CHAPTER 6

(Salen)chromium(III) complex catalyzed oxidation benzylic alcohols by Oxone®

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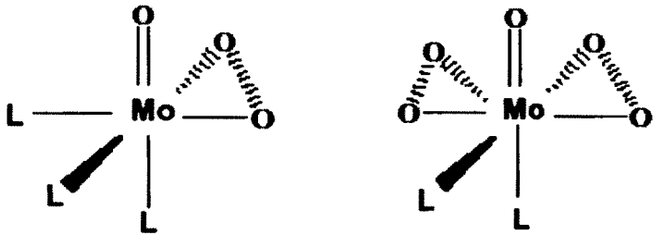
6.1 Introduction

Research involving application of transition metal complexes in chemical processes has attracted much interest over the last century. Reasons are the novelty of the chemistry involved, its great potential and the practical applications, as proven in numerous examples. All kinds of inorganic and organometallic compounds are used as catalysts or as reactants in a vast number of chemical reactions [1]. Some of the important processes include hydrogenation of alkenes (Wilkinson catalyst), hydroformylation (cobalt and rhodium catalyst, oxo process), alkene oxidation, Wacker process), polymerization (Ziegler-Natta catalyst) and alkene isomerization (nickel catalyst).

The oxidation of alkenes to epoxides, aldehydes, ketones and glycols is a large and growing part of homogeneous catalysis with direct industrial applications [2,3]. The oxidation of organic substrates by direct oxygen atom transfer from transition metal complexes is of fundamental importance and has been investigated

extensively. Reasons for this interest are the necessity for functionalization of lower alkenes, interest in understanding reactions of biological importance, the need for partial selective oxidation and the preparation of compounds with a specific spatial structure. The transition metal complexes seem to fulfil some of these requirements and many different systems are available that can utilize a variety of oxygen sources for these oxidation reactions. The active catalytic oxidant has been described as a mono- or bidentate coordinated alkyl hydroperoxide (hydrogen peroxide) or a bidentate co-ordinated peroxo group for the transition metal catalyzed epoxidations using group **4** and **5** metals. The type of active catalytic oxidant for group **6** and **7** transition metal epoxidations is an oxo metal complex. Hydroperoxides, hydrogen peroxide and molecular oxygen are used to generate the active oxidant for group **4** and **5** transition metal complexes, while for the group **6** and **7** transition metal complexes, iodosyl compounds, N-oxides, hypoclorite as well as various other oxidants are available to generate the active catalytic oxidant [4] Oxochromium(V) complexes formed from chromium(III)-salen [salen= ,Nethylenebis(salicyldeneaminato) ligand] or –TPP (-Tl'P = mesotetraphenylporphyrinato) complexes can achieve the conversion of an alkene to its epoxide [4]. Monoperoxo-molybdenum complexes, $[MoO(O_2)Ln]$ (**1**), and diperoxomolybdenum complexes, $[MoO(O_2)2L_1L_2]$ (**2**), were also found to epoxidize many different types of alkenes [4,5].



1 2

(1). Monoperoxo-molybdenum complex and (2). Diperoxomolybdenum complexes

$[MoO(O_2)(2,6\text{-dipic})]\cdot H_2O$, $[MoO(O_2)(PhCON(Ph)O)_2]$ and $[MoO(O_2)Cl(pic)]$ are some of the monoperoxo-molybdenum complexes that have been synthesized and $[MoO(O_2)_2\cdot HMPA]\cdot H_2O$ is one example of a large variety of diperoxo - molybdenum complexes. The tungsten-peroxo complexes show similar behaviour to the molybdenum complexes and both mono- and diperoxo species are known. However, because of the low solubility of the tungsten complexes, their reactivity has not been studied to any large extent. The manganese complexes that are commonly used as catalysts for alkene epoxidation are porphyrin type complexes [4,5]. The main reason is the relationship of these manganese porphyrin complexes to the biological oxidation systems. Oxomanganese(V)-salen complexes, formed from manganese(III)-salen complexes, show catalytic epoxidation activity as well [6]. The catalytic activities of the rhenium complexes, which have also been tested, seem to be comparable to that of technetium and have low activity [4].

Pioneering work by Groves and coworkers has led to widespread interest in the reactivity of oxo-metal complexes of porphyrins and other macrocycles [7,8]. Nowadays, it is generally accepted that the catalysis of oxygen-atom transfer by chromium, manganese, iron, and ruthenium porphyrins involves oxo-metal species as key intermediates, reminiscent of the mechanism of action of cytochrome P-450 [9]. Moreover, similar mechanisms and intermediates have been proposed for

many other types of catalytic oxidations [10]. Remarkably, even after years of research on porphyrins containing the aforementioned four metals, only oxochromium(IV) and dioxoruthenium(VI) derivatives have been fully characterized [11,12].

Selective oxygenations of hydrocarbons are important reactions. Owing to the fact that dioxygen is a triplet and therefore will not react readily with singlet molecules, activation is required, often involving free radicals or metal ions. For practical reasons, one would like to stop the oxidation process at an intermediate stage, like aldehyde or epoxide. An attractive reaction model is one in which a metal ion could split dioxygen producing a metal oxo species that could oxygenate a substrate. A mechanism of this type is the so-called oxo-rebound, which was first proposed by Groves [13,14]. To drive the first half of the reaction (dioxygen cleavage) the metal oxo bond has to be strong, but the second half requires a weak bond. The question has remained open whether both half reactions can run smoothly employing a single metal complex.

The catalytic activity in oxo-rebound mechanism of metal complexes found to depend on periodic trends of the metals. Metal-oxo bonds tend to weaken as one moves up and to the right of the transition metal series. The first row is a classic example. Titanium and vanadium tend to form very strong bonds with oxygen, to such an extent that V(III) is used as an oxygen abstraction reagent, turning NO-metal species into nitrido compounds [15]. Moving to the right yields progressively more reactive species, with Fe and Mn oxo's being the most reactive, whose oxo compounds have to be generated with an oxidant and are generally too unstable to be isolated. Iron is of course the most biologically relevant metal due to its presence in enzymes such as P-450 where an oxo metal species is presumed to

be part of the cycle. Moving past iron is problematic due to what is known as the oxo wall. Previous work, in this group in particular is focused on the use of perhalogenated porphyrins [16-18] and vanadium salen compounds [19] as catalysts. While the observed catalytic activity was not due to oxo transfer chemistry rather, the reactions proceed via the well-known peroxo-radical mechanism [20]. In both the cases, it was apparent that oxo chemistry did not happen, owing either to a too reactive or a too stable metal oxo species. Of the remaining metals in the first row, only Cr forms oxo compounds that are more stable than those of Fe. Cr-oxo porphyrins were first reported by Groves [7]. of the two oxo oxidation states (V and IV), complexes in the former are too reactive to be isolated, while the latter are stable and can be spontaneously formed from the corresponding chromium(II) species [7a]. The first isolable Cr(V)O species was reported by Kochi using a salen ligand [7b]. However, the increased stability of the compound was still not high enough to observe a spontaneous oxidation of the Cr(III) species.

6.1.2 Some aspects of industrial reactions and emerging technologies of Transition-metal complexes for liquid-phase catalytic oxidations

Homogeneous oxidation catalysis is used in many industrial scale procedures. These include the production of acetaldehyde from ethylene, of adipic acid [2] from cyclohexane, of terephthalic acid from *p*-xylene [21-24] and also that of propylene oxide by the epoxidation of propylene [2]. The conversion of ethylene, C_2H_4 into acetaldehyde, CH_3CHO (the Wacker process) implies some of the fundamental concepts of palladium organometallic chemistry and two elementary redox processes. On the basis of experiments with deuterium-labelled ethylene it appears that the nucleophilic attack of water on ethylene coordinated to

palladium is a key reaction for this purely heterolytic (non-radical) process [25,26]. In this case, the involvement of dioxygen and an oxidant (copper(II) salts, heteropolyacids, "$H_{3+n}[PMo_{12-n}V_nO_{40}]_{aq}$", quinone, *etc.*) allows a stoichiometric reaction to be turned into a catalytic process. At present, this synthesis route is not so important as it was in the 1960s, due to the development of the Monsanto [24] and Cativa [27] processes leading directly to acetic acid. On the other hand, the oxidations of cyclohexane and *p*-xylene by dioxygen in air are chain reactions which imply organic free-radicals; these are considered as homolytic processes. In these systems, cobalt (III and II) and/or manganese (III and II) ions can catalyze the initiation steps. Reactions of this type, in which the organic substrates are directly oxidized by air or by pure dioxygen, are often classified as autoxidation processes [28]. The conversion of propylene into its oxide implies the selective transfer of a peroxygen atom O(-I) by a heterolytic mechanism, without modification of the formal oxidation state (or oxidation number) of the metallic centre. This type of process has given rise to a new, creative chemistry for better-tuned catalytic oxidation reactions. The origin of the oxygen atom is rarely dioxygen itself; another peroxygen atom-donor oxidant must be used. This can be an organic hydroperoxide, ROOH, aqueous hydrogen peroxide, H_2O_2 or performic, or peracetic acids, HC(O)OOH and $CH_3C(O)OOH$, usually prepared *via* an equilibrium reaction. For most carboxylic acids, a strong acid catalyst must be added in order to achieve an acceptable rate of reaction. The *in situ* generation of percarboxylic acids has important applications in the production of epoxides without transition metal catalysts. Many medicines and intermediates in fine chemistry have functional groups, which can be derived from epoxides. During the last 30 years, homogeneous oxidation catalysis has been used for the synthesis of

epoxide intermediates and, to a lesser extent, of aldehydes or ketones. Research in this area is very active, notably inspired by enzymatic transformations which are particularly selective. Besides these oxidation reactions which have led to industrial processes, there are many other reactions for which catalytic systems have overall superiority, because of better economics, environmental constraints and the need for high selectivity. Much work is related to the "Green Chemistry" trend, aimed at converting often stoichiometric procedures generating large quantities of waste into simple catalytic processes without serious effluent problems, in the name of the principle of "atom economy" [29].

6.1.3 Different types of oxygen-donor oxidants

Here are some of the selected (Table 1) industrial oxygen-donating oxidants (hydrogen peroxide, *tert*-butyl hydroperoxide, nitric acid, *etc.*) and others, with more specific uses, like iodosylbenzene, PhIO, applied in very sophisticated oxidation systems with "fragile" catalysts, whose ligands are sensitive to oxidation. Economic factors and ecological constraints lead to a preference for oxidations involving dioxygen, hydrogen peroxide, alkyl hydroperoxides such as *t*-BuOOH (*tert*-butyl hydroperoxide). However, an oxidant such as concentrated nitric acid has been chosen for certain industrial processes (*vide infra*), even if it does not correspond, far from it, to an economy of matter and a chemistry which respects the environment in its initial design. It should be added that ozone, O_3, as long as it is prepared and used on the site, leads to industrial productions worthy of interest (15000 tons/year of glyoxylic acid by DSM-Chemie Linz) [30-32].

Table 1. Some Oxygen-donor Oxidants

Oxidant	Active oxygen (wt%)	By-product
H_2O_2	47.1	H_2O
t-BuOOH	17.8	*t*-BuOH
HNO3	25.0	NO*x*, N_2O, N_2
N_2O	36.4	N_2
NaClO	21.6	NaCl
$NaClO_2$	35.6	NaCl
NaBrO	13.4	NaBr
[a]$C_5H_{11}NO_2$	13.7	$C_5H_{11}NO$
[b]"$KHSO_5$"	10.5	$KHSO_4$
$NaIO_4$	29.9[c]	NaI
PhIO	7.3	PhI

a *N*-Methylmorpholine *N*-oxide (NMO). *b* Stabilized and commercialized as the "triple salt": $2KHSO_5$- $KHSO_4$-K_2SO_4 (oxone®). *c* Assuming all 4 oxygen atoms are used.

6.2 Present Work

There has been much research on the oxidation, especially the search for versatile and selective reagents. Among the most widely used are chromium compounds; infact, chromic acid is one of the most powerful and universal oxidants [35]. The Jones reagent (chromiutrioxide/H_2SO_4), the Collent reagent (chromiumtrioxide/pyridine complex), pyridinium chlorochromate (PCC), poly(vinylpyridinium) chlorochromate (PVPCC), and pyridinium dichromate (PDC) are some of the more popular commercially available chromium based oxidants used for such transformations.

The main drawback of these reagents is that in addition to their lack of generality, they have to be applied in stiochiometric amounts or even in large excess to effect complete conversion of the substrate. However, in view of the carcinogenity of chromium compounds, health and environmental concerns limit

their use for large-scale and industrial applications. Although much effort has been made in the development of methods for chromium based catalytic oxidations in recent years [34], there is still need for catalytic oxidation of alcohols with wide scope and applicability. Indeed, ongoing research has been directed toward the development of such methods, especially for selective oxidations [35]. For example, oxochromium(V) heteropolytungstate were reported to effect the catalytic allylic oxidation of cyclohexenol [35c]. recently, chromium (VI)-catalysed oxidation of allylic alcohols by tert-butyl hydroperoxide to carbonyl products has been developed [36].

In this chapter, we slightly shifted our attention towards transition metal complexs as catalysts for the oxidation of alcohols with Oxone® as the oxidant.

In continuation of our work on explorations of Oxone® oxidations, we wish to report on the selective (Salen)chromium(III) (Figure. I) catalyzed oxidation of a series of alcohols to the corresponding acids with Oxone® as the oxygen source (Scheme 1).

6.3 Experimental

The catalyst (Salen)chromium (III) was prepared by the previously reported method [37]. All the products are known compounds and were identified by comparison of their physical & spectral data with those of authentic samples. Melting points were determined in open capillaries and are uncorrected. IR was recorded as neat films or as KBr pellet on a Thermo Nicolet spectrometer. All alcohols are commercial materials and were purchased from S D Fine chemicals (Mumbai India) and Lancaster. Potassiun peroxomonosulphate was purchased from Across Chemicals. Acetonitrile and dichloromethane were purchased from S

D fine chemicals (Mumbai India) and were used without further purification. Yields reported refer to isolated products of the carbonyl compounds.

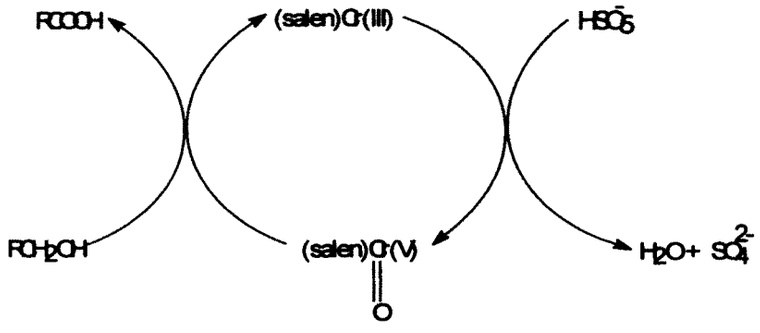
Preparation of *N,N'*-Ethylenebis(salicylideneiminato)chromium-(III) Chloride 1.

To a suspension of 2.59 g (9.96 mmol) of bis(salicyliden)ethylenediamine in 50 mL of absolute ethanol was added a suspension of 1.31 g (10.7 mmol) of anhydrous chromous chloride in ethanol (20 mL) within 15 min with vigorous stirring under an N_2-gas atmosphere at room temperature (ca. 20 °C) for 1 h. The dark-brown solution was allowed to reflux in the presence of air for 2 h. The solvent was removed (ca. 20 °C, ca. 20 Torr), and the residue was suspended in water (50 mL) and allowed to stir for 2 h in the presence of air at ca. 20 °C. The undissolved, yellowish-brown material was collected by filtration on a G4 sintered-glass funnel and was washed with water (3 x 10 mL). The material was extracted with water (2 x 500 mL) by heating in an open glass beaker, with vigorous stirring for 2 h. After filtration and concentration of the filtrate at normal pressure by evaporation, a reddish brown material precipitated; more material precipitated on cooling overnight, which was collected and dried under reduced pressure (120 °C, ca. 10-2 Torr, P_2O_5, 12 h) to afford 1.2 g dark-brown, hygroscopic product, m.p (dec) 338-340 °C. IR (KBr): 3026, 1800, 1496, 1027, 893 cm-1.

General Procedure for the Oxidation of Benzylic alcohols.

4-Nitro benzyl alcohol (2.2 mmol) and Oxone (1 mmol) were taken in 50% aqueous acetonitrile mixture in a round-bottomed flask fitted with reflux condenser. Catalyst 1 (5 mol%) was added and the reaction mixture was refluxed on water bath for appropriate time (See Table 1). The progress of the reaction was monitored by TLC. After the reaction was complete, the aqueous acetonitrile was

removed under reduced pressure and the residue was washed with ethyl acetate and the organic layer was dried over $MgSO_4$ and concentrated to afford pure carboxylic acid. The oxidation of primary aliphatic alcohols were sluggish yielded mixture of acid and carbonyl compounds even after 5 hours under reflux. Hence, the benzylic substrates were selected for the further study.



Scheme 1. Catalytic cycle for the oxidation of alcohols to acids by (Salen)Cr(III)/Oxone®

6.4 Results and Discussion

The in-situ generated (salen)oxochromium(V) complex is proposed as the actual oxidant. Such (salen)oxochromium(V) complexes have been previously isolated and subsequently used in the epoxidation of olefins by Kochi's group [38]; the asymmetric version was recently established [39].

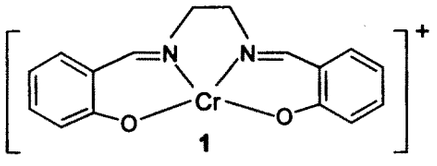
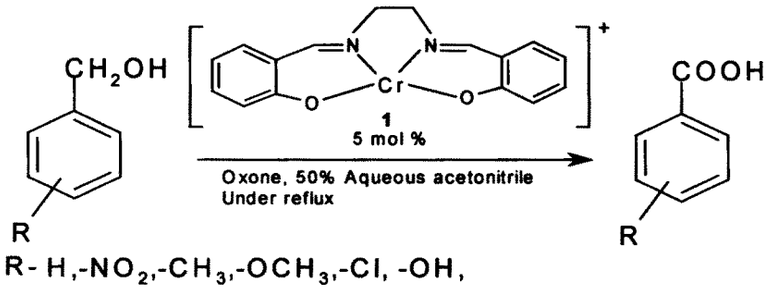


Figure I: (Salen)chromiun (III) Complex

In the presence of **1**, the oxidation of 4- Nitrobenzyl alcohol was examined with Oxone® in aqueous acetonitrile under reflux. We found that the alcohol was oxidized to the corresponding acid within three hours in 89% yield (Table 1, entry 3). A controlled experiment in the absence of **1** using the same reaction conditions gave no reaction and the starting alcohol was recovered. The oxidations of other alcohols were then examined using the optimized reaction conditions. (Table 1)



Scheme2. Oxidation of alcohols

Although not surprisingly, the substituted benzylic substrates like 2-nitro-, 4-Nitro- , 4-Chloro- and 4-Methoxybenzyl alcohol were more reactive than the 4-Methylbenzyl alcohol. It is noteworthy to mention that no oxidation was observed in the aromatic ring of the benzylic substrates.

The oxidation of cinnamyl alcohol was also examined; however it mainly afforded benzoic acid due to the cleavage of the carbon-carbon double bond. This type of carbon-carbon double bond cleavage was also noticed in the catalytic oxidatons of alcohols by a cobalt (II) complex [40].

Test for Free radicals

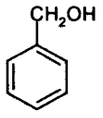
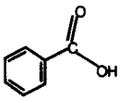
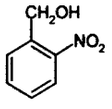
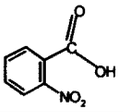
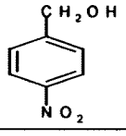
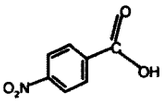
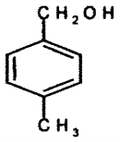
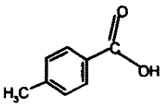
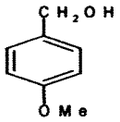
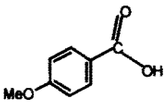
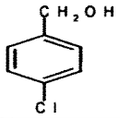
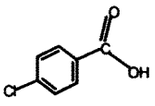
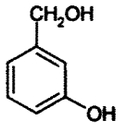
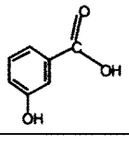
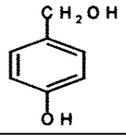
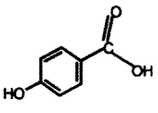
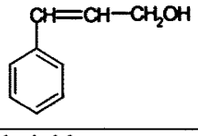
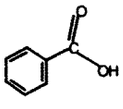
In order to understand the electron transfer mechanism from (Salen)chromium (III) complex, oxidation of 4-Nitrobenzyl alcohol was carried out in the presence of acrylonitrile (0.5 ml) as a radical scavenger. Single electron

transfer reactions are known to induce polymerization of acrylonitrile. But in our case, we did not noticed polymerization of acrylonitrile. Hence it is confirmed to be a two-electron transfer reaction, hence, there is in-situ formation of oxochromium (V) species as the active oxidant.

6.5 Conclusions

In conclusion, the catalyst (Salen)chromium (III), **1** is found to be an effective homogeneous catalyst for the oxidation of benzylic alcohols to their corresponding acids with Oxone®.

Table 1. Oxidation of alcohols by (Salen)chromium(III) complex / Oxone®

Srl No.	Substrate	Product	Time (hr)	Yield (%)[a,b] Isolated	M.P
1			4.5	91	122-123
2			2.5	89	148
3			3	93	238-240
4			5	77	177-179
5			3	87	181-184
6			3	96	242-244
7			4	83	201-203
8			4	87	215-217
9			3	93	119-122

[a]Isolated yield.

6.6 References

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