



Epoxidation of α,β -unsaturated carbonyl compounds in ionic liquid/water biphasic system under mild conditions

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Abstract

The epoxidation reactions of electron-deficient α,β -unsaturated carbonyl compounds were investigated in ionic liquid (IL)/water biphasic system using hydrogen peroxide as an oxidant at room temperature. By optimizing the reaction conditions, including reaction time, temperature, the amount of oxidant and sodium hydroxide, 100% conversion and 98% selectivity could be achieved in the epoxidation of mesityl oxide. The mass transfer model for the epoxidation of α,β -unsaturated carbonyl compounds in the 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4MIm][PF_6]$)/water biphasic system has been proposed.

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1. Introduction

Epoxides are well known as one of the most valuable building blocks, which can be used as intermediates and precursors for chemicals production. Therefore, epoxidation reaction is an important transformation of olefins. Particularly, the epoxidation reactions of electron-deficient olefins such as α,β -unsaturated carbonyl compounds, which are widely applied in the synthesis of intermediates in pharmaceutical and fine chemicals, are usually unsatisfactory because of poor reactivity of those unsaturated compounds. To achieve high selectivity, some research works have focused on this type of reactions. Phase transfer cata-

lysts (PTCs) have been considered as quite effective reagents to carry out this transformation with mild and inexpensive oxidant such as H_2O_2 [1,2], due to their easy transformation to the corresponding active species (ammonium hydrogen peroxide). Quite recently, the molecular sieve TS-1 was also successfully used in this area [3]. The epoxidation reactions mentioned above were required to be performed either at low temperature or in a dropwise charging for the sake of obtaining high selectivity and avoiding the ring-opening hydrolysis of epoxyketone in the strongly basic conditions [4,5].

Ionic liquids (ILs), or room temperature molten salts, have attracted increasing interest over recent years, particularly in the area of green chemistry [6,7]. Since the thermodynamics and kinetics of reactions carried out in ionic liquids are very different from those in traditional molecular solvents, they have been

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found to be promising solvents for a wide range of industrial applications from petrochemicals [8], and bulk chemicals [9], to fine chemicals [10] and the treatment of nuclear waste [11], etc. Recently, Song and Roh reported the asymmetric epoxidation of olefins catalyzed by (salen)Mn^{III} using sodium hypochlorite (NaOCl) as an oxidant in 1-butyl-3-methylimidazolium hexafluorophosphate ([C₄MIm][PF₆]) ionic liquid [12]. Additionally, methyltrioxorhenium-catalyzed epoxidation of olefins was also successfully carried out in 1-ethyl-3-methylimidazolium tetrafluoroborate ([C₂MIm][BF₄]) ionic liquid using urea hydrogen peroxide as the source of oxygen [13]. Lau et al. performed an epoxidation reaction in ionic liquid using enzyme as a catalyst, employing a clean and inexpensive oxidant of hydrogen peroxide [14]. However, the catalytic system was so sensitive and the demands for experimental operations were so strict that its applications would be narrow.

In this paper, we report the epoxidation of α,β -unsaturated carbonyl compounds in an ionic liquid/water biphasic system under mild reaction conditions.

2. Experimental

2.1. Materials and reagents

All solvents and chemicals used were commercially available and used without further purification unless otherwise stated. *N*-methylimidazole, 1-chloropropane, 1-chlorobutane, 1-chloropentane, and 1-chlorohexane were purchased from Aldrich. Mesityl oxide, chalcone, cyclohexenone, naphthoquinone, methylcinnamate and benzylideneacetone were obtained from Strem Chemicals. Ammonium hexafluorophosphate, tetrabutylammonium bromide and benzyltrimethylammonium chloride were received from Shanghai Chemicals Co. Toluene was distilled over sodium-benzophenone prior to use.

2.2. Preparations of ionic liquids

Ionic liquids, 1-propyl-3-methylimidazolium hexafluorophosphate ([C₃MIm][PF₆]), [C₄MIm][PF₆], 1-pentyl-3-methylimidazolium hexafluorophosphate ([C₅MIm][PF₆]) and 1-hexyl-3-methylimidazolium hexafluorophosphate ([C₆MIm][PF₆]) were prepared by following the procedure for [C₄MIm][PF₆]: (1) *N*-methylimidazole was quaternized with 1-chlorobutane to form 1-butyl-3-methylimidazolium chloride; (2) 1-butyl-3-methylimidazolium chloride was treated with ammonium hexafluorophosphate in water to obtain [C₄MIm][PF₆] ionic liquid, and then [C₄MIm][PF₆] was further purified at 80 °C under vacuum. The detailed synthesis and purification of the ionic liquids were analogous to the procedure reported in previous literatures [15], and their FT-IR (Bruker, IFS120HR) spectra accorded with those of the references.

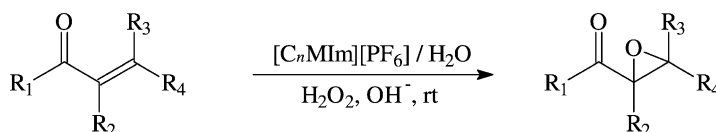
2.3. Epoxidation reaction

All the epoxidation reactions (Scheme 1) were performed in a 25 ml round-bottom flask equipped with a magnetic stirrer. For a typical reaction, 1.5 ml ionic liquid, 4.4 mmol α,β -unsaturated carbonyl compound, 0.5–5 ml aqueous hydrogen peroxide solution (30%) and 0.2–4.4 ml 1N sodium hydroxide aqueous solution were successively charged into the reactor, and then the content was stirred for 40–180 min at room temperature (15 ± 1 °C). At the end of the reaction, the mixture was extracted with toluene (2 ml × 3), and the combined toluene phase was analyzed by GC/MS.

The epoxidation reactions in the organic solvent/water biphasic system were performed as described above.

2.4. Qualitative and quantitative analysis

The qualitative analysis of liquid reaction mixture was carried out on a Hewlett-Packard 6890/5793



Scheme 1.

GC/MS equipped with an HP 5MS column (30 m) with helium as carrier gas. The column temperature was raised from 80 to 260 °C at a heating rate of 10 °C min⁻¹.

The quantitative analysis of the extract solution was carried out on a temperature-programmed Hewlett-Packard GC-5790 equipped with a ϕ 3 × 3000 mm PTFE column, using 2-butanone as the internal standard.

3. Results and discussion

3.1. Epoxidation in [C₄MIm][PF₆]/H₂O and traditional PTC system

The epoxidation reaction of mesityl oxide were performed in both [C₄MIm][PF₆]/H₂O biphasic catalytic system and traditional organic solvent/H₂O phase transfer catalyst (PTC) system, respectively, and the results are listed in Table 1.

In the [C₄MIm][PF₆]/H₂O system, the epoxidation of mesityl oxide was obviously dependent on the bases used. A neutral condition did not exhibit the catalytic activity in this system leaving the starting material mesityl oxide intact (entry 1). Under a weakly basic condition (entry 2), the conversion of mesityl oxide did not exceed 4%. When Na₂CO₃ was used in place of NaHCO₃, the conversion was much improved, but the selectivity to α,β -epoxyketone was poor. A satisfying result was achieved by using NaOH as a base and all mesityl oxide was almost converted to the corresponding α,β -epoxyketone (entry 4). Above all, a

strong base was necessary for the epoxidation reaction in the [C₄MIm][PF₆]/H₂O biphasic catalytic system, and NaOH was found to be the best in this study. Additionally, the reaction temperature was very important for the epoxidation reaction. As the temperature increased from 15 to 25 °C, the selectivity to α,β -epoxyketone decreased by about 10% while the conversion of mesityl oxide was still kept at 100% (entry 5). The decrease in selectivity was supposed to be due to the ring-opening of the α,β -epoxyketone at higher temperature.

As a contrast, the epoxidation was performed in the CH₂Cl₂/H₂O PTC system using TABA as a catalyst under the same conditions (entry 6). In this case, mesityl oxide was only converted by 5% and the selectivity to the α,β -epoxyketone just reached 85%. Thus, it can be seen that the [C₄MIm][PF₆]/H₂O system was more efficient for epoxidation of α,β -unsaturated carbonyl compounds than the traditional CH₂Cl₂/H₂O system under those mild conditions. Wynberg and Marsman reported that, in the traditional CH₂Cl₂/H₂O system, the yields of the α,β -epoxyketones were very poor unless the reaction temperature was limited to below zero degree [4].

3.2. Optimizing reaction conditions

3.2.1. Effect of reaction time

Fig. 1 shows the effect of reaction time on epoxidation of α,β -unsaturated carbonyl compound in the [C₄MIm][PF₆]/H₂O biphasic system using mesityl oxide as substrate. The epoxidation was very slow at the beginning and only 6% of mesityl oxide reacted

Table 1

Epoxidation of mesityl oxide in the [C₄MIm][PF₆]/H₂O biphasic catalytic system and organic solvent/H₂O PTC system^a

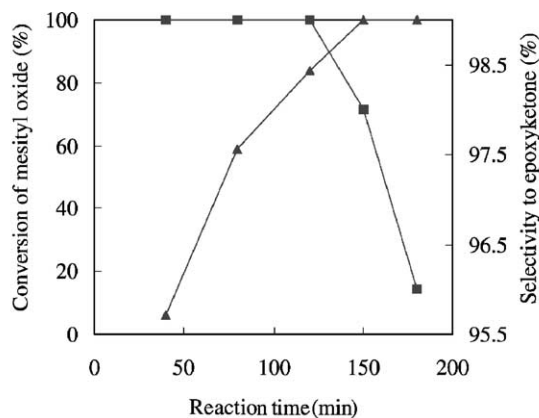
Entry	Catalytic system	Catalyst	Base	Temperature (°C)	Conversion (%) ^b	Selectivity (%) ^c
1	[C ₄ MIm][PF ₆]/H ₂ O	–	–	15	1	95
2	[C ₄ MIm][PF ₆]/H ₂ O	–	Na ₂ CO ₃	15	86	91
3	[C ₄ MIm][PF ₆]/H ₂ O	–	NaHCO ₃	15	4	96
4	[C ₄ MIm][PF ₆]/H ₂ O	–	NaOH	15	100	98
5	[C ₄ MIm][PF ₆]/H ₂ O	–	NaOH	25	100	88
6	CH ₂ Cl ₂ /H ₂ O	TBAB ^d	NaOH	15	5	85

^a Reaction conditions: 0.5 ml mesityl oxide; 1.5 ml ionic liquid or 2 ml organic solvent; 2.5 ml aqueous hydrogen peroxide solution (30%); 0.9 ml aqueous NaOH solution (1N); 0.12 mmol catalyst for entry 6; 2.5 h.

^b Conversion of mesityl oxide.

^c Selectivity to α,β -epoxyketone.

^d Tetrabutylammonium bromide.



—▲— Conversion of mesityl oxide —■— Selectivity to epoxyketone

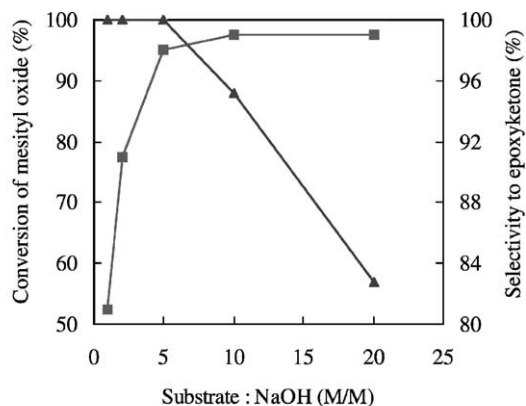
Fig. 1. Effect of reaction time on epoxidation of mesityl oxide in the $[\text{C}_4\text{MIm}][\text{PF}_6]/\text{H}_2\text{O}$ biphasic system. Reaction conditions: 0.5 ml mesityl oxide; 1.5 ml ionic liquid; 2.5 ml aqueous hydrogen peroxide solution (30%); 0.9 ml aqueous NaOH solution (1N); 15 °C.

after 40 min. This slow initial stage of the epoxidation in the $[\text{C}_4\text{MIm}][\text{PF}_6]/\text{H}_2\text{O}$ biphasic system could be related to its reaction mechanism (Section 3.5.2). Subsequently, the conversion increased rapidly and the reaction completed at 150 min. The selectivity to α,β -epoxyketone was always maintained at 98% in 150 min; afterwards, the selectivity further decreased gradually with the reaction time. In this way, 150 min could be optimal for epoxidation of mesityl oxide in the $[\text{C}_4\text{MIm}][\text{PF}_6]/\text{H}_2\text{O}$ biphasic system.

3.2.2. Effect of substrate/sodium hydroxide molar ratio

In the traditional PTC system, substrate/sodium hydroxide molar ratio is critical for epoxidation of α,β -unsaturated carbonyl compounds. We investigated the effect of substrate/sodium hydroxide molar ratio on the epoxidation using mesityl oxide as a substrate in our $[\text{C}_4\text{MIm}][\text{PF}_6]/\text{H}_2\text{O}$ biphasic system, and the results are shown in Fig. 2.

As expected, a lower mesityl oxide/NaOH ratio could benefit for conversion of substrate, but it is detrimental to selectivity of α,β -epoxyketone. Although a higher mesityl oxide/NaOH ratio is favorable for the selectivity, mesityl oxide could not be completely converted. Consequently, a 5:1 of substrate/

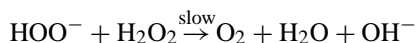
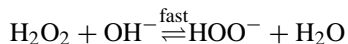


—▲— Conversion of mesityl oxide —■— Selectivity to epoxyketone

Fig. 2. Effect of substrate to sodium hydroxide ratio on the epoxidation of mesityl oxide in the $[\text{C}_4\text{MIm}][\text{PF}_6]/\text{H}_2\text{O}$ biphasic system. Reaction conditions: 0.5 ml mesityl oxide; 1.5 ml ionic liquid; 2.5 ml aqueous hydrogen peroxide solution (30%); 15 °C; 2.5 h.

NaOH ratio resulted in 100% conversion with α,β -epoxyketone selectivity of 98%.

In the presence of bases, the decomposition of H_2O_2 is inevitable. The NaOH-initiated decomposition of H_2O_2 could be illustrated as follows [16]:



Apparently, the pH value of the whole aqueous phase affects directly the decomposition of H_2O_2 . When $[\text{H}_2\text{O}_2] = [\text{HOO}^-]$, the pH value of aqueous phase equals to the $\text{p}K_a$ value of H_2O_2 , namely 11.13, and at this point, the maximum decomposition of H_2O_2 would be reached [17]. At the optimal substrate/NaOH ratio, namely 5:1, the pH value is much higher than 11.13 in the aqueous phase. Thus, the decomposition of H_2O_2 would be suppressed effectively. Consequentially it is beneficial for the conversion of mesityl oxide.

3.2.3. Effect of hydrogen peroxide/substrate molar ratio

A cost-efficient ratio of H_2O_2 to substrate should be favorable for the practical application of catalytic system when H_2O_2 is used as an oxidant. In our

Table 2
Effect of H₂O₂ to substrate ratio on the epoxidation of mesityl oxide in the [C₄MIm][PF₆]/H₂O biphasic system^a

Entry	H ₂ O ₂ /substrate (M/M)	Conversion (%) ^b	Selectivity (%) ^c
1	1	45	98
2	3	79	98
3	5	100	98
4	7	100	98

^a Reaction conditions: 0.5 ml mesityl oxide; 1.5 ml ionic liquid; 0.9 ml aqueous NaOH solution (1N); 15 °C; 2.5 h.

^b Conversion of mesityl oxide.

^c Selectivity to α,β -epoxyketone.

[C₄MIm][PF₆]/H₂O biphasic system, mesityl oxide have been used to examine the effect of hydrogen peroxide/substrate molar ratio on epoxidation of α,β -unsaturated carbonyl compounds and the results are listed in Table 2.

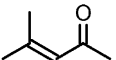
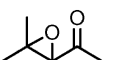
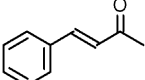
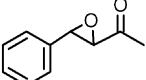
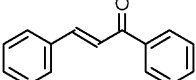
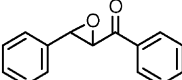


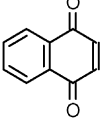
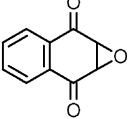
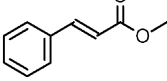
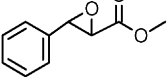
The conversion of mesityl oxide increased markedly with increasing H₂O₂ to substrate ratio and reached

a complete conversion at the ratio of 5:1. It is worthy of noting that selectivity to α,β -epoxyketone was constant at 98% in all the range of the ratios. Therefore, the ratio of 5:1 was believed to be optimal in the ionic liquid system, which comparable to that in the traditional PTC system [18].

3.3. Epoxidation of α,β -unsaturated carbonyl compounds with different structures in [C₄MIm][PF₆]/H₂O biphasic system

The epoxidation of a variety of α,β -unsaturated carbonyl compounds were carried out using these optimized conditions in the [C₄MIm][PF₆]/H₂O biphasic system and the results are summarized in Table 3. The model substrate, mesityl oxide (entry 1) could be effectively converted to corresponding α,β -epoxyketone with excellent selectivity. In other cases, the reaction time were extended in order to achieve high conversions. At 180 min of reaction time, benzylideneacetone

Table 3
Epoxidation reactions of various α,β -unsaturated carbonyl compounds in the [C₄MIm][PF₆]/H₂O biphasic system^a

Entry	Substrate	Products	Time (min)	Conversion (%) ^b	Selectivity (%) ^c
1			150	100	98
2			180	96	99
3			180	96	100
4 ^d			180	90	99
5			180	54	96
6 ^d			480	65	98

^a Reaction conditions: 4.4 mmol substrate; 1.5 ml ionic liquid; 2.5 ml aqueous hydrogen peroxide solution (30%); 0.9 ml aqueous NaOH solution (1N); 15 °C; 2.5 h.

^b Conversion of substrate.

^c Selectivity to epoxyketone.

^d Carried out at 25 °C.

was converted to desired α,β -epoxyketone in 96% conversion and 99% selectivity. Similarly, the epoxidation of chalcone under these conditions provided the 2,3-epoxy-1,3-diphenyl-1-propanone in 96% conversion without any hydrolysis of the α,β -epoxyketone. In the case of cyclohexenone, the epoxidation reaction was carried out at 25 °C since low conversion was observed at 15 °C.

The epoxidation of dicarbonyl unsaturated compound was also evaluated under these reaction conditions. For example, naphthoquinone was converted to corresponding α,β -epoxyketone in a modest conversion of 54%. This method was shown not to be limited to α,β -unsaturated ketones since the epoxidation of the methyl cinnamate provided 3-phenyl-oxiranecarboxylate in a conversion of 65% and a 98% of selectivity. This low conversion would be attributed to its oxygen atom of ester group sharing the conjugated π^* electron of ene-carbonyl to decrease the activity of β -position. Although the conversion of 65% is unsatisfactory, it is still an improved value compared to the reported one [19], indicating the usefulness of the present procedure.

Thus, it can be seen that the $[\text{C}_4\text{Mim}][\text{PF}_6]/\text{H}_2\text{O}$ biphasic catalytic system has exhibited considerable activities for epoxidation of a variety of α,β -unsaturated carbonyl compounds. Moreover, good selectivity for the α,β -epoxyketones is essentially different from the traditional PTC catalytic systems.

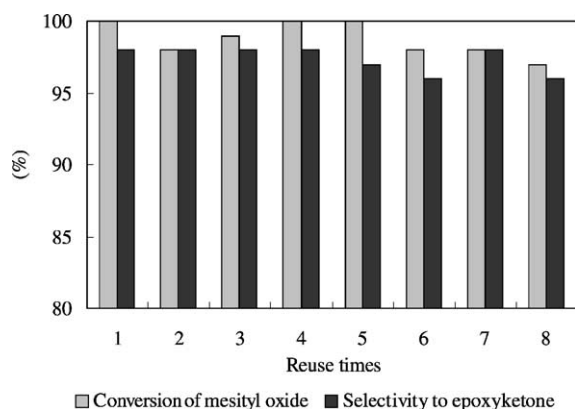


Fig. 3. Reuse of $[\text{C}_4\text{Mim}][\text{PF}_6]$ in the epoxidation of mesityl oxide. Reaction conditions: 0.5 ml mesityl oxide; 1.5 ml ionic liquid; 2.5 ml aqueous hydrogen peroxide solution (30%); 0.9 ml aqueous NaOH solution (1N); 15 °C; 2.5 h.

3.4. Reuse of ionic liquid

In this study, $[\text{C}_4\text{Mim}][\text{PF}_6]$ was separated from the ionic liquid/ H_2O biphasic system after the first run and then directly used in the next run. Although aqueous NaOH solution could result in a little volumetric expansion of $[\text{C}_4\text{Mim}][\text{PF}_6]$, the reuse of $[\text{C}_4\text{Mim}][\text{PF}_6]$ was still possible. As shown in Fig. 3, $[\text{C}_4\text{Mim}][\text{PF}_6]$ almost maintained its original activity for mesityl oxide even after having been used eight times.

3.5. Mechanism of epoxidation reaction in ionic liquid/ H_2O biphasic systems

3.5.1. Comparison of different ionic liquid/water systems

For understanding the reaction mechanism of epoxidation in the ionic liquid/water biphasic system, $[\text{C}_n\text{Mim}]\text{PF}_6$ ($n = 3, 4, 5, 6$) ionic liquids with different hydrophobicity were used as a hydrophobic phase to investigate the epoxidation of mesityl oxide (Table 4). It can be seen that, with the increase in length of the side chain attached to organic cation of ionic liquids, the conversion of mesityl oxide decreased and the selectivity to α,β -epoxyketone increased. It is evident that as the hydrophobicity of ionic liquid increased, the conversion of mesityl oxide was retarded but the selectivity to α,β -epoxyketone did not [20].

3.5.2. Mass transfer model for epoxidation reaction in $[\text{C}_4\text{Mim}][\text{PF}_6]/\text{water}$ biphasic system

The mass transfer model for the epoxidation of α,β -unsaturated carbonyl compounds in the traditional organic solvent/ H_2O biphasic system has been

Table 4
Epoxidation of mesityl oxide in different ionic liquid/water biphasic systems^a

Catalytic system	Conversion (%) ^b	Selectivity (%) ^c
$[\text{C}_3\text{Mim}][\text{PF}_6]/\text{H}_2\text{O}$	100	97
$[\text{C}_4\text{Mim}][\text{PF}_6]/\text{H}_2\text{O}$	100	98
$[\text{C}_5\text{Mim}][\text{PF}_6]/\text{H}_2\text{O}$	95	99
$[\text{C}_6\text{Mim}][\text{PF}_6]/\text{H}_2\text{O}$	84	99

^a Reaction conditions: 0.5 ml mesityl oxide; 1.5 ml ionic liquid; 2.5 ml aqueous hydrogen peroxide solution (30%); 0.9 ml aqueous NaOH solution (1N); 15 °C; 2.5 h.

^b Conversion of mesityl oxide.

^c Selectivity to α,β -epoxyketone.

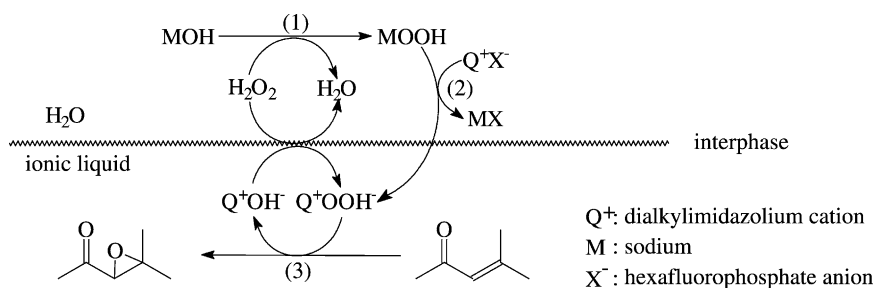


Fig. 4. Mass transfer model of epoxidation of mesityl oxide in the $[C_4MIm][PF_6]/H_2O$ biphasic system.

carefully studied [21]. It has been confirmed that the active species, OOH^- , could be transferred into the organic phase from aqueous solution by interfacial extraction or a PTC process [22]. We believe that in the ionic liquid/ H_2O biphasic system, the epoxidation also starts from the transport of OOH^- from the aqueous phase to ionic liquid, and followed by inverted transport of OH^- . To be specific, process (1): OH^- could be transformed to OOH^- in the presence of H_2O_2 in the aqueous phase; process (2): HOO^- combines with a cation (Q^+) of ionic liquid dissolved into water to form Q^+OOH^- and then enters to the ionic liquid phase; process (3): Q^+OOH^- initiates epoxidation reaction and itself transforms to Q^+OH^- . A graphic explanation is shown in Fig. 4.

Although $[C_4MIm][PF_6]$ dissolved into water is negligible, it is crucial for the process (2). The latest literature has reported that the solubility of $[C_4MIm][PF_6]$ in water is less than 2.5 wt.% below $50^\circ C$ [23], which is just as much as the catalyst amount required in the traditional PTC system. It is noted that $NaPF_6$ is symbiotic with Q^+OOH^- in process (2). Because of the solubility of $NaPF_6$ in water comparable with $[C_4MIm][PF_6]$, the transformation from $[C_4MIm][PF_6]$ to $NaPF_6$ could be unfavorable in the aqueous phase. Consequently, the process (2) was so slow that the concentration of the hydroperoxide anion (OOH^-) in ionic liquid may be limited. As a result, the rate of epoxidation reaction was slow in the $[C_4MIm][PF_6]/water$ biphasic system and the most hydrophobic ionic liquid, $[C_6MIm][PF_6]$, would give a lowest conversion.

In addition, Q^+OH^- produced in process (3) should be insignificant due to the low concentration of Q^+OOH^- in the $[C_4MIm][PF_6]$ phase. Meanwhile, most of Q^+OH^- will rapidly transfer into aqueous

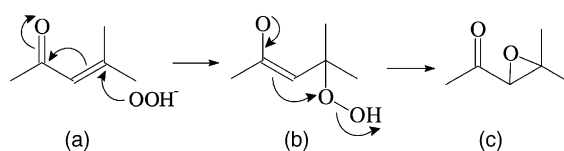


Fig. 5. Mechanism of epoxidation of mesityl oxide in the $[C_4MIm][PF_6]/H_2O$ biphasic system.

phase because of Q^+OH^- bearing a strong hydrophilic function group OH^- . As a result, the concentration of OH^- could be further decreased in the ionic liquid phase. Thus, in hydrophobic phase, the ring-opening hydrolysis of α,β -epoxyketones resulting from OH^- could be efficiently restricted. Compared with traditional PTC systems, the high selectivity to α,β -epoxyketone obtained in the ionic liquid/water system was reasonable. Similarly, the more hydrophobic ionic liquid was, the lower the concentration of OH^- in ionic liquid would be, and so the higher selectivity to α,β -epoxyketone.

3.5.3. Mechanism of epoxidation reaction

The present studies have revealed that the epoxidation reaction could be initiated by OOH^- . The mechanism of epoxidation involves two steps (Fig. 5): (1) OOH^- undergoes a nucleophilic addition to mesityl oxide to give an intermediate b; (2) intermediate b loses OH^- anion to afford desired α,β -epoxyketone [19].

4. Conclusion

The epoxidation reactions of electron-deficient α,β -unsaturated carbonyl compounds have been

carried out in $[C_nMIm]PF_6/H_2O$ ($n = 3, 4, 5, 6$) biphasic systems by using hydrogen peroxide as oxidant under mild conditions. Under optimized reaction conditions, where the molar ratios of substrate/NaOH and H_2O_2 /substrate was both 5:1, α,β -unsaturated carbonyl compounds such as mesityl oxide, benzylideneacetone and chalcone have been almost completely converted to the corresponding α,β -epoxyketones. Compared with traditional PTC systems, $[C_4MIm][PF_6]/H_2O$ biphasic catalytic system has exhibited excellent selectivity to α,β -epoxyketones. Additionally, $[C_4MIm][PF_6]$ almost retained its original activity for the epoxidation of mesityl oxide even after having been used eight times.

According to the mass transfer model, a small quantity of $[C_4MIm][PF_6]$ dissolved into water exchanged its anion with H_2O_2 to form Q^+OOH^- , and then Q^+OOH^- transferred into the $[C_4MIm][PF_6]$ phase to initiate the epoxidation reaction. Just due to the peculiar properties of the $[C_4MIm][PF_6]$, the ring-opening hydrolysis of α,β -epoxyketones was suppressed efficiently, resulting in the high selectivity to α,β -epoxyketones.

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