Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

An Efficient Aerobic Oxidation for *p*-Xylene to *p*-Toluic Acid using Azacrown Ether-tethered Mn(III) Schiff Base Complexes as Catalysts

Wei Zeng[a]; Jianzhang Li[a]; Shengying Qin[a]
[a] Department of Chemistry, Sichuan University, Chengdu, P. R. China

To cite this Article Zeng, Wei , Li, Jianzhang and Qin, Shengying(2004) 'An Efficient Aerobic Oxidation for *p*-Xylene to *p*-Toluic Acid using Azacrown Ether-tethered Mn(III) Schiff Base Complexes as Catalysts', Supramolecular Chemistry, 16: 8, 569 — 572

To link to this Article: DOI: 10.1080/10610270412331315217

URL: http://dx.doi.org/10.1080/10610270412331315217

Supramolecular Chemistry, December 2004 VOL. 16 (8), pp. 569–572

Taylor & Francis
Taylor & Francis Group

An Efficient Aerobic Oxidation for *p*-Xylene to *p*-Toluic Acid using Azacrown Ether-tethered Mn(III) Schiff Base Complexes as Catalysts

WEI ZENG, JIANZHANG LI and SHENGYING QIN*

Department of Chemistry, Sichuan University, Chengdu 610064, P. R. China

Received (in Southampton, UK) 23 April 2004; Accepted 14 June 2004

The oxidation of *p*-xylene to *p*-toluic acid with air at 110°C under normal atmospheric pressure occurs efficiently in the presence of crown Mn(III) Schiff base complexes $\mathrm{MnL}_2^n\mathrm{Cl}$ ($n = 1-4$). Significant conversion levels (up to 75%) and selectivity (up to 92–96%) are obtained; the effect of the azacrown ether pendants in Mn(III) Schiff base complexes on the oxidation of *p*-xylene are also investigated by comparison with the crown-free analogues $\mathrm{MnL}_2^5\mathrm{Cl}$. Moreover, addition of alkali metal ions accelerates the rate of conversion of *p*-xylene to *p*-toluic acid.

Keywords: Azacrown; Mn(III) Schiff base complexes; Aerobic oxidation

INTRODUCTION

Substituted benzoic acids are very important materials in the chemical and pharmaceutical industries [1,2]. In recent years, many studies on the oxidation of *p*-xylene to *p*-toluic acid catalyzed by $Co(OAc)_2/NaBr/AcOH$, $Co(C_{18}H_{35}O_2)_2/NH_4Br$ or Schiff base complexes have been reported; however, using these conditions, the yield (<60%) and the selectivity (<25%) for *p*-toluic acid are low [3,4]. On the other hand, to the best of our knowledge, no studies on the oxidation of alkyl compounds catalyzed by azacrown substituted Schiff base complexes have so far been reported. Crown rings with a special configuration will endow crown functional molecules such as hydroxamic acid and receptor molecules *et al.* with a novel performance and character with a hydrophobicity of outer ethylene groups and orderly arrangement of inner oxa atoms [5,6]. Moreover, crown ether-containing Schiff bases are well known to bind cations in the crown ether cavity in addition to the coordination of a transition metal center through the N_2O_2 donor atoms. Co-complexation of a hard cation close to the transition-metal center is believed to play an important role in perturbing its oxygen-binding properties. Recent work by others and us has showed that when transition-metal complexes with azacrown pendants were complexed with alkali or alkaline earth metal ions, significantly improved dioxygen affinities, compared to their crown-free analogues, were obtained [7,8,9]. A previous paper [9] has reported the synthesis, crystal structure and dioxygen affinities of $\mathbf{CoL}_2^n$ ($n = 1-5$) (Scheme 1), in connection with a further research program aimed at the effect of the bonded azacrown ring appended in the ligand and the added alkali metal ions into the reactive system on the catalytic oxidation performance of Schiff base Mn (III) complexes. Herein we report the homogeneous direct catalytic oxidation of *p*-xylene to *p*-toluic acid by air in the presence of the Schiff base Mn(III) complexes $\mathbf{MnL}_2^n\mathbf{Cl}$ ($\mathrm{n} = 1-5$) (Scheme 1) under the mild conditions.

EXPERIMENTAL

Apparatus and Reagents

Melting points were determined on a Yanaco MP-500 micro-melting point apparatus and are uncorrected. The IR spectra were obtained on a Nicolet-1705X IR

---

*Corresponding author. Tel.: +86-028-85471565. E-mail: zengwei109@hotmail.com

ISSN 1061-0278 print/ISSN 1029-0478 online © 2004 Taylor & Francis Ltd
DOI: 10.1080/10610270412331315217

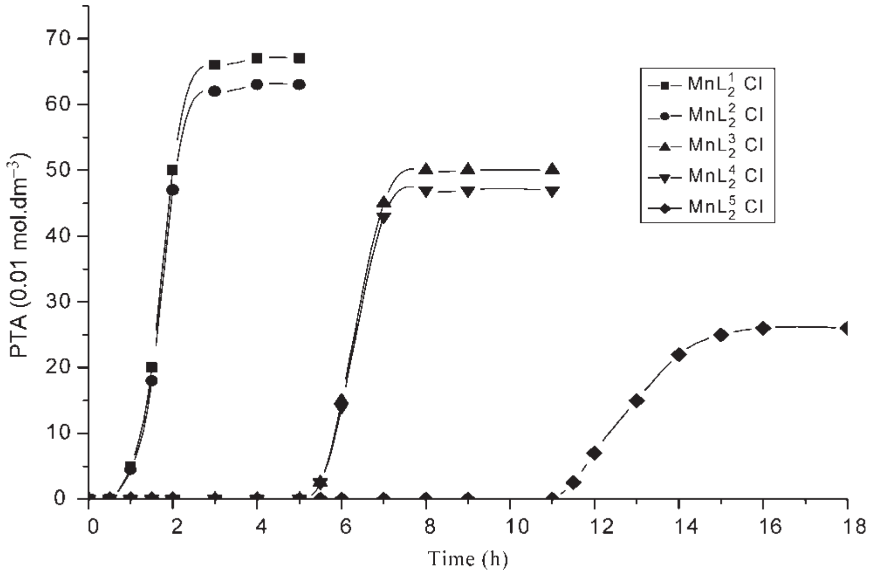
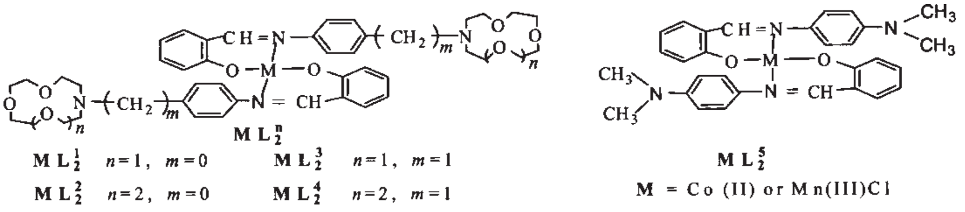


FIGURE 1 Influence of the azacrown ring pendants in Mn(III) Schiff base complexes on the oxidation of *p*-xylene. Reaction conditions: Air flow rates: 0.05 L h^{-1}; *p*-xylene (1.62×10^{-1} mol, 20 ml); Mn(III) Schiff base complex (2.0×10^{-5} mol); axial base pyridine (2.0×10^{-5} mol); normal atm of air; reaction temperature: 110°C.

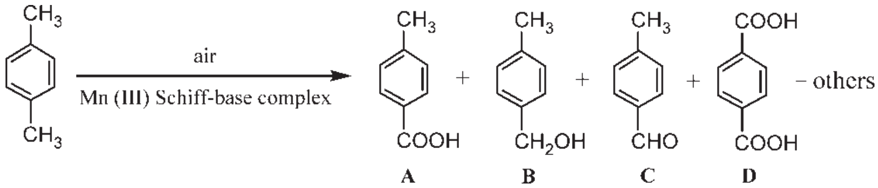
spectrometer. Pyridine, fresh air and *p*-xylene were purchased from China. Standard samples of *p*-toluic acid, *p*-tolyl alcohol, *p*-tolyl aldehyde and terephthalic acid were obtained from Aldrich Co.; pyridine and *p*-xylene were purified prior to use. The Schiff base ligands **HL**^{n} ($n = 1$–5) were synthesized according to published procedures [9]; the general procedure for the synthesis of Mn(III) Schiff base complexes **MnL$_2^n$Cl** ($n = 1$–5) was similar to the literature [10]. **MnL$_2^1$Cl** : purple, 58% yield, mp 191–194°C. IR (KBr, film) ν_{max}: 1637, 1126, 1121 cm^{-1}. Anal. Calcd for $MnC_{42}H_{50}N_4O_8Cl$: C, 60.80; H, 6.03; N, 6.67. Found: C, 60.61; H, 5.88; N, 6.93. Λ_m (s cm^2 mol^{-1}) 138.3. **MnL$_2^2$Cl** : purple, 51% yield, mp 225–229°C. IR (KBr, film) ν_{max}: 1626, 1123 cm^{-1}. Anal. Calcd for $MnC_{46}H_{58}N_4O_{10}Cl$: C, 60.23; H, 6.33; N, 6.11. Found: C, 60.56; H, 6.28; N 6.02. Λ_m (s cm^2 mol^{-1}) 140.5. **MnL$_2^3$Cl** : purple, 61% yield, mp 198–200°C. IR (KBr, film) ν_{max}: 1637, 1127, 1132 cm^{-1}. Anal. Calcd for $MnC_{44}H_{55}N_4O_8Cl$: C, 61.61; H, 6.30; N, 6.53. Found: C, 61.48; H, 6.42; N, 6.68. Λ_m (s cm^2 mol^{-1}) 156.1. **MnL$_2^4$Cl** : purple, 56% yield, mp 157–160°C. IR (KBr, film) ν_{max}: 1629, 1226, 1128 cm^{-1}. Anal. Calcd for $MnC_{48}H_{62}N_4O_{10}Cl$: C, 60.95; H, 6.56; N, 5.96. Found: C, 61.13; H, 6.39; N, 6.18. Λ_m (s cm^2 mol^{-1}) 143.9.

General Procedure for the Oxidation of *p*-xylene to *p*-toluic Acid (PTA) with Air

The oxidation of *p*-xylene was carried out in a general gas-liquid reactor. Fresh air was bubbled at a flow rate of 0.05 L h^{-1} 110°C into a mixture of *p*-xylene (1.62×10^{-1} mol, 20 ml), Mn(III) Schiff base complex (2.0×10^{-5} mol) and axial base pyridine (2.0×10^{-5} mol).The oxidation products were analyzed at regular intervals by high performance liquid chromatography (HPLC) (Agilent 1100LC) with Hypersil ODS (100 mm × 4.6 mm, 5 μm) as the chromatographic column. Authenticated standard samples were used to confirm the identity of products. The oxidation was stopped upon reaching the maximum value of accumulated content of PTA, and the total conversion and product distribution were evaluated by using calibration curves, which were obtained by injecting a known amount of authenticated standard. Conversions and selectivity were calculated based on the amount of



SCHEME 1



SCHEME 2

TABLE I Mn(III) Schiff-base complexes catalytic oxidation for *p*-xylene to PTA at 110°C*

				Selectivity (wt.%)				
Entry	Catalyst	Convn. (wt.%)	TOF (h^{-1})	A	B	C	D	Others
1	$\mathbf{MnL_2^1Cl}$	58	157	96	2	1	0.5	0.5
2	$\mathbf{MnL_2^2Cl}$	56	152	94.5	1.5	2	1	1
3	$\mathbf{MnL_2^3Cl}$	23	62	92	2	3	1	2
4	$\mathbf{MnL_2^4Cl}$	27	73	93	2	2	2	1
5	$\mathbf{MnL_2^5Cl}$	8	21	31	28	25	10	6

* A = *p*-toluic acid, B = *p*-tolyl alcohol, C = *p*-tolyl aldedyhe, D = terephthalic acid, TOF = Turnover frequency (mole *p*-xylene converted per mole catalyst per hour); reaction conditions: Air flow rates: 0.05 L h^{-1}; *p*-xylene (1.62×10^{-1} mol, 20 mL); Mn(III) Schiff base complex (2.0×10^{-5} mol); axial base pyridine (2.0×10^{-5} mol); normal atm of air; reaction temperature: 110°C.

p-xylene reacted and oxidation products formed estimated by HPLC.

RESULTS AND DISCUSSION

The oxidation of *p*-xylene to PTA was carried out using Mn(III) Schiff base complexes as the catalyst (Scheme 2).

The plots of the accumulated content of PTA *vs.* reaction time (Fig. 1) indicated that the induction periods required for initiating the oxidation of *p*-xylene catalyzed by the crown Mn(III) Schiff base complexes (~ 0.5, 0.5, 5 and 5 h for $\mathbf{MnL_2^1Cl}$, $\mathbf{MnL_2^2Cl}$, $\mathbf{MnL_2^3Cl}$ and $\mathbf{MnL_2^4Cl}$, respectively) are shorter than that for the oxidation of *p*-xylene catalyzed by the crown-free Mn(III) Schiff base complexes $\mathbf{MnL_2^5Cl}$ (~ 11 h). The time taken for PTA to reach the maximum concentration during the oxidation of *p*-xylene catalyzed by the crown Mn(III) complexes is also shorter than that for $\mathbf{MnL_2^5Cl}$. This may be due to the presence of the azacrown ring which controls efficiently the microenvironment of the active center with its hydrophobicity of outer ethylene groups and orderly arrangement of inner oxa atoms.

Moreover, as shown in Table I;, it can be seen that the selectivity for the oxidation product PTA, conversion and Turnover frequency (TOF) for the oxidation of *p*-xylene catalyzed by crown Mn(III) Schiff base complexes are also excellent compared with that of the oxidation of *p*-xylene catalyzed by the crown-free Schiff base $\mathbf{MnL_2^5Cl}$. Comparing the catalytic oxidation activities of $\mathbf{MnL_2^1Cl}$ and $\mathbf{MnL_2^2Cl}$ (entries 1 and 2), there seems to be little effect of the size of the azacrown ring on oxidation, the same phenomenon was also observed for $\mathbf{MnL_2^3Cl}$ and $\mathbf{MnL_2^4Cl}$ (entries 3 and 4). It is noteworthy that the catalytic oxidation activities of $\mathbf{MnL_2^1Cl}$ and $\mathbf{MnL_2^2Cl}$ are higher than that of $\mathbf{MnL_2^3Cl}$ and $\mathbf{MnL_2^4Cl}$, respectively. This may be due to the presence of an extra methylene (-CH_2-) between the aromatic ring bonded to the -N=CH and azacrown ring. For $\mathbf{MnL_2^3Cl}$ and $\mathbf{MnL_2^4Cl}$, the methylene (-CH_2-) between the aromatic ring and azacrown ring makes the azacrown ring far away from the coordination center and thus leads to poorer control of the microenvironment of the active center; $\mathbf{MnL_2^3Cl}$ and $\mathbf{MnL_2^4Cl}$ thus show poorer catalytic activities than $\mathbf{MnL_2^1Cl}$ and $\mathbf{MnL_2^2Cl}$.

It is interesting that the addition of alkali metal nitrate (nitrate/$\mathbf{MnL_2^nCl}$ = 2 : 1 mol/mol) can enhance the catalytic activity of the $\mathbf{MnL_2^nCl}$ (n = 1–4), especially in the case of $\mathbf{MnL_2^2Cl}$ (Table II),

TABLE II Effect of addition of alkali metal salt (2.0×10^{-5} mol) on the catalytic performance of $\mathbf{MnL_2^2Cl}$*

				Selectivity (wt.%)				
Entry	Catalyst	Convn. (wt.%)	TOF (h^{-1})	A	B	C	D	Others
1	$NaNO_3$ instead of Mn(III) schiff base complexes	0	0	0	0	0	0	0
2	$\mathbf{MnL_2^2Cl}$ + $LiNO_3$	69	188	95	2	1	1	1
3	$\mathbf{MnL_2^2Cl}$ + $NaNO_3$	75	204	96	2	1	0.5	0.5
4	$\mathbf{MnL_2^2Cl}$ + KNO_3	67	182	95	2	2	0.5	0.5
5	$\mathbf{MnL_2^5Cl}$ + $NaNO_3$	9	24	33	25	26	12	4

* A = *p*-toluic acid, B = *p*-tolyl alcohol, C = *p*-tolyl aldedyhe, D = terephthalic acid, TOF = Turnover frequency (mole *p*-xylene converted per mole catalyst per hour.); reaction conditions are the same as those in Table I; nitrate/$\mathbf{MnL_2^nCl}$ = 2 : 1 mol/mol.

where the TOF values were significantly improved by 130% (entry 3). On the contrary, the above phenomenon was not observed when $NaNO_3$ was added to the uncrowned $\mathbf{MnL_2^5Cl}$ (entry 5). This may be because the dimension of the alkali metal Na^+ ($d = 1.90$ Å) [11] matched well with that of crown ring (N–15–5) cavity ($d = 1.7 \sim 2.2$ Å) [11] and was located near to the coordination center, moreover, the Na^+ with the positive charge may enable the molecular oxygen to be activated more easily.

In conclusion, this study demonstrates that selective oxidation for *p*-xylene to *p*-toluic acid can successfully occur in the presence of azacrown Mn(III) Schiff base complexes, which display a much bettter catalytic activity than the crown-free Mn(III) complexes do. The crown ether-alkali metal complementarity can improve the conversion and TOF of the oxidation for *p*-xylene. Further studies into the mechanism and scope of this catalytic oxidation are now underway in our laboratory.

Acknowledgement

Financial support from the National Natural Science Foundation of China (Grant No. 29572059).

References

[1] Hudlicky, M. *Oxidation in Organic Chemistry, ACS Monograph 186*; American Chemical Society: Washington, DC, 1990.
[2] Trost, B. M. *Comprehensive Organic Synthesis (Oxidation)*; Pergamon: New York, 1991.
[3] Jacob, C. R.; Varkey, S. P.; Ratnasamy, P. *Appl. Catal. A* **1999**, *182*, 91.
[4] Fang, F.; Sun, J.; Zheng, R.; Qiu, W. W.; Tang, J.; He, M. Y. *Tetrahedron* **2004**, *60*, 1225.
[5] Hochisako, H.; Ihara, H.; Kamiya, J.; Hirayama, C.; Yamnda, K. *Chem. Commun.* **1997**, 19.
[6] Galon, A.; Andreu, D.; Echavarren, A. M.; Prades, P.; de. Mendoza, J. *J. Am. Chem. Soc.* **1992**, *114*, 1511.
[7] Gebbink, R. J. M. K.; Martens, C. F.; Feiter, M. C.; Karlin, K. D.; Nolte, R. J. M. *Chem. Commun.* **1997**, 389.
[8] Lu, X. X.; Qin, S. Y.; Zhou, Z. Z.; Yam, V. W. W. *Inorg. Chem. Acta* **2003**, *346*, 49.
[9] Zeng, W.; Li, H. B.; Xiang, R. L.; Wei, X. Y.; Qin, S. Y. *Chin. J. Chem.* **2003**, *23*, 510.
[10] Srinivasan, K.; Michaud, P.; Kochi, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 2309.
[11] Vögtle, F.; Weber, E.; Elben, U. *Kontakte (Darmstadt)* **1980**, *2*, 36.