

A Simple and Effective Catalytic System for Epoxidation of Aliphatic Terminal Alkenes with Manganese(II) as the Catalyst

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Abstract: A simple catalytic system that uses commercially available manganese(II) perchlorate as the catalyst and peracetic acid as the oxidant is found to be very effective in the epoxidation of aliphatic terminal alkenes with high product selectivity at ambient temperature. Many terminal alkenes are epoxidised efficiently on a gram scale in less than an hour to give excellent yields of isolated product (> 90 %)

of epoxides in high purity. Kinetic studies with some C₉-alkenes show that the catalytic system is more efficient in epoxidising terminal alkenes than internal alkenes, which is contrary to most commonly known epoxidation systems. The

Keywords: alkenes • epoxidation • homogeneous catalysis • manganese • oxidation

reaction rate for epoxidation decreases in the order: 1-nonene > *cis*-3-nonene > *trans*-3-nonene. ESI-MS and EPR spectroscopic studies suggest that the active form of the catalyst is a high-valent oligonuclear manganese species, which probably functions as the oxygen atom-transfer agent in the epoxidation reaction.

Introduction

Epoxidation of alkenes is an industrially important reaction because epoxides are valuable chemicals widely used as intermediates in organic syntheses and as raw materials in the manufacture of commodity products such as epoxy resins, paints and surfactants.^[1,2] Thus, there is a continuous motivation to develop new catalytic systems for the production of epoxides with high yield and selectivity in a cost-effective manner.^[3] Transition-metal-catalysed epoxidation is one of the most effective approaches for this transformation.^[4] Among the various transition-metal catalysts for epoxidation, manganese stands out as the most efficient, economical and environmentally benign. Various manganese complexes ligated with salens,^[5] porphyrins^[6] and aromatic N-donor ligands^[7] are known to be efficient catalysts for the epoxidation of a wide range of alkenes. The ligands can often provide selectivity in the epoxidation process (e.g. the chiral

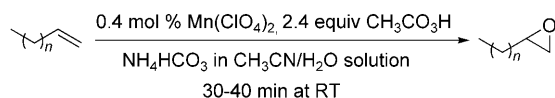
salen ligand in Jacobsen's catalyst for asymmetric epoxidation of alkenes). However, cost effectiveness and robustness are the major obstacles associated with the application of these metal complexes in industrial processes. Although manganese(II) sulfate in combination with bicarbonate and hydrogen peroxide is known to be an effective catalytic system for epoxidation of certain alkenes,^[4c,8] this system can only be applied to electron-rich and substituted alkenes, and is inactive towards electron-deficient and aliphatic terminal alkenes. There remains a need to develop an effective method based on inexpensive and non-toxic catalysts for the epoxidation of aliphatic terminal alkenes under mild conditions. Herein, we report a simple and highly efficient catalytic system, which uses commercially available manganese(II) perchlorate (Mn(ClO₄)₂) as the catalyst and peracetic acid (CH₃CO₃H) as the oxidant for the epoxidation of aliphatic terminal alkenes with high selectivity at ambient temperature (Scheme 1).

Results and Discussion

Screening of oxidants and metal salts: The reactivity and selectivity of catalytic epoxidation reactions usually show a strong dependence on the reaction conditions and are particularly sensitive to the nature of the metal catalysts and oxidants. In the trial experiments for screening possible re-

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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.200800759>.



Scheme 1. Catalytic epoxidation of terminal alkenes.

agents, a number of inexpensive oxidants and transition-metal salts were studied systematically with 1-decene as the substrate. Amongst the five commercial oxidants, only peracetic acid shows excellent reactivity (> 99% conversion) and epoxide yield (93%) with $\text{Mn}(\text{ClO}_4)_2$ as the catalyst in acetonitrile/water (Figure 1). No epoxidation was observed with other oxidants such as hydrogen peroxide, *tert*-butyl hydroperoxide and cumene hydroperoxide. In general, good yields of epoxides and high selectivity were obtained by using 2.4 equivalents of peracetic acid with respect to alkene substrates (Figure 1, insert).

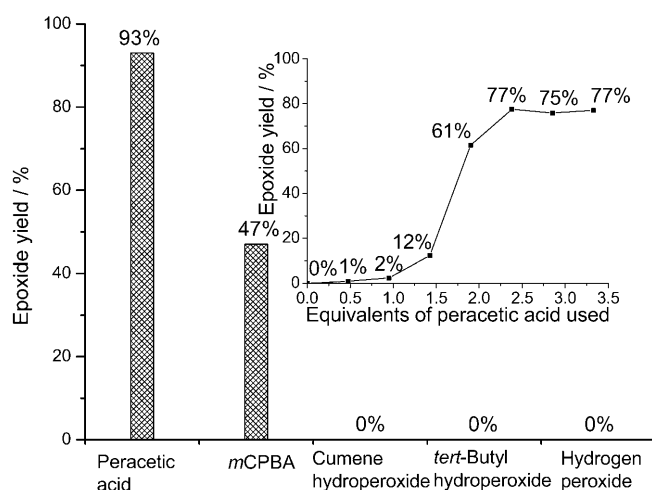


Figure 1. Effects of oxidants on the epoxidation of 1-decene with 0.4 mol % of $\text{Mn}(\text{ClO}_4)_2$ salt in acetonitrile/water at room temperature; epoxide yields determined by GC after 30 min. The insert shows the epoxide yields as a function of peracetic acid loading with 1-decene as the substrate; epoxide yields were determined by GC after reaction of 15 min.

Control experiments indicate that the presence of the Mn^{II} catalyst is crucial in the epoxidation because there is no background reaction observed. To compare the catalytic abilities of other metal salts in the epoxidation of the terminal alkenes, some metal salts were screened under similar reaction conditions (Figure 2). Along the first row of transition-metal salts (i.e. Sc^{III} , Ti^{IV} , V^{IV} , Cr^{III} , Mn^{II} , Mn^{III} , Fe^{III} , Co^{II} , Ni^{II} , Cu^{II} and Zn^{II}), all metal salts except those of Mn were inactive towards 1-decene as they all gave epoxide yields of less than 10%. The Mn^{II} salt, which gave excellent selectivity and a 93% yield of the epoxide in 30 min at room temperature, was unique in that it catalysed this reaction effectively. In addition, a similar epoxidation reactivity with a comparable yield (91%) was observed by using a manganese(III) salt. These results indicate that manganese

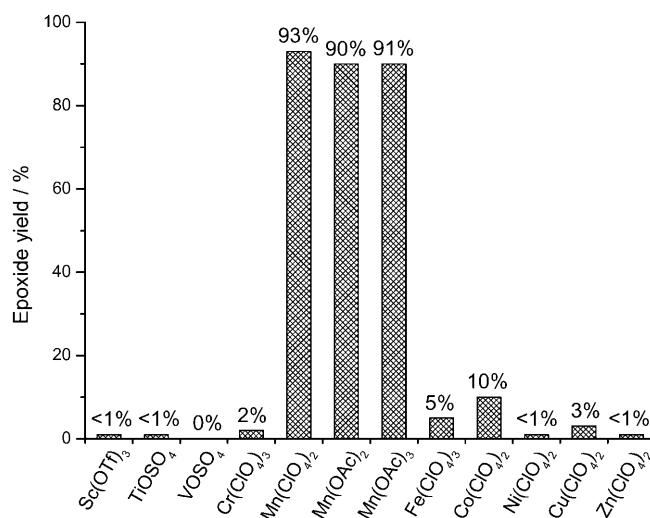


Figure 2. Effects of transition metals on the epoxidation of 1-decene with 2.4 equivalents of $\text{CH}_3\text{CO}_3\text{H}$ as the oxidant in acetonitrile/water at room temperature. Epoxide yields were determined by GC after 30 min.

salts are the only candidates suitable for the epoxidation of aliphatic terminal alkenes under such simple oxidation conditions with peracetic acid as the oxidant. After optimisation, only 0.4 mol % of $\text{Mn}(\text{ClO}_4)_2$ with respect to alkene substrates was found to be sufficient to obtain good epoxide yields (see Figure S1 in Supporting Information).

Optimisation of epoxidation conditions with $\text{Mn}(\text{ClO}_4)_2$ as the catalyst:

The excellent reactivity and selectivity results of the Mn-catalysed epoxidation in the preliminary studies prompted us to investigate the system in detail by focusing on the effects of buffer additives, solvent and water content in the reaction mixture. With respect to the reported studies,^[8a,b] the manganese/bicarbonate catalytic system is strongly influenced by pH and buffer additives because the epoxidation reaction involves the formation of pH-sensitive peroxymonocarbonate as the key intermediate. In our system, the additives are interestingly found not to participate in the catalytic process; they intrinsically only act as pH buffers to maintain slightly alkaline conditions in the reaction media. As shown in Figure 3, several commercial buffer additives were examined in the epoxidation of 1-decene. Acidic and neutral buffer additives such as acetic acid, dihydrogen phosphate and hexametaphosphate all gave almost no epoxide in comparison with the background level of epoxidation. On the other hand, dramatically enhanced catalytic activities in the epoxide production (85–93% epoxide yields) were observed when alkaline buffers such as acetates, tartrates, formates, carbonates, bicarbonates and hydroxides were used in the epoxidation reaction. Among them, the best additive was ammonium bicarbonate, which gave the highest yield of 1,2-epoxydecane (93%). This is probably related to its better solubility in the acetonitrile/water.

The optimal amounts of basic ammonium bicarbonate salt used for the Mn-catalysed epoxidation were determined by

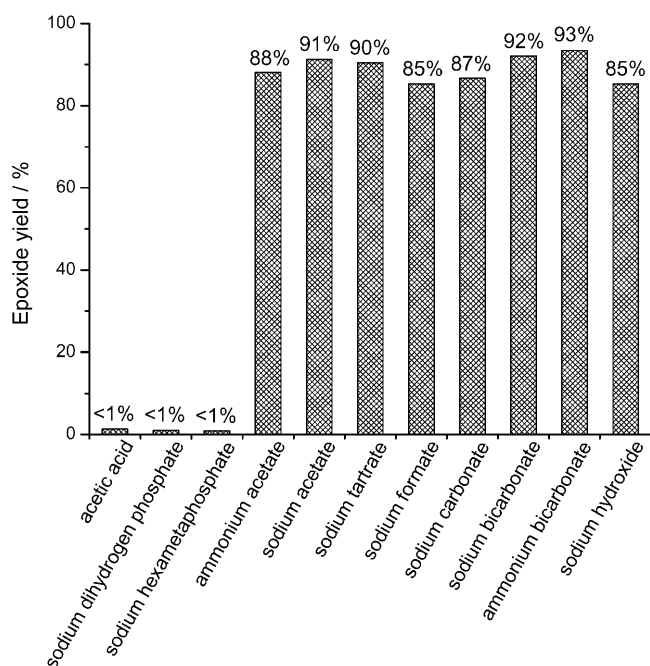


Figure 3. Effects of buffer additives on the Mn-catalysed epoxidation of 1-decene. Epoxide yields were determined by GC after 30 min.

kinetic studies (see Figure S2 in Supporting Information). Experimentally, small amounts of the bicarbonate buffer (0.13 equivalents with respect to peracetic acid) were enough to attain maximum epoxide production with high selectivity. The addition of excess buffer showed no detrimental effect on the catalytic reaction as the epoxide yields were still maintained. By calculation, the minimum amount of the bicarbonate salt that must be added to the reaction aliquot is just sufficient to neutralise the H_2SO_4 (≈ 4.2 mol %), which acts as the stabiliser in the commercial peracetic acid stock solution.

Analytically, the H_2SO_4 content was simply extrapolated from the titration of the peracetic acid with 0.5 M ammonium bicarbonate standard solution (see Figure S3 in Supporting Information). Upon titration, three inflection points are remarkably observed at pH 2.6, 6.2 and 10.6 which correspond to the titration endpoints of H_2SO_4 , $\text{CH}_3\text{CO}_2\text{H}$ and $\text{CH}_3\text{CO}_3\text{H}$, respectively. As predicted from the titration curve, when all the H_2SO_4 content in the peracetic acid was neutralised, the pH of the Mn-catalysed epoxidation system shifted to less acidic. Through destabilising the peracetic acid, it is believed that the peroxy oxygen atom could be actively transferred to the Mn^{II} catalyst to form high-valent Mn-oxo species for catalysis.^[9]

The solvent resistance to oxidation, the ability of the solvent to form a complex with the Mn^{II} catalyst and the versatility of in situ generated Mn^{II} -solvent complexes all control the effectiveness of the catalytic reaction. Hence, the nature of the solvent is another critical factor in this Mn-catalysed epoxidation system. As shown in Figure 4, a number of common solvents were screened as possible epoxidation media. Among them, acetonitrile gave the best reactivity

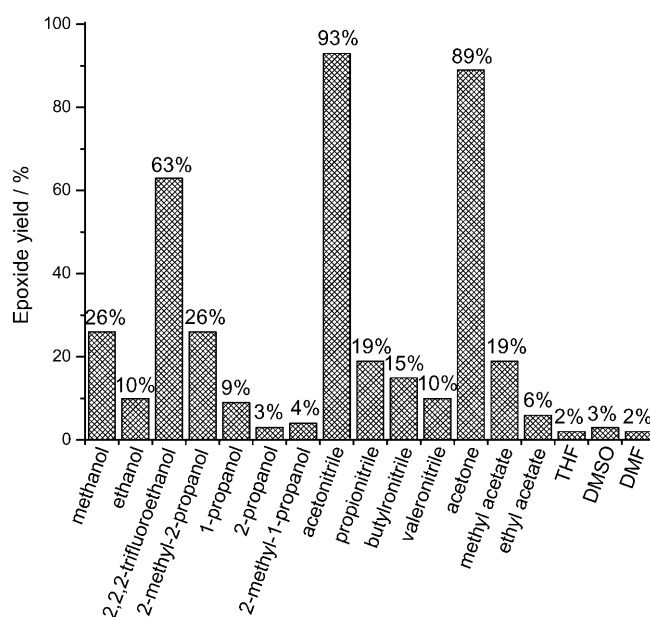


Figure 4. Effects of solvents on the Mn-catalysed epoxidation of 1-decene. Epoxide yields were determined by GC after reaction of 30 min.

with an epoxide yield of 93%. Other solvents, regardless of their protic or aprotic characters, afforded poor yields of 1,2-epoxydecane because they are susceptible to oxidation under such conditions. For example, stable 2,2,2-trifluoroethanol gave a 63% yield of epoxide which was comparatively much higher than the other non-fluorinated alcohols. On the other hand, strong chelating solvents (e.g. DMF and DMSO (DMSO = dimethyl sulfoxide)) also retarded the catalytic activity as their Mn^{II} -solvent complexes are intrinsically inactive in the catalysis.

Besides, the compatibility between solvents, substrates, the Mn catalyst and the bicarbonate buffer seems to determine the success of the epoxidation reaction. A comparison of acetonitrile with its analogues (i.e. propionitrile, butyronitrile and valeronitrile) indicates that acetonitrile was the best choice as the reaction medium and the yields of 1,2-epoxydecane dropped remarkably (from 93% to 19%) with the chain length of alkyl nitrile under similar reaction conditions (Figure 4). This can be attributed to the reduced solubilities of the Mn catalyst and the bicarbonate buffer with increasing hydrophobicity of the solvent. It is also consistent with the experimental results, which show that the catalytic activity was promoted significantly by addition of water (10% (v/v)) to the acetonitrile mixture as the epoxide yields were found to increase from 3% to 77% in the first 15 min of the reaction (see Figure S4 in Supporting Information).

Epoxidation of different aliphatic terminal alkenes with the $\text{Mn}(\text{ClO}_4)_2/\text{CH}_3\text{CO}_3\text{H}/\text{NH}_4\text{HCO}_3$ catalytic system in acetonitrile/water: The fruitful results of this simple Mn-catalysed epoxidation system with 1-decene prompted us to investigate its ability with other alkenes.^[10] In Table 1, most terminal aliphatic alkenes were epoxidised efficiently

Table 1. Epoxidation of terminal aliphatic alkenes with the Mn catalyst and peracetic acid in acetonitrile/water at room temperature.^[a]

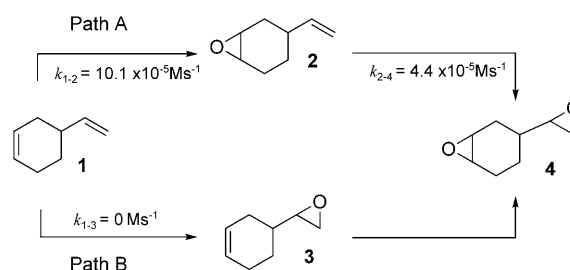
Entry	Substrate	Conversion, [%]	GC Yield ^[b] , [%]	Yield [%]
1	1-octene	>99	86	83
2	1-nonene	>99	91	87
3	1-decene	>99	93	90
4	1-undecene	>99	94	87
5	1-dodecene	>99	92	91
6	1-tridecene	>99	93	90
7	1-tetradecene	90	85	–
8	1-pentadecene	75	63	–
9 ^[c]	1,7-octadiene	>99	78	62
10 ^[c]	1,8-nonadiene	>99	91	88
11 ^[c]	1,9-decadiene	>99	92	90
12	vinylcyclohexane	>99	91	85
13	allylcyclohexane	>99	94	88
14 ^[d]	1H,1H,2H-perfluoro-1-octene	43	36	–
15 ^[d]	1,1,2-trifluoro-1-octene	0	0	–

[a] Reaction conditions: alkenes (7 mmol), Mn(ClO₄)₂ salt (0.4 mol %), NH₄HCO_{3(aq)} (0.5 M, 4.2 mL), CH₃CO₃H (2.4 equiv, 3.4 mL), acetonitrile (34 mL), 40 min reaction time. [b] GC yields were determined by GC with tetradecane as the internal standard. [c] Small-scale reaction: alkene (0.5 mmol), Mn(ClO₄)₂ salt (0.64 mol %), CH₃CO₃H (4.8 equiv), NH₄HCO_{3(aq)} (0.5 M, 0.6 mL), acetonitrile (4.8 mL); diepoxides were formed as the products. [d] Small-scale reaction: alkene (0.5 mmol), Mn(ClO₄)₂ salt (0.4 mol %), CH₃CO₃H (2.4 equiv), NH₄HCO_{3(aq)} (0.5 M, 0.3 mL), acetonitrile (2.4 mL).

(>99% conversion) with the Mn^{II} catalyst on a gram scale within 40 min. No reaction was observed even if 10 equivalents of peracetic acid were used under the Mn^{II}-free conditions. The Mn-catalysed system generally demonstrates excellent epoxide selectivity between alkenes with different alkyl chain lengths. For the C₈–C₁₃ terminal alkenes (Table 1, entries 1–6), both GC yields and yields of isolated epoxide were found on average to be above 90%. As the chain length got longer (Table 1, entries 7, 8), the conversion and epoxide yields obviously declined. This is attributed to poor solubility of the alkenes with longer alkyl chains in the acetonitrile/water medium.

The terminal dienes, illustrated in entries 9–11 (Table 1), can also be transformed into the corresponding diepoxides effectively in the same manner. In particular, the conversions of all the dienes were found to be over 99%. Good yields of epoxides were obtained for both 1,9-decadiene (90% yield) and 1,8-nonadiene (88% yield); however, the epoxidation reaction only gave a fair yield of 1,2,7,8-diepoxyoctane (62% yield). Meanwhile, the attachment of bulky functional groups to the terminal C=C double bond, such as vinyl cyclohexane and allyl cyclohexane (Table 1, entries 12 and 13), has no influence on the effectiveness of this Mn^{II} catalyst. Both the substrates can achieve high conversions (>99%) with excellent epoxide selectivities (>90%). Attempts were made to epoxidise the electron-deficient fluorinated terminal alkenes (entries 14 and 15). However, only 1H,1H,2H-perfluoro-1-octene showed very limited reactivity in the catalytic process with a 36% yield of epoxide by GC.

Kinetic and mechanistic studies of the Mn(ClO₄)₂/CH₃CO₃H/NH₄HCO₃ catalytic system in epoxidation of terminal alkenes: To have a better understanding of the reactivity and regioselectivity of the Mn-catalysed system towards terminal and internal alkenes, a number of kinetic experiments were carried out with 4-vinyl-1-cyclohexene as the model substrate. 4-Vinyl-1-cyclohexene was used because it is a non-conjugated alkadiene that bears one terminal and one internal C=C double bond in the chemical structure. As shown in Scheme 2, there are two possible



Scheme 2. The regioselectivity of the Mn-catalysed epoxidation of 4-vinyl-1-cyclohexene.

stepwise-reaction pathways (Paths A and B) for the epoxidation of 4-vinyl-1-cyclohexene (1). These include the formation of diepoxides 4-epoxyethyl-1-cyclohexene 1,2-epoxide (4) via intermediate 4-vinyl-1-cyclohexene 1,2-epoxide (2) and via intermediate 4-epoxyethyl-1-cyclohexene (3). With respect to the kinetic diagram (Figure 5), the initial rate of the monoepoxide 2 formation ($k_{1,2} = 10.1 \times 10^{-5} \text{ Ms}^{-1}$) is much faster than that of the monoepoxide 3 ($k_{1,3} = 0 \text{ Ms}^{-1}$) in the Mn-catalysed reaction. Over 60% of the monoepoxide 2 was produced but no monoepoxide 3 was observed in

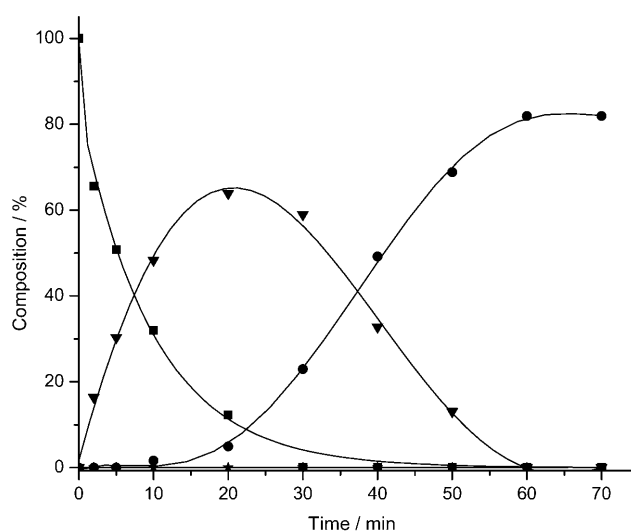


Figure 5. Kinetic study of 4-vinyl-1-cyclohexene epoxidation with the Mn catalyst in acetonitrile/water at 25°C. 4-Vinyl-1-cyclohexene (1: ■); 4-vinyl-1-cyclohexene 1,2-epoxide (2: ▼); 4-epoxyethyl-1-cyclohexene (3: ★); 4-epoxyethyl-1-cyclohexene 1,2-epoxide (4: ●).

the first 20 min. These results indicate that the Mn catalyst preferentially epoxidises the electron-rich internal C=C double bond even if it faces more steric hindrance in the catalytic process. When the diene **1** content in the reaction mixture dropped to 15% after 20 min, subsequent epoxidation of the monoepoxide **2** got faster ($k_{2-4}=4.4\times 10^{-5}\text{ ms}^{-1}$) and eventually it was converted to diepoxide **4** as the final product. A control experiment without the Mn^{II} catalyst only showed the background epoxidation to form the monoepoxide **2** at a very slow reaction rate ($k_{\text{control}}=1.3\times 10^{-5}\text{ ms}^{-1}$) (see Figure S5 in the Supporting Information).

A comparison of the initial rates of formation of the monoepoxide **2** ($k_{1-2}=10.1\times 10^{-5}\text{ ms}^{-1}$) and monoepoxide **3** ($k_{1-3}=0\text{ ms}^{-1}$) proved that the Mn-catalysed epoxidation reaction highly preferred to go through Path A rather than Path B to produce diepoxide **4**. This is easily understood by the involvement of active high-valent Mn-oxo species, which are typically electrophilic and attack effectively the electron-rich internal C=C double bond in the catalytic process. However, when the same studies were carried out independently with different analogues of 4-vinyl-1-cyclohexene (i.e. cyclohexene and vinylcyclohexane), the reactivity was an amusing contrast. As listed in Table 2, the rate of formation of 1,2-epoxycyclohexane (entry 2) was found to be $9.8\times 10^{-5}\text{ ms}^{-1}$ which is comparable to that of monoepoxide **2** (entry 1). Interestingly, the initial rate to produce the terminal epoxide ($k=20.8\times 10^{-5}\text{ ms}^{-1}$) from vinylcyclohexane (entry 3) is two times faster than the reaction to form 1,2-epoxycyclohexane (entry 2). By considering these kinetic results (Table 2, entries 1–3), the active Mn-oxo species generated in situ in the reaction mixture show better catalytic activity in the epoxidation of terminal C=C double bonds; nevertheless, they attack the sterically hindered dialkyl-substituted position in the diene **1** readily in the intramolecular

competition reaction. The reactivity and regioselectivity are unambiguously different from the general findings with internal electron-rich alkenes, which gives exclusive privileges in catalytic epoxidation processes.^[11]

A similar observation was also found in the epoxidation of aliphatic 1-nonene and its geometric isomers by using the Mn^{II} catalyst. As shown in entries 4–6 (Table 2), the initial rate of terminal 1,2-epoxynonane formation was found to be $15.8\times 10^{-5}\text{ ms}^{-1}$ without any background epoxidation (entry 4). The catalytic rate is considerably faster than the oxidation of *cis*-3-nonene (entry 5) as the peracetic acid itself reacts with the *cis*-isomer readily under Mn^{II} -free conditions ($k=4.9\times 10^{-5}\text{ ms}^{-1}$). This is in good agreement with the results of the cyclohexene and vinylcyclohexane oxidations (entries 2 and 3) reported above. Generally, there is no significant catalytic effect observed for the Mn catalyst on the *trans* isomer (entry 6) probably due to the steric hindrance.

In the 1-nonene/*cis*-3-nonene intermolecular competition experiment, the rate of the Mn-catalysed *cis*-3-nonene epoxidation ($k=10.3\times 10^{-5}\text{ ms}^{-1}$) was maintained at a comparable level in the reaction mixture; however, a remarkable drop (≈ 8 times) of 1-nonene epoxidation rate ($k=1.6\times 10^{-5}\text{ ms}^{-1}$) was observed (entry 7). As the active Mn catalyst shows a higher preference to attack *cis*-type alkenes with electron-rich C=C double bonds, the epoxidation rate for 1-nonene always lags behind *cis*-3-nonene for the first 20 min of the competition reaction, according to the kinetic diagram (Figure 6). A remarkable turning point appeared after 20 min, at which the rate of 1,2-epoxynonane formation drastically increased five times to $k=7.9\times 10^{-5}\text{ ms}^{-1}$ (compared with its initial rate $k=1.6\times 10^{-5}\text{ ms}^{-1}$), when almost all the *cis*-3-nonene was consumed. This unpredictable kinetic behaviour in the competition experiment is consistent

Table 2. The kinetic studies of the Mn-catalysed epoxidation of alkenes with peracetic acid as the oxidant in acetonitrile/water at 25°C.^[a]

Entry	Substrate	Rate constant $k, \times 10^{-5}\text{ ms}^{-1}$	
		with Mn catalyst	No catalyst
1 ^[b]	4-vinyl-1-cyclohexene	10.1 (0.5 ^[c] , 4.4 ^[d])	1.3
2	cyclohexene	9.8	2.7
3	vinylcyclohexane	20.8	0
4	1-nonene	15.8	0
5	<i>cis</i> -3-nonene	14.2	4.9
6	<i>trans</i> -3-nonene	2.8	2.3
7 ^[e]	1-nonene versus <i>cis</i> -3-nonene	1.6 (7.9 ^[f]), 10.3	0, 4.1
8 ^[e]	1-nonene versus <i>trans</i> -3-nonene	1.9 (5.4 ^[e]), 2.6	0, 1.7
9 ^[e]	<i>cis</i> -3-nonene versus <i>trans</i> -3-nonene	13.5, 2.4	2.0, 1.5

[a] Reaction conditions for the kinetic studies: alkene substrates (1 mmol) in of acetonitrile (4.8 mL), $\text{Mn}(\text{ClO}_4)_2$ salt (0.4 mol %), $\text{NH}_4\text{HCO}_3(\text{aq})$ (600 μL , 0.5 M), and peracetic acid (500 μL) at 25°C; the initial rates (k) were determined from the reaction profiles at low conversion of substrates ($<20\%$). [b] The initial rates of monoepoxide **2** formation were determined by using 0.5 mmol of substrate. [c] The rate of diepoxide **4** formation before all diene **1** was completely converted. [d] The rate of diepoxide **4** formation after all diene **1** was completely converted. [e] Intermolecular competition experiments. [f] Reaction rate after 20 min. [g] Reaction rate after 140 min.

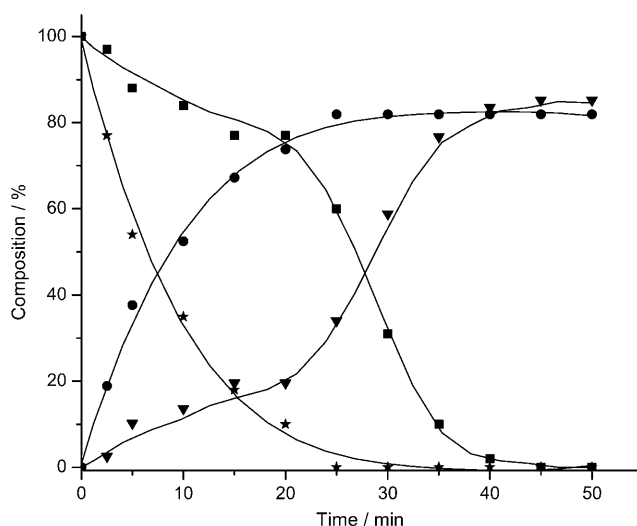


Figure 6. The competition study of 1-nonene versus *cis*-3-nonene in the Mn-catalysed epoxidation reactions in acetonitrile/water at 25°C. 1-Nonene (■), 1-nonene oxide (▼), *cis*-3-nonene (★), and *cis*-3-nonene oxide (●).

with that observed in the intramolecular competition with 4-vinyl-1-cyclohexene as the substrate (Figure 5). In both cases, the epoxidation rates of terminal alkenes were found to be much faster in the independent kinetic studies (entries 2–5) even though the internal C=C double bonds behave more competitively with the Mn catalyst (entries 1 and 7). Based on these kinetic results, the internal alkenes seem not only to be competitors, but also to block the active sites of the Mn catalyst for the attachment to the C=C double bond of the terminal alkenes.

To account for this unusual reactivity of the Mn-catalysed system, we postulate that the active species for the epoxidation are high-valent Mn–oxo complexes with oxidation states of +5 or even higher because most Mn^{IV}–oxo complexes reported in the literature are generally not active in the epoxidation of aliphatic terminal alkenes.^[12] During the competition reaction, the Mn–oxo oxygen atom transfers to the alkenes through electrophilic attack of the C=C double bond in which the effectiveness depends on the density of the π electrons. As the dialkyl-substituted internal alkenes (e.g. *cis*-3-nonene) donate more electrons to the C=C double bond compared with the terminal alkenes (e.g. 1-nonene), they are more susceptible to attack with the active Mn–oxo species (Table 2, entries 1 and 7). However, the reactivity showed an opposite trend in that the C=C double bonds in the terminal alkenes were epoxidised faster in the independent experiments (Table 2, entries 2–5). These findings possibly indicate that the reaction rate is dependent on the oxygen atom-transfer process.

In the kinetic studies of 1-nonene/*cis*-3-nonene intermolecular competition (Figure 6), the catalytic epoxidation of *cis*-3-nonene was dominant in the first 20 min with a net reaction rate of $6.2 \times 10^{-5} \text{ ms}^{-1}$ due to its structural superiority in competing for the Mn–oxo active sites. When over 85% of the *cis*-3-nonene was consumed after 20 min, the epoxidation rate of 1-nonene was getting faster remarkably with $k = 7.9 \times 10^{-5} \text{ ms}^{-1}$ as the unusual competition from *cis*-3-nonene decreased. In a rough estimation, the epoxidation rate of 1-nonene was five times faster than its initial rate as well as that of *cis*-3-nonene even if the peracetic acid concentration was supposed to be much lower. When the reaction profiles of 1-nonene epoxidation were followed in this competition reaction, it was found, interestingly that the terminal alkenes were intrinsically less effective than the internal alkenes at coordination with the Mn–oxo species. However, once the active sites were available, an enhanced epoxidation rate was obtained. These results confirm that the oxygen atom-transfer process is the rate-determining step rather than the preference in binding to the Mn–oxo species.

To get further justification, the 1-nonene/*trans*-3-nonene intermolecular competition reaction was carried out under similar conditions. *trans*-3-Nonene was used as a competitor because it is a geometric isomer of 1-nonene with an internal C=C double bond and this *trans*-type double bond is inert in the Mn-catalysed epoxidation system (Table 2, entry 6). In Figure 7, the kinetic diagram indicates that 1-

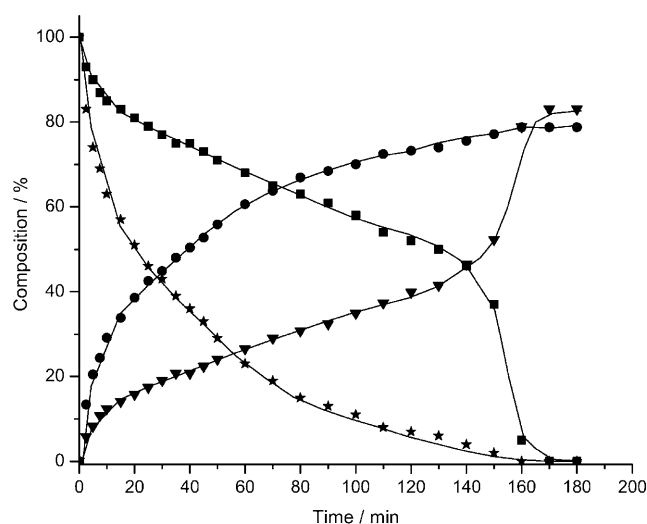


Figure 7. The competition study of 1-nonene versus *trans*-3-nonene in the Mn-catalysed epoxidation reactions in acetonitrile/water at 25°C. 1-Nonene (■), 1-nonene oxide (▼), *trans*-3-nonene (★), and *trans*-3-nonene oxide (●).

nonene took almost 3 h for complete conversion, which is almost four times longer than the reaction time used in the 1-nonene/*cis*-3-nonene system. Furthermore, it is noteworthy that the turning point for the dramatic increment in the epoxidation rate observed in the 1-nonene/*cis*-3-nonene competition reaction at 20 min did not occur. This is attributed to the suppression of *trans*-3-nonene by blocking the active Mn–oxo from the coordination to 1-nonene because over 50% of the *trans*-alkene still remained in the reaction mixture. It is also in good agreement with the results obtained in all of the kinetic studies. After 140 min, the turning point of the reaction clearly appeared when over 95% of *trans*-3-nonene was consumed by background oxidation and meanwhile, the Mn–oxo active sites became available.

Referring to the kinetic results listed in Table 2, the Mn-catalysed epoxidation reaction is found to be controlled by two key steps; that is, binding of the substrate onto the active Mn–oxo and transfer of the Mn–oxo oxygen atom to the C=C double bond. The binding affinity is mainly determined by the nucleophilicity of alkene C=C double bonds towards the active Mn–oxo species. Hence, the internal alkenes (e.g. *cis*-2-nonene and cyclohexene) showed a high preference to react faster in the competition reaction. The rate-determining step in this Mn-catalysed reaction was proven to be the process of Mn–oxo oxygen atom transfer and therefore, the terminal alkenes (e.g. 1-nonene and vinylcyclohexane) gave higher epoxidation rates in the independent experiments. In terms of the structural geometry (Table 2, entries 5, 6 and 9), it also indicates that the Mn catalyst is highly sensitive to steric hindrance because only the terminal alkenes and *cis*-isomers are readily epoxidised in the catalytic manner (for the kinetic diagrams of these experiments, see Figures S6 and S7 in the Supporting Information). To compare, these experimental results apparently contrast with the reported Mn-based systems^[4–8] and give a clue that the active species, generated in situ in the reaction

media, are not simply just the ligated or solvated Mn–oxo complexes because these complexes generally show no such regioselective properties. By combining these interesting results, it is suggested that the active Mn–oxo species in the catalytic epoxidation could be some complicated polymetallic Mn–oxo clusters rather than simple solvent–Mn–oxo complexes.

To obtain more concise information to confirm the existence of the polymetallic Mn–oxo clusters during the catalysis, ES-IMS measurements were conducted on the reaction mixture to look for the possible species. As expected, a number of high molecular mass species with manganese bi- or oligonuclear structures were detected by using positive-ion mode. In the control experiments without addition of peracetic acid or by using acetic acid instead under similar conditions, no such molecular ions were observed in the ES-IMS analysis and hence, these could be the fragments or molecules of the active species.^[13]

The detectable fragment ions are summarised and assigned based on their major isotopic peaks (see Table S1 in Supporting Information for detailed assignments). The assignment was attributed by comparing the isotopic ratios of the chlorine atoms in the spectrum with the calculated values because the isotopic contribution made by carbon, hydrogen, oxygen and manganese atoms is insignificant in the fragment ions. Undoubtedly, the mass series in the spectrum are dominated by the chlorine isotopes with a 2 amu difference in the same mass range. In all cases, the assignment of different fragment/molecule ions was found to be in excellent agreement with the simulation on the isotopic ratios. One of the fragment/molecule ions is selected and shown in Figure 8 as an example (see the Supporting Information for more detectable Mn–oxo cluster species).

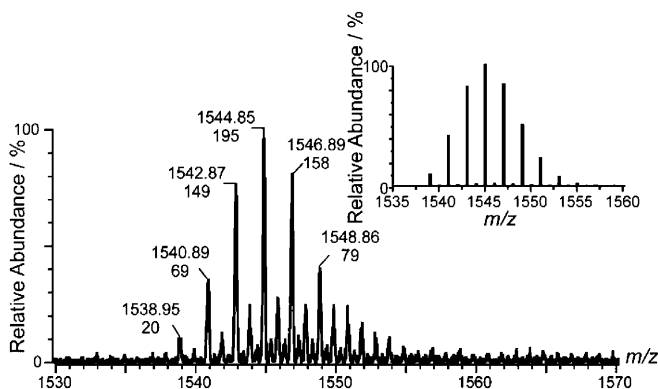


Figure 8. The mass spectrum of the $[\text{Mn}_3(\text{ClO}_4)_{13}(\text{O})(\text{H}_2\text{O})_4]^+$ fragment ion observed in the ESI-MS measurements. The insert is the simulated isotopic distribution based on theoretical calculation.

Based on the ESI-MS information, the active species were depicted as high-valent polymetallic Mn–oxo complexes or clusters with rigid and giant structures formed in situ under the reaction conditions.^[14] Through simple calculations, the possible oxidation states of the Mn in the spectrum are estimated to be +4, +5 and +6. In addition, mixed valence systems^[15] with +4/+5 and +5/+6 are also found in the bi-

and trinuclear Mn fragment ions as listed in Table S1 in the Supporting Information. However, the exact structures and conformations of the active Mn–oxo species are not yet completely resolved.

The oxidation states of the Mn components were also monitored by EPR spectroscopy during the epoxidation reaction. As shown in Figure 9, the initial solution containing peracetic acid and 1-decene in acetonitrile (without Mn^{II} species) gave no visible signal (line a). After the Mn^{II} salt

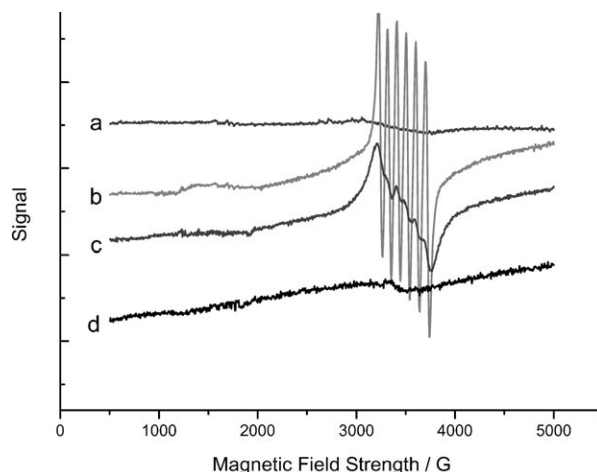


Figure 9. EPR spectra of the Mn-catalysed reaction mixture: a) Control experiment without $\text{Mn}(\text{ClO}_4)_2$; b) experiment with $\text{Mn}(\text{ClO}_4)_2$; c) measurement at $t = 2$ s after addition of $\text{NH}_4\text{HCO}_3(\text{aq})$; d) measurement at $t = 5$ min after addition of $\text{NH}_4\text{HCO}_3(\text{aq})$. Experimental conditions: $\text{Mn}(\text{ClO}_4)_2$ (1.3 mM), 1-decene (42.7 mM), $\text{NH}_4\text{HCO}_3(\text{aq})$ (50 mM) and peracetic acid (9.6 equiv, 32 wt. %) in acetonitrile/water (9:1 v/v). EPR spectra: 9.4 GHz with 2 mW microwave power at 77 K.

was added, a remarkable signal appeared with a six-line pattern centred at around $g = 2$ (line b), which is consistent with high-spin Mn^{II} ($S = 5/2$) species. When $\text{NH}_4\text{HCO}_3(\text{aq})$ was injected all at once in the reaction mixture, this signal rapidly diminished in amplitude in the first 2 s (line c) and no new EPR signal was observed. On the basis of these preliminary results, we are speculating that the active species for the catalytic reaction could be in low spin state because the species are EPR silent in the measurements.^[16]

Manganese clusters are the well-known catalysts in photosystem II and behave as the water-oxidising complexes in plants. However, to the best of our knowledge, there are no literature reports of their applications in the epoxidation of terminal alkenes. The structure of the Mn catalyst in its active state during the catalysis is not clear yet. Nevertheless, we are speculating that it might be the polymetallic manganese clusters (Mn_3 , Mn_4 or higher nuclearity) with high-valent Mn^{V} -oxo for oxygen atom transfer in the epoxidation reaction.^[17] The oxygen-transfer process in the catalysis presumably follows the concerted mechanism because the Mn catalyst gave epoxides with high stereospecificity. This is also consistent with the observations that both mono-alkyl- and *cis*-alkenes are epoxidised much more efficiently than *trans*-alkenes in the kinetic studies.

Safety note: Manganese perchlorate salt is potentially explosive and should always be handled with appropriate care although we have not experienced any problems in these experiments.

Conclusion

A simple catalytic system for the epoxidation of aliphatic terminal alkenes has been successfully developed by using commercially available manganese(II) perchlorate salt as the catalyst and peracetic acid as the oxidant. Based on the ESI-MS and EPR spectroscopy results, the active intermediate formed in situ is proposed to be the high-valent oligonuclear manganese species, which were first applied in the epoxidation of terminal alkenes as effective catalysts. A number of terminal alkenes were found to be epoxidised efficiently (<40 min) on a gram-scale with excellent yields of the isolated products (>90%). The kinetic studies revealed that the Mn-catalysed system shows higher catalytic activity towards the terminal alkenes. The catalytic rate of epoxidation was found to decrease in the order of 1-nonene > *cis*-3-nonene > *trans*-3-nonene, which is a consequence of the giant structure of the Mn-oxo species. To have a better understanding of the nature of the active catalyst in this system, work is ongoing to isolate and obtain the structures of the Mn-oxo clusters, which may lead to a new class of catalysts for alkene epoxidation.

Experimental Section

Materials: All the solvents were of analytical reagent grade and were used without further purification. Alkenes and epoxides were obtained from Aldrich or Acros Organic and were used as received unless otherwise noted. The standard compounds 1,2,7,8-diepoxyoctane, 1,2,8,9-diepoxyoctane, 1,2,9,10-diepoxydecane, 1-cyclohexyl-2,3-epoxypropane and epoxyethylcyclohexane were synthesised and characterised following the literature methods.^[18] Transition-metal salts, peracetic acid (32 wt % in dilute acetic acid), H₂O₂ (35 wt % solution in water), *tert*-butyl hydroperoxide (70 wt % in water), cumene hydroperoxide (88% in cumene) and *meta*-chloroperoxybenzoic acid (purity ≈ 77%) were purchased from Aldrich. The double-deionised water was purified by filtration through an ion-exchange resin purification train (Millipore).

Instrumentation: A Hewlett-Packard 8900 GCMS equipped with EC-1 or EC-WAX columns (Alltech Associates, Inc.) was used for yield determination and identification. ¹H and ¹³C NMR spectra were recorded on a Bruker DPX-400 MHz NMR spectrometer. Tetradecane was used as an internal standard in the quantitative GCMS measurements. EPR spectra (77 K) were recorded at the X-band (9.4 GHz microwave frequency), 2 mW power and 25G modulation amplitude on a Bruker EMX EPR spectrometer. Samples were placed in a 5 mm quartz tube and frozen in liquid N₂ before spectral measurement. ESI-MS analysis was carried out by using a VG Micromass 7070F Mass Spectrometer.

General procedures for gram-scale catalytic epoxidation of terminal alkenes: Alkene (7 mmol), acetonitrile (34 mL), NH₄HCO_{3(aq)} (4.2 mL, 0.5 M in water) and Mn(ClO₄)₂ (1.4 mL, 0.4 mol %, 0.02 M in acetonitrile) were added to a 100 mL round-bottomed flask equipped with a magnetic stirrer. After the flask was sealed with a rubber septum, peracetic acid (3.4 mL, 32 wt % in dilute acetic acid) was added dropwise by using a syringe over 5 minutes. The reaction mixture was then vigorously stirred for another 45 min. **CAUTION! The reaction is highly exothermic if per-**

acetic acid is added too quickly. The epoxide product was extracted into pentane (3 × 40 mL), washed with 1 M NaHCO_{3(aq)} and dried over sodium sulfate. The organic solvent was removed under vacuum by rotary evaporator. The crude product was purified by a silica gel column with dichloromethane as the eluent to give the desired epoxides as a colourless liquid. The epoxides were characterised by GCMS and ¹H NMR spectrum, and compared with the known compounds.

Epoxidation of 1,7-octadiene: Following the general procedure with 1,7-octadiene (0.5 mmol), Mn(ClO₄)₂ salt (0.64 mol %, 100 μL, 0.02 M in acetonitrile), peracetic acid (500 μL, 4.8 equiv), NH₄HCO_{3(aq)} (600 μL, 0.5 M in water) in acetonitrile (4.8 mL) gave 1,2,7,8-diepoxyoctane (62% yield). ¹H NMR (400 MHz, CDCl₃): δ = 2.84 (m, 2H), 2.68 (dd, 2H), 2.39 (dd, 2H), 1.52–1.37 ppm (m, 8H); GCMS: *m/z*: 142.

Epoxidation of 1,8-nonadiene: Following the general procedure with 1,8-nonadiene (0.5 mmol), Mn(ClO₄)₂ salt (0.64 mol %, 100 μL of 0.02 M acetonitrile), peracetic acid (500 μL, 4.8 equiv), NH₄HCO_{3(aq)} (600 μL, 0.5 M in acetonitrile) (4.8 mL) gave 1,2,8,9-diepoxyoctane (88% yield). ¹H NMR (400 MHz, CDCl₃): δ = 2.85 (m, 2H), 2.69 (dd, 2H), 2.41 (dd, 2H), 1.52–1.32 ppm (m, 10H); GCMS: *m/z*: 156.

Epoxidation of 1,9-decadiene: Following the general procedure with 1,9-decadiene (0.5 mmol), Mn(ClO₄)₂ salt (0.64 mol %, 100 μL of 0.02 M in CH₃CN), peracetic acid (500 μL, 4.8 equiv) and 0.5 M NH₄HCO_{3(aq)} (600 μL) in acetonitrile (4.8 mL) gave 1,2,9,10-diepoxydecane (90% yield). ¹H NMR (400 MHz, CDCl₃): δ = 2.86 (m, 2H), 2.71 (dd, 2H), 2.41 (dd, 2H), 1.52–1.32 ppm (m, 8H); GCMS: *m/z*: 170.

Epoxidation of allylcyclohexane: Following the general procedure gave 1-cyclohexyl-2,3-epoxypropane (88% yield). ¹H NMR (400 MHz, CDCl₃): δ = 2.92 (m, 1H), 2.73 (dd, 1H), 2.41 (dd, 1H), 1.75–1.66 (m, 6H), 1.42–1.22 (m, 5H), 1.12–0.83 ppm (m, 2H); GCMS: *m/z*: 140.

Epoxidation of vinylcyclohexane: Following the general procedure gave epoxyethylcyclohexane (85% yield). ¹H NMR (400 MHz, CDCl₃): δ = 2.69 (m, 2H), 2.49 (dd, 1H), 1.86 (d, 1H), 1.73–1.63 (m, 4H), 1.22–1.07 ppm (m, 6H); GCMS: *m/z*: 126.

Conditions for kinetic and competition experiments: The activity and selectivity of the catalytic system were determined by performing kinetic experiments in a thermostatted bath at 25 °C. The experiments were typically conducted with the Mn^{II} salt (0.4 mol %) in a 10 mL round-bottomed flask equipped with stirrer bar. Alkene substrates (1 mmol) in acetonitrile (4.8 mL), Mn(ClO₄)₂ salt (0.32 mol %), NH₄HCO_{3(aq)} (600 μL, 0.5 M) and peracetic acid (500 μL, 32 wt %) were added to the flask. The reaction mixture was stirred vigorously. At regular time intervals, 50 μL of the reaction mixture was withdrawn and diluted with pentane to 5 mL in a volumetric flask. The sample was then analysed by GCMS with tetradecane as the internal standard.

Conditions for ESI-MS analysis of the Mn-oxo cluster: The sample for ESI-MS analysis was prepared in an ice bath at 0 °C. In a 5 mL round-bottomed flask, Mn(ClO₄)₂ (0.02 M) acetonitrile (100 μL) was added into acetonitrile (2.4 mL) containing 0.5 M NH₄HCO_{3(aq)} (300 μL) and peracetic acid (250 μL). The resulting mixture was stirred for 1 min and then kept in a freezer at –25 °C for another 12 h. The resulting solution was directly examined by ESI-MS without further dilution.

Acknowledgement

We acknowledge the support from the Hong Kong Polytechnic University and the Research Grants Council Central Allocation Fund (CityU 2/06C).

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Received: April 22, 2008
Published online: July 10, 2008