Oxidation of organic substrates catalyzed by novel mixed-ligand manganese(III) complexes

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Abstract

Novel [Mn^{III}(amp)(bipy)(Cl)] (**1**) (H$_2$amp: *N*-(hydroxyphenyl)salicyldimine; bipy: 2,2′-bipyridyl) and [Mn^{III}(app)(bipy)-(Cl)]$^+$ (**2**) (H$_2$app: *N*-(hydroxyphenyl)pyridine-2- carboxaldimine; bipy: 2,2′-bipyridyl) complexes have been synthesized and characterized by physico-chemical methods. Complexes **1** and **2** have been employed as catalysts in the oxidation of both saturated and unsaturated hydrocarbons using *tert*-butylhydroperoxide (*t*-BuOOH). A mechanism involving formation of and transfer from a reactive highvalent Mn(V)-oxo species as catalytic intermediate is proposed for the catalytic processes. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Oxo transfer reaction catalyzed by transition metal complexes is of abiding import in inorganic research. In this regard metalloporphyrins have been used [1] extensively owing to their direct relationship to enzymatic oxidation with cytochrome P-450 [2,3]. Parallel to these porphyrin chemistries, the same catalytic reactions that are mimicked by various transition metal complexes [4–14], in particular ruthenium complexes [15–26] containing non-porphyrinic ligands, viz. polyaminopolycarboxylate, Schiff-bases, polypyridyl ligands, etc. have concerned us [27–33]. Evaluation of metal complexes with the requisites necessary for effective and selective catalytic transformation is our goal. Ruthenium complexes by virtue of their wide range of reversible and accessible oxidation states have proved to be useful catalysts for oxidation of myriad of a organic substrates using various terminal oxidants. However, manganese complexes with reportedly notable catalytic properties towards hydrocarbon oxidation in homogeneous [7,10,12] as well as in heterogenized-homogeneous conditions [34–37] should be potentially interesting. This prompted us to undertake the present research and we have thus undertaken an investigation of hydrocarbon oxidation with *t*-BuOOH catalyzed by new [Mn^{III}(amp)(bipy)(Cl)] (**1**) (H$_2$amp: *N*-(hydroxyphenyl)salicyldimine; bipy: 2,2′-bipyridyl) and [Mn^{III}(app)(bipy)(Cl)]$^+$ (**2**) (H$_2$app: *N*-(hydroxyphenyl)pyridine-2-carboxaldimine; bipy: 2,2′-bipyridyl) complexes. The use of *t*-BuOOH is of particular interest with regard to the negligible use of this potentially strong terminal oxidant in the catalytic processes involving manganese complexes. Further, safety and environmental concerns have attached special importance to the use

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of alkyl hydroperoxide and hydrogen peroxide in the catalytic scheme. The present paper reports the synthesis and characterization of complexes **1** and **2** along with their reactivities toward oxidation of saturated and unsaturated hydrocarbons in presence of *t*-BuOOH under ambient conditions.

2. Experimental

2.1. Materials

The [Mn^{III}(amp)(bipy)(Cl)]·H_2O complex (**1**) was synthesized by interacting $MnCl_2$·$4H_2O$ with *N*-(2-hydroxyphenyl)salicyldimine (H_2amp) [38] and 2,2′-bipyridyl (bipy) in a stoichiometric ratio. To a methanolic solution of $MnCl_2$·$4H_2O$ (0.396 g, 2 mmol in 10 ml) solution of (15 ml) of H_2amp (0.426 g, 2 mmol) containing KOH (4 mmol, 224 mg) was added and resultant mixture was stirred for 10 min. On addition of 2,2′-bipyridyl (0.312 g, 2 mmol) to this solution, the orange colour changed to dark brown. The mixture was refluxed for 8 h. A dark solid separated, which was filtered, washed with water and little methanol, and finally dried in decicator over $CaCl_2$; yield (80%). Anal. Calculated for $MnC_{23}N_3O_3H_{19}Cl$: C, 58.24; H, 4.11; N, 7.88. Found: C, 58.04; H, 3.99; N, 7.91. UV–VIS data in CH_3CN (λ_{max}, nm (ε_{max}, M^{-1} cm^{-1}): 235 (30944), 252 (22477), 324 (9215), 431(2832). IR(cm^{-1}) as KBr pellet: 3391, 2361, 1598, 1467, 1301, 758,356. $\mu_{eff} = 5.17$ BM.

The [Mn^{III}(app)(bipy)(Cl)]Cl complex (**2**) was synthesized by following the same procedure as adapted for complex **1**. Salicyldehyde was replaced by 2-pyridine carboxaldehyde in this instant. To a methanolic solution (10 ml) of $MnCl_2$·$4H_2O$ (0.595 g, 3 mmol in 10 ml) methanolic solution (15 ml) of 2-aminophenol (0.327 g, 3 mmol) and 2-pyridine carboxaldehyde (0.3 ml, 3 mmol) was added and stirred for 10 min. 2,2′-Bipyridyl (0.469 g, 3 mmol) was then added and the resultant mixture was further refluxed for 8 h. The dark brown solution, which upon evaporation to dryness yielded a solid, which was washed thoroughly with water–methanol (8:2) mixture, and finally dried in decicator over $CaCl_2$; yield (70%). Anal. Calculated for $MnC_{22}N_4OH_{17}Cl_2$: C, 57.24; H, 4.55; N, 11.32. Found: C, 56.94; H, 4.23; N, 11.69. UV–VIS data in CH_3CN (λ_{max}, nm (ε_{max},

M^{-1} cm^{-1}): 235 (19661), 282 (16960), 411 (4127), 431 (3931), 435 (1758). IR (cm^{-1}) as KBr pellet: 3068, 2358, 1594, 1438, 773, 414. $\mu_{eff} = 4.91$ BM.

All other chemicals and solvents were of analytical reagent grade and used as obtained. Doubly-distilled water was used throughout the experiments.

2.2. Instrumentation

The electronic absorption spectra were measured with a GBC Cintra 10 spectrophotometer. Infrared spectra were obtained on a Perkin-Elmer (Model 783) spectrometer (using KBr pellets). Electrochemical studies were carried out in acetonitrile medium by using tetrabutylammoniumperchlorate (TBAP) as supporting electrolyte. A PAR Electrochemical equipment (Model 174A) equipped with a platinum working electrode and standard calomel electrode (SCE) as reference were used for this purpose. All potentials are expressed against SCE. Magnetic susceptibility was measured by using a PAR-155 vibrating sample magnetometer. A Perkin-Elmer 240C elemental analyzer was used to collect micro analytical data (C, H, N).

2.3. Procedure of catalytic studies

In a typical experiment 0.1 mmol of catalyst complex **1/2**, 0.1 mmol of benzyltributylammoniumchloride (phase transfer catalyst, PTC) and 10.0 mmol of substrate in 10 ml of CH_2Cl_2 were magnetically stirred with 10.0 mmol *t*-BuOOH (70% aqueous solution) at room temperature. Aliquots of the CH_2Cl_2 layer was withdrawn at chosen interval of time subjected to gas chromatographic (GC) analysis for product(s). Gas chromatographic analysis were performed with a Carlo Erba GC 8000^{Top} series on a Tenax column connected with a FID detector. GC parameters were quantified by the authentic product samples prior to the analysis.

3. Results and discussion

The structural representation (tentative) of the complexes **1** and **2** is shown in Fig. 1. The IR spectra of the complexes show all the expected bands for coordinated Schiff-base type (amp/app) and bipy ligands.
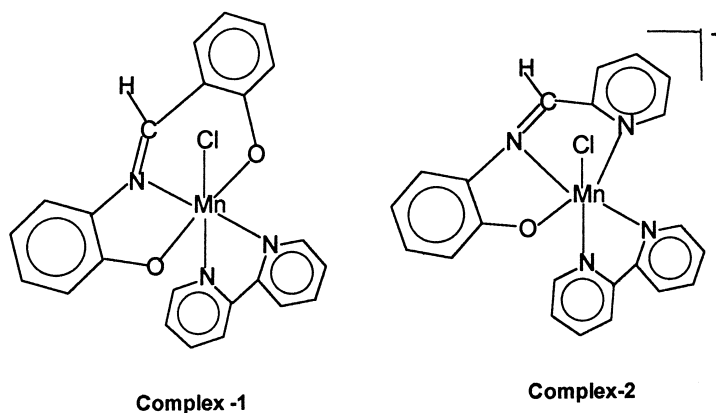
Fig. 1. Schematic representation of complex **1**.

The bands at $1580\,cm^{-1}$ and $1240\,cm^{-1}$ are assigned to coordinated C=N– and C–O– stretchings, respectively. Complexes **1** and **2** afford reddish brown solutions in organic solvents. A number of bands, charge transfer in nature, are observed in UV–VIS region (see Section 2). Representative example is shown in Fig. 2. The magnetic moments of complexes **1** and **2** conform to the high spin d^4 configuration. The UV–VIS spectrum of complex **1** in CH_3CN (Fig. 2) is characterized by charge transfer bands. Complexes **1** and **2** were electrochemically examined at a platinum working electrode in acetonitrile solution and found that both the complexes undergo reductive degradation in CH_3CN. A large anodic current noticed on the reverse scan was exhibitive of the electrode pollution, which was further corroborated by electrode deposition.

Catalytic oxidations of the organic substrates (S) was carried out in a biphasic medium (CH_2Cl_2/H_2O) in presence of a phase transfer catalyst (PTC) benzyltributylammonium chloride. The potency of catalyst complexes was examined under a standard set of conditions (see Section 2 for reaction conditions). Blank experiments demonstrated that each component is essential for an effective catalytic transformation. The results of the catalytic reactions summarized in Table 1 indicate that the complexes **1** and **2** are not strongly
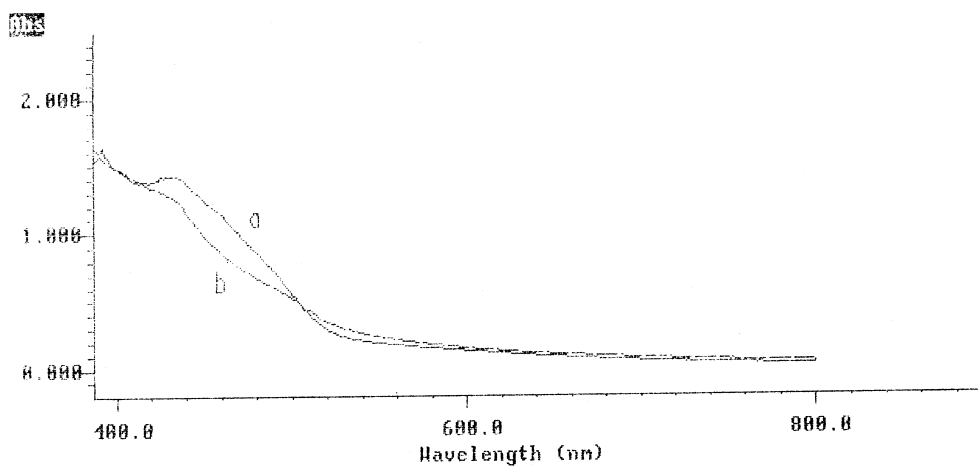

Fig. 2. Spectra of (a) complex **1** in CH_3CN and (b) immediately after addition of *t*-BuOOH.

Table 1
Results of the catalyzed oxidation of organic substrates with *t*-BuOOH[a]

Substrate	Product(s)[b]	Complex **1** Yield (%)[c]	Complex **2** Yield (%)[c]
Cyclohexene	Cyclohexene-1-ol	14	21
	Cyclohexepoxide	5	3
Cyclohexane	Cyclohexanol	6	8
	Cyclohexanone	2	10
Cyclohexanol	Cyclohexanone	15	17
cis-Stilbene	Benzaldehyde	13	21
	cis-Stilbeneoxide	28	5
	trans-Stilbeneoxide	57	70
trans-Stilbene	Benzaldehyde	9	13
	cis-Stilbeneoxide	25	4
	trans-Stilbeneoxide	71	76
Tetrahydrofuran	γ-Butyrolactone	36	33
Toluene	Benzylalcohol	11	10
Benzylalcohol	Benzaldehyde	6	13
	Benzaldehyde	42	43
Indene	Indeneoxide	36	25

[a] See Section 2 for reaction condition.
[b] After 4 h of reaction.
[c] Based on substrate concentration.

differentiated in their competency to produce olefin epoxide. With each catalyst cyclohexene is converted to its epoxide together with cyclohexene-1-ol. Formation of allylic oxidation product cyclohexene-1-ol in appreciable yields as compared to Mn-salen complexes [7] necessarily indicates the higher electrophilic nature (owing to the presence of bipy ligand) of oxomanganese(V) intermediates expectantly formed in the present catalytic process. Further, free access of allylic C–H bond (to the Mn=O bond) through side on approach [39] is favoured as the coordinated 'amp^{2-}'/'app^{-}' ligand is flat. Present catalytic system oxidizes stilbenes to epoxides (with the loss of configuration) and benzaldehyde (Table 1). The formation of epoxides in case of stilbenes oxidation are explicable with regards to the fact that it must add an oxygen atom to preserve the coordination number 4 at carbon. Electron transfer, followed by O insertion in the acyclic intermediate appears to be the main pathway for the oxidation of both *cis*-stilbene and *trans*-stilbene. Furthermore, in both cases, the lack

of streospecificity in stilbene epoxidation (Table 1) suggests the radicaloid nature of the proposed oxo-manganese(V) catalytic intermediate leading to long-life intermediate in the case of olefins containing aromatic substituents on sp^2 carbon atom. A similar observation was reported earlier [40] in oxidation of stilbene catalyzed by porphyrinatomanganese(III) complex. Steric repulsion of the phenyl rings perhaps favours rotation into less-strained '*trans*' arrangement prior to the ring closure step. For *cis*-stilbene the rotation process (*cis*- to *trans*-) vies with ring closure in *cis*-orientation and produce mixture of *cis*- and *trans*-epoxides. Formation *trans*-epoxide together with small amount of its *cis*-isomer observed in the reaction mixture for oxidation of *trans*-stilbene (Table 1) is presumably due to the fact that the rotation toward the *cis*-orientation is energetically uphill and cannot compete efficiently with the ring closure in *trans* configuration. In order to know the reaction pathway for the formation of benzaldehyde, oxidation of *cis*- and *trans*-stilbene epoxides was examined and found benzaldehyde is the reaction product both the cases, but in poor yield. This suggests that the benzaldehyde formation does not take place through any rearranged pathway. Formation of benzaldehyde in oxidation of stilbenes (Table 1) is, therefore, attributable to the oxidative cleavage of C=C double bond. Another important observation of the present investigations that both complexes **1** and **2** can readily catalyze the oxo-functionalization of C–H bond of various organic substrates. It is capable of oxidizing cyclohexane to cyclohexanol, toluene to benzyl alcohol and tetrahydrofuran to γ-butyrolactone. For alcohols, it oxidizes cyclohexanol to cyclohexanone and benzyl alcohol to benzaldehyde, but could not oxidize *t*-BuOH. This supports the need for an α-hydrogen adjacent to the hydroxyl group for hydride transfer.

4. Conclusions

Present studies persuasively demonstrates the catalytic ability of the reported complexes **1** and **2** for oxo-functionalization of unsaturated and saturated hydrocarbons using *t*-BuOOH. A highvalent Mn(V)-oxo complex is proposed to be the active species in the catalytic process. The presence of 'bipy' (which makes the oxo group adequately electrophilic in nature) and

flat 'amp^{2-}'/'app^{-}' (which comply with the steric requirement for free advance of C–H bond orthogonal to Mn=O bond) probably responsible for observing hydroxylated product in the reported catalytic system.

Acknowledgements

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