Catalysis Letters Vol. 96, Nos. 3–4, July 2004 (© 2004)

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

S.P. Maradur[a], S.B. Halligudi[b], and G.S. Gokavi[a,*]

[a]*Department of Chemistry, Shivaji University, Kolhapur-416004, Maharashtra, India*
[b]*Catalysis Division, National Chemical Laboratory, Pune, India*

Received 8 April 2004; accepted 30 April 2004

$$R_1R_2CH_2OH \xrightarrow[\text{50\% Aqueous acetonitrile}]{[Co^{II}(W_{12}O_{40})]^{6-}/\text{Oxone}} R_1R_2CHO$$

A Keggin-type polyoxometalate (POM) 12-tungstocobaltate (II) ($[Co^{II}(W_{12}O_{40})]^{6-}$) 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 potassium peroxomonopersulphate.

KEY WORDS: homogeneous catalysis; oxidation; alcohols; polyoxometalates (POM); Oxone®.

1. Introduction

The selective oxidation [1a–d] 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 [2] 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 [3] and specific catalysts under phase transfer conditions with co-catalysts like TEMPO [4] (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 [5], ruthenium catalyst [6], vanadium containing polymolybdates [4] or enzyme catalysts have also been reported. However, they suffer general applicability, high catalytic loads, and use of oxidatively unstable ligands and modest conversions.

Polyoxometalates (POM) find application in various organic functional group transformations due to their tailor made characteristics [1]. The properties of the POM 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 [7].

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 [8] even though the procedure may be environmentally begin. 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 [9] 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 [10–15]. 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) [16,17] and for *N*,*N*-diaryl hydrazine [18]. 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 paper we demonstrate the efficient oxidation of alcohols to their corresponding aldehydes and ketones with Oxone® catalyzed by a Keggin-type POM, 12-tungstocobaltate (II).

---

*To whom correspondence should be addressed.
E-mail: gsgokavi@hotmail.com

1011-372X/04/0700–0165/0 © 2004 Plenum Publishing Corporation

2. Experimental

The catalyst $[Co^{II}(W_{12}O_{40}]^{6-}$ was prepared by the previously reported method [19] and standardized spectrophotometrically. 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 SD Fine chemicals (Mumbai, India) and Lancaster. Potassium peroxomonosulphate was purchased from Across Chemicals. Acetonitrile, dichloromethane purchased from SD fine chemicals (Mumbai, India) and were used without further purification. Yields reported refer to isolated products of the carbonyl compounds.

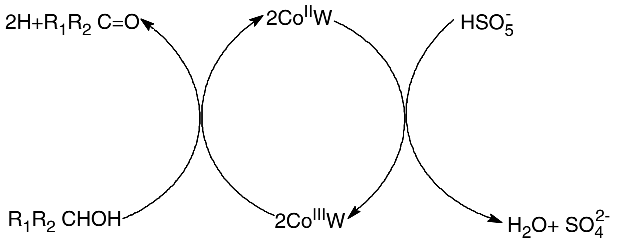
2.1. General Procedure

Alcohol (2.2 mmol) and oxone (1 mmol) 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 °C for 2–3 h. The progress of the reaction was monitored by TLC. After the completion of the reaction, the resulting solution was extracted with dichloromethane (20 mL × 2). 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 carbonyl compound, which was purified by crystallization, distillation or chromatography as appropriate.

3. Results and discussion

In the present study, a method for efficient oxidation of alcohols by oxone in presence of catalytic concentration of 12-tungstocobaltate (II) is described. The uncatalysed 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 aldehyde is the only product obtained in comparatively high yields without further conversion of aldehyde 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 1.



Scheme 1. Proposed catalysed path of the reaction.

Table 1
Oxidation of alcohols to carbonyl compounds catalysed by Potassium dodecatungstocobaltate $(II)^-$/oxone

S. No	Reactant	Product	Reaction time, *t* (h)	Yield (%) Isolated[a]	MP/BP of carbonyl compound *T*(°C)	MP of 2,4-DNP derivative *T*(°C)
1	*n*-Propanol	*n*-Propanaldehyde	3	70[b]	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

[a] Yield of pure product after crystallization or distillation or chromatography over silica gel.
[b] Estimated by gas chromatography.

The first dissociation of H_2SO_5 is rapid, as it is equivalent to sulphuric acid proton [20]. 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 2.

$$\begin{aligned}
&[Co^{II}W_{12}O_{40}]^{6-} + HSO_5^- \\
&\quad \xrightarrow{k_1} [Co^{III}W_{12}O_{40}]^{5-} + HSO_5^{2-} \\
&H^+ + [Co^{II}W_{12}O_{40}]^{6-} + HSO_5^{2-} \\
&\quad \xrightarrow{Fast} [Co^{III}W_{12}O_{40}]^{5-} + H_2O + SO_4^{2-} \\
&[Co^{III}W_{12}O_{40}]^{5-} + R_1R_2CHOH \\
&\quad \xrightarrow{Fast} + [Co^{II}W_{12}O_{40}]^{6-} + R_1R_2C^{\bullet}OH + H^+ \\
&[CO^{III}W_{12}O_{40}]^{5-} + R_1R_2C^{\bullet}OH \\
&\quad \xrightarrow{Fast} + [Co^{II}W_{12}O_{40}]^{6-} + R_1R_2C{=}O + H^+
\end{aligned}$$

Scheme 2.

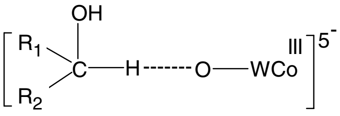


Figure 1.

$$\text{Rate} = k[Co^{II}W_{12}O_{40}]^{6-} + [HSO_5^-] \tag{1}$$

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

The reaction between 12-tungstocobaltate (II) and oxone occurs through an outer-sphere path [21] 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 colour 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 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. Conclusions

To conclude, we have shown that the Keggin-type POM 12-tungstocobaltate (II) catalyse the homogeneous liquid phase peroxomonosulphate (Oxone®) selectively oxidizes aliphatic and benzylic alcohols to the corresponding carbonyl compounds.

Acknowledgment

This work was supported by a Grant-in-Aid (12-29/2003[SR]) from University Grants Commission (UGC) New Delhi, India. SPM thank UGC New Delhi for research fellowship.

References

[1] (a) R.A. Sheldon and J.K. Kochi, *Metal-catalysed Oxidations of Organic Compounds*, Academic Press, New York, 1981; (b) S.V. Ley, J. Norman, W.P. Griffith and 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 and A. Dijksman, Catal. Today. 57 (2000) 157.

[2] G. Caincilli and G. Cardillo, *Chromium Oxidations in Organic Chemistry*, Springer, Berlin, 1984.

[3] D. Sloboda-Rozner, P.L. Alsters and R. Neumann. J. Am. Chem. Soc. 125 (2003) 5280.

[4] R. Ben-Daniel, P. Alsters and R. Neumann. J. Org. Chem. 66 (2001) 8650.

[5] M.F. Semmelhack, C.R. Schmid, D.A. Cortes and C.S. Chou. J. Am. Chem. Soc. 106 (1984) 3374.

[6] A. Dijksman, I.W.C.E. Arends and R.A. Sheldon, Chem. Commun. (1999) 1591.

[7] I.N. Lykakis, C. Tanielian and M. Orfanopoulos, Org. Lett. 5 (2003) 2875 (and refs cited therein).

[8] R.A. Sheldon, J. Chem. Technol Biotechnol. 68 (1997) 381.

[9] (a) A. Berkessel and C.A. Sklorz, Tetrahedron Lett. 40 (1999) 7065; (b) J. Brinksma, M.T. Ripens, R. Hage and B.L. Feringa, Inorg. Chem. Acta. 337 (2002) 75; (c) Ligtenbary, A.G.J. Ousting, P. Roelfes, G. La Crois, R.M. Hage, R. Feringa, B.L. Lutz, and M. Spek, A.L. Chem. Commun. (2001) 385.

[10] L.A. Wozniak and W.J. Stec, Tetrahedron Lett. 40 (1999) 2637.

[11] L.A. Wozniak, M. Koziolkiewicz, A. Kobylanska and W. J. Stec, Bioorg. Med. Chem. Lett. 8 (1998) 2641.

[12] K.S. Webb and D. Levy, Tetrahedron Lett. 36 (1995) 5117.

[13] K.S. Webb and S.J. Ruszkay, Tetrahedron 54 (1998) 401.

[14] B.M. Trost and D.P. Curran, Tetrahedron Lett. 22 (1981) 1287.

[15] A.L. Baumstark, M. Beeson and P.C. Vasquez, Tetrahedron Lett. 30 (1989) 5567.

[16] R.W. Murray, Chem. Rev. 89 (1989) 1187.

[17] S.E. Denmark, D.C. Forbes, D.S. Hays, J.S. Depue and R.G. Wilde, J. Org. Chem. 60 (1995) 1391.

[18] P.P. Kulkarni, A.J. Kadam, U.V. Desai, R.B. Mane and P.P. Wadgaonkar, J. Chem. Res-(S) (2000) 184.

[19] L.C. Baker and T.P. Mccutcheon, J. Am. Chem. Soc. 78 (1956) 4503.

[20] D.L. Ball and J.O. Edwards, J. Am. Chem. Soc. 78 (1956) 1125.

[21] A.L. Nolan, R.C. Burns and G.A. Lawrence, J. Chem. Soc, Dalton Trans. (1998) 3041.