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Aerobic Oxidation of *p*-Toluic Acid to Terephthalic Acid over T(*p*-Cl)PPMnCl/Co(OAc)$_2$ Under Moderate Conditions

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Abstract The aerobic oxidation of *p*-toluic acid to terephthalic acid over tetra(*p*-chlorophenylporphinato)manganese (T(*p*-Cl)PPMnCl)/cobalt acetate was reported for the first time. The co-catalysis of T(*p*-Cl)PPMnCl/Co(OAc)$_2$ was also studied. The studies indicated that the PTA oxidation was influenced by the catalyst composition, catalyst concentrations and reaction conditions. A preliminary mechanism of this co-catalyzed oxidation reaction was proposed based on experimental observations.

Keywords Metalloporphyrin · Cobalt acetate · co-Catalysis · *p*-Toluic acid · Oxidation · Terephthalic acid

1 Introduction

The preparation of terephthalic acid (TPA) via the aerobic oxidation of *p*-xylene (PX) is a very important industrial process from both economical and environmental aspects [1, 2]. In practice, the oxidation of PX with air to TPA is now carried out in HOAc (80%) using Co(OAc)$_2$/Mn(OAc)$_2$/HBr as catalysts on an industrial scale worldwide. The low concentration of the reactants and the use of the bromide make the low efficiency and high environmental impact and corrosion of reactors becoming the major shortcomings [3, 4]. The development of new PX oxidation processes fitting the requirements of green chemistry still remains a challenge.

In fact, the difficulty of the aerobic oxidation of PX to TPA lies in the oxidation of *p*-toluic acid (PTA) with air to TPA. Chemically, the aerobic oxidation of PX to TPA involves the aerobic oxidation of PX to PTA and the subsequent oxidation of PTA with air to TPA. However, the oxidation of PTA to TPA is much more difficult than the oxidation of PX to PTA [5]. So the effective oxidation of PTA to TPA with air becomes the key step of the aerobic oxidation of PX to TPA. The methyl group of PTA will be deactivated by the electron withdrawing effect of the –COOH group once one methyl group of PX is oxidized, and the reactivity of PTA is only about one-tenth of PX [2]. So it is feasible to realize the effective oxidation of PX to TPA through two steps. The work we have reported [6, 7] has solved the step of the oxidation of PX to PTA, however, the oxidation of PTA to TPA still remains a challenge to the oxidation of PX to TPA. So it is essential to explore how to oxidize PTA to TPA effectively under moderate conditions.

Since 1960s, people have been trying to discover better catalytic ways for PTA oxidation and much progress has been achieved. Higashijima and Nagayama [8] carried out the PTA oxidation with molecular oxygen over ruthenium-substituted heteropolyanion in water under the conditions of 200 °C and 6 MPa. Toland et al. [9] developed the method of PTA oxidation with aqueous base and sulfur at high-pressure over 15 MPa. Emerson et al. [10] conducted the PTA oxidation with oxygen in the presence of Fe_2O_3 and K_2CO_3 in KOH solution at high-pressure (700 psi) and 240 °C. Ishii et al. [11] developed a new bromide free method for the oxidation of PTA in HOAc with 10% of NHPI, 0.5% of Co(OAc)$_2$ and 0.5% of Mn(OAc)$_2$ as catalyst at 100 °C to yield TPA. Givens et al. [12] reported that the oxidation of PTA could be accomplished by cobalt and N-hydroxysuccinimide co-catalyzed reactions with dioxygen under the conditions of 25 °C and 233 psi in

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24 h. Zuo et al. [13] made use of a unique combination of $Co(OAc)_2$ with zirconium tetrakis(acetylacetonate) to realized the oxidation of PTA using ketones as promoters under the conditions of 100 °C and 60 bar in 24 h. Saha and Espenson [14] carried out the autoxidation of PTA with the $Co(OAc)_2/Mn(OAc)_2/Br^-$ catalyst in the presence of trifluoroacetic acid. However, above achievements did not agitate the industrial preparation of TPA catalyzed by $Co(OAc)_2/Mn(OAc)_2/Br$ and these catalyst system still suffered from high catalyst concentration, the use of bromide as a promoter, high solvent proportion, serious decarboxylation and rigorous reaction conditions.

This paper describes the aerobic oxidation of PTA to TPA over T(*p*-Cl)PPMnCl/$Co(OAc)_2$ under moderate reaction conditions. The T(*p*-Cl)PPMnCl/$Co(OAc)_2$ system has the advantage of low catalyst loading, friendly environmental effects, moderate reaction conditions, and low proportion of the solvent. Mechanism of this co-catalyzed oxidation reaction was proposed based on experimental observations.

2 Experimental

2.1 Instruments and Reagents

MS spectra were determined on an Agilent 1100 LC–MS. A Bruck 400 MHz spectrometer was used for ^{1}HNMR analysis of porphyrins in $CDCl_3$. IR spectra were recorded on a PE-783 Spectrometer. UV–Vis spectra were obtained on a ShimadzuUV-2450 spectrometer. A Perkin-Elmer 2400 elementary analyzer was used for elemental analysis. The high-pressure reactor with high speed magnetic agitating and CYS-1 automatic oxygen-measuring instrument is similar to that reported previously [15]. Cobalt acetate was synthesized according to a previously published procedure [16], and the conversion of cobaltous acetate to cobaltic acetate as determined by iodometric titration was 54%. T(*p*-Cl)PPMnCl was synthesized and purified according to documented procedures [17]. The structure was characterized by UV–Vis,IR,MS and ^{1}HNMR, and analytical data were consistent with the document [7]. PTA was purified by recrystallization and analyzed by HPLC to ensure the absence of impurities before use. Other reagents were of analytical grade all.

2.2 General Procedure for PTA Oxidation

2.2.1 *Oxidation of PTA at Elevated Pressure*

The procedures of PTA oxidation with air catalyzed by manganeseporphyrin and cobalt acetate were carried out as following: 100 g PTA, 100 g acetic acid, 1.19×10^{-5} mol T(*p*-Cl)PPMnCl and 4.02×10^{-4} mol $Co(OAc)_2 \cdot 4H_2O$ were charged into the reactor; nitrogen was injected to maintain the pressure of 1.2 MPa at first in order to heat the mixtures to 190 °C and assure the non-occurrence of reactions during the stage of heating; the mixtures were heated to 190 °C, then air was injected at the speed of 160 L/h and the reaction system pressure was maintained at 1.2 MPa. An automatic gas-measuring instrument was used to measure the O_2 concentration of tail gas on-line. After the reaction completed, the autoclave was cooled to room temperature and the products were quantitatively analyzed by HPLC as reported previously [7].

2.2.2 *Oxidation of PTA at Atmospheric Pressure*

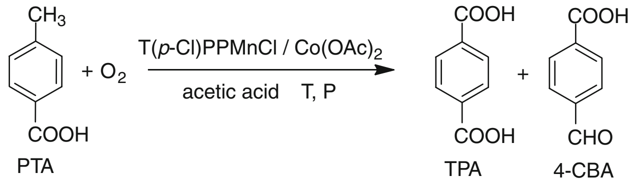
Oxidation of PTA at atmospheric pressure was carried out according to the following procedure: 1.5 g of PTA and 25 mL of HOAc as well as precisely weighed catalyst were placed in a 100-mL three-necked flask (in dark) equipped with condenser and magnetic stirring. Oxygen (0.1 MPa) was continuously introduced into the flask at flow rate of 4.2 L/h while the temperature was kept at 391 K. The contents of hydroperoxides of the oxidation products were determined by an iodometric method.

3 Results and Discussion

3.1 Aerobic Oxidation of PTA over T(*p*-Cl)PPMnCl/$Co(OAc)_2$

The products of PTA aerobic oxidation over T(*p*-Cl)PPMnCl/$Co(OAc)_2$, identified by LC–MS and also by HPLC co-injection of commercially available authentic samples, consisted mainly of terephthalic acid (TPA) and 4-carboxybenzalaldehyde (4-CBA), as shown in Scheme 1.

The changes of the yield and selectivity of products with the reaction time were shown in Fig. 1a and b, respectively. The plots showed that the yield of TPA increased rapidly in the initial 3 h, and the TPA selectivity increased from 76.2% of 0.5 h to 92.7% of 3 h, and the increase rate of TPA slowed with the further increase of time. The yield of 4-CBA changed slowly after 0.5 h, and the selectivity of 4-CBA reduced rapidly from 23.8% (0.5 h) to 9.21% (2 h)



Scheme 1 Oxidation of *p*-toluic acid with air over T(*p*-Cl)PPMnCl/$Co(OAc)_2$

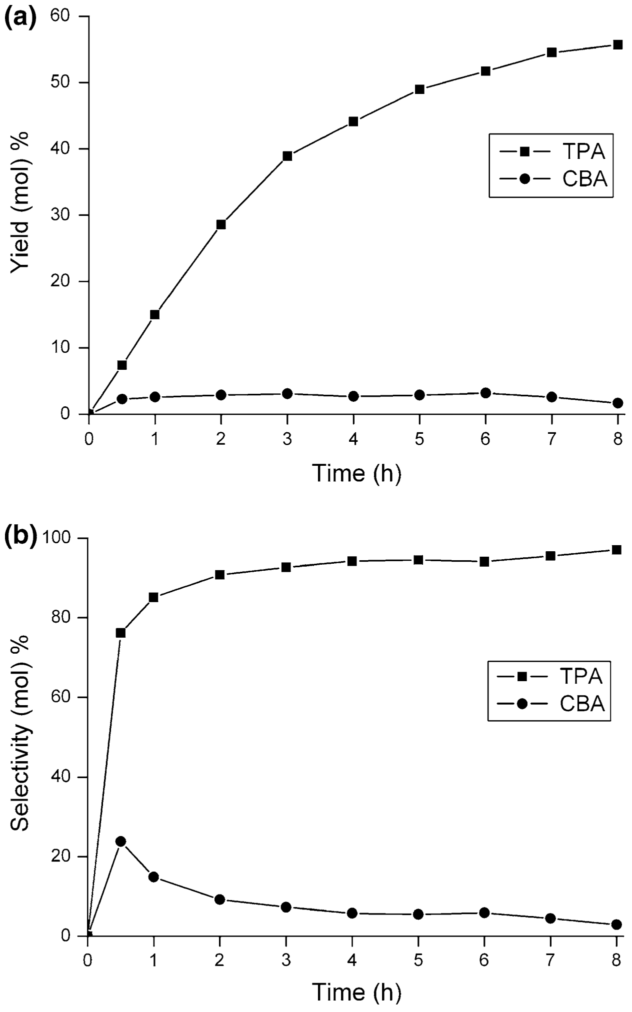


Fig. 1 Effect of reaction time on the products yield (**a**) and selectivity (**b**). Reaction conditions: PTA, 100 g; HOAc, 100 g; T(*p*-Cl)PPMnCl, 16.2 ppm; Co(OAc)$_2$·4H$_2$O, 548 ppm; air pressure, 1.2 MPa; 190 °C; air flow, 160 L h^{-1}

in the initial 2 h followed by a slow decrease in the next 6 h. The yield of TPA reached 54.5%, and 95.5% of selectivity was produced at 7.0 h. The result showed that the PTA could be effectively oxidized to TPA with air over T(*p*-Cl)PPMnCl/Co(OAc)$_2$.

3.2 Comparison of Catalyst system Composition

The aerobic oxidation of PTA was carried out using four different catalyst systems, i.e., T(*p*-Cl)PPMnCl, Co(OAc)$_2$, Mn(OAc)$_2$/Co(OAc)$_2$ and T(*p*-Cl)PPMnCl/Co(OAc)$_2$, and the results were summarized in Table 1.

When Co(OAc)$_2$ was used as the catalyst at 190 °C under 1.2 MPa and 160 L h^{-1} airflow for 7 h, the reaction conversion reached 45.1% while the selectivity of TPA was 94.3%. When the catalyst was switched to T(*p*-Cl)PPMnCl, there was no TPA produced while 1.1% of PTA reacted. The conversion was only 45.6% in the presence of 16.2 ppm Mn(OAc)$_2$ and 548 ppm Co(OAc)$_2$ for 7 h. To our surprise, when the same amount of T(*p*-Cl)PPMnCl was added to the reaction mixture over Co(OAc)$_2$, the conversion reached 57.1% which was much higher than that when the two components were used alone and the selectivity of TPA increased to 95.5% in 7 h. Both the PTA conversion and TPA yield could be increased significantly when T(*p*-Cl)PPMnCl and Co(OAc)$_2$ were used together. The results suggest that co-catalysis between the two catalysts may be operative in the aerobic oxidation of PTA.

3.3 Effect of Catalyst Concentration

3.3.1 Effect of Co(OAc)$_2$ Concentration

One can see from Table 2 that when the concentration of Co(OAc)$_2$ increased from 1.37 × 10^2 ppm to 1.10 × 10^3 ppm, the PTA conversion and the selectivity of TPA increased first, and then decreased. The optimal concentration of Co(OAc)$_2$ was 5.48 × 10^2 ppm. When the concentration of Co(OAc)$_2$ was either higher or lower than the optimal concentration, the PTA conversion and selectivity of TPA all suffered. The PTA conversion increased from 14.6% to 51.9% and the selectivity of TPA increased from 81.8 to 94.5% with the increases of the concentration of Co(OAc)$_2$ from 1.37 × 10^2 ppm to 5.48 × 10^2 ppm. However, the conversion decreased with the further increase of the Co(OAc)$_2$ concentration. It may be relative to the different Co^{3+}/Co^{2+} and the 4-carboxyl benzolperoxy chain radicals concentration [18] at the different concentration of Co(OAc)$_2$.

3.3.2 Effect of T(p-Cl)PPMnCl Concentration

The concentration of T(*p*-Cl)PPMnCl influenced the oxidation of PTA as well. We can see from Table 3 that the optimal concentration of T(*p*-Cl)PPMnCl is 16.2 ppm. When the concentration of T(*p*-Cl)PPMnCl increased from 3.2 to 16.2 ppm, the PTA conversion increased from 45.3 to 51.9%. But the PTA conversion decreased with the further increase of T(*p*-Cl)PPMnCl concentration when the concentration of T(*p*-Cl)PPMnCl was more than 16.2 ppm. Moreover, the PTA conversion was only 47.1% when 22.7 ppm T(*p*-Cl)PPMnCl was used as catalyst. This behavior was identified as the 'catalyst-inhibitor conversion' [19]. A possible reason related to this phenomenon was that metalloporphyrin could react with oxo-radical RO to produce the non-radical product, and the chain initiation was terminated. In addition, the metalloporphyrins tend to form catalytically inactive dimeric μ-oxo- and/or μ-peroxo-bridged dimetal species when its concentration surpassed the critical value, which was not in fovor of the catalysis

Table 1 Effect of catalyst system composition on PTA oxidation

Catalyst composition	Reaction time (h)	Conversion (%)	Selectivity (%)	
			TPA	CBA
$Co(OAc)_2$	3	39.0	92.0	8.0
$Co(OAc)_2$	5	43.7	94.1	5.9
$Co(OAc)_2$	7	45.1	94.3	5.7
T(*p*-Cl)PPMnCl	7	1.1	0	100
$Co(OAc)_2$/T(*p*-Cl)PPMnCl	3	42.0	92.7	7.3
$Co(OAc)_2$/T(*p*-Cl)PPMnCl	5	51.9	94.5	5.5
$Co(OAc)_2$/T(*p*-Cl)PPMnCl	7	57.1	95.5	4.5
$Co(OAc)_2$/$Mn(OAc)_2$	7	45.6	94.5	5.5

Reaction conditions: PTA, 100 g; HOAc, 100 g; T(*p*-Cl)PPMnCl, 16.2 ppm; $Co(OAc)_2 \cdot 4H_2O$, 548 ppm; $Mn(OAc)_2 \cdot 4H_2O$, 16.2 ppm; temperature, 190 °C; air pressure, 1.2 MPa; air flow, 160 L h^{-1}

Table 2 Effect of the concentration of $Co(OAc)_2$ on PTA oxidation

$Co(OAc)_2$ conc. (ppm)	Conversion (%)	Selectivity (%)	
		TPA	CBA
1.37×10^2	14.6	81.8	18.2
2.74×10^2	47.8	94.8	5.2
5.48×10^2	51.9	94.5	5.5
1.10×10^3	45.4	93.8	6.2

Reaction conditions: PTA, 100 g; HOAc, 100 g; T(*p*-Cl)PPMnCl, 16.2 ppm; air pressure, 1.2 MPa; 190 °C; air flow, 160 L h^{-1}; reaction time, 5 h

Table 4 Effect of temperature on the PTA oxidation

Temperature (°C)	Conversion (%)	Selectivity (%)	
		TPA	CBA
160	11.5	82.6	17.4
180	44.1	94.9	5.1
190	51.9	94.5	5.5
210	56.4	97.6	2.4
220	52.9	97.1	2.9

Reaction conditions: PTA, 100 g; HOAc, 100 g; T(*p*-Cl)PPMnCl, 16.2 ppm; $Co(OAc)_2 \cdot 4H_2O$, 548 ppm; air pressure, 1.2 MPa; air flow, 160 L h^{-1}; reaction time, 5 h

Table 3 Effect of the concentration of T(*p*-Cl)PPMnCl on PTA oxidation

T(*p*-Cl)PPMnCl conc. (ppm)	Conversion (%)	Selectivity (%)	
		TPA	CBA
3.2	45.3	94.1	5.9
9.7	46.8	94.3	5.7
13.0	48.9	94.3	5.7
16.2	51.9	94.5	5.5
22.7	47.1	93.9	6.1

Reaction conditions: PTA, 100 g; HOAc, 100 g; $Co(OAc)_2 \cdot 4H_2O$, 548 ppm; air pressure, 1.2 MPa; 190 °C; air flow, 160 L h^{-1}; reaction time, 5 h

[20]. Similar phenomena were also observed in our previous works [6, 15].

3.4 Effect of Reaction Temperature

The influence of reaction temperature on the oxidation reaction was investigated and the results were shown in Table 4. When the temperature was below 210 °C, the PTA conversion and TPA selectivity enhanced with the increasing of the temperature, and there was a sharp increase in the PTA conversion and the TPA yield (11.5–51.9% for conversion, 9.5–49.0% for the TPA yield) when the temperature was changed from 160 to 190 °C. The selectivity of TPA changed from 82.6 to 94.5% with the increases of the temperature from 160 to 190 °C. These indicated that the increase of temperature was helpful to the oxidation of PTA. But when the temperature was higher than 210 °C, the PTA conversion and TPA yield began to decrease. It might be caused by decarboxylation of the TPA at exorbitantly high temperature.

3.5 Effect of PTA Concentration

It could be seen from Table 5 that the optimized concentration of PTA was up to 65% which was enormously higher than the concentration of PTA in other new catalyst systems, and the system gave the highest conversion 62.9% and TPA selectivity 96.8%. When the PTA concentration was below 65%, the conversion and TPA selectivity were increasing with the increase of the PTA concentration. This might be because the reduction of solvent led to the increase of the catalyst concentration. But the conversion and TPA selectivity decreased with the further increase of PTA concentration. It might be relative to the changes of reaction system's viscosity and polarity [21, 22] and the

Table 5 Effect of the PTA concentration on PTA oxidation

PTA conc. (mass%)	Conversion (%)	Selectivity (%)	
		TPA	CBA
35	33.4	92.7	7.3
50	51.9	94.5	5.5
65	62.9	96.8	3.4
80	50.8	95.5	4.5
90	26.3	92.0	8.0

Reaction conditions: PTA, 100 g; T(*p*-Cl)PPMnCl, 16.2 ppm; Co(OAc)$_2$·4H$_2$O, 548 ppm; air pressure, 1.2 MPa; 190 °C; air flow, 160 L h^{-1}; reaction time, 5 h

shift of the metalloporphyrin's redox electric potential [23, 24] in different amount of HOAc.

3.6 The Preliminary Mechanism of co-Catalysis Between T(*p*-Cl)PPMnCl and Co(OAc)$_2$ in the Aerobic Oxidation of PTA to TPA

The selective oxidation of hydrocarbons with oxygen over metalloporphyrins is a biomimetic catalytic process mimicking the cytochrome P450 monoxygenase [25]. When 2,6-di-tertbutyl-p-cresol as a free inhibitor was added into the oxidation system, the reaction was substantially quenched. The result suggested that the reaction proceeded via a radical process.

Hydroperoxides could be produced under moderate conditions by the use of metalloporphyrin as catalyst [26]. The changes of peroxides content with reaction time in different catalyst system were investigated and the results were shown in Fig. 2. The concentration of peroxides was much higher over T(*p*-Cl)PPMnCl than Co(OAc)$_2$. Results suggest that metalloporphyrin excels Co(OAc)$_2$ in producing peroxides as catalyst.

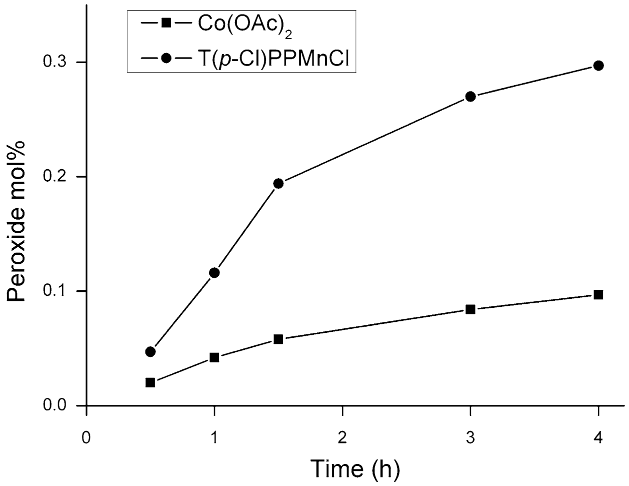


Fig. 2 Changes of content of peroxides with reaction time in different catalyst system. Reaction conditions (in dark): PTA, 1.5 g; HOAc, 25 mL; O$_2$ pressure, 0.1 MPa; temperature, 391 K; O$_2$ flow rate, 4.2 L/h; catalyst: T(*p*-Cl)PPMnCl, 8.7 × 10^{-3} mmol; Co(OAc)$_2$·4H$_2$O, 8.7 × 10^{-3} mmol

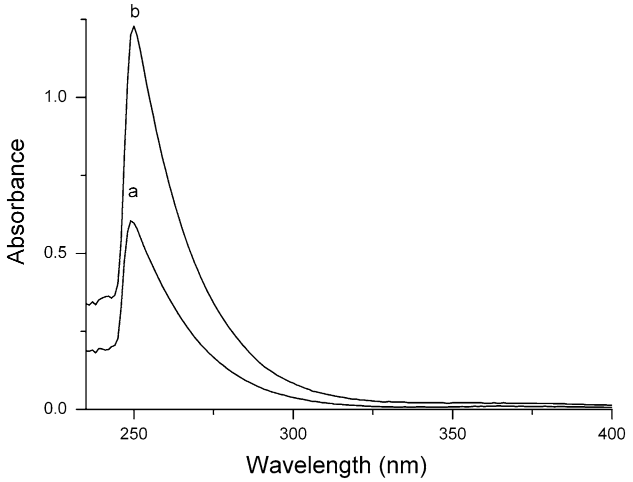


Fig. 3 Absorption spectrum of a solution (**a**) of peracetic acid (4.1 × 10^{-2} M, 3.5 mL) and a mixed solution (**b**) of peracetic acid after adding Co(OAc)$_2$·4H$_2$O (3.6 mg) (glacial acetic acid solvent)

The peroxides formed in the hydrocarbon oxidation play an important role in the initiation of the chain reaction of the hydrocarbon oxidation [27]. In order to find out the relationship between cobaltous acetate and peroxide mostly stemmed from the catalysis of metalloporphyrin, spectroscopic investigations were conducted. The UV spectra of the peracetic acid was shown as Fig. 3a. When Co(OAc)$_2$ was added into peracetic acid representing for hydroperoxide, the solution turned green and the UV spectra was shown as Fig. 3b. A new absorption peak at 250 nm where the absorption of Co(OAc)$_2$ and HOAc at 250 nm was negligible appeared. This phenomenon indicated Co^{2+} could react with peracetic acid. The solution was then evaporated at decompressed pressure, and the green product obtained was dried. The UV–vis spectra of the green product (Fig. 4) showed that there was one intense absorption band of 254 nm. The charge-transfer band at 254 nm indicated the cobalt(III)-oxygen bonding [28]. Therefore, the green solid obtained was cobaltic acetate. Results suggested that hydroperoxides could oxidize Co^{2+} into Co^{3+} (see Eq. 1):

$$\begin{aligned}&\mathrm{RCOOOH} + 2\,\mathrm{Co}^{2+} + 2\mathrm{H}^{+}\\&\quad\rightarrow \mathrm{RCOOH} + 2\,\mathrm{Co}^{3+} + \mathrm{H_2O}\end{aligned} \tag{1}$$

It was reported that the key step of cobalt-catalyzed hydrocarbon oxidation was the reaction between the Co^{3+} with the hydrocarbon to form alkyl free radicals [29, 30]. In order to investigate the effect of Co^{3+}concentration on the PTA oxidation with air, the aerobic oxidation of PTA to TPA over T(*p*-Cl)PPMnCl/Co(OAc)$_2$ was run with the Co(OAc)$_3$ instead of Co(OAc)$_2$. The oxidation results were

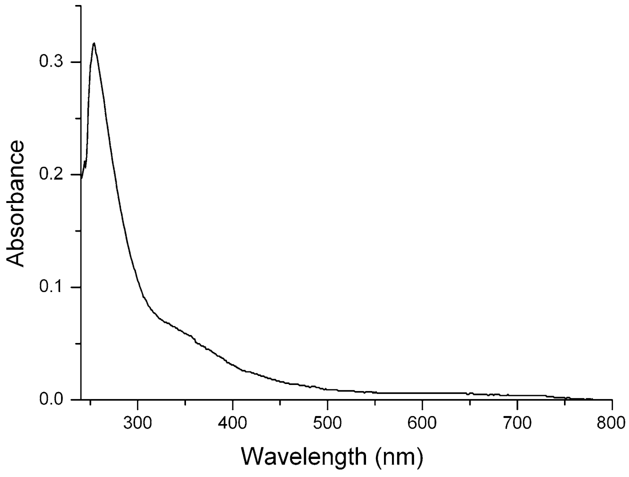


Fig. 4 Absorption spectrum of a solution of cobaltic acetate (2.4×10^{-5} M) (glacial acetic acid solvent)

listed in Table 6. When equal amount of Co^{2+} substituted for Co^{3+}, the PTA conversion increased from 51.9% to 56.8% and the selectivity of TPA increased from 94.5 to 96.5%. The duplicate runs had been done, and the data was consistent. It appears to be similar to that of cobalt acetate-catalyzed autoxidation. The results showed that Co^{3+} obtained by the reaction of peroxides and Co^{2+} could promote the PTA oxidation. This might be because Co^{3+} abstracted one hydrogen atom of the substrates to form free radicals. Once the concentration of Co^{3+} was increased, more free radicals were produced and chain initiation was accelerated.

According to the above experimental results and reported facts [26, 27, 29–33], a preliminary mechanism of co-catalysis between T(*p*-Cl)PPMnCl and $Co(OAc)_2$ in the aerobic oxidation of PTA to TPA is proposed (see Scheme 2).

The LC–MS analysis of the PTA oxidation products showed that there were no 4-(hydroxymethyl)benzoic acid and esterification reaction products of the hydroxymethyl group produced. It seemed that the formation of aralkyl free radical included a deoxy process of the alkoxy free radical in this system. For the co-catalysis between metalloporphyrin and cobalt acetate, the function of T(*p*-Cl)PPMnCl might be to produce more peroxides from the PTA (step a in Scheme 2), and then more Co^{3+} was formed from the oxidation of the Co^{2+} with peroxides (step b). Moreover, Co^{3+} promoted the PTA oxidation due to the ease of the free radicals' formation (step c). Further studies of the mechanism are underway, with the precise details yet unknown.

4 Conclusions

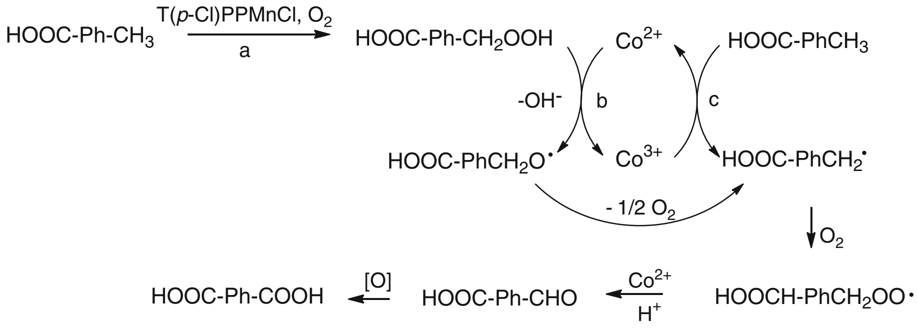
The PTA was oxidized to TPA with air by the catalysis of T(*p*-Cl)PPMnCl/$Co(OAc)_2$, The aerobic oxidation of PTA was influenced by the catalyst composition and the concentrations of the catalyst as well as reaction conditions. Both the PTA conversion and TPA yield increased significantly when the a small amount of T(*p*-Cl)PPMnCl was added to the PTA-O_2-$Co(OAc)_2$ system. By the use of 548 ppm $Co(OAc)_2$ and 16 ppm T(*p*-Cl)PPMnCl as the catalysts, PTA oxidation under the optimum conditions of 190 °C, 1.2 MPa and 160 L h^{-1} airflow produced TPA at 96.8% selectivity and 62.9% conversion of PTA in 5 h. For the co-catalysis between metalloporphyrin and cobalt acetate, the function of T(*p*-Cl)PPMnCl might be to

Table 6 Comparison of the catalytic power between $Co(OAc)_3$ and $Co(OAc)_2$ in combination with metalloporphyrin

Catalyst	Co^{2+} (mol)	Co^{3+} (mol)	Conversion (%)	Selectivity (%)	
				TPA	CBA
$Co(OAc)_2$/T(*p*-Cl)PPMnCl	4.01×10^{-4}	0	51.9	94.5	5.5
$Co(OAc)_2$/$Co(OAc)_3$/T(*p*-Cl)PPMnCl	2.98×10^{-4}	1.03×10^{-4}	56.8	96.5	3.5

Reaction conditions: PTA, 100 g; T(*p*-Cl)PPMnCl, 16.2 ppm; air pressure, 1.2 MPa; 190 °C; air flow, 160 L h^{-1}; reaction time, 5 h

Scheme 2 Preliminary mechanism of co-catalysis between T(*p*-Cl)PPMnCl and $Co(OAc)_2$ in the aerobic oxidation of PTA to TPA



produce more peroxides from the PTA, and then more Co^{3+} was formed from the oxidation of the Co^{2+} with peroxides. Moreover, Co^{3+} promoted the PTA oxidation due to the ease of the free radicals' formation.

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