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Catalytic alcoholysis of quinolin-8-yl esters by manganese complexes

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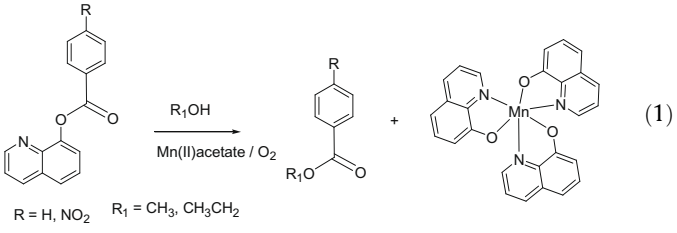
ABSTRACT

The role of different oxidation states of manganese in manganese(II) acetate promoted methanolysis reaction of *p*-nitrobenzoic acid quinolin-8-yl ester is presented.

Quinoline derivatives are used as drugs for malaria, arthritis, and lupus [1]. Control release of such drugs is essential in curing and there exists a reasonable amount of scope to study and design probes for monitoring degradation of quinoline derivatives for such studies [2]. Bio-compatible methods, for such study is of prime concern [3]. We show here the use of near-IR spectroscopy as a tool to study the alcoholysis of *p*-nitrobenzoic acid quinolin-8-yl ester for its transformation to manganese(III) complex and also compare such results with other related systems to establish the catalytic role of manganese.

The reaction between the *p*-nitrobenzoic acid quinolin-8-yl ester and methanol or ethanol is catalysed by manganese(II) acetate tetrahydrate under aerobic conditions [4]. In the process the manganese(II) gets oxidized to manganese(III). The *tris*-(8-oxyquinolato) manganese(III) is formed during these reactions (Eq. (1)).



(1)

We have also confirmed the formation of *tris*-(8-oxyquinolato) manganese(III) by solving its crystal structure. It is reported in literature that the reaction of manganese(II) acetate with 8-hydroxyquinoline under aerobic condition leads to the formation of *tris*-(8-oxyquinolinato)manganese(III) [5]. Manganese(III) complexes are useful catalysts for hydrolysis reactions of esters [6]. The manganese(II) complexes can be easily oxidized from +2 to +3 oxidation state in presence of oxygen as oxidizing agent. The complex *tris*-(8-oxyquinolinato)manganese(III) has a d^4-electronic configuration and it posses a near-IR absorption at 950 nm due to *d*–*d* transition between $d_{x^2-y^2}$ and d_z^2 orbitals arising from Jahn–Teller distortion. Similar near IR absorptions are reported in manganese(III) complexes [7]. The formation of *tris*-(8-oxyquinolinato)manganese(III) can be monitored by recording the changes in absorbances at 950 nm. It shows that the within 90 min complete formation of *tris*-(8-oxyquinolinato)manganese(III) takes place from the reaction of manganese(II) acetate with 8-hydroxyquinoline in methanol. Since in the alcoholysis of *p*-nitrobenzoic acid quinolin-8-yl ester the complex *tris*-(8-oxyquinolinato)manganese(III) was formed, the formation of ester could be monitored by the increase in absorbance of this peak. The reactions were monitored at 950 nm and it was found that complete conversion to *tris*-(8-oxyquinolinato)manganese(III) from *p*-nitrobenzoic acid quinolin-8-yl ester on reaction with manganese(II) acetate (3:1 molar ratio) in methanol took about 160 min, whereas the similar reaction of benzoic acid quinolin-8-yl ester took approximately 1100 min. The change of absorption at 950 nm in the two cases is illustrated in Fig. 1a and b. The similar reaction with ethanol was also carried out and observed that ethanolysis of *p*-nitrobenzoic acid quinolin-8-yl ester in the presence manganese(II) acetate (3:1 molar ratio); it took place in 140 min. The alcoholysis in other solvents such as *iso*-propanol, *t*-butanol, were attempted and they were found to be not effective and in these cases hydrolysis took place rather than alcoholysis with the traces of moisture present in the system.

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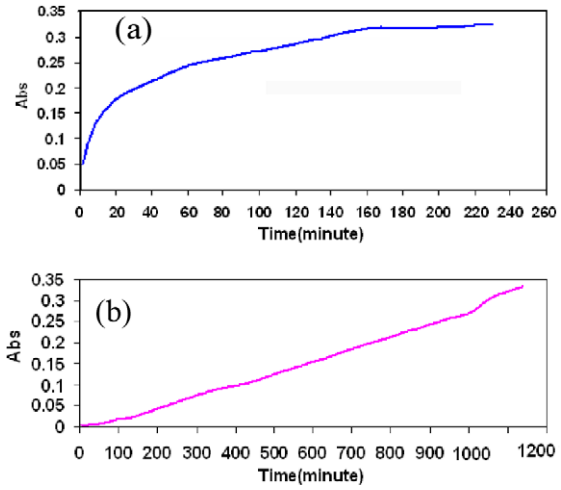


Fig. 1. The changes in absorbance at 950 nm in the reaction of manganese(II) acetate with (a) *p*-nitrobenzoic acid quinolin-8-yl ester; (b) benzoic acid quinolin-8-yl (1:3 molar ratio) in methanol.

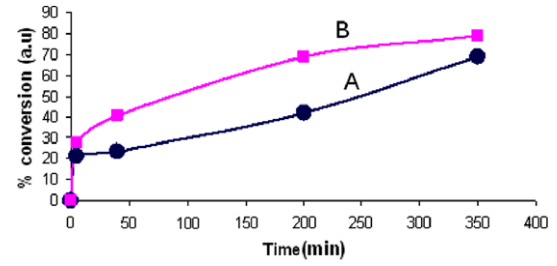


Fig. 2. Plot of % conversion of *p*-nitrobenzoic acid quinolin-8-yl ester to 8-hydroxyquinoline with time: by catalytic amount of (A) *tris*-(8-oxyquinolinato)manganese(III) (5 mol%); (B) *tris*-acetylacetonato manganese(III) (5 mol%).

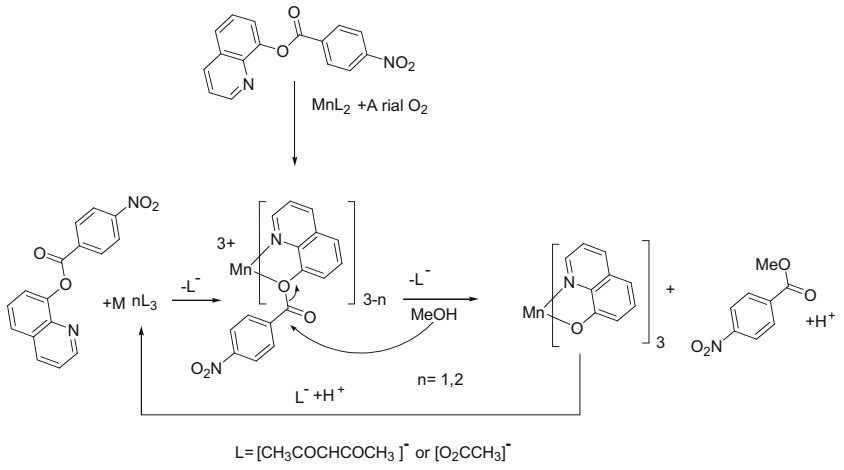
Since *tris*-(8-oxyquinolinato)manganese(III) was easily formed in these reactions we had independently studied the catalytic reactions of this complex for methanolysis of *p*-nitrobenzoic acid quinolin-8-yl ester. The catalytic methanolysis was monitored by using GC–MS and the percentage conversion vs time is presented in Fig. 2. It was found that the reaction is also catalysed by *tris*-(8-oxyquinolinato)manganese(III) complex. Thus, it is the manganese(III) ion, that is responsible for these catalytic reactions. Based on the above observations the mechanistic path for the catalytic reactions can be described by Scheme 1. The manganese(III) complexes are generally labile, upon interaction with the ligand they activate the ester group of the *p*-nitrobenzoic acid quinolin-8-yl ester for nucleophilic attack by methanol. In the process the manganese(III) oxy-quinolinato complex is formed, and along with this protons are liberated. The liberated protons further triggers the catalytic cycle and a catalytic reaction is observed. In the case of manganese(II) acetate, the manganese(II) gets converted to a manganese(III) by arial oxygen; which in turns further takes part in the catalytic cycle.

Further proof to the catalytic role of manganese(III) comes from the catalytic ability of *tris*-acetylacetonato manganese(III) on the methanolysis of *p*-nitrobenzoic acid quinolin-8-yl ester. In this case we had observed a higher catalytic ability of *tris*-acetylacetonato manganese(III) over *tris*-(8-oxyquinolinato)manganese(III). This ability is attributed to the lability of the two ligands in the complexes. The acetylacetonato groups of the *tris*-acetylacetonato manganese(III) can be replaced by 8-oxyquinolinato group easily. Thus, the *tris*-(8-oxyquinolinato)manganese(III) can be easily prepared from a methanolic solution of *tris*-acetylacetonato manganese(III) as illustrated in Eq. (2):

$$\mathrm{Mn(AcAc)_3 + HQ \overset{MeOH}{\rightarrow} Mn(HQ)_3} \qquad (2)$$

where AcAc = acetylacetonato anion.

In order to understand the reaction further we have checked the reactivity of benzoic acid naphthalene-1-yl ester and *p*-nitrobenzoic acid naphthalene-1-yl ester with methanol in the presence of manganese(II) acetate. We have tried the catalytic methanolysis reaction of *N*-quinolin-8-yl-benzimide and observed no reactions. However, the reaction of manganese(II) acetate with 8-aminoquinoline and benzoic acid together lead to a trinuclear complex **I** (Eq. (3)). The trinuclear complex **I** (Fig. 3, left) is characterized by solving its crystal structure [8] and similar trinuclear complexes are well known in literature [9]. The reaction of methyl cinnamate with ethanol was studied with manganese(II) acetate catalyst but we have not observed catalytic reaction at ambient condition. However, in the reaction of cinnamic acid with manganese(II) acetate we observed the formation of co-ordination polymer **II** (Eq. (4)). The polymer comprises of two bridging carboxylates and two aqua ligands (Fig. 3, right). It has distorted octahedral geometry around the each manganese center [8]:



Scheme 1.

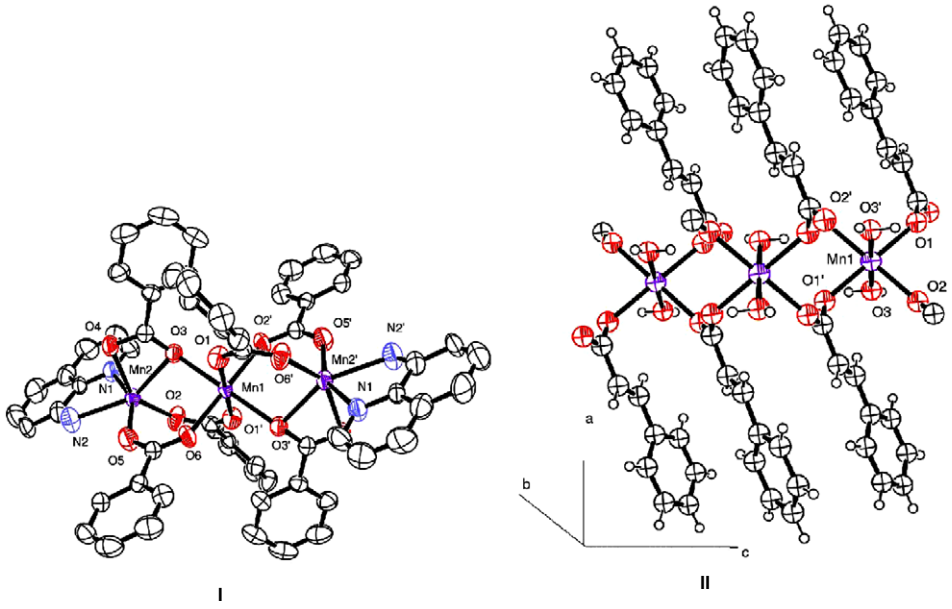
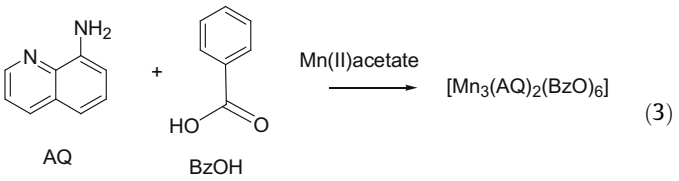
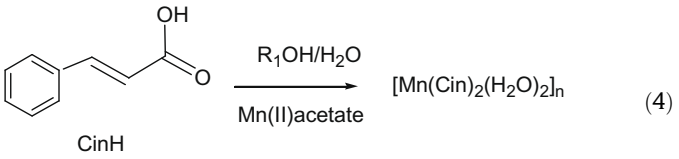


Fig. 3. The crystal structures of left **I** (hydrogen atoms in **I** are omitted for clarity) and right is the crystal structure of polymer **II**.



I



II

These results also showed that some of the esters like methyl cinnamate or *N*-quinolin-8-yl-benzimide do not undergo catalytic hydrolysis; whereas, cinnamic acid or aminoquinoline which can be derived from such hydrolysis of such esters lead to stable manganese(II) complexes. On the other hand, in the case of *p*-nitrobenzoic acid quinolin-8-yl ester a manganese(III) complex is formed on reaction with manganese(II) acetate, which also can be prepared directly by reacting manganese(II) acetate with 8-hydroxyquinoline. This depicts that, the propensity for oxidation of manganese(II) to form labile manganese(III) chelate complex along with the ease of triggering of protons from the esters by attack of an alcohol, are the two important factors that decides the described catalytic process.

Acknowledgements

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Appendix A. Supplementary material

CCDC 677170 and 710241 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2009.04.023.

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[4] In a typical experiment manganese(II) acetate tetrahydrate (0.005 g, 0.02 mmol) was added to a well stirred solution of *p*-nitrobenzoic acid quinolin-8-yl ester (0.25 g, 1 mmol) in 10 ml methanol, and the reaction mixture was stirred at room temperature for 12 h. The reaction mixture turned black. To the reaction mixture 10 ml water was added. The reaction mixture was further extracted with ethylacetate (30 ml). The ethylacetate extract was dried over anhydrous sodiumsulphate; the extract was concentrated and purified by column chromatography using silica gel and using ethylacetate (5%) in petroleum ether as eluent. On purification methyl-*p*-nitrobenzoate was obtained in 98% yield.
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[8] Crystal data for **I**: $C_{60}H_{46}Mn_3N_4O_{12}$, Mr = 1179.83, Triclinic, space group *P*-1, $a = 10.9221(3)$ Å, $b = 11.4069(3)$ Å, $c = 12.1288(3)$ Å, $\alpha = 65.8510(10)°$, $\beta = 78.658(2)°$, $\gamma = 78.180(2)°$, $V = 1338.79(6)$ Å^3, $Z = 1$, density = 1.463 g/cm^3, $F(0\,0\,0) = 605$, Abs. Coeff./mm^{-1} = 0.765, 12132 reflection collected, 4609 unique, R indices $[I > 2\sigma(I)] = 0.0393$, R indices (all data) = 0.0512, and gof = 1.028. For **II**: $C_{18}H_{18}MnO_6$, Mr = 385.26, Monoclinic, space group, *C*2/*c*, $a = 37.038(4)$ Å, $b = 6.4832(6)$ Å, $c = 7.4521(7)$ Å, $\alpha = 90.00°$, $\beta = 91.787(10)°$, $\gamma = 90.00°$, $V = 1788.6(3)$ Å^3, $Z = 4$, density = 1.431 g/cm^3, $F(0\,0\,0) = 796$, Abs. Coeff./mm^{-1} = 0.768, 6851 reflection collected, 1615 unique, R indices $[I > 2\sigma(I)] = 0.0753$, R indices (all data) = 0.0875, and gof = 1.238.
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