

Selective Oxidation of Alcohols to Aldehydes by Hydrogen Peroxide Using Hexamolybdochromate(III) as Catalyst

S.P. Mardur and G.S. Gokavi*

*Kinetics and Catalysis Laboratory, Department of Chemistry, Shivaji University
Kolhapur-416004, Maharashtra State, India*

(Received 24 April 2009, Accepted 26 July 2009)

Anderson type hexamolybdochromate(III) was utilized as a catalyst for facile conversion of various aliphatic, benzylic and heterocyclic alcohols to corresponding aldehydes and ketones in good yields. The reaction was carried out in 50% aq. acetonitrile using hydrogen peroxide as the oxidant at 50 °C. The reaction was found to involve oxidation of the catalyst to its active Cr(V) intermediate by hydrogen peroxide.

Keywords: Anderson type, Alcohols, Oxidation, Homogeneous catalysis, Hydrogen peroxide

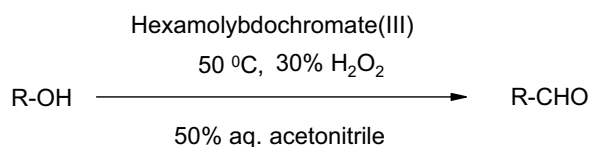
INTRODUCTION

Oxidation is a core technology wherein the general methods are unacceptable for practical synthesis. The heavy metal oxidants form toxic wastes, and known organic stoichiometric oxidants are usually very expensive [1-2]. Thus, there is need for clean, safe oxidation procedures. Molecular oxygen is obviously an ideal oxidant [3], but aerobic oxidation is often difficult to control. Hydrogen peroxide, H₂O₂, is a very attractive oxidant for liquid-phase reactions [4]. 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 also waste-avoiding oxidant only when it is used in a controlled manner without organic solvents and other toxic compounds. These oxidations, however, require an efficient catalyst. Other methods for the preparation of carbonyl compounds utilizing sodium nitrate in the presence of an acidic ionic liquid [5] and methyl triphenylphosphonium peroxydisulfate [6], either from the corresponding alcohols or

from oximes and phenylhydrazones respectively, have also been reported.

Polyoxomolybdates have been attracting considerable interest over recent years as oxidation catalysts for both gas and liquid phase oxidation reactions [7-11]. They were utilized as co-catalysts in various oxidations of terminal alkenes [12], followed later on by various catalytic oxidations of alcohols, ketones [13] and amines [14-15], phenols [16], alkyl aromatics [17], dienes [18], alkanes [19] and sulfur containing compounds [20]. Although Keggin and Dawson are known to be active catalysts in several [8] industrial processes, the application of Anderson type heteropolyoxomolybdates is only starting. 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 structure has been confirmed by Perloff [21] who found that it resembles that of [TeMo₆O₂₄]⁶⁻. Most of the polyoxometalate catalysis

*Corresponding author. E-mail: gsgokavi@hotmail.com

*Scheme 1*

reported in the literature are based on the utilization of Keggin or Dawson-type polyoxometalates. In continuation of our work on organic oxidations catalysed by polyoxometalates [22-23], 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) as shown in Scheme 1. The conversion of alcohols into corresponding carbonyl compounds can also be effected by using carcinogenic chromium reagents [24]. However, the present method utilizes the chromium reagent in a catalytic amount rather than stoichiometric amount.

EXPERIMENTAL

All the products are known compounds and were identified by comparison of their physical and 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 were commercial materials purchased from S. D. Fine Chemicals (Mumbai India) and Lancaster. Acetonitrile and dichloromethane were purchased from S. D. Fine Chemicals (Mumbai India) and used without further purification. Yields reported refer to the isolated products of the carbonyl compounds.

Catalyst Preparation

The catalyst sodium hexamolybdochromate(III) was prepared using the previously reported method [21]. 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 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 h. 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.

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%).

General Procedure for Oxidation of Alcohols

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 $\text{Na}_3[\text{CrMo}_6\text{O}_{24}\text{H}_6]$ (0.4 mmol) 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 \times 2) and the organic phase 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. Since the carbonyl compounds are all known compounds, they are characterized by comparing the physical constants (M.P or B. P.) of the product with their corresponding 2,4,DNP derivatives.

RESULTS AND DISCUSSION

To study the catalytic oxidation of alcohols mediated by $\text{Na}_3[\text{CrMo}_6\text{O}_{24}\text{H}_6] \cdot 8\text{H}_2\text{O}$, benzyl alcohol was chosen as a model compound and the reaction conditions were optimized. The effect of catalyst between 1.0 mmol to 4.0 mmol by keeping the amount of hydrogen peroxide constant was studied (Table 1) and the maximum yield of benzaldehyde was obtained within three hrs when the concentration of the catalyst was 4.0 mmol. Therefore, keeping the catalyst concentration

Selective Oxidation of Alcohols to Aldehydes by Hydrogen Peroxide

Table 1. Effect of Hydrogen Peroxide and Catalyst on the Yield of Benzaldehyde During Oxidation of Benzyl Alcohol after 3 h

Catalyst (mmol)	H ₂ O ₂ (mmol)	Yield (%) ^b
0.0	4.5	0
0.1	4.5	55
0.2	4.5	60
0.3	4.5	70
0.4	4.5	85
0.4	0.0	0

^bIsolated yield.

(4.0 mmol) constant, other substrates were oxidized. The reaction did not occur within 3 h, when only the catalyst or only hydrogen peroxide was present (Table 1). To assess the general scope of the catalytic oxidation, the saturated and benzylic, primary and secondary alcohols were chosen as substrates. The results of this study are shown in Table 2 for various alcohols which show that the carbonyl compound is the only product obtained in comparatively high yields. Not surprisingly, the substituted benzylic substrates like 2-Nitro-, 4-Nitro-, 4-Chloro- and 4-Methoxybenzyl alcohols were more reactive than the 4-Methylbenzyl alcohol. It is worth mentioning that no oxidation was observed in the aromatic ring of the benzylic substrates. Cinnamyl alcohol and furfuryl alcohol were also oxidized neatly without forming any side

Table 2. Sodium Hexamolybdochromate(III) Catalyzed Oxidation of Alcohols to Carbonyl Compounds by H₂O₂

Sr. No.	Reactant	Product	Reaction time (h)	Yield (%) ^b	M.P./B.P. of product (°C)	M.P. of 2,4-DNP derivative (°C)
1	2-Propanol	Acetone	4	72	56	150
2	n-Butanol	n-Butaraldehyde	4	78	76	122
3	2-Butanol	Iso-butaraldehyde	4	81	66	185
4	Sec-butanol	Ethyl methyl ketone	4	75	80	115
5	n-Octanol	n-Octaldehyde	4.5	80	170	106
6	Benzyl alcohol	Benzaldehyde	3	85	179	235
7	2-Nitro benzyl alcohol	2-Nitobenzaldehyde	2.5	92	45	264
8	4-Nitro benzyl alcohol	4-Nitro benzaldehyde	2.5	92	104	>300
9	4-Chloro benzyl alcohol	4-Chlorobenzaldehyde	2.5	87	47	263
10	4-Methyl benzyl alcohol	4-Methylbenzaldehyde	3	81	204	231
11	4-Methoxy benzyl alcohol	4-Methoxy benzaldehyde	2.5	83	248	254
12	4-Hydroxy benzyl alcohol	4-Hydroxy benzaldehyde	3	81	117	280
13	Cinnamyl alcohol	Cinnamaldehyde	3	62	125	-
14	Fufuryl alcohol	Furfural	3	87	161	-
15	Benzhydrol	Benzophenone	3	87	49	238

^bIsolated yield.

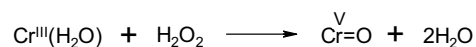
products. Generally, over-oxidation of the primary alcohols to the corresponding acids occurs with other catalysts, but in the presence of hexamolybdochromate(III) the formation of acids was not observed. Although numerous methods have been reported in the literature for the selective oxidation of alcohols to corresponding carbonyl compounds, the present method is compared with some recently [25-30] reported methods (Table 3). The advantage of the present method over the others is that it does not require any activator [25] like Na_2HPO_4 or phase transfer reagent like IRS400 [27] and tetraalkylpyridinium ion [29] to effect the oxidation. Therefore, the present method gives selectively good yield in reasonable time.

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, the oxidation of 4-nitrobenzyl alcohol was carried out using the optimized conditions in the presence of 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 oxidized sodium hexamolybdochromate(V). The FT-IR spectra of both unoxidized and oxidized sodium hexamolybdochromate were recorded as KBr pellet. The comparison of the two spectra indicated that the polyoxometalate characteristic M-O_c-M peak at 643 cm^{-1} splitted into two peaks in the oxidized form due to the change in the oxidation state of chromium. There was also a new peak at 829 cm^{-1} characteristic of $\text{Cr}^{\text{V}}=\text{O}$ in the FT-IR of the oxidized form of sodium hexamolybdochromate [31]. On the basis of FT-IR spectral examination of both unoxidized and oxidized forms of hexamolybdochromate, the formation of Cr^{V} can be shown as in the following equation where the formed $\text{Cr}^{\text{V}}=\text{O}$ acts as an oxidant in the present study.

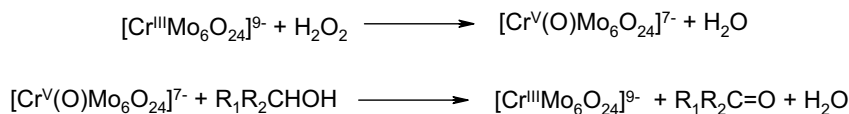


Since, under the reaction conditions studied, but in the absence of POM, the oxidation of alcohols did not take place, we surmised that the initial activation mechanism worked through an interaction between the H_2O_2 and the POM as shown in

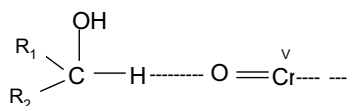
Table 3. Comparison of the Reported Methods with the Present Method for Oxidation of Benzyl Alcohol to Benzaldehyde

Sr. No.	Catalyst	Conditions	Yield (%)	Ref.
1	$\text{Na}_2\text{WO}_4/\text{Na}_2\text{HPO}_4$	Dimethylacetamide, 90 °C, 1 h	99	[25]
2	8-HydroxyquinolinatoMn(III) complexes	Acetone, 25 °C, 3 h	82	[26]
3	$\text{Na}_2\text{WO}_4/\text{IRA 400 Resin}$	Acetonitrile, reflux, 4-6 h	83	[27]
4	$\text{H}_3\text{PW}_{12}\text{O}_{40}$	Butanol, reflux (60-70 °C), 2.5 h	78	[28]
5	Tetraalkylpyridinium octamolybdate	Water, reflux, 1.7 h	93.6	[29]
6	[LMn(O) ₃ MnL] (L = 1,4,7 trimethyl, 1,4,7 triazacyclononane)	Acetonitrile, 22 °C, 24 h	43.5	[30]
7	Hexmolybdochromate(III)	Acetonitrile, 50 °C, 3 h	85	Present work

Selective Oxidation of Alcohols to Aldehydes by Hydrogen Peroxide



Scheme 2.



Scheme 3

Scheme 2. The possible transition state of the mechanism which involves the development of negative charge is shown in the Scheme 3. Such a transition state is largely stabilized by electron withdrawing substrates and makes the reaction to occur faster. Moreover, the 4-nitro and 4-chloro benzyl alcohols reacted at a faster rate than that of the benzyl alcohol.

CONCLUSIONS

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 the formation of a Cr(V) POM anion which in turn leads to the formation of carbonyl derivatives as the 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. The method is environmentally benign as water is the only byproduct.

ACKNOWLEDGEMENTS

We gratefully acknowledge the generous grant received from University Grants Commission [grant No. F.12-29/2003 (SR)] to carry out this research project.

REFERENCES

[1] M. Hudlicky, *Oxidations in Organic Chemistry*, ACS

Monograph Ser. (186), American Chemical Society, Washington, DC, 1990.

- [2] B.M. Trost, I. Fleming, *Comprehensive Organic Synthesis*, Pergamon Press, 1st ed., Oxford, 1991.
- [3] R.A. Sheldon, J.K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, 1981.
- [4] G. Strukul, *Catalytic Oxidations with Hydrogen Peroxide as Oxidant*, Kluwer Academic, Dordrecht, The Netherlands, 1992.
- [5] A.R. Hajipour, F. Rafii, A.E. Ruoho, *Synlett*. 7 (2007) 1118.
- [6] A.R. Hajipour, S. Zahmatkesh, A.E. Ruoho, *J. Iranian Chem. Soc.* 5 (2008) S54.
- [7] M.T. Pope, *Isopoly and Heteropoly Anions*, Springer: Berlin, Germany, 1983.
- [8] A. Muller, *Polyoxometalate Chemistry*, Kluwer Academic: Dordrecht, The Netherlands, 2001.
- [9] I.V. Kozhevnikov, *Catalysis by Polyoxometalates*, Wiley: Chichester. U.K., 2002.
- [10] C.L. Hill, C.M. Prosser-McCartha, *Coord. Chem. Rev.* 143 (1995) 407.
- [11] a) N. Mizuno, M. Misono, *Chem. Rev.* 98 (1998) 171; b) R. Neumann. *Prog. Inorg. Chem.* 47 (1998) 317.
- [12] K. Bergstad, H. Grennberg, J.E. Backvall, *Organometallics* 17 (1998) 45.
- [13] R. Ben-Daniel, R. Neumann, *Angew. Chem. Int. Ed.* 42 (2003) 92.
- [14] R. Ben-Daniel, P.L. Alsters, R. Neumann, *J. Org. Chem.* 66 (2001) 8650.
- [15] A.M. Khenkin, I. Vigdergauz, R. Neumann, *Chem. Eur. J.* 6 (2000) 875.
- [16] I.G. Kolesnik, E.G. Zhizhina, K.I. Matveev, *J. Mol. Catal. A* 153 (2000) 147.
- [17] A.M. Khenkin, L. Weiner, Y. Wang, R. Neumann, *J. Am. Chem. Soc.* 123 (2001) 8531.

- [18] a) R. Neumann, M. Lissel, *J. Org. Chem.* 54 (1989) 4607; b) R. Neumann, M. Levin, *J. Am. Chem. Soc.* 114 (1992) 7278.
- [19] A.M. Khenkin, R. Neumann, *J. Am. Chem. Soc.* 123 (2001) 6437.
- [20] N.M. Okun, J.C. Tarr, D.A. Hilleshiem, K.I. Hardcastle, C.L. Hill, *J. Mol. Cat. A* 246 (2006) 11.
- [21] A. Perloff, *Inorg. Chem.* 9 (1970) 2228.
- [22] S.P. Maradur, S.B. Halligudi, G.S. Gokavi, *Catal. Lett.* 96 (2004) 165.
- [23] S.D. Kadam, A.R. Supale, G.S. Gokavi, *Z. Phys. Chem.* 222 (2008) 635.
- [24] A.R. Hajipour, H.R. Bagheri, A.E. Ruoho, *Bull. Korean Chem. Soc.* 25 (2004) 1238.
- [25] T. Hida, H. Nogusa, *Tetrahedron* 65 (2009) 270.
- [26] Z. Ye, Z. Fu, S. Zhong, F. Xie, X. Zhou, F. Liu, D. Yin, *J. Catal.* 261 (2009) 110.
- [27] N. Bhati, K. Sharma, A. Goswami, *Synth. Commun.* 38 (2008) 1416.
- [28] R. Taebee, M.H. Alizadeh, *Curr. Sci.* 93 (2007) 133.
- [29] G. Ming-Lin, L. Hui-Zhen, *Green Chem.* 9 (2007) 421.
- [30] V.A. dos Santos, L.S. Shul'pina, D. Veghini, D. Mandelli, G.B. Shul'pin, *React. Kinet. Catal. Lett.* 88 (2006) 339.
- [31] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed., 1978.