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Ionic liquids as reaction media in catalytic oxidations with manganese and iron pyridyl triazacyclononane complexes

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ABSTRACT

A family of bioinspired iron and manganese complexes of general formula $[M^{II}(CF_3SO_3)_2(^{Me,X}PyTACN)]$, where $^{Me,X}PyTACN$ = 1-[2′-(6–Rpyridyl)methyl]-4,7-dimethyl-1,4,7-triazacyclononane, R=H,Me and M = Fe, and Mn has been studied as efficient catalytic systems for hydrogen peroxide oxidation reactions. Previous work revealed that the manganese derivative $[Mn^{II}(CF_3SO_3)_2(^{Me,H}PyTACN)]$, **1**, in acetonitrile exhibits a high catalytic activity in the epoxidation of a wide range of olefins (TON: 810–4500), using acetic acid and hydrogen peroxide as primary oxidant. The analogous iron based complex $[Fe^{II}(CF_3SO_3)_2(^{Me,H}PyTACN)]$, **2a** and $[Fe^{II}(CF_3SO_3)_2(^{Me,Me}PyTACN)]$, **2b** promote the high added value oxidation reaction of alkanes in mild conditions. In this work sustainability and selectivity of the oxidative system is improved with the use of the ionic liquids (ILs) as reaction medium. The possibility to recycle the catalytic phase without loss of the activity with respect to the original reaction in acetonitrile (MeCN) is reported.

1. Introduction

The development of efficient and sustainable systems for oxidation reactions, combining the use of hydrogen peroxide as primary oxidant, a non-toxic metal source and a recyclable reaction medium, is one of the biggest challenges in the catalysis field. Environmentally benign and selective epoxidation reactions are important targets in up-to-date research. Diverse epoxy compounds are widely used as intermediates to obtain value added chemical products; therefore a broad substrate scope is crucial in proposing new oxidative methodologies/catalysts. Activation of peroxides by transition-metal catalysts definitely is a central topic in oxidation chemistry from many points of view: i.e., efficiency, sustainability, substrate tolerance etc.

Bioinspired iron and manganese coordination complexes with tetradentate nitrogen based ligands have emerged as powerful alkane and alkene oxidation catalysts, and some of them have also found use in asymmetric catalysis [1–13]. Iron and manganese complexes containing tetradentate ligands based in the triazacyclononane ring, appended with a methylpyridine arm ($[M^{II}(CF_3SO_3)_2(^{Me,}RPyTACN)]$, where $^{Me,}RPyTACN$ = 1-[2′-(6-X-pyridyl)methyl]-4,7-dimethyl-1,4,7-triazacyclononane, and M = Fe, and Mn, Fig. 1) belong to this type of compounds and their catalytic activity in oxidation reactions with H_2O_2 was reported. These complexes have also coincident structural elements with the well-studied Mn(TMTACN) (TMTACN = *N*,*N′*,*N″*-trimethyl-1,4,7-triazacyclononane) system, which shows excellent performance in a number of oxidative processes, including olefin epoxidation and *cis*-dihydroxylation reactions [14–18].

With the manganese catalyst $[Mn(CF_3SO_3)_2(^{Me,H}PyTACN)]$ a very efficient and regioselective epoxidation of a wide range of olefins was obtained [19], while the corresponding iron complexes show remarkably efficient conversion of H_2O_2 into alkane oxidized products, with retention of the configuration [20]. The elucidation of the reaction mechanisms operating in these bioinspired oxidation reactions is of great importance in order to increase the knowledge of similar reactions taking place at biological systems, and also to improve the general efficiency of the reactions with the objective of developing synthetic methods. The reactive intermediate involved in the oxidation of olefins and alkanes catalyzed by the iron complexes **2** has been proposed to be a $Fe^V(O)(OH)$ species on the basis of product analysis and computational methods. More recently [21,22] such species has been characterized through variable temperature mass spectroscopy (VT-MS), contributing to provide a general tool in the identification of catalytic intermediates. Such innovative technique, coupled with isotopic labeling experiments, allows to follow the oxygen atom transfer, demonstrating that the active species contains an oxygen atom from H_2O_2 and a second oxygen atom from water. This formulation thus provides further evidence about its possible generation via a water-assisted heterolytic O–O breakage in the precursor

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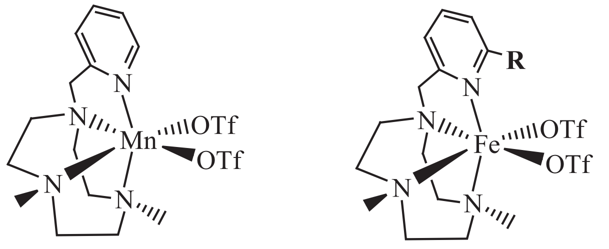


(1)

R = H (2a), Me (2b)

Fig. 1. Bioinspired manganese and iron complexes with a pyridyl triazacyclononane ligand (pyTACN) used in this study.

$Fe^{III}(OOH)(OH_2)$ species [23,24]. Furthermore, optimized conditions, in terms of yields and also of selectivity towards oxidation of methylene sites of alkanes oxidation have been recently described [25]. The versatility of the iron triazacyclononane complex **2a** and **2b** also concerns the possibility to mediate efficient chemically driven water oxidation employing CAN (cerium^{IV} ammonium nitrate) as sacrificial chemical oxidant [26]; mechanistic studies reveal that the oxidizing intermediates formed in the catalytic cycle of WO are the same as those involved in alkane hydroxylation and olefin *cis*-dihydroxylation reactions using H_2O_2, allowing the development of a catalytic system that uses CAN as single-electron oxidant and water as oxygen-atom source [27].

Beyond the use of H_2O_2 and O_2 as oxidant, the design of alternative reaction media to VOC's (volatile organic compounds) is crucial for the sustainability improvement of modern industrial processes [28,29]. Ionic liquids (ILs) represent the state of the art in this field and in the last decades several examples regarding their positive effects in synthetic chemistry, in terms of stabilization of reactive intermediates and transition states, are widely documented in literature [30–32]. The tunable chemical and physical properties of ILs, such as the prospect to modify their molecular structure to give specific properties, allow to design a tailored medium for each case of interest; in addition, a proper choice of cation and anion provide a fine tuning of their solubility in water or organic solvent. An ever-increasing interest has been dedicated to ionic liquids as media for catalysis, both in biphasic and homogeneous conditions [33–38]. In particular, metal catalysts, having polar or ionic character are often fully dispersed or immobilized into ionic liquid, at odd with the less polar organic substrates, so that the catalytic phase can be easily separated from reaction mixture and suitably recycled.

In the present work, the possibility to improve the environmental and economic sustainability and the selectivity in the final products distribution, in the oxidation reactions catalyzed by the iron and manganese complexes of the pyTACN ligand, namely **1** and **2**, is reported.

2. Experimental

2.1. Reagents and instruments

Reagents and HPLC solvents were purchased from Sigma–Aldrich and used without further purification. Pyridine and 1-methylimidazole used for the synthesis of ILs were distilled from KOH prior the use. The titer of the 30% commercial solution of hydrogen peroxide was determined by iodometric titration. GC analyses were performed with a Varian 3900 chromatograph equipped with a FID 1770 detector and a Supelco SPB-5 column. For the HPLC measurements a Shimadzu LC-10ADvp with a UV–vis detector and a C_{18} inverse phase column was used. The identification and the purity of the ILs were checked through the ^1H NMR spectroscopy with a Bruker Advance 300 MHz instrument. A high vacuum pump with a pressure of 0.1 mbar was used.

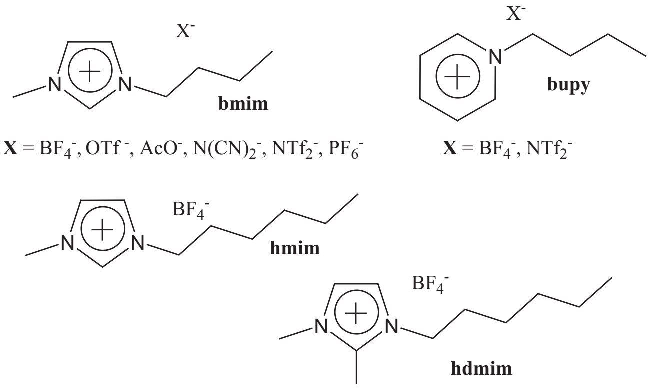


Fig. 2. Molecular structures of the ionic liquids utilized as reaction media.

2.2. Ionic liquids synthesis

The ILs (Fig. 2) are prepared according to literature procedures [39–43]; details concerning the ^1H NMR characterization of the precursor salts are reported in the supplementary information.

2.3. Catalysts synthesis

The pyridyl triazacyclononane ligands and the corresponding manganese (**1**) and iron (**2a**, **2b**) complexes were prepared following previously reported experimental procedures [20,44].

2.4. General catalytic procedures

The epoxidation reactions catalyzed by $[Mn^{II}(CF_3SO_3)_2(^{Me,H}PyTACN)]$ complex **1** were carried out in several ILs with styrene and cyclooctene (COT) as reference alkenes.

In a Schlenk tube containing catalyst (0.3 mg, 0.44 μmol, 0.1% mol), 4 ml of IL, previously dried with a high vacuum pump, olefin (0.44 mmol) and acetic acid (14 eq, 6.2 mmol, 0.35 ml) were added. The system was kept under vigorous magnetic stirring at 0 °C in an ice bath. A H_2O_2 30%: H_2O 1:1 solution (1.2 eq, 0.53 mmol, 100 μl) was gradually injected within half an hour. After further hour of reaction the ionic liquid mixture was analyzed by HPLC and repeatedly extracted with diethyl ether in order to isolate the residue alkene and the epoxide, and to recover the catalytic phase IL/**1**. Water and acetic acid were removed drawing the mixture under high vacuum at 60 °C for an hour.

The oxidation reaction catalyzed by $[Fe^{II}(CF_3SO_3)_2(^{Me,H}PyTACN)]$ **2a** and $[Fe^{II}(CF_3SO_3)_2(^{Me,Me}PyTACN)]$ **2b** was investigated considering cyclohexane as reference alkane.

In a Schlenk tube containing catalyst (2.5 μmol, 0.1% mol), 2 ml of IL, previously dried with a high vacuum pump, and cyclohexane (2.5 mmol) were added and kept under vigorous magnetic stirring at 25 °C. A solution of 0.4 ml of H_2O_2 30% (0.25 mmol, 25 μl) in CH_3CN was gradually injected within half an hour. The mixture was then stirred for an additional 10 min and repeatedly extracted with diethyl ether. The organic phase was filtered on silica gel to remove traces of the IL and analyzed by gas chromatography after the addition of naphthalene as internal standard.

2.5. Quantitative analyses

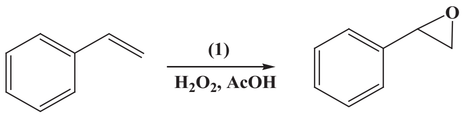
The quantitative appraisal of oxidation products was performed either by GC or HPLC measurements; in particular the HPLC analyses were performed when decomposition of the oxidation products in the GC injector was detected.

3. Results and discussion

The Mn complex $[Mn^{II}(CF_3SO_3)_2(^{Me,H}PyTACN)]$ **1** shows efficient catalytic activity in the epoxidation reactions with different oxidants [45], in particular with peracetic acid [44]. In a more convenient and sustainable process the mixture of acetic acid and H_2O_2 has been used instead of peracetic acid, leading to the *in situ* formation of the active oxidant. Unfortunately, in the absence of carboxylic acids **1** catalyzes the decomposition of hydrogen peroxide. Instead, addition of large excesses of acetic acid is required to achieve quantitative conversion of the substrate. The catalytic mechanism is not yet completely clear and further studies are needed, similarly to other manganese catalyzed oxidations [1,46]. Previous isotopic labeling studies show that the main source of oxygen atoms incorporated into the epoxide derive from the H_2O_2. Moreover olefins, easily subjected to isomerization, are epoxidized with retention of configuration. The experimental data available for olefin epoxidation reactions mediated by **1** are consistent with two mechanistic scenarios; oxygen atom transfer may be executed by a high valent peroxidic intermediate $Mn^{IV}(OOAc)$, as early proposed by Busch and co-workers [47]. Alternatively, acetic acid may assist the heterolytic rupture of the peroxide O–O bond, forming a high valent $Mn^{V}(O)$ as active species. Involvement of dinuclear manganese reactive intermediates as proposed for the Mn(TMTACN) catalyzed oxidations appears in this system unlikely [46,48].

Ionic liquids (ILs) have been used as “greener” alternative to the MeCN reaction medium employed in the original procedure, with the aim to recover the catalytic phase and reuse it in a subsequent cycle of reaction. A broad variety of ILs in terms of structural, coordination ability and hydrophilic character has been studied. The specific combination between cations and anions influences the chemical and physical properties of the medium and so its role in the catalytic efficiency. Also the absence of impurities in ILs is of primary importance in catalytic processes. Several precautions on synthetic strategy have been taken to remove traces of inorganic salts, basic or acid species in order to prepare ILs with a high purity grade [49].

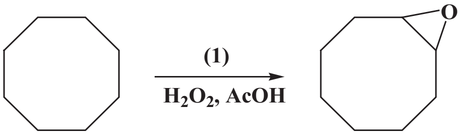
Table 1
Oxidation of styrene catalyzed by **1** in ILs.[a]



Entry	Solvents	Conversion %[b]	Yield %[c]
1[d]	MeCN	100	94
2	$bmimBF_4$	98	99
3	bmimOTf	13	–
4	$bmimNTf_2$	0	0
5	$bmimPF_6$	0	0
6	bmimOAc	0	0
7	$bmimN(CN)_2$	0	0
8	$hmimBF_4$	88	93
9[f]	$hdmimBF_4$	30	33
10	$bupyBF_4$	83	–[e]
11[f]	$bupyNTf_2$	100	–

[a] 1: 1200: 1000 cat.: H_2O_2: styrene, HPLC yields.
[b] Conversion% = (final mols of substrate/initial mols of substrate) %.
[c] Yield% = (mols of product/mols of substrate) %.
[d] Previous work.
[e] Yield could not be measured because the IL exhibits absorbance that overlaps with that of the product.
[f] GC yields.

Table 2
Oxidation of cyclooctene (COT) catalyzed by **1** in ILs.[a]



Entry	Solvents	Conversion %	Yield %
1[b]	MeCN	100	95
2	$bmimBF_4$	0	0
3	$bupyNTf_2$	100	89

[a] 1: 1100: 1000 cat.: H_2O_2: COT; GC yields.
[b] Previous work.

The results on the reactivity of **1** in epoxidation reaction carried out in different ionic liquids are collected in Tables 1 and 2. In general, product yields obtained in ionic liquids are very similar to that observed in acetonitrile. Styrene was used as model substrate in these reactions because of its general solubility in ILs, and because both the substrate and the corresponding epoxide can be detected and quantified by means of a diode array detector, taking advantage of the absorbance of the aromatic ring. Therefore, products have been quantified with HPLC measurements through a simple direct analysis of the ionic liquid mixtures.

Results in Table 1 reveal that the choice of the anionic partner in the IL appears to play a key role in the outcome of the reaction. Better results have been obtained when low-coordinating tetrafluoroborate anion is used (Entries 2,8–10). While, when anions characterized by higher coordinating ability, such as triflate or acetate (Entries 3,6), were present unsatisfactory or absence of catalytic activity was detected. The hydrophobic character of the IL does not appear crucial, in fact, positive results for olefin conversions have been obtained by using $hmimBF_4$ and $bupyNTf_2$ (Entries 8,11). Styrene epoxidation reaction appears not to be a viable process in $bupyNTf_2$ because of the higher acidity of acetic acid in this medium, which caused ring opening of the epoxide product (Entry 11). Furthermore, when styrene was insoluble in the IL (Entries 4,5) no catalytic activity was detected.

The influence of the cationic moiety in the outcome of reaction can be also explored comparing several type of imidazolium BF_4^- based ILs. The catalytic activity of **1** decreases passing from the typical 1-butyl-3-methylimidazolium, to the longer alkyl chain analogous, or to the trialkylimidazolium cation (Entries 2,8,9). Such structural modification leads to a significant alteration in the cation symmetry, cation–anion interaction and in the intermolecular dynamics of the IL, which results in a different degree of viscosity [50]. In fact such property reasonably affects both the solubility of the reagents, and the mass transfer rate during the reaction. The great importance of the cation nature is particularly visible in the case of the reaction performed in $bmimNTf_2$ and $bupyNTf_2$ (Entries 4,11); a higher viscosity of the latter could be responsible of the unsatisfactory results obtained, with respect to the total styrene conversion in the pyridinium analogue.

Also cyclooctene (COT) epoxidation was attempted. However due to its low solubility in $bmimBF_4$, the oxidation was feasible only in $bypyNTf_2$ with a quantitative conversion of the substrate and an interesting yield of 89% in the corresponding *cis*-COT oxide

Table 3
Olefins conversion in the IL/**1** catalytic phase recycle.

	bmimBF_4 (%)	Styrene		COT
		hmimBF_4 (%)	bupyBF_4 (%)	bupyNTf_2 (%)
I cycle	98	88	83	100
II cycle	95	43	81	88
III cycle	–	–	–	–

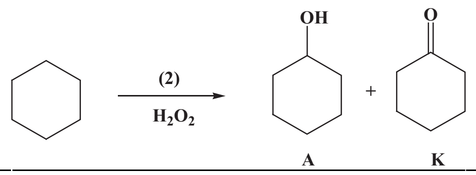
(Entries 2,3). This result once more demonstrates that suited IL's can be found for diverse catalytic processes [51].

In order to explore the synthetic applicability of the ILs based procedure, after the complete consumption of the oxidant, the catalytic phase was recharged with substrate and H_2O_2 two more times and a single final work up of the reaction mixture was done. Unfortunately, with this protocol, it was observed that no more epoxide was obtained with respect to the single substrate/H_2O_2 addition. Indeed catalytic activity was not resumed even in a second cycle of reaction, demonstrating that the ionic liquid regeneration to the initial reaction condition are required.

Consequently, we explored a recycling procedure (see Section 2 for details) involving separation of the products after completion of the oxidation and subsequent reuse of the catalytic ionic phase plus new substrate and primary oxidant. In this case, two cycles are possible with minor loss of catalytic activity in three IL (bmimBF_4, bupyBF_4 and bupyNTf_2, see Table 3), but a third cycle was ineffective in producing more epoxide. A tentative explanation could be a progressive degradation of the catalyst and/or its leaching from the IL phase during the work up. It may be anticipated that the utilization of a continuous flow reactor could greatly improve the efficiency of the process in the ionic medium.

Within the framework of the olefins oxidation, the use of the iron catalysts **2a** and **2b** represents an interesting alternative to **1**, because the iron catalysts promote not only epoxidation but also *cis*-dihydroxylation of olefins, employing H_2O_2 as oxidant [20]. Considering the interest in the development of environmentally benign oxidation systems, and the advantage of avoiding the use of acetic acid, attempts to perform the iron catalyzed COT oxidation in ILs were carried out. Unfortunately the formation of *cis*-COT oxide and *cis*-diol was not observed, in 1-butyl-3-methylimidazolium $^-BF_4$, ^-OTf and $^-NTf_2$. Indeed, in reaction times similar to those necessary for the completion of the oxidation in MeCN, hydrogen peroxide is not consumed, thus indicating either a catalyst inhibition or degradation of the iron complexes in this media. In spite of these unsatisfactory results with COT, the reactivity of the iron catalytic system in ILs was investigated in cyclohexane oxidation reactions. To this purpose, bupyNTf_2 was chosen because of the better cyclohexane solubility. Although the catalytic activity observed in these reactions (Table 4) is less than that observed in MeCN, product yields are still higher than those obtained with most non heme iron catalysts studied to date in acetonitrile [52]. Most remarkably, a notable tendency toward the alcohol derivative formation was obtained, an indication that reactions in these ionic liquids remain metal based processes, distinct from free diffusing radicals; in particular the use of the ionic liquid promotes a selectivity two-times higher than that obtained in molecular solvent. Considering that a large excess of alkane is used to avoid overoxidation reaction, such evidence probably validates the involvement of even more selective metal-centered oxidant in ILs. These preliminary results open the possibility to investigate a better tailored IL able to improve the alkane conversion besides the selectivity in the products distribution.

Table 4
Oxidation of cyclohexane catalyzed by **2a** and **2b**.[a]



Entry	Solvents	Catalyst	Yield %	A:K
1[b]	MeCN	2a	39	2.6
2[b]	MeCN	2b	64	4.3
3	bupyNTf_2	2a	7	4
4	bupyNTf_2	2b	20	8

[a] 1: 100: 1000 cat.: H_2O_2: cyclohexane.
[b] Previous work; GC yields.

4. Conclusions

In conclusion we have demonstrated the efficiency of epoxidation of olefins catalyzed by **1** in ILs, and the possibility to carry out two cycles of the reaction with the same catalytic phase. Moreover a oxidation of cyclohexane catalyzed by **2a** and **2b** has been detected.

It was noted that the success of the epoxidation reaction depends not only on the choice of ILs, which should contain a low-coordinating anion, but, on the basis of the unsatisfactory results obtained with the more viscous ILs (bmimNTf_2 and hdmimBF_4), also viscosity of the ionic medium appears to play an important role. It was also shown that the reaction cannot be generalized, because the oxidation of a particular olefin is obtained only when the appropriate IL is used. The bupyNTf_2 appears to be a good and versatile solvent when poorly soluble olefins are oxidized, i.e., COT, but its use is not possible when sensitive products are formed. Preliminary results in the alkane oxidation have shown a promising selectivity in the products distribution with the use of bupyNTf_2 as reaction medium.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2013.10.016.

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