

Epoxidation of alkenes with hydrogen peroxide catalyzed by iron(III) porphyrins in ionic liquids[†]

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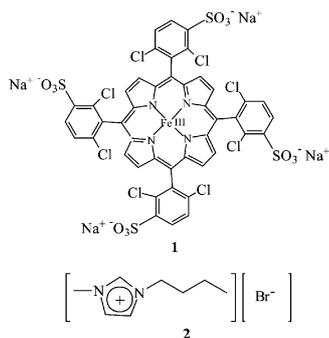
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An efficient procedure is described for catalyst recycling and easy product isolation in alkene epoxidation with hydrogen peroxide catalyzed by water-soluble iron(III) porphyrins in environmentally benign and ambient temperature ionic liquids.

Metalloporphyrins as model catalysts of cytochrome P450 have been used to mimic various oxidation reactions such as hydroxylation of hydrocarbons, epoxidation of olefins and oxidation of other organic substrates with hydrogen peroxide in homogeneous organic and aqueous reaction media.^{1–4} The intermolecular self-destruction and recovery of the expensive catalysts are the general problems encountered in homogeneous reaction media with metalloporphyrins. Therefore, various heterogeneous methods have been developed to make catalyst recovery easy and to enhance the catalytic activity.^{5–7}

Ambient room temperature ionic liquids have recently gained recognition as environmentally benign solvents due to their unique physical properties such as non-volatility, non-flammability, and thermal stability.^{8–11} They have been employed as solvents for liquid–liquid separations, extractions and for recycling homogeneous catalysts *etc.*^{12–14} Ionic liquids have also been used as novel reaction media for economically and environmentally attractive processes in aqueous mono- and biphasic systems.^{15,16} Herein, we report the oxidation of selected olefins with H₂O₂ catalyzed by anionic water-soluble porphyrins in ionic liquids under different reaction conditions.



The catalyst tetrakis(2',6'-dichloro-3'-sulfonatophenyl)porphyrinato iron(III) [Cl₈TPPS₄Fe(III)] (**1**) was immobilized in 1-butyl-3-methylimidazolium bromide {[Bmim][Br]} (**2**) due to its ionic character. The epoxidation of alkenes with hydrogen peroxide catalyzed by **1** was carried out under biphasic conditions: a mixture of styrene in dichloromethane and **1** in **2** was stirred with hydrogen peroxide under a nitrogen atmosphere for 4 h to give styrene epoxide (**4a**) and phenylacetaldehyde (**5a**) in 74% and 16% yield, respectively. Similarly, the oxidation of *p*-chlorostyrene (**3b**) with hydrogen peroxide and **1** in **2** gave *p*-chlorostyrene epoxide (**4b**) and *p*-chlorophenylacetaldehyde (**5b**) in 70% and 14% yield, respectively (Table 1). The oxidation of cyclohexene (**6**) with

hydrogen peroxide and **1** in **2** gave epoxy-cyclohexane (**7**), 2-cyclohexenol (**8**) and 2-cyclohexenone (**9**) in 42, 35, 12%, respectively, but cyclooctene (**10**) gave only epoxy-cyclooctane (**11**) in 81% yield (Fig. 1).

The organic phase containing product was separated after the completion of the reaction leaving behind the catalyst immobilized in ionic liquid. The recovered brown oily ionic liquid containing **1** could be reused for further catalytic reactions (Table 2). The catalytic activity of catalyst **1** immobilized in ionic liquid **2** in alkene epoxidation is comparable to the activity obtained when the same catalyst was supported on other heterogeneous systems.^{6,18} Further, the efficiency of catalyst **1** in ionic liquid **2** and in homogeneous solution (water–acetonitrile, 1:1 v/v) was compared using epoxidation of styrene and cyclooctene. The epoxide yields were very low in homogeneous solution (17% in the case of styrene and 21% in the case of cyclooctene). The mechanism of epoxide formation is believed to proceed in a similar manner to that of

Table 1 Alkene epoxidation with hydrogen peroxide catalyzed by **1** immobilized in **2** under a nitrogen atmosphere^{a,†}

Entry	Substrate	Time/h	Yield (%) ^b epoxide	Turnovers ^c
1	3a	4	74 ^d	1.38 × 10 ³
2	3b	5	70 ^e	1.23 × 10 ³
3	6	5	42 ^f	6.4 × 10 ²
4	10	4	81	1.35 × 10 ³

^a † See footnote. ^b Yield is based on the substrate and is determined by GC. ^c Turnovers calculated from epoxide yield. ^d Phenylacetaldehyde in 16% yield was also obtained. ^e *p*-Chlorophenylacetaldehyde in 14% yield was also obtained. ^f Cyclohexen-2-ol and cyclohexen-2-one were also obtained in 35 and 12% yield, respectively.

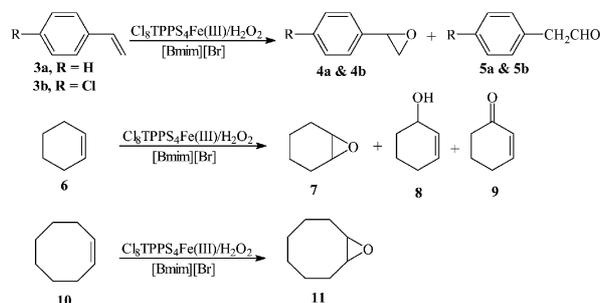


Fig. 1 The epoxidation of alkenes by hydrogen peroxide catalyzed by **1** immobilized in **2**.

Table 2 Catalytic activity of the recovered catalyst **1** immobilized in ionic liquid **2** in the epoxidation of styrene with H₂O₂

Run	1	2	3	4	5
Yield (%) ^a	74	73	71	68	62

^a Based on the substrate and GC analysis.

[†] Electronic supplementary information (ESI) available: experimental. See <http://www.rsc.org/suppdata/cc/b2/b207072n/>

homogeneous medium and proceeded through an iron-*oxo* intermediate. Further, the formation of aldehyde may be due to the rearrangement of an initially formed complex of iron-*oxo* intermediate and alkene.¹⁹

It is noteworthy that the recycled metalloporphyrin **1** in ionic liquid **2** showed comparable activity even after 4–5 runs in the oxidation of styrene with hydrogen peroxide (Table 2). However, the addition of excess oxidant to the reaction mixture resulted in the degradation of catalyst.

In summary, the present method of epoxidation by using ionic liquid as a biphasic system is useful for recycling the expensive metalloporphyrin catalyst from the reaction mixture. The activity of the catalyst in ionic liquid is greater than that in conventional solvents.

Notes and references

‡ The required ionic liquid [Bmim][Br] was prepared using a literature method.¹⁷ The catalyst Cl₈TPPS₄Fe(III) is readily soluble in [Bmim][Br] and its behaviour in [Bmim][Br] is similar to that in conventional solvents.

A typical procedure for the epoxidation of alkenes using Cl₈TPPS₄Fe(III) immobilized in ionic liquid [Bmim][Br]: The catalyst Cl₈TPPS₄Fe(III) (1.25 mmol) was dissolved in [Bmim][Br] (2 cm³). To this solution, alkene (125 mmol) in dichloromethane (5 cm³) and hydrogen peroxide (30%, 125 mmol) were added under a nitrogen atmosphere. The two-phase system was stirred at room temperature for 4–5 h. Progress of the reaction was monitored by GC. The organic phase was separated, washed with water and dried with anhydrous Na₂SO₄. The solvents were removed under reduced pressure and the residue was chromatographed on silica gel. The formation

of different products has been confirmed by ¹H NMR, and other spectroscopic data.

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