspective.
Another part of the work will be devoted to the synthesis and characterization of IL, and the **electroless epoxidation** of cyclooctene, as model substrate, and Mn(TPP)OAc, as model catalyst, without or with US. Under electroless conditions, H2O2 will be used as oxidant to serve as a reference for the sono-electrochemical transformation. Ionic liquids will be chosen based on previous studies involving ionic liquids and electrochemistry, or epoxidation using porphyrins under ultrasonic irradiation .
Finally, catalysts will be tested for **electro-epoxidation**. The best experimental conditions (potentials, electrode materials…) will be evaluated and the best catalysts will be also tested upon immobilization onto the electrode surface. In parallel, a **laboratory-scale's sono-electroreactor will be designed to implement sono-electro-epoxidation experiments**.

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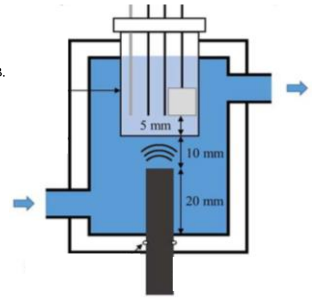

Skills

Chemical engineering and chemistry
Taste for teamwork,
Good experimental skills and Adaptability

Key words

Chemical Reaction, Catalysis,
Electrochemistry,
Ultrasound, Sustainable processes

Job Information

Candidate before	31/05/2024		
Date of beginning	01/09/2024	Duration	36 month
French Level required	None	English Level required	B2

Program managers	Patrick COGNET	patrick.cognet@ensiacet.fr
	Laurie BARTHE	laurie.barthe@ensiacet.fr