Epoxidation of cyclooctene catalyzed by dioxomolybdenum(VI) complexes in ionic liquids

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Abstract

A series of room temperature ionic liquids (RTILs) were tested as solvents for dioxomolybdenum(VI) complexes in the catalytic epoxidation of *cis*-cyclooctene, using *tert*-butyl hydroperoxide (TBHP) as the mono-oxygen source. In general, the best results were obtained using the RTIL 1-*n*-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIM]NTf$_2$). Upon addition of cyclooctene and TBHP (in decane) to solutions of MoO$_2$X$_2$(*p*-tolyl-(CH$_3$-DAB)) [X = Cl, Me; *p*-tolyl-(CH$_3$-DAB) = *N,N-p*-tolyl-2,3-dimethyl-1,4-diazabutadiene] in [BMIM]NTf$_2$, biphasic mixtures were obtained. The epoxidation reactions proceeded with 100% selectivity to cyclooctene oxide, but activities were lower than those observed for the same catalysts in the absence of any additional solvent (other than decane). By contrast, in the presence of the novel cationic complex [MoO$_2$Cl(Bn$_3$Me$_3$-tame)]BF$_4$ [Bn$_3$Me$_3$-tame = *N,N′,N″*-tribenzyl-1,1,1-tris(methylaminomethyl)ethane] and [BMIM]NTf$_2$, the catalytic activity was higher than that achieved with no additional solvent, although a minor amount of 1,2-cyclooctane diol was formed as a by-product. This system gave the best results in terms of catalyst/solvent recycling (carried out by extracting the reactants and products with *n*-hexane). There was a loss of catalytic activity from the first to the second run, but thereafter tended to stabilise. Interestingly, selectivity to the desired epoxide increased upon recycling, reaching 100% in the third run.
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Keywords: Olefin epoxidation; Dioxomolybdenum(VI) complexes; Ionic liquids; Catalyst recycling; *tert*-Butyl hydroperoxide

1. Introduction

High-valent d^0 transition metal complexes, such as Mo^{VI}, V^V and Ti^{IV}, are versatile catalysts for the epoxidation of alkenes [1–3]. Molybdenum catalysts in the homogeneous phase (Arco and Halcon processes) are commercially applied to the production of propylene oxide using alkyl hydroperoxides as oxidants [4,5]. In recent years, complexes of the type MoO(O$_2$)$_2$(L$_1$)(L$_2$) and MoO$_2$X$_2$(L$_1$)(L$_2$) (X = Cl, Br, CH$_3$), with different combinations of base ligands L$_1$ and L$_2$, have been experimentally characterised and tested as catalysts for epoxidation reactions, usually employing *tert*-butyl hydroperoxide (TBHP) as the mono-oxygen source [6–17]. Important properties, such as the solubility of the complex and the Lewis acidity of the metal centre, can be fine-tuned by variation of either X or L. However, homogeneous catalytic processes often suffer from drawbacks such as the laborious separation of the reagents and products from the catalyst and catalyst recycling is often not feasible, originating chemical waste, which is of ecological and economical concern. One way to address these problems is to immobilise the homogeneous catalysts on solid supports [18,19]. These approaches generally require additional modification of the catalyst, frequently lead to partial loss of activity,

sometimes due to metal leaching from the solid into solution, making them unattractive for industrial applications.

A promising alternative to the above catalytic systems is to immobilise the catalyst in a room temperature ionic liquid (RTIL), i.e. an organic salt with a melting point below ambient temperature. These novel reaction media are interesting solvents, particularly for catalysis since they are non-volatile, non-flammable and thermally stable and possess enhanced potential for catalyst separation and recycling, and accelerating reactions [20–26]. RTIL have been used for several types of organic reactions, but their use as solvents for oxidation reactions is only just emerging. Imidazolium-based ionic liquids are stable enough to air, moisture and heat and have been successfully employed for immobilising Ni(acac)₂ in the catalytic oxidation of aromatics [27], Pd in the oxidation of benzyl alcohol [28], PdCl₂ in Wacker-type reactions [29] and Sharpless catalytic asymmetric dehydroxylation [30,31]. Transition metal (Mn, Cr) salen complexes immobilised in BMIM-based ionic liquids (BMIM = 1-butyl-3-methylimidazolium) constitute recyclable catalyst/solvent systems for the asymmetric epoxidation of olefins and ring-opening of epoxides [32,33]. More recently, the catalytic epoxidation of alkenes has been successfully carried out by manganese porphyrin in [BMIM]PF₆ with advantages over an organic catalytic phase, such as higher reaction rates and efficiency and the RTIL/catalyst system could be recycled [34,35].

To the best of our knowledge, the use of ionic liquids in Mo^{VI} catalyst systems has yet to be investigated. Herein we report on the catalytic performance of dioxomolybdenum(VI) complexes for the epoxidation of *cis*-cyclooctene using TBHP as the oxidant and an ionic liquid as additional solvent. The results are compared with "conventional" one-phase homogeneous catalysis.

2. Experimental

2.1. Materials and methods

The compounds MoO₂Cl₂ [36,37], MoO₂Cl₂(THF)₂ [38], N,N-p-tolyl-2,3-dimethyl-1,4-diazabutadiene [p-tolyl-(CH₃-DAB)] [39], MoO₂Cl₂(p-tolyl-(CH₃-DAB)) (**1**) [40] and 1,1,1-tris(methylaminomethyl)ethane (Me₃-tame) [41] were prepared as described in the literature (see compounds **1** and **2**).
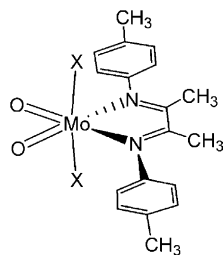
X = Cl (**1**), Me (**2**)

Published procedures were also employed for the synthesis of the ionic liquids [BMIM]PF₆, [BMIM]NTf₂, [C₈MIM]PF₆, [BdMIM]NTf₂, [C₅O₂MIM]PF₆ and [(d-h)₂dmg]PF₆ [42–46]. Microanalyses for C, H and N were carried out at the ITQB. Mo was determined by ICP-AES at the Central Laboratory for Analysis, University of Aveiro (E. Soares). IR spectra were obtained as KBr pellets using a FTIR Mattson-7000 infrared spectrophotometer. ¹H NMR spectra were recorded at 300 MHz using a Bruker CXP 300 spectrometer. ¹³C NMR spectra were recorded at 100.28 MHz using a Bruker Avance DPX-400 spectrometer. Mass spectra were acquired on Bruker esquire 3000⁺.

2.2. MoO₂Me₂(p-tolyl-(CH₃-DAB)) (2)

A solution of MoO₂Cl₂(THF)₂ (1.03 g, 3.0 mmol) in dry THF (20 mL) was treated with p-tolyl-(CH₃-DAB) (0.79 g, 3.0 mmol) and the mixture stirred vigorously for 30 min. After this time the mixture was cooled to −20 °C (isopropanol bath) and a solution of CH₃MgCl in THF (3 M, 2.0 mL, 6.0 mmol) added slowly. The reaction was then allowed to warm up to room temperature and stirred for 1 h. The dark red suspension was taken to dryness and ice-cold distilled water added. The product was extracted with CH₂Cl₂ and the organic phase dried over anhydrous Na₂SO₄. Finally, the solvent was removed under reduced pressure and the resulting red residue recrystallized from CH₂Cl₂/diethyl ether (1.06 g, 90%). Found: C, 56.72; H, 6.16; N, 6.58. C₂₀H₂₆MoN₂O₂ requires C, 56.87; H, 6.20; N, 6.63%. Selected FTIR (KBr, cm⁻¹): ν = 934 vs (ν$_{sym}$ Mo=O), 907 vs (ν$_{asym}$ Mo=O). ¹H NMR (300 MHz, CDCl₃, Si(CH₃)₄, 20 °C): δ = 7.21 (d, 4H), 6.90 (d, 4H), 2.31 (s, 6H), 2.25 (s, 6H), 0.82 (s, 6H). ¹³C NMR (100.28 MHz, CDCl₃, Si(CH₃)₄, 20 °C): δ = 165.1, 146.8, 137.0, 129.8, 120.4, 21.1, 20.0.

2.3. N,N′,N″-tribenzyl-1,1,1-tris(methylaminomethyl)ethane (Bn₃Me₃-tame)

Potassium hydroxide powder (210 mg, 3.90 mmol; 3.1 eq.) and benzyl bromide (460 μl, 3.90 mmol; 3.1 eq.) were added to a solution of Me₃-tame (200 mg, 1.26 mmol) in dry toluene (4 mL). The reaction mixture was heated overnight at 90 °C under nitrogen. After cooling to room temperature more potassium hydroxide (35 mg, 0.63 mmol; 0.5 eq.) and benzyl bromide (75 μL, 0.63 mmol; 0.5 eq.) were added and heating was continued at 90 °C for 1 h after which time an additional amount of KOH (100 mg) was added to the reaction mixture at room temperature. After filtration of solid KBr the solvent was removed by evaporation. The pure Bn₃Me₃-tame was obtained as a colourless oil (489 mg, 91%) after flash chromatography (elution with hexane:ethyl acetate 8:2). FTIR (neat, cm⁻¹): ν = 3084, 3027, 2944, 2837, 2780, 1494, 1452, 1364, 1025, 715, 697. ¹H NMR (300 MHz, C₆D₆, rt): δ = 7.40–7.11 (m, 15H), 3.54 (s, 6H), 2.54 (s, 6H), 2.18 (s, 9H), 1.18 (s, 3H). ¹³C NMR (100.28 MHz, C₆D₆, rt): 140.9, 128.8, 128.5, 127.1,

65.4, 65.1, 45.3, 45.1, 21.2. Mass spectrum, m/z (intensity) ESI 430.2 $(M + 1)^+$ (100%).

2.4. $[MoO_2Cl(Bn_3Me_3$-tame$)]BF_4$ (3)

A solution of silver tetrafluoroborate (73 mg, 0.373 mmol) in THF (2 mL) was added to a solution of MoO_2Cl_2 (75 mg, 0.373 mmol) in THF (5 mL) under nitrogen. The reaction mixture was left to stir for 2 h at room temperature. After filtering to remove the precipitate, a solution of Bn_3Me_3-tame (160 mg, 0.373 mmol) in THF (15 mL) was added dropwise to the clear filtrate, resulting in the immediate formation of a white precipitate. Stirring was continued for 1 h at room temperature and then the solid product was recovered by filtration. Washing with diethyl ether and drying in vacuum gave $[MoO_2Cl(Bn_3Me_3$-tame$)]BF_4$ (3) (218 mg, 85%) as a pale blue powder, soluble in DMF. Found: C, 51.12; H, 5.56; N, 5.93. $C_{29}H_{39}N_3MoO_2ClBF_4$ requires C, 51.24; H, 5.78; N, 6.18%. IR (KBr, cm^{-1}): 3464 w, 3034, 2966, 2927, 2646 w, 1648, 1456 s, 1382 m, 1060 s, 948 s, 913 s, 749 s, 702 s. ^1H NMR (300 MHz, d_7-DMF, rt): $\delta = 7.55$–7.44 (m, 15H), 4.18 (s, 6H), 3.49 (s, 2H), 3.23 (s, 4H), 2.7 (s, 9H), 1.48 (s, 3H).

2.5. Catalysis

The epoxidation of cis-cyclooctene was carried out under air in a micro reaction vessel equipped with a magnetic stirrer, which was loaded with 36 μmol of complex, 3.6 mmol cyclooctene (1% molar ratio of catalyst/substrate), 5.5 mmol TBHP (5.5 M in decane) and, optionally, either 200 μL 1,2-dichloroethane (DCE) or RTIL. The products were analysed using a gas chromatograph (Varian 3800) equipped with a capillary column (SPB-5, 20 m × 0.25 mm × 0.25 μm) and a flame ionisation detector.

3. Results and discussion

The Mo^{VI} organometallic complex $MoO_2Me_2(p$-tolyl-(CH_3-DAB)) 2 was prepared by the treatment of the dichloro complex $MoO_2Cl_2(p$-tolyl-(CH_3-DAB)) 1 (prepared in situ) with the Grignard reagent CH_3MgCl. Elemental analysis, FTIR and solution NMR data confirmed that the desired complex was obtained in high purity. The cationic complex 3 was obtained as described in Scheme 1.

Octahedral dioxomolybdenum(VI) complexes containing 1,4-diazabutadienes (DAB) have previously been shown to be active and stable homogeneous catalysts for the epoxidation of olefins using TBHP [13,14]. The oxidation of cis-cyclooctene using TBHP as oxidant in the presence of complexes 1 and 2 yields cyclooctene oxide as the only product (Table 1). Without additional solvent homogeneous mixtures are formed and cyclooctene oxide is yielded quantitatively after 4 h (Fig. 1). Compared to previous catalyst systems based on dioxomolybdenum(VI) complexes [14,15], including those containing other types of DAB ligands, complexes 1 and 2 possess outstanding catalytic activity. The kinetic profile shown in Fig. 1 for the dimethyl complex 2 is typical of $MoO_2X_2L_2$-type complexes used

Table 1
Cyclooctene epoxidation using TBHP in the presence of dioxomolybdenum(VI) complexes 1–3

Solvent/catalyst	Temperature (°C)	TOF[a] (mol mol$_{Mo}^{-1}$ h^{-1})	Conversion[b] (%)	Select. to epoxide[c] (%)	Phase system
None/1	55	(55)[d]	100	100	L
DCE/1	55	11 (32)	94	100	L
[BMIM]PF$_6$/1	55	7 (77)	73	100	L–L
None/2	55	(73)	100	100	L
DCE/2	55	12 (53)	100	100	L
[BMIM]PF$_6$/2	55	8 (24)	90	100	L–L
[BMIM]PF$_6$/2[e]	55	6	73	100	L–L
[BMIM]PF$_6$/2[e]	35	2	34	100	L–L
[C$_8$MIM]PF$_6$/2	55	8 (25)	94	100	L–L
[BMIM]NTf$_2$/2	55	10 (34)	96	100	L–L
[BdMIM]NTf$_2$/2	55	4 (7)	53	100	L–L
[C$_5$O$_2$MIM]PF$_6$/2	55	1 (2)	14	100	L–L
[(d-h)$_2$dmg]PF$_6$/2	55	9 (27)	92	100	L
None/3	55	8 (48)	64	75[f]	C[g]
DCE/3	55	6 (19)	71	97[f]	C
[BMIM]PF$_6$/3	55	9 (40)	71	85[f]	C–L
[BMIM]NTf$_2$/3	55	11 (47)	93	85[f]	C–L

[a] Turnover frequency calculated at ca. 8 h reaction.
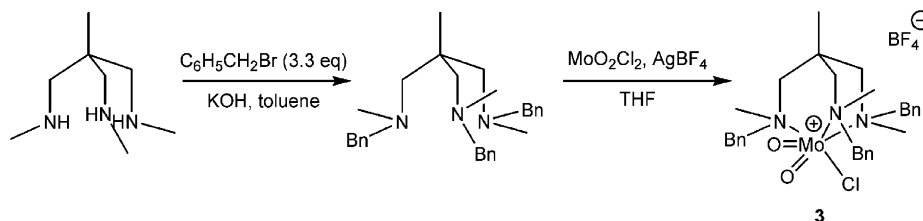[b] Cyclooctene conversion after 30 h.
[c] Selectivity calculated at 30 h.
[d] Values in brackets correspond to turnover frequency calculated at ca. 1 h reaction.
[e] Equimolar amounts of substrate/TBHP were used instead of 0.65.
[f] 1,2-Cyclooctanediol was formed.
[g] Colloidal suspension.

Scheme 1.

as epoxidation catalysts with TBHP. Initially, the reaction is fast but then slows down, which has been attributed to the formation of *tert*-butyl alcohol, a by-product of the epoxidation, which competes with TBHP for co-ordination to the Mo^{VI} centre [15]. Homogeneous one-phase catalyst systems were also obtained when 1,2-dichloroethane was used as solvent. However, the oxidation reaction was slower than that observed without additional solvent, proceeding to ca. 90% cyclooctene conversion within 8 h in the case of **2**, giving a TOF of 12 mol mol_{Mo}^{-1} h^{-1} (Table 1).

The epoxidation of cyclooctene was subsequently carried out using the RTIL [BMIM]PF$_6$ (Plate 1) as a solvent for the catalyst precursors **1** and **2**. Upon addition of *cis*-cyclooctene and TBHP (in decane) the reaction systems become biphasic. The catalyst precursor **2** dissolves in the RTIL to give a deep red solution, while decane and cyclooctene are immiscible with the RTIL, and TBHP is soluble in the RTIL. It was noted that after addition of the oxidant, the upper organic phase, containing the substrate and products, adopted a pale orange colour suggesting that some molybdenum species transferred from the ionic liquid phase. The conversion of substrate after 8 h was 60%,

corresponding to a TOF of 8 mol mol_{Mo}^{-1} h^{-1} (Table 1). A conversion of 90% was only achieved after 30 h (cf. 73% for **1**). The reactions under biphasic conditions are therefore slower than in homogeneous phase, probably due to mass transfer limitations. When the molar ratio of complex **2**/substrate was decreased from 1 to 0.5% the TOF decreased from 8 to 5 mol mol_{Mo}^{-1} h^{-1} and conversion after 8 h decreased from 60 to 34%. With equimolar amounts of cyclooctene and TBHP the oxidation of cyclooctene was slower, proceeding to 73% olefin conversion at 30 h (Table 1). Lowering the temperature from 55 to 35 °C decreased cyclooctene conversion at 30 h by ca. 50%.

The recyclability of the [BMIM]PF$_6$/**2** system was first examined by carrying out a second reaction run using equimolar amounts of olefin and TBHP at 35 °C. In order to recover the ionic mixture containing the catalyst, a liquid extraction was performed using *n*-hexane (3 × 2 mL), which is immiscible with the RTIL. This solvent was chosen amongst several others (cyclohexene, cyclopentene, diethyl ether) in order to obtain a better separation of the reagents and products relative to the catalyst. *n*-Hexane was added to the reaction mixture followed by agitation, after which two clear liquid layers were separated by decantation. When the [BMIM]PF$_6$/**2** system was recycled and reused partial loss of catalytic activity (evaluated as olefin conversion at 30 h) was observed (Fig. 2). The first hexane extract was yellow (and no solid could be separated by centrifuging) suggesting
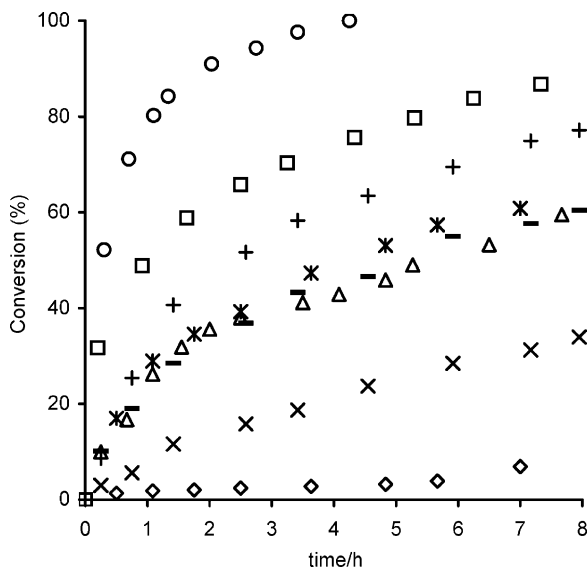

Fig. 1. Kinetic profiles of cyclooctene epoxidation in the presence of MoO$_2$Me$_2$(*p*-tolyl-(CH$_3$-DAB)) **2** without additional solvent (○) or using DCE (□), [BMIM]PF$_6$ (△), [C$_8$MIM]PF$_6$ (▬), [BMIM]NTf$_2$ (+), [BdMIM]NTf$_2$ (×), [C$_5$O$_2$MIM]PF$_6$ (◇) or [(d-h)$_2$dmg]PF$_6$ (✖) as solvent at 55 °C.
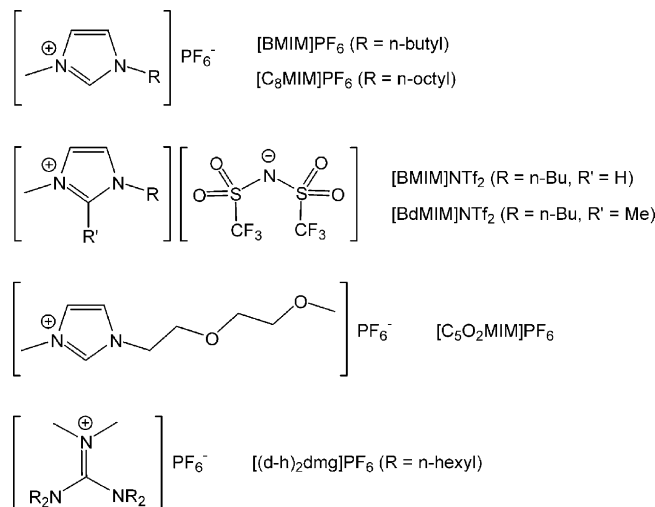

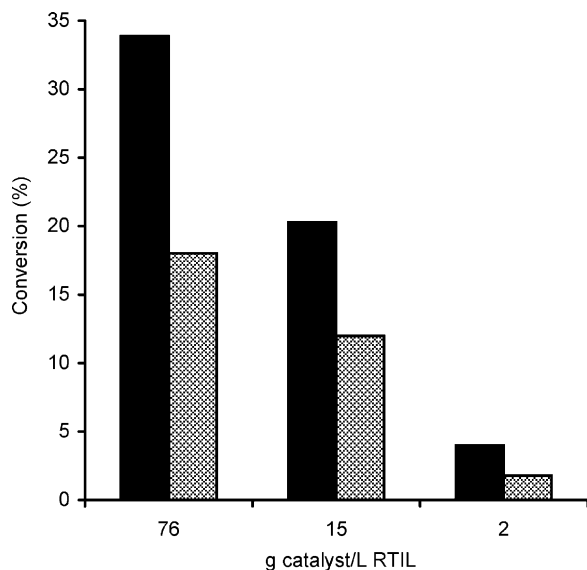Plate 1. Room temperature ionic liquids used in this work.

Fig. 2. Influence of the amount of [BMIM]PF$_6$ on the catalytic performance of MoO$_2$Me$_2$(p-tolyl-(CH$_3$-DAB)) **2** at 35 °C (first run—black; second run—diamonds).

that a fraction of molybdenum species were also extracted in this multicomponent system. The leaching of active catalytic species from the RTIL phase, both during the reaction and recycling, is probably one reason why catalytic performance is poor in the second run. It is noteworthy that it is only the first 2 mL extraction solution that turns yellow; the additional fresh solvent in subsequent single stage extractions remains colourless. These results suggest that the loss of Mo takes place mainly during the first extraction, being removed together with the less hydrophobic organic phase containing cyclooctene and polar reaction products, such as *tert*-butanol and cyclooctene oxide. Hence, the recyclability of this system may depend on the partition of the catalyst in the RTIL and organic phase. The [BMIM]PF$_6$/**1** system was also recycled but in a second reaction run substrate conversion after 30 h at 55 °C was less than 4%. Further experiments were restricted to systems containing the dimethyl complex **2**.

The influence of the amount of RTIL on the catalytic performance was studied under similar conditions at 35 °C, using the same initial amount of complex **2**. With increasing amounts of ionic liquid the reaction rate decreased significantly, most likely due to increasing mass transfer limitations (Fig. 2). For all recycling tests using different amounts of RTIL, cyclooctene conversion decreased at least 40% from the first to the second run. Further experiments were performed with the [BMIM]PF$_6$/**2** system using an excess of TBHP, 76 g catalyst/L RTIL, at 55 °C. Under these conditions, considerable loss of activity was observed (olefin conversion after 30 h decreased from 90% in the first run to 6% in the second run). In an attempt to minimise the loss of molybdenum during the extraction operation the experiments were repeated using two other solvents instead of *n*-hexane, namely *n*-pentane and cyclohexane, in which

complex **2** is also insoluble. These experiments gave similar catalytic results to those obtained using *n*-hexane, i.e. olefin conversion decreased at least 83% from the first to the second run. The loss of activity decreases with temperature probably because heating enhances the weight-fraction of the catalyst in the upper organic phase.

Several other RTILs (Plate 1) were tested as immobilising agents for **2** and catalytic tests carried out using 76 g catalyst/L RTIL, at 55 °C. No significant differences in catalytic activity are observed between [BMIM]PF$_6$, [C$_8$MIM]PF$_6$ or [(d-h)$_2$dmg]PF$_6$ (Table 1). The oxidation reaction in the presence of [C$_5$O$_2$MIM]PF$_6$ was rather sluggish, yielding 14% epoxide after 30 h. The highest reaction rate was observed for [BMIM]NTf$_2$ (TOF = 10 mol mol$_{Mo}^{-1}$ h^{-1}). When the different RTIL/catalyst systems were recycled under the same conditions, cyclooctene conversion after 30 h decreased ca. 94% for [BMIM]PF$_6$ and [C$_8$MIM]PF$_6$, whereas for [BMIM]NTf$_2$ and [BdMIM]NTf$_2$ the loss was less than 40% (Fig. 3). These results suggest that the type of anion plays an important role in the catalytic performance of complex **2**, with NTf$_2$ giving better results than PF$_6$. A possible explanation is the different solubility of the complex in the RTILs, accounting for variable losses of molybdenum during the extraction operation. The amount of Mo present in [BMIM]PF$_6$ and [BMIM]NTf$_2$ after two runs was estimated by ICP-AES, which gave a maximum of 43 and 26 wt.% metal loss, respectively.

This study was further extended to the ionic dioxomolybdenum(VI) complex **3**, for which the catalytic performance was evaluated under typical reaction conditions, either with no additional solvent, or with DCE, [BMIM]PF$_6$ or [BMIM]NTf$_2$, at 55 °C (Table 1). The complex is not
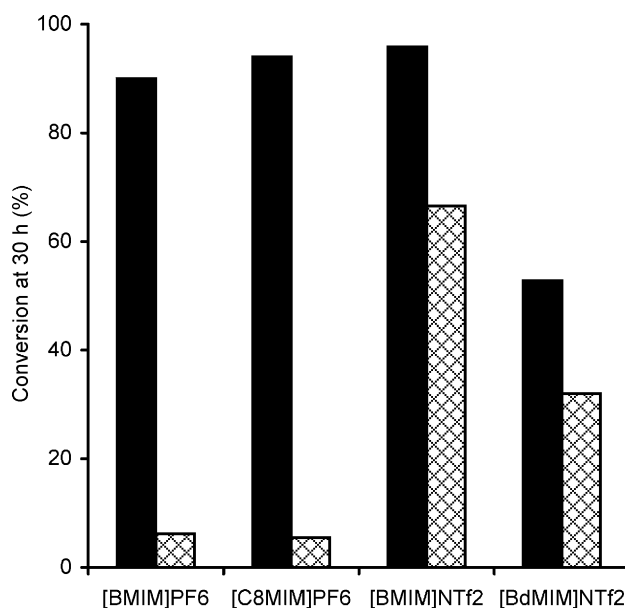

Fig. 3. Influence of the type of RTIL on the catalytic performance of MoO$_2$Me$_2$(p-tolyl-(CH$_3$-DAB)) **2** at 55 °C (first run—black; second run—diamonds).

completely soluble in any of these reaction systems, forming a colloidal suspension. Without additional solvent the oxidation of cyclooctene with TBHP proceeded at a TOF of $8 \, \text{mol} \, \text{mol}_{\text{Mo}}^{-1} \, \text{h}^{-1}$. Cyclooctene oxide was the main reaction product, which underwent consecutive epoxide ring-opening to give 25% 1,2-cyclooctanediol after 30 h. The ring-opening reaction could be due to the increased Lewis-acidity of the catalyst **3**. When DCE was used the reaction rate decreased, as observed for complexes **1** and **2** (Table 1). Interestingly, in the case of complex **3**, the TOF was higher when [BMIM]PF$_6$ or [BMIM]NTf$_2$ were used, contrary to that observed for complexes **1** and **2**. Apparently, the solubility of complex **3** in these RTILs is higher than in DCE or without additional solvent, which can explain the higher TOF obtained in the RTIL.

Recycling tests were performed for [BMIM]PF$_6$/**3** and [BMIM]NTf$_2$/**3** systems, at 55 °C. Since the complex is insoluble in *n*-hexane, this solvent was used for extraction between successive runs. The recyclability of complex **3** in these RTILs is much superior to that observed for complex **2** (compare Figs. 3 and 4). Partial loss of activity was observed from the first to the second run, but then tends to remain constant, giving a TON of 144 and 229 mol mol$_{\text{Mo}}^{-1}$ for [BMIM]PF$_6$ and [BMIM]NTf$_2$, respectively, after three runs. The molybdenum content in [BMIM]PF$_6$ after three runs was at least 90 wt.% of the initial amount. The loss of Mo is therefore lower than that observed for complex **2**, under the same conditions. This is probably related to the lower solubility of complex **3** in the less dense organic phase (decane/cyclooctene), leading to small losses of metal during the extraction of the reagents and products. Selectivity towards epoxide formation increases in consecutive reaction runs. Since the complex is ionic, some changes in the catalyst precursor may occur in the presence of RTIL under the applied reaction conditions.

4. Conclusion

This study shows that the use of RTILs for recycling homogeneous dioxomolybdenum(VI) complexes may be promising if the right RTIL is chosen for a certain catalyst as well as the recycling conditions, such as the extraction solvent used for separating the reactants and products from the RTIL/catalyst system.

Complexes **2** and **3** are interesting catalysts for the oxidation of *cis*-cyclooctene using TBHP as oxidant. In particular, MoO$_2$Me$_2$(*p*-tolyl-(CH$_3$-DAB)) possesses excellent selectivity towards the formation of the epoxide and relatively high activity is observed without additional solvent, with a chlorinated solvent or an adequate RTIL. The [BMIM]PF$_6$/MoO$_2$Me$_2$(*p*-tolyl-(CH$_3$-DAB)) catalytic system conducts the reaction at room temperature using equimolar amounts of olefin:TBHP. Loss of catalytic activity is observed from the first to the second reaction run, which is attributed to the loss of some Mo species from the ionic liquid both during the reaction and the extraction of the reagents and products. Amongst several RTIL tested for recycling complex **2**, the best results were observed for [BMIM]NTf$_2$, using *n*-hexane as extraction solvent.

The catalytic performance of a new ionic complex **3** was studied without additional solvent and using DCE or RTIL, under similar reaction conditions. The catalyst yields cyclooctene oxide as the major product and 1,2-cyclooctanediol as a by-product, as a result of epoxide ring-opening. The highest TOF values are observed using [BMIM]PF$_6$ or [BMIM]NTf$_2$ instead of DCE or no additional solvent. In these RTILs, complex **3** could be recycled without significant loss of activity after the first run and selectivity to the epoxide increased in consecutive runs.

Fig. 4. Catalytic performance of complex **3** in [BMIM]X {X = PF$_6$ or NTf$_2$} in consecutive reaction runs at 55 °C (where X_n stands for [BMIM]X used in *n* runs): cyclooctene conversion (black bars) and selectivity towards epoxide formation (bricks) at 30 h, and TOF at 8 h (white bars).

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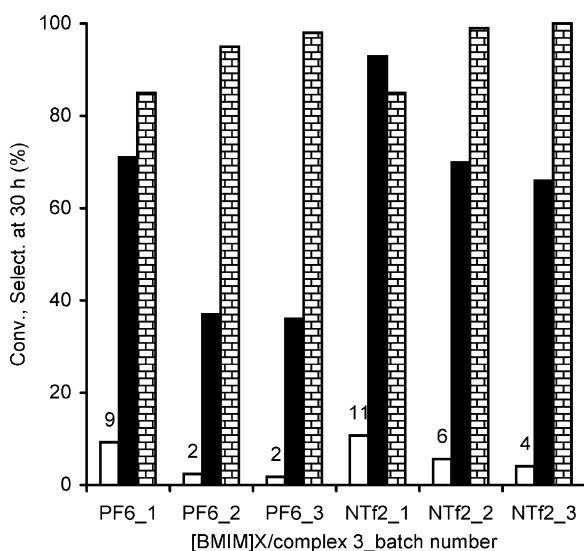[3] K.A. Jörgensen, Chem. Rev. 89 (1989) 431.

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