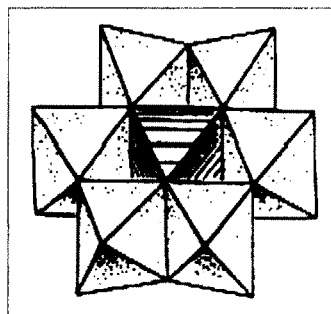


CHAPTER 4



*Catalytic activity of Anderson-type:
sodium hexamolybdochromate (III) in
alcohol oxidations by hydrogen peroxide*

4.0 Catalytic activity of Anderson-type:sodium hexamolybdochromate (III) in alcohol oxidations by hydrogen peroxide

4.1 Introduction

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4.1 Introduction

Oxidation is a core technology for converting petroleum-based materials to useful chemicals of a higher oxidation state. However, oxidation is among the most problematic processes. Many textbook oxidation methods are unacceptable for practical synthesis; the heavy metal oxidants form toxic wastes, while known organic stoichiometric oxidants are usually very expensive [1]. Nitric acid, the most conventional industrial oxidant [2], is cheap but unavoidably forms various nitrogen oxides. Thus, there is a need for the invention of clean, safe oxidation procedures. Molecular oxygen is obviously an ideal oxidant [3], but aerobic oxidation is often difficult to control and sometimes results in combustion and the reaction is performed with a low conversion to avoid over-oxidation. Furthermore, although both oxygen atoms in O₂ may be utilized for oxidation (100% atom efficiency) [4,5], only one oxygen atom has been used in most reactions (50% atom efficiency) [6], so the oxidation often requires certain reducing agents to

capture the extra oxygen atom during the reaction [7]. In some cases, the initial oxidation products such as (hydro)peroxides are reduced to obtain the desired products.

Hydrogen peroxide, H_2O_2 , is a very attractive oxidant for liquid-phase reactions [8]. H_2O_2 is an adduct of H_2 and O_2 that is also viewed as an adduct of an O atom and an H_2O molecule. It can oxidize organic compounds with an atom efficiency of 47% and with the generation of water as the only theoretical co-product. It is relatively cheap and about 2.4 million metric tons are produced for use, mainly as bleach [9]. It should be noted that H_2O_2 can be an ideal, waste-avoiding oxidant only when it is used in a controlled manner without organic solvents and other toxic compounds. Thus, the discovery of an efficient catalyst and the choice of reaction conditions are the keys to realizing an ideal oxidation procedure. The reaction should be achieved with an H_2O_2 concentration of <60%, because the use, storage, and transportation of higher concentrations of H_2O_2 are not desirable for safety reasons [10]. The H_2O_2 oxidation is particularly useful for the synthesis of high-value fine chemicals, pharmaceuticals or agrochemicals, and electronic materials which require high chemical purity. It may also be used for improving the environment by oxidative removal of very small amounts of toxic compounds. However, despite a sustained effort in industry, the current cost of H_2O_2 still does not allow for the economical production of inexpensive compounds in large quantities. There will be significant changes depending on the development of low cost H_2O_2 production, demand for high product quality, stringent environmental regulations, changes in public opinion, legislation, and taxation policy regarding environment protection. In fact, there is a trend to use H_2O_2 as an oxidant for large volume processes such as caprolactam synthesis

(Sumitomo Chemical Co.) [11] and propylene oxidation (BASF and Dow Chemical Co.) [12]. H_2O_2 oxidation methods may switch to in situ or on-site technology using H_2 and O_2 . Since the structures of chemical substances are diverse and reaction volumes are variable depending on whether the purpose is research or production, no synthetic methods can be universal. One of the major advantages of the H_2O_2 oxidation is the high tunability of the reaction parameters. It is known that H_2O_2 and O_2 (or air) are complementary useful clean oxidants in practical chemical synthesis. Oxidation by hydrogen peroxide can be achieved under neutral, acid or alkaline conditions, as well as in the presence of catalysts. In some applications however, the oxidising power of hydrogen peroxide is insufficient, the help of a metal catalyst is often required, and in recent years a considerable effort has been devoted to the search for new efficient metal derivatives suited to this purpose.

Polyoxomolybdates have been attracting considerable interest over recent years as oxidation catalysts for both gas and liquid phase oxidation reactions. For example, the Polyoxomolybdates of the kegglin structure, $H_{3+x}PV_xMo_{12-x}O_{40}$ (especially $X=0-2$), have been used as oxidation catalysts for both gas phase and liquid-phase oxidations [13], the earliest use was as cocatalysts in Wacker type oxidations of terminal alkenes [14], followed later on by various catalytic oxidations of halides [15], alcohols, ketones and amines [16], phenols [17], (alkyl)aromatics [18], dienes [19], alkanes [20], and sulfur containing compounds [21]. Although the Keggin and Dawson are known to be active catalysts in several industrial processes, the application of Anderson type (Fig. 1) heteropolyoxomolybdates is only starting. These have been scarcely proved as hydrotreating catalysts [22], but the characterization and performance of the phases

containing Pt have been recently studied for hydrogenolysis and NO-CO reactions [22–25].

The Anderson Structure and Derived Compounds

The Anderson structure may be described as an isopolyoxometalate containing a crown of six octahedrons sharing edges. The center may be occupied or not. In the chromium-containing compound structure, there are six hydrogen atoms, the positions of which are considered to be the six OH groups bridging the central atom to the molybdenum-containing crown octahedrons. The oxidation state of chromium may be easily deduced from the charge since it is well known that there usually is molybdenum(VI).

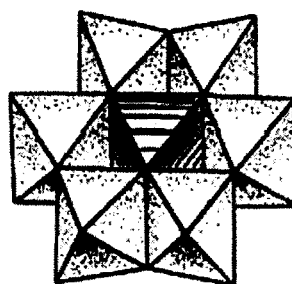


Figure. 1. Structure of the typical Anderson heteropolymolybdate.

Prior work [26-30] has established the existence and probable isomorphism for the heteropoly 6-molybdo anions of the following central trivalent ions: Cr, Al, Fe, Co, Rh and Ga. Later it was shown that these anions have a -3 charge in solution [27,31] and that the central ion is octahedrally co-ordinated [29,32,33]. The observation that some of these salts could be completely dehydrated at moderate temperatures (200°C or less) without, apparently, destroying the anion was originally interpreted [27] as an evidence that all of the water in these salts was merely water of crystallization. This conclusion led to the postulation of an erroneous dimeric structure [27]. However, later work by some of the same

workers [31] and others [34] definitely established the monomeric nature of the anion in solution. In 1960, Agarawala [35] investigated the 6-tungstonickelate (II) anion and concluded that this complex definitely contained constitutional water and had the formula $[\text{NiW}_6\text{O}_{24}\text{H}_6]^{4-}$. The heavy atom arrangement was found to be consistent with the structure originally proposed by Anderson [36] and later found by Evans [37] in the $[\text{TeMo}_6\text{O}_{24}]^{6-}$ anion. The similarity of the 6-molybdo and 6-tungsto anions and the evidence already cited concerning the anion charge and monomeric nature, led Tsigdinos [29] to conclude that the 6-molybdochromate anion and its structure are same as proposed by Anderson. Later, Perloff [38] investigated the detailed structure of the of the heteropolysalt of $\text{Na}_3[\text{CrMo}_6\text{O}_{24}] \cdot 8\text{H}_2\text{O}$ and established that the anion has the same structure as the $[\text{TeMo}_6\text{O}_{24}]^{6-}$ anion with excellent agreement and concluded that the hydrogen atoms of the anion are bonded to the oxygen atoms which are coordinated to the Cr atom.

4.2 Present Work

Most of the polyoxometalate catalysis reported were based on the utilization of Keggin or Dawson-type polyoxometalates. In chapter 2 and chapter 3 we have reported on the Keggin-type polyoxometalate, 12-tungstocobaltate (II), and the oxidant, Oxone®. Though Oxone® is economical and a good oxidant, is not a green oxidant as it generates salts. In continuation of our work on organic oxidations catalysed by polyoxometalates [39], we now present our studies on a novel system; the oxidation of alcoholic substrates to aldehydes and ketones using hydrogen peroxide catalysed by an Anderson-type polyoxomolybdate, sodium hexamolybdochromate (III). To the best of our knowledge this is the first report on

alcohol oxidations by hydrogen peroxide catalysed by an Anderson-type polyoxometalate, sodium hexamolybdochromate (III).

4.3 Experimental

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

4.3.1 Catalyst Preparation:

The catalyst Sodium hexamolybdochromate (III) was prepared by the previously reported method [38]. The pH of a solution containing 14.5 g of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ in 30 ml of water was adjusted to 4.5 with concentrated HNO_3 . A second solution was made by dissolving 4.0 g of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 5 ml of water. Both the solutions were mixed together, and the mixture was boiled for 1 min and filtered while hot. The filtrate was set aside for crystallization and crystals started to appear in 1 hr. the solution was allowed to stand for 2 weeks before the precipitate was filtered off and washed several times with cold water. Reddish purple crystals were obtained.

4.3.2 Quantitative analysis of the Catalyst

The complex $\text{Na}_3[\text{CrMo}_6\text{O}_{24}\text{H}_6]\cdot 8\text{H}_2\text{O}$ was studied by AAS analysis. 100 mg of recrystallised sample was dissolved in doubly glass-distilled water. 5 ml of this stock solution was diluted to 100 ml and used for AAS analysis of Cr and Mo metals using Perkin-Elmer AAnalyst-300. The complex $\text{Na}_3[\text{CrMo}_6\text{O}_{24}\text{H}_6]\cdot 8\text{H}_2\text{O}$ shows (Theoretical): Na- 5.6303 % (5.6052 %), Cr- 4.2227 % (4.2242 %) and Mo-46.217 % (46.2109 %)

4.3.3 Catalytic Runs

To start with, the oxidation of 4-nitrobenzyl alcohol was studied. In a typical experiment 4-nitrobenzyl alcohol (2.2 mmol) and H_2O_2 (4.5 mmol) were taken in 50:50 % aqueous acetonitrile mixture in a round-bottomed flask fitted with reflux condenser. Catalyst $\text{Na}_3[\text{CrMo}_6\text{O}_{24}\text{H}_6]$ (4.0×10^{-4} mol) was added. The reaction mixture was stirred at 50°C for 2-3 hours. The progress of the reaction was monitored by TLC. After the completion of the reaction, the resulting solution was extracted with dichloromethane (20ml x2). The combined organic layer was washed with a solution of NaHCO_3 and dried over MgSO_4 , filtered, and the solution was concentrated to afford the crude 4-nitrobenzaldehyde, which was further purified by column chromatography (petroleum ether-ethyl acetate, 9:1). The oxidations of other alcohols were then examined using the optimized reaction conditions.

4.4 Results and Discussion:

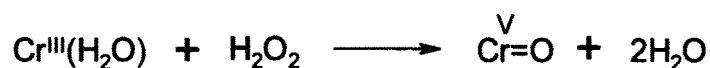
To assess the general scope of the catalytic oxidation mediated by the $\text{Na}_3[\text{CrMo}_6\text{O}_{24}\text{H}_6]\cdot 8\text{H}_2\text{O}$, the saturated and benzylic, primary and secondary alcohols were chosen as substrates and H_2O_2 as oxygen source. The uncatalyzed

oxidation of alcohols did not occur under the experimental conditions. The results of this study are shown in Table 1 for various alcohols which shows that the carbonyl compound is the only product obtained in comparatively high yields. 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. Cinnamyl alcohol and furfuryl alcohol were also oxidised neatly without forming any side products.

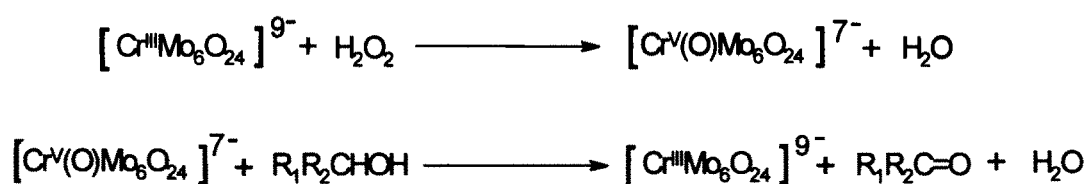
4.4.1 Mechanistic Insights

In the context of this research, we were also interested in gaining insight into the mechanism of these reactions. To establish the electron transfer mechanism of POM in oxidations, oxidation of 4-nitrobenzyl alcohol was carried out using the optimised conditions in the presence 0.5 ml of acrylonitrile we did not notice polymerization of acrylonitrile. Hence it is confirmed to be a two-electron transfer reaction. The two electron path of the reaction occurs due to the formation of Chromium (V) in-situ as a result of the oxidation of Sodium hexamolybdochromate (III) by hydrogen peroxide. The violet solution of Sodium hexamolybdochromate (III) was treated with hydrogen peroxide and the resulting green solution was evaporated to get the crystals of oxidised Sodium hexamolybdochromate (V). The FT-IR spectra (Figure 3) of both unoxidised and oxidised Sodium hexamolybdochromate were recorded as KBr pellet. The comparison of both the spectra indicated that the polyoxometalate characteristic M-O_c-M peak at 643 cm⁻¹ was found to be splitted into two peaks in the oxidised form due to the change in the oxidation state of chromium. There was also a new peak at 829 cm⁻¹ characteristic of Cr^V=O in the FT-IR of the oxidised form of

Sodium hexamolybdochromate [40]. On the basis of FT-IR spectral examination of both unoxidised and oxidised form of hexamolybdochromate the formation of Cr^V can be shown as in equation and the formed Cr^V=O acts as an oxidant in the present study.



Since, under the reaction conditions studied, but in the absence of POM, the oxidation of alcohols did not take place, we surmised that the initial activation mechanism was by an interaction between the H₂O₂ and the POM as shown in the scheme 1.



Scheme 1. Reaction Pathway for the Oxidation of alcohols by H₂O₂ Catalyzed by Na₃[CrMo₆O₂₄H₆]•8H₂O

The possible Transition State of the mechanism is shown in the Figure 2

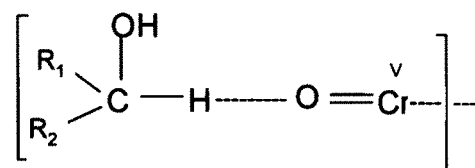


Figure.2

which involves the development of negative charge. Such transition state is more stabilized by electron-withdrawing substrates and makes the reaction to occur faster. In the present study also the 4-nitro and 4-chloro benzyl alcohols reacts at a faster rate than that of the benzyl alcohol.

4.5 Conclusion

In this new catalytic application of the Anderson type polyoxometalate, $\text{Na}_3[\text{CrMo}_6\text{O}_{24}\text{H}_6]\cdot 8\text{H}_2\text{O}$, it has been shown that the reaction of the polyoxometalate with the H_2O_2 leads to formation of a Cr(V) POM anion leading to the formation of carbonyl derivatives as final products. The possible synthetic outcome of such a procedure has been noted for a series of aliphatic and benzylic alcohols and even the heterocyclic alcohols were converted into carbonyl compounds without the formation of any side products.

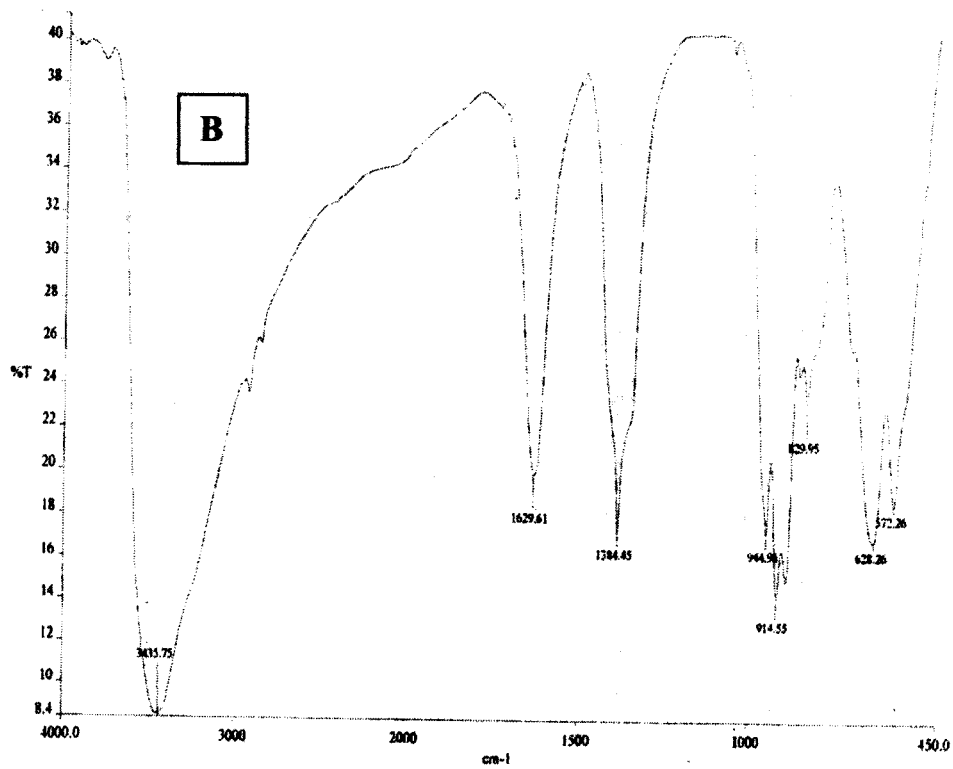
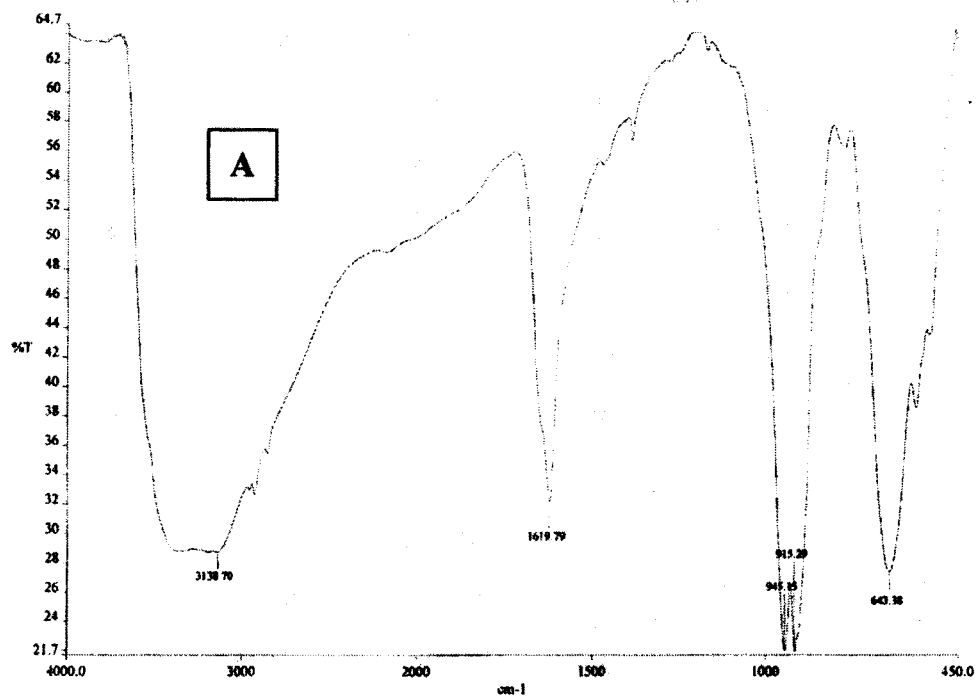
Table 1: Oxidation of alcohols to carbonyl compounds catalysed by Sodium hexamolybdochromate (III) /H₂O₂

Srl No	Reactant	Product	Reaction time (t/h)	Yield (%) [†]	M.P of carbonyl compound T/ ^o C
1	2-Propanol	Acetone	4	72 [‡]	liquid
2	n-Butanol	n-Butraldehyde	4	78	liquid
3	2-Butanol	Iso-butraldehyde	4	81	liquid
4	Sec-Butanol	Ethyl methyl ketone	4	75	liquid
5	n-Octanol	n-Octaldehyde	4.5		liquid
6	Benzyl alcohol	Benzaldehyde	3	85	liquid
7	2-Nitrobenzyl alcohol	2-Nitro benzaldehyde	2.5	92	43-45
8	4-Nitrobenzyl alcohol	4-Nitro benzaldehyde	2.5	92	104
9	4-chlorobenzyl alcohol	4-Chloro benzaldehyde	2.5	87	47
10	4-Methoxybenzyl alcohol	4-Methoxy benzaldehyde	2.5	83	248
11	4-Methylbenzyl alcohol	4-Methyl benzaldehyde	3	81	201-204
12	4-Hydroxybenzyl alcohol	4-Hydroxy benzaldehyde	3		117-119
13	Cinnamyl alcohol	Cinnamaldehyde	3	87	liquid
14	Furfuryl alcohol	Furfuraldehyde	3	79	liquid
15	Pyridine-3-methanol	Pyridine-3-aldehyde	3	83	liquid
16	Benzhydrol	Benzophenone	3	87	liquid

[†] Yield of pure product after crystallization or chromatography over silica gel.

[‡] Estimated by Gas Chromatography.

Figure 3. FT-IR Spectra of (a) hexamolybdochromate (III) and (b) hexamolybdochromate (V)



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