



Short communication

# A surfactant-like ionic liquid with permanganate dissolved as a highly selective epoxidation system

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## ABSTRACT

A ligand-free catalytic epoxidation system using permanganate in a surfactant-like ionic liquid (IL) medium was developed. The results indicate that the IL takes crucial effects in the epoxide selectivity. The loading of permanganate is also found critical in preventing over-oxidation of epoxides. The system with 0.3 mol% permanganate and 3.5-equivalent  $\text{CH}_3\text{CO}_3\text{H}$  is able to achieve excellent yields and selectivity of epoxides. The study of epoxidation with  $\text{KMnO}_4$  in IL medium reveals an unusual oxidation behavior of permanganate not found in traditional solvents.

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## 1. Introduction

Oxidation of alkenes to epoxides is an important industrial process [1–3]. Chemists are searching for new technology to use green reagents, solvents, and reaction media for epoxidation [4–6]. Potassium permanganate ( $\text{KMnO}_4$ ) is an inexpensive and widely used oxidant for organic oxidations [7]. The process is also recognized as environmental-friendly because manganese dioxide can be separated and recycled [8]. Nonetheless, some practical problems of over-oxidations, degradations, and formation of a multitude of products are observed occasionally.

In recent years, a number of new oxidation systems have been reported with  $\text{KMnO}_4$  in IL including oxime derivative oxidation [9], oxidative deprotection of aromatic hydrazones [10], oxidation of arenes [11] and alcohols [12,13]. Among these examples, ILs were addressed to play crucial roles. Recent studies also demonstrate that reactions in ILs show different thermodynamic and kinetic behaviors from conventional solvents [14]. Some systems are known to improve reaction performance to give better reaction rate, selectivity, and yields [15–18].

Epoxidation of alkenes with 1-methyl-3-butylimidazoliumdecylsulfate in [bmim][ $\text{BF}_4$ ] was reported [19], while permanganate in IL has not been investigated although many epoxidation reactions and inert alkane oxidations are investigated with Mn-catalysts [20–23]. In this study, we reported a new system with permanganate in a surfactant-like IL for transformation of terminal alkenes to epoxides.

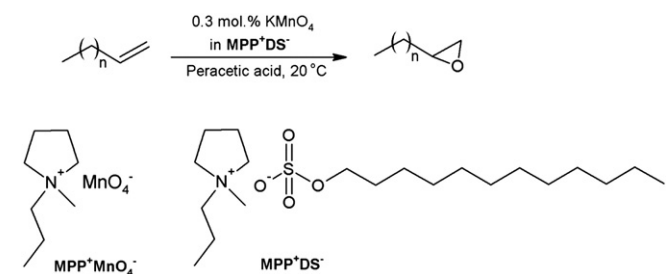
## 2. Results and discussion

$\text{MPP}^+\text{DS}^-$  is composed of 1-methyl-1-propylpyrrolidinium cation and a long-chained alkyl sulfate anion and is able to accommodate both inorganic salts and non-polar aliphatic alkenes as a homogenous phase for catalysis because dodecyl sulfate is an excellent phase transfer agent.  $\text{MPP}^+\text{DS}^-$  is thus prepared as a recyclable medium for catalysis.  $\text{MPP}^+$  is able to form an ionic chelation with  $\text{MnO}_4^-$  in-situ to enhance the miscibility of the reaction mixture (Scheme 1).

$\text{MPP}^+\text{DS}^-$  is not a room temperature IL (m.p. 64 °C). It is a hygroscopic salt absorbing moisture to form a viscous gel. Using small amounts of de-ionized water (0.4 mL/g) is able to prepare a viscous solution. A homogenous gel was obtained by mixing  $\text{MPP}^+\text{DS}^-$  with  $\text{KMnO}_4(\text{aq})$ . The gel was characterized with ESI-MS and UV-vis (Fig. 1) and it was found that  $\text{MnO}_4^-$  was trapped by  $\text{MPP}^+$  as the species of  $[\text{MPP}^+]_2\text{MnO}_4^-$  is identified with the corresponding mass ( $m/z$ ) = 374.86 Da. The species corresponding to  $[\text{MPP}^+]_2\text{DS}^-$  ( $m/z$  = 521.24 Da) is also observed. This indicates that the permanganate is “dissolved” in  $\text{MPP}^+\text{DS}^-$  through ionic exchange. In addition, a set of characteristic permanganate absorption peaks from 450 to 600 nm ( $\lambda_{\text{max}}$  = 457, 475, 488, 506, 526, 546, and 569 nm) is observed in the UV-visible spectrum.

$\text{KMnO}_4$  is a well-known oxidant for C–H bond oxidation but no report was found for alkenes epoxidation [20,21].  $\text{KMnO}_4$  in IL system was investigated in the epoxidation reaction with 1-octene and commercial  $\text{CH}_3\text{CO}_3\text{H}$ . Table 1 summarizes the experimental results. In general, reactions were found very effective and rapid to produce epoxides in excellent yields and selectivity. Control experiments, without using IL as the medium or in the absence of  $\text{KMnO}_4$ , showed poor reactivity with  $\text{CH}_3\text{CO}_3\text{H}$  as the oxidant (Table 1, entries 1–2). However, when adding

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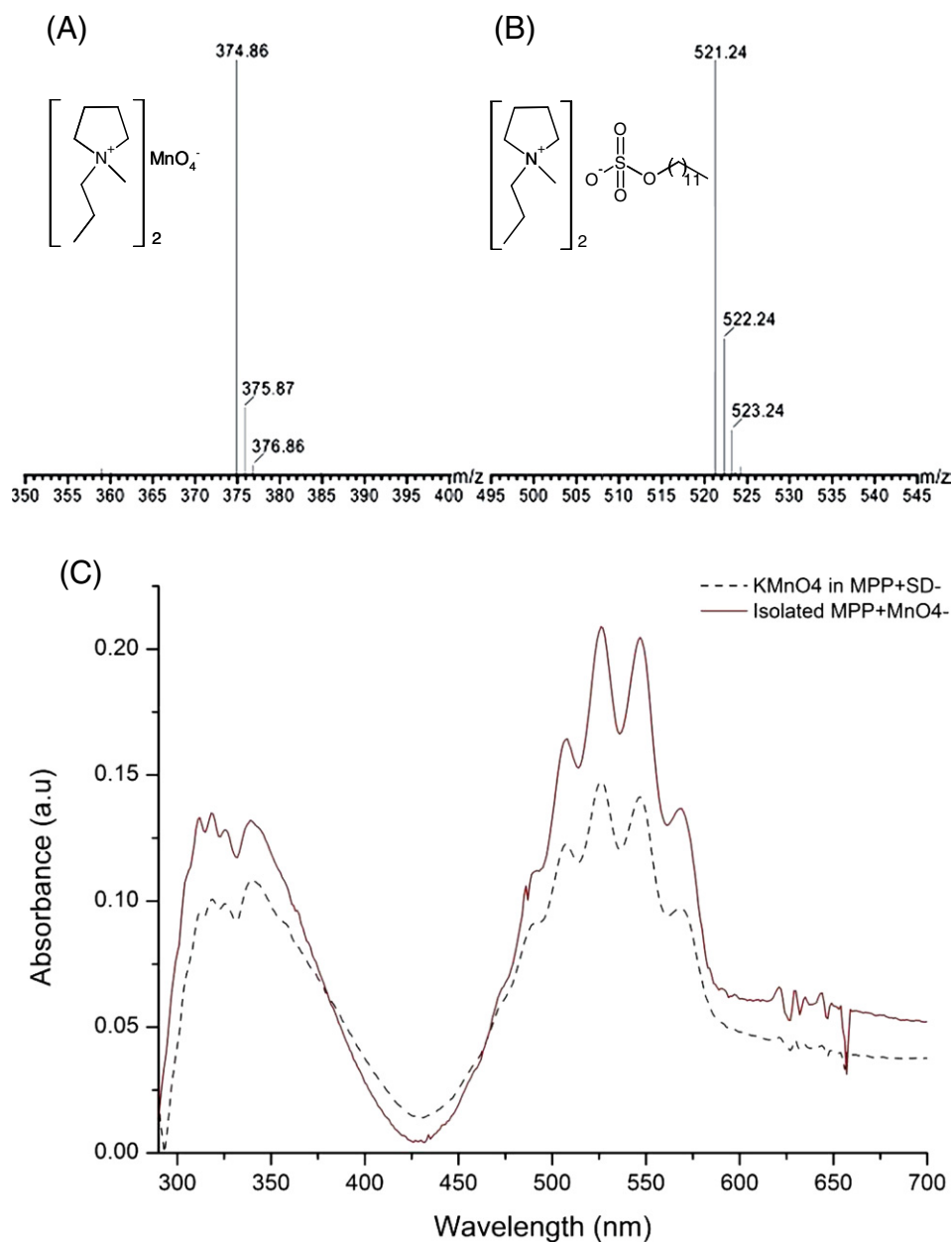


**Scheme 1.** Epoxidation of aliphatic terminal alkenes in  $\text{MPP}^+\text{DS}^-$  medium with  $\text{KMnO}_4$  or isolated catalyst  $\text{MPP}^+\text{MnO}_4^-$  using  $\text{CH}_3\text{CO}_3\text{H}$  as the oxidant.

0.15 mol%  $\text{KMnO}_4$  into  $\text{MPP}^+\text{DS}^-$  with  $\text{CH}_3\text{CO}_3\text{H}$ , the reaction was proceeded effectively. As shown in Table 1 (entry 3), 1-octene was oxidized to 1,2-epoxyoctane selectively without over-oxidation occurred;

however, the reaction was not completed. As increasing  $\text{KMnO}_4$  loading to 0.3 mol%, the epoxidation was efficiently to achieve 100% conversion within 30 min (Table 1, entry 4). Further increasing  $\text{KMnO}_4$  (0.6 mol%) did not give extra improvements in both reactivity and reaction time for complete conversion but slightly reducing the yield of epoxides (Table 1, entry 6). The reactions were able to achieve high yields of epoxide (>92%) under optimized conditions.

The comparison of using isolated  $\text{MPP}^+\text{MnO}_4^-$  and  $\text{KMnO}_4$  in  $\text{MPP}^+\text{DS}^-$  for epoxidation was studied. Under the same conditions, 99% conversion and 93% epoxide yield were obtained with  $\text{MPP}^+\text{MnO}_4^-$  as the catalyst. The result is very comparable with  $\text{KMnO}_4$  (Table 1, entry 5). The findings imply that no significant difference from using isolated  $\text{MPP}^+\text{MnO}_4^-$  or  $\text{KMnO}_4$  in IL medium because in both cases they are likely having the same active Mn-oxo species for epoxidation. It is noteworthy that the present epoxidation system does not give observable alkyl peroxides, which are found as the primary products and



**Fig. 1.** (A) ESI-MS analysis (positive mode) of IL medium, and (B) a MS spectrum of IL trapped with  $\text{MnO}_4^-$  as the counter-ion after the addition of  $\text{KMnO}_4$  to  $\text{MPP}^+\text{DS}^-$ ; (C) the UV-vis spectrum of the mixture of  $\text{KMnO}_4$  in  $\text{MPP}^+\text{DS}^-$  and the isolated  $\text{MPP}^+\text{MnO}_4^-$ .

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