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Oxyfunctionalization of Cyclohexane Catalyzed by Oxo-bridged Manganese Schiff Base Complexes

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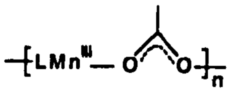
Abstract: Oxo-bridged polynuclear manganese Schiff base complexes catalyzed the oxidation of cyclohexane to cyclohexanol and cyclohexanone in the presence of tert-butyl hydroperoxide or hydrogen peroxide.

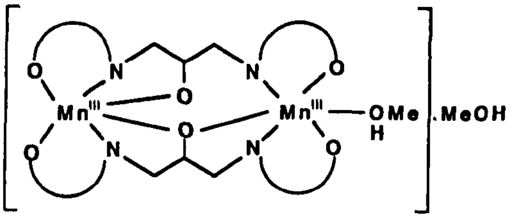
Selective and catalytic oxyfunctionalization of alkanes under homogeneous condition is an important research objective.[1] Currently, there is a great deal of interest in the biomimetic models of methane monooxygenase (MMO) enzyme. Spectroscopic studies on the MMO enzyme established that the catalytic site is comprised of a μ-hydroxo diiron core with bridging and terminal carboxylate anions.[2] A few models of MMO, consisting of μ-oxo and μ-hydroxo-bridged diiron non-haem complexes, have been shown to catalyze oxidation of alkanes to alcohols (and ketones) with dioxygen in conjunction with an electron donor or a single oxygen donor such as alkylhydroperoxide or hydrogen peroxide.[3] Recently, a few manganese analogues of this system have also been reported to effect the oxidation of alkanes.[4] Herein we report, for the first time, easily accessible polynuclear manganese Schiff base complexes, containing a variety of oxo-bridged structural features, as catalysts for oxyfunctionalization of cyclohexane with tert-butyl hydroperoxide (TBHP) or hydrogen peroxide.

The complexes were prepared by literature methods[5] and characterized by elemental analysis, IR and UV-vis spectroscopy. These metal complexes possess structural features that are uncommon to the earlier reported[4] manganese systems for the catalytic oxidation of alkanes. The Mn complex 1 is polymeric in nature where the metal ions are bridged by acetate groups. The unsymmetrical binuclear complex 2 has a μ-alkoxo bridge. The complex 3 has two Mn(IV) ions linked by a di-μ-oxo bridge.

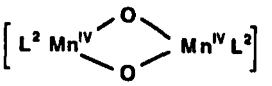
The oxidation reactions with these complexes were performed as follows. TBHP (2 mmol) was added to a solution of the manganese complex (0.02 mmol) and cyclohexane (20 mmol) in acetonitrile (15 ml) and the solution stirred at room temperature under argon atmosphere. the products were estimated by gas chromatography analysis using internal standard method. The results are shown in the Table 1.



1



2, Ligand = L^1



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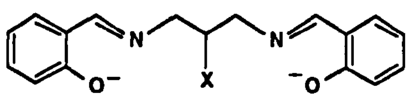
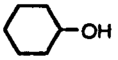
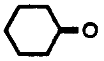


L, X = OH; L^1, X = O$^-$; L^2, X = H

No oxidation of cyclohexane occurred in the absence of the catalyst. The complex 1 catalyzed the oxidation of cyclohexane with TBHP to give cyclohexanol and cyclohexanone in a combined yield (based on TBHP taken) of 72% in 3 h (run 1) which increased to 84% in 6 h (run 2). The complex 2 showed similar catalytic activity for the oxidation of cyclohexane (runs 4, 5). However, the complex 3 was found to be a poor catalyst (run 6), which may be due its partial solubility in acetonitrile under the reaction conditions. The reaction was faster when higher amounts (3 mmol) of TBHP were used, as evident from the comparison of the catalyst turnover numbers in runs 1 and 3. The catalytic turnover numbers and yields of cyclohexanol and cyclohexanone with the complexes 1 and 2 are significantly higher than those for the recently reported[4e,f] Mn complexes for the oxidation of cyclohexane.

In all the reactions, oxidation of cyclohexane gave cyclohexanol and cyclohexanone in nearly 1:1 ratio, which appears to be independent of the nature of the catalyst. The ability of the system to catalyze the oxidation of cyclohexanol to cyclohexanone was confirmed as follows. In an independent experiment, oxidation of cyclohexanol (1 mmol) with TBHP (2 mmol) and complex 1 (0.02 mmol) under similar conditions gave cyclohexanone in 20% yield (molar yield based on TBHP taken) in 3 h, which increased to 23% in 6 h. However, the rate of cyclohexanone formation in the

Table 1. Oxidation of cyclohexane by tert-butyl hydroperoxide or hydrogen peroxide catalyzed by Mn complexes[a]

				Yield[b] (%)		
Run	Catalyst	Oxidant	t/h			TON[c]
1	1	TBHP	3	24	48	72
2	1	TBHP	6	28	56	84
3	1	TBHP[d]	3	19	36	83
4	2	TBHP	3	21	39	60
5	2	TBHP	6	23	47	70
6	3[e]	TBHP	3	1	2	3
7	4[f]	TBHP	3	6	11	17
8	1	H_2O_2[d]	3	3	3	9
9	2	H_2O_2[d]	3	3	4	11
10	3	H_2O_2[d]	3	1	<1	2

[a] Mn complex (0.02 mmol), TBHP (2 mmol) and cyclohexane (20 mmol) were taken. Catalyst:oxidant:substrate mole ratio 1:100:1000. [b] Yields are based on TBHP taken. The yields of cyclohexanone take into account the fact that two equivalents of TBHP are required to produce one equivalent of cyclohexanone. [c] Turnover number = (moles of cyclohexanol + 2 x moles of cyclohexanone)/moles of catalyst. [d] 3 mmoles of oxidant were used. Catalyst:oxidant:substrate mole ratio 1:150:1000. [e] Only partially soluble. [f] 4 = Manganese(III) acetate dihydrate.

above reaction is lower than that in the oxidation of cyclohexane by TBHP and 1, where such yields are 24 and 28%, respectively (runs 1,2). This indicates formation of cyclohexanone directly from cyclohexane without the intermediacy of cyclohexanol even though *in situ* oxidation of cyclohexanol can give cyclohexanone. Such a catalytic activity has been demonstrated in the oxidation of cyclohexane by TBHP in the presence of μ-oxo-bridged diferric complexes.[3a] Manganese(III) acetate dihydrate[6] (4), which is proposed to be a trinuclear metal cluster with oxo- and acetato-bridges[7], also catalyzed the oxidation of cyclohexane with TBHP (run 7).

Hydrogen peroxide was less effective as an oxidant as compared to TBHP for the oxidation of cyclohexane with catalysts 1-3 (runs 8-10). No oxidation of cyclohexane was observed with complex 1 and dioxygen as an oxidant. This rules out the possibility of oxidation of cyclohexane by the Mn complexes and dioxygen that might be formed by decomposition of TBHP during the reaction.

Addition of 2,6-di-t-butyl-4-methylphenol (10 equiv.) as a radical scavenger to the reaction in run 1 did not affect the yields of the oxidation products. This result implies that free alkoxyl or peroxyl radicals are not involved in these oxidation reactions. The mechanism of oxyfunctionalization and activity of these complexes for the oxidation of other alkanes, arenes and alkenes are under investigation.

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