A role of ionic liquid as an activator for efficient olefin epoxidation catalyzed by polyoxometalate

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Ionic liquid (IL), such as 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]), as an activator for the epoxidation of a wide variety of olefins with H_2O_2 catalyzed by Keggin polyoxometalate [bmim]$_3PW_{12}O_{40}$ has been demonstrated. Use of IL results both in significant enhancement of TOF and selectivity for olefin epoxidation compared to that of traditional organic solvents, *e.g.* 289 times TOF and 1.3 times selectivity as found in CH_2Cl_2 for the epoxidation of *cis*-cyclooctene. The kinetic ^{31}P NMR spectra uncover that the active peroxotungstate $[PO_4\{W(O)(O)_2\}_4]^{3-}$ (Venturello complex), contributing to the epoxidation, can be readily generated in the presence of [bmim][PF_6]. Furthermore, the counterion such as PF_6^- and $[(CF_3SO_2)_2N]^-$ is evidenced to play a crucial role in the epoxidation of olefin. BF_4^- as counterion, instead of PF_6^-, is found to reduce TOF and selectivity for *cis*-cyclooctene epoxidation dramatically from 289 to less than 1 and from 99% to 12%, respectively.

Introduction

In recent years, tungsten-based polyoxometalates have received an increasing interest in selective oxidation of organic compounds with hydrogen peroxide, *i.e.* Ishii–Venturello chemistry, due to their high efficiency and the use of the environmentally friendly oxidant.[1–10] However, a series of drawbacks, for example, the use of toxic and carcinogenic chlorinated solvents and the difficulty in reuse of catalyst and separation of products in traditional biphasic or homogeneous systems, diminish their advantages.

Much recent research in catalysis is associated with manipulation and optimization of reaction media to achieve high efficiency and to decrease the environmental load.[11,12] Ionic liquids, which possess many desirable properties such as negligible vapor pressure, high thermal stability, good solvency of organic and inorganic materials and the possibility to influence the chemical reaction process, are usually used as "green" and recyclable media for chemical processes including organometallic catalysis, electrochemistry and organic synthesis.[13–19] However, only a few examples of polyoxometalates used as catalyst in ionic liquids have been reported. For example, Tandon and co-workers reported the oxidation of alcohols with hydrogen peroxide catalyzed by a imidazolium ion based peroxotungstophosphate in the ionic liquid [bmim][BF_4].[20] However, no polyoxometalate-catalyzed epoxidation of olefins in ionic liquids was reported so far, although it has been extensively investigated in other media. Moreover, some studies show that, besides as "green" reaction media, ionic liquids seem to play some special roles in catalytic reactions. For example, Song and Roh showed that the addition of ionic liquid could clearly accelerate the epoxidation of 2,2-dimethylchromene in Jacobsen's chiral (salen)Mn catalytic system.[15] Sun *et al.* reported that an ionic liquid was beneficial for the oxidation of alcohols in a copper(II) chloride catalytic system.[21] Hardacre and co-workers reported the superior rates and selectivities for the sulfoxidation in ionic liquids compared with molecular solvents with catalysts Ti-SBA-15 and UL-TS-1.[22] Mizuno and co-workers found that peroxotungstate immobilized by an ionic liquid on SiO_2 particles exhibited superior activity with respect to that of triethylammonium cation for the epoxidation of olefins.[23] However, the mechanism underlying the enhancement in reactivity of ionic liquids is not clear.

We herein exploit the hydrophobic 1-butyl-3-methylimidazolium ionic liquid (*e.g.* [bmim][PF_6]) as a solvent for epoxidation of olefins by the imidazolium-based Keggin polyoxometalate ([bmim]$_3PW_{12}O_{40}$) with aqueous hydrogen peroxide. It was found that [bmim]$_3PW_{12}O_{40}$ could epoxidize olefins with aqueous hydrogen peroxide at a much more rapid rate in ionic liquids than that in classical organic solvents. The epoxidation reaction in CH_3CN was also greatly promoted upon the addition of the ionic liquid. The unique role of the ionic liquid as a cocatalyst in olefin epoxidation catalyzed by polyoxometalate was demonstrated based on kinetics, solvent effect, ion effect and spectroscopic experiments. It is suggested that the ionic liquid could not only be used as solvent for the reuse of catalyst, but also supply the special microenvironment to facilitate the formation of the active peroxotungstate from [bmim]$_3PW_{12}O_{40}$ and H_2O_2.

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Experimental

Materials and catalysts

cis-Cyclooctene, cyclohexene, 1-octene, styrene, α-methylstyrene, *trans*-2-octene, 2-methyl-1-heptene, 2-methyl-2-heptene and *trans*-β-methyl were purchased from Aldrich and Across Co. and were used as received. Hydrogen peroxide (30 wt%), Keggin polyoxometalate ($H_3PW_{12}O_{40}$) and tetrabutylammonium bromide were obtained from Beijing Chemicals Co. All other chemicals were of laboratory reagent grade quality and were used without further purification. 1-Butyl-3-methylimidazolium chloride salt ([bmim]Cl) was prepared as described previously.[24] 1-Butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) was prepared with [bmim]Cl and KPF_6: [bmim]Cl (0.1 mol) and KPF_6 (0.1 mol) were added into distilled water. The obtained ionic liquid organic phase was washed thoroughly with distilled water, and then dried for 1 h using anhydrous $MgSO_4$;[24] δ_H (400 MHz; acetone-d$_6$; Me_4Si) 0.92 (3H, t), 1.32 (2H, m), 1.80 (2H, m), 3.82 (3H, s), 4.12 (2H, t), 7.35 (1H, s), 7.38 (1H, s) and 8.45 (1H, s). Similarly, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([bmim][NTf_3])[25] and 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4])[24] were prepared by the method of ion exchange. $[bmim]_3PW_{12}O_{40}$ was precipitated from aqueous solutions of $H_3PW_{12}O_{40}$ by the addition of excess [bmim]Cl.[26] The white solids were collected, washed thoroughly with H_2O, and dried under vacuum overnight; ν_{max}(film)/cm^{-1} 3441, 3149, 3116, 2961, 2932, 2870, 1636, 1563, 1459, 1384, 1164, 1079, 979, 895, 806, 747, 650, 621, 521. $[Bu_4N]_3PW_{12}O_{40}$ and $[C_5H_5N(CH_2)_{15}CH_3]_3PW_{12}O_{40}$ were prepared with tetrabutylammonium bromide and cetylpyridinium bromide, respectively, by a similar method.

Oxidation of olefins

In a typical reaction, the catalyst $[bmim]_3PW_{12}O_{40}$ (8 mg, 2.4 μmol) was dissolved in [bmim][PF_6] (1 cm^3). Substrate (0.8 mmol) was added and followed by adding of hydrogen peroxide (30% in water) (1.2 mmol). The reaction mixture was stirred at 60 °C for 1 h. After completion of the reaction, the reaction mixture was extracted with diethyl ether (3 × 3 cm^3). The extract layer was collected and then a definite amount of toluene was added as an internal standard for GC analysis. The ionic liquid phase including the catalyst was washed with diethyl ether and dried prior to being recycled. The same reaction conditions were used in other solvents. For classical organic solvents, the reaction mixture was diluted to about 9 cm^3 with diethyl ether after reaction for 1 h and then toluene was added as an internal standard for GC analysis.

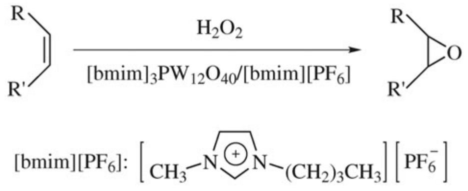
Instrumentation and methods

The epoxidation yield was determined by GC using a gas chromatograph Hitachi G-3900 equipped with a flame ionization detector and a 30 m × 0.25 mm DB-5 capillary column. The oxidation products were identified by means of GC-MS and GC using authentic samples. For GC-MS analyses, a Finnigan Trace GC ultra gas chromatograph equipped with a Finnigan TraceDSQ mass spectrometer was used. The IR spectra were recorded in KBr on a DigiLab FTS 3500 Fourier Transfer Infrared Spectrometer (Tekmar Dohrmann). The ionic liquids were characterised using ESI-MS (APEX α model FT-TCR mass spectrograph). A Bruker 300 MHz instrument and Bruker 400 MHz instrument were used for NMR spectra. Chemical shifts of ^{31}P NMR were referenced with respect to external 85% H_3PO_4.

Results and discussion

The activity of catalyst for epoxidation of olefins (Scheme 1) under different conditions is shown in Table 1. For the epoxidation of *cis*-cyclooctene, the catalytic reaction in the ionic liquid [bmim][PF_6] exhibited both a high yield of 87% and a high selectivity of 99% (entry 1), and the efficiency of H_2O_2 utilization was determined as *ca.* 87%.[27] In the blank experiments, no reaction occurred in the absence of oxidant H_2O_2 or $[bmim]_3PW_{12}O_{40}$. Other olefins, including other cyclic olefins, long-chain olefins and olefins with electron-withdrawing groups, could be efficiently epoxidized in the $[bmim]_3PW_{12}O_{40}/H_2O_2/[bmim][PF_6]$ system (entries 2–7). Notably, 2-octene could be readily epoxidized into its epoxide, while 1-octene was oxidized at rather low rate. As is known, epoxidation is an electrophilic reaction, and the methyl moiety is a good electron-donating group. The high activity of 2-octene compared to that of 1-octene could be ascribed to the effect of electron-donating methyl substitution. Similarly, styrene with an electron-withdrawing aromatic group was epoxidized with rather low yield and selectivity. However, *trans*-β-methylstyrene with an electron-donating methyl group exhibited an increased reactivity. Another important fact for the present catalytic system is that the configuration around the double bond of olefins was completely retained in the corresponding epoxides in the epoxidation of *cis*- and *trans*-olefins. The stability and the recyclable of the $[bmim]_3PW_{12}O_{40}/[bmim][PF_6]$ catalytic system was examined by repetitive use of the catalyst and the ionic liquid. It was found that five recycles for epoxidation of *cis*-cyclooctene led to no significant decrease in reactivity and selectivity.

Other solvents were also examined for the epoxidation reaction (Table 1, entries 8–12). Another ionic liquid [bmim][$(CF_3SO_2)_2N$] exhibited similar yield (82%) and selectivity (94%). Interestingly, the ionic liquid [bmim][BF_4] with $[BF_4]^-$ as counterion showed very low catalytic activity. The influence of the possible impurities in the ionic liquid was checked. Halides, such as chloride or fluoride ions, and acid, are considered as the most possible impurities, which are derived from the preparation of the ionic liquid and hydrolysis of the $[BF_4]^-$ or $[PF_6]^-$, respectively. No notable decrease in the reaction activity was observed when hydrochloric acid and/or hydrofluoric acid ($\leq 1 \times 10^{-3}$ M) were added to the



Scheme 1 Epoxidation of olefins in the ionic liquid [bmim][PF_6].

Table 1 Epoxidation of olefins with H_2O_2 catalyzed by $[bmim]_3PW_{12}O_{40}$[a]

	Substrate	Solvent	Product	Yield[b] (%)	Selectivity[c] (%)	TON[d]
1	*cis*-Cyclooctene	$[bmim][PF_6]$	Cyclooctene oxide	87	99	289
2	Cyclohexene	$[bmim][PF_6]$	Cyclohexene oxide	36	80	121
3	1-Octene	$[bmim][PF_6]$	1,2-Epoxyoctane	12	86	40
4	*trans*-2-Octene	$[bmim][PF_6]$	*trans*-2,3-Epoxyoctane	37	94	125
5	2-Methyl-2-heptene	$[bmim][PF_6]$	2-Methyl-2,3-epoxyheptane	67	89	223
6	Styrene	$[bmim][PF_6]$	Styrene oxide	9	32	31
7	*trans*-β-Methylstyrene	$[bmim][PF_6]$	*trans*-β-Methylstyrene oxide	22	67	74
8	*cis*-Cyclooctene	$[bmim][(CF_3SO_2)_2N]$	Cyclooctene oxide	82	94	274
9	*cis*-Cyclooctene	$[bmim][BF_4]$	Cyclooctene oxide	Trace	12	<1
10	*cis*-Cyclooctene	CH_3CN	Cyclooctene oxide	1	77	3
11	*cis*-Cyclooctene	CH_3OH	Cyclooctene oxide	Trace	40	1
12	*cis*-Cyclooctene	CH_2Cl_2	Cyclooctene oxide	Trace	75	1

[a] *Reaction conditions*: 0.8 mmol substrate; 1.2 mmol H_2O_2; 2.4 μmol catalyst; 1 cm^3 solvent; reaction temperature 60 °C; reaction time 1 h. [b] Yield for epoxides based on substrate. [c] Selectivity for epoxides determined by GC analysis. [d] Turnover number (TON) = mol products per mol catalyst.

most effective catalytic system ($[bmim]_3PW_{12}O_{40}$–[bmim]-$[PF_6]$–H_2O_2). Besides, the presence of water is another potential problem for $[bmim][BF_4]$ ionic liquid system due to its good aqueous solubility. In this study, the dried ionic liquid and the optimum amount of aqueous H_2O_2 for the catalytic activity were used to decrease the influence on the activity efficiently. It is obvious that the effect of the possible impurities can be excluded under the same experimental conditions. Therefore, the anion of the ionic liquid may play a key role in the $[bmim]_3PW_{12}O_{40}$-based selective oxidation process. In all tested classical organic solvents, including CH_2Cl_2, CH_3CN and CH_3OH, only little cyclooctene oxide was produced under otherwise identical conditions. In CH_2Cl_2, in which the $[bmim]_3PW_{12}O_{40}$ is insoluble, a trace of cyclooctene oxide was produced. Even in the miscible solvents CH_3CN and CH_3OH, the reactivity for the epoxidation was also rather low, which suggests that the solubility was not the only cause for the high yield of epoxides in ionic liquids.

In order to illuminate the effect of ionic liquid clearly, a mixed solvent of $[bmim][PF_6]$ and acetonitrile was used in the epoxidation of *cis*-cyclooctene (Fig. 1). Epoxidation reaction was rather slow (less than 1%) when only acetonitrile was used as solvent. However, when $[bmim][PF_6]$ was added to acetonitrile to form a homogeneous solution, the catalytic activity was markedly enhanced. After addition of 10% of ionic liquid, about 50% of initial *cis*-cyclooctene was epoxidized to cyclooctene oxide in 1 h. When the content of ionic liquid in the mixed solvent was more than 30%, the disappearance of the cyclooctene and the yield of epoxide tended to remain constant. It is notable that the total mass was well-balanced for all the ratios, indicating the good selectivity of the mixed solvent system.

Tetraalkylammonium salts have been widely used as phase transfer agents in polyoxometalate-based catalysts. In the present study, different types of organic ion salts (C^+A^-) were also used to determine the effect of the ions (Fig. 2). Results indicated that neither the short-chain tetrabutylammonium bromide ($[Bu_4N]Br$) nor the long-chain cetyltrimethylammonium bromide ($[CH_3(CH_2)_{15}(CH_3)_3N]Br$) exhibited much accelerative effect on the epoxidation. As observed in the pure ionic liquid system, replacing the $[PF_6]^-$ counterion by Cl^- and $[BF_4]^-$, in ionic liquids [bmim]Cl and $[bmim][BF_4]$, led to negligible promotive effect, which indicates again that the anion, besides the cation, in the ionic liquid presents important effects on the activity of catalyst.

^{31}P NMR spectra have proved to been a strong tool for the determination of ^{31}P species derived from $PW_{12}O_{40}$.[3–5,28,29] However, most of the reported experiments were carried out under static conditions, *i.e.* the NMR spectra were recorded at different $PW_{12}O_{40}{}^{3-}$: H_2O_2 ratios after a given reaction time. In the present study, the time-dependent ^{31}P NMR spectra of the polyoxometalate species during the reaction were monitored to reveal their evolvement process. As shown in Fig. 3, after $[bmim]_3PW_{12}O_{40}$ was treated with 50 equivalents of H_2O_2 in the mixed solvent acetonitrile–$[bmim][PF_6]$ (1 : 1) at 50 °C for 15 min, the peak for the original $PW_{12}O_{40}{}^{3-}$ (−14.4 ppm) became very low. Concomitantly, new species with resonances at 4.1, −12.0 and −12.1 ppm appeared (Fig. 3(A), curve b). The peak at 4.1 ppm has been assigned to be the catalytically active species $[PO_4\{W(O)(O)_2\}_4]^{3-}$

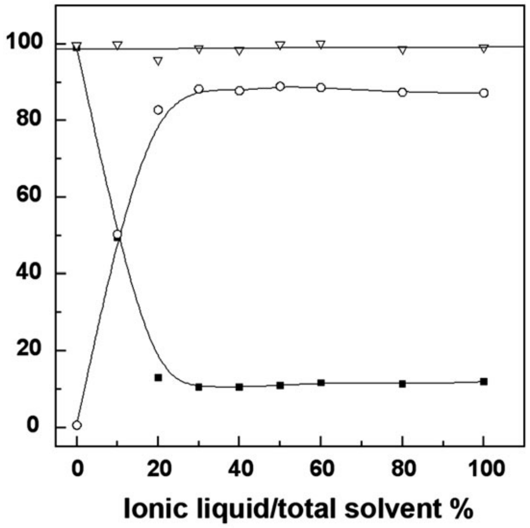


Fig. 1 Effect of $[bmim][PF_6]$ in mixed solvents (acetonitrile and ionic liquid) on the epoxidation of *cis*-cyclooctene at 60 °C for 1 h: (■) amount of *cis*-cyclooctene remaining (%); (○) yield of cyclooctene oxide (%); (▽) the total mass balance (%). [Catalyst] = 2.4 mM, [substrate] = 0.8 M and $[H_2O_2]$ = 1.2 M.

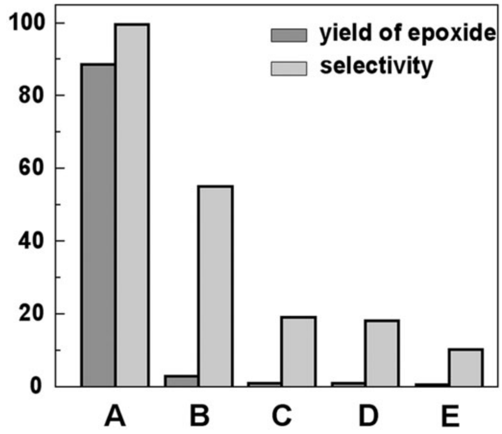


Fig. 2 Effect of ion salts on epoxidation of *cis*-cyclooctene with H_2O_2 catalyzed by $[bmim]_3PW_{12}O_{40}$ in acetonitrile at 60 °C for 1 h. [Catalyst] = 2.4 mM, [substrate] = 0.8 M and $[C^+A^-]/[Cat.] = 1000$. Ion salts (C^+A^-): A: $[bmim][PF_6]$; B: tetrabutylammonium bromide; C: cetyltrimethylammonium bromide; D: [bmim]Cl; E: $[bmim][BF_4]$.

(Venturello complex).[28] The signals near −12 ppm can be attributed to polyoxometalates with peroxo groups (usually expressed as PW_xO_y).[28] Further reaction led to the loss of the signals at −12.0 and −12.1 ppm. We also notice that part of the species caused the buildup of the resonance at 4.1 ppm as the other part of the species reconverted to the initial phosphotungstate (Fig. 3(A), curves c and d). It is implied that the PW_xO_y species are probably intermediates in the formation of the catalytically active Venturello complex. When *cis*-cyclooctene (20 mM) was added into the system, the peak at 4.1 ppm disappeared immediately (Fig. 3(A), curve f), which confirms that the species with a signal at 4.1 ppm is the active species for the epoxidation of olefins. When $[C_5H_5N(CH_2)_{15}CH_3]_3PW_{12}O_{40}$ was treated with H_2O_2 in acetonitrile at 50 °C, besides the signal from the original $PW_{12}O_{40}{}^{3-}$ (−13.8 ppm), a weak peak at 1.3 ppm appeared and became stronger with reaction time (Fig. 3(B)). The addition of *cis*-cyclooctene did not affect the intensity of this peaks, suggesting that the peak could not represent an active species. In pure acetonitrile solvent and in the presence of $[bmim]_3PW_{12}O_{40}$ and H_2O_2, the peak of the original polyoxometalate was located at −14.0 ppm, and new small peaks were observed during reaction at 50 °C (Fig. 3(C)). All these results are in good accord with those in the activity experiments (Table 1 and Fig. 2). Therefore, it is evident that the ionic liquid $[bmim][PF_6]$ could promote the formation of the active peroxotungstate in the polyoxometalate catalytic system.

It was reported that phosphotungstate has no catalytic activity for the epoxidation of olefins until the active peroxotungstate forms at an appreciable concentration.[5] A induction period for the formation of epoxides is expected when the $PW_{12}O_{40}{}^{3-}$ is used as precursor and if the active peroxotungstate is formed in a slow rate. In this study, the epoxidation of *cis*-cyclooctene was kinetically studied in the $[bmim]_3PW_{12}O_{40}–H_2O_2$ system in order to examine the induction period. In the ionic liquid $[bmim][PF_6]$, epoxidation was determined to show first-order kinetics (Fig. 4(A)), and the apparent rate constant was evaluated to be 0.060 min^{-1}. There is no apparent induction period, indicating that the initial formation of the active peroxo species from the precursor $[bmim]_3PW_{12}O_{40}$ and H_2O_2 in the ionic liquid is considerably fast with respect to the epoxidation reaction. By contrast, in pure acetonitrile, although a very low conversion was observed, the formation of epoxide exhibited an evident induction period (Fig. 4(B)), which is in agreement with the results by Alsters and co-workers.[30]

During the Ishii–Venturello reaction, the polyoxometalate precursor ($PW_{12}O_{40}{}^{3-}$ in this study) must first transform to the active epoxidizing species $[PO_4\{W(O)(O)_2\}_4]^{3-}$ in the presence of excess hydrogen peroxide. Brégeault and co-workers[28] reported that if the H_2O_2 was first mixed with the polyoxometalate in an aqueous solution to form the Venturello complex before the phase transfer, good catalytic activity was obtained. In contrast, when the hydrogen peroxide was introduced after the transfer of precursor into organic phase by

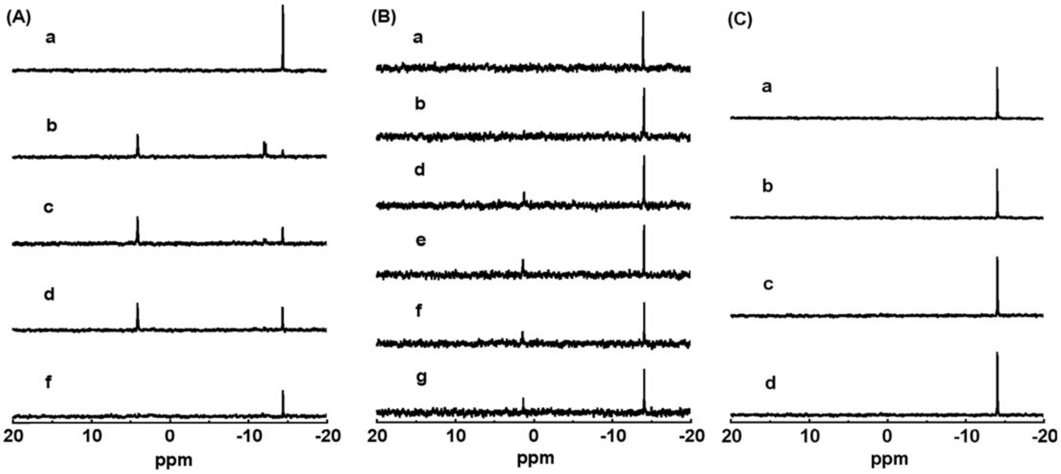


Fig. 3 Time-dependent ^{31}P NMR spectra at 50 °C: (A) $[bmim]_3PW_{12}O_{40}$ reacted with 50 equivalents of H_2O_2 in a mixed solvent (acetonitrile–$[bmim][PF_6]$ (1 : 1)); (B) $[C_5H_5N(CH_2)_{15}CH_3]_3PW_{12}O_{40}$ reacted with H_2O_2 in acetonitrile; (C) $[bmim]_3PW_{12}O_{40}$ reacted with H_2O_2 in acetonitrile. Reaction time: (a) 0 min; (b) 15 min; (c) 30 min; (d) 45 min; (e) 90 min. Reaction time after the addition of substrate *cis*-cyclooctene: (f) 0 min; (g) 10 min.

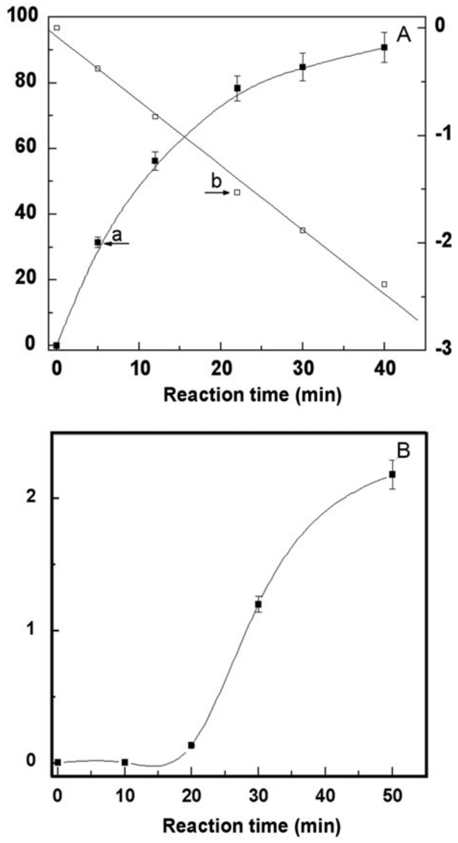


Fig. 4 Kinetic profiles in [bmim]$_3$PW$_{12}$O$_{40}$-catalyzed epoxidation of *cis*-cyclooctene with hydrogen peroxide at 60 °C in different solvents: (A) in [bmim][PF$_6$]: (a) the formation of epoxide and (b) the rate of the epoxide formation *vs.* reaction time. (B) The formation of epoxide *vs.* reaction time in acetonitrile. [Catalyst] = 2.4 mM and [substrate] = 0.8 M.

phase transfer agent, the polyoxometalate exhibited little catalytic activity. In this case, H_2O_2 is not accessible to the precursor, and the active species is difficult to generate. In our study, acetonitrile is miscible both with aqueous hydrogen peroxide, with the substrates and with [bmim]$_3$PW$_{12}$O$_{40}$. However, little active species (Fig. 3(C)) and low epoxidation rate (Table 1 and Fig. 4(B)) were obtained in acetonitrile, indicating that the reaction media can greatly affect the formation of active species and hence significantly change the epoxidation reaction rate. In a controlled experiment, [PO$_4${W(O)(O)$_2$}$_4$]$^{3-}$ with the counterion [bmim]$^+$, [Bu$_4$N]$^+$ or [CH$_3$(CH$_2$)$_{15}$-(CH$_3$)$_3$N]$^+$ was used directly as catalyst. The epoxidation reaction could occur efficiently in both [bmim][PF$_6$] and pure acetonitrile, indicating that the former process (*i.e.* the formation of the active species) is blocked in the pure acetonitrile environment. Another evidence for the slow formation of active species in acetonitrile is the existence of an induction period (Fig. 4(B)). The slow formation of active species also gives a good interpretation of the low epoxidation rate in other media, such as [bmim][BF$_4$], CH_3OH and CH_2Cl_2 (Table 1).

From the above results, it is evident that the some ionic liquid can provide a special microenvironment for the formation of the active peroxotungstate in the Ishii–Venturello reaction. It has been reported that the nature of the imidazolium ionic liquid depends on the three-dimensional network of anions and cations by weak interaction (such as hydrogen bonds, van der Waals and Coulombic forces).[12,31–33] The anion identity has an important impact on its properties, such as viscosity, polarity, and H-bond strength.[34] In this study, the inefficiency of epoxidation in [bmim][BF$_4$] (Table 1, entry 9) indicates that the anionic counterion plays an important role in the formation of the microenvironment. Furthermore, in the studies on the physicochemistry of ionic liquids, negative excess molar volumes were always observed when ionic liquids (such as [bmim][PF$_6$]) were mixed with organic solution (such as acetonitrile), indicating that the nanostructural organization from the ion–ion interactions of ionic liquids does not have to be broken in the organic solvent, even at very low concentration of the ionic liquid.[35–37]

To further reveal the interaction and association between the [bmim]$^+$ and counterion [PF$_6$]$^-$, the electrospray ionization (ESI) spectra were examined. As shown in Fig. 5, the ESI experiment evidently indicated the presence of the monocharged species [(bmim)$_2$(PF$_6$)]$^+$ and [(bmim)(PF$_6$)$_2$]$^-$ in the acetonitrile solution of the ionic liquid [bmim][PF$_6$]. Similar results had been reported by Dupont[32] and Zhao.[38] In addition, the relative intensity of [(bmim)(PF$_6$)$_2$]$^-$ increased with the increase in the concentration of [bmim][PF$_6$] (Fig. 6). This change was in accordance with activity of epoxidation in the acetonitrile solution of the ionic liquid. Accordingly, [bmim][PF$_6$] when dissolved in acetonitrile can form a special structure, which could enhance the activation of catalyst, and, consequently, exhibit a good activity of epoxidation.

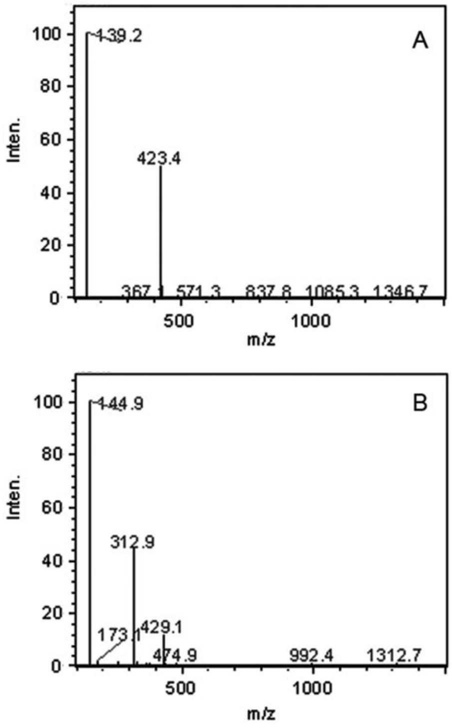


Fig. 5 ESI-MS spectra of acetonitrile solutions of [bmim][PF$_6$]: (A) the positive ion mode: m/z 139.2 [bmim]$^+$ and m/z 423.4 [bmim–PF$_6$–bmim]$^+$; (B) the negative ion mode: m/z 144.9 [PF$_6$]$^-$ and m/z 429.1 [PF$_6$–bmim–PF$_6$]$^-$.

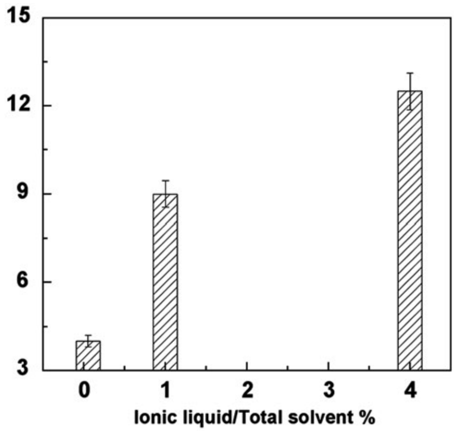


Fig. 6 The effect of the ion pair aggregate of different concentrations of [bmim][PF_6] in acetonitrile. The target ion pair [PF_6–bmim–PF_6]$^-$ (CA_2^-) of m/z 429.1 was indicated through ESI-MS spectra in the negative ion mode.

It is also noted that there are some differences in the chemical shifts of ^{31}P NMR spectra of the original $PW_{12}O_{40}{}^{3-}$ (−14.4 ppm for [bmim]$_3PW_{12}O_{40}$ in acetonitrile–[bmim][PF_6] (1 : 1) mixed solvent, −14.0 ppm for [bmim]$_3PW_{12}O_{40}$ in acetonitrile and −13.8 ppm for [$C_5H_5N(CH_2)_{15}CH_3$]$_3PW_{12}O_{40}$ in acetonitrile) (Fig. 3), which confirms that the ionic liquid, even mixed with CH_3CN, can provide a special microenvironment for the polyoxometalate species. Therefore, it is reasonable to propose that the cations and anions of the ionic liquid could form a microenvironment with nonpolar and polar regions,[39–41] which means that the unique structure is derived from the anions and the cations arranged in specific dimensions, and here they can interact with the polyoxometalate and hydrogen peroxide, which can accelerate the activation reaction of polyoxometalate by hydrogen peroxide to generate the catalytically active species.

Conclusions

Ionic liquids could not only be used as solvent for the reuse of catalyst, but also be beneficial to epoxidation of olefins catalyzed by [bmim]$_3PW_{12}O_{40}$ and H_2O_2. In the ionic liquid, the special microenvironment was supplied by the interactions of cations and anions, in which the generation of the active peroxotungstate from [bmim]$_3PW_{12}O_{40}$ and H_2O_2 could be accelerated significantly. In some sense, the ionic liquid [bmim][PF_6] could be considered as a cocatalyst to promote the formation of active peroxotungstate from phosphotungstate and hydrogen peroxide.

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