Ultrasonics Sonochemistry 19 (2012) 390–394

Contents lists available at SciVerse ScienceDirect

Ultrasonics Sonochemistry

journal homepage: www.elsevier.com/locate/ultsonch

Short Communication

Ultrasound and ionic liquid: An efficient combination to tune the mechanism of alkenes epoxidation

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ARTICLE INFO

Article history:
Received 5 September 2011
Received in revised form 7 October 2011
Accepted 9 October 2011
Available online 20 October 2011

Keywords:
Epoxidation
Alkenes
Ionic liquids
Mn porphyrin
Ultrasound

ABSTRACT

In this proof of concept study, the advantageous properties of both H_2O_2/$NaHCO_3$/imidazole/Mn(TPP)OAc oxidation system and MOPyrroNTf$_2$ ionic liquid have been combined under ultrasonic irradiation to give an exceptionally favorable environment for Mn(TPP)OAc catalyzed olefin oxidations. The results reveal the crucial role played by the ultrasonic irradiations that influence drastically the oxidation process. In MOPyrroNTf$_2$ and under ultrasonic irradiation, the mechanism probably involves an oxo-manganyl intermediate at the expense of the classical bicarbonate-activated peroxide route.

1. Introduction

Utilization of hydrogen peroxide, H_2O_2, as an oxidant has received much attention in the recent years because of its low environmental impact. In addition, it is reasonably cheap [1], safely storable [2] and generates water as only theoretical co-product [1]. Moreover, H_2O_2 is more accessible than other oxidizing agents such as organic peracids and organic hydroperoxides for liquid phase reactions and it advantageously exhibits a high active oxygen content [3]. However, it is a rather slow oxidizing agent in the absence of activators such as bicarbonate ions [4]. Accordingly, the use of bicarbonate-activated hydrogen peroxide system (BAP) was proven to be very versatile, allowing the epoxidation of both lipophilic and hydrophilic alkenes [1a].

Olefin epoxidation, catalyzed by iron or manganese metalloporphyrin complexes [5], constitutes a milestone in the rapid evolution of this research area including in a chiral form [6]. Recently, the combination of H_2O_2/$NaHCO_3$/imidazole/Mn(TPP)OAc has been proposed in the literature for the selective oxidation of olefins [7]. However, in the latter report, one cannot exclude an important contribution of the metal-free BAP process, as it has been shown that a combination of hydrogencarbonate and H_2O_2 (10 equiv.) allows the epoxidation of variously substituted alkenes with conversions ranging from 20% to 90% [1a]. In addition, most reactions were carried out in a volatile, often toxic organic solvent and bleaching of the catalyst was observed.

In the recent years, the use of ionic liquids has become a topic of much interest. Their application as reaction media for a wide variety of synthetic processes is an area of intense research and new approaches involving ionic liquids are proposed for catalyst separation and recycling [8]. Ionic liquids display many interesting properties which make them very attractive for catalysis. In these almost vapourless, air and moisture stable solvents, polar or ionic catalysts can be immobilized without any post-functionalization, allowing easy recycling.

Ultrasound-promoted synthesis has attracted much attention during the past few decades. The most successful applications of ultrasound were found in the field of heterogeneous chemistry involving solids and metals. In fact, ultrasound is known to enhance some processes [9] through a physical phenomenon called cavitation, which is the formation, growth and collapse of bubbles in an elastic liquid. By imploding, these bubbles create locally high pressure (up to 1000 bar) and temperature (up to 5000 K) that lead to high-energy radical mechanisms but also generate some interesting physical effects [10]. Thus, the enhancement of catalyst activity by low frequency ultrasonic irradiation (e.g. $f = 20$ kHz) is due to (1) the improvement of mass transfer between the liquid

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doi:10.1016/j.ultsonch.2011.10.007

and the catalyst surface, (2) reduction of particle size, increase of surface area and (3) acceleration of suspended particle motion induced by shock waves and microstreaming.

Recent reports in the literature describe the use of manganese [11] or molybdenum [12] salts for promoting the epoxidation of olefins in an ionic liquid medium. While environmentally friendly and very efficient, this strategy is limited to achiral transformations. Herein, we demonstrate that under ultrasound activation in an appropriate ionic liquid, it is possible to completely by-pass the ligand-free mechanism and induce a metalloporphyrin based route.

2. Experimental

2.1. Reagent, apparatus and analysis

^{1}H NMR and ^{13}C DEPT NMR spectra were recorded in $CDCl_3$ (Euriso-Top, Saint Aubin, France) at 23 °C using a Bruker DRX300 spectrometer, at 300 MHz and 75.5 MHz for ^{1}H and ^{13}C, respectively. Chemical shifts (δ) are reported in ppm relative to tetra-methylsilane (TMS). Gas chromatography was performed on a GC9000series gas chromatograph from Fisons Instruments using flame-ionization detector and equipped with an UB1P capillary column (dimethylpolysiloxane 30 m × 0.32 mm × 0.25 μm) from Interchim. Mass spectra were taken on a HP 5973 MSD coupled to a HP 6890 GC and equipped with an Optima 5 capillary column (dimethylpolysiloxane 30 m × 0.32 mm × 0.25 μm) from Macherey-Nagel. FTIR spectra were recorded on a Nicolet 380 spectrometer and reported in cm^{-1}. Ultrasound was generated by a Digital Sonifier® S-250D from Branson (P_{elec} = 11 W). A 3 mm diameter tapered microtip probe operating at a frequency of 20 kHz was used and its acoustic power in water ($P_{acous.vol}$ = 0.667 W mL^{-1}) was determined by calorimetry using a procedure described in the literature [13]. Viscosity measurements were recorded on a Anton Paar AMVn Viscosimeter at 20 °C, associated with water content measurements on Metrohm 831KF coulometer (Karl Fisher method).

Except pyrrolidine that was distilled under reduced pressure, chemicals used during these investigations were obtained and used without further purification. 1-methylpyrrolidine, 1-octylbromide, ethyl acetate, cyclooctene, styrene, α-pinene, hydrogen peroxide (30%: wt.% solution in water), imidazole and sodium bicarbonate were purchased from Acros. Pyrrole was purchased from Alfa Aesar, benzaldehyde and cyclohexene from Aldrich, cyclohexane from Chimie-Plus Laboratoires and $LiNTf_2$ was obtained from Solvionic.

2.2. Synthesis of Mn(TPP)OAc

Tetraphenylporphyrin (TPP) was prepared in propionic acid according to the literature method [14].

TPP (732 μmol, 0.450 g, 1 equiv.), CH_3COONa (4.4 mmol, 0.360 g, 6 equiv.) and manganese acetate (11.0 mmol, 1.9 g, 15 equiv.) were refluxed in glacial acetic acid under an argon atmosphere for 3 h. Complexation was monitored by TLC. After evaporation of the solvent under reduced pressure (rotary evaporator), the residue was solubilized in CH_2Cl_2 and filtered through a 10 cm high alumina pad to remove the remaining TPP free base in the first fraction, before increasing the polarity of the eluent with EtOH and collect the porphyrin manganese complex as a greenish band. Then, the solvents were evaporated and the solid was dried under reduced pressure (2×10^{-3} bar) to afford 517 mg of Mn(TPP)OAc as green crystals in 97% yield.

2.3. Synthesis of MOPyrroBr

A solution of 1-methylpyrrolidine (400 mmol, 41.6 mL, 1.2 equiv.) in ethyl acetate (250 mL) was degassed for 15 min by argon bubbling. Then, 1-octylbromide (333 mmol, 58.0 mL, 1 equiv.) was added and the resulting mixture was refluxed for 17 h under argon. Finally, the solvent was evapored under reduced pressure (rotary evaporator). The residue was washed thoroughly with ethyl acetate (3 × 100 mL) and dried under reduced pressure to afford the MOPyrroBr first generation ionic liquid as an hygroscopic white solid in 92% yield.

MOPyrroBr: mp 98 °C. H NMR (δ ppm, $CDCl_3$, 300 MHz): δ 3.84–3.85 (m, 4H), 3.62–3.68 (m, 2H), 3.30 (s, 3H), 2.30–2.31 (m, 4H), 1.73–1.83 (m, 2H), 1.27–1.36 (m, 10H), 0.88 (t, 3H, J = 6.6 Hz). ^{13}C DEPT NMR (δ ppm, $CDCl_3$, 75.5 MHz): CH_2 δ 64.8 (2C), 64.5 (2C), 32.0, 29.6, 29.4, 26.8, 24.5, 22.9, 22.1. CH_3 δ 49.1, 14.4.

2.4. Synthesis of $MOPyrroNTf_2$

MOPyrroBr (307 mmol, 85.3 g, 1 equiv.) was added to a solution of $LiNTf_2$ (245 mmol, 70.4 g, 0.8 equiv.) in distilled water (200 mL). The mixture was stirred at room temperature under argon for 5 h and extracted with CH_2Cl_2 (3 × 70 mL). The combined organic phases were then washed with water (3 × 20 mL), brine (2 × 15 mL) and dried over $MgSO_4$. After filtration and evaporation under reduced pressure (rotary evaporator, 2×10^{-3} mbar), the desired $MOPyrroNTf_2$ second generation ionic liquid was obtained as a pale yellow liquid in 93% yield.

$MOPyrroNTf_2$: ^{1}H NMR (δ ppm, $CDCl_3$, 300 MHz): δ 3.57 (m, 4H), 3.37 (m, 2H), 3.06 (s, 3H), 2.21 (m, 4H), 1.65–1.76 (m, 2H), 1.20–1.33 (m, 10H), 0.83 (t, 3H).

^{13}C DEPT NMR (δ ppm, $CDCl_3$, 75.5 MHz): CH_2 δ 64.0 (2C), 63.9 (2C), 31.0, 28.4, 28.3, 25.6, 23.3, 21.9, 20.8. CH_3 δ 13.4, 47.8. IR (ATR, ZnSe crystal, neat): ν_{max} 2958, 2930, 2861, 1487, 1349, 1180, 1134, 1054 cm^{-1}.

2.5. General procedure for the epoxidation of alkenes in $MOPyrroNTf_2$

Mn(TPP)OAc (1.5 μmol, 1.1 mg) was dissolved in $MOPyrroNTf_2$ (3 mL) under sonication for 2 min. Imidazole (15 μmol, 1.0 mg), sodium bicarbonate (0.25 mmol, 21 mg, 0.25 equiv.) and alkene (1 mmol, 0.13 mL, 1 equiv.) were added to the solution thermostated at 25 °C (minichiller cooler). Hydrogen peroxide (2.5 mmol, 0.25 mL, 2.5 equiv., 30% solution in water) was added under ultrasonic irradiation (3 mm Ø tapered microtip probe, P_{elec} = 11 W). Additional amounts of sodium bicarbonate (0.25 mmol, 21 mg, 0.25 equiv.) and hydrogen peroxide (2.5 mmol, 0.25 mL, 2.5 equiv.) were added portion-wise every 15 min over 1 h. After 1 h of sonication (Fig. 1), the reaction mixture was throughly washed with an ether/cyclohexane (3:2 v/v) mixture (5 × 2 mL) to extract the remaining alkene and the newly formed products. The ether/cyclohexane phase was analyzed by gas chromatography. The chemical yields were determined by ^{1}H NMR after purification by column chromatography on silica gel with cyclohexane as eluent.

3. Results and discussion

The hydrophilicity of the aqueous bicarbonate-activated H_2O_2 system and the lipophilicity of alkenes urged us to develop a favorable ionic liquid system which can provide a suitable reaction environment for both hydrophilic and hydrophobic molecules. For these reasons, we decided to carry out the catalytic reaction in $MOPyrroNTf_2$ (Fig. 2) [15], an air, moisture and electrochemically stable hydrophobic ionic liquid. Indeed, $MOPyrroNTf_2$ displays a water content of 1165.2 ± 13.9 ppm and exhibits a low viscosity of (η = 237, 15 mm^2 s^{-1} at 20 °C) allowing a perfect solubilization of the porphyrin catalyst. Hence, $MOPyrroNTf_2$ affords an ideal interfacial contact area for mass transfer between the water and the organic phases.

Fig. 1. Ultrasonic experimental equipment.

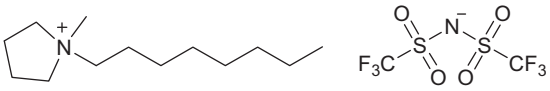


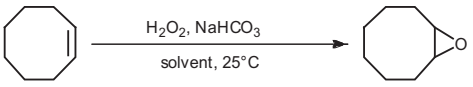
Fig. 2. Structure of the MOPyrroNTf$_2$ ionic liquid.

As detailed in Table 1, the BAP system affords the selective formation of cyclooctene oxide in modest yields at 25 °C in silent conditions when acetonitrile is used as solvent (even if one equivalent of $NaHCO_3$ is added portionwise). But, as the reaction time increases, the yield of cyclooctene oxide increases too. These results suggest that, in agreement with literature data [3a], the catalyst-free bicarbonate-activated H_2O_2 constitutes an efficient, but slow oxidizing system for the selective epoxidation of cyclooctene in acetonitrile. Under ultrasonic activation (Table 1, entry 3) the reaction is still selective but the yield in cyclooctene oxide is reduced by a factor of three suggesting a deactivation of the hydrogencarbonate-activated H_2O_2. The BAP system relies on the formation of the active peroxymonocarbonate ion, HCO_4^- according to the reaction $H_2O_2 + HCO_3^- \leftrightarrow HCO_4^-$ [1a] (the desired epoxidation reaction does not occur in the absence of sodium hydrogencarbonate). However, as mentioned above, under ultrasonic irradiation, the high cavitational intensity favors the H_2O_2 dissociation resulting in an immediate decrease in H_2O_2 concentration [16]. The net result is an instantaneous decrease in formation of the active oxidant-(peroxomonocarbonate ion) and a subsequent decrease in olefin oxidation. When MOPyrroNTf$_2$ was used as solvent (Table 1, entries 4 and 5) almost no reaction occured, both in silent conditions and under ultrasonic activation, showing a crucial solvent effect in the extent of reaction completion.

As MOPyrroNTf$_2$ partly dissolves cyclooctene, it forms at least a biphasic medium with the oxidant slowly transferring from the aqueous phase to the organic one, hence limiting the conversion. An attempt was made to increase the rate of mass transfer [16] using ultrasonic irradiation. However, this had no significant effect in the absence of catalyst. Keeping in mind that the development of an environmentally benign and versatile methodology for enantioselective epoxidation of olefins constitutes the ultimate goal in catalysis, we then explored the use of the model Mn(TPP)OAc to perform the oxygen transfer from H_2O_2/$NaHCO_3$ to the olefin substrates. The reaction was first carried out with cyclooctene as substrate according to the conditions previously described [7].

Catalytic tests in acetonitrile resulted in all cases in catalyst bleaching. In addition, as shown in Table 2 (entries 1 and 2), when acetonitrile was used as reaction medium, conversions of cyclooctene to cyclooctene oxide were comparable to those obtained without catalyst whatever the reaction time (Table 1, entries 1 and 2). This suggests that the catalyst does not play any key role in the oxidation process under those experimental conditions, and that the oxidation proceeds according to the classical BAP mechanism. Conversely, when the reaction was carried out under ultrasonic irradiation (Table 2, entry 3) the yield of epoxide remained in the 30% range whereas it was limited to 8% in the absence of Mn(TPP)OAc (Table 1, entry 3). This observation suggests that under ultrasound activation the mechanism is different, and probably involves the manganese porphyrin possibly through the already known oxo-manganyl intermediate [17]. This hypothesis was further verified when the reaction was carried out in MOPyrroNTf$_2$. In this reaction medium and in silent conditions, the catalyst does not bleach; but, probably due to the limited mass transfer afforded by mechanical stirring, a low 12% conversion was obtained after 5 h of reaction at room temperature (Table 2, entry 4). Interestingly, upon ultrasound activation the rate transfer of oxidizing species is enhanced, resulting in 72% conversion in only 1 h (Table 2, entry 5). This result undoubtedly confirms that under ultrasonic irradiation, the BAP-epoxidation does not occur. Even more, it highlights the crucial role played by the porphyrin catalyst that is prevented from bleaching by the ionic liquid.

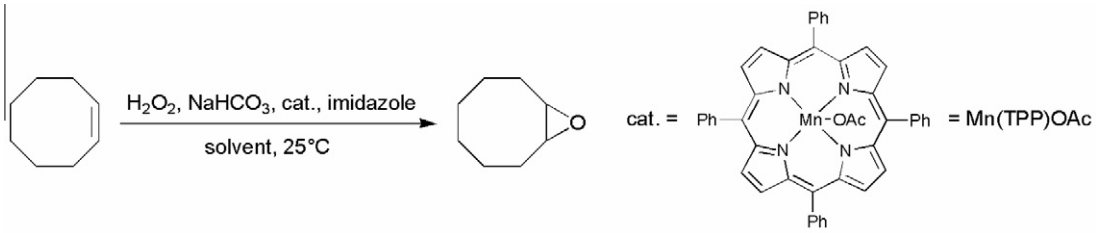
Table 1
BAP-mediated epoxidation of cyclooctene.



Entry	Solvent	Activation method	Time (h)	Epoxide yield[a](%)	Selectivity (%)
1	CH_3CN	–	1	26[b] (4[d])	100
2	CH_3CN	–	5	54[b]	100
3	CH_3CN	))))	1	8[c]	100
4	MOPyrroNTf$_2$	–	1	1[b] (<1[d])	100
5	MOPyrroNTf$_2$	))))	1	3[c]	>99

[a] GC-yield (based on starting cyclooctene) measurements.
[b] Optimized reaction conditions: 1 equiv. substrate, 10 equiv. H_2O_2, 0.53 equiv. $NaHCO_3$, 3 mL solvent, T = 25 °C.
[c] Optimized reaction conditions: 1 equiv. substrate, 10 equiv. H_2O_2, 4 × 0.25 equiv. $NaHCO_3$, 3 mL solvent,)))) ultrasonic irradiation: f = 20 kHz, P = 11 W (electric).
[d] Portionwise addition of the oxidant (4 × 0.25 equiv.).

Table 2
Effect of catalysis.



Entry	Solvent	Activation method	Time (h)	Epoxide yield[a] (%)	Selectivity (%)
1	CH_3CN	–[d]	1	34[b] (5[e])	100
2	CH_3CN	–[d]	5	54[b]	100
3	CH_3CN	))))[d]	1	33[c]	100
4	$MOPyrroNTf_2$	–	5	12[b]	100
5	$MOPyrroNTf_2$	))))	1	72[c] (66[f])	>99

[a] GC-yield (based on starting cyclooctene).
[b] Optimized reaction conditions: 1 equiv. substrate, 10 equiv. H_2O_2, 0.53 equiv. $NaHCO_3$, 1.5 mol% imidazole, 0.15 mol% Mn(TPP)OAc, 3 mL solvent, $T = 25$ °C.
[c] Optimized reaction conditions: 1 equiv. substrate, 10 equiv. H_2O_2, 4 × 0.25 equiv. $NaHCO_3$, 1.5 mol% imidazole, 0.15 mol% Mn(TPP)OAc, 3 mL solvent,)))) ultrasonic irradiation: $f = 20$ kHz, $P = 11$ W(electric).
[d] Bleaching of catalyst.
[e] Portionwise addition of the oxidant (4 × 0.25 equiv.).
[f] Isolated yield.

Table 3
Epoxidation of various alkenes.

Entry	Substrate	Solvent	Catalyst	Activation method	Epoxide yield[a] (%)	Selectivity (%)
1	Cyclohexene	CH_3CN	None	–	99[b] (99[e])	100
2	Cyclohexene	CH_3CN	Mn(TPP)OAc[d]	–	98[b]	>99
3	Cyclohexene	$MOPyrroNTf_2$	None	))))	1[c]	>99
4	Cyclohexene	$MOPyrroNTf_2$	Mn(TPP)OAc	))))	95[c] (91[f])	>99
5	Styrene	CH_3CN	None	–	61[b] (60[e])	97
6	Styrene	CH_3CN	Mn(TPP)OAc[d]	–	73[b]	>99
7	Styrene	$MOPyrroNTf_2$	None	))))	7[c]	96
8	Styrene	$MOPyrroNTf_2$	Mn(TPP)OAc	))))	86[c] (74[f])	91
9	α-Pinene	CH_3CN	None	–	10[b] (2[e])	100
10	α-Pinene	CH_3CN	Mn(TPP)OAc[d]	–	11[b]	>99
11	α-Pinene	$MOPyrroNTf_2$	None	))))	2[c]	>99
12	α-Pinene	$MOPyrroNTf_2$	Mn(TPP)OAc	))))	49[c] (39[f])	82

[a] GC-yield (based on starting cyclooctene).
[b] Optimized reaction conditions: 1 equiv. substrate, 10 equiv. H_2O_2, 0.53 equiv. $NaHCO_3$, 1.5 mol% imidazole, 0.15 mol% Mn(TPP)OAc, 3 mL solvent, $T = 25$ °C, 1 h.
[c] Optimized reaction conditions: 1 equiv. substrate, 10 equiv. H_2O_2, 4 × 0.25 equiv. $NaHCO_3$, 1.5 mol% imidazole, 0.15 mol% Mn(TPP)OAc, 3 mL solvent,)))) ultrasonic irradiation: $f = 20$ kHz, $P = 11$ W (electric), 1 h.
[d] Bleaching of catalyst.
[e] Portionwise addition of the oxidant (4 × 0.25 equiv.).
[f] Isolated yield.

Based on literature about Mn-porphyrin catalytic epoxidation with H_2O_2, imidazole was added in reaction medium (Tables 2 and 3). Indeed, epoxide yields obtained without imidazole are very low and axial ligand role of imidazole (proximal effect) was shown by Mansuy and co-workers [17,18].

The combination ionic liquid/ultrasound leads to better conversions with, in addition, a decreased reaction time. These optimized conditions were applied to a series of substrates displaying different electronic and/or steric properties and the results were gathered in Table 3.

Analysis of Table 3 (entries 1, 2 and 4) reveals that cyclohexene oxidation readily affords the corresponding epoxide, whatever the experimental conditions. However, entry 3 (Table 3) confirms that in the absence of catalyst, the BAP system is deactivated under ultrasound irradiation. A similar trend is observed when styrene and α-pinene are used as substrates (Table 3, entries 7 and 11). For all investigated reactions, the best conditions involve the use of $MOPyrroNTf_2$ as solvent, Mn(TPP)OAc as catalyst and ultrasonic irradiation. Under these conditions, the challenging trisubstituted α-pinene double bond is selectively epoxidised in an encouraging 49% yield (Table 3, entry 12), whereas the silent conditions afforded the corresponding epoxide in a limited 10% conversion (Table 3, entry 9). The isolated yields confirmed that almost no degradation occured using our optimized conditions. Indeed, in all cases, the yields are good to excellent – 66%, 91%, 74% and 39% – for cyclooctene oxide, cyclohexene oxide, styrene oxide and α-pinene oxide, respectively, and the selectivity is close to 100% despite a limited decrease under ultrasound activation.

4. Conclusion

In our work the use of ultrasonic irradiation in $MOPyrroNTf_2$ prevents the olefin epoxidation via the bicarbonate-activated hydrogen peroxide system in the presence of a manganese porphyrin. In the afore-mentioned conditions, epoxidation most likely takes place via a classical high-valent oxo-managanese porphyrin complex. Indeed, our study demonstrates that ultrasound favor the fast degradation of the transient oxidant active peroxymonocarbonate intermediate (half life ~5 min, pH 7.4 under silent

conditions) allowing a fast epoxidation via the porphyrin complex [17]. Thus, the unique combination of ultrasound activation and ionic liquid should allow the use of a chiral complex for the enantioselective epoxidation of olefins in the presence of the environmentally benign H_2O_2/$NaHCO_3$ combination. Further work is currently in progress in our laboratories to develop enantioselective epoxidation of olefins under this smart ultrasound/ionic liquid system.

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