Pronounced Catalytic Activity of Manganese(III) – *Schiff* Base Complexes in the Oxidation of Alcohols by Tetrabutylammonium Peroxomonosulfate

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A novel and practical catalytic method for efficient and highly selective oxidation of a wide range of benzylic, allylic, aliphatic, primary, and secondary alcohols to the corresponding aldehydes and ketones using tetrabutylammonium peroxomonosulfate catalyzed by tetradentate *Schiff* base – Mn^{III} complexes has been developed. Electron-deficient and hindered alcohols required longer reaction times for oxidation in this catalytic system. The electron-poor and hindered salicylidene ring of the ligand enhanced the catalytic activity and stability of Mn catalysts. The desired turnover numbers obtained in the oxidation reactions indicated the high efficiency and relative stability of these simple *Schiff* base complexes in this catalytic system.

Introduction. – Oxidations of alcohols to the corresponding carbonyl compounds are pivotal reactions in organic synthesis [1] [2], and catalytic methodologies employing salen [3–11] and porphyrin [12] complexes as catalysts are particularly attractive from biological point of view. It is well-known that the copper metalloenzyme, galactose oxidase (GOase) [13], and also cytochrome P-450, a monooxygenase enzyme [14], catalyze oxidation of alcohols to the corresponding carbonyl compounds. In the last decade, *Schiff*-base ligands have received more attention, mainly because of their extensive applications in the fields of synthesis and catalysis [15–18]. They have been recognized as powerful homogeneous and heterogeneous catalysts in the oxidation reactions by various oxygen donors [3–11] [15]. However, the efficacy of these easily prepared catalysts for activation of tetrabutylammonium peroxomonosulfate (Bu_4NHSO_5) as a commercially available and easily prepared organic-soluble O-source in the oxidation of organic compounds still lags behind [19–21]. In continuation of our ongoing research on the application of Bu_4NHSO_5 in the oxidation of various organic substrates under catalytic [12] [22–24] and non-catalytic conditions [25] [26], now we describe the high efficiency of simple Mn^{III} – *Schiff* base complexes for activation of this versatile O-source in the highly selective oxidation of alcohols in desired times (*Scheme*). The influence of electronic and structural features of the substrate and also *Schiff*-base ligand in Mn catalysts on the reaction rates has also been investigated in this study (*Fig. 1*).

Results and Discussion. – The oxidation of benzyl alcohol ($PhCH_2OH$) with Bu_4NHSO_5, which proceed sluggishly in the absence of catalyst under mild conditions,

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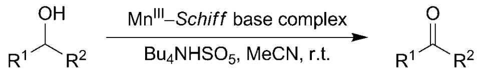
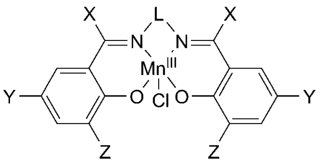
Scheme. *Oxidation of Different Alcohols Using* Bu_4NHSO_5 *Catalyzed by* Mn^{III}*–*Schiff *Base Complexes*



R^1, R^2 = H, Alkyl, Benzyl, Aryl (see *Table 2*)



	L	X	Y	Z
Mn-1	C_6H_4	H	H	H
Mn-2	C_6H_4	Me	H	H
Mn-3	C_6H_4	H	MeO	H
Mn-4	C_6H_4	H	NO_2	H
Mn-5	C_6H_4	H	*t*-Bu	*t*-Bu
Mn-6	$(CH_2)_2$	H	H	H
Mn-7	$(CH_2)_3$	H	H	H
Mn-8	$(CH_2)_4$	H	H	H
Mn-9	$(CH_2)_6$	H	H	H
Mn-10	$(CH_2)_2$	Me	H	H
Mn-11	$(CH_2)_3$	Me	H	H
Mn-12	$(CH_2)_4$	Me	H	H
Mn-13	$(CH_2)_6$	Me	H	H

Fig. 1. *Mn–*Schiff *base complexes employed in this study*

was used as a model reaction in $CHCl_3$ (23% after 24 h). To find optimum reaction conditions, the influence of different factors, affecting the conversion and selectivity of the oxidation reaction, such as catalyst concentration, solvent nature, and ligand structure, was investigated. Performing the oxidation reaction of $PhCH_2OH$ in the presence of 1 mol-% of [Mn(salphen)Cl] catalyst (salphen = *N*,*N′*-bis(salicylidene)-phenylenediamine dianion ligand; *Fig. 1*; **Mn-1**) and 1.7 equiv. of Bu_4NHSO_5 in $CHCl_3$ enhanced the conversion markedly (70% after 5 min). The increase of the mole percentage up to 10 mol-% of Mn catalyst did not affect the conversion rate of oxidation. Also the influence of imidazoles and pyridines as axial nitrogenous bases, having dramatic effects on the rate and selectivity in the oxidation reaction catalyzed by various transition-metal complexes such as porphyrin [27] and salen catalysts [28], has been studied. In the present oxidation method, however, the same yields and selectivity were obtained for alcohol oxidation in the presence or in the absence of various N-donors such as imidazole, pyridine, and 4-methylmorpholine 4-oxide.

Then, the influence of solvent nature in this catalytic system has been studied. Examination of five solvents such as CH_2Cl_2, $CHCl_3$, acetone, MeCN, MeOH, and EtOH in this catalytic reaction revealed MeCN as the best solvent in terms of conversion rate and benzaldehyde yield (*Table 1*). Complete conversion of $PhCH_2OH$ occurred under these conditions, and PhCHO was obtained in 95% yield within 3 min without any formation of over-oxidation product.

The Catalytic Oxidation of Alcohols Using Bu_4NHSO_5. To establish the general applicability of the catalytic system, a wide range of primary and secondary aliphatic, allylic and benzylic alcohols were subjected to oxidation under the optimized

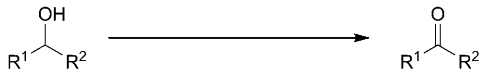
Table 1. *Influence of the Solvent on the Oxidation of* $PhCH_2OH$ *Using* Bu_4NHSO_5 *Catalyzed by* **Mn-1**[a])

Solvent	PhCHO Yield [%][b])
EtOH	21
MeOH	28
$CHCl_3$	70
Me_2CO	80
CH_2Cl_2	86
MeCN	100

[a]) The reactions were run under air at room temperature, and the molar ratio of $PhCH_2OH/Bu_4NHSO_5$/catalyst was 100 : 170 : 1. [b]) GC Yield, based on xylene as internal standard, after 3 min.

conditions in the presence of 1 mol-% of easily prepared and efficient **Mn-1** catalyst (*Table 2*). Benzylic alcohols are generally excellent substrates for this catalyst (*Table 2*, *Entries 1–14*), with electron-rich ones leading to faster reaction rates. However, electronic and steric effects do not seem to have a significant effect on the yields for electron-rich and electron-poor benzylic alcohols. The application of the reaction

Table 2. *The Oxidation of Different Alcohols Using* Bu_4NHSO_5 *Catalyzed by* **Mn-1** *in MeCN*[a])[b])



Entry	R^1	R^2	Yield [%][c])	Time [min]
1	Ph	H	100 (95)[d])	3
2	$2\text{-Me}-C_6H_4$	H	90	5
3	$4\text{-}{}^t\text{Bu}-C_6H_4$	H	100	< 1
4	$4\text{-MeO}-C_6H_4$	H	100	1
5	$2\text{-MeO}-C_6H_4$	H	95	5
6	$4\text{-Cl}-C_6H_4$	H	97	3
7	$2\text{-Cl}-C_6H_4$	H	95	5
8	$4\text{-NO}_2-C_6H_4$	H	93	5
9	$2\text{-NO}_2-C_6H_4$	H	92	10
10	Ph	Me	100 (93)[d])	1
11	Ph	Ph	100	3
12	2,3-Dihydro-1*H*-inden-1-yl		97	3
13	1,2,3,4-Tetrahydronaphthalen-1-yl		95	3
14	Ph	PhC(O)	96 (90)[d])	3
15	Cyclohex-2-en-1-yl		98	5
16	PhCH=CH	H	92	5
17	Cyclohexyl		100	20
18	2-Methylcyclohexyl		93	20
19	$MeCH_2CH_2CH_2CH_2CH_2$	Me	82 (77)[d])	20
20	$MeCH_2CH_2CH_2$	H	63	20

[a]) The reactions were run under air at room temperature, and the molar ratio of alcohol/Bu_4NHSO_5/catalyst was 100 : 170 : 1. [b]) All products were identified by their IR, ^1H-NMR, and GC/MS data in comparison with authentic samples. [c]) GC Yield based on the xylene as internal standard. [d]) Yield of isolated material.

conditions to allylic alcohols gave the corresponding α,β-unsaturated carbonyl compounds in high yields with no trace of epoxidation products (*Table 2*, *Entries 15* and *16*). When we applied this catalytic system in the oxidation of secondary and primary saturated alcohols, the good-to-high yields of ketones and aldehydes were secured by longer reaction times (*Table 2*, *Entries 17–20*). It is noteworthy that, in the oxidation of benzylic and primary alcohols, no over-oxidation to the related carboxylic acids was observed.

It seems that the rate of oxidation with this catalytic system is dependent on the electronic and steric demands of the substrate. To examine the electronic influence of substituent on the reactivity of the substrate, the turnover number (TON: mole product/mole catalyst) of **Mn-1** catalyst per min (turnover frequency: TOF/min) of the oxidation of different benzylic alcohols was determined under similar conditions using 2000 : 3400 : 1 molar ratio for alcohol/Bu_4NHSO_5/catalyst. It was observed that electron-donating and electron-withdrawing substituents on the phenyl ring of alcohol have a pronounced effect on the rate of oxidation. The presence of electron-donating MeO and *t*-Bu group in the *para*-position of benzyl alcohol enhanced the TOF in comparison with alcohols having no substituent at the ring (960/min for 4-methoxybenzyl- and 1620 for 4-(*tert*-butyl)benzyl alcohol *vs.* 652/min for benzyl alcohol). A substrate with a strong electron-withdrawing NO_2 group at the phenyl ring displayed a lower TOF than benzyl alcohol (274/min) under the same conditions. The influence of steric factors in this catalytic system is also noteworthy. The lower yields of *ortho*-substituted alcohols in comparison with the corresponding non-hindered alcohols at similar reaction times may be related to the steric hindrance at the Mn center of active oxidant in this catalytic oxidation method (TOF 568/min for 2-methylbenzyl alcohol *vs.* 652/min for benzyl alcohol; *Table 2*, *Entries 2*, *5*, *7*, *9*, and *18*, compared to *Entries 1*, *4*, *6*, *8*, and *17*). These relatively high turnover rates obtained in the oxidation of different alcohols highlight the high efficiency of the Mn catalyst in the present oxidation method.

The facile and high-yielding preparation of the **Mn-1** catalyst, which was used in a very low concentration in this oxidation procedure, offered ready scalability of the method. Performing the oxidation reaction using 100 mmol of $PhCH_2OH$ in the presence of only 1 mol-% of the catalyst gave 92% PhCHO after purification over silica gel.

The Influence of Ligand Nature on the Catalytic Activity and Stability of Mn – Schiff *Base Complexes.* To explore the influence of ligand nature on the catalytic activity of Mn complexes in the alcohol oxidation, a number of tetradentate Mn^{III} – *Schiff* base complexes (*Fig. 1*) have been examined in the oxidation of $PhCH_2OH$ under similar conditions (*Table 3*). The results in the presence of [Mn(salen)Cl] (salen = *N,N′*-bis(salicylidene)ethylenediamine dianion ligand) and the related derivatives are compiled in *Table 3* (*Entries 3–10*). It was observed that all [Mn(salen)Cl] complexes employed in this study were less active than **Mn-1**; however, for salens derived from 2-hydroxybenzaldehyde, the longer the alkyl chain of *Schiff* base ligand (*Table 3*; **Mn-6** to **Mn-9**), the higher is the conversion. For ligands derived from 2-hydroxyacetophenone, lower yields were obtained by using the phenylene group (*Table 3*; **Mn-2**) or an increasing number of CH_2 units (*Table 3*; **Mn-10** to **Mn-13**) between the azomethin moieties.

Table 3. *Influence of the Ligand Nature on the Catalytic Activity of Mn Catalyst in the Oxidation of $PhCH_2OH$ Using Bu_4NHSO_5*[a])

Entry	Mn Complex	PhCHO Yield [%][b])
1	**Mn-1**	95
2	**Mn-2**	54
3	**Mn-6**	61
4	**Mn-7**	67
5	**Mn-8**	70
6	**Mn-9**	75
7	**Mn-10**	54
8	**Mn-11**	51
9	**Mn-12**	48
10	**Mn-13**	44

[a]) The reactions were run under air in MeCN at room temperature, and the molar ratio of $PhCH_2OH$/Bu_4NHSO_5/catalyst was 100 : 170 : 1. [b]) GC Yield, based on xylene as internal standard, after 3 min.

Furthermore, the influence of electronic and structural features of the salicylidene ring of the ligand on the catalytic activity and also the stability of *Schiff*-base complexes [29] have been examined. The TON of electronically and structurally different Mn-(salphen) complexes (*Fig. 1*; **Mn-3** to **Mn-5**) has been compared with that of **Mn-1** in the oxidation of $PhCH_2OH$ after 1 min (TOF) and also 24 h (TON) under similar conditions using 2000 : 3400 : 1 molar ratio for $PhCH_2OH$/Bu_4NHSO_5/catalyst (*Fig. 2*). The order of activity of different Mn-(salphen) complexes was found to be: **Mn-5** > **Mn-1** > **Mn-4** > **Mn-3**. Thus, whilst unsubstituted complex, **Mn-1**, displayed more efficiency than those having electronic demands with very similar steric environments at their Mn centers, *i.e.*, **Mn-3** and **Mn-4**, a negative influence of an electron-donating group on the salicylidene ring of the *Schiff*-base ligand on the activity (TOF 652/min, 340/min, and 460/min for **Mn-1**, **Mn-3**, and **Mn-4**, resp.) and also stability of the catalyst (TON 912/24 h; 600/24 h, 696/24 h for **Mn-1**, **Mn-3**, and **Mn-4**, resp.) was observed. Moreover, the introduction of the bulky *t*-Bu groups on the phenyl ring of salicylidene

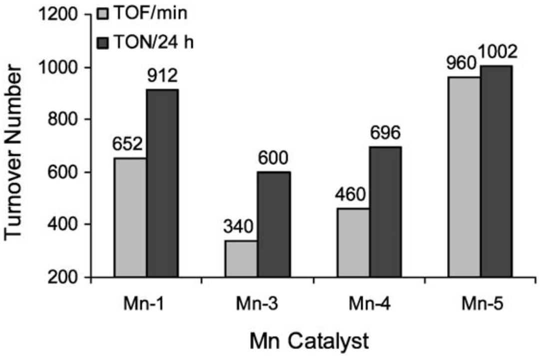


Fig. 2. *The turnover numbers of substituted Mn^{III}-salphen complexes in the oxidation of $PhCH_2OH$ alcohol using Bu_4NHSO_5 in MeCN at room temperature.* The molar ratio of $PhCH_2OH$/Bu_4NHSO_5/catalyst was 2000 : 3400 : 1.

(*i.e.*, **Mn-5**) enhanced the catalytic performance and also the stability of the hindered catalyst (TOF 960/min; TON 1002/24 h). The UV/VIS-spectral study of the **Mn-5** catalyst during the oxidation of the less reactive octan-2-ol showed that 81% of the catalyst remain intact. Probably, the prevention of the formation of catalytically inactive species such as μ-oxo dimer by hindered *t*-Bu groups near the coordination sites may be a reason for increasing the activity and stability of the catalyst [16]. It is noteworthy that, in the case of simple **Mn-1** in the oxidation of octan-2-ol, the percentage of the remaining catalyst was 64%, which is a promising result for the stability of a simple *Schiff*-base complex against oxidative degradation in this oxidation method.

Conclusions. – The catalytic efficiency and excellent selectivity of tetradentate Mn^{III}–*Schiff* base complexes in the oxidation of alcohols to the corresponding aldehydes and ketones using Bu_4NHSO_5 under mild conditions were established. The presence of an electron-donating group on the phenyl ring of the benzyl alcohol increased the reactivity of the substrate, while electron-withdrawing and bulky groups on the *Schiff*-base ligands enhanced the catalytic activity of the Mn catalyst. The applicability of this simple catalytic system to a wide variety of primary and secondary benzylic, allylic, and also saturated cyclic and alicyclic alcohols with excellent selectivity, combined with high turnover rates and ready scalability of the method, makes it attractive for practical purposes.

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Experimental Part

Typical Procedure for Oxidation of Benzyl Alcohol. To a mixture of $PhCH_2OH$ (1 mmol, 0.108 g) and [Mn(*Schiff*-base)Cl] [30–32] (0.01 mmol) in MeCN (5 ml) was added Bu_4NHSO_5 [33][34] (1.7 mmol, 0.7 g). The mixture was stirred at 25° for an appropriate reaction time, and the reaction was followed by TLC or GC. After completion of the reaction, PhCHO was isolated by silica-gel chromatography with hexane/AcOEt 10:1. Liquid. B.p.: 178°. IR (neat): 1701, 1600, 1460, 1312, 1204, 827, 749. ^{1}H-NMR (250 MHz): 7.45–7.67 (*m*, 3 H); 7.87–7.90 (*m*, 2 H); 10.02 (*s*, 1 H). ^{13}C-NMR (63 MHz): 128.8; 129.7; 134.4; 136.5; 192.3. MS: 106 (M^+).

REFERENCES

[1] R. A. Sheldon, J. K. Kochi, 'Metal-Catalyzed Oxidation of Organic Compounds', Academic Press, New York, 1981.

[2] J.-E. Bäckvall, 'Modern Oxidation Methods', Wiley-VCH, Weinheim, 2004.

[3] G. Wu, X. Wang, J. Li, N. Zhao, W. Wei, Y. Sun, *Catal. Today* **2007**, *131*, 402.

[4] V. B. Sharma, S. L. Jain, B. Sain, *J. Mol. Catal. A: Chem.* **2004**, *212,* 55.

[5] K. Kervinen, P. Lahtinen, T. Repo, M. Svahn, M. Leskeläa, *Catal. Today* **2002**, *75*, 183.

[6] W. Adam, F. G. Gelacha, C. R. Saha-Möller, V. R. Stegmann, *J. Org. Chem.* **2000**, *65*, 1915.

[7] S. L. Benjamin, K. Burgess, *Chem. Rev.* **2003**, *103*, 2457.

[8] W. Adam, S. Hajra, M. Herderich, C. R. Saha-Möller, *Org. Lett.* **2000**, *218*, 2773.

[9] B. Bahramian, V. Mirkhani, M. Moghadam, A. H. Amin, *Appl. Catal., A* **2006**, *315*, 52.

[10] T. Linker, *Angew. Chem., Int. Ed.* **1997**, *36*, 2060.

[11] H. R. Mardani, H. Golchoubian, *Tetrahedron Lett.* **2006**, *47*, 2349.

[12] A. Rezaeifard, M. Jafarpour, G. Kardan Moghaddam, F. Amini, *Bioorg. Med. Chem.* **2007**, *15*, 3097.

[13] F. Thomas, G. Gellon, I. Gautier-Luneau, E. Saint-Aman, J.-L. Pierre, *Angew. Chem., Int. Ed.* **2002**, *41*, 3047.
[14] A. D. N. Vaz, M. J. Coon, *Biochemistry* **1994**, *33*, 6442.
[15] E. M. McGarrigle, D. G. Gilheany, *Chem. Rev.* **2005**, *105*, 1563.
[16] P. G. Cozzi, *Chem. Soc. Rev.* **2004**, *33*, 410.
[17] T. Katsuki, *Chem. Soc. Rev.* **2004**, *33*, 437.
[18] K. C. Gupta, A. K. Sutar, *Coord. Chem. Rev.* **2008**, *252*, 1420.
[19] P. Pietikäinen, *Teterahedron Lett.* **1999**, *40*, 1001.
[20] P. Pietikäinen, *Teterahedron* **2000**, *56*, 417.
[21] P. Pietikäinen, A. Haikarainen, *J. Mol. Catal. A: Chem.* **2002**, *180*, 59.
[22] A. Rezaeifard, M. Jafarpour, S. Rayati, R. Shariati, *Dyes Pigm.* **2009**, *80*, 80.
[23] N. Iranpoor, D. Mohajer, A.-R. Rezaeifard, *Tetrahedron Lett.* **2004**, *45*, 3811.
[24] D. Mohajer, A. Rezaeifard, *Tetrahedron Lett.* **2002**, *43*, 1881.
[25] A. Rezaeifard, M. Jafarpour, M. A. Naseri, R. Shariati, *Dyes Pigm.* **2008**, *76*, 840.
[26] D. Mohajer, N. Iranpoor, A. Rezaeifard, *Tetrahedron Lett.* **2004**, *45*, 631.
[27] D. Mohajer, L. Sadeghian, *J. Mol. Catal. A: Chem.* **2007**, *272*, 191.
[28] I. V. Khavrutskii, R. R. Rahim, D. G. Musaev, K. Morokuma, *J. Phys. Chem. B* **2004**, *108*, 3845.
[29] N. S. Venkataramanan, S. Premsingh, S. Rajagopal, K. Pitchumani, *J. Org. Chem.* **2003**, *68*, 7460.
[30] A. Z. El-Sonbati, A. A. El-Bindary, I. G. A. Rashed, *Spectrochim. Acta, Part A* **2002**, *58*, 1411.
[31] A. Haikarainen, J. Sipilä, P. Pietikäinen, A. Pajunen, I. Mutikainen, *J. Chem. Soc., Dalton Trans.* **2001**, 991.
[32] J. Tong, Y. Zhang, Z. Li, C. Xia, *J. Mol. Catal. A: Chem.* **2006**, *249*, 47.
[33] B. R. Travis, B. P. Ciaramitaro, B. Borhan, *Eur. J. Org. Chem.* **2002**, 3429.
[34] S. Campestrini, B. Meunier, *Inorg. Chem.* **1992**, *31*, 1999.

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