



## Surfactant encapsulated cobalt complex catalyst for environmental friendly oxidation of alcohols

Babasaheb Bhosale

Assistant Professor, Chemistry Department, Rajaram College, Kolhapur- 416004

*Received: 20-01-2021 / Revised Accepted: 25-02-2021 / Published: 28-02-2021*

### ABSTRACT

The surfactant encapsulated cobalt complex, keggin type 12-tungstocobaltate (II) is prepared using cationic surfactant and characterized which is used for environmental friendly oxidation of many simple aliphatic, aromatic and substituted alcohols. This encapsulated catalyst can be recycled number of times without losing its activity more than 5%. To understand the mechanism of the oxidation, kinetic study of oxidation is also studied.

**Keywords:** Encapsulated, Cobalt Complex, Alcohol, Oxidation

### INTRODUCTION

Many of the present oxidizing agents used for oxidation of alcohols are hazardous and carcinogenic. In search of green and environmental friendly oxidation, we prepared surfactant encapsulated cobalt complex and used it for oxidation reactions as a catalyst using hydrogen peroxide as a green oxidizing agent

All the solutions required throughout the work were prepared in doubly distilled water, and standardized before starting the experiment. The cobalt complexes  $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$  and  $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$  were prepared<sup>1</sup> by the reported method. The solutions of  $\text{K}_5[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]$  and  $\text{K}_6[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]$  were standardized spectrophotometrically<sup>2</sup> ( at 388 nm for  $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$  and at 624 nm for  $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$  respectively ) using cystronic 119 UV-VIS spectrophotometer. All other chemicals were of

analytical reagent grade used without further purification. The organic solvents like acetonitrile and 1-4, Dioxon were of spectroscopy grade used without further purification.

### RESULTS AND DISCUSSION

The oxidation of aliphatic alcohols by hydrogen peroxide catalyzed by surfactant encapsulated keggin type 12-tungstocobaltate (II), prepared by using cationic surfactant and characterized by IR, and C, H, N, analysis, has been carried out in buffer as well as weak acid solution. The oxidation of aromatic and substituted aromatic alcohols by hydrogen peroxide catalyzed by surfactant encapsulated keggin type 12-tungstocobaltate (II) has been studied in 50% aqueous acetonitrile solution. Alcohol (2.2 mmol) and Hydrogen peroxide (10 mmol) were taken in a buffer of  $\text{pH} = 4$  and the catalyst  $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$  (0.4gm) was

**Address for Correspondence:** Babasaheb Bhosale, Assistant Professor, Chemistry Department, Rajaram College, Kolhapur- 416004, India; E-mail: babasahebbhosale23@gmail.com

**How to Cite this Article:** Babasaheb Bhosale. Surfactant encapsulated cobalt complex catalyst for environmental friendly oxidation of alcohols. World J Pharm Sci 2021; 9(3): 170-172.

This is an open access article distributed under the terms of the Creative Commons Attribution-NonCommercial-ShareAlike 4.0 International License, which allows adapt, share and build upon the work non-commercially, as long as the author is credited and the new creations are licensed under the identical terms.

added. In case of benzyl and substituted benzyl alcohols, 50-50% acetonitrile was used as solvent. The reaction mixture was stirred at 40°C for 5-10 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the resulting solution was extracted with dichloromethane. The combined organic layer was washed with a solution of NaHCO<sub>3</sub> and dried over MgSO<sub>4</sub>. The products of oxidation of primary alcohols are respective

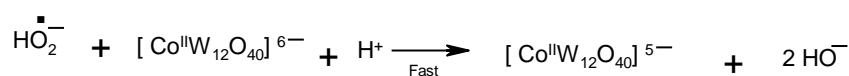
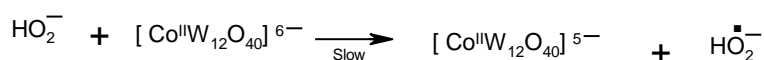
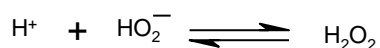
aldehydes and secondary alcohols are ketones. The organic solution was then filtered and concentrated to obtain the crude carbonyl compound. The melting points of the 2-4 DNP derivatives of the products obtained agree well with the literature values (Some examples are given in table 1) confirming the aldehydes or ketones as the oxidation products in the case of all the alcohols studied.

**Table- 1**

Alcohol	Melting Point of 2,4 DNP	
	Observed	Literature
Methyl alcohol	165	166
Ethyl alcohol	170	168
n-Propyl alcohol	154	155
Isopropyl alcohol	127	128
n-butyl alcohol	120	123
Isobutyl alcohol	185	187
Hexyl Alcohol	235	265
Benzyl alcohol	264	265
2-nitro-benzyl alcohol	300	302
4- nitro-benzyl alcohol	263	265
4- chloro-benzyl alcohol	231	233

To understand the mechanism of the reaction, various effects like effect of H<sup>+</sup> ion concentration, catalyst concentration and substitution concentration in case of benzyl alcohol is studied. With the help of kinetic results and activation

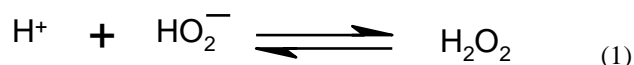
parameters obtained, the following mechanism is proposed for the reaction. The mechanism of oxidation of [Co<sup>II</sup>W<sub>12</sub>O<sub>40</sub>]<sup>6-</sup> by hydrogen peroxide was studied separately in our laboratory and found to be as represented in *Scheme 1*.



The kinetic data of both aliphatic and benzyl alcohols suggest that the initiation of the reaction occurs by interaction of the catalyst and oxidant generating oxidized form of the catalyst, 12-tungstocobaltate (III), which then oxidizes the substrate in a rate determining step. In order to

understand the nature of the active species of the reactants the effect of pH was studied. In case of aliphatic alcohols the time of reaction decreases with increase in pH of the solution which is due to prior protonation equilibria. Here unprotonated form the reactant, HO<sub>2</sub><sup>-</sup> is an active species. Since

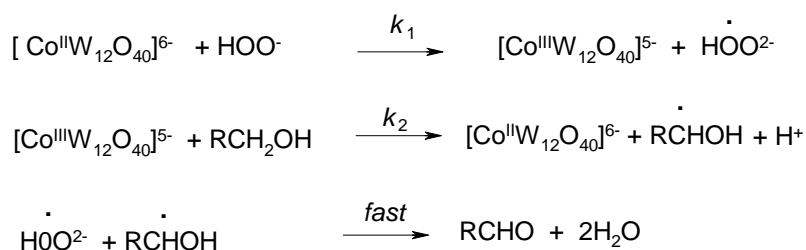
catalyst, 12- tungstocobaltate(II), do not undergo protonation as evidenced by spectroscopic studies<sup>3</sup> and alcohol also do not undergo protonation. It is protonation of the oxidant which affects the time of



Since the rate of reaction increase with increase in pH or decrease in  $[\text{H}^+]$ , the unprotonated  $\text{HO}_2^-$  is the active species in the present study. There is no significant variation in the reaction time even when the nature of alcohol is changed; it indicates that the initiation of the reaction is due to the interaction of oxidant and the catalyst,  $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ . The detailed study of the mechanism reaction between oxidant and the catalyst was found to involve two single-electron transfer steps (*Scheme 1*) with  $\text{HO}_2^-$  as the oxidant species. In the  $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$  catalyzed alcohol oxidation also, the reaction proceeds with the generation of  $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$  in the slow step which then abstracts an electron from

the reaction as the pH changes. The oxidant, Hydrogen peroxide, in aqueous solution exists as  $\text{HO}_2^-$  and gets protonated as shown in equilibrium 1.

the alcohol to produce an alcohol-free radical. The concentration of the catalyst used is of the order of  $4.0 \times 10^{-5}$  and that of the oxidant is very high, of the order  $3.0 \times 10^{-2}$ , making dependence of the overall reaction on oxidant concentration negligible. The effect of pH on the reaction also justifies earlier results considering  $\text{HO}_2^-$  as the active oxidant species. The concentration of the species increases with pH leading to the enhancement of the rate of the reaction. Therefore, the general mechanism of the  $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$  catalyzed oxidation of alcohols by hydrogen peroxide can be represented as in Scheme 2.



**Scheme 2**

The catalyst,  $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$  is recovered by simple filtration and it can be recycled number of times without losing its catalytic activity in measurable

percentage or more than 5%. This catalyst can be stored without taking so much precaution and undergo heterogeneous reaction.

## REFERENCES

- Judd, D. A.; Nettles, J. H.; Nevins, N.; Snyder, J. P.; liotta, D. C.; Ermolieff, J.; Hill, C. L. J Am. Chem. Soc., 2001, 5, 886-897.
- Shaoqin, L.; Dirk, G. K.; Helmuth, M.; Volkmer, D. Adv. Mater., 2002, 14, 225-228.
- A.L. Nolan, R.C. Burns, G.A. Lawrance. J. Chem. Soc. Dalton Trans., 1998, 3041-3048.
- Sadakane, M.; Steckhan, E. Chem. Rev., 1998, 219-237.
- Chester, A. W. J. Org. Chem., 1970,35, 1797-1800.
- Lambert, A.; Derouane, G. E.; Kozhevnikov1, I. V. J. Catalysis, 2002, 211,445-450.
- Hasure, A. M.; Gokavi, G.S. React. Kinet. Catal. Lett., 2003, 80, 59-65.
- Banerjee, P.; Saha, S. K.; Gupta, M. J. Chem. Soc. Perkin Trans.II 1988, 1781- 1785.
- Girgor'eva, A.; Chernaya, S. S.; Trusov, S. Russ. J. Appl. Chem. 2001, 74, 2021-2026.
- Anitha, N.; Rangappa, K. S.; Raj, K. M. Indian J. Chem. Sect B 1999, 38, 1046-1051.
- Firsova, Y. N.; Ryabov, A. D. Russ. Chem. Bl. 1997, 46, 1700-1706.
- Baker, L. C.; McCutcheon, T. P. J Am Chem Soc.,1956, 78, 4503-4510.
- Rasmussen, P.G.; Brubaker, C.H. Inorg Chem., 1964, 3, 977-980.
- Goyal, B.; Prakash, A.; Mehrotra, R. N. Indian J Chem., 1999, 38 A, 541-546.
- Reddy, C. S.; Kumar, T. V. Indian J Chem., 1995, 34 A, 615.
- Sengupta, K. K.; Sengupta, S.; Basu, S. N. Carbohydrate Res. 1979, 75-84.