Epoxidation in ionic liquids: A comparison of rhenium(VII) and molybdenum(VI) catalysts

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ABSTRACT

Complexes of the type (dimethyl-bpy)MoO$_2$Cl$_2$ and Schiff/Lewis-base complexes of methyltrioxorhenium (MTO), being efficient homogeneous catalysts for the epoxidation of olefins, have been examined with respect to their catalytic performance at 55 and 25 °C in systems employing room temperature ionic liquids (RTILs) of composition [BMIM]NTf$_2$, [BMIM]PF$_6$, [BMIM]BF$_4$ and [C$_8$MIM]PF$_6$ as solvents. The performance in the cyclooctene epoxidation was observed to be strongly dependent on the water content of the system and the catalyst solubility in the RTIL. MTO based systems prove to be superior with respect to lower energy consumption, higher stability and higher product yields compared to the investigated Mo(VI) system under the conditions applied.

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1. Introduction

In the last decade room temperature ionic liquids (RTILs) have been used in a variety of catalytic reactions [1]. Their unique physical properties, such as low volatility, low flash point, thermal stability and high polarity make them an attractive alternative to organic solvents [2]. Inorganic or organometallic complexes, sometimes immiscible with hydrocarbons, are often soluble in RTILs. RTILs provide therefore a non-aqueous alternative for two-phase catalysis, in which the catalyst is immobilized in the ionic liquid phase and is easily separated from the products. RTILs have been used for several types of reactions, such as hydrogenation, hydrosilylation and oligomerisation of olefins. Song and Roh reported the first manganese(III) (salen) complex, capable of catalyzing an asymmetric epoxidation in an ionic liquid less than a decade ago [3]. Since then, RTILs have been successfully applied in olefin epoxidation with manganese(III) porphyrins [4]. A series of imidazolium-based RTILs have been tested in this work as solvents for the catalytic cyclooctene epoxidation.

1.1. MTO derivatives as catalysts

Methyltrioxorhenium (MTO) is an extremely efficient catalyst precursor for a variety of organic reactions, as has been previously demonstrated, mainly by the research groups of Espenson and Herrmann [5]. Olefin epoxidation is yet the best examined of the many applications of this versatile catalyst [6]. The reaction mechanism has been studied in great detail, both from a kinetic and theoretical point of view in homogeneous and heterogeneous variations of the reaction [7]. Due to its Lewis acidity, MTO promotes ring-opening reactions of sensitive epoxidation products, which lead to the formation of diols [8]. It was recognized quite early that the presence of Lewis bases, for example nitrogen donor ligands, suppresses unwanted side reactions [9]. Nevertheless, the activity of MTO–Lewis base adducts was originally found to be significantly lower than that of MTO itself [10]. The use of aromatic N-donor ligands in 5–12 fold excess however, leads to higher activities and selectivities in epoxidation catalysis than with MTO alone [11]. Both mono- and bidentate aromatic Lewis bases with N-donor ligands display this behavior [12]. Many N-base adducts of MTO have been isolated and characterized and in several cases *in situ* employed for olefin epoxidation catalysis [13]. Re(V)-oxo complexes bearing Schiff-base ligands have also been investigated extensively [14], and Schiff-base adducts of MTO were also synthesized and applied as epoxidation catalysts in organic solvents [15]. In the latter case ligand excess proved to be unnecessary to achieve selective olefin epoxidations.

Owens and Abu-Omar examined the epoxidation of different olefins using MTO as a catalyst and urea hydrogen peroxide (UHP) with the ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate, [EMIM]BF$_4$, as a solvent. This oxidation system is nearly water-free, so the conversion of the substrates yields primarily the epoxides and not diols [16].

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1.2. Molybdenum systems as catalysts

Molybdenum(VI) complexes are also versatile catalysts for the epoxidation of olefins. It has been shown that compounds of the type $MoO_2X_2L_2$ (L = Lewis base) and $Cp'Mo(CO)_3Cl$ can be used as olefin epoxidation catalysts or catalyst precursors. The latter compounds are undergoing oxidation *in situ* with TBHP to the Mo(VI) catalyst. $Cp'Mo(CO)_3R$ (R = alkyl or ansa-alkyl) complexes show a catalytic activity comparable to their chloro analogues [17]. The byproduct of the oxidation of olefins with TBHP in the presence of Mo(VI) dioxo complexes is *t*-BuOH, which decreases the velocity of the catalytic reaction with increasing concentration [18a–c]. The $Cp'Mo(CO)_3R$ catalysts (Cp' = Cp, Cp*; R = Cl, Me) were investigated in RTILs and it was observed that among all examined catalysts the best epoxid yields are obtained for [BMIM]NTf_2-containing systems [19]. Valente et al. examined two other Mo(VI) catalysts – MoO_2Me_2(*p*-tolyl-(CH_3–DAB)) and the cationic complex [MoO_2-Cl(Bn_3Me_3-tame)]BF_4 (tame = *tert*-amylmethylether) – for the epoxidation of olefins. Both catalysts lead to the highest yields when using [BMIM]NTf_2 as a solvent [20]. Among the large variety of RTILs available in the literature, in this study RTILs of the imidazolium salt type were chosen with different anions as solvents due to their high oxidation stability as well as their ease of accessibility in terms of synthesis [2,21].

2. Results and discussion

Compound **1**, a very simple and straightforward Lewis base adduct of dichloro dioxo molybdenum(VI) (see Scheme 1), was used as a catalyst for olefin epoxidation. Compound **2** and **3** (same ligand as in compound **1**) were added to the reaction solution together with MTO to form the active catalysts *in situ*. Such an *in situ* formation of MTO based catalysts is well established in the literature (see above). Table 1 shows the results of the catalytic epoxidation of *cis*-cyclooctene with the molybdenum system **1**.

In all examined cases for epoxidation reactions catalyzed by Mo systems in RTILs the reaction leads to the highest yields when using [BMIM]NTf_2 as solvent (Table 1, Fig. 1). The low water content of this RTIL [2] allows a longer survival of the water sensitive Mo(VI) species. However, compared to the performance under solvent free conditions (Fig. 2) the yields obtained for compound **1** in ionic liquids are not particularly impressive. This is, most likely, due to phase transfer problems between the viscous RTIL and the substrate and in particular to the mentioned instability of Mo(VI) in water-containing systems, leading to catalyst decomposition. According to its high water content, [BMIM]BF_4 leads to the lowest product yield. The progress of reactions is quite independent from the different solvents, which can be deduced from the general shape of the curves in Fig. 1.

In addition to the molybdenum system, two MTO derivatives have been investigated. The influence of a Lewis base ligand was

Table 1
Catalytic results for compound **1** as the catalyst with different RTILs as solvents under laboratory atmosphere with water equilibrated RTILs and TBHP as oxidizing agent.

Solvent	Yield [%] after 4 h	Yield [%] after 24 h	TOF[a] (mol/mol * h)
[BMIM]BF_4	21	27	36
[BMIM]PF_6	26	33	55
[C_8MIM]PF_6	22	30	64
[BMIM]NTf_2	31	43	113

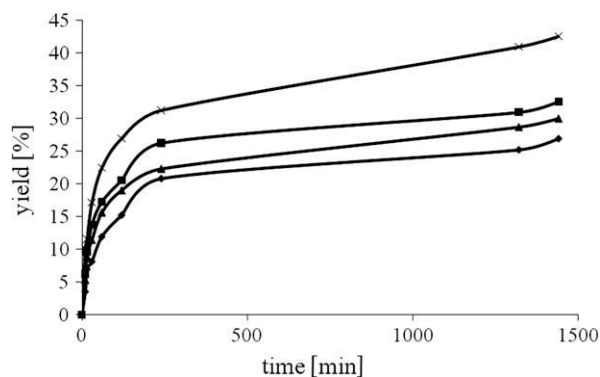[a] Determined after 5 min reaction time.

Fig. 1. Kinetics of cyclooctene epoxidation in the presence of the complex **1** using [BMIM]BF_4 (♦), [BMIM]PF_6 (■), [BMIM]NTf_2 (×) or [C_8MIM]PF_6 (▲) as solvents.
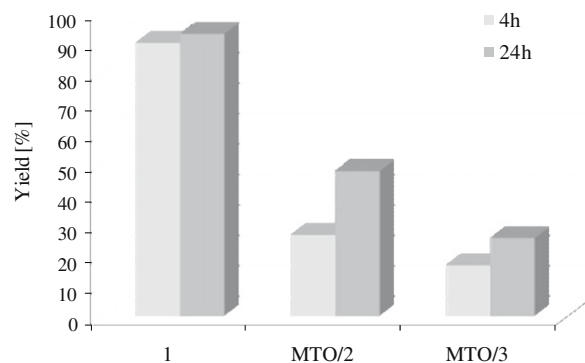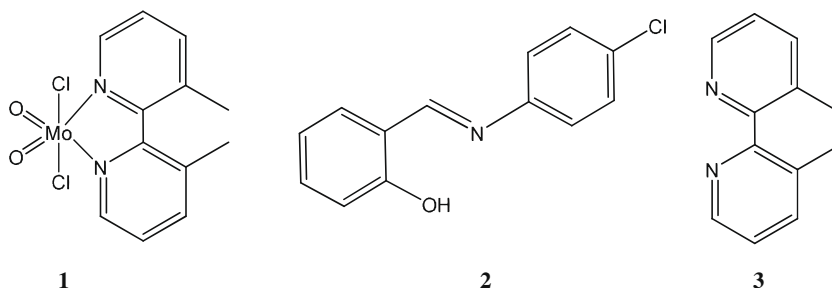

Fig. 2. Catalytic results for compounds **1**, MTO/**2** and MTO/**3** as the catalyst under solvent free condition in laboratory atmosphere.

to be evaluated in comparison to the previous examinations that had been executed with MTO alone. The respective ligand is added

Scheme 1.

directly to the solution and readily forms a complex with MTO as described in the literature [12b,15a]. The catalytic activity of both MTO complexes was examined as mentioned for the molybdenum system (see Table 2).

By comparing complexes of MTO with ligand **2** and MTO with ligand **3** a clear trend can be observed. In all cases the MTO/**2** system leads to higher yields compared with MTO/**3**. Both catalytic systems have the highest activity when [BMIM]PF$_6$ is used as solvent. Interestingly, the addition of the Schiff-base has a considerable effect on the activity of the catalyst when the reaction is taking place in [BMIM]PF$_6$. In this work it was found that the cyclooctene oxide yield rises by 25% after 24 h in comparison to pure (Lewis base ligand free) MTO. Figs. 3 and 4 give more details concerning the progress of reaction. Furthermore it should be mentioned that in all RTILs the MTO adducts produce a higher yield of cyclooctene oxide than the pure MTO. This fact does not surprise, because ring-opening reactions are suppressed with the ligated system. However, with MTO alone diol formation occurs.

In summary [BMIM]PF$_6$ is the most appropriate solvent for both examined base adducts of MTO, leading to the highest yields among the systems studied. The use of RTILs in this reaction is meaningful, as higher yields were obtained in all cases compared to solvent free systems. It should be finally mentioned that the catalytic reactions with the molybdenum system are performed at 55 °C with TBHP as oxidizing agent while the base adducts of MTO we applied at room temperature and with H$_2$O$_2$ as oxidant. In addition, all RTILs were water equilibrated and the reactions are performed under laboratory atmosphere. This fact leads to a very convenient and straight forward procedure. Interestingly, comparison between the yields of **1** and MTO/**3** shows that the rhenium system leads to much higher conversion although the ligand is the same. Furthermore, the water content of the RTIL, being very

important for the water sensitive Mo(VI) catalyst **1** is not a concern for the MTO based systems, which produce water as byproduct of the epoxidation with H$_2$O$_2$ anyway. Based on these promising findings additional MTO systems with chiral Lewis bases as epoxidizing catalysts are currently under way in our laboratory.
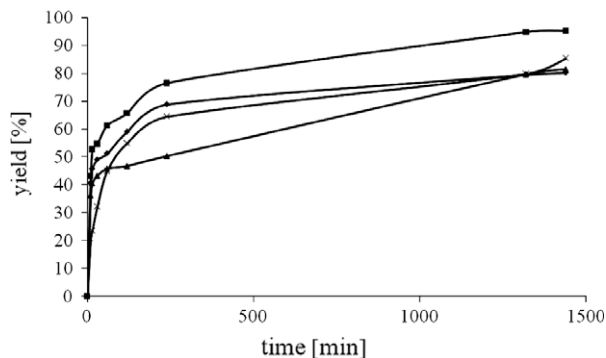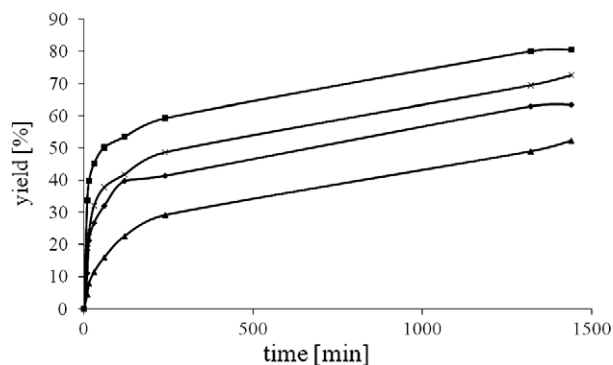
Fig. 4. Kinetics of cyclooctene epoxidation in the presence of MTO/**3** using [BMIM]BF$_4$ (♦), [BMIM]PF$_6$ (■), [BMIM]NTf$_2$ (×) or [C$_8$MIM]PF$_6$ (▲) as solvents.

3. Experimental part

All preparations were performed under laboratory atmosphere. TBHP was purchased from Aldrich as 5.0–6.0 M solution in *n*-decane and used after drying over molecular sieves to remove the water (<4% when received). ^{1}H, ^{13}C, and ^{19}F NMR spectra were obtained using a 400-MHz Bruker Avance DPX-400 spectrometer. Catalytic runs were monitored by GC methods on a Hewlett–Packard instrument HP 5890 Series II equipped with a FID, a Supelco column Alphadex 120 and a Hewlett–Packard integration unit HP 3396 Series II.

3.1. Synthesis of ionic liquids

The RTILs [BMIM]PF$_6$, [C$_8$MIM]PF$_6$, [BMIM]NTf$_2$ and [BMIM]BF$_4$ were prepared and purified as described in the literature [2,22]. Their spectroscopic data are in accordance with the data reported previously. MTO was prepared according to literature procedures [23] and MoO$_2$Cl$_2$ was purchased from Sigma–Aldrich.

3.2. Catalytic reactions

All catalytic reactions were performed under laboratory atmosphere and the course of the product formation was monitored by GC analysis. During the first 30 min of the reaction samples were taken every 5 min, afterwards every 30 min. After reacting for 24 h, magnetic stirring was stopped. If the two phases could be easily recognized, the samples were taken from the upper phase. If not, 2 mL of *n*-hexane was added and the mixture was stirred until two layers could be clearly seen (after allowing the mixture to settle). The samples were treated with a catalytic amount of MnO$_2$ to destroy remaining peroxide. Then, methylene chloride was added to get the right concentration for the GC analysis. Finally the sample was treated with a catalytic amount of MgSO$_4$ to remove residual water. The resulting slurry was filtered and the filtrate injected into a GC column. The yield of cyclooctene was calculated from calibration curves recorded prior to the reaction course.

Cyclooctene epoxidation with the Mo(VI) system: After preheating the oil bath to 55 °C, the reaction vessel was charged with *cis*-cyclooctene (800 mg, 7.3 mmol) and internal standard

Table 2
Catalytic results for MTO with compound **2** and **3** with different solvents under laboratory atmosphere with water equilibrated RTILs and H$_2$O$_2$ as oxidizing agent.

Solvent	MTO/**2**			MTO/**3**		
	Yield [%] after 4 h	Yield [%] after 24 h	TOF[a] (mol/mol h)	Yield [%] after 4 h	Yield [%] after 24 h	tOF[a] (mol/mol * h)
[BMIM]BF$_4$	69	80	451	41	63	122
[BMIM]PF$_6$	77	95	479	59	81	374
[C$_8$MIM]PF$_6$	50	81	402	29	52	51
[BMIM]NTf$_2$	64	85	230	49	73	210

[a] Determined for the first 5 min of reaction time.

Fig. 3. Kinetics of cyclooctene epoxidation in the presence of MTO/**2** using [BMIM]BF$_4$ (♦), [BMIM]PF$_6$ (■), [BMIM]NTf$_2$ (×) or [C$_8$MIM]PF$_6$ (▲) as solvents.

mesitylene (0.5 g). Afterwards TBHP (2.65 mL, 5.5 M in *n*-decane) and RTIL (0.5 mL) were added and the mixture was stirred for 10 min. With the addition of the catalyst (73 μmol, 1 mol%) the catalytic reaction was started.

Cyclooctene epoxidation with the Re(VII) systems: The reaction vessel was charged with *cis*-cyclooctene (800 mg, 7.3 mmol) and internal standard mesitylene (0.5 g). Afterwards H_2O_2 (1.62 mL, 30% aqueous solution) and RTIL (0.5 mL) were added and the mixture was stirred for 10 min. With the addition of MTO (73 μmol, 1 mol%) and the ligand (73 μmol) the catalytic reaction was started.

4. Conclusion

For the epoxidation of cyclooctene in ionic liquids four different RTILs were examined as solvents for the catalysts. They served as solvents for catalytic reactions with MTO and base adducts as catalysts. Additionally, a molybdenum(VI) system was investigated for sake of comparison. Since the MTO- and Mo-catalyzed epoxidations are well examined in the literature, this work may provide further insight into the recommendability of replacing the conventional solvent DCM by ionic liquids in lab scale reactions. The MTO containing catalysts in [BMIM]PF$_6$ (particularly the MTO/**2** system) show the highest yield, which turns out to be higher than in conventionally used DCM or in solvent free epoxidation systems. Moreover, the easy product separation in case of the biphasic system may contribute larger scale applications. The reaction with the molybdenum system as catalyst leads to the highest yield in [BMIM]NTf$_2$, correlating well with published Mo systems, which in all cases gave the highest yields in [BMIM]NTf$_2$ [19]. This is due to the low water content in this RTIL which prolongs the life time of the water sensitive Mo(VI) species. However, under the applied conditions – which require no further precautions and can be easily executed under lab atmosphere the MTO/**2**/H_2O_2/[BMIM]PF$_6$ system is the most efficient one. Based on these promising findings additional MTO systems with chiral Lewis bases as epoxidizing catalysts are currently under examination in our laboratory.

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