



# A moderate and efficient method for oxidation of ethylbenzene with hydrogen peroxide catalyzed by 8-quinolinolato manganese(III) complexes

Chunli Lu, Zaihui Fu\*, Yachun Liu, Fenglan Liu, Youyu Wu, Jinwei Qin, Xiangling He, Dulin Yin

Key Laboratory of Resource Fine-Processing and Advanced Materials of Hunan Province and Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Ministry of Education of China), College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, China

## ARTICLE INFO

### Article history:

Received 16 December 2009  
Received in revised form 20 July 2010  
Accepted 7 August 2010  
Available online 14 August 2010

### Keywords:

Ethylbenzene  
Catalysis  
Hydrogen peroxide  
8-Quinolinolato Mn(III) complexes  
Selective oxidation

## ABSTRACT

The oxidation of ethylbenzene with 30% aqueous hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) in an acetone–water medium at 30 °C was investigated using hexadentate 8-quinolinolato manganese(III) complexes ( $\text{Q}_3\text{Mn}^{\text{III}}$ ) as catalysts. The results indicated that the  $\text{Q}_3\text{Mn}^{\text{III}}$  complexes, with ammonium acetate and acetic acid as additives, selectively catalyzed the side chain oxidation of ethylbenzene at secondary carbon atoms, affording acetophenone as a major product. Among the  $\text{Q}_3\text{Mn}^{\text{III}}$  complexes examined, the 5,7-dibrominated  $\text{Q}_3\text{Mn}^{\text{III}}$  catalyst was the most active, and provided the ethylbenzene conversion of 26.1% and the oxidation yield of 65% under the optimum conditions. The influence of various parameters on the reaction was checked in detail. Based on the UV–vis spectra, a free radical mechanism for the  $\text{Q}_3\text{Mn}^{\text{III}}$  catalytic system was also proposed.

© 2010 Elsevier B.V. All rights reserved.

## 1. Introduction

Acetophenone as an important intermediate is increasingly used for the synthesis of some perfumes, pharmaceuticals, resins, alcohols, esters, aldehydes and tear gas, and as a solvent for cellulose ethers. Therefore, there has been considerable interest in the development of highly efficient processes for the production of acetophenone from ethylbenzene. Among these processes reported to date, the air oxidation process of ethylbenzene based on Co(II) and Mn(II) catalysts in acetic acid media is known [1]. However, the operation conditions in this process are often harsh, the reagent mixture is corrosive (bromide is used as a promoter) and the chemistry is rarely selective. N-Hydroxyphthalimide (NHPI) is usually used to improve the air oxidation of ethylbenzene [2–12], but the use of toxic acetonitrile ( $\text{CH}_3\text{CN}$ ) solvent and costly NHPI hampers its industrial application. The oxidation process of ethylbenzene with t-butyl hydroperoxide (TBHP) as the oxidant has been reported widely [13–17], but a higher TBHP wastage and the use of poisonous reagents make this process lose the competitive capacity. Aqueous hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) would be the ultimate green oxidant since it produces water as the sole by-product, and it is easy to be dealt with after reactions. The latest studies have therefore focused on the catalytic oxidation of ethylbenzene with  $\text{H}_2\text{O}_2$  as the terminal oxidant [18–27]. However, some of the

oxidation systems reported to date have one or more disadvantages, including the use of toxic reagents [19–21,26,27], relatively high operation temperature [19–21], low ethylbenzene concentration [22,26], and unsatisfactory  $\text{H}_2\text{O}_2$  efficiency [19]. Still it is highly desirable to develop an environmentally acceptable catalytic partial oxidation of ethylbenzene that operates under moderate conditions in the liquid phase with a high degree of selectivity.

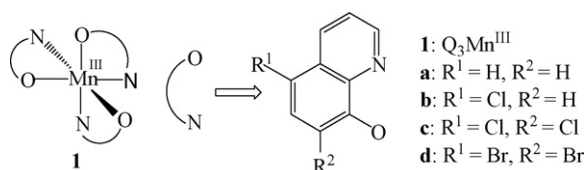
In our previous works, we have found that hexadentate 8-quinolinolato manganese(III) complexes ( $\text{Q}_3\text{Mn}^{\text{III}}$  presented in Scheme 1) can efficiently catalyze the epoxidation of olefins [28,29], the oxidation of alcohols [30] and the oxidation of thioanisole [31] with  $\text{H}_2\text{O}_2$  in a green water–acetone or pure acetone medium. Based on the recent successful applications of  $\text{Q}_3\text{Mn}^{\text{III}}$  catalysts in the reactions mentioned above, we are interested in the potential of  $\text{Q}_3\text{Mn}^{\text{III}}$  catalysts for ethylbenzene oxidation. Here, we report initial results from using  $\text{Q}_3\text{Mn}^{\text{III}}$  complexes to catalyze ethylbenzene oxidation with aqueous  $\text{H}_2\text{O}_2$  in a water–acetone medium containing ammonium acetate ( $\text{NH}_4\text{OAc}$ ) and acetic acid ( $\text{HOAc}$ ).

## 2. Experimental

### 2.1. Preparation and characterization of $\text{Q}_3\text{Mn}^{\text{III}}$ complexes

8-Hydroxyquinoline (8-HQ (**a**)), 5-chloro-8-HQ (**b**), 5,7-dichloro-8-HQ (**c**) and 5,7-dibromo-8-HQ (**d**) were purchased from Alfa Aesar. The other commercially available chemicals, such as ethylbenzene, acetone, ammonium acetate, acetic acid, 30 wt% aqueous  $\text{H}_2\text{O}_2$  and solvents, were laboratory-grade reagents from local sup-

\* Corresponding author. Tel.: +86 731 88872576; fax: +86 731 88872531.  
E-mail address: [fzhnu@tom.com](mailto:fzhnu@tom.com) (Z. Fu).



**Scheme 1.** The structures of  $Q_3Mn^{III}$  complexes.

pliers.  $Q_3Mn^{III}$  complexes **1a–1d** (Scheme 1) were prepared and characterized as following a reported procedure [28]. The liquid UV–vis spectral measurement for the  $Q_3Mn^{III}$ -catalyzed ethylbenzene oxidation process was recorded from 200 to 700 nm on a UV-3310 spectrophotometer (Hitachi) with a scanning rate of 800 nm/min at room temperature and the measured process described as follows. At room temperature (20 °C), 1  $\mu$ mol of **1d** was dissolved to 100 ml of acetone to obtain a slight yellow solution with **1d** concentration of  $1 \times 10^{-5}$  M. After scanning the UV–vis spectrum of **1d** solution (4 ml), 1.5 ml of aqueous solution containing 40  $\mu$ mol  $NH_4OAc$  and 20  $\mu$ mol  $HOAc$  were added to 10 ml of **1d** solution. After recording the spectral change of this solution, 20  $\mu$ mol of ethylbenzene was further added to the solution and then its spectral curve was measured. Finally, 30%  $H_2O_2$  (0.9  $\mu$ l, 8  $\mu$ mol) was added to the solution and its spectral change with time was recorded.

## 2.2. Procedure of oxidation

The general procedure for ethylbenzene oxidation is described as follows. At ambient temperature (30 °C), to stirred water–acetone (v/v, 1.5:5, 6.5 ml) a mixture of ethylbenzene (10 mmol), catalyst  $Q_3Mn^{III}$  (0.01 mmol),  $NH_4OAc$  (0.4 mmol), and  $HOAc$  (0.2 mmol), 30%  $H_2O_2$  (3 mmol) was added dropwise

during an appointed period (generally within half an hour). After  $H_2O_2$  was consumed completely, as shown by an inspection with potassium iodide–starch test paper, the catalyst was separated from the reaction mixture by filtration. The filtrate was analyzed on an Agilent 6890N gas chromatograph (GC) with an SE-54 quartz capillary column (30 m  $\times$  0.32 mm  $\times$  0.25  $\mu$ m) and flame ionization detector (FID) using bromobenzene as an internal standard. The column temperature was 120 °C. Both injector and detector temperatures were set at 250 °C. The isolated acetophenone and 1-phenylethanol were satisfactorily identified by comparing the MS spectra with those of both the authentic samples. In addition, treating the filtrate for 1 h with triphenylphosphine hardly changed the selectivity of products, which showed the absence of alkyl hydroperoxide in the products [23].

## 3. Results and discussion

### 3.1. Characterizations of $Q_3Mn^{III}$ complexes

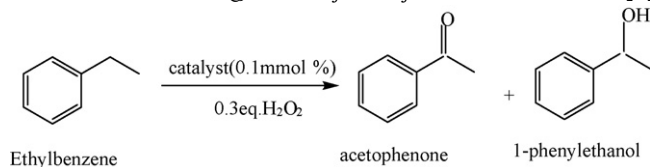
In our previous works, we showed that the  $Q_3Mn^{III}$  complexes (**1a–1d**) had a hexadentate structure with the distorted octahedral geometry via CHN and Mn elemental analyses, as well as a diffuse reflectance UV–vis spectroscopy technique [28,29]. Moreover, the B3LYP/6-311G+ (d) calculation indicated that the halogenated  $Q_3Mn^{III}$  complexes had a stronger distortion effect than **1a** [31].

### 3.2. Catalytic tests

Table 1 summarizes the data for  $Q_3Mn^{III}$ -catalyzed ethylbenzene oxidation with  $H_2O_2$  in acetone–water media. In the absence of catalyst, this reaction did not occur at 30 °C (entry 1), but it could proceed efficiently in the presence of  $Q_3Mn^{III}$  catalysts and  $NH_4OAc$ – $HOAc$  additives (entries 2–5), and the oxidation

**Table 1**

The results obtained from  $Q_3Mn^{III}$ -catalyzed ethylbenzene oxidation with  $H_2O_2$ <sup>a</sup>.



Entry	Catalyst	Additive (mmol)	Time (h)	TON <sup>b</sup>	Selectivity <sup>c</sup> (%)		Oxidation yield <sup>d</sup> (%)
					Ketone	Alcohol	
1 <sup>c</sup>	–	$NH_4OAc$ (0.4) + $HOAc$ (0.2)	24	–	–	–	–
2	<b>1a</b>		5	94	82	18	31
3	<b>1b</b>		5	105	79	21	35
4	<b>1c</b>		5	90	73	27	30
5	<b>1d</b>		6	142	74	26	47
6	<b>1d<sup>e</sup></b>		7	224	78	22	56
7	<b>1d<sup>f</sup></b>		5	256	80	20	51
8 <sup>g</sup>	<b>1d</b>		7	11.5	61	27	6
9 <sup>h</sup>	<b>1d</b>		1.5	150	100	–	75
10 <sup>i</sup>	–	–	7	3.5 <sup>i</sup>	51	25	–
11	<b>1d</b>	No additive	24	52	80	20	17
12	<b>1d</b>	$Na_2HPO_4$ (0.2)	6	60	80	20	20
13	<b>1d</b>	$NH_4OAc$ (0.4)	5	80	80	20	27
14	<b>1d</b>	$HOAc$ (0.2)	20	70	80	20	23

<sup>a</sup> Reaction conditions: Ethylbenzene (EB), 10 mmol; catalyst, 0.01 mmol; 30%  $H_2O_2$ , 3 mmol and water/acetone (3/10, 6.5 ml) at 30 °C. Conversion and selectivity were determined by GC using an internal standard technique.

<sup>b</sup> Number of moles of ethylbenzene consumed per mol of Mn ion.

<sup>c</sup> Selectivity for acetophenone (ketone) and 1-phenylethanol (alcohol).

<sup>d</sup> Mol% yield of oxidation products based on the amount of  $H_2O_2$ .

<sup>e</sup> 30%  $H_2O_2$ , 4 mmol.

<sup>f</sup> 30%  $H_2O_2$ , 5 mmol.

<sup>g</sup> Catalyst, 0.02 mmol; 30%  $H_2O_2$ , 4 mmol; 2,4-di-tert-butylphenol, 0.02 mmol.

<sup>h</sup> Using 1-phenylethanol (1 mmol), 30%  $H_2O_2$  (0.4 mmol) and catalyst **1d** (0.002 mmol).

<sup>i</sup> Using 15% peracetic acid (4 mmol) as an oxidant, given ethylbenzene conversion.

**Table 2**  
The effect of the concentration of ethylbenzene<sup>a</sup>.

Entry	EB (mmol)	H <sub>2</sub> O <sub>2</sub> (mmol)	Time (h)	EB conversion (mol%)	Oxidation yield (%)	Product selectivity (%)	
						Ketone	Alcohol
1	4.0	1.6	6	16.7	42	69	31
2	6.0	2.4	6	20.1	50	74	26
3	8.0	3.2	6	24.4	61	73	27
4	10.0	4.0	6	26.1	65	70	30
5 <sup>b</sup>	10.0	4.0	7	4.3	11	73	27
6	12.0	4.8	6	19.8	50	70	30
7	14.0	5.6	6	17.6	44	70	30

<sup>a</sup> Reaction conditions: Catalyst **1d**, 0.02 mmol; acetone, 5 ml; water, 1.5 ml; HOAc, 0.2 mmol; NH<sub>4</sub>OAc, 0.4 mmol; temperature, 30 °C.

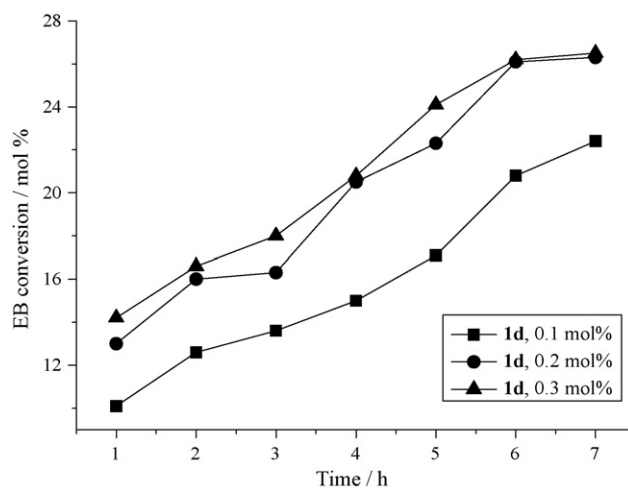
<sup>b</sup> **1d** system was treated with H<sub>2</sub>O<sub>2</sub> for 30 min before ethylbenzene was added.

products obtained were acetophenone (selectivity, 73–82%) and 1-phenylethanol (selectivity, 18–27%), arising from the side chain oxidation of ethylbenzene at secondary carbon atoms. Among the Q<sub>3</sub>Mn<sup>III</sup> complexes examined, the 5,7-dibrominated Q<sub>3</sub>Mn<sup>III</sup> (**1d**) was most active for this reaction, affording a high turnover number (TON, 142) and moderate oxidation yield (ca. 47%) at H<sub>2</sub>O<sub>2</sub>/ethylbenzene molar ratio of 0.3 (entry 5), which was likely due to the stronger distortion effect of **1d** than that of the other Q<sub>3</sub>Mn<sup>III</sup> complexes, as supported by the DFT calculations [31]. Entries 5–7 illustrate the effect of the amount of H<sub>2</sub>O<sub>2</sub> on the reaction. An increase in the amount from 3 to 4 mmol resulted in increased TON from 142 to 224 and oxidation yield from 47 to 56%. However, an attempt to further increase the amount from 4 to 5 mmol resulted in a marginal decrease of the oxidation yield from 56 to 51% (entries 5 vs 7). It is noteworthy that the selectivity of acetophenone slightly increased with the amount owing to further oxidation of 1-phenylethanol. Entry 8 demonstrates that the catalytic reaction was restrained markedly in the presence of 2,4-di-tert-butylphenol, indicating that it owns a feature of free radical mechanism. Entry 9 illustrates that 1-phenylethanol was oxidized easily to the corresponding acetophenone by H<sub>2</sub>O<sub>2</sub> in the coexistence of **1d** and NH<sub>4</sub>OAc–HOAc. Entry 10 shows that 3.5% of ethylbenzene was oxidized directly to acetophenone (51%), 1-phenylethanol (25%) and benzaldehyde (24%) while using 0.4 equiv. of peracetic acid.

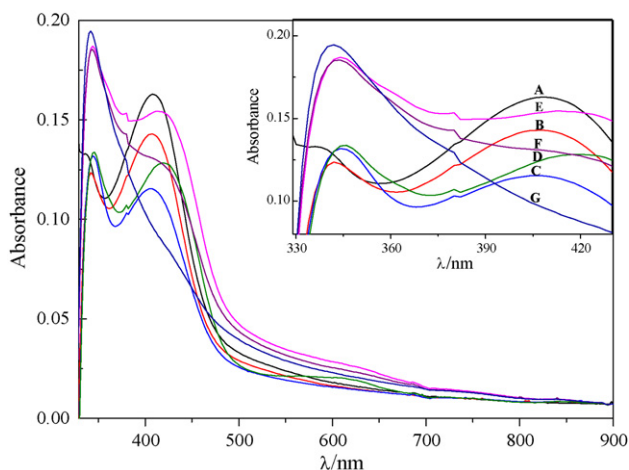
The effect of additives on the reaction was further investigated by using the most efficient **1d** as a catalyst (entries 11–14). Entry 11 illustrates that the reaction proceeded very slowly in the absence of additives and gave a relatively low TON (ca. 52) after 24 h. Among the additives examined, Na<sub>2</sub>HPO<sub>4</sub> (pH = 8.6 in the water–acetone medium) obviously accelerated reaction but hardly improved TON (entry 12). NH<sub>4</sub>OAc (pH = 8.1 here) significantly enhanced reaction rate and slightly improved TON (entry 13), whereas the use of HOAc (pH = 5.2 here) in place of NH<sub>4</sub>OAc resulted in a dramatic retardation of the reaction rate (entry 14). The best result was achieved upon using NH<sub>4</sub>OAc and HOAc mixtures as the additives (pH = 7.1 here), indicating that the pH value and OAc<sup>−</sup> ions play key role in the catalytic reaction. While using NH<sub>4</sub>OAc or NH<sub>4</sub>OAc–HOAc mixture as the additive, two different roles are possible. First, the weak basic NH<sub>4</sub>OAc, as proposed for salen–Mn<sup>III</sup>-catalyzed epoxidation of alkenes with H<sub>2</sub>O<sub>2</sub> [32,33], can promote the formation of HO<sub>2</sub><sup>−</sup> from H<sub>2</sub>O<sub>2</sub> which facilitates the formation of a hydroperoxy complex (Q<sub>3</sub>Mn<sup>III</sup>–OOH from Q<sub>3</sub>Mn<sup>III</sup>). This was supported by the fact that a weak basic Na<sub>2</sub>HPO<sub>4</sub> had an outstanding accelerated effect on this reaction but a weak acidic HOAc did not. Another possibility is that OAc<sup>−</sup> ions likely participate in this catalytic oxidative process via the formation of a peroxyacylmanganese(III) species (Q<sub>3</sub>Mn<sup>III</sup>–OOAc), as proposed by Montanari and co-workers for porphyrin–Mn<sup>III</sup>-catalyzed epoxidation of alkenes with H<sub>2</sub>O<sub>2</sub> in the presence of a lipophilic nitrogen heterocycle ligand and a carboxylic acid cocatalyst [34].

In the following experiments, the influence of the concentration of catalyst **1d** on the reaction was checked at H<sub>2</sub>O<sub>2</sub>/ethylbenzene molar ratio of 0.4. As illustrated in Fig. 1, the reaction rate and ethylbenzene conversion were dependent on the concentration of **1d**, when the concentration was ca. 0.1 mol%, the conversion smoothly increased with time and eventually got up to ca. 22.4% after H<sub>2</sub>O<sub>2</sub> was consumed (about 7 h). When the concentration increased to ca. 0.2 mol%, the reaction was accelerated, eventually affording the conversion of 26.1% and the oxidation yield of 65% after 6 h. However, an attempt to further increase the concentration (0.3 mol%) was actually invalid in improving the conversion. By the way, the selectivity of products was hardly influenced by the concentration of catalyst and reaction time.

Finally, the effect of ethylbenzene amount on the reaction was investigated using **1d** catalyst (0.02 mmol) at H<sub>2</sub>O<sub>2</sub>/ethylbenzene molar ratio of 0.4, and the results are listed in Table 2. Using the amount from 4 to 10 mmol resulted in the continuous and considerable increases of ethylbenzene conversion from 16.7 to 26.1% and oxidation yield from 42 to 65%, respectively (see entries 1–4 in Table 2). Notably, while adding H<sub>2</sub>O<sub>2</sub> for 30 min and then ethylbenzene, the catalysis efficiency was very low (see entry 5). This is likely because **1d** reacts with H<sub>2</sub>O<sub>2</sub> in advance to form some inactive intermediates for ethylbenzene oxidation in this situation and the pre-existence of ethylbenzene may efficiently restrain the formation of these intermediates, as supported by the following UV–vis spectral characterizations. This restraint effect should strengthen with ethylbenzene concentration, which can lead to the aforementioned concentration effect. However, an attempt to further increase the concentration actually resulted in the decreased ethylbenzene conversion and oxidation yield (entries 6–7). It is likely



**Fig. 1.** The effect of the concentration of catalyst on the oxidation of ethylbenzene (reaction conditions: ethylbenzene (10 mmol); 30% H<sub>2</sub>O<sub>2</sub> (4 mmol); water/acetone (1.5 ml/5 ml) at 30 °C).

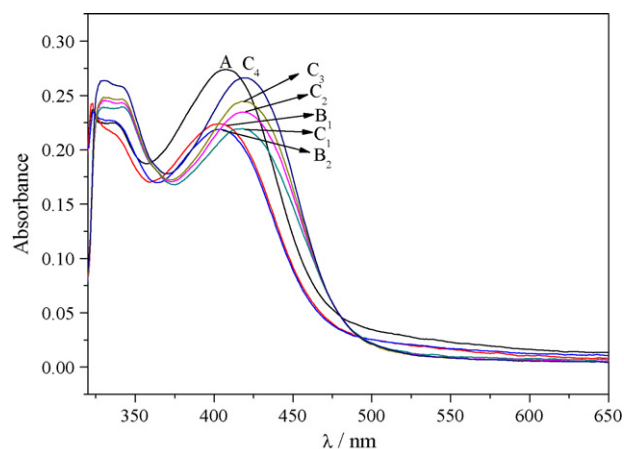


**Fig. 2.** UV-vis spectra of (A) a solution of **1d** in acetone ( $1.0 \times 10^{-5}$  M, 4 ml); (B) adding 40  $\mu\text{mol}$   $\text{NH}_4\text{OAc}$  and 20  $\mu\text{mol}$   $\text{HOAc}$  aqueous solution; (C) 10 min later of adding 20  $\mu\text{mol}$  ethylbenzene to the solution B; (D) 20 min later of adding 30%  $\text{H}_2\text{O}_2$  (8  $\mu\text{mol}$ ) to the solution C; (E) 30 min later; (F) 1 h later; (G) 8 h later. Inset is the amplified traces.

that the solubility of ethylbenzene becomes worse at the higher concentration, which can lead to an increase in the transfer mass resistance.

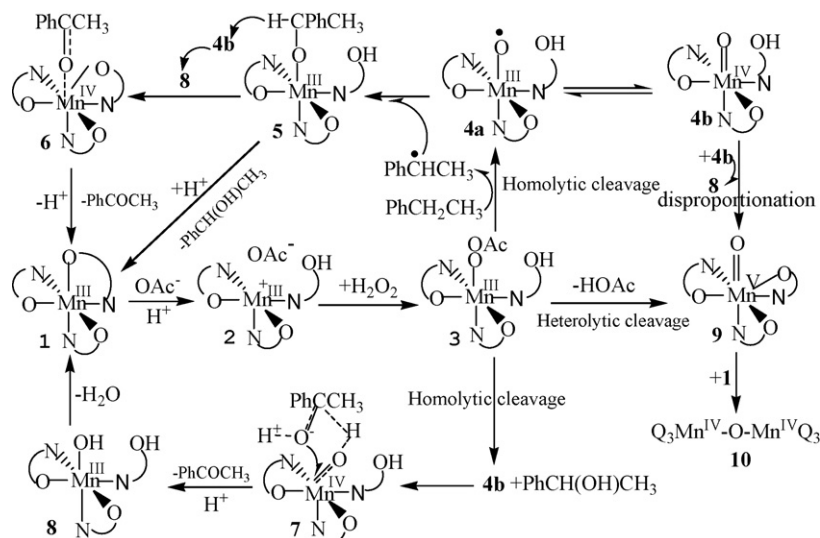
### 3.3. Reaction mechanism

The  $\text{Q}_3\text{Mn}^{\text{III}}$ -catalyzed ethylbenzene oxidation process was further monitored by a UV-vis spectroscopy technique. Fig. 2 is a stepwise overlay of UV-vis spectra for the **1d** complex in an acetone medium at room temperature. In this, curve A is the spectrum of **1d** in acetone. The absorption band with  $\lambda_{\text{max}} \sim 408$  nm can be assigned to the metal to ligand charge transfer (MLCT) [35]. When the  $\text{NH}_4\text{OAc}$ - $\text{HOAc}$  aqueous solution was added to the A solution, the MLCT band experienced a decrease in intensity (see curve B). After adding ethylbenzene to the B solution during 20 min, the MLCT absorbance decreased further (see curve C). This hypochromic effect is likely originated from the transformation of hexadentate  $\text{Q}_3\text{Mn}^{\text{III}}$  (**1** in Scheme 2) to the corresponding pentadentate one (**2**) in the presence of  $\text{NH}_4\text{OAc}$ - $\text{HOAc}$ , which can lead to a decrease in its coordination capacity. On adding

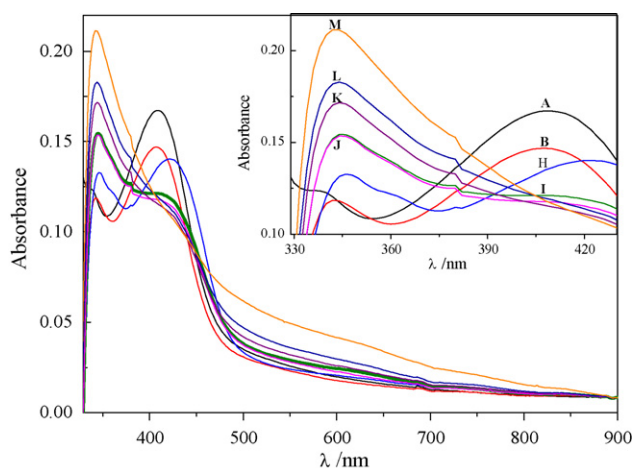


**Fig. 3.** UV-vis spectra of (A) a solution of **1d** in acetone-water ( $1.0 \times 10^{-5}$  M, 4 ml); (B<sub>1</sub>) adding 8  $\mu\text{mol}$  peracetic acid to the A solution after 10 min; (B<sub>2</sub>) 30 min later; (C<sub>1</sub>) 10 min later of using  $\text{NH}_3 \cdot \text{H}_2\text{O}$  to adjust the pH value of B<sub>2</sub> solution to 7.5; (C<sub>2</sub>) 20 min later; (C<sub>3</sub>) 30 min later; (C<sub>4</sub>) 50 min later.

$\text{H}_2\text{O}_2$  to the C solution further, the MLCT band immediately shifted to  $\lambda_{\text{max}} \sim 424$  nm, and its intensity increased obviously (see curve D). Notably, the reaction **1d** with peracetic acid in acidic acetone-water media resulted only in a marginal blue-shift and significant decrease of the MLCT band, indicating that the formation of peroxyacyl manganese(III) species ( $\text{Q}_3\text{Mn}^{\text{III}}\text{-OOAc}$ ) does not lead to the red-shift of MLCT band. When the pH value of this reaction mixture was adjusted to 7.5 with  $\text{NH}_3 \cdot \text{H}_2\text{O}$ , the red-shift immediately occurred (see Fig. 3), which was likely assigned to the ligand to metal charge transfer (LMCT) of the  $\text{Mn}^{\text{IV}}=\text{O}$  species generated via a homolytic cleavage of peroxyacyl manganese(III) species ( $\text{Q}_3\text{Mn}^{\text{III}}\text{-OOAc}$ ), as reported by Groves and co-workers for the reaction of porphyrin- $\text{Mn}^{\text{III}}$  and porphyrin- $\text{Fe}^{\text{III}}$  with *m*-chloro-peroxybenzoic acid in basic or neutral conditions [36,37]. Subsequently, the  $\text{Mn}^{\text{IV}}=\text{O}$  species gradually became obscure with time, and eventually disappeared after 8 h (see curves E-G). At the same time, the trace in 380–400 nm ran up in 30 min (see curve E), and then dropped slowly with time, finally disappeared after 8 h (curves F-G), as observed by us for the  $\text{Q}_3\text{Mn}^{\text{III}}$ -catalyzed cyclohexanol oxidation with  $\text{H}_2\text{O}_2$  [30]. While the absorbance in 500–700 nm, which was assigned to the LMCT band of the  $\text{Mn}^{\text{V}}=\text{O}$  generated through a heterolytic cleavage of O-O bond

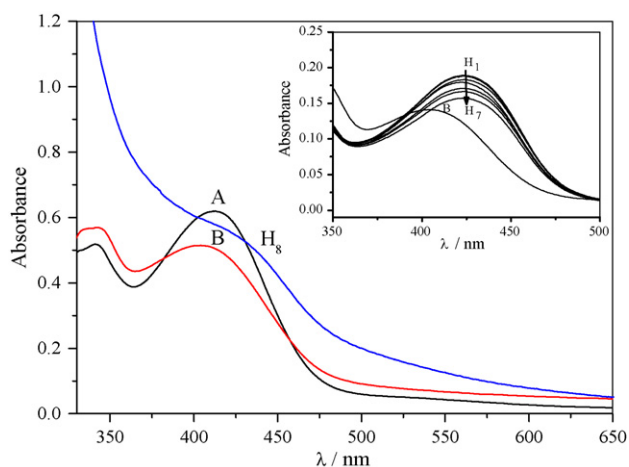


**Scheme 2.** Possible catalytic pathways for  $\text{Q}_3\text{Mn}^{\text{III}}$ -catalyzed ethylbenzene.



**Fig. 4.** UV-vis spectra of (A) a solution of **1d** in acetone ( $1.0 \times 10^{-5}$  M, 4 ml); (B) adding  $40 \mu\text{mol}$   $\text{NH}_4\text{OAc}$  and  $20 \mu\text{mol}$   $\text{HOAc}$  aqueous solution; (H) adding  $30\%$   $\text{H}_2\text{O}_2$  ( $8 \mu\text{mol}$ ) to the solution B; (I) 30 min later; (J) 30 min later after adding  $20 \mu\text{mol}$  ethylbenzene to the solution I; (K) 30 min later; (L) 1 h later; (M) 8 h later. Inset is the amplified traces.

[33,34], still existed in the whole process although its intensity decreased slightly. These spectral changes likely imply that the  $\text{Mn}^{\text{IV}}=\text{O}$  species plays a key role in the oxidation of ethylbenzene, but the  $\text{Mn}^{\text{V}}=\text{O}$  species should not be mainly responsible for the present oxidation process, which was further confirmed by the following spectral experiments. Namely, (i) if the B solution was treated with  $\text{H}_2\text{O}_2$  for 30 min before adding ethylbenzene, its  $\text{Mn}^{\text{V}}=\text{O}$  absorbance became more strong and the spectral change in  $380\text{--}400$  nm was obscure (see curves H–M in Fig. 4). And (ii) if the B solution was only treated with  $\text{H}_2\text{O}_2$  for 8 h, its spectral change could very clearly sketch the formation of  $\text{Mn}^{\text{IV}}=\text{O}$  species and its final transformation to the  $\text{Mn}^{\text{V}}=\text{O}$  although the deactivation of catalyst caused by its dimerization and oxidative degradation, inevitably occurred under such situation (see Fig. 5). Both the spectral experiments clearly indicate that the  $\text{Mn}^{\text{IV}}=\text{O}$  species is easy to be converted to the nonsignificant  $\text{Mn}^{\text{V}}=\text{O}$  and deactivated species in the absence of ethylbenzene, which can lead a very low catalysis efficiency, as supported by the foregoing catalytic experiment (see entry 5 in Table 2).



**Fig. 5.** UV-vis spectra of (A) a solution of **1d** in acetone ( $1.0 \times 10^{-5}$  M, 4 ml); (B) adding  $40 \mu\text{mol}$   $\text{NH}_4\text{OAc}$  and  $20 \mu\text{mol}$   $\text{HOAc}$  aqueous solution; ( $\text{H}_8$ ) 8 h later after adding  $30\%$   $\text{H}_2\text{O}_2$  ( $8 \mu\text{mol}$ ) to the solution B; inset shows an initial visible absorption spectral changes after adding  $30\%$   $\text{H}_2\text{O}_2$  ( $8 \mu\text{mol}$ ) to the solution B, spectral scanning is taken at average 3 min intervals ( $\text{H}_1\text{--H}_7$ ).

From the above facts, the  $\text{Q}_3\text{Mn}^{\text{III}}$ -catalyzed oxidation of ethylbenzene with  $\text{H}_2\text{O}_2$  is envisioned to proceed via a following radical pathway (see Scheme 2), as supported by the above experiment of using 2,4-di-tert-butylphenol as a radical eliminating species (see entry 8 in Table 1). First,  $\text{Q}_3\text{Mn}^{\text{III}}$  (**1** in Scheme 2) easily cleaved the longest Mn–O bond to form a pentadentate  $[\text{Q}_3\text{Mn}^{\text{III}}]^+\text{OAc}^-$  with a pendant hydroxyl group (**2**) in the presence of  $\text{NH}_4\text{OAc}\text{--HOAc}$  or  $\text{NH}_4\text{OAc}$ . Then, **2** reacts with  $\text{H}_2\text{O}_2$  to form a  $\text{Q}_3\text{Mn}^{\text{III}}\text{--OOAc}$  species (**3**). Finally, **3** rapidly undergoes a homolytic cleavage of

its O–O bond to a  $\text{Q}_3\text{Mn}^{\text{III}}\text{--O}^\bullet$  (**4a**) and  $\text{PhCHCH}_3$  free radicals in the participation of ethylbenzene, as described in some literatures [36–39]. Notably, **4a**, as reported by Groves and co-workers for the homolytic O–O bond cleavage reaction of acylperoxomanganese(III) porphyrin [37], is quickly and reversibly converted to  $\text{Q}_3\text{Mn}^{\text{IV}}=\text{O}$  (**4b**) through one electron transfer of metal to oxygen, which just accords with the feature of the aforementioned  $\text{Mn}^{\text{IV}}$  species in UV-vis spectra. A pathway is possible to result in the generation of  $\text{PhCH}(\text{OH})\text{CH}_3$ . First, **4a** easily combines with

$\text{PhCHCH}_3$  to give  $\text{Q}_3\text{Mn}^{\text{III}}\text{--O--CH}(\text{CH}_3)\text{Ph}$  (**5**) before its transformation to **4b**, subsequently, the decomposition of **5** can result in the formation of  $\text{PhCH}(\text{OH})\text{CH}_3$  and the regeneration of catalyst  $\text{Q}_3\text{Mn}^{\text{III}}$ . Two pathways are possible to result in the generation of  $\text{PhCOCH}_3$ . First, another secondary H atom on **5** may be further abstracted by **4b** to produce an  $\text{Mn}^{\text{IV}}\text{--OCCH}_3\text{Ph}$  species **6** before its decomposition. Then, **6** is decomposed to give  $\text{PhCOCH}_3$  and the regenerated catalyst **1**. Another possibility is that **4b** may oxidize the fresh formation of  $\text{PhCH}(\text{OH})\text{CH}_2$  to give a  $\text{Mn}^{\text{IV}}$  species (**7**), then, **7** is decomposed to generate a  $\text{PhCOCH}_3$  and  $\text{Q}_3\text{Mn}^{\text{III}}\text{--OH}$  species (**8**), finally, the intramolecular dehydration of **8** can lead to the regeneration of catalyst **1**, as reported by us for the  $\text{Q}_3\text{Mn}^{\text{III}}$ -catalyzed oxidation of alcohols with  $\text{H}_2\text{O}_2$  [30]. Notably, the above reaction results, in which a high ketone/alcohol molar ratio was obtained and this ratio was independent on the time, support that the formation of  $\text{PhCOCH}_3$  is mainly originated from the first pathway. By the way, the disproportionation of **4b**, as reported by some literature [36,40,41], can lead to the generation of  $\text{Q}_3\text{Mn}^{\text{V}}=\text{O}$  (**9**) and **8** although the formation of **9** via a heterolytic cleavage of O–O bond of **3** cannot be excluded in the present conditions. It is anticipated that this disproportionate reaction occurs more easily in the absence of ethylbenzene, as observed in the UV-vis spectra. The combination of **9** with **1** can lead to the formation of a deactivated  $\mu$ -oxomanganese(IV) dimer  $\text{Q}_3\text{Mn}^{\text{IV}}\text{--O--Mn}^{\text{IV}}\text{Q}_3$  (**10**) with a characteristic absorption band at  $\lambda_{\text{max}} \sim 364$  nm, as reported by Srinivasan et al. for the salen- $\text{Mn}^{\text{III}}$ -catalyzed epoxidation of olefins [42].

#### 4. Conclusions

For the first time we have developed an efficient and moderate method for ethylbenzene oxidation with  $\text{H}_2\text{O}_2$  catalyzed by hexadentate  $\text{Q}_3\text{Mn}^{\text{III}}$  complexes in acetone–water media, and proposed a free radical mechanism for the  $\text{Q}_3\text{Mn}^{\text{III}}$ -mediated catalytic oxidation system. Having found these kinds of  $\text{Q}_3\text{Mn}^{\text{III}}$  complexes, we are interested in exploiting the potential applications of the other 8-quinolinolato metal complexes in organic synthesis.

#### Acknowledgements

We acknowledge the financial support for this work by the National Natural Science Foundation of China (20873040, 20573035) and the Youth Foundation of Hunan Normal University (53112-1658).

## References

- [1] H. Ma, J. Xu, C. Chen, Q.H. Zhang, J.B. Ning, H. Miao, L.P. Zhou, X.Q. Li, *Catal. Lett.* 113 (2007) 3–4.
- [2] S.S. Bhoware, S. Shylesh, K.R. Kamble, A.P. Singh, *J. Mol. Catal. A* 255 (2006) 123–130.
- [3] I.C. Chisem, K. Martin, M.T. Shieh, J. Chisem, J.H. Clark, R. Jachuck, D.J. Macquarrie, J. Rafelt, C. Ramshaw, K. Scott, *Org. Process Res. Dev.* 1 (1997) 365–369.
- [4] T. Hara, T. Iwahama, S. Sakaguchi, Y. Ishii, *J. Org. Chem.* 66 (2001) 6425–6431.
- [5] W.W.Y. Lam, S.M. Yiu, J.M.N. Lee, S.K.Y. Yau, H.K. Kwong, T.C. Lau, D. Liu, Z.Y. Lin, *J. Am. Chem. Soc.* 128 (2006) 2851–2858.
- [6] C. Walling, C. Zhao, G.M. El-Taliaw, *J. Org. Chem.* 48 (1983) 4910–4914.
- [7] T. Dohi, N. Takenaga, A. Goto, H. Fujioka, Y. Kita, *J. Org. Chem.* 73 (2008) 7365–7368.
- [8] R. Alcántara, L. Canoira, P.G. Joao, J.M. Santos, I. Vázquez, *Appl. Catal. A* 203 (2000) 259–268.
- [9] R. Alcántara, L. Canoira, P.G. Joao, J.P. Pérez-Mendo, *Appl. Catal. A* 218 (2001) 269–279.
- [10] Y. Ishii, T. Iwahama, S. Sakaguchi, K. Nakayama, Y. Nishiyama, *J. Org. Chem.* 61 (1996) 4520–4526.
- [11] I. Hermans, J. Peeters, P.A. Jacobs, *J. Org. Chem.* 72 (2007) 3057–3064.
- [12] S.D. George, S.C. Sherman, A.V. Iretskii, M.G. White, *Catal. Lett.* 65 (2000) 181–183.
- [13] S. Vetrivel, A. Pandurangan, *J. Mol. Catal. A* 217 (2004) 165–174.
- [14] K. George, S. Sugunan, *Catal. Commun.* 9 (2008) 2149–2153.
- [15] T.H. Bennur, D. Srinivas, S. Sivasanker, *J. Mol. Catal. A* 207 (2004) 163–171.
- [16] M. Rogovin, R. Neumann, *J. Mol. Catal. A* 138 (1999) 315–318.
- [17] S. Boitsov, A. Riahi, J.C.R. Muzart, *Surf. Chem. Catal.* 3 (2000) 747–750.
- [18] M.R. Maurya, M. Kumar, U. Kumar, *J. Catal. Mol. A* 273 (2007) 133–143.
- [19] M.R. Maurya, A. Arya, P. Adao, J. Costa Pessoa, *Appl. Catal. A* 351 (2008) 239–252.
- [20] N.K. Mal, A.V. Ramaswamy, *Appl. Catal. A* 143 (1996) 75–85.
- [21] T. Radhika, S. Sugunan, *Catal. Commun.* 8 (2007) 150–156.
- [22] M. Klopstra, R. Hage, R.M. Kellogg, B.L. Feringa, *Tetrahedron Lett.* 44 (2003) 4581–4584.
- [23] G.B. Shul'pin, T. Sooknoi, L.S. Shul'pina, *Petrol. Chem.* 48 (2008) 36–39.
- [24] H.R. Lucas, L. Li, A.A.N. Sarjeant, M.A. Vance, E.I. Solomon, K.D. Karlin, *J. Am. Chem. Soc.* 131 (2009) 3230–3245.
- [25] M. Szalaniec, M. Witko, J. Heider, *J. Mol. Catal. A* 286 (2008) 128–136.
- [26] V. Bolland, D. Mathieu, N. Pons-Y-Moll, J.F. Bartoli, F. Banse, P. Battioni, J.J. Girerd, D. Mansuy, *J. Mol. Catal. A* 215 (2004) 81–87.
- [27] K.O. Xavier, J. Chacko, K.K. Mohammed Yusuff, *Appl. Catal. A* 258 (2004) 251–259.
- [28] S. Zhong, Y.M. Tan, Z.H. Fu, Q.J. Xie, F. Xie, X.P. Zhou, Z.P. Ye, G.S. Peng, D.L. Yin, *J. Catal.* 256 (2008) 154–158.
- [29] S. Zhong, Y.M. Tan, Z.H. Fu, Q.J. Xie, F. Xie, X.P. Zhou, Z.P. Ye, G.S. Peng, D.L. Yin, *Adv. Synth. Catal.* 350 (2008) 802–806.
- [30] Z.P. Ye, Z.H. Fu, S. Zhong, F. Xie, X.P. Zhou, F.L. Liu, D.L. Yin, *J. Catal.* 261 (2009) 110–115.
- [31] X. Fang, Z.H. Fu, S. Zhong, Z.P. Ye, X.P. Zhou, F.L. Liu, C.Y. Rong, L.Q. Mao, D.L. Yin, *J. Mol. Catal. A* 307 (2009) 93–97.
- [32] A.M.d'A. Rocha Gonsalves, R.A.W. Johnstone, M.M. Pereira, J. Shaw, *J. Chem. Soc. Perkin Trans. 1* (1991) 645–649.
- [33] P. Pietikäinen, *Tetrahedron* 54 (1998) 4319–4326.
- [34] P.L. Anelli, S. Banfi, F. Montanari, S. Quici, *J. Chem. Soc. Chem. Commun.* (1989) 779–780.
- [35] S.M. Crawford, *Spectrochim. Acta* 19 (1963) 225–270.
- [36] J.T. Groves, M.K. Stern, *J. Am. Chem. Soc.* 109 (1987) 3812–3814.
- [37] J.T. Groves, Y. Watanabe, *Inorg. Chem.* 25 (1986) 4808–4810.
- [38] J.T. Groves, Y. Watanabe, *J. Am. Chem. Soc.* 110 (1988) 8443–8452.
- [39] S. Ban, M. Cavazzini, F. Coppa, S.V. Barkanova, O.L. Kaliya, *J. Chem. Soc. Perkin Trans. 2* (1997) 1577–1583.
- [40] J.T. Groves, T. Takahashi, *J. Am. Chem. Soc.* 105 (1983) 2073–2074.
- [41] C.L. Hill, F.J. Hollander, *J. Am. Chem. Soc.* 104 (1982) 7318–7319.
- [42] K. Srinivasan, P. Michaud, J.K. Kochi, *J. Am. Chem. Soc.* 108 (1986) 2309–2320.