

Oxidation of primary aromatic amines to azo derivatives with sodium periodate using polystyrene-bound manganese(III) porphyrin

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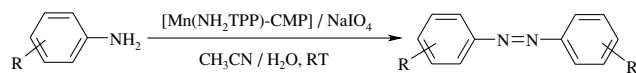
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The manganese (III) complex of 5,10,15,20-tetrakis(4-aminophenyl)porphyrin covalently bound to crosslinked chloromethylated polystyrene [Mn(H₂NTPP)-CMP] can act as an efficient catalyst for oxidation of primary aromatic amines to the corresponding azo compounds by sodium periodate in the presence of imidazole as axial ligand.

Keywords: primary aromatic amines, sodium periodate, manganese(III) porphyrin

The heme-containing monooxygenase cytochrome P-450 oxidises a wide variety of organic compounds.¹ Among the more biologically significant of these processes are *O*- and *N*-dealkylation,² olefin and arene epoxidation,^{3,4} alkane hydroxylation⁵ and oxidation of nitroso⁶ and primary aromatic amines to nitro derivatives.⁷ Various single oxygen-atom donors such as iodobenzene, hypochlorites, potassium monopersulfate and periodates^{8–13} have been used for these oxygenation reactions. However, instability of metalloporphyrins toward oxidative degradation and difficulty in recovery of the expensive catalyst, limit the practical applications of metalloporphyrin catalysts in both synthetic and industrial processes. On the other hand, immobilisation of metalloporphyrin complexes on solid supports can provide catalysts, which are easier to handle, and may exhibit improved selectivities and activities because of the support environment. To date, different approaches have been taken in the design of heterogeneous metalloporphyrin catalysts including: (i) electrostatic binding of charged porphyrins to counter-charged supports, (ii) intercalation or entrapment of porphyrin between the layers of clays or within the pores or matrices of solids, (iii) axial ligation to surface bound ligands and (iv) covalent bonding to the supports.^{14–20}

In our interest in the oxidation of amines,^{21,22} here we report the use of [Mn(H₂NTPP)-CMP] as a heterogeneous catalyst in the oxidation of primary aromatic amines to azo derivatives with sodium periodate. The catalyst exhibits a high activity and stability in the oxidation of amines with NaIO₄ in the presence of imidazole as axial ligand (Scheme 1)



Scheme 1

Results and discussion

Oxidation of primary aromatic amines with sodium periodate catalyzed by [Mn(H₂NTPP)-CMP]: The potential of this supported manganese(III) porphyrin as catalyst for oxidation of primary aromatic amines was initially investigated with *p*-toluidine in the presence of sodium periodate. The reaction was carried in 1:1 acetonitrile/water mixture, in which a higher azo yield was observed. Control experiments showed that in the absence of catalyst no oxidation to azo compounds

occurs. The effect of different axial ligands upon the oxidation rate decreased in the order: imidazole > *t*-butylpyridine > 4-methylpyridine > 2-methylpyridine > pyridine. The optimum condition used for the oxidation of *p*-toluidine with this heterogeneous system, was catalyst, oxidant, imidazole and substrate in a molar ratio of 0.02: 2: 0.2: 1, respectively.

Polystyrene-supported tetrakis(4-aminophenyl)porphyrinato manganese(III) was used in the reaction of a wide range of substituted amines (Table 1). The conditions used for oxidation of other primary aromatic amines were identical to the procedure described above for *p*-toluidine. Evidently, this is an efficient catalyst for oxidation of these amines. The results which are summarised in Table 1 show that this catalytic system can oxidize the primary aromatic amines to azo compounds with NaIO₄ in good isolated yields (54–89%) at room temperature.

Comparison of this heterogeneous system with previous reported homogeneous systems^{21,22} showed that in the former the yields are the same but the reaction times are longer.

Catalyst reuse and stability: The stability of [Mn(H₂NTPP)-CMP] was studied in repeated oxidation reactions. The oxidation of *p*-toluidine was chosen as a model substrate for the study of catalyst reuse and stability. The reaction was carried out as described above. At the end of the reaction, the catalyst was removed by filtration and washed with water and acetonitrile and reused. The dried catalyst was consecutively reused four times. After the use of catalyst for four consecutive times, the azo yield was 80%. The amount of leached Mn (1.2%) was determined by atomic absorption (Table 2).

Experimental

The porphyrin ligand, 5,10,15,20-tetrakis-(4-aminophenyl)porphyrin, was prepared and metalated according to the literature procedures.²³ Amines were obtained from Merck or Fluka and were passed through a column containing active alumina to remove peroxidic impurities.

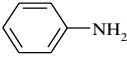
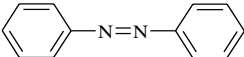
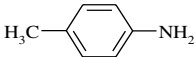
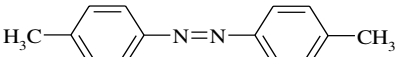
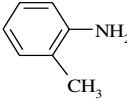
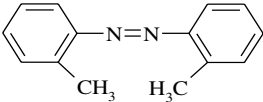
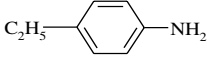
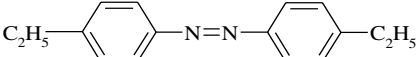
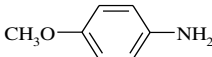
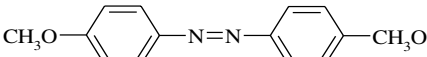
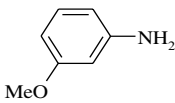
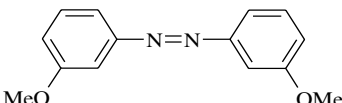
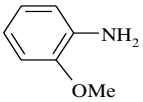
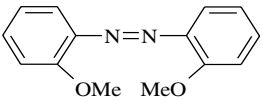
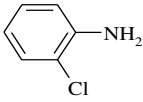
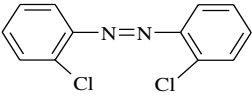
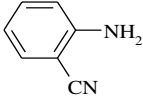
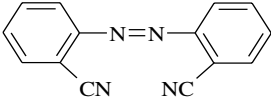
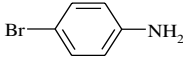
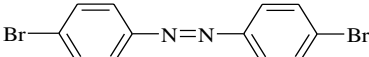
Preparation of polystyrene-bound manganese(III)5,10,15,20-tetrakis-(4-aminophenyl) porphyrin: Chloromethylated polystyrene crosslinked with 2% divinylbenzene (Merck) (2.0g) was suspended in DMF (100 ml) and manganese(III)5,10,15,20-tetrakis-(4-aminophenyl)porphyrin (1.67 g (2.48 mmol)) and triethylamine (5 ml) was added. The mixture was refluxed for 72 h in the dark under N₂ atmosphere while being stirred magnetically and then cooled to room temperature. The dark green coloured resin was suction filtered, washed thoroughly with DMF, methanol and then acetone, and dried under vacuum at room temperature for 24 h.

General procedure for oxidation of primary aromatic amines to azo compounds: A 25 ml flask was charged with amine (1 mmole), polystyrene-bound manganese porphyrin (150 mg), imidazole (0.2 mmole) and CH₃CN (10 ml). After addition of sodium periodate solution (2 mmole in 10 ml H₂O), the mixture was stirred

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† This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.

Table 1 Oxidation of primary aromatic amines to azo derivatives with NaIO₄ catalysed by [Mn(H₂NTPP)-CMP] in the presence of imidazole

Row	Substrate	Products	Time(h)	Yield ^a /%	M.p./°C Found(reported) ²⁴
1			3	80	69(71)
2			3	85	145(144–145)
3			3	82	57(55)
4			3	89	139(140–141)
5			2.5	87	118(118–119)
6			2.5	82	75(73–74)
7			3	84	152(153)
8			5.5	55	56(57–58)
9			5.5	60	56(57–58)
10			5.5	55	203(205)

^aIsolated yields based on starting aromatic amine.

Table 2 The results of [Mn(H₂NTPP)-CMP] catalyst recovery and the manganese leached in the oxidation of *p*-toluidine with sodium periodate

Run	Conversion/% ^a	Mn leached/% ^b	Time/h
1	85	1.2	3
2	83	0.9	3
3	80	0.7	3
4	80	0	3

^aGLC yield based on starting *p*-toluidine.

magnetically at room temperature for 3–5.5 h. Progress of the reaction was followed by GLC. After the reaction was completed, the polymer beads were filtered off and the filtrates were extracted with CH₂Cl₂ and were purified by silica gel plate or silica gel column (eluent: CCl₄-Et₂O). The identities of products were confirmed by IR and ¹H NMR spectral data.

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