

Letter

Oxidation of cyclohexane by tert-butyl hydroperoxide catalyzed by manganese(II) *N,N'*-ethylene bis(salicylideneaminato) and analogous complexes

Pralhad A. Ganeshpure^{*}, Gopal L. Tembe, Sheo Satish

Research Center, Indian Petrochemicals Corporation Limited, Vadodara 391 346, India

Received 5 June 1996; accepted 25 August 1996

Abstract

Manganese(II) *N,N'*-ethylene bis(salicylideneaminato) (1) and analogous manganese(II) complexes 2–5 catalyzed oxyfunctionalization of cyclohexane by tert-butyl hydroperoxide to give cyclohexanol and cyclohexanone in high yields at room temperature in acetonitrile solution. A pathway involving oxomanganese intermediate is suggested for the reaction.

Keywords: Oxidation; Manganese(II) complexes; tert-Butyl hydroperoxide; Cyclohexane; Adamantane

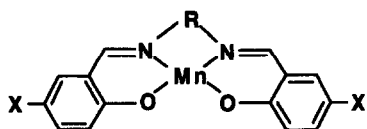
Selective and catalytic hydroxylation of alkanes under mild conditions is still an important challenge for chemists [1]. The oxidation of alkanes by tert-butyl hydroperoxide (TBHP) in the presence of μ -oxo-bridged diiron complexes as catalysts is of current interest [2,3]. These complexes containing Fe–O–Fe unit provide structural models for the active site in methane mono-oxygenase (MMO) enzyme. Recent investigations on MMO have shown that the active site has μ -hydroxo diiron core, where they catalyze variety of oxidation reactions [4]. Analogous μ -oxo-bridged binuclear manganese complexes have also been reported to catalyze oxidation of alkanes by TBHP to alcohols and

ketones [5–9]. We have observed, for the first time, that even mononuclear manganese(II) Schiff base complexes can be employed in the above system to catalyze oxidation of alkanes in a similar manner. Herein, we report manganese(II) salen and analogous complexes as catalysts for the oxidation of cyclohexane by TBHP at room temperature in acetonitrile solution.

The manganese(II) Schiff base complexes 1–5 were prepared by the literature procedures [10,11] and characterized by elemental analysis and IR spectroscopy. A typical procedure for the oxidation reaction is as follows. TBHP (4 mmol) was added to a solution of Mn complex (0.04 mmol) and cyclohexane (40 mmol) and the resultant homogeneous solution stirred at room temperature under argon atmosphere. The

^{*} Corresponding author.

products were analyzed by GC using internal standard method. The results are shown in Table 1.



- 1 R = (CH₂)₂, X = H 2 R = (CH₂)₂, X = OCH₃
 3 R = 1,2-C₆H₄, X = H 4 R = (CH₂)₃, X = H
 5 R = (CH₂)₃N(CH₂)₃, X = H
 |
 CH₃

No oxidation of cyclohexane occurred in the absence of the catalyst. The manganous salt, Mn(OAc)₂ · 4H₂O did not catalyze oxidation of cyclohexane under the above conditions. Oxidation of cyclohexane in the presence of Mn^{II}(salen) (**1**) gave cyclohexanol and cyclohexanone, as the only products, in 74% yield (combined yield based on TBHP taken) with a catalyst turnover number (TON) of 74 (run 1).

Table 1
Oxidation of cyclohexane by TBHP catalyzed by Mn^{II} complexes ^a

Run	Complex	Yield ^b (%)		TON ^c
		Cyclohexanol	Cyclohexanone	
1	1	21	53	74
2 ^d	1	12	33	90
3	2	19	43	62
4	3	20	30	50
5	4	10	22	32
6	5	18	44	62
7 ^e	1	15	51	66
8 ^f	1	13	54	67

^a Mn complex (0.04 mmol), TBHP (4 mmol) and cyclohexane (40 mmol) were taken. Catalyst:oxidant:substrate molar ratio 1:100:1000. Reaction time 3 h.

^b Yield based on TBHP taken. Cyclohexanone yields were calculated considering the requirement of 2 mol of TBHP to produce 1 mol of ketone.

^c Turnover number = (mol of cyclohexanol + 2 × mol of cyclohexanone)/mol of catalyst.

^d Additional amount of TBHP (4 mmol) was added after 3 h and stirred further for 3 h. Catalyst:oxidant:substrate molar ratio 1:200:1000.

^e 2,6-Di-tert-butyl-4-methylphenol (0.4 mmol) was added.

^f 2,6-Di-tert-butyl-4-methylphenol (1.2 mmol) was added.

Addition of further amounts of TBHP (4 mmol) increased the catalyst TON to 90 (run 2). Similarly, Mn(II) complexes **2–5** catalyzed the oxidation of cyclohexane to give moderate to high yields of cyclohexanol and cyclohexanone (runs 3–6). The yields of cyclohexanol and cyclohexanone in the present system are substantially higher than those reported for the oxo-bridged binuclear Mn complexes catalyzed oxidation of cyclohexane [5–8].

Oxidation of adamantane by TBHP in the presence of complex **1** gave 1-adamantanol as a major product with 2-adamantanone in 20% yield together (catalyst:oxidant:substrate mole ratio 1:100:100). Oxidation of *cis*-cyclooctene by TBHP and **1** afforded corresponding epoxide in 17% yield. The system was able to catalyze oxidation of secondary alcohols to ketones as demonstrated by the following example. Oxidation of cyclohexanol (2 mmol) with TBHP (4 mmol) in the presence of complex **1** (0.04 mmol) gave cyclohexanone (0.7 mmol) in 3 h. It was noted that the yield of cyclohexanone in the above reaction is lower than that in the oxidation of cyclohexane with TBHP and **1** where such yield is 1.06 mmol. This indicates formation of part of the cyclohexanone directly from cyclohexane without the intermediacy of cyclohexanol as observed in the systems using μ -oxo-bridged diferric complexes and TBHP [2].

In the oxidation reactions a dark brown precipitate is observed at the end of all the runs. This indicates transformation of the metal complex into an insoluble species which causes termination of the catalytic cycle. The nature of the insoluble dark brown species is under investigation.

No oxidation of cyclohexane occurred with complex **1** and dioxygen as an oxidant. The reaction in run 1 under dioxygen atmosphere (O₂ balloon) gave the same yields and cyclohexanol/cyclohexanone ratio. Therefore, dioxygen that might be formed by decomposition of TBHP does not appear to be involved in the reaction unlike in cases of some TBHP/Fe systems [12,13]. Addition of 2,6-di-tert-butyl-

4-methylphenol (10 and 30 eq.), as a free radical inhibitor, did not significantly alter the yields of the oxidation products in the oxidation of cyclohexane catalyzed by $Mn^{II}(\text{salen})$ (runs 7 and 8). The results imply that long chain radical processes are not involved in the reaction [12]. No free radical coupling products such as tert-butylperoxycyclohexane or dicyclohexyl were detected in runs 1–8. This indicates that the mechanism of the present reaction is different from that of the traditional radical autoxidation.

Mechanism of oxygen transfer from alkyl hydroperoxides to alkanes in the presence of transition metal complexes may proceed either by heterolytic cleavage of the peroxide bond to give the putative oxo-metal intermediate or via homolysis involving alkoxy and/or peroxy free radicals [14]. The mechanistic path will depend on the nature of the metal complex and also on the oxidant employed [14]. Recently, heterolytic mechanisms implicating high-valent oxomanganese species have been proposed for several metal catalyzed oxidations of alkanes by TBHP [3,6,14,15]. By analogy to these systems and considering the apparent nonradical character of the present reaction, we propose that the mechanism might involve formation of $LMn-O(H)-O^tBu$ intermediate followed by heterolysis of O–O bond to generate high-valent oxomanganese species, responsible for the catalytic oxidations. However, the possibility of a free radical pathway operating simultaneously cannot be ruled out.

Acknowledgements

We thank P.J. Patel and R. Antony for their assistance in carrying out the experiments.

References

- [1] C.L. Hill ed., *Activation and Functionalization of Alkanes* (Wiley, New York, 1989).
- [2] S. Menage, J.M. Vincent, C. Lambeaux, G. Chottard, A. Grand and M. Fontecave, *Inorg. Chem.* 32 (1993) 4766 and references therein.
- [3] R.A. Leising, J. Kim, M.A. Perez and L. Que, Jr., *J. Am. Chem. Soc.* 115 (1993) 9524.
- [4] A.C. Rosenzweig, C.A. Frederick, S.J. Lippard and P. Nordlund, *Nature (London)* 366 (1993) 537.
- [5] C.M. Che, W.T. Tang, K.Y. Wong, W.T. Wong and T.F. Lai, *J. Chem. Res. (S)* (1991) 30.
- [6] S. Menage, M.N. Collomb-Dunand-Sauthier, C. Lambeaux and M. Fontecave, *J. Chem. Soc., Chem. Commun.* (1994) 1885.
- [7] J.M. Vincent, S. Menage, C. Lambeaux and M. Fontecave, *Tetrahedron Lett.* 35 (1994) 6287.
- [8] D. Tetard, A. Rabion, J.B. Verlhac and J. Guilhem, *J. Chem. Soc., Chem. Commun.* (1995) 531.
- [9] P.A. Ganeshpure, G.L. Tembe and S. Satish, *Tetrahedron Lett.* 36 (1995) 8861.
- [10] K. Srinivasan, P. Michaud and J.K. Kochi, *J. Am. Chem. Soc.* 108 (1986) 2309.
- [11] C.P. Horwitz, P.J. Winslow, J.T. Warden and C.A. Lisek, *Inorg. Chem.* 32 (1993) 82.
- [12] R.H. Fish, K.J. Oberhausen, S. Chen, J.F. Richardson, W. Pierce and R.M. Buchanan, *Catal. Lett.* 18 (1993) 357.
- [13] D.H.R. Barton, S.D. Beviere, W. Chavasiri, D. Doller and B. Hu, *Tetrahedron Lett.* 33 (1992) 5473.
- [14] W.A. Lee and T.C. Bruice, *J. Am. Chem. Soc.* 107 (1985) 513.
- [15] S.-I. Murahashi, Y. Oda, T. Naota and T. Kuwabara, *Tetrahedron Lett.* 34 (1993) 1299.