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High frequency ultrasound for investigating H2O2-mediated cis-cyclooctene epoxidation mechanism

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PURPOSE OF THE ABSTRACT

Epoxides constitute an important class of oxygenated intermediates used in the manufacture of a wide range of daily live products including epoxy resins, cross-linked polymers, surfactants, plasticizers, paints or surface coating agents. [1] Unfortunately, their synthesis usually involves iodosylbenzenes, chlorate and perchlorate salts, amine and pyridine N-oxides, peracids and peroxides, that are converted into undesirable by-products and must be treated. [1] In the context of more sustainable production of epoxides, hydrogen peroxide has received a growing attention thanks its numerous advantages: non-toxic oxidant, it is low cost and only releases water as by-product. Among literature discussing eco-friendly epoxidations with H2O2, tungsten-based catalysts have been described for decades thanks to their high activity and non-toxicity. To assess their catalytic action, cis-cyclooctene has been extensively studied as model compound thanks to the high affinity of its double bond toward electrophilic oxidants. [2] Nevertheless, its fast epoxidation kinetics did not allow any in-detail study of reaction parameters on the outcomes of the reaction. Moreover, no explicit contribution of HO° radical species, commonly coming from homolytic dissociation of H2O2, has been proposed to date to complete the proposed mechanisms.

For the past few decades, ultrasound-mediated syntheses have witnessed a growing interest thanks to the multiple physical and chemical effects induced by ultrasonic waves. As an illustration, low frequency ultrasound has been well studied thanks to the enhanced mass transfer, reduced reaction times and decreased use of harmful compounds observed for many examples of epoxidations with hydrogen peroxide. [3] However, to date, no example of study of this reaction under high frequency irradiation has been exposed.

In this context, this presentation describes how a high frequency sonoreactor enables to collect mechanistic information on cis-cyclooctene epoxidation and to optimize critical reaction parameters. Step by step optimization under ultrasound leads to high epoxidation yields and enhanced selectivity compared to silent conditions.

FIGURES

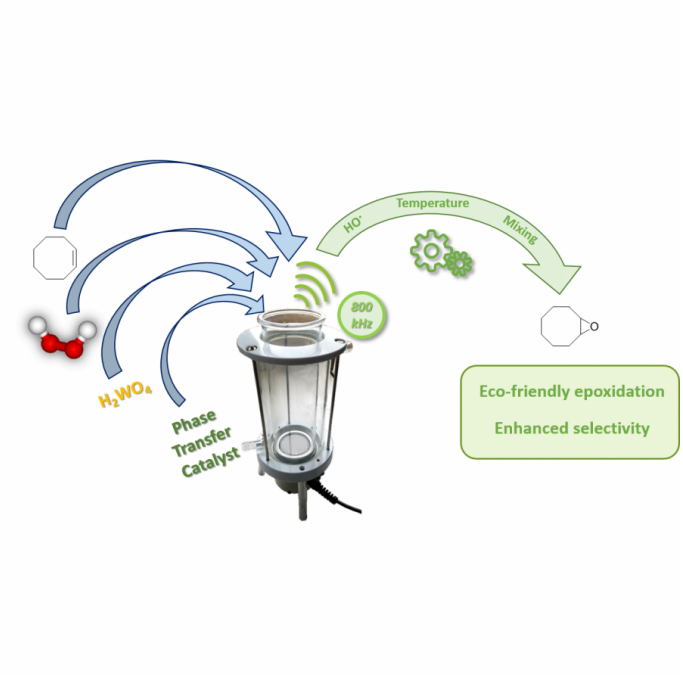

FIGURE 1

Figure

Schematic representation of mechanistic information brought by high frequency ultrasound during cis-cyclooctene epoxidation with H2O2.

FIGURE 2

KEYWORDS

Epoxidation | Cis-cyclooctene | Hydrogen peroxide | Ultrasound

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