Synergistic Catalytic Action of Cobalt(II) Hydroxamates and N-Hydroxyphthalimide in the Aerobic Oxidation of *p*-Xylene

Jian LIANG, Jian Zhang LI, Bo ZHOU, Sheng Ying QIN*
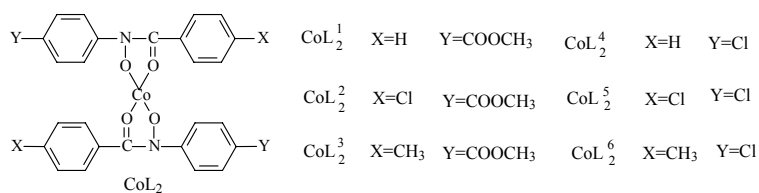
Department of Chemistry, Sichuan University, Chengdu 610064

Abstract: The catalytic performance of a series of cobalt(II) hydroxamates (CoL$_2$) and the synergistic catalytic action of the cobalt complexes combined with N-hydroxyphthalimide (NHPI) in the aerobic oxidation of *p*-xylene to *p*-toluic acid (PTA) were investigated. The results showed that the existing synergistic action in the catalytic oxidation can shorten the induction period of the radical reaction and improve the yield of PTA.

Keywords: Catalysis, N-hydroxyphthalimide (NHPI), cobalt(II) hydroxamates, oxidation of *p*-xylene.

Hydroxamic acids, an important class of metal chelators[1], were broadly researched in coordination chemistry[2], analytical chemistry[3] and medicine chemistry[4]. Previously, we reported the dioxygen affinities and biomimetic catalytic oxidation performance of transition-metal hydroxamates[5]. Recently the oxidation of *p*-xylene into *p*-toluic acid (PTA) catalyzed by cobalt(II) hydroxamates was also reported[6]. As one kind of co-catalyst, N-hydroxyphthalimide (NHPI) has been widely applied in the catalytic oxidation of various organic compounds[7]. For example, the catalytic oxidation of alkanes was promoted by a new catalytic system, NHPI combined with Co(acac)$_2$ at around 100 ℃[8]. In order to achieve better catalytic results in the aerobic oxidation of *p*-xylene, we used CoL$_2^1$-CoL$_2^6$ as catalyst, NHPI as a co-catalyst, and examine their synergistic action in the oxidation of *p*-xylene to PTA. The structures of the investigated complexes (CoL$_2$) are illustrated as **Figure 1**.

Figure 1 Cobalt(II) complexes with N-phenyl hydroxamic acid

CoL$_2^1$	X=H	Y=COOCH$_3$	CoL$_2^4$ X=H Y=Cl
CoL$_2^2$	X=Cl	Y=COOCH$_3$	CoL$_2^5$ X=Cl Y=Cl
CoL$_2^3$	X=CH$_3$	Y=COOCH$_3$	CoL$_2^6$ X=CH$_3$ Y=Cl

CoL$_2$

---

* E-mail: qin-shengying@163.com

Figure 2   Catalytic oxidation of CoL_2 in the absence of NHPI

CoL_2^1 - CoL_2^6: 1.0×10^{-3} $mol \cdot L^{-1}$
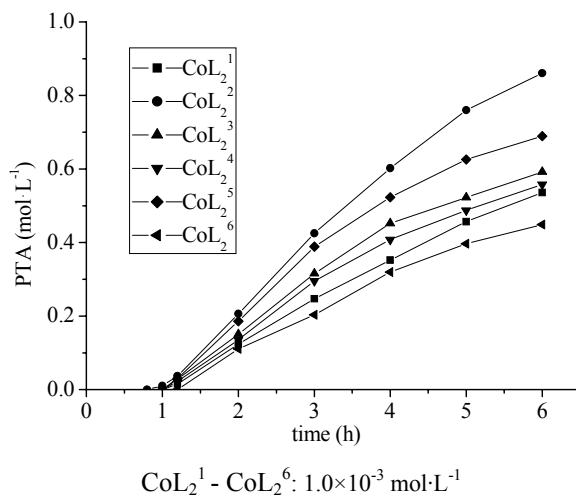
CoL_2^4 - CoL_2^6 complexes were prepared according to published procedures[9,10], the other complexes CoL_2^1 - CoL_2^3 were supplied by our laboratory.

The oxidation of *p*-xylene to *p*-toluic acid (PTA) is carried out in general gas-liquid phase reactor. Into the mixture of *p*-xylene (15 mL), and CoL_2 (1.0×10^{-3} $mol \cdot L^{-1}$), is bubbled air at the flow rate of 2.8 $L \cdot L^{-1} \cdot min^{-1}$ at 115 ℃. The reaction mixture (0.1 mL) was abstracted by pipet at regular intervals, and diluted with ethanol (15 mL), then the cumulative content of PTA was calculated by standard acid-base titration.

Figure 2 shows that there is the effect of substitution in the catalytic oxidation of *p*-xylene by these cobalt(Ⅱ) complexes. Except CoL_2^1 and CoL_2^4 show the similar catalytic activity, the complexes (CoL_2^2 and CoL_2^3) containing $COOCH_3$ in the ligand show higher catalytic activity compare to the corresponding complexes (CoL_2^5 and CoL_2^6) without $COOCH_3$. This is possibly due to the better solubility of the complexes containing $COOCH_3$ in *p*-xylene. CoL_2^2 (X=Cl, Y=$COOCH_3$), which is the best among the six catalysts, shows higher catalytic activity than CoL_2^3 (X=CH_3, Y=$COOCH_3$). It is due to that the aromatic ring in the ligand of CoL_2^2 is deactivated by the mild electron-drawing halogen atom (X=Cl), which can prevent the catalyst from oxidation degradation. On the other hand, the π-awarding is increased through *p*-π conjugation between halogen atom and aromatic ring[5].

In order to evaluate the features of NHPI as co-catalyst, the aerobic oxidation of *p*-xylene was examined under the same procedures as illustrated above, except for the addition of NHPI (1.0×10^{-2} $mol \cdot L^{-1}$). These results indicated that the induction period of the oxidation reactions for *p*-xylene is shortened, and the PTA accumulative concentration is increased rapidly. For example, the induction periods of CoL_2^2 (CoL_2^6) and NHPI+CoL_2^2 (NHPI+CoL_2^6) were about 0.8 h (1.2 h) and 0.5 h (0.7 h), respectively. **Figure 3** shows the difference of catalytic activity between CoL_2^2 and NHPI+CoL_2^2 as well as CoL_2^6 and NHPI+CoL_2^6.

Figure 3 Catalysis of CoL_2^2 and CoL_2^6 in the absence or in the presence of NHPI
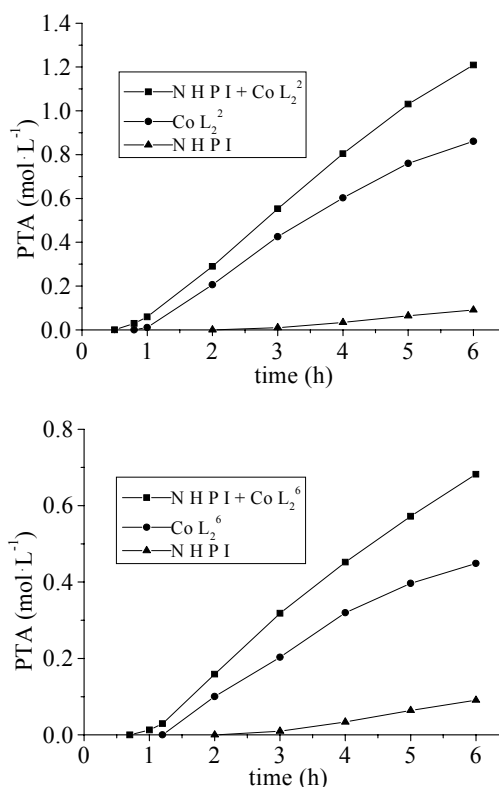
NHPI: 1.0×10^{-2} mol·L^{-1}; CoL_2^2, CoL_2^6: 1.0×10^{-3} mol·L^{-1}

Table 1 The influence of NHPI concentration on the catalytic oxidation

system	induction period (h)	PTA yield (wt %)
CoL_2^2	0.8	13.2
NHPI (1.0×10^{-3} mol·L^{-1}) + CoL_2^2	0.6	15.9
NHPI (1.0×10^{-2} mol·L^{-1}) + CoL_2^2	0.5	17.2
NHPI (1.0×10^{-1} mol·L^{-1}) + CoL_2^2	0.5	17.6

CoL_2^2: 1.0×10^{-3} mol·L^{-1}; time: 6 hrs

When the concentration of NHPI was changed, the oxidation results showed that higher the concentration of NHPI is, stronger the catalytic capacity of the corresponding system is.   The influence of NHPI concentration on the catalytic oxidation is illustrated as **Table 1**.

In order to examine the synergistic action of cobalt(Ⅱ) hydroxamates and NHPI in the oxidation of *o*-xylene or *m*-xylene, we designed the same procedures as that in *p*-xylene.   The results, showed in **Table 2,** illustrated that the addition of NHPI can also shorten the induction period and improve the yield of the corresponding toluic acid.

Table 2   Catalytic oxidation of *o*-xylene or *m*-xylene by CoL_2^2 for 6 h

substrate	system	induction period (h)	toluic acid yield (wt %)
o-xylene	CoL_2^2	1.0	10.6
o-xylene	$NHPI+CoL_2^2$	0.7	14.1
m-xylene	CoL_2^2	1.2	8.2
m-xylene	$NHPI+CoL_2^2$	0.9	11.9

NHPI: 1.0×10^{-2} mol·L^{-1}; CoL_2^2: 1.0×10^{-3} mol·L^{-1}

Although NHPI can improve the catalytic capacity of cobalt(Ⅱ) hydroxamates, NHPI alone has less effect in the catalytic oxidation as showed in **Figure 3**. These phenomena indicated that the catalytic capacity of cobalt complexes combined with NHPI is stronger than the corresponding cobalt complexes or NHPI, alone respectively. It is possibly due to that NHPI can easily form phthalimide-N-oxyl (PINO) in the presence of cobalt(Ⅱ) complexes, then PINO, a highly reactive free radical[7,8], can shorten the induction period of the radical reaction and improve the yield of PTA.

References

1. W. Zeng, G. Y. Zeng, S. Y. Qin, *Chinese J. Org. Chem.*, **2003**, *23*, 1213.
2. B. Kurzak, H. Kozlowski, E. Farkas, *Coord. Chem. Rev.*, **1992**, *114*, 169.
3. S. Hutchinson, *Anal. Chem. Acta.*, **1994**, *291*,269.
4. H. R. Bravo, *Phytochemistry*, **1993**, *33*, 569.
5. H. Yang, S. Y. Qin, X. X. Lu, *Chin. Chem. Lett.*, **1999,** *10*, 79.
6. C. C. Zhang, W. Zeng, J. Z. Li, S. Y. Qin, *Chin. Chem. Lett.*, **2003,** *14*, 627.
7. Y. Ishii, T. Iwahama, S. Sakaguchi, *J. Org. Chem.*, **1996**, *61*, 4520.
8. Y. Yoshino, Y. Hayashi, T. Iwahama, S. Sakaguchi, Y. Ishii, *J. Org. Chem.*, **1997**, *62*, 6810.
9. H. E. Baumgarten, A. Staklis, E. M. Miller, *J. Org. Chem.*, **1965**, *30*, 1203.
10. D. R. Agrawal, S. G. Tandon, *J. Chem. Eng. Data*, **1972**, *17*, 257.