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Methyltrioxorhenium-catalyzed epoxidation of olefins with hydrogen peroxide as an oxidant and pyridine N-oxide ionic liquids as additives

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ABSTRACT

Four ionic liquids (ILs) with both a pyridine N-oxide moiety and an imidazolium moiety combined by an amide spacer were synthesized through a series of reactions including amidation, peroxidation, quaterization and anion exchange reaction. Their structures were fully characterized by ^{1}H NMR, FT-IR, UV–vis and HR–MS. The ionic liquids were used respectively as additives in the methyltrioxorhenium (MTO) catalyzed epoxidation of olefins with 30% H_2O_2 as an oxidant. The catalytic results displayed that the ILs had excellent performances in suppressing epoxide ring-opening reaction, which led to the significant improvement of the selectivity of the MTO-catalyzed epoxidation with low loadings compared to other substances as additives. The coexistence of the pyridine N-oxide and imidazolium moieties in the structures of ILs is necessary in improving the MTO-catalyzed epoxidation reaction. It was also displayed that the improvement degree on the selectivity of epoxidation depended on the type of anion of the ILs, but not the position of the substituent with imidazolium moiety in the ring of pyridine N-oxide. Meanwhile, the results also showed that the introduction of the ILs caused the decrease of the epoxidation rate, but this side effect was small compared to those of other substances used as additives.

1. Introduction

Epoxides are valuable intermediates in organic chemical, fine chemical and pharmaceutical synthesis. The epoxidation of olefins is one of the most efficient strategies for obtaining epoxides [1]. Among all of the procedures the epoxidation of olefins with hydrogen peroxide (H_2O_2) as an oxidant has received special attention due to its high atom efficiency and environment friendliness [2–5]. However, the oxidation activity of H_2O_2 is so weak that generally appropriate catalysts such as transition metal complexes are needed to activate it [3,6,7]. In 1991, Herrmann and co-workers [8,9] found that methyltrioxorhenium(VII) (CH_3ReO_3, MTO) as a catalyst was very powerful in the epoxidation of olefins with H_2O_2 as an oxidant. However, the MTO/H_2O_2 catalytic system is not perfect due to the fact that the strong Lewis acidity of central rhenium atom (Re) can promote the ring opening of epoxides leading to the formation of diols in the presence of water during the reaction, meanwhile, MTO and the active species derived from MTO decompose in the aqueous solutions [10–13]. When trying to overcome both the problems it was found that the addition of Lewis base ligands, containing nitrogen and (or) oxygen donor atoms, could reduce the Lewis acidity of MTO and increase the selectivity of the epoxides. Therefore, a wide range of ligands has been chosen or synthesized to evaluate their improvement on the MTO-catalyzed epoxidation [14–37]. We also synthesized some Schiff-bases as ligands for the MTO-catalyzed epoxidation of olefins with 30% H_2O_2 as an oxidant, which showed excellent selectivity for the formation of epoxides with moderate or poor catalytic activity [38–41]. All previous results have shown that pyridine and its derivatives are among the most efficient additives at increasing the selectivity of the reaction. However, generally significant excess of the Lewis base additives is necessary to achieve excellent catalytic performance in such cases [17,21,27], which is unfavorable from the viewpoints of cost and separation. Besides, if the additives are too basic, then, MTO will decompose to catalytically inert perrhenic acid and methanol [11,25,26,32]. Much efforts have been made to seek additives that can suppress the ring opening side reaction in low loading, while not promote the decomposition of MTO or its derivatives. It was found that some oxygen donor ligands can coordinate with MTO to form stable complexes [19,31,33–37]; the complexes pre-prepared or generated in situ not only suppressed the ring opening side reaction, but also showed long lifetime compared to the cases with nitrogen donor ligands as additives in epoxidation of olefins. Moreover, in contrast to N-donor adducts, no pronounced ligand excess is necessary to achieve high yields and selectivity in olefin epoxidation catalysis.

On the other hand, MTO-catalyzed epoxidations carried out in ILs were reported in literature [42–44]. Several olefinic substrates with different structure characters were oxidized at room temperature (RT) to the corresponding epoxides with fair to excellent

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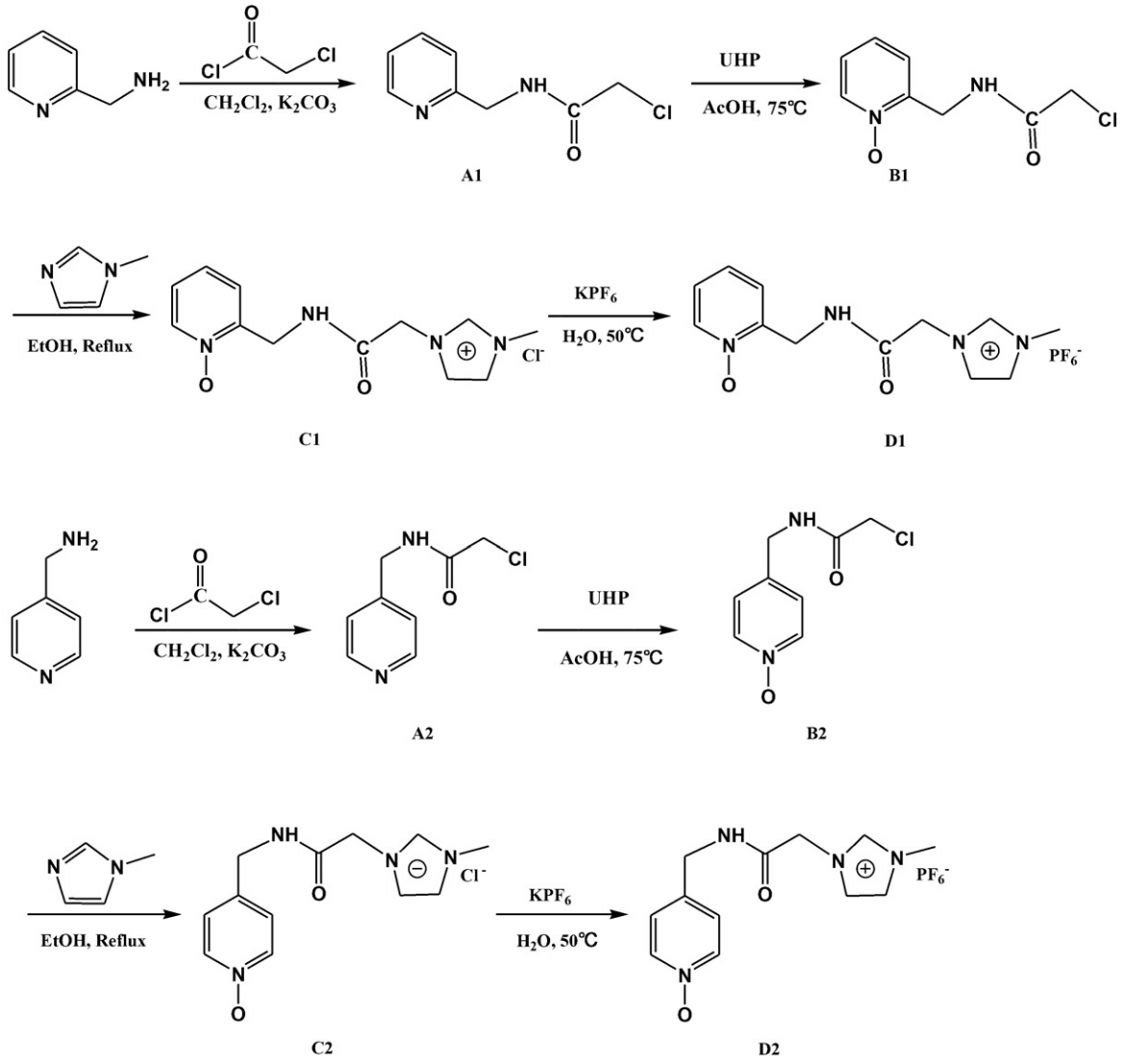

Scheme 1. Synthesis of pyridine N-oxide ionic liquids.

yields. In most cases, the epoxidation rates are at least comparable, if not higher than those reported previously. For example, the epoxidation of cyclooctene in four different water-equilibrated ILs, [BMIM]NTf_2, [BMIM]PF_6, [BMIM]BF_4, and [C_8MIM]PF_6, with H_2O_2 as an oxidant and Schiff- and Lewis-base adducts of MTO acting as active catalytic species gave higher yields compared to the solvent-free systems [43]. Recently, we found that 1-methyl-3-(butyl-4-sulfonate) imidazoliumbetaine (MBSIB), a zwitter ionic compound similar to ILs in structure, showed good performances as an additive in enhancing the MTO-catalyzed epoxidation of alkenes with 30% H_2O_2 as an oxidant [45]. The introduction of 10-fold excess MBSIB significantly improved the selectivity of epoxide without reducing the reaction rate. Furthermore, the MTO–MBSIB system was stable throughout the entire catalytic run and increased the TON of the epoxidation of alkenes. Our work in combination with the literature described above encourages us to design some new type ligands with both oxygen donor and ionic liquid moieties as shown in Scheme 1. As expected, the catalytic results showed that low loadings of the ligands can suppress the ring opening of epoxides and extend the lifetime of MTO in the MTO-catalyzed epoxidation of olefins with 30% H_2O_2 as an oxidant. Besides, the high stability and solubility of the ligands in water make them easy separation with the organics and recycling. Herein, we reported the results.

2. Experimental

2.1. Materials and reagents

2-Aminomethyl pyridine and methyltrioxorhenium (MTO) were purchased from Alfa Aesar. Cyclohexene (99%), 1-octene (99%) and styrene (99%) were purchased from Acros. Pyridine N-oxide (PyNO) was prepared according to a previously reported method [46]. 1-n-Butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6) was prepared as described in literature [47]. 4-Aminomethyl pyridine was prepared by us in high purity. All of the other reagents and solvents were obtained from commercial sources and used as received without further purification.

2.2. Physical measurements

The ^{1}H NMR spectra were recorded on a Bruker AC-P400 instrument using $CDCl_3$, DMSO or D_2O as solvent and TMS as internal

standard. IR spectra were recorded on a Bruker Vector-22 spectrophotometer using KBr pellets as the IR matrix. The UV–vis spectra were recorded on a Varian Cary 300 spectrophotometer. Melting points were determined on a Perkin XT-4 microscopic analyzer. ESI mass spectra were recorded on a LCQ Advanced high-resolution mass spectrometer.

2.3. Preparation of the pyridine N-oxide ionic liquids

2.3.1. Synthesis of **A1** and **A2**

2-Chloro-N-(pyridin-2-ylmethyl)acetamide (**A1**). To a suspension of 2-aminomethyl pyridine (6.0 g, 0.056 mol) and K_2CO_3 (4.0 g, 0.028 mol) in dichloromethane (50 mL) was slowly added 2-chloroacetyl chloride (3.3 g, 0.028 mol) in dichloromethane (20 mL) at 0 °C under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 1 h, then the mixture was filtered and the filtrate was evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of EtOAc/petroleum ether (30–60 °C) 1:1 as eluent to afford product **A1** as a yellowish liquid (90%). ^{1}H NMR ($CDCl_3$) δ: 4.13(s, 2H, COCH_2Cl), 4.61(d, J = 5.2 Hz, 2H, PyCH_2NHCO), 7.21–7.28(m, 2H, *Py.H*), 7.66(d, J = 1.6 Hz, 1H, *Py.H*), 7.85(s, 1H, N*H*), 8.58(d, J = 4.8 Hz, 1H, *Py.H*); IR (KBr) ν: 3430, 3069, 1694, 1632, 1562, 1517, 1461, 1362, 1259, 1101, 1026, 777 cm^{-1}; UV–vis ($CHCl_3$) λ_{max}: 267 nm.

2-Chloro-N-(pyridin-4-ylmethyl)acetamide (**A2**). The reaction procedure of preparing **A2** is similar to that of **A1**. The residue was purified by flash column chromatography on silica gel using a mixture of EtOAc/petroleum ether (30–60 °C) 1:1 mixed with appropriate amount of acetic acid as eluent. The eluent was evaporated in vacuum to give **A2** acetate as a yellowish liquid. The product was used for the next step directly.

2.3.2. Synthesis of **B1** and **B2**

2-Chloro-N-(N-oxide-pyridin-2-ylmethyl)acetamide (**B1**). A solution of **A1** (13.3 g, 0.018 mol) and urea hydrogen peroxide (UHP) (2.0 g, 0.011 mol) in acetic acid (20 mL) was stirred at 75 °C for 3 h. Then additional UHP (4.0 g, 0.022 mol) was added to this solution and the mixture was stirred at 75 °C for further 7 h. After evaporation of the solvent, the resulting residue was neutralized with saturated aqueous K_2CO_3, and then extracted with chloroform. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to give yellowish oil. The oil was recrystallized from ethanol–cyclohexane to give **B1** as a white solid (70%): m.p. 119.5–120.5 °C. ^{1}H NMR ($CDCl_3$) δ: 4.0(s, 2H, COCH_2Cl), 4.68(d, J = 6.0 Hz, 2H, PyCH_2NHCO), 7.26–7.29(m, 2H, *Py.H*), 7.45–7.49(t, J = 4.8 Hz, 1H, *Py.H*), 8.05(s, 1H, *NH*), 8.25–8.27(m, 1H, *Py.H*) ppm; IR (KBr) ν: 3430, 1663, 1543, 1440, 1432, 1271, 1212, 1112, 1027, 761 cm^{-1}; UV–vis ($CHCl_3$) λ_{max}: 271 nm.

2-Chloro-N-(N-oxide-pyridin-4-ylmethyl)acetamide (**B2**). The reaction procedure of preparing **B2** is similar to that of **B1**. The reaction mixture was evaporated under vacuum to remove the solvent. The resulting residue was dissolved in methanol and the solution was neutralized with solid Na_2CO_3. Then the mixture was filtered and the filtrate was evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of EtOAc/MeOH 15:1 as eluent to give product **B2** as a yellowish liquid after removing the solvent in vacuum. ^{1}H NMR (DMSO) δ: 4.13(s, 2H, COCH_2Cl), 4.25(d, J = 6.0 Hz, 2H, PyCH_2NHCO), 7.22–7.26(m, 2H, *Py.H*), 8.11–8.15(m, 2H, *Py.H*), 8.91(s, 1H, *NH*) ppm.

2.3.3. Synthesis of **C1** and **C2**

1-Methyl-3-(2-oxo-2-(N-(N-oxide-pyridin-2-ylmethyl))-ylamine)ethyl-imidazolium chloride (**C1**). A solution of **B1** (13 g, 0.015 mol) and 1-methylimidazole (1.9 g, 0.023 mol) in absolute ethanol was stirred at 75 °C for 5 h under nitrogen atmosphere. After evaporation of ethanol, acetonitrile was added to the mixture causing precipitation of **C1** as a white solid. This solid was recovered by filtration, washed twice with acetonitrile and dried in vacuum. Finally the product was obtained in 89% yield. m.p. 210.5–212.5 °C; ^{1}H NMR (D_2O) δ: 3.82(s, 3H, NCH_3), 4.56(s, 2H, COCH_2), 5.08(s, 2H, PyCH_2NHCO), 7.37(s, 2H, *IMI.H*), 7.42–7.50(m, 2H, *Py.H*), 7.61(d, J = 8.0 Hz, 1H, *Py.H*), 8.26(d, J = 6.8 Hz, 1H, *Py.H*), 8.69(s, 1H, *IMI.H*) ppm; IR (KBr) ν: 3424, 1686, 1567, 1493, 1433, 1265, 1221, 1177, 1111, 1031 cm^{-1}; UV–vis (CH_3OH) λ_{max}: 214, 262 nm; MS(ESI) m/z: 247.1190 [M$^+$−HCl].

1-Methyl-3-(2-oxo-2-(N-(N-oxide-pyridin-4-ylmethyl))-ylamine)ethyl-imidazolium chloride (**C2**). **C2** was prepared similar to **C1**. Yield 75%; m.p. 105.0–107.5 °C; ^{1}H NMR (D_2O, 400 MHz) δ: 3.71(s, 3H, NCH_3), 4.33(s, 2H, COCH_2), 4.97(s, 2H, PyCH_2NHCO), 7.26–7.27(m, 2H, *IMI.H*), 7.31(d, J = 6.8 Hz, 2H, *Py.H*), 8.05–8.07(t, J = 4.8 Hz, 2H, *Py.H*), 8.60(s, 1H, *IMI.H*) ppm; IR (KBr) ν: 3424, 1696, 1563, 1495, 1432, 1270, 1227, 1175, 1109, 1029 cm^{-1}; UV–vis (CH_3OH) λ_{max}: 214, 262 nm; MS(ESI) m/z: 247.1189 [M$^+$−HCl].

2.3.4. Synthesis of **D1** and **D2**

1-Methyl-3-(2-oxo-2-(N-(N-oxide-pyridin-2-ylmethyl))-ylamine)ethyl-imidazolium hexafluorophosphate (**D1**). To a solution of **C1** (13.5 g, 0.012 mol) in water (25 mL) was added potassium hexafluorophosphate (4.7 g, 0.024 mmol), and the mixture was stirred at 50 °C for 30 h. After removal of water in vacuum, the residue was dissolved in acetonitrile and the insoluble salt precipitate was removed by filtration. Finally, the filtrate was concentrated in vacuum to give **D1** as a yellowish solid in a yield of 95%. m.p. 172.0–174.5 °C; ^{1}H NMR (D_2O) δ: 3.86(s, 3H, NCH_3), 4.60(s, 2H, COCH_2), 5.11(s, 2H, PyCH_2NHCO), 7.41(s, 2H, *IMI.H*), 7.48–7.53(m, 2H, *Py.H*), 7.63 (d, J = 7.6 Hz, 1H, *Py.H*), 8.29(d, J = 6.4 Hz, 1H, *Py.H*), 8.72(s, 1H, *IMI.H*) ppm; IR (KBr) ν:3425, 1698, 1562, 1492, 1438, 1369, 1232, 1179, 1113, 1037, 843 cm^{-1}; UV–vis (CH_3OH) λ_{max}: 214, 262 nm.

1-Methyl-3-(2-oxo-2-(N-(N-oxide-pyridin-4-ylmethyl))-ylamine)ethyl-imidazolium hexafluorophosphate (**D2**). **D2** was prepared similar to **D1**. Yield 75%; m.p. 85.0–87.5 °C; ^{1}H NMR (D_2O, 400 MHz) δ: 3.88(s, 3H, NCH_3), 4.63(s, 2H, COCH_2), 5.14(s, 2H, PyCH_2NHCO), 7.43(s, 2H, IMI.H), 7.50–7.56(m, 2H, Py.H), 7.65 (d, J = 6.4 Hz, 1H, Py.H), 8.32(d, J = 4.4 Hz, 1H, Py.H), 8.75(s, 1H, IMI.H) ppm; IR (KBr) ν: 3425, 1693, 1558, 1497, 1433, 1273, 1221, 1111, 1029, 842 cm^{-1}; UV–vis (CH_3OH) λ_{max}: 214, 262 nm.

2.4. Catalytic reaction

The epoxidation reactions were performed in a 25 mL round bottomed flask immersed in a temperature-controlled water bath. In a typical experiment, 5 mmol of substrate, 7 mL of methanol and 0.05 mmol of MTO were mixed in this flask. Subsequently, aqueous H_2O_2 (30 wt.%, 10 mmol) was added to initiate the reaction. Samples were collected at regular intervals and analyzed by a Shandong Lunan Ruihong Gas Chromatograph (SP-6800A) equipped with a 30 m × 0.25 mm SE 30 capillary column and an FID detector.

2.5. Lifetime test

Once the previous substrate was exhausted, fresh substrate and aqueous H_2O_2 were sequentially added into the reaction mixture, and the reaction was run again and monitored by GC.

2.6. Recovery of **C1**

After the first run, the reaction mixture was evaporated under high vacuum at 40 °C to remove the methanol, water,

cyclohexene oxide and trace of cyclohexanediol formed in the catalytic run. The residue was analyzed by GC to make sure no presence of cyclohexene oxide and cyclohexanediol. Then the residue was subjected to the next catalytic run as described in Section 2.4.

3. Results and discussion

3.1. Preparation and characterization of *C1*, *C2*, *D1* and *D2*

Herein, the ionic liquids (ILs, **C1, C2, D1** and **D2**) with both a pyridine N-oxide moiety and an imidazolium moiety were prepared as shown in Scheme 1. The two moieties were combined with an amide spacer (–CH_2CONH–). First, 2(or 4)-aminomethyl pyridine reacted with 2-chloroacetyl chloride in dichloromethane in the presence of potassium carbonate to afford 2-chloro-N-(N-oxide-pyridin-2(or 4)-ylmethyl)acetamide **A1** (or **A2**) smoothly. **A1** or **A2** was oxidized with UHP in acetic acid to give 2-chloro-N-(N-oxide-pyridin-2(or 4)-ylmethyl)acetamide **B1** or **B2** in good yield. Respective quaternization of 1-methylimidazole with **B1** and **B2** afforded 1-methyl-3-(2-oxo-2-(N-(N-oxide-pyridin-2-ylmethyl))-ylamine)ethyl-imidazolium chloride (**C1**) and 1-methyl-3-(2-oxo-2-(N-(N-oxide-pyridin-4-ylmethyl))-ylamine)ethyl-imidazolium chloride (**C2**) in excellent and good yields. Finally, the ILs **D1** and **D2** were obtained in high yields by anion exchange reaction to replace chloric anion for hexafluorophosphate. The ILs **C1**, **C2**, **D1** and **D2** were characterized by ^{1}H NMR, FT-IR, UV–vis and high resolved MS.

3.2. Test of ILs as additives in the MTO-catalyzed epoxidation

3.2.1. The epoxidation of different olefins catalyzed by MTO/pyridine N-oxide ionic liquids

In the beginning, methanol, methylene chloride and acetonitrile were chosen as solvents to investigate the influence of the four ILs on the MTO-catalyzed epoxidation with 30% H_2O_2 as an oxidant. The results showed that the epoxidation could not undergo smoothly in methylene chloride and acetonitrile due to the insolubility of the ILs in the solvents. Therefore, all the epoxidation reactions were run in methanol. Cyclohexene, styrene and 1-octene were chosen as the substrates with different structure characters to evaluate the effect of the four ILs as additives on the MTO-catalyzed epoxidation of olefins with 30% H_2O_2 as an oxidant at 0 °C and 20 °C, respectively, and the results are summarized in Table 1. It can be seen that all the substrates underwent epoxidation reaction under the conditions employed, however, the epoxidation rate are different. Cyclohexene is epoxidized most easily, followed by styrene, and 1-octene is epoxidized with the most difficulty. Similar phenomenon was also observed in the cases with other substances as additives [17,32,38–42]. Herein, the conversion of cyclohexene reached higher than 97% in all cases when the reaction was run at 0 °C for 6 h (entries 2–5, Table 1); however, the conversions of styrene and 1-octene were only about 47% and 27%, respectively, even if the reaction was run for 12 h (entries 12–15, 23–26, Table 1). The results in Table 1 displayed that the four ILs as additives dramatically increased the selectivity of the epoxidation reaction for all the substrates especially at higher temperature, however, decreased the reaction rate in some degree compared to the neat MTO-catalyzed epoxidation, which were also

Table 1
The epoxidation of different olefins catalyzed by MTO/pyridine N-oxide ionic liquids.

Entry	Substrate	Temperature (°C)	Catalyst	Time (h)	Conversion (%)	Selectivity (%)
1	Cyclohexene	0	MTO	6	99	70
2		0	MTO/**C1**	6	97	99
3		0	MTO/**D1**	6	98	99
4		0	MTO/**C2**	6	97	99
5		0	MTO/**D2**	6	97	99
6		20	MTO	1.5	99	27
7		20	MTO/**C1**	1.5	92	95
8		20	MTO/**D1**	1.5	93	90
9		20	MTO/**C2**	1.5	92	95
10		20	MTO/**D2**	1.5	93	90
11	Styrene	0	MTO	12	60	13
12		0	MTO/**C1**	12	46	85
13		0	MTO/**D1**	12	47	81
14		0	MTO/**C2**	12	47	86
15		0	MTO/**D2**	12	47	82
16		20	MTO	3	61	6
17		20	MTO/**C1**	3	44	84
18		20	MTO/**D1**	3	48	69
19		20	MTO/**C2**	3	44	86
20		20	MTO/**D2**	3	49	72
21		20	MTO/**C1**[a]	3	84	99
22	1-Octene	0	MTO	12	30	85
23		0	MTO/**C1**	12	26	99
24		0	MTO/**D1**	12	27	99
25		0	MTO/**C2**	12	26	99
26		0	MTO/**D2**	12	26	99
27		20	MTO	12	85	78
28		20	MTO/**C1**	12	48	98
29		20	MTO/**D1**	12	67	87
30		20	MTO/**C2**	12	48	99
31		20	MTO/**D2**	12	68	88
32		20	MTO/**C1**[a]	12	86	99

Reaction conditions: olefin 5 mmol, 30% H_2O_2 10 mmol, MTO 0.05 mmol, ligand 0.05 mmol, methanol 7 mL.
[a] MTO 0.10 mmol; **C1** 0.10 mmol.

observed in other basic additives promoted MTO-catalyzed epoxidation [27,40].

It is noteworthy that the effects of ILs on the epoxidation depended on the type of anion in some degree. The ILs with Cl^- as anion performed better in improving the selectivity of the epoxides than the ones with PF_6^- as anion. And the higher the reaction temperature was, the more obvious difference between the two anions was observed (entries 7–10, 17–20, 28–31, Table 1). For example, when the epoxidation of cyclohexene was run at 20 °C for 1.5 h with **C1** and **D1** or **C2** and **D2** as additives, respectively, the magnitudes of the selectivity of the epoxide were about 95% and 90%, respectively (entries 7–10, Table 1). The reason of **D1** and **D2** inferior to **C1** and **C2** in improving epoxidation selectivity may be the instability of PF_6^- anion toward hydrolysis in contact with moisture, which has been noted in a number of reports [49–51]. However, the position of the substitute with imidazolium moiety in the pyridyl ring seems not important, because no difference between **C1** and **C2** or **D1** and **D2** in effecting the epoxidation reaction was observed throughout the reactions of all the substrates at different temperature. For example, when the epoxidation of cyclohexene was run at 20 °C for 1.5 h, the selectivity of the epoxide was around 95%, the conversion of cyclohexene was 92% in both cases of **C1** and **C2** as additives, respectively (entries 7, 9, Table 1); and in the same reaction conditions the selectivity of the epoxide and the conversion of cyclohexene were 90% and 93% in both cases of **D1** and **D2** as additives (entries 8, 10, Table 1), respectively. From the structures of the ILs, it is expected that only N-oxide group as an electron donor can coordinate with the center Re of MTO to generate the complexes in situ as shown in Fig. 1. No difference between **C1** and **C2** or **D1** and **D2** as additives in effecting the epoxidation reaction indicated that the amide spacer between the pyridyl N-oxide and the imidazolium moiety in both the structures is long enough to avoid the steric hindrance of imidazolium moiety in the epoxidation reaction.

Moreover, the influence of the loading amount of MTO and **C1** (MTO:**C1** = 1:1) on the epoxidation of styrene and 1-octene was also investigated. As show in Table 1, with the increasing of MTO and **C1** loadings from 1 mol% to 2 mol%, both the conversion of olefins and selectivity of the epoxides were improved (entries 17, 21, 28, 32, Table 1). When the epoxidation of styrene catalyzed by 2 mol % MTO/**C1** was run at 20 °C for 3 h, the conversion of styrene and the selectivity of epoxide were 84% and 99% corresponding to 44% and 84% in case of 1% of MTO/**C1** loading (entries 17, 21, Table 1); when the epoxidation of 1-octene was run at 20 °C for 12 h, the conversion of 1-octene increased from 48% to 86%, meanwhile, the selectivity of epoxide increased from 98% to 99% with the increasing of MTO/**C1** from 1% to 2% mol (entries 28, 32, Table 1). This results showed that increasing the loading amount of catalyst accelerated the epoxidation reaction, meantime, decreased the exposure time of the generated epoxides with water, therefore, decreased the amount of epoxide to 1,2-diols owing to ring-opening of epoxides.

Table 2
The effect of the molar ratio of **C1** to MTO on the epoxidation of cyclohexene.

Entry	**C1**/MTO (molar ratio)	Time (h)	Conversion (%)	Selectivity (%)
1	0/1	1.5	99	27
2	0.5/1	2	99	86
3	1/1	3	99	93
4	2/1	3	75	95

Reaction conditions: cyclohexene 5 mmol, 30% H_2O_2 10 mmol, MTO 0.05 mmol, methanol 7 mL, reaction temperature 20 °C.

3.2.2. *Effect of **C1** to MTO molar ratio on the epoxidation of olefins*

Because the four ILs had similar performances in improvement of the MTO-catalyzed epoxidation, **C1** was used as a representative to evaluate the effect of IL to MTO molar ratio on the epoxidation of olefins and the results are given in Table 2. It was found that the selectivity of the epoxide increased with the increasing of **C1** to MTO molar ratio. The observed results seem consistent with the view that the enhanced selectivity was due to the in situ coordination of the pyridine N-oxide moiety of **C1** to MTO (as shown in Fig. 1), which decreased the acidity of the Re, thereby inhibiting epoxide ring-opening. Accordingly, with the increasing of **C1** the equilibrium shifted toward the MTO–**C1** adduct, which promoted the concentration of adduct in solution and decreases the acidity of MTO, so that the selectivity of the epoxide increased. Meanwhile, it was also noted that only 2 percentage point increase of the selectivity of epoxide was received with the increasing of **C1** to MTO molar ratio from 1:1 to 2:1, indicating that low concentration of **C1** was enough to suppress the epoxide ring opening (entries 3 and 4, Table 2). The observed results indicated that **C1** is different from those ones that generally high molar ratio of additive to MTO was necessary to suppress the side reaction [17,18].

3.2.3. *Comparison of different ligands on the epoxidation of cyclohexene*

The results displayed that low loading of **C1** can suppress the epoxide ring opening, meanwhile, not slow down the epoxidation reaction significantly compared to other additives reported in the literature [10,42,48]. For understanding the mechanism leading to the excellent performance of **C1** as an additive in the MTO-catalyzed epoxidation, some other substances including [bmim]PF_6, pyridine N-oxide and **B1** were respectively used as additives in the reaction, their effects on the reaction were examined and compared with that of **C1** by keeping the epoxidation at the same progress (99% conversion). It can be seen from Table 3 that when the molar ratio of [bmin]PF_6 to MTO was 1:1 in the MTO-catalyzed epoxidation of

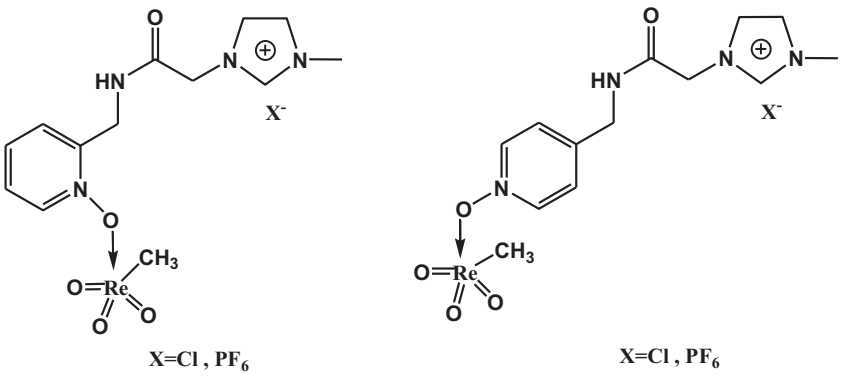

Fig. 1. Coordination of ILs with MTO.

Table 3
Effects of different ligands on the epoxidation of cyclohexene.

Entry	Additive	Time (h)	Conversion (%)	Selectivity (%)
1	None	6	>99	70
2	[bmim]PF_6	6	>99	68
3	[bmim]PF_6[a]	5	>99	45
4	PyNO	7.5	>99	84
5	**B1**	7.5	>99	85
6	Pyridine	8	>99	92
7	Pyridine[b]	8	97	>99
8	**C1**	8	>99	>99

Reaction conditions: cyclohexene 5 mmol, 30% H_2O_2 10 mmol, MTO 0.05 mmol, ligand 0.05 mmol, methanol 7 mL, reaction temperature 0 °C.
[a] [bmim]PF_6 0.5 mmol.
[b] Pyridine 0.6 mmol.

cyclohexene, [bmin]PF_6 almost had no effect, neither on the rate of the reaction nor the selectivity of epoxide (entries 1 and 2, Table 3). With the molar ratio of [bmin]PF_6 to MTO increasing to 10:1, the conversion of cyclohexene reached 99% within 5 h, however, the selectivity decreased to 45% (entry 3, Table 3). It is obvious that large excess of [bmin]PF_6 accelerated both the epoxidation and the epoxide ring-opening rate at the same time. In cases of PyNO and **B1** as additives, both of which have the pyridine N-oxide moiety as that in **C1**, the selectivity of epoxide was around 85%, respectively, when the conversion of cyclohexene reached 99% (entries 4 and 5, Table 3). And longer time (7.5 h) was needed to finish the epoxidation reaction similar to that with 3-cyanopyridine N-oxide as an additive in literature [25]. In case of pyridine as an additive, as high as 12:1 of molar ratio of pyridine to MTO was needed to suppress the epoxide ring-opening reaction, however, the epoxidation reaction was slowed down compared to the case of **C1** as an additive (entries 7, 8, Table 3). Based on the above results, we can conclude that for the simple structural additives the coordination capability of the additive to MTO plays an central role in suppressing the epoxide ring-opening reaction as reported in literature [20,40], the stronger the coordination capability is, the higher the selectivity of epoxide is obtained. However, when we consider **C1**, it is not appropriate just attributing the enhanced selectivity of epoxide to the in situ coordination of the pyridine N-oxide moiety of **C1** to MTO, because the coordination capacity of pyridine is stronger than that of **C1** in principle. Moreover, PyNO and **B1** just lack the imidazolium moiety compared to **C1** from the structural point of view; however, their improvement on the epoxidation reaction is inferior to that of **C1**. Therefore, the coexistence of pyridine N-oxide and quaternary ammonium in one structure is necessary to greatly enhance the capacity to suppress the epoxide ring-opening, without slowing down the epoxidation reaction largely. It is difficult to clarify what causes this result. In the beginning, we attributed this to the simultaneous binding of pyridine N-oxide and quaternary ammonium with MTO to stabilize MTO and reduce the acidity of the center Re atom of MTO. DFT calculation results did not support this assumption. The possible reason is the salvation of the quaternary ammonium moiety [52], which enhanced the solubility and stabilize the complexes as shown in Fig. 1 in the reaction mixture.

3.2.4. *Effect of the reaction time on the epoxidation of cyclohexene catalyzed by MTO/**C1***

The effect of **C1** on the epoxidation of cyclohexene at different reaction time is shown in Fig. 2. It can be seen that the conversion of cyclohexene with **C1** as an additive increased with time as expected, and reached about 100% in 3 h; while in case of neat MTO catalyzed epoxidation of cyclohexene the reaction completed within 1.5 h, indicating that the introduction of **C1** decreased the epoxidation rate. On the other hand, the introduction of **C1** is favorable to increase the selectivity of epoxidation. One will see that the

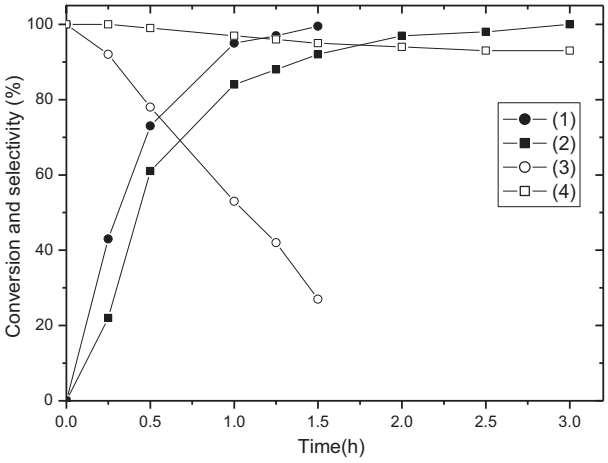

Fig. 2. Effect of the reaction time on the epoxidation of cyclohexene catalyzed by MTO/**C1**. (1) MTO conversion, (2) MTO/**C1** conversion, (3) MTO selectivity and (4) MTO/**C1** selectivity. Reaction conditions: cyclohexene 5 mmol, 30% H_2O_2 10 mmol, MTO 0.05 mmol, **C1** 0.05 mmol, methanol 7 mL, reaction temperature 20 °C.

selectivity of epoxide decreased dramatically with time in the case of neat MTO-catalyzed epoxidation, and to 27% when the reaction finished; however, the selectivity of epoxide decreased very slowly and as high as 93% of the selectivity of epoxide was received at the stage of reaction completion in case of **C1** as an additive. The results displayed in Fig. 2 clearly illustrated that **C1** suppressed the epoxide ring-opening in the MTO-catalyzed epoxidation of cyclohexene.

3.3. *The lifetime of MTO/**C1** catalytic system*

To further certify the stabilization effect of ILs on MTO or its mono and bisperoxo derivatives in the epoxidation process, fresh cyclohexene and 30% H_2O_2 were introduced into the reaction mixture after the completion of each catalytic reaction. The results are summarized in Table 4. It can be seen from Table 4, that the conversion of cyclohexene remained nearly constant in the first 5 runs, though the selectivity decreased in some degree. The results indicated that MTO or its mono and bisperoxo derivatives were stable throughout the epoxidation process and the activity of MTO was maintained in all the time due to the presence of **C1**. The gradual decreasing of the selectivity of the epoxide is due to the accumulation of water from 30% H_2O_2. In addition, epoxide generated during the process was not separated from the reaction mixture after each run, which increased the concentration of the epoxide and the contact time of the epoxide with water. As a result, more epoxide ring-opening was observed. With more and more water was accumulated with the catalytic running times, the concentration of H_2O_2 was lower and lower, therefore, the epoxidation rate decreased gradually too. Anyway, the introduction of the ILs is in favor of stabilizing the MTO and its active derivatives in the

Table 4
The lifetime of MTO/**C1** catalytic system.

Entry	Running times	Time	Conversion (%)	Selectivity (%)
1	1	8	>99	>99
2	2	8	>99	99
3	3	8	>99	97
4	4	8	>99	94
5	5	8	>99	81
6	6	8	85	62
7	6	11	>99	48

Reaction conditions: cyclohexene 5 mmol, 30% H_2O_2 10 mmol, MTO 0.05 mmol, **C1** 0.05 mmol, methanol 7 mL, reaction temperature 0 °C.

epoxidation process and the increasing of the selectivity of the epoxidation.

3.4. Recycling test of *C1*

By evaporating the reaction mixture at high vacuum, we tried to recover both MTO and **C1** from the MTO/**C1** catalyzed epoxidation of cyclohexene with aqueous H_2O_2 as an oxidant. When the residue was subjected to epoxidation of cyclohexene directly, no reaction was observed. However, when fresh MTO was introduced into the reaction mixture, the epoxidation reaction proceeded smoothly again. Analysis results showed that the conversion of cyclohexene and the epoxide selectivity were same as those in the case of fresh **C1** as an additive. The results indicated that **C1** was recyclable due to its stability in the catalytic and recovery processes.

4. Conclusions

The four ionic liquids with pyridine N-oxide moiety as designed and synthesized showed excellent performances in the MTO-catalyzed epoxidation of olefins with 30% H_2O_2 as an oxidant. The catalytic results displayed that low loading amount of the ILs compared to other substances as additives could suppress the epoxide ring-opening, which led to the significant increase of selectivity of the epoxide. Though the introduction of the ILs caused the decrease of the epoxidation rate, the side effect was much smaller than those of other substances being used as additives. We concluded that the coexistence of pyridine N-oxide and imidazolium moieties in the ILs was important to deduce of the acidity of the central Re atom meanwhile stabilize MTO or its derivatives in the epoxidation process, which led to the excellent performances in improvement of the selectivity of the epoxidation and the lifetime of MTO. It was also displayed that the improvement degree on the selectivity of epoxidation depended on the type of anion of the ILs, but not the position of the substituent with imidazolium moiety in the ring of pyridine N-oxide.

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