

Electrosynthesis of hydrogen peroxide in room temperature ionic liquids and *in situ* epoxidation of alkenes†

Michael Chi-Yung Tang, Kwok-Yin Wong and Tak Hang Chan*

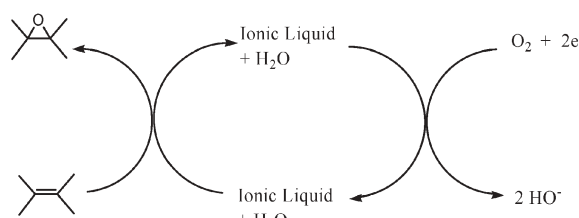
Received (in Cambridge, UK) 9th November 2004, Accepted 21st December 2004

First published as an Advance Article on the web 19th January 2005

DOI: 10.1039/b416837b

Hydrogen peroxide can be electrosynthesized from oxygen in [bmim][BF₄]-water and used *in situ* for the epoxidation of alkenes.

Even though it is generally recognised that room temperature ionic liquids (RTILs) have a wide electrochemical window and are thermally stable, electrochemical applications of RTILs to organic synthesis have not been extensively explored.¹ Some recent examples include reduction of dimethyl maleate and benzaldehyde,² polymerization of arenes³ and preparation of functionalized siloxanes.⁴ Hydrogen peroxide has recently been advocated as a green oxidant because it leaves no hazardous residues, only oxygen and water, after reaction. It has been widely applied to the paper pulp bleaching process, degradation of hazardous organic molecules in effluents treatment, and chemical synthesis. However, the usual method of production of hydrogen peroxide (the anthraquinone process)^{5,6} involves the use of large amounts of organic solvents and the consumption of alkylated anthraquinones. Furthermore, because of the potential hazards of neat hydrogen peroxide, it is generally used as a 30% aqueous solution, which adds to high transportation costs. Recently, Weidner *et al.*^{7,8} demonstrated that the stable superoxide ion can be electrogenerated from oxygen in the ionic liquid, 3-butyl-1-methylimidazolium hexafluorophosphate, [bmim][PF₆]. Since the superoxide ion can be rapidly reduced in water to give hydrogen peroxide,⁹ we reasoned that hydrogen peroxide can be generated by electroreduction of oxygen in water-containing ionic liquids. In this communication, we provide the first report on the electrosynthesis of hydrogen peroxide from oxygen in the ionic liquid, 3-butyl-1-methylimidazolium tetrafluoroborate, [bmim][BF₄]. We also demonstrate that the hydrogen peroxide in [bmim][BF₄] can be used *in situ* for the epoxidation of alkenes (Scheme 1). Furthermore, the whole cycle can be repeated with high efficiency.

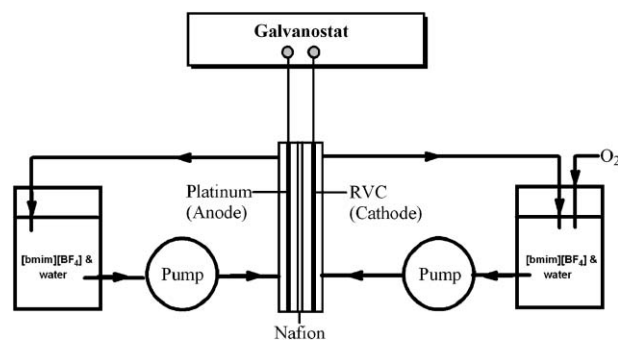


Scheme 1

† Electronic supplementary information (ESI) available: experimental procedures for the electrosynthesis of hydrogen peroxide and the epoxidation of alkenes. See <http://www.rsc.org/suppdata/cc/b4/b416837b/> *bcchanth@polyu.edu.hk

Investigations into the optimal operational parameters (optimal applied potential and volume ratio of [bmim][BF₄] to water) were performed using a H-cell with batch electrolysis (see supporting information†).¹⁰ The anion [BF₄] was used in lieu of [PF₆] because of the known hydrolytic instability of [PF₆].¹¹ In addition, the ionic liquid [bmim][BF₄] was known to be stable towards relatively high concentrations of hydrogen peroxide.¹²

A micro flow cell (Scheme 2) was used for galvanostatic continuous flow electrolysis to generate hydrogen peroxide for the epoxidation. Oxygen electroreduction occurred at the reticulated vitreous carbon (RVC) cathode while the anode was a platinum gauze and each compartment was separated by Nafion[®]. Both compartments consisted of the optimized volume ratio of [bmim][BF₄] to water (8 : 2 v/v). All measurements were carried out in controlled current (60 mA). Hydrogen peroxide concentration was determined using standard titration methods with potassium permanganate. The results are summarized in Table 1. The applied potential and the amount of water in [bmim][BF₄] were the significant factors which affected the yield of hydrogen peroxide. Different potentials from -600 mV to -750 mV (*vs.* SCE) were applied and different volume ratios of [bmim][BF₄] to water were investigated. The optimal conditions were found to be -650 mV (*vs.* SCE) and 8 : 2 (v/v) respectively. Under these operational conditions, the yield of hydrogen peroxide increased steadily with time, and reached a value of 102 mM after 4 h with an initial current efficiency of 62%. Electrogeneration of hydrogen peroxide in [bmim][BF₄]-water (8 : 2 v/v) mixture was also performed with a slightly alkaline solution (0.04 M NaOH). Under alkaline conditions, the formation of the hydroperoxide ion is expected to be favoured because the hydrogen peroxide is a stronger acid than water ($pK_a = 11.64$ at 25 °C).¹³ This was found to be the case (Table 1) with a yield of 124 mM of hydrogen peroxide after 4 h and an initial current efficiency of 71%. Table 1 also compares the yields of hydrogen peroxide in RTILs with the



Scheme 2

Table 1 Comparison of hydrogen peroxide concentration and current efficiencies in different electrolytes under continuous flow electrolysis




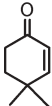
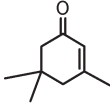
	[bmim][BF ₄] + H ₂ O ^a	[bmim][BF ₄] + 0.04 M NaOH ^a	2 M NaOH ^b	Organic phase ^c + 2 M NaOH (1 : 9 v/v) ^b
[H ₂ O ₂]/mM	102 ^d	124 ^d	50	150
Current efficiency (%)	62	71	40	60
Time/h	4	4	4	4

^a Electrolysis current 0.6 A, projected area 6.7 mA cm⁻². ^b Electrolysis current 1.37 A, projected area 22.5 mA cm⁻². See ref. 14. ^c Tributylphosphate and diethylbenzene were added to 2 M NaOH. See ref. 14. ^d H₂O₂ concentration was determined by standard titration methods with KMnO₄.

traditional electrochemical syntheses. Based on a similar electrochemical setup, the yield of hydrogen peroxide in aqueous 2 M NaOH electrolyte¹⁴ only is half of that in the [bmim][BF₄]-water mixture. This is presumably because of the low oxygen solubility in aqueous solution. Under the biphasic system of tributyl phosphate-diethylbenzene and aqueous NaOH,¹⁴ the yield of hydrogen peroxide after 4 h is higher than that of the [bmim][BF₄]-NaOH mixture but with a lower initial current efficiency.

We demonstrated that the hydrogen peroxide thus generated in RTIL can be used *in situ* for oxidation without the need for extraction or isolation of the hydrogen peroxide. We chose epoxidation of alkenes for demonstration because of the industrial significance of epoxides. There have been extensive studies on the epoxidation of alkenes in clean solvents such as water¹⁵ or ionic liquids^{12,16} employing hydrogen peroxide as oxidant. The alkaline hydrogen peroxide generated in the [bmim][BF₄]-NaOH mixture was used successfully for the epoxidation of a number of α,β -unsaturated ketones. The results are summarized in Table 2 showing that several different electrophilic alkene substrates have

Table 2 Epoxidation of electrophilic alkenes^a

Entry	Substrate	Time/min	Yield (%)
1		1	92
2		5	91
3		8	86
4		8	80
5		120	65

^a Reaction conditions: 0.37 mmol substrate, 78 mmol of electrogenerated hydrogen peroxide in 12 mL [bmim][BF₄]-NaOH mixture, room temperature. Epoxides were extracted by diethyl ether. Yields were determined by GC-MS *versus* an internal standard and all epoxides were isolated and identified by ¹H NMR spectroscopy.

been converted to epoxides with yields ranging from fair to good after isolation by extraction with diethyl ether.¹⁷ The yields of the epoxides compare well with those in the literature using 2 M hydrogen peroxide in [bmim][BF₄].¹⁶

Finally, we demonstrated that it was possible to recycle the electrolyte for the regeneration of hydrogen peroxide. After diethyl ether extraction of the epoxide (from 3,5-dimethylcyclohexen-1-one, entry 3 in Table 2) in the first cycle, the [bmim][BF₄]-NaOH mixture was recovered without loss of the ionic liquid. However, because of the loss of water in the course of extraction, compensation of water was necessary in order to retrieve the optimized volume ratio of [bmim][BF₄] to NaOH for the next electrochemical cycle. The correction of the volume ratio was achieved according to the calibration curve of the density of the [bmim][BF₄]-NaOH mixture *versus* the volume ratio of [bmim][BF₄] to NaOH. After measuring the density of the recovered [bmim][BF₄]-NaOH mixture, an appropriate volume of water was added to the mixture to give the optimized 8 : 2 v/v ratio. The mixture was then reused for the electrochemical generation of hydrogen peroxide, and used *in situ* again for the epoxidation. The results are summarized in Table 3. It can be seen that the [bmim][BF₄]-NaOH mixture can be recycled for at least four cycles with little diminution of the yield of hydrogen peroxide. The slight decline in the yield of epoxide in the 4th cycle was attributed to the formation of side products as the alkene substrate was completely converted.

In summary, we have shown that [bmim][BF₄]-water or NaOH mixtures can be used as promising electrolytes for the effective electrogeneration of hydrogen peroxide which is subsequently used for the epoxidation of alkenes. The whole process can be regarded as a totally clean system as only oxygen, water and electricity are required.

We thank the University Grants Committee Area of Excellence Scheme in Hong Kong (Project No AoE/P-10/01) and the Hong Kong Polytechnic University Area of Strategic Development Fund for financial support of this research.

Table 3 Recovery and reuse of [bmim][BF₄] for the epoxidation of 3,5-dimethylcyclohexen-1-one^a

Cycle	1	2	3	4
[H ₂ O ₂]/mM	78	79	79	80
Time/h ^b	2	1.5	1.5	1.5
Epoxide yield (%) ^c	86	84	83	80

^a A suitable amount of water was added to optimize the volume ratio of [bmim][BF₄] to NaOH in cycles 2 to 4. ^b Time for electrolysis under the same conditions as in Table 1. ^c Epoxidation was carried out under the same conditions as in Table 2. Yields were determined by GC-MS and the products identified by ¹H NMR spectroscopy.

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- 16 O. Bortolini, V. Conte, C. Chiappe, G. Fantin, M. Fogagnolo and S. Maietti, *Green Chem.*, 2002, **4**, 94.
- 17 It is presumed that the epoxides can be extracted by supercritical carbon dioxide in place of diethyl ether. See: O. Bortolini, V. Conte, C. Chiappe, G. Fantin, M. Fogagnolo and S. Maietti, *Eur. J. Org. Chem.*, 2003, 4804. In the event that CO₂ would react with the NaOH in the electrolyte, Na₂CO₃ instead of NaOH can be used for the electrosynthesis of hydrogen peroxide (see ESI†).