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Manganese Acetate in Pyrrolidinium Ionic Liquid as a Robust and Efficient Catalytic System for Epoxidation of Aliphatic Terminal Alkenes

Kam-Piu Ho, Wing-Leung Wong, Lawrence Yoon Suk Lee, Kin-Ming Lam, Tak Hang Chan, and Kwok-Yin Wong^{*[a]}

In recent years, growing attention has been paid to the applications of room temperature ionic liquids (RTILs) as a new class of reaction media in diverse chemical processes. The characteristics and the most important applications of ionic liquids (ILs) have been comprehensively reviewed in the past decade.^[1] The unique properties of ILs, for instance, low melting point and negligible vapour pressure with essentially no volatile organic emission, make them a good candidate to comply with contemporary environmental standards and economical requirements.^[2]

Intense interests on the use of ILs in catalytic reactions stem from their potential benefits, particularly the ease of product separation and therefore high recyclability of the catalysts.^[1,3] Numerous possible combinations of cations and anions offer convenient ways to fine-tune the physicochemical properties of ILs, such as polarity, viscosity, and miscibility with other reagents. Most metal catalysts are soluble in ILs without the modification of ligands, and usually the noncoordinating anions of ILs leave the active sites of catalysts still available for the substrates. These distinctive properties are advantageous in improving biphasic catalytic systems, which often suffer from problems associated with the incompatibility amongst the reaction components.^[1a,4-6]

One of the most extensively studied catalytic reactions in which ILs are used as a reaction medium is the oxidation of organics, such as epoxidation of alkenes. Since the first report on manganese(III)-salen complex which successfully catalyzed the epoxidation of alkenes in IL,^[7] a series of imidazolium-based ILs have been tested.^[1a-c,3a-b,8] Although these newly developed IL-based catalytic systems seem to

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achieve excellent results comparable to those of the homogeneous catalysis in organic solvents,^[9] the successful examples are usually limited to internal alkenes. The epoxidation of terminal alkenes in IL, particularly of long-chained aliphatic alkenes, often face difficulties owing to poor miscibility among the reaction components, which leads to slow reaction rate and low conversion yield. Effective catalytic epoxidation of aliphatic terminal alkenes and unfunctionalized olefins in ILs still remains as a challenge.

Our group has been interested in the development of ILs as "green" media for metal-catalyzed oxygenations of organic molecules.^[10] The epoxidation of alkenes catalyzed by manganese (Mn) salts is particularly attractive, because they are inexpensive, relatively non-toxic, and very effective in catalyzing the epoxidations.^[11] We have previously demonstrated the catalytic oxidation of alkenes by Mn^{II}/ Me₄NHCO₃ in a RTIL (1-butyl-3-methylimidazolium tetrafluoroborate, $[bmim]BF_4$) with H_2O_2 as the terminal oxidant.^[10a,c] Unfortunately, the [bmim]BF₄-Mn^{II}/Me₄NHCO₃ system is inactive towards aliphatic terminal alkenes. In general, we experienced two major difficulties in using $[bmim]BF_4$ as the medium for oxidations: (i) the low miscibility of non-polar aliphatic terminal alkenes, such as 1octene, with the polar [bmim]BF4 medium; and (ii) the instability of [bmim]BF₄ under very oxidizing conditions. Despite the extended reaction time and excessive amount of oxidant used, only moderate conversions with poor epoxide selectivity were observed. Herein, we report a novel and robust IL system for the rapid epoxidation of a number of aliphatic terminal alkenes under relatively mild conditions using Mn^{II} acetate (Mn(OAc)₂) as an effective ligand-free catalyst precursor (Scheme 1). This homogeneous catalytic system is designed to be simple, recyclable, easy to separate the products, resistant to oxidative degradation, scalable, and efficient for the oxidation of unfunctionalized terminal alkenes.

The surfactant-like IL, $1 \cdot C_{12}H_{25}SO_4$ (Scheme 1, 1=1methyl-1-propylpyrrolidinium, $C_{12}H_{25}SO_4$ = dodecyl sulfate), was used as a reaction medium for the epoxidation of alkenes with Mn(OAc)₂ as the catalyst. From our previous

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[[]a] Dr. K.-P. Ho, Dr. W.-L. Wong, Dr. L. Y. S. Lee, K.-M. Lam, Prof. T. H. Chan, Prof. K.-Y. Wong Department of Applied Biology and Chemical Technology The Hong Kong Polytechnic University Hung Hom, Kowloon, Hong Kong SAR (China) Fax: (+852)2364 9932 E-mail: bckywong@polyu.edu.hk



Scheme 1. Catalytic epoxidation of aliphatic terminal alkenes in a simple ionic liquid-manganese(II) catalyst system.

study in ligand-free Mn-catalyzed epoxidation of alkenes in acetonitrile using peracetic acid as the oxidant, the active species is likely to be a high-valent polymetallic manganese(V) oxo species which is EPR silent.^[10e] In addition, the main key to successful conversion is the compatibility between reaction medium, inorganic metal catalyst, buffer solution, and the substrate. 1.C12H25SO4 was designed to accommodate the inorganic salts $(Mn(OAc)_2 \text{ and } NaHCO_3)$, water, and non-polar organic substrates in order to form a homogenous phase for catalysis. The dodecyl sulfate, a common phase transfer agent, was selected as a counterion to enhance the compatibility with aliphatic terminal alkenes. In this study, the pyrrolidinium cation was chosen rather than imidazolium or pyridinium because of its stability against oxidative degradation. Structurally, the C-C and C-N bonds in pyrrolidinium are less susceptible to oxidation than the unsaturated C=C and C=N bonds in the other cations. The stability of different ILs against the oxidative degradation was compared by reacting them with peracetic acid for 30 min at 20 °C (Figure 1). The amount of peracetic acid



Figure 1. A comparison of the stability of different ionic liquids in peracetic acid (CH₃CO₃H, 32 wt.% in dilute acetic acid) at 20°C for 30 min.

consumed in the reaction indicates the degree of IL degradation, thus the stability of IL. The pyridinium and imidazolium-based ILs used up significant amounts of peracetic acid (8–26%) and exhibited obvious color changes. In the case of $1 \cdot C_{12}H_{25}SO_4$, only 2% of peracetic acid was used up without any change in color. These results confirmed that $1 \cdot C_{12}H_{25}SO_4$ is more robust and suitable as a medium for our study.

Once the IL medium was optimized for the stability and compatibility with reaction reagents, the catalytic ability of the $1 \cdot C_{12}H_{25}SO_4$ -Mn(OAc)₂ system for the oxidation of ali-

phatic terminal alkenes was investigated using 1-octene as the model substrate and peracetic acids (32 wt.% in dilute acetic acid) as the oxidant at 20 °C (Table 1). Control experi-

Table 1. The epoxidation of 1-octene catalyzed by $Mn(OAc)_2$ in $1\text{-}C_{12}H_{25}SO_4.^{[a]}$

Entry	$Mn(OAc)_2$ [mol %]	1-Octene [mmol]	Conv. [%]	Yield ^[b] [%]	Selectivity [%]	TOF $[h^{-1}]$
1 ^[c]	0.5	2.5	0	0	-	_
2	0.2	2.5	65	63	97	650
3	0.4	2.5	90	87	97	450
4	0.5	2.5	100	94	94	400
5	0.6	2.5	100	93	93	333
6 ^[d]	0.5	2.5	23	23	100	92
7 ^[e]	0.5	2.5	67	67	100	268
8 ^[f]	0.5	20	100	82 ^[g]	82	240

[a] Reaction conditions: $1-C_{12}H_{25}SO_4$ (1.0 g), NaHCO₃ (150 mg), H₂O (0.38 mL), CH₃CO₃H (3.4 equiv), at 20 °C, 30 min. [b] Yield estimated by GC with tetradecane as an internal standard. [c] Control experiment using water instead of $1-C_{12}H_{25}SO_4$. [d] Using 1.4 equiv of CH₃CO₃H. [e] Using 2.4 equiv of CH₃CO₃H. [f] Reaction time: 50 min. [g] Yield of isolated product.

ments performed in water instead of $1-C_{12}H_{25}SO_4$ or in the absence of Mn(OAc)₂ showed poor reactivity. When 0.2 mol% of Mn(OAc)₂ was used in $1-C_{12}H_{25}SO_4$, only 65% of 1-octene was converted. However the reaction proceeded smoothly with a good selectivity (97%) of 1,2-epoxyoctane (Table 1, entry 2). As the catalyst loading was increased to 0.5 mol%, the epoxidation was greatly improved to achieve complete conversion and excellent yield within 30 min (94%, Table 1, entry 4). It was found that 0.5 mol% of Mn-(OAc)₂ is optimal and further increase in catalyst loading (0.6 mol%) has no effect on either the reaction time or the epoxide selectivity. Under these optimized conditions, high conversions (>99%) and excellent yields of epoxide (>93%) were achieved.

In order to explore the potential of this system for the large scale synthesis of aliphatic terminal epoxides, 20 mmol of 1-octene was used under the same conditions (Table 1, entry 8).^[12] The reaction was completed in 50 min and the product of 1,2-epoxyoctane was isolated in good yield (82%). The crude product collected by simple extraction and decantation from the IL medium showed excellent purity in GC-MS, ¹H and ¹³C NMR characterizations, even without further purification by flash column chromatography.

The catalytic epoxidation of other terminal alkenes were also surveyed under similar conditions. In most cases, complete conversion with high selectivity was achieved (Table 2). Aliphatic terminal alkenes such as 1-heptene, 1nonene, and 1-decene were oxidized smoothly to give over 80% yields of isolated products (Table 2, entries 1–3). However, as the chain length of the substrate increases to C₁₁, that is, 1-undecene, the catalytic reactivity declined considerably because of its poor miscibility with the reaction medium. The conversion was not completed (74%) even after the prolonged reaction time of 50 min, and 69% yields of 1,2-epoxyundecane oxide was isolated.^[13] For 1-dodecene

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Table 2. Epoxidation of various terminal alkenes in the $1{\cdot}C_{12}H_{25}SO_{4}{-}Mn{\cdot}(OAc)_2$ catalytic system. $^{[a]}$

Entry	Alkenes	Conversion [%]	Yield of isolated product [%]
1	M_4	100	81
2	M_6	100	87
3	M7	100	87
4	M8	74	69
5	\bigcirc	100	89
6		100	87 ^[b]
7	M_5	100	82 ^[b]
8	M_6	100	88 ^[b]
9		100	0 ^[c]

[a] Reaction conditions: $1-C_{12}H_{25}SO_4$ (1.0 g), NaHCO₃ (150 mg), H₂O (0.38 mL), alkene (2.5 mmol), Mn(OAc)₂ (0.5 mol%), peracetic acid (3.4 equiv), at 20°C for 30 min. [b] Only di-epoxides were produced and yields were estimated by GC with tetradecane as an internal standard. The di-epoxides were identified with the known compounds by GC-MS. [c] No styrene oxide was obtained; styrene was over-oxidized to benzoic acid.

cellent conversion (100%) and yield (94%) obtained in $1 \cdot C_{12}H_{25}SO_4$ (Table 3, entry 4) can be attributed to the stability of pyrrolidinium cation under strongly oxidizing reaction conditions. As noted previously, oxidant was wasted in the degradation of pyridinium or imidazolium-based ILs.

The stability and reusability of the 1-C₁₂H₂₅SO₄ medium was tested by successively repeating the epoxidation of 1octene. Upon the completion of each reaction, the product was extracted with pentane and the remaining 1.C12H25SO4 medium was reused upon addition of fresh peracetic acid. For the first three cycles, comparable yields of isolated product were obtained. However, during the recycling process, insoluble sodium acetate (from peracetic acid) and manganese oxide were formed and accumulated in the IL medium. It seems that these insoluble substances affect the catalytic activity of the system significantly as they accumulated up to a certain concentration (Figure 2). For example, at the 4th cycle the conversion dropped to 45% because of salting out effect caused by high concentration of acetate leading to poor solubility of $Mn(OAc)_2$ in the IL. The precipitates were then filtered off and the IL was reused with fresh Mn- $(OAc)_2$ catalyst (0.5 mol %) added to the medium, and com-

(C₁₂), the conversion dropped to 38% under the same conditions. In general, the reactivity was found to decrease as the alkyl chain of the terminal alkene gets longer (>C₁₀).

The $1 \cdot C_{12}H_{25}SO_4$ -Mn(OAc)₂ system can epoxidize sterically bulky terminal alkenes. Vinyl-cyclohexane (Table 2, entry 5), was epoxidized smoothly to afford a good isolated yield of 89%, which is comparable to those of straight-chained alkenes. Moreover, di-enes such

Table 3. A comparison of different ionic liquids used as the reaction medium for the catalytic epoxidation of 1-octene.^[a]

Entry	Ionic Liquids	Conversion [%]	Yield of epoxide ^[b] [%]			
1	⁺ N-C ₁₂ H ₂₅ SO ₄ -	65	63			
2	~_N+N ∕ C ₁₂ H ₂₅ SO₄`	74	69			
3	_N_+N_C ₁₂ H ₂₅ SO₄ ⁻	84	77			
4	N ⁺ C ₁₂ H ₂₅ SO ₄ ⁻	100	94			



as 4-vinyl-1-cyclohexene, 1,8-nonadiene, and 1,9-decadiene were successfully converted into the corresponding di-epoxides in good yields (yields of isolated products > 82%) under similar conditions (Table 2, entries 6–8). Competition experiments were carried out using 4-vinyl-1-cyclohexene as the model substrate. It was found that epoxidation occurs through a stepwise-reaction. The internal cyclic C=C bond was oxidized first and then followed by the terminal C=C bond. The reaction eventually gave the di-epoxide as a sole product.^[14]

The effect of using different IL media in the catalytic epoxidation of 1-octene was also investigated by comparing the conversion rate and epoxide yield. For all the ILs studied, $C_{12}H_{25}SO_4^-$ was used as a common counterion and only the cationic component was varied. Table 3 shows that when the reaction was carried out in pyridinium or imidazolium-based ILs, the conversions were incomplete. The epoxide yields in those ILs were less than 77%. Presumably, the ex-



Figure 2. Reuse of $1-C_{12}H_{25}SO_4$ medium with Mn(OAc)₂ as catalyst for epoxidation of 1-octene. (At cycle 5 and 8, precipitates of manganese oxide and sodium acetate were filtered off; and fresh Mn(OAc)₂ catalyst (0.5 mol%) was added to the ionic liquid medium for further experiments).

plete conversion with good yields of isolated product were achieved in subsequent catalytic cycles (from 5th to 7th cycle, 100% conversion, ~80% yield of isolated product). The catalytic system shows stable performance as the excess sodium acetate and manganese oxide were removed regularly and fresh $Mn(OAc)_2$ was added as the catalyst (Figure 2, 8th and 9th cycles). Under such circumstances, the ionic liquid (1-C₁₂H₂₅SO₄) medium can be reused constantly.

In conclusion, a novel and simple $1 \cdot C_{12}H_{25}SO_4$ -Mn(OAc)₂ catalytic system has been successfully developed for the rapid and selective oxidation of aliphatic terminal alkenes to epoxides. It has been demonstrated that the $1 \cdot C_{12}H_{25}SO_4$ -Mn(OAc)₂ system is an efficient, recyclable, and scalable protocol for green and large scale synthesis of epoxides from various terminal alkenes. More importantly, the simple ligand-free catalytic system is used with other non-toxic and inexpensive reagents under mild reaction conditions, which makes this system more practical and applicable to the industry.

Experimental Section

Experimental details on the synthesis and characterizations of $1\text{-}C_{12}H_{25}SO_4$ and recycling studies are available in Supporting Information.

Typical procedures for the catalytic epoxidation of terminal alkenes in $1-C_{12}H_{25}SO_4-Mn(OAc)_2$: $1-C_{12}H_{25}SO_4$ (1.0 g), H_2O (0.38 mL), $Mn(OAc)_2$ (100 µL ,0.075 M in H_2O), NaHCO₃ (150 mg), and 1-octene (2.5 mmol) were added to a 10 mL round-bottomed flask fitted with a water-cooling jacket. The flask was then sealed with a rubber septum. Peracetic acid (3.4 equiv, 1.8 mL, 32 wt.% in dilute acetic acid) was added in a dropwise manner over 1 min. The mixture was stirred vigorously for 30 min at 20 °C. Crude products were extracted with pentane (4×6 mL), washed with 1 M NaHCO₃ solution, and then dried over sodium sulfate. After the removal of solvents, 1,2-epoxyoctane oxide was isolated as a colourless liquid. The epoxide was characterized by GC-MS, ¹H NMR, and ¹³C NMR.

Recycling procedures of the $1-C_{12}H_{2s}SO_4$ medium with $Mn(OAc)_2$ as catalyst for the epoxidation of 1-octene: After each experiment, the residual pentane in $1-C_{12}H_{2s}SO_4$ was removed by a rotary evaporator. The recovered brownish ionic liquid was then reused for the next run. After every three cycles of reaction, the ionic liquid medium was diluted with dichloromethane (5 mL) and the insoluble manganese oxides and sodium acetates were filtered off. The ionic liquid was reused for catalysis after the removal of organic solvent under vacuum and with the addition of new $Mn(OAc)_2$ catalyst (0.5 mol%, 0.04 m in water).

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- [12] Caution: Large scale reaction is highly exothermic and the peracetic acid should be added slowly. The reaction should be proceeded with care.
- [13] The modified reaction conditions for 1-undecene, such as increased Mn(OAc)₂ or peracetic acid loading and longer reaction time, resulted in poor epoxide selectivity owing to the over-oxidation.
- [14] For detailed experimental results of the competition study, see the Supporting Information.

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