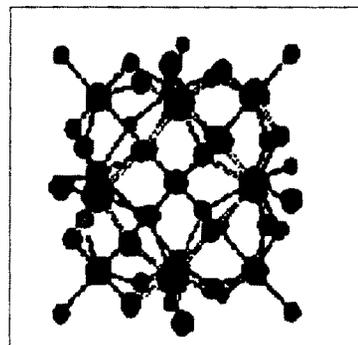


CHAPTER 2



*Oxidation of aliphatic and benzylic
alcohols by Oxone[®], catalysed by
12-tungstocobaltate (II)*

2.0 Oxidation Of aliphatic and benzylic alcohols by Oxone[®], catalysed by 12-tungstocobaltate (II)

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2.1 Introduction

Catalysis by heteropolyoxometalates (HPAs) and related compounds is a field of increasing importance[1-9], several features making them economically and environmentally attractive.. In the last two decades, the broad utility of polyoxometalates has been demonstrated by a wide variety of synthetically useful selective transformations of organic-substrates. The properties of the HPA's can be altered by both changing the heteroatom and the oxometalate moiety. Thus making them suitable for particular research. They are used in oxidation of hydrocarbons, alcohols, substituted phenols and amines [10]. Several new industrial processes based on POM catalysis, such as oxidation of methacrolein, hydration of olefins, polymerization of tetrahydrofuran, etc., have been developed and commercialized [6].

Many isopoly- and heteropolyoxometalate (POM) anions are ideal candidates for the observation of homogeneous-phase outer-sphere electron-transfer processes and for comparison of experimentally determined rate constants with those predicted by the theoretical models of Marcus, Sutin, and others. At the same time, where one or more addendum atoms usually V(V), Mo(VI), or W(VI) of the POM cluster have been substituted by d-electron-containing first- or second-row transition-metal cations, more rapid inner-sphere electron-transfer pathways are often accessible. The elegance and utility of Marcus's theory of outer-sphere electron transfer were recognized in 1992 with a Nobel Prize in chemistry, and its historical development was outlined in his Nobel Lecture [11]. Shortly after publication of Marcus's seminal papers on this topic [12-14], it was recognized that POM anions were likely to exchange electrons via an outer-sphere mechanism: (1) As a class, POM anions possess charge densities considerably lower than those observed in traditional low-charge-density (non-coordinating) anions, such as ClO_4^- and NO_3^- ; (2) the partial negative charges on the oxide anion ligands within POM structures are quite low (the $\text{p}K_a$ values of many POM anions are below 1, and the partial negative charges residing on the outermost terminal oxide ligands, $\text{M}=\text{O}$, are generally lower than those on the bridging oxide anions embedded within the clusters); and (3) many POM anions, and in particular those possessing the Keggin structure, are close to spherical in shape, a geometric consideration important for application of the electrostatic laws upon which much of Marcus's development was predicated. The first detailed kinetic study and theoretical analysis of electron transfer involving POM anions was reported by Rasmussen and Brubaker in 1964, only shortly after the foundations of Marcus's work had been laid [15]. Rasmussen and Brubaker studied the self-exchange reaction between

$[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ and its 1- e^- oxidized derivative, $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$. In addition to the general considerations listed above, both these complexes are substitutionally inert with respect to the ligand environments of the cobalt ions [16]. In 1970 Chester recognized the potential utility of $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ as a well-defined probe for determining the nature of outer-sphere oxidations of alkyl aromatic hydrocarbons [17]. His aim was to determine whether such processes were feasible. An additional rationale for using $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ was the expectation that reduction of tetrahedrally coordinated Co(III) ions (ground-state electronic configuration $e^3t_2^3$, 5E) to tetrahedral Co(II) ($e^4t_2^3$, 4A) would occur rapidly in the absence of electronic excitation. In contrast, addition of an electron to an e_g orbital of low spin octahedral Co(III) ($t_2^6e^0$, 1A) is formally a spin-forbidden process. Hence, *$[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ anions were expected to be more kinetically facile oxidants than the octahedral cobalto-organic complexes, such as cobalt(III)acetate, typically used in the oxidation of organic substrates.* The possible effects of Jahn-Teller distortion on the inner-sphere reorganization energy associated with the 1- e^- reduction of $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ were not considered. These, and related structural and electronic issues, will assume greater importance in evaluation of the role of inner-sphere reorganization energies, and of the potential for nonadiabatic behavior, in electron self-exchange between $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ and $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ and between other POM anion pairs. Since publication of Chester's work in 1970, $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ and related POM anions have been used as well-defined outer-sphere electron-transfer agents in over 50 published studies. Indeed, the $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ anion has, with good reason, been referred to as a "soluble anode" [18]. Meanwhile, the potential utility of numerous POM anions as electron-transfer agents in the selective

catalytic oxidations of inorganic and organic substrates of practical importance has been recognized.

The selective oxidation [19] of alcohols to the corresponding carbonyl compounds is a key transformation in organic chemistry. Traditional methods used for such transformations generally involve either inorganic oxidants in stoichiometric quantities like chromium (VI) reagents [20] or use of stoichiometrically excess peroxy compounds like hydrogen peroxide, in presence of a catalyst. The latter method is environmentally friendly but requires long hours of reaction time, higher temperature [21] and specific catalysts under phase transfer conditions with co-catalysts like TEMPO²² (the oxidation of alcohol may continue up to carboxylic acid stage). Apart from the above methods intrinsically waste free aerobic oxidation methods using copper catalyst [23], ruthenium catalyst [24] vanadium containing polymolybdates [22] or enzyme catalysts have also been reported. However, they suffer general applicability, high catalytic loads, and use of oxidatively unstable ligands and modest conversions.

Development of new catalytic methods for selective oxidation of alcohols to carbonyl compounds finds applications in fine chemical synthesis. For smaller operations the complications due to use of oxygen gas as an oxidant may be avoided [25] even though the procedure may be environmentally benign. Further, it is also advantageous to use water-soluble catalyst for practical and industrial applications. Because, in the methods where the catalyst is made soluble in organic solvents either by using hydrophobic phase transfer reagents or by using ligands [26] like polyamine inherently requires separation of the catalyst from the product which also makes recovery of the catalyst difficult. Whereas, if the catalyst is soluble in aqueous medium, oxidation of liquid alcohols to corresponding

carbonyl compound and their separation becomes convenient leaving behind the catalyst in aqueous phase. Thus making it available for recycling.

Oxone® used in the present study is a convenient, readily available and economical, which is utilized for various transformations in organic synthesis [27-32]. The active ingredient of Oxone® is potassium peroxymonosulfate, KHSO_5 , commonly known as potassium monopersulfate, which is present as a component of a triple salt with the formula $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$ [potassium hydrogen peroxymonosulfate sulfate (5:3:2:2)]. The oxidation potential of Oxone® is derived from its peracid chemistry; it is the first neutralization salt of peroxymonosulfuric acid H_2SO_5 (also known as Caro's acid).

$\text{K}^+\text{O-S(=O)}_2\text{(OOH)}$. The standard electrode potential (E°) of Oxone® is shown in the following reaction:

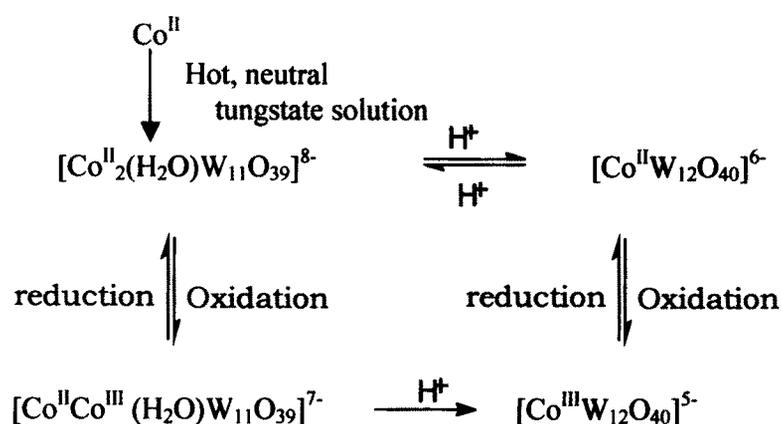
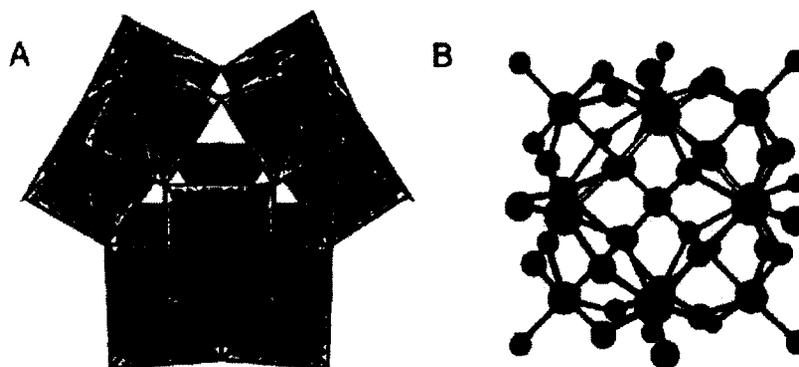


This potential is high enough for many room temperature oxidations, including halide to halogen or hypohalite, ferrous ion to ferric, and manganous ion to manganic. The compounds containing boron, nitrogen, phosphorous and sulfur have been selectively oxidized by oxone. It was also used for the preparation of reagent dimethyldioxirane (DMDO) [33,34] and for N,N-diaryl hydrazine [35]. Generally the oxidations by oxone occurs with very low rates necessitating the presence of a catalyst which increases the rate by offering an alternative path.

In this Chapter we demonstrate the efficient oxidation of alcohols to their corresponding aldehydes and ketones with Oxone® catalysed by a Keggin-type polyoxometalate, 12-tungstocobaltate (II).

2.2 Experimental

The cobalt complexes, $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$, were prepared by the reported method [36,37] as: 198 gm of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (SD fine) was dissolved in 400 ml water and the pH of the solution was adjusted to a value between 6.5 to 7.5 by the addition of 40 ml glacial acetic acid (BDH). A separate solution was prepared by dissolving 24.9 gms of cobaltous acetate tetrahydrate in 125 ml of warm water to which few drops of glacial acetic acid had been added. The sodium tungstate solution was brought to boil and cobaltous acetate solution was added to it slowly with stirring. Small amount of transitory pink precipitate appeared and re-dissolved very rapidly forming a deep green solution. After all the cobaltous acetate solution was added and the resultant solution was boiled for ten minutes and then filtered hot to remove traces of insoluble matter. To this extremely soluble sodium salt of $[\text{Co}^{\text{II}}_2(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{8-}$ a hot saturated solution containing 130 gms of potassium chloride was added. The green crystals of potassium salt were separated on cooling. The product was recrystallised with water containing 2 ml of acetic acid. The product obtained was potassium salt of $[\text{Co}^{\text{II}}_2(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{8-}$ (salt I). The recrystallised product (20 gms) was dissolved in 100 ml of 0.1 mol dm^{-3} HCl and evaporated on steam bath until green needle like crystals of $\text{K}_6[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]$ were begun to form and cooled in ice box. The resulting crystals (salt II) were recrystallised from water. The scheme for the above preparation is given as in Scheme-I, whose structure is as in Figures A and B, which was described by Keggin.



Scheme I

The solution $\text{K}_6[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]$ was standardized spectrophotometrically [38] at 624 nm for $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ respectively) using an Elico SL 159 UV-VIS spectrophotometer.

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. The Gas Chromatographic analysis was carried out on Shimadzu GC-14B (HP 5 cross-linked 5% PHME silicone capillary column). All alcohols are commercial materials and were purchased from S D Fine chemicals (Mumbai India) and

Lancaster. Potassium peroxomonosulphate was purchased from Across Chemicals. 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.

2.3 Present work

Carbonyl compounds in the fine chemicals industry are precursors with wide applicability from drugs to fragrances. The oxidation of alcohols to carbonyl products is an important transformation in organic chemistry [39], which has received most attention over the years, especially the search for versatile and selective reagents in catalytic applications [40]. Methods which are available for selective oxidation of alcohols to the corresponding carbonyl compounds are not free from some disadvantages and there still exist a need for new methods. The main requirements are simplicity of the method, selectivity, in particular with regard to over-oxidation of carbonyl compounds to carboxylic acids, effectiveness and mildness of the reaction conditions. Thus, most of the current industrial oxidation processes are outmoded and are used polluting oxidants in solution like the heavy metals Cr(VI) or Mn(VI), and industries are under pressure to replace them with catalytic processes using clean oxidants, such as oxygen, H₂O₂ and other inexpensive and environmentally friendly oxidants.

During the past few years much of the work has been done on 12-tungstocobaltate in our laboratory. The main focus of our research group was utilization of 12-tungstocobaltate (III) as an oxidant. The POM, has been successfully utilized in the oxidation of various inorganic and organic substrates. To list few of them are, oxidation of thallium(I) by 12-tungstocobaltate(III) in aqueous hydrochloric acid medium [41], oxidation of antimony(III) by Keggin type 12-tungstocobaltate(III)

in aqueous hydrochloric acid [42], ruthenium(III) catalysed oxidation of thallium(I) by 12-tungstocobaltate(III) in hydrochloric acid medium [43], chromium(VI), chromium(V) and chromium(IV) oxidation of 12-tungstocobaltate(II) [44], Outer-sphere electron transfer from platinum(II) to Keggin-type 12-tungstocobaltate(III) in presence and absence of chloride ions [45], Oxidation of arsenous acid by 12-tungstocobaltate(III) catalysed by ruthenium(III) in aqueous acid medium [46].

Lawrence et.al [47] reported the oxidation of 12-tungstocobaltate(II) by Oxone[®] to 12-tungstocobaltate(III). In continuation of our work on POMs we planned to develop the catalytic cycle: 12-tungstocobaltate(II) /Oxone[®], where in the oxidant Oxone[®] will oxidise 12-tungstocobaltate(II) to 12-tungstocobaltate(III), which in turn will oxidise alcohols to carbonyl compounds.

To start with, the oxidation of 4-nitrobenzyl alcohol was studied. In a typical experiment 4-nitrobenzyl alcohol (2.2 mmol) and Oxone[®] (1mmol) were taken in 50:50 % aqueous acetonitrile mixture in a round-bottomed flask fitted with reflux condenser. Catalyst 12-tungstocobaltate (II) (4×10^{-4} mol) was added. The reaction mixture was stirred at 50^oC 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 x 2). The combined organic layer was washed with a solution of NaHCO₃ and dried over MgSO₄ 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. (Table 1)

2.4 Results and Discussion

Catalyst Characterization

The FT-IR spectrum of catalyst (Fig 1) shows fundamental bands at 933, 862, and 756 cm^{-1} corresponding to W-O_d , $\text{W-O}_b\text{-W}$ and $\text{W-O}_c\text{-W}$ stretching motion of the Keggin structure. The broad peak centered at 3392 cm^{-1} and sharp peak at 1619 cm^{-1} indicate the water associated with the Keggin structure of the catalyst as either in the lattice or in the co-ordinated form.

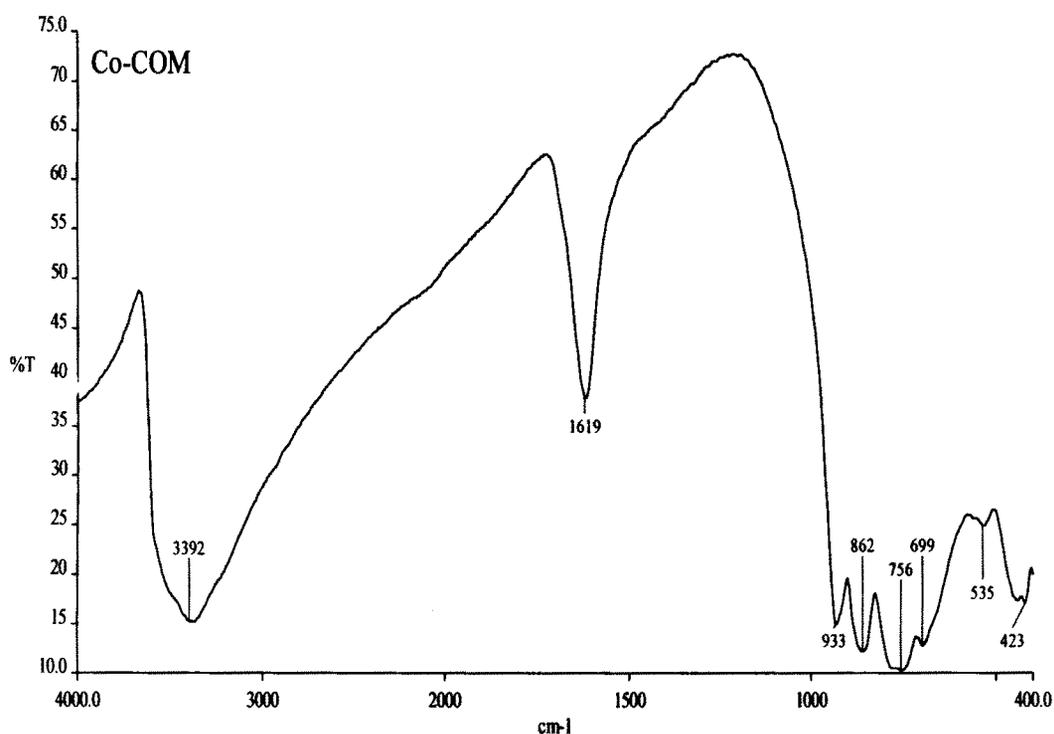
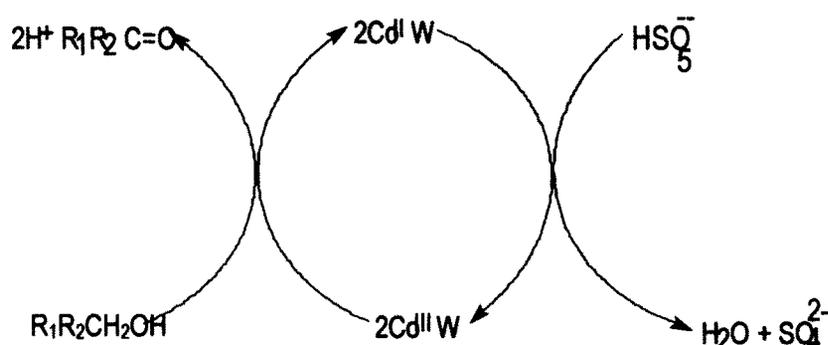


Figure. 1. FT-IR Spectrum of 12-Tungstocobaltate (II)

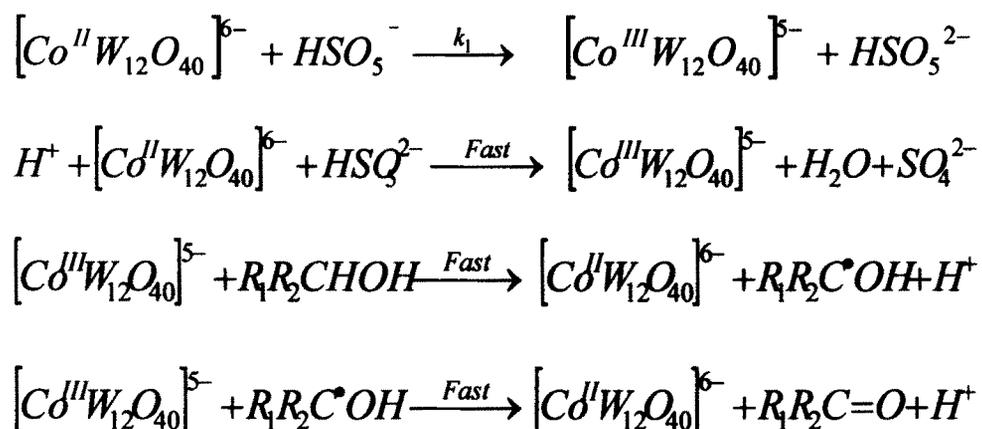
The uncatalyzed oxidation of alcohols did not occur under the experimental conditions. The results of this study are shown in Table 1 for various alcohols which shows that the carbonyl compound is the only product obtained in comparatively high yields without further conversion to carboxylic acid.

The rates of oxidation of representative aliphatic alcohol IPA were studied in aqueous medium, following the reaction by determining the remaining oxidant iodometrically. It was found that the reaction was independent of both substrate and oxidant concentration and increases linearly with the concentration of catalyst, 12-tungstocobaltate (II). Therefore, the reaction is initiated by the oxidation of 12-tungstocobaltate (II) by oxone and converting it into 12-tungstocobaltate (III), an outer-sphere oxidant (Known as soluble anode). This oxidant generated in situ will react with the alcohol in a rate-determining step. Therefore, the catalysed path of the reaction can be represented as in Scheme 2.



Scheme 2: Proposed catalysed path of the reaction.

The first dissociation of H_2SO_5 is rapid, as it is equivalent to sulphuric acid proton. [48]. Whereas the dissociation constant of second proton has a very low value therefore, in aqueous solutions the predominant species of oxone would be HSO_5^- the mechanism of 12-tungstocobaltate (II) catalysed oxidation of alcohols may be represented by Scheme 3.



Scheme 3

$$Rate = k [Co^{II}W_{12}O_{40}]^{6-} [HSQ_5^-] \quad 1$$

$$k_{obs} = k_1 [Co^{II}W_{12}O_{40}]^{6-} \quad 2$$

The reaction between 12-tungstocobaltate (II) and oxone occurs through an outer-sphere path [47] in which two moles of 12-tungstocobaltate (II) are oxidized per mole of oxone. It was observed that when catalyst and oxidant were mixed in absence of alcohol the blue color of the catalyst changes to yellow oxidized form. The corresponding rate law is given by equation (1) and since, the oxidant used is in excess, the rate constant would be given by equation (2), which makes it independent of substrate and oxidant concentration.

The possible Transition State of the mechanism is shown in the Figure 1

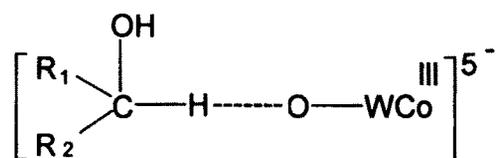


Figure.1

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.

2.5 Conclusions

A Keggin-type polyoxometalate (POM) 12-tungstocobaltate (II) ($[\text{CoII}(\text{W}_{12}\text{O}_{40})]^{6-}$) has been used as a catalyst for the oxidation of aliphatic and benzylic alcohols to the corresponding carbonyl compounds. The reduced (POM) formed in the oxidation of alcohols is re-oxidized by Oxone® (potassium peroxomonopersulphate). Further more we did not noticed the over oxidation of the products to the corresponding acids. The catalytic method: 12-tungstocobaltate (II)/ Oxone® demonstrated this chapter will be effective for the oxidation of alcohols.

Table 1: Oxidation of alcohols to carbonyl compounds catalysed by Potassium dodecatungstocobaltate (II)⁻ /oxone

Srl No	Reactant	Product	Time (t/h)	Yield (%) Isolated [†]	M.P/B.P of carbonyl compound T ^o C	M.P of 2,4-DNP derivative T ^o C
1	n-Propanol	n-Propanaldehyde	3	70 [‡]	47-48	154
2	2-Propanol	Acetone	3	72	56	127
3	n-Butanol	n-Butraldehyde	3	78	76	120
4	2-Butanol	Iso-butraldehyde	3	81	66	185
5	Sec-Butanol	Ethyl methyl ketone	3	75	80	146
6	Benzyl alcohol	Benzaldehyde	3	85	179	235
7	2-Nitro benzyl alcohol	2-Nitro benzaldehyde	2.5	92	43-45	264
8	4-Nitro benzyl alcohol	4-Nitro benzaldehyde	2.5	92	104	>300
9	4-chloro benzyl alcohol	4-Chloro benzaldehyde	2.5	87	47	263
10	4-Methoxy benzyl alcohol	4-Methoxy benzaldehyde	2.5	83	248	254
11	4-Methyl benzyl alcohol	4-Methyl benzaldehyde	3	81	201-204	231

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

[‡] Estimated by Gas Chromatography.

2.6 References

1. K. I. Mateev. *Kinet. Katal.* 18 (1977) 862.
2. J. M. Thomas.; K. I. Zamaraev. *Perspective in Catalysis*, Blackwell, London, (1992) 431.
3. I. V. Kozhevnikov.; *Catal Rev Sci Eng.* 37 (1995) 311.
4. M. Misono. *Catal Rev Sci Eng.* 30 (1988) 339.
5. N. Mizuno.; M. Misono. *Chem Rev.* 98 (1998) 199.
6. (a) M. Misono.; N. Nojiri. *Appl Catal.* 64 (1990) 1.; (b) N. Nojiri.; M. Misono. *Appl Catal.* 95 (1993) 559.
7. Y. Izumi.; K. Urabe.; M. Onaka. *Zeolite, Clay and Heteropoly Acid in Organic reactions*. Kodansha/VCH, Tokyo. (1992) 99.
8. T. Okahara.; N. Mizuno.; M. Misono. *Adv Catal.* 41(1996) 113.
9. C. L. Hill.; C. M. Prosser-McCartha. *Coord Chem Rev*, 143 (1995) 407.
10. I. N. Lykakis.; C. Tanielian.; M. Orfanopoulos. *Org. Lett.* 5 (2003) 2875. and refs cited therein.
11. R. A. Marcus. *Angew. Chem., Int. Ed. Engl.* 32 (1993) 1111.
12. R. A. Marcus. *Discuss. Faraday Soc.* 29 (1960) 21.
13. R. A. Marcus. *J. Phys. Chem.* 67 (1963), 853.
14. R. A. Marcus. *Annu. Rev. Phys. Chem.* 15 (1964), 155.
15. P. G. Rasmussen.; C. H., Jr. Brubaker. *Inorg. Chem.* 3 (1964) 977.
16. G. Geier.; C. H. Jr. Brubaker. *Inorg. Chem.* 5 (1966), 321.
17. A. W. Chester. *J. Org. Chem.* 35 (1970) 1797.
18. L. Ebersson.; L.-G. Wistrand. *Acta Chem. Scand. B* 34 (1980) , 349.
19. (a) R. A. Sheldon.; J. K. Kochi. *Metal-catalysed Oxidations of Organic Compounds*, Academic Press, New York, (1981).; (b) S. V. Ley.; J. Norman.; W. P. Griffith.; S. P. Marsden. *Synthesis* (1994) 639.; (c) M. Hudlicky. *Oxidations in Organic Chemistry*, ACS, Washington DC, (1990).; (d) R. A. Sheldon.; I. W. C. E. Arends.; A. Dijkstra, *Catalysis Today*. 57 (2000) 157.
20. G. Cincilli.; G. Cardillo. *Chromium Oxidations in Organic Chemistry*, Springer, Berlin, (1984).

21. D.Sloboda-Rozner.; P. Alsters.; R. Neumann. *J. Am. Chem. Soc.* 125 (2003) 5280.
22. R.Ben-Daniel.; P. Alsters.; R. Neumann. *J. Org. Chem.* 66 (2001) 8650.
23. M. F. Semmelhack.; C. R.Schmid.; D. A. Cortes.; C. S. Chou. *J. Am. Chem. Soc.* 106 (1984) 3374.
24. A.Dijksman,.; I. W. C. E. Arends.; R. A. Sheldon. *Chem. Commun.* (1999) 1591.
25. R. A. Sheldon. *J. Chem. Technol Biotechnol.* 68 (1997) 381.
26. (a) A. Berkessel.; C. A. Sklorz. *Tetrahedron Lett.* 40 (1999) 7065.; (b) J. Brinksma.; M. T. Ripens.; R. Hage.; B. L. Feringa. *Inorg Chem. Acta.* 337 (2002) 75.; (c) A. G. J. Ligtenbary.; P. Ousting.; G. Roelfes.; R. M. La Crois.; R. Hage.; B. L. Feringa.; M. Lutz.; A. L. Spek. *Chem. Commun.* (2001) 385.
27. L. A.Wozniak.; W. J. Stec. *Tetrahedron Lett.* 40 (1999) 2637.
28. L. A.Wozniak.; M. Koziolkiewicz.; A. Kobylanska.; W. Stec, *J. Bioorg. Med. Chem. Lett.* 8 (1998) 2641.
29. K. S. Webb.; D. Levy. *Tetrahedron Lett.* 36 (1995) 5117.
30. K. S. Webb.; S. J. Ruskay. *Tetrahedron.* 54 (1998) 401.
31. B. M. Trost.; D. P. Curran. *Tetrahedron Lett.* 22 (1981) 1287.
32. A. L.Baumstark.; M. Beeson.; P. C. Vasquez. *Tetrahedron Lett.* 30 (1989) 567.
33. R. W . Murray. *Chem. Rev.* 89 (1989) 1187.
34. S. E.Denmark.; D. C. Forbes.; D. S. Hays.; J. S. Depue.; R. G. Wilde. *J. Org. Chem.* 60 (1995) 1391.
35. P. P. Kulkarni.; A. J. Kadam.; U. V. Desai.; R. B. Mane.; P. P. Wadgaonkar. *J. Chem Res (S)* (2000) 184.
- 36.. L. C. Baker.; T. P. McCutcheon. *J. Am. Chem. Soc.* 78 (1956) 4503.
37. P. G. Rasmussen.; C. H. Brubaker. *Inorg. Chem.* 3 (1964) 977.
38. B. Goyal.; A. Prakash.; R. N. Mehrotra. *Indian. J. Chem.* 38A (1999) 541.
39. B. M. Trost. *Comprehensive Organic Synthesis (Oxidation)* , Pergamon; New York. 7 (1991).
40. J. Muzart. *Chem. Rev.* 92 (1992) 113.

41. A. M. Hasure.; G. S. Gokavi. *Transition Metal Chemistry*. 27 (2002) 497.
42. B.D.Bhosale.; G.S.Gokavi. *Int. J. Chem. Kinetics* 34 (2002) 589.
43. A. M. Hasure.; G. S. Gokavi. *React. Kinetics. Catal. Lett.* 80 (2003) 59.
44. A.M. Hasure.; G. S. Gokavi. *Transition .Metal Chem.* 29 (2004) 231.
45. B. D. Bhosale.;G. S. Gokavi. *Indian J. Chemistry*. 43A (2004) 799.
46. B. D. Bhosale.;G. S. Gokavi. *Inorganic Reaction Mechanism 5 (2004)* 79.
47. A. L. Nolan.; R. C. Burns.; G. A. Lawrance. *J. Chem. Soc. Dalton. Trans.* (1998) 3041.
48. D. L. Ball.; J. O. Edwards. *J. Am. Chem. Soc.* 78 (1956) 1125.