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High frequency ultrasound as a tool for elucidating mechanistic elements of *cis*-cyclooctene epoxidation with aqueous hydrogen peroxide

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ABSTRACT

The use of high frequency ultrasound (800 kHz) highlights the non-radical character of the *cis*-cyclooctene epoxidation mediated by H₂O₂ and H₂WO₄. Combination of moderate mixing brought by the ultrasonic irradiation with precise thermoregulation of the double jacketed sonoreactor demonstrates the potential of this technique for studying and optimizing all the reaction parameters. The results not only reveal that the optimized ultrasonic conditions lead to excellent epoxidation outcomes with 96% yield and 98% selectivity but also to higher selectivities toward the epoxidation product compared with silent conditions.

1. Introduction

Epoxides are important oxygenated intermediates leading to a large variety of daily products including epoxy resins, surfactants, cross-linked polymers, plasticizers, paints or surface coating agents [1]. However, the synthesis of epoxides usually involves non-environmentally-friendly oxidants such as iodobenzene, chlorate and perchlorate salts, amine and pyridine-N-oxides, peracids and peroxides [1–3]. Despite their high oxidizing potential these species are converted into undesirable by-products such as halogenated salts, amines, pyridines, acids or alcohols and that must be treated.

For this reason, the development of clean and efficient processes for the manufacture of epoxides is a great challenge. Over the past few decades, hydrogen peroxide has witnessed a growing interest for oxidation reactions thanks to its low environmental impact. Indeed, it is non-toxic and only releases water as theoretical by-product [4]. In addition, with a production of 4.5 metric tons/year, H₂O₂ is a readily available and cheap oxidant [4–6]. After molecular oxygen, it is thereby more accessible than other oxidizing compounds and displays high oxygen content [2].

Epoxidation reactions with H₂O₂ are also discussed intensively in the literature. More specifically, the use of transition metal based catalysts under solvent-free conditions have received much attention to develop eco-friendly epoxidations [2]. Among them, tungsten-based catalysts have been studied recently thanks to their high oxidizing potential, non-toxicity and low cost [7–9].

Study of their activity is often assessed with the epoxidation of *cis*-cyclooctene as a model compound. High affinity of its double-bond towards electrophilic oxidants makes it a substrate of interest [3,10]. As an illustration, with the W-H₂O₂ based oxidizing systems, *cis*-cyclooctene is commonly epoxidized 2 to 5 times faster than other olefins with conversions and yields above 90% [3,11,12]. Nevertheless, in spite of the well documented literature dealing with this reaction, higher reaction kinetics observed with this model compound did not allow any in-detail description on the reaction parameters on the outcome of the reaction. Besides, no clear explanation on the contribution of HO[•] that is commonly produced from H₂O₂ has been proposed to date to complete the proposed mechanisms.

Ultrasound-assisted syntheses have received a growing attention over the past few decades thanks to the multiple effects brought by ultrasonic waves to the media [13]. Indeed, ultrasonic effects are the consequence of cavitation phenomenon occurring through nucleation, growth and brutal collapse of micrometric bubbles in elastic media leading to modifications of different nature. When imploding, these bubbles create local zones where intense temperatures (up to 5000 K) and very high pressures (up to 1000 atm) are reached, leading to both important physical and chemical effects. At low frequencies, physical effects resulting from violent microjets and shearing forces are preferentially observed while chemical effects coming from solvent sonolysis and radical formation prevail under high frequency ultrasound [14,15].

Recent studies reported the multiple benefits brought by low

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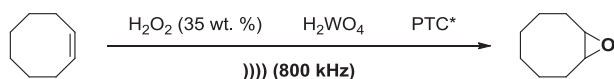


Fig. 1. *Cis*-cyclooctene epoxidation mediated by hydrogen peroxide and high frequency ultrasound. *PTC = Phase Transfer Catalyst.

frequency ultrasound for H_2O_2 -mediated epoxidations, including enhanced mass transfer, reduced reaction times and decreased use of harmful compounds [16–21]. Conversely, very few examples relate the use of high frequency ultrasound for organic synthesis. Actually, the corresponding reports mainly focused on alkylpolyglycoside polymerization or oxidation of hexoses to uronic acids [22,23]. To date, no use of high frequency ultrasound has been described to carry out H_2O_2 -mediated epoxidations. In this study, we demonstrate that a high frequency ultrasonic reactor (800 kHz) cannot only reveal elements of *cis*-cyclooctene epoxidation that are not accessible under silent conditions but also enhances its environmental performances (Fig. 1).

2. Results and discussion

Among the literature describing the *cis*-cyclooctene epoxidation with H_2O_2 and a tungsten-based catalyst, the results presented by Reedijk *et al.* are the most interesting in terms of green chemistry [12]. Indeed, the solvent-free conditions used involve a catalytic system made of 0.2 mol% of Na_2WO_4 , H_2WO_4 , Aliquat 336® as Phase Transfer Catalyst (PTC) and chloroacetic acid as promoter. After 30 min at 60 °C in the presence of 1.5 eq H_2O_2 (50% in water), cyclooctene is epoxidized in 89% yield and 99% selectivity. These excellent results led us to use similar conditions in order to compare the kinetics of this reaction between silent conditions and ultrasonic irradiation. As illustrated in Fig. 2, even in the absence of chloroacetic acid, a catalyst loading of 0.2 mol % affords very good results after 30 min of reaction under silent conditions. Interestingly, over this period, the conversion and the yield increase very sharply almost reaching their final values after 15 min (TOF = 1350 h^{-1} over 15 min). As already observed in the literature, these results illustrate faster kinetics for the *cis*-cyclooctene epoxidation than with other substrates under similar conditions [3,11,12]. Interestingly, in the meantime, the temperature also strongly increases from 25 °C to almost 95 °C within only 10 min due to the exothermic character of the epoxidation. To assess the potential contribution of the temperature increase to the fast improvement of the conversion and yield, the reaction was carried out using a double-jacketed high frequency ultrasound reactor (picture in ESI). An acoustic power of 0.66 $\text{W}\cdot\text{mL}^{-1}$ was applied in order to ensure a steady 60 °C temperature

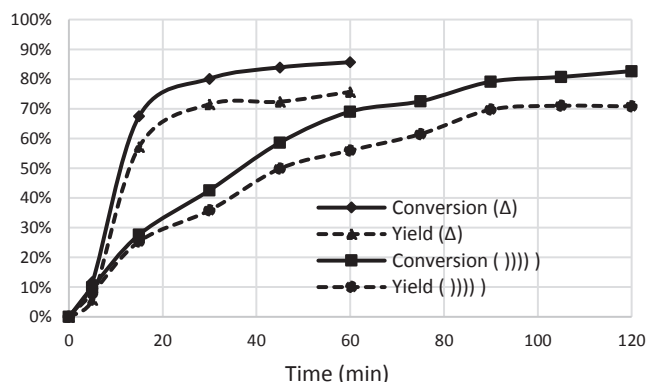


Fig. 2. Evolution of *cis*-cyclooctene epoxidation results under silent and ultrasonic conditions versus time. *Cis*-cyclooctene (280 mmol), H_2O_2 (35 wt%, 1.5 eq.), H_2WO_4 (0.2 mol%), Aliquat 336® (0.2 mol%), 25–60 °C. Silent conditions (Δ): 1,000 rpm. Ultrasonic conditions (□): $f = 800$ kHz, $P_{\text{acous}} = 0.66$ $\text{W}\cdot\text{mL}^{-1}$. Conversion (transformed starting material) and epoxide yield (on the basis on starting *cis*-cyclooctene) calculated by internal quantification during GC analysis.

during sonication. Under ultrasonic conditions, both conversion and yield increase slower than under silent conditions (Fig. 2). Indeed, while the reaction is almost completed after 30 min reaction under magnetic stirring, 90 min are needed to reach final conversion and maximum yields under ultrasound. Such slower kinetics can be attributed to the precise control of the temperature imposed by the water-cooled reactor as the reaction mixture did not exceed 60 °C during sonication. These preliminary results reveal that a thermo-regulated reactor and the use of high frequency ultrasound lead to a slower increase of conversion and yield against time (TOF = 380 h^{-1} over 15 min). The moderate conditions reached thanks to the ultrasonic reactor allowed us to study the influence of each reaction parameter and to optimize them independently.

The most critical reaction parameters for *cis*-cyclooctene epoxidation were determined using high frequency ultrasound. As total electric consumption becomes higher under ultrasound than under silent conditions after 1 h, optimization was made over 1 h studies (See example of energy consumptions under optimized conditions in Fig. S2 in ESI). Firstly, we investigated the chemical action of high frequency ultrasound on aqueous hydrogen peroxide. Indeed, as exposed previously, the subsequent formation, growth and collapse of the cavitation bubbles under high frequency irradiation leads to the homolytic cleavage of water O–H bonds (Fig. 3, Eq. (1)) [24,25]. This reaction leads to the formation of highly reactive HO^\bullet radicals that can also be produced through homolytic scission of the hydrogen peroxide O–O bond (Fig. 3, Eq. (2)). Thus, the reactivity of such species toward the double bond of cyclooctene can be studied.

The chemical action of high frequency ultrasound on water homolysis has been determined by measuring the HO^\bullet production kinetics thanks to a chemical dosimeter based on the Weissler reaction [26]. Under a selected acoustic power of 0.58 $\text{W}\cdot\text{mL}^{-1}$, the open-air ultrasonic irradiation of 50 mL deionized water leads to the production of HO^\bullet radicals at a rate of 0.784 $\text{mmol L}^{-1}\text{h}^{-1}$.

As exposed above, hydroxy radicals can also be produced by sonolysis of the H_2O_2 peroxide bond. In order to assess the amount of hydrogen peroxide decomposed under high frequency ultrasound, we studied the degradation of H_2O_2 under ultrasonic irradiation over 1 h (Fig. 4). Fig. 4 reveals that hydrogen peroxide is little decomposed under these conditions. After 1 h of ultrasonic irradiation, less than 2% loss of hydrogen peroxide is observed. In order to evaluate the effect of the catalyst on H_2O_2 decomposition under ultrasound, the study was undertaken in the presence of tungstic acid used in a 5 times higher concentration than the one used previously for *cis*-cyclooctene epoxidation. Interestingly, even the addition of tungstic acid does not catalyze hydrogen peroxide decomposition under ultrasonic conditions. This observation can be illustrated by the formation of stable peroxotungstates from the reaction between H_2WO_4 and H_2O_2 preventing hydrogen peroxide from decomposition [27,28]. These results indicate that, in the absence of any organic substrate, HO^\bullet radicals formed from water or hydrogen peroxide sonolysis do not undergo side reactions leading to progressive H_2O_2 decomposition. Thus, the ability of tungstic acid to preserve hydrogen peroxide from degradation under ultrasound and its very good activity toward *cis*-cyclooctene epoxidation led us to select this catalyst to start optimization study.

In order to complete the catalytic system used to study *cis*-cyclooctene epoxidation under biphasic conditions and ultrasound, we selected $\text{Oct}_3\text{MeN}^+\text{HSO}_4^-$ as PTC. The choice of this onium salt was driven by the excellent results reported by Noyori *et al.* for alkene

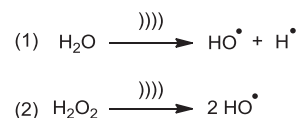


Fig. 3. HO^\bullet formation under ultrasonic irradiation of aqueous solution of hydrogen peroxide.

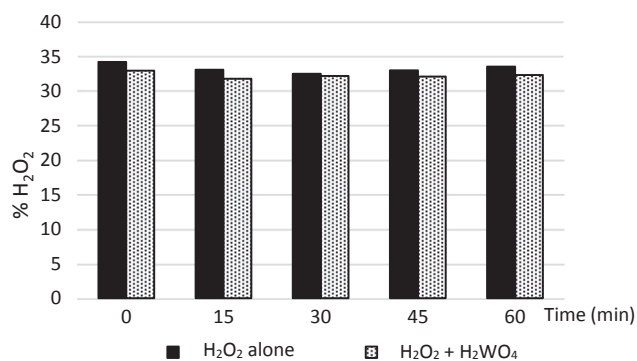


Fig. 4. Evolution of %H₂O₂ during high frequency sonication of aqueous hydrogen peroxide solution alone or in the presence of H₂WO₄ versus time-H₂O₂ (35 wt%, 50 mL), H₂WO₄ (6 mmol), $f = 800$ kHz, $P_{\text{acoustic}} = 0.58$ W.mL⁻¹.

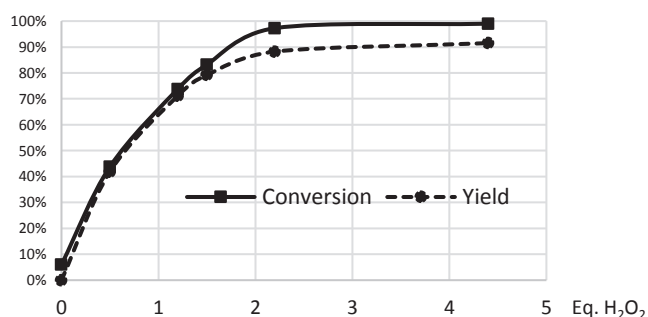


Fig. 5. Influence of the H₂O₂ amount on the results of *cis*-cyclooctene epoxidation under high frequency ultrasound. *Cis*-cyclooctene, H₂O₂ (35 wt%), H₂WO₄ (1 mol%), Oct₃MeN⁺ HSO₄⁻ (1 mol%), 25–50 °C, 1 h. Ultrasonic conditions: $f = 800$ kHz, $P_{\text{acoustic}} = 0.58$ W.mL⁻¹. Cyclooctene and H₂O₂ amounts are determined to reach a 50 mL reaction volume. Conversion (transformed starting material) and epoxide yield (on the basis on starting *cis*-cyclooctene) calculated by internal quantification during GC analysis.

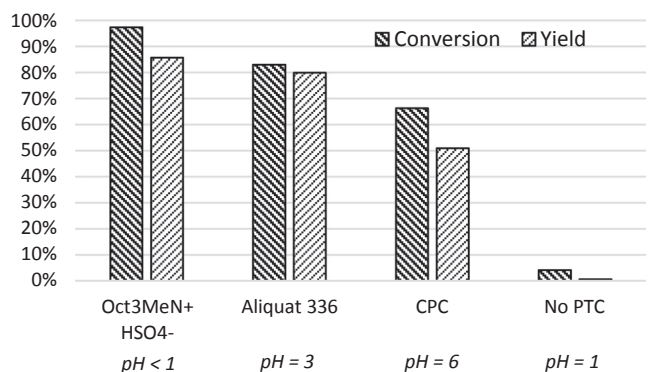


Fig. 6. Influence of different Phase Transfer Catalysts (PTC) on the results of *cis*-cyclooctene epoxidation under high frequency ultrasound. *Cis*-cyclooctene (185 mmol), H₂O₂ (35 wt%, 275 mmol, 1.5 eq.), H₂WO₄ (1 mol%), PTC (1 mol%), 25–50 °C, 1 h, $f = 800$ kHz, $P_{\text{acoustic}} = 0.58$ W.mL⁻¹. Conversion (transformed starting material) and epoxide yield (on the basis on starting *cis*-cyclooctene) calculated by internal quantification during GC analysis.

epoxidation, alcohol oxidation and alkene oxidative cleavage applied for a broad substrate scope [27,29,30]. The optimization study started by investigating the influence of the amount of H₂O₂ on the outcomes of the reaction (Fig. 5).

As illustrated in Fig. 5, when the reaction is performed in the only presence of water (0 equivalent of H₂O₂), a very small amount of *cis*-cyclooctene is converted (6%) and no epoxide is observed (0%). It is worth noting that also no epoxide is formed without H₂WO₄ under

these conditions. These observations suggest that the HO[•] radicals formed from the sonolysis of water do not have a significant impact on the reaction. Study of the reaction in the presence of 0.5 equivalents of H₂O₂ allowed us to assess the influence of OH[•] radicals originating from hydrogen peroxide sonolysis. Under high frequency ultrasound, O-O homolytic cleavage of 0.5 equivalent of H₂O₂ leads to the theoretical formation of 1 equivalent of HO[•]. However, under these conditions, conversion and yield did not exceed 50% (44% and 42% respectively), indicating that molecular hydrogen peroxide is the limiting reactant. The limited effect of the HO[•] radicals on this reaction may be correlated to the *cis*-cyclooctene aqueous solubility. Indeed, even if the addition of HO[•] radicals on *cis*-cyclooctene proceeds faster than their recombination into H₂O₂ (rate constants: 3.1×10^{10} against 6.2×10^9 L.mol⁻¹.s⁻¹, calculated from refs [13,31]), the aqueous solubility of *cis*-cyclooctene (from 22.9 to 43.5 mg.L⁻¹ in temperature range of the study, calculated from ref [32]) is too low to react quantitatively with HO[•] in aqueous phase. In order to confirm that HO[•] radicals do not have influence on epoxidation results, the reaction has been undertaken in the presence of *tert*-butanol as radical inhibitor. By carrying out the epoxidation in the presence of 0.5 equivalent of H₂O₂, similar conversion and yield as those observed without radical inhibitor have been found (48% and 46% respectively).

Consequently, these results show that HO[•] radicals do not contribute to *cis*-cyclooctene epoxidation: the reaction occurs through a non-radical mechanism under high frequency ultrasound. In our conditions, the chemical action of high frequency ultrasound does not affect the epoxidation mechanism: it can be compared to a physical activation technique. Consequently, this reaction can be classified as type II reaction, also known under “false sonochemistry” [14,33]. In spite of excellent results obtained with 2.2 equivalents of H₂O₂, the use of 120% stoichiometric excess of hydrogen peroxide is not attractive in terms of Atom Economy. Besides, conversion and yield reached under these conditions are too high (97% and 88% respectively) to adjust the other reaction parameters to enhance epoxidation results. Since lower conversion (83%) and yield (79%) obtained in the presence of 1.5 H₂O₂ equivalents are high enough to study the influence of reaction parameters, we decided to set the amount of H₂O₂ at 1.5 equivalents for the rest of this study.

The nature of the PTC on the results of epoxidation was next studied. To this end, 3 common onium salts used in the literature with tungsten-based catalysts were compared (Fig. 6): Oct₃MeN⁺ HSO₄⁻, Oct₃MeN⁺ Cl⁻ (Aliquat 336®), and (C₁₆H₃₂)C₅H₅N⁺ Cl⁻ (Cetylpyridinium Chloride = CPC). All of these phase transfer catalysts have been selected for their activity in a large variety of epoxidation and oxidation reactions with tungsten-based catalysts [27,30,34–36]. The presence of these compounds in the catalytic system was justified by studying the reaction without any phase transfer material. As shown in Fig. 6, very low conversion and yield were observed in the absence of PTC. Conversely, the addition of selected onium salts resulted in moderate to high epoxidation yields. These results highlight the crucial role of the phase transfer catalyst for the effective catalytic conversion of *cis*-cyclooctene into epoxide. Besides, it is noteworthy that even under the moderate mixing reached by high frequency ultrasonic irradiation, high epoxidation results were obtained when using PTC. Under these conditions, ultrasound showed that a strong mixing is not necessary to afford very good conversion. Comparison of the results obtained in the presence of onium salts revealed that best epoxidation yields are reached with Oct₃MeN⁺ HSO₄⁻ and Aliquat 336® with yields above 80%. Indeed, the tricaprilmethylammonium cation forming these onium salts displayed a higher activity than cetylpyridinium cation present in CPC that led to moderate 51% yield. The nature of the anion on the pH of the media also greatly influenced the results of the reaction. On the one hand, while cyclooctene is almost converted quantitatively in the presence of Oct₃MeN⁺ HSO₄⁻, Aliquat 336® only affords 83% conversion. These results can be explained by the lower pH brought by the hydrogen sulfate anion (pH < 1) during the reaction

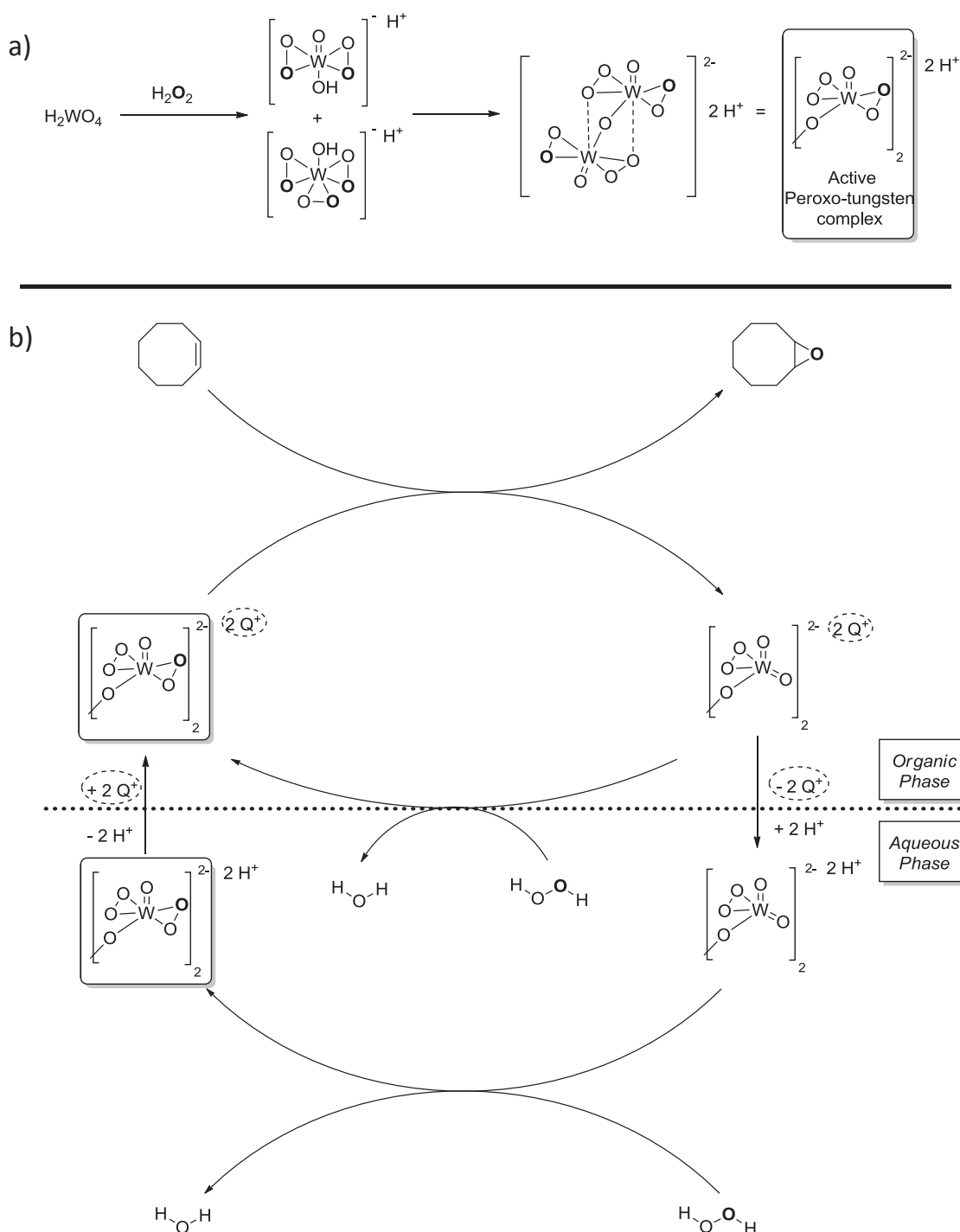
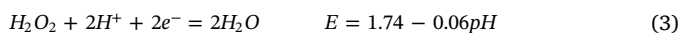


Fig. 7. Hypothesis of mechanism of H_2O_2 mediated *cis*-cyclooctene epoxidation under high frequency ultrasound a) Formation of active peroxy-tungsten complex. b) Detailed epoxidation mechanism under phase transfer catalysis conditions (Aliquat 336[®]: $\text{Oct}_3\text{MeN}^+ \text{Cl}^- = \text{Q} + \text{X}^-$) Adapted from [27,28,37].

leading to enhanced oxidizing power of hydrogen peroxide. Indeed, equation of Eh-pH diagram of hydrogen peroxide (Eq. (3)) reveals that H_2O_2 redox potential increases at lower pH ranges [7]:



Activation of W-based catalyst by H_2O_2 is thus favored to form active peroxy species as pH decreases [27,28,35]. On the other hand, very acidic conditions brought by the hydrogen sulfate anion during the reaction led to the formation of a higher amount of by-products from *cis*-cyclooctene. Indeed, epoxide ring opening is favored in such acidic conditions. In contrast, mild acidic conditions (pH = 3) reached thanks

to the buffering action of Aliquat 336[®] during the reaction resulted in less side reactions. As it is low cost, commercially available and shows very good epoxidation results, Aliquat 336[®] has been selected as optimal PTC for the reaction.

Catalytic involvement of Aliquat 336[®] on epoxidation has been assessed by studying the reaction in the only presence of H_2O_2 35% and Aliquat 336[®] (1.5 eq and 1% respectively); it led to a conversion below 10% and 0% epoxide after 1 h of reaction. In a similar way, 0% epoxide is observed with 1.5 eq H_2O_2 only. These results indicate that PTC has no direct interaction with H_2O_2 during the reaction. These observations are consistent with mechanisms proposed in the literature showing that

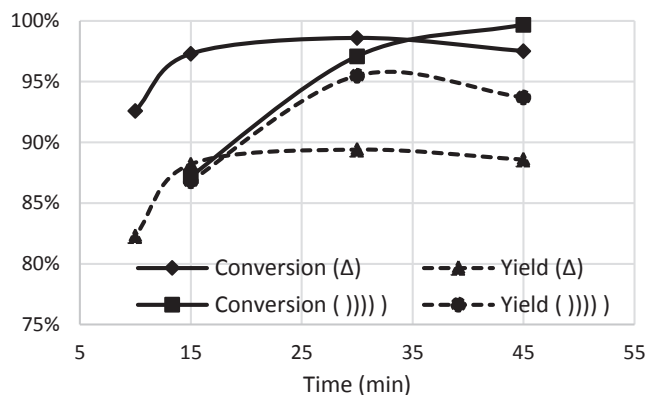


Fig. 8. Results of *cis*-cyclooctene epoxidation under high frequency ultrasound and silent conditions *versus* time. *Cis*-cyclooctene (185 mmol), H₂O₂ (35 wt%, 275 mmol, 1.5 eq), H₂WO₄ (0.75 mol%), Aliquat 336® (0.75 mol%), 25–80 °C. Silent conditions (Δ): 1,000 rpm. Ultrasonic conditions ()): *f* = 800 kHz, P_{acous} = 0.61 W.mL⁻¹. Conversion (transformed starting material) and epoxide yield (on the basis on starting *cis*-cyclooctene) calculated by internal quantification during GC analysis.

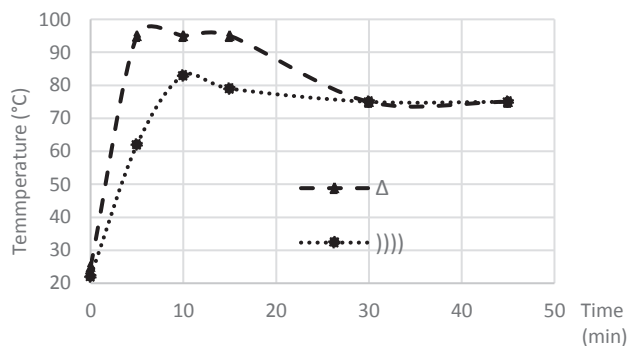


Fig. 9. Temperature profiles during *cis*-cyclooctene epoxidation at 80 °C under silent and ultrasonic conditions. *Cis*-cyclooctene (185 mmol), H₂O₂ (35 wt%, 275 mmol, 1.5 eq), H₂WO₄ (0.75 mol%), Aliquat 336® (0.75 mol%), 25–80 °C. Silent conditions (Δ): 1,000 rpm. Ultrasonic conditions ()): *f* = 800 kHz, P_{acous} = 0.61 W.mL⁻¹.

PTC allows bringing active peroxy-tungsten species from aqueous phase to organic phase to epoxidize *cis*-cyclooctene.

Based on results on the investigation of *cis*-cyclooctene epoxidation under high frequency ultrasound and proposed mechanisms in the literature, mechanism occurring through a molecular pathway was suggested (Fig. 7) [27,28,37].

In aqueous phase, the reaction between H₂WO₄ and H₂O₂ results in the formation of mononuclear tungsten peroxy-species that lead to an active dimeric peroxy-tungsten complex (Fig. 7a). This complex ([W₂O₃(O₂)₄]²⁻) is transferred from the aqueous phase to the organic phase by 2 quaternary ammonium moieties of Aliquat 336® (Oct₃MeN⁺ = Q⁺ in Fig. 7b) where epoxidation of *cis*-cyclooctene occurs. The efficiency of [Oct₃MeN]₂[W₂O₃(O₂)₄] for alkene epoxidation has been shown to derive from the presence of the two asymmetrically bounded η²-peroxide ligands in [W₂O₃(O₂)₄]²⁻ making the W-O bond weaker and easier to break [37]. The catalyst is then renewed by reacting with another molecule of H₂O₂ at the interface between organic and aqueous phase or in aqueous phase after cation exchange of Q⁺ by H⁺.

Further optimizations on the temperature, the amount of catalysts and the acoustic power led us to use only 0.75 mol% of H₂WO₄ and Aliquat 336® and high frequency ultrasound at an acoustic power of 0.61 W.mL⁻¹ at 80 °C. Finally, optimization of reaction time under ultrasound showed that the best epoxidation results are obtained in 30 min. Indeed, as illustrated in Fig. 8, when reaction time exceeds 30 min, selectivity decreases from 98 to 94%. Under high frequency

ultrasound, the best results are reached in only 30 min of reaction at 80 °C where cyclooctene oxide is obtained with 96% yield and 98% selectivity.

A comparative study was next carried out under magnetic stirring at 80 °C. Under silent conditions, conversion and yield reach their final values after 15 min reaction. Interestingly, between 15 and 45 min reaction, the selectivity toward epoxide is always higher under ultrasound than under silent conditions. Indeed, under silent conditions, the selectivity did not exceed 91% while the reaction afforded cyclooctene oxide in 94 to 99% selectivity under ultrasonic activation. These observations can be explained by the faster temperature increase observed under magnetic stirring. Actually, under silent conditions at 1,000 rpm, the temperature measured in the medium showed a sharp increase from 25 to 95 °C in 5 min only and remained constant for 10 min (Fig. 9). Strong mixing of biphasic media under such temperatures would thereby lead to more side reactions. Conversely, precise thermoregulation and moderate mixing provided by our high frequency ultrasound reactor allowed a good control of the temperature at 80 °C after 10 min of irradiation, leading to high selectivity toward epoxidation product. Thus, the high frequency ultrasound reactor is not only an efficient tool to unveil mechanistic aspects of *cis*-cyclooctene epoxidation but is also an innovative direct activation technique. More specifically, the unique combination of mild mixing brought by ultrasonic activation and precise temperature control allowed enhancing the selectivity of the reaction. Besides, the sonoreactor enables lowering the overall energy consumption compared to silent conditions contributing to enhance the green character of the reaction (See energy calculations under Fig. S2 in ESI).

3. Experimental section

3.1. Reagents, apparatus and analysis

Gas chromatography was performed on a HP 6890 Series gas chromatograph from Hewlett Packard using a flame-ionization detector and equipped with an Optima-5MS Accent capillary column (dimethylpolysiloxane, 30 m × 0.25 mm × 0.25 μm) from Marchery Nagel.

The high frequency ultrasonic cup-horn system is shown in ESI. It is made up of a jacketed Pyrex reaction cell (internal diameter × height: 60 × 185 mm) equipped with a high frequency transducer which resonance frequency was measured at 807 ± 1 kHz. Cooling of the piezoelectric transducer was ensured by a fan to avoid degradation from heating due to Joule effect. A homemade 800 kHz generator was used to supply energy to the high frequency transducer (in the presence of 50 mL of deionized water: P_{acous} = 0.58 W.mL⁻¹ for P_{elec} = 60 W; P_{acous} = 0.66 W.mL⁻¹ for P_{elec} = 73 W). A Minichiller Huber cooling system (Offenburgh, Germany) was filled with deionized water and used for thermoregulated experiments. The temperature was measured by a Pt-100 resistance probe (100 Ω at 0 °C; 119 Ω at 50 °C) within about 0.1 °C precision. The total liquid volume reached 50 mL for the whole reactions.

Acoustic power of ultrasonic reactor was determined in deionized water using calorimetry according to procedure described in the literature [38]. Kinetic of formation of HO· radicals was evaluated by iodide dosimetry using UV-Vis spectroscopy [26,39,40].

All chemicals were obtained and used without further purification. *Cis*-cyclooctene, and potassium permanganate were purchased from Acros. Tungstic acid and methyltriethylammonium hydrogensulfate were obtained from Aldrich. Aliquat 336® and hexadecylpyridinium chloride were provided by Alfa Aesar. Hydrogen peroxide (aqueous solution, 35 wt%) and potassium iodide were purchased from Honeywell. Permanganate titration of hydrogen peroxide solution was performed regularly according to literature procedure for accurate determination of H₂O₂ concentration [41].

3.2. General procedures

3.2.1. Cis-cyclooctene epoxidation under silent conditions

In a 250 mL round bottom flask, aqueous solution of hydrogen peroxide (280 mmol, 27.90 g, 1.5 eq, 35 wt% solution) was added to a mixture of H₂WO₄ (1.4 mmol, 0.346 g, 0.75 mol%) and Aliquat 336® (1.4 mmol, 0.56 g, 0.75 mol%). The aqueous solution was stirred at room temperature for 2 min before adding cis-cyclooctene (185 mmol, 21.44 g). Round bottom flask was equipped with a condenser and the biphasic mixture was stirred at 80 °C without any incubation period at 1,000 rpm. After 1 h reaction, aqueous phase is separated from the organic layer and thoroughly washed with CH₂Cl₂ (3 × 30 mL) in order to extract remaining cyclooctene and newly formed products. After evaporation of the solvent under reduced pressure, remaining liquid residue and organic phase were analysed by gas chromatography for quantification by internal standard method (dodecane used as internal standard).

3.2.2. Cis-cyclooctene epoxidation under high frequency ultrasound

Reactants were introduced into the high frequency sonochemical reactor according to the same procedure as previously before closing head of reactor with rubber plug. Double-Jacket of sonochemical reactor was then filled with water at 25 °C thanks to a Minichiller Huber cooling system and the mixture was subjected to 800 kHz ultrasonic irradiation (60 mm diameter piezoelectric ceramic, P_{elec} = 67 W, P_{acous} = 0.61 W.mL⁻¹) for 1 h. Reactor was degassed at regular intervals to avoid pressure increase. At the end of reaction, aqueous and organic phases were treated and analysed following the same procedure as previously.

Note: as sonochemical efficiency of a sonoreactor was demonstrated to depend on liquid height [40], amounts of reactants were calculated to reach a total volume of 50 mL during optimization study.

3.2.3. Kinetic studies of cis-cyclooctene epoxidation

Reactants were prepared following the same procedures as previously as well as under ultrasonic as under silent conditions. During the reaction, stirring or irradiation was stopped for a few seconds to allow sampling of organic phase at regular intervals. Reaction was monitored analysing samples by gas chromatography. Final results were confirmed by analysing both phases according to the same procedure as previously.

4. Conclusion

In this work, the use of high frequency ultrasound proved that H₂O₂-mediated epoxidation of cis-cyclooctene with a tungsten-based catalyst involves a non-radical mechanism. Study on the nature of the PTC not only revealed the crucial role of this compound in the catalytic conversion of cis-cyclooctene but also that mild mixing brought by ultrasonic irradiation is sufficient to lead to high yields. The unique combination of high frequency ultrasound with a double-jacket reactor thereby allowed the independent study and optimization of critical reaction parameters to lead cis-cyclooctene epoxidation with 96% yield and 98% selectivity in only 30 min. More specifically, accurate temperature control coupled with moderate mixing brought by ultrasound proved to limit the initial temperature increase of the reaction leading to higher selectivity toward epoxidation product compared to silent conditions. These results revealed high frequency ultrasonic reactor as a direct activation technique that enables study, optimization and enhancement of performances of radical non-sensitive reactions. Application of this innovative tool for the efficient and environmentally benign epoxidation of other olefinic substrates is currently under study.

Conflicts of interest

There are no conflicts to declare.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ultsonch.2018.12.038>.

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