Journal of Molecular Catalysis A: Chemical 372 (2013) 84–89

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Remarkable effect of simple aliphatic alcohols on the controlled aerobic oxidation of toluene catalyzed by (T(*p*-Cl)PP)MnF/NHPI

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ARTICLE INFO

Article history:
Received 12 December 2012
Received in revised form 7 February 2013
Accepted 17 February 2013
Available online xxx

Keywords:
Toluene
Metalloporphyrin
Dioxygen
Benzaldehyde
Catalytic oxidation

ABSTRACT

The remarkable effect of simple aliphatic alcohols on the controlled oxidation of toluene with molecular oxygen over [5,10,15,20-tetrakis(*p*-chlorophenyl)porphinato]manganese fluoride (T(*p*-Cl)PPMnF) and *N*-hydroxyphthalimide (NHPI) was reported. The influences of reaction conditions such as the concentration and structure of alcohols, temperature and catalyst concentration on the promotion effect were also studied. UV–vis spectra were used to investigate the possible structure of reaction intermediate derived from the catalyst (T(*p*-Cl)PP)MnF in the toluene oxidation systems in the presence of methanol. The results showed that the added methanol interacted with catalyst (T(*p*-Cl)PP)MnF to form the coordination compound $[(T(p\text{-Cl})PP)Mn^{III}(ROH)_2]^+$, which subsequently was transformed into a high valent manganese-oxo radical cation intermediate $[(T(p\text{-Cl})PP)Mn^{IV}(O)(CH_3OH)]^{+\bullet}$ in the oxidation systems. We deduce that the formation of $[(T(p\text{-Cl})PP)Mn^{IV}(O)(CH_3OH)]^{+\bullet}$ and its higher reactivity toward toluene may be responsible for the better results observed. On the basis of the results obtained, a possible mechanism of the controlled oxidation of toluene with dioxygen over (T(*p*-Cl)PP)MnF/NHPI in the presence of the aliphatic alcohols was proposed.

1. Introduction

The controlled oxidation of toluene to benzaldehyde (BA), benzyl alcohol (BAL) is an important transformation in chemical industry because benzaldehyde and benzyl alcohol are widely used to synthesize a large variety of diverse chemicals such as pharmaceuticals, foodstuff, dyes, perfume, and resins [1,2]. Currently, benzaldehyde and benzyl alcohol are mainly produced via chlorination of toluene followed by hydrolysis [3,4], which generates large quantities of toxic waste, thus causing serious pollution problems. More importantly, the products produced in the above process are prohibited to be used in the pharmaceutical and foodstuff fields because they contain some of the chlorinated impurities. As a result many researchers have been striving to develop new routes for the production of benzaldehyde and benzyl alcohol through the controlled oxidation of toluene using molecular oxygen. Until now several catalyst systems including g-C_3N_4 nanocomposite [5,6], copper-based oxides [7], Mn(salen) complex [8], and NHPI [9] have been reported as effective catalyst for the selective oxidation of toluene with different oxidants. However, one of the major problems associated with the existing technologies is that the conversion of toluene has to be kept below 10% to obtain relative high selectivity of benzaldehyde and benzyl alcohol [5–12] since benzaldehyde is easily overoxidized in the oxidation system to benzoic acid (BAC). So far, most of the selectivities of benzaldehyde and benzyl alcohol reported are lower than 60%. Consequently, the controlled aerobic oxidation of toluene to benzaldehyde and benzyl alcohol in good yield and with excellent selectivity remains as a challenge [13,14].

Metalloporphyrins, which are widely recognized as environmentally benign catalysts, have attracted extensive interest for their excellent catalytic performances in the controlled oxygenation of hydrocarbons with molecular oxygen under mild conditions [10,15–20]. Our group has investigated the selective aerobic oxidation of toluene using simple metalloporphyrin as the catalyst and selectivity of benzaldehyde and benzyl alcohol up to 60% with the conversion of toluene up to 8.9% was achieved [10]. Though the results are comparable to those previously reported, they are far from practical and there is still much room left to be improved. Since *N*-hydroxyphthalimide (NHPI) has been reported as an effective cocatalyst for the metalloporphyrin catalyzed aerobic oxidation of hydrocarbons in mild conditions [9,21–24], we wonder whether adding some NHPI in our reaction mixture could improve our reaction. Furthermore, researchers have reported that some protic solvents such as aliphatic alcohols, acting as ligands, can markedly affect the catalytic activity of metalloporphyrin in the oxidation of hydrocarbons or epoxidation of olefins with peroxides [20,25–27]. So we decided to probe the effect of adding some alcohols in the T(*p*-Cl)PPMnF/NHPI catalyzed aerobic

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http://dx.doi.org/10.1016/j.molcata.2013.02.012

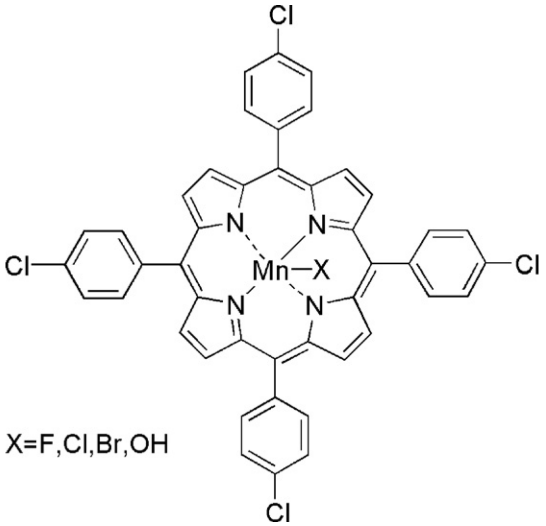


Fig. 1. T(*p*-Cl)PPMnX.

oxidation of toluene system. We were pleased to discover that the catalytic activity of (T(*p*-Cl)PP)MnF could be remarkably enhanced by adding some aliphatic alcohol into the reaction mixture in the aerobic controlled oxidation of toluene. Both the toluene conversion and the selectivity of benzaldehyde and benzyl alcohol could be significantly improved. UV–vis spectra of the toluene reaction mixture showed that (T(*p*-Cl)PP)MnF can be coordinated axially with aliphatic alcohol to form $[(T(p\text{-Cl})PP)Mn(ROH)_2]^+$, which is transformed in the reaction mixture to high-valent manganese-oxo redical cations $[(T(p\text{-Cl})PP)Mn^{IV}(O)(CH_3OH)]^{+\bullet}$, which we believe is the active species for oxidation of hydrocarbon [26]. We reasoned that the addition of aliphatic alcohol can facilitate the formation of $[(T(p\text{-Cl})PP)Mn^{IV}(O)(CH_3OH)]^{+\bullet}$ intermediates during the reaction process. According to these results, a possible mechanism of the aerobic oxidation of toluene over the manganese porphyrin and NHPI was proposed.

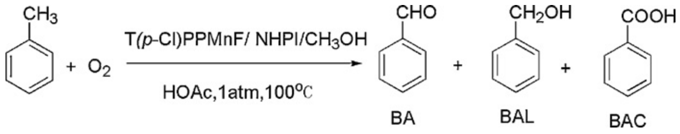
2. Experimental

2.1. Instruments and materials

GC analysis was performed on a Shimadzu GC-2010 equipped with a 0.5 mm i.d. 25 m PEG 20M capillary column and a flame ionization detector. MS spectra were measured on a Class-5000 GC–MS spectrometer and an Agilent 1100 LC–MS. UV–vis absorption spectra and changes in absorbance with time were recorded on a PE L-17 spectrometer. Toluene was purified and analyzed by GC to ensure the absence of impurities before use. Pyrrole was redistilled before use. Other reagents were all analytical grade and used as received. T(*p*-Cl)PPMnX (X = F, Cl, Br, OH) (structure as Fig. 1) were synthesized and purified according to documented procedures [28,29].

2.2. Toluene oxidation over (T(p-Cl)PP)MnX/NHPI

The catalytic oxidation of toluene with molecular oxygen at atmospheric pressure was performed according to the following typical procedure: desired amount of reactants and precisely weighted catalysts were added into a 100 ml three-neck flask equipped with a reflux condenser and a magnetic stirrer. Then the flask was heated to reaction temperature while the solution was agitated by a magnetic stirrer. Upon reaching the reaction temperature, oxygen was continuously introduced into the flask through a flowmeter. The mixture of toluene oxidation was sampled at regular intervals, identified by GC–MS, and quantified with GC using bromobenzene as the internal standard [10]. The contents of hydroperoxides were determined by iodometric method.



Scheme 1. (T(*p*-Cl)PP)MnF/NHPI catalyzed toluene oxidation.

3. Results and discussion

3.1. The promotional effect of simple aliphatic alcohols on the toluene oxidation

The oxidation of toluene catalyzed by (T(*p*-Cl)PP)MnX/NHPI with molecular oxygen and the influence of simple aliphatic alcohols on the oxidation were investigated. Analysis showed that the same oxidation products were obtained in all reactions whether alcohol was added or not (Scheme 1). Out of the four different metalloporphyrin catalysts tested (T(*p*-Cl)PP)MnX (X = F, Cl, Br, OH)), (T(*p*-Cl)PP)MnF was found to give slightly better results (Table 1). As a result, T(*p*-Cl)PP)MnF was chosen as the standard catalyst to study the controlled oxidation of toluene. In a typical experiment without the addition of aliphatic alcohol, the toluene conversions is 12.8%, the selectivity of benzaldehyde was 39.6%, and the selectivity of benzyl alcohol was 4.7% at 100 °C when the reaction time was 10 h (Table 2, entry 4). However, when some amount of aliphatic alcohol such as methanol or ethanol was added, the toluene conversion was increased to 38.2%, 32.1%, while the selectivities of benzaldehyde and benzyl alcohol reached 37.5%, 6.3%, respectively (Table 2, entries 6 and 8). These results are summarized in Table 2.

Interestingly, at 8 h when the conversion of toluene was around 14–15%, the selectivity of benzaldehyde was as high as 62.4–64.8% (Table 2, entries 5 and 7). When the catalyst was switched from (T(*p*-Cl)PP)MnF/NHPI to $Mn(OAc)_2$/NHPI, the promotional effect observed with methanol or ethanol was not observed (Table 2, entries 9 and 10).

3.2. The effect of methanol on (T(p-Cl)PP)MnF in the toluene oxidation

The UV–vis spectral changes accompanying the toluene oxidation reaction could be attributed to the change of the (T(*p*-Cl)PP)MnF catalyst. So in order to investigate the change of (T(*p*-Cl)PP)MnF catalyst, the UV–vis spectra of the toluene reaction mixture have been measured and analyzed. Fig. 2 shows the spectral changes of toluene oxidation over (T(*p*-Cl)PP)MnF/NHPI in 10 h with or without the addition of some CH_3OH. When 0.08 mol methanol was added, as can be seen from the part A of Fig. 2, only one characteristic peak (468 nm) could be observed at the beginning of the toluene oxidation (shown as the bold solid line in Fig. 2). According to the reported literature [30], this absorbance

Table 1
The catalytic efficiency of (T(*p*-Cl)PP)MnX on the toluene oxidation.

(T(*p*-Cl)PP)MnX	Conv. (mol %)	Selectivity (mol%)		
		BA	BAL	BAC
(T(*p*-Cl)PP)MnF	38.2	37.5	6.3	55.3
(T(*p*-Cl)PP)MnCl	35.7	38.4	5.8	54.4
(T(*p*-Cl)PP)MnBr	29.8	42.9	7.2	47.2
(T(*p*-Cl)PP)MnOH	37.5	37.1	6.5	55.1

Reaction conditions: toluene 0.13 mol, CH_3OH 78.1 mmol, (T(*p*-Cl)PP)MnX 20 ppm, NHPI 5 mol%, HOAc 20 ml, O_2 0.05 L/min, temperature 100 °C.

Table 2
Selective oxidation of toluene with molecular oxygen.

Entry	Catalysts		Additives	Time (h)	Con. (mol%)	Selectivity (mol%)		
						BA	BAL	BAC
1	–	–	–	10	Traces	–	–	–
2	(T(*p*-Cl)PP)MnF	–	–	7	Traces	–	–	–
3	(T(*p*-Cl)PP)MnF	–	MeOH	10	Traces	–	–	–
4	(T(*p*-Cl)PP)MnF	NHPI	–	10	12.8	39.6	4.7	54.3
5	(T(*p*-Cl)PP)MnF	NHPI	MeOH	8	15.6	64.8	9.1	24.8
6	(T(*p*-Cl)PP)MnF	NHPI	MeOH	10	38.2	37.5	6.3	55.3
7	(T(*p*-Cl)PP)MnF	NHPI	EtOH	8	14.5	62.4	10.3	25.1
8	(T(*p*-Cl)PP)MnF	NHPI	EtOH	10	32.1	42.4	7.1	49.2
9	$Mn(OAc)_2$[a]	NHPI	MeOH	10	5.8	17.4	4.3	74.2
10	$Mn(OAc)_2$[a]	NHPI	–	10	6.3	14.2	3.1	79.4
11	–	NHPI	–	10	0.13	38.5	15.4	0.0

Reaction conditions: toluene 0.13 mol, CH_3OH 78.1 mmol, (T(*p*-Cl)PP)MnF 20 ppm, NHPI 5 mol%, HOAc 20 ml, O_2 0.05 L/min, temperature 100 °C.

[a] $Mn(OAc)_2$ 20 ppm.

peak at 468 nm could be ascribed to the Soret absorbance of $[(T(p\text{-}Cl)PP)Mn(CH_3OH)_2]^+$, which came from the (T(*p*-Cl)PP)MnF coordinated with CH_3OH in the reaction solution. In order to further confirm the structure of methanol complexed (T(*p*-Cl)PP)MnF, a dichloromethane solution of (T(*p*-Cl)PP)MnF was added methanol until the concentration of methanol in dichloromethane reached 3–10 M. Fig. 3 shows the UV–vis spectral changes observed in this experiment. With the increasing amount of methanol added, the spectrum shows a decrease in the Soret absorbance (λ_{max} = 458 nm) for (T(*p*-Cl)PP)MnF with concomitant increase of absorbance at 468 nm, the peak of which was also observed in the toluene oxidation at the same position, which was also consistent with that of $[(T(p\text{-}Cl)PP)Mn(CH_3OH)_2]^+$ reported in literature [30]. As the toluene oxidation began to take place, two new absorbance peaks at 421 and 556 nm appeared, and as the reaction progressed, the intensity of the Soret band at 468 nm decreased significantly accompanied with substantial increase of absorbance at 421 nm. For their assignment, we took note of similar metalloporphyrin complexes in early reports [26,31–33]. It was reported that hydrogen peroxides could coordinate axially with iron porphyrin [26], then the oxygen–oxygen bond of the hydrogen peroxide molecule coordinated with iron porphyrin could undergo either heterolytic or homolytic cleavage. The former process will lead to $Fe^{IV}(O)P^{+\bullet}$, an active catalyst for olefin epoxidation with $Fe^{IV}(OH)P$ species produced, while the latter produces $Fe^{IV}(OH)P$ directly. Some researchers [20,34,35] also found that aliphatic alcohols could modify the electronic properties of metalloporphyrin and facilitate the heterolytic cleavage of the oxygen–oxygen bond of hydrogen peroxide. So in our case, we deduced that the absorbance at 421 nm could be assigned to $[(T(p\text{-}Cl)PP)Mn^{IV}(O)(CH_3OH)]^{+\bullet}$, which could be generated in the reaction of $[(T(p\text{-}Cl)PP)Mn^{III}(ROH)_2]^+$ with benzyl hydrogen peroxides. This assignment of the absorbance peak at 421 nm is consistent with the reported $Mn^{IV}(O)P$ complexes in known literatures [31–33]. $[(T(p\text{-}Cl)PP)Mn^{IV}(O)(CH_3OH)]^{+\bullet}$ should have higher reactivity toward toluene oxidation than $[(T(p\text{-}Cl)PP)Mn^{III}(ROH)_2]^+$, and this could explain why higher conversion of toluene and selectivity toward benzaldehyde and benzyl alcohol were achieved in the presence of alcohol. It should be pointed out that similar results were also reported by Groves in the study of the interaction between cis-β-methylstyrene and oxomanganese(IV) porphyrin [31]. In order to show the differences, the UV–vis spectra of toluene oxidation mixture without methanol have been measured as well and the results were shown as the part B of Fig. 2. Only one absorbance peak at 470 nm could be observed which could be assigned to the coordination compound (T(*p*-Cl)PP)MnF complexed with acetic acid. During the reaction, the absorbance at 470 nm remained unchanged. The results implied that it was more difficult for ((T(*p*-Cl)PP)MnF to form the active intermediate $[(T(p\text{-}Cl)PP)Mn^{IV}(O)(CH_3OH)]^{+\bullet}$ in the oxidation of toluene in acetic acid without the addition of alcohol.

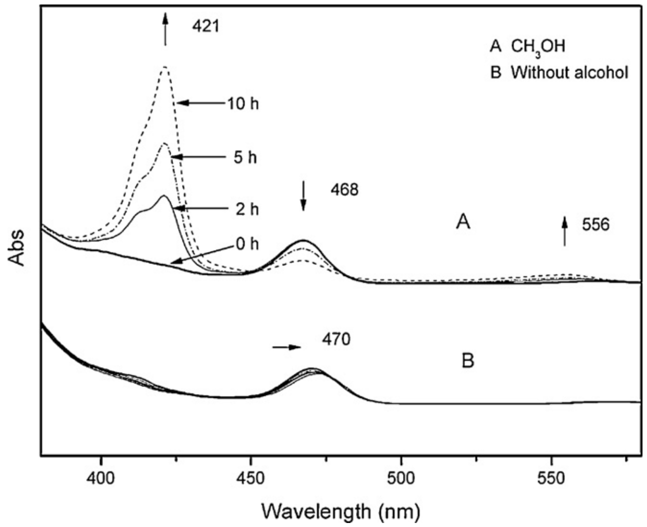


Fig. 2. UV–vis absorption spectral changes observed during toluene oxidation. Reaction conditions: toluene 0.13 mol, (T(*p*-Cl)PP)MnF 20 ppm, NHPI 5 mol%, HOAc 40 ml, O_2 0.05 L/min, temperature 100 °C, reaction time 10 h; A: CH_3OH 78.1 mmol, B: without alcohols.

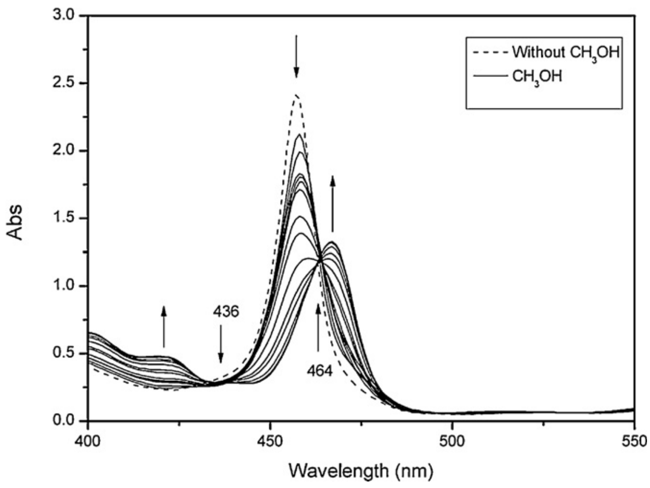


Fig. 3. UV–vis spectral changes of (T(*p*-Cl)PP)MnF with CH_3OH in CH_2Cl_2. Reaction conditions: CH_3OH: 3.00–10.00 M. (T(*p*-Cl)PP)MnF: 1.2×10^{-5} M.

Table 3
Effect of the concentration of methanol on the toluene oxidation.

CH_3OH (mmol)	Con. (mol%)	Selectivity (mol%)		
		BA	BAL	BAC
15.6	13.2	63.9	5.8	29.2
31.2	15.4	58.7	6.2	33.1
46.9	24.5	50.4	5.6	42.5
78.1	38.2	37.5	6.3	55.3

Reaction conditions: toluene 0.13 mol, NHPI 5 mol%, (T(*p*-Cl)PP)MnF 20 ppm, HOAc 20 ml, O_2 0.05 L/min, temperature 100 °C, reaction time 10 h.

3.3. *The effect of other reaction parameters on the toluene oxidation*

3.3.1. *The effect of the amount of methanol*

In order to further study the influence of alcohol on the toluene oxidation catalyzed by (T(*p*-Cl)PP)MnF/NHPI, the changes of the toluene conversion and the selectivity of benzaldehyde and benzyl alcohol were investigated by varying the amount of methanol added into the reaction solution. The results are listed in Table 3. When the amount of methanol added was 15.6 mmol, the conversion of toluene and the selectivities of benzaldehyde and benzyl alcohol are 13.2%, 63.9%, 5.8% respectively. When the amount of methanol added was further increased, the conversion and the yield of benzaldehyde and benzyl alcohol increased rapidly. When 78.1 mmol of methanol was added, the conversion went up to 38.2% and the selectivity of benzaldehyde dropped to 37.5%, in other words, the total yield of benzaldehyde and benzyl alcohol was 16.2%. This is understandable since at higher conversion, more aldehyde and alcohol were converted to benzoic acids, thus lowering the selectivities. However, the yield increase can be rationalized by better coordination of methanol with (T(*p*-Cl)PP)MnF at higher concentrations. When the methanol concentration was lower, only some of the (T(*p*-Cl)PP)MnF catalysts were coordinated axially with methanol. When the methanol concentration was higher, most of the (T(*p*-Cl)PP)MnF catalysts were converted to the stable $[(T(p\text{-}Cl)PP)Mn(CH_3OH)_2]^+$ or $[(T(p\text{-}Cl)PP)Mn^{IV}(O)(CH_3OH)]^{+\bullet}$ in the process of toluene oxidation. Some literatures [30,34] have also reported that the increase of alcohol concentration could change the reductive potentials of metalloporphyrins, thus influencing their catalytic ability in chemical reactions.

3.3.2. *The effect of aliphatic alcohol structure*

In order to gain further insight into the effect of aliphatic alcohol on the catalytic ability of manganese porphyrin, the changes of toluene conversion and yields of benzaldehyde and benzyl alcohol were investigated by adding different aliphatic alcohols. The results are shown in Table 4. The influences of different aliphatic alcohols on the toluene oxidation over (T(*p*-Cl)PP)MnF/NHPI are significant different. Straight-chain alcohols, such as methanol, ethanol, and propanol which have smaller steric hindrance, can promote the catalytic ability of manganese porphyrin and higher conversions of toluene oxidation are obtained. In contrast, when some amount of isopropanol or tert-butyl alcohol with larger steric hindrance was added in the reaction solution, the oxidation of toluene was slowed down considerably. It could be attributed to the larger steric hindrance of branched-chain alcohols prohibiting molecular oxygen from getting near the catalyst after the catalyst (T(*p*-Cl)PP)MnF was coordinated with the added alcohol, consequently the ability of (T(*p*-Cl)PP)MnF activating dioxygen was decreased and the rate of toluene oxidation was slowed down. Similar phenomenon was also observed in the investigation of the aerobic oxidation of *p*-xylene influenced with *p*-toluic alcohol by our research group [36].

Table 4
Effect of different aliphatic alcohols on the toluene oxidation.

Alcohols	Conversion (mol%)	Selectivity (mol%)		
		BA	BAL	BAC
–	12.8	39.6	4.7	54.3
CH_3OH	38.2	37.5	6.3	55.3
CH_3CH_2OH	32.1	42.4	7.1	49.2
$CH_3CH_2CH_2OH$	17.5	56.2	7.8	34.5
$(CH_3)_2CHOH$	8.4	75.0	9.4	14.1
$(CH_3)_3COH$	7.5	69.0	8.3	20.8

Reaction conditions: toluene 0.13 mol, NHPI 5 mol%, (T(*p*-Cl)PP)MnF 20 ppm, alcohol 78.1 mmol, HOAc 20 ml, O_2 0.05 L/min, temperature 100 °C, reaction time 10 h.

Table 5
Effect of the concentration of (T(*p*-Cl)PP)MnF on the toluene oxidation.

(T(*p*-Cl)PP)MnF (ppm)	Conversion (mol%)	TON (mol/mol)	Yield (mol%)		
			BA	BAL	BAC
0	0.13	–	0.05	0.02	0.00
10	34.0	155,135	11.5	2.1	19.8
20	38.2	174,333	14.3	2.4	21.1

Reaction conditions: NHPI 5 mol%, CH_3OH 78.1 mmol, HOAc 20 ml, O_2 0.05 L/min, temperature 100 °C, reaction time 10 h.

3.3.3. *The effect of the concentration of (T(p-Cl)PP)MnF*

The catalyst concentration is a key factor influencing the conversion and product selectivity in metalloporphyrin-catalyzed alkane oxidations [10,17]. In order to understand the effect of the concentration of (T(*p*-Cl)PP)MnF on the toluene oxidation, we investigated the changes of the toluene conversion and the selectivity of benzaldehyde and benzyl alcohol with different (T(*p*-Cl)PP)MnF concentrations, and the results are shown in Table 5. With no catalyst, the toluene conversion was about 0.13%. When 10 or 20 ppm of (T(*p*-Cl)PP)MnF was used in the reaction, the toluene conversion was increased to above 34% while the yield of benzaldehyde was between 11 and 14%. In contrast the yield of benzyl alcohol was only around 2%. It should be noted that the molar turnover numbers were more than 150,000 in these reactions. These results illustrate that the toluene conversion and benzaldehyde/benzyl alcohol yield increased significantly when a small amount of (T(*p*-Cl)PP)MnF was added, and the metalloporphyrin catalyst is a highly efficient catalyst for the selective oxidation of toluene.

3.3.4. *The effect of reaction time on the toluene oxidation*

The changes of toluene conversion and the selectivity of benzaldehyde and benzyl alcohol of the toluene oxidation with reaction time are shown in Fig. 4. The plot shows that the conversion of toluene increased and the selectivity to benzaldehyde and benzyl alcohol decreased with reaction time. When the reaction time was 10 h, the maximum conversion of toluene was up to 12.8%, and the selectivities of benzaldehyde and benzyl alcohol was 37.5% and 6.3%, respectively, in the absence of any alcohol. When methanol or ethanol was added into the reaction solution, the maximum conversion of toluene was increased significantly to 38.2% or 32.1% respectively, and the selectivities of benzaldehyde and benzyl alcohol were maintained between 37.5 and 42.4% and 6.3 and 7.1%, respectively.

3.3.5. *The effect of reaction temperature on the toluene oxidation*

Normally temperature is very important on the metalloporphyrin catalyzed reactions. Increasing reaction temperature can shorten the induction period and accelerate the reaction rate of metalloporphyrin catalyzed reactions [37,18]. In this paper, the influence of reaction temperature on the toluene oxidation catalyzed by (T(*p*-Cl)PP)MnF/NHPI with methanol at the temperature range of 70–100 °C was investigated. As illustrated in Table 6, the conversion of toluene was influenced significantly by the

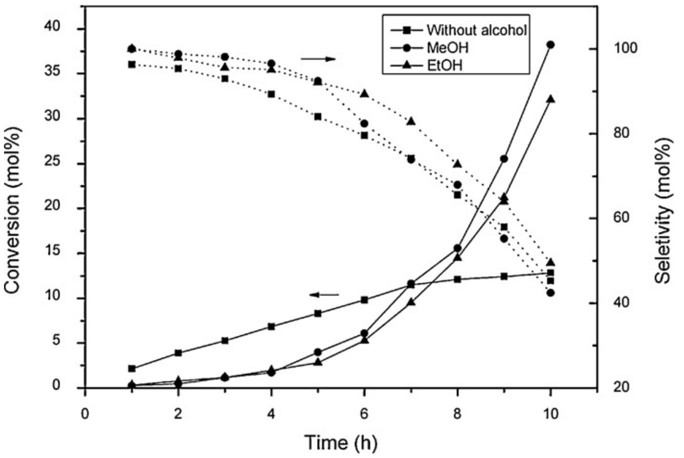


Fig. 4. Changes of toluene conversion and the selectivity of BA and BAL with the reaction time. Reaction conditions: toluene 0.13 mol, NHPI 5 mol%, (T(*p*-Cl)PP)MnF 20 ppm, alcohol 78.1 mmol, HOAc 20 ml, O_2 0.05 L/min, reaction time 10 h.

reaction temperature. The rate of toluene oxidation was so slow at 70 °C that there was very little product when the reaction was run for 10 h. With the increase of reaction temperature, the conversion of toluene and the yield of benzaldehyde and benzyl alcohol increased rapidly, although the selectivity of benzaldehyde and benzyl alcohol decreased somewhat. That could be due to the fact that benzaldehyde and benzyl alcohol could be oxidized easily at higher temperature.

3.4. The preliminary mechanism for the (T(p-Cl)PP)MnF/NHPI catalyzed-alcohol promoted selective oxidation of toluene with dioxygen

The mechanisms of hydrocarbon oxidations with molecular oxygen catalyzed by metalloporphyrins [24,33,37,18,39–42], or metalloporphyrins with co-catalysts [20,21] have been extensively investigated. All previous literatures have suggested that the aerobic oxidations of hydrocarbons catalyzed by metalloporphyrins involve a free radical reaction, which is typically initiated from alkyl hydroperoxides [10,21]. NHPI can be an excellent radical catalyst promoter for the aerobic oxidation of hydrocarbons through an active intermediate PINO to produce alkyl hydroperoxides [9,22]. For the aerobic controlled oxidation of toluene over (T(*p*-Cl)PP)MnF/NHPI, benzyl hydrogen peroxide was found to be produced in the reaction mixture, and its yield was 6.2 mol% when the reaction time was 5 h. We propose that benzyl hydrogen peroxide comes from the reaction of molecular oxygen with toluene catalyzed by (T(*p*-Cl)PP)MnF/NHPI [15,21,26,35]. Then the benzyl hydrogen peroxide can coordinate axially to (T(*p*-Cl)PP)MnF and the oxygen–oxygen bond of the coordinated benzyl hydrogen peroxide can undergo cleavage to produce a high-valent manganese-oxo porphyrin species through two pathways. One is through a homolytic cleavage to produce $[(T(p\text{-Cl})PP)Mn^{IV}(OH)]^+$ [26,35], which is less active for the toluene oxidation, the other is through a heterolytic cleavage to produce a two-electron oxidized $[(T(p\text{-Cl})PP)Mn^{IV}(O)(CH_3OH)]^{+\bullet}$ and benzyl alcohol [15,35]. And the heterolytic cleavage could be accelerated by adding some simple aliphatic alcohol in the reaction solution [34]. In other words, the added alcohol not only can modify the electronic properties of metalloporphyrin catalyst but also can facilitate the formation of $[(T(p\text{-Cl})PP)Mn^{IV}(O)(CH_3OH)]^{+\bullet}$. The more active $[(T(p\text{-Cl})PP)Mn^{IV}(O)(CH_3OH)]^{+\bullet}$ then can react with toluene to produce a benzyl radical. This hypothesis is corroborated by the observation that higher selectivity of benzyl alcohol vs benzaldehyde was achieved when some methanol was added into the reaction solution. The whole reaction process might be as follows:

Table 6
Effect of temperature on the toluene oxidation.

Temperature (°C)	Conv. (mol%)	Selectivity (mol%)[a]		
		BA	BAL	BAC
70	Traces	–	–	–
80	1.2	85.2	13.1	0.0
90	18.6	58.9	9.6	30.2
100	38.2	37.5	6.3	55.3

Reaction conditions: toluene 0.13 mol, NHPI 5 mol%, (T(*p*-Cl)PP)MnF 20 ppm, CH_3OH 78.1 mmol, HOAc 20 ml, O_2 0.05 L/min, reaction time 10 h.

[a] Yields were determined by GC analyses based on substrates used.

$$RCH_3 + O_2 \xrightarrow[\text{NHPI}]{[(T(p\text{-Cl})PP)Mn^{III}]^+} RCH_2OOH \quad (1)$$

$$[(T(p\text{-Cl})PP)Mn^{III}]^+ + R^1OH \rightarrow [(T(p\text{-Cl})PP)Mn^{III}(R^1OH)_2]^+ \quad (2)$$

$$[(T(p\text{-Cl})PP)Mn^{III}(R^1OH_2)]^+ + RCH_2OOH \xrightarrow{R^1OH} [(T(p\text{-Cl})PP)Mn^{IV}(O)(R^1OH)]^{+\bullet} + RCH_2OH \quad (3)$$

$$[(T(p\text{-Cl})PP)Mn^{III}]^+ + RCH_2OOH \rightarrow [(T(p\text{-Cl})PP)Mn^{IV}(OH)]^+ + RCH_2O^\bullet \quad (4)$$

$$[(T(p\text{-Cl})PP)Mn^{IV}(O)(R^1OH)]^{+\bullet} + RCH_3 \rightarrow [(T(p\text{-Cl})PP)Mn^{IV}(OH)(R^1OH)]^+ + RCH_2^\bullet \quad (5)$$

$$[(T(p\text{-Cl})PP)Mn^{IV}(OH)]^+ + RCH_2OOH \rightarrow [(T(p\text{-Cl})PP)Mn^{III}]^+ + RCH_2OO^\bullet \quad (6)$$

4. Conclusions

In summary, we discovered that suitable aliphatic alcohols can exert remarkable beneficial effect on the aerobic controlled oxidation of toluene over (T(*p*-Cl)PP)MnF/NHPI and good conversion and product selectivity toward benzaldehyde and benzyl alcohol were achieved. The UV–vis spectral analysis of the toluene oxidation mixture showed that an active intermediate species $[(T(p\text{-Cl})PP)Mn^{IV}(O)(CH_3OH)]^{+\bullet}$ could be generated in the oxidation. We deduced that the formation of $[(T(p\text{-Cl})PP)Mn^{IV}(O)(CH_3OH)]^{+\bullet}$ is related to the better results observed. Current efforts are underway to elucidate the reaction mechanism further and the results will be reported in due course.

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