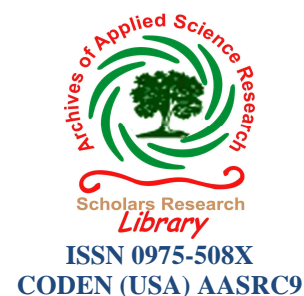




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Kinetics and mechanism of oxidation of benzyl alcohol by Oxone catalyzed by Keggin type 12-tungstocobaltate(II)

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ABSTRACT

The oxidation of benzyl alcohol [B.A.] by Oxone catalyzed by Keggin type $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ has been studied in the temperature range 303-318 K. The reaction proceeds by the oxidation of $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ to $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ by Oxone, which then oxidizes benzyl alcohol [B.A.] in a rate determining step generating alcohol free radical. The reaction was found to be inhibited by increase in the $[\text{H}^+]$ due to protonation equilibria of HSO_5^{2-} which is the active species in rate determining step. Decreasing the relative permittivity of the medium increases the rate of the reaction which is attributed to the formation of an outer-sphere complex between the reactants. The activation parameters were also determined and the values support the proposed mechanism.

Key Words: kinetics, mechanism, Keggin type 12-tungstocobaltate(II), benzyl alcohol, oxidation

INTRODUCTION

Transition metal substituted heteropolyoxometalates¹ are very good candidates for homogeneous outer-sphere electron transfer processes. These are also used extensively as model systems for fundamental research providing unique opportunities for mechanistic studies on molecular level. They exhibit diverse chemical and electrochemical properties, which makes them attractive for catalytic¹⁻⁴ and electrocatalytic⁵ applications. These attractive features include stability under highly oxidizing conditions, availability of a

variety of transition metal ions which can be incorporated into heteropolymetalate structure, reversible oxidation and reduction of the incorporated metal ion and the ability to modify the formal redox potentials. Peroxo compounds like peroxomonosulphate, perborate and organic peroxides are used for the oxidation of organic compounds⁶. The active ingredient of potassium monopersulphate, commonly known as oxone is KHSO_5 . But under ordinary conditions oxidation by this reagent is slow and requires various metal ions as catalysts⁷. The preliminary step of catalyzed path is oxidation of metal ion to its higher oxidation state which then oxidizes the substrate. Therefore, in continuation of our earlier work^{3,4} on the catalysis by polyoxometalates, herein we report the 12-tungstocobaltate(II) catalyzed oxidation of benzyl alcohol by oxone.

MATERIALS AND METHODS

Reagent grade chemicals and doubly distilled water were used throughout. The cobalt complex $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ was prepared by literature method^{8,9} and standardized spectrophotometrically¹⁰ at 624 nm using an Elico SL 159 UV-vis spectrophotometer. The solutions of oxone (Lancaster) were freshly prepared and standardized iodometrically. The solutions of benzyl alcohol (Merck) were prepared by dissolving the required quantities in aqueous acetonitrile. The reactions were studied under pseudo first-order conditions by keeping large excess of benzyl alcohol over oxone and the unreacted oxidant was determined iodometrically. The rate constants were obtained from linear ($r > 0.966$)

log[oxone] against time plots. The rate constants were reproducible to within $\pm 5\%$ up to 75% completion of the reaction.

RESULTS AND DISCUSSION

The stoichiometry for the reaction between oxone and benzyl alcohol in presence of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ was studied by keeping the concentration of benzyl alcohol ($4.0 \times 10^{-3} \text{ mol dm}^{-3}$) constant and varying the oxone concentration from 0.5 to $1.5 \times 10^{-2} \text{ mol dm}^{-3}$. The reactants were mixed and the concentration of oxone was determined iodometrically after 24 h. The stoichiometry was found to be 2 moles of benzyl alcohol per mole of oxone. The progress of the reaction was followed by TLC. The benzaldehyde was found as the product of oxidation and was identified by its 2,4-DNP derivative (m.p. 235°C , lit. 237°C).

Effect of reactant concentration:

The effect of oxone, oxidant, was studied between the concentration range of 0.5×10^{-2} to $5.0 \times 10^{-2} \text{ mol dm}^{-3}$ keeping alcohol concentration constant at 0.2 mol dm^{-3} and $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ at 4×10^{-4} . The pseudo-first order rate constants remain unchanged. The effect of alcohol concentration was studied between 5.0×10^{-2} to $5.0 \times 10^{-1} \text{ mol dm}^{-3}$ by keeping concentration of oxone constant at $2.0 \times 10^{-2} \text{ mol dm}^{-3}$ and catalyst concentration at $4.0 \times 10^{-4} \text{ mol dm}^{-3}$. The reaction was found to be independent of alcohol concentration.

Effect of catalyst concentration:

The effect of catalyst was studied by varying catalyst concentration between 1.0×10^{-4} to $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ keeping concentrations of oxone at $2.0 \times 10^{-2} \text{ mol dm}^{-3}$ and alcohol concentration at 0.2 mol dm^{-3} . The pseudo-first-order rate constants increase with increase in concentration of the catalyst. The plots of pseudo-first-order rate constant against concentration of catalyst were found to be almost linear without any intercept showing first order dependence of reaction on catalyst concentration.

Effect of Hydrogen ion concentration:

In order to understand the effect of hydrogen ion concentration on benzyl alcohol oxidation, the sulphuric acid concentration was varied from 0.02 to 0.2 mol dm^{-3} . The order in hydrogen ion concentration was found to be negative and reaction rate was found to be retarded by the H^+ ion concentration increases.

Effect of ionic strength and solvent polarity:

The effect of ionic strength was studied using Na_2SO_4 and it was found that there was no effect of ionic strength, hence no attempt was made to keep ionic strength constant during the course of study. The effect of solvent polarity was studied by varying percentage of acetonitrile from 45% to 65% (v/v) by keeping concentration of oxone at $2.0 \times 10^{-2} \text{ mol dm}^{-3}$, benzyl alcohol at 0.2 mol dm^{-3} and catalyst concentration at $4.0 \times 10^{-4} \text{ mol dm}^{-3}$. It was found that the decrease in the dielectric constant of the medium increases the rate of the reaction.

Test for polymerization:

The intervention of free radical was examined by adding a known quantity of acrylonitrile to the reaction mixture. The reaction mixture on dilution with methanol forms precipitate showing intervention of free radical in the reaction.

Effect of Temperature:

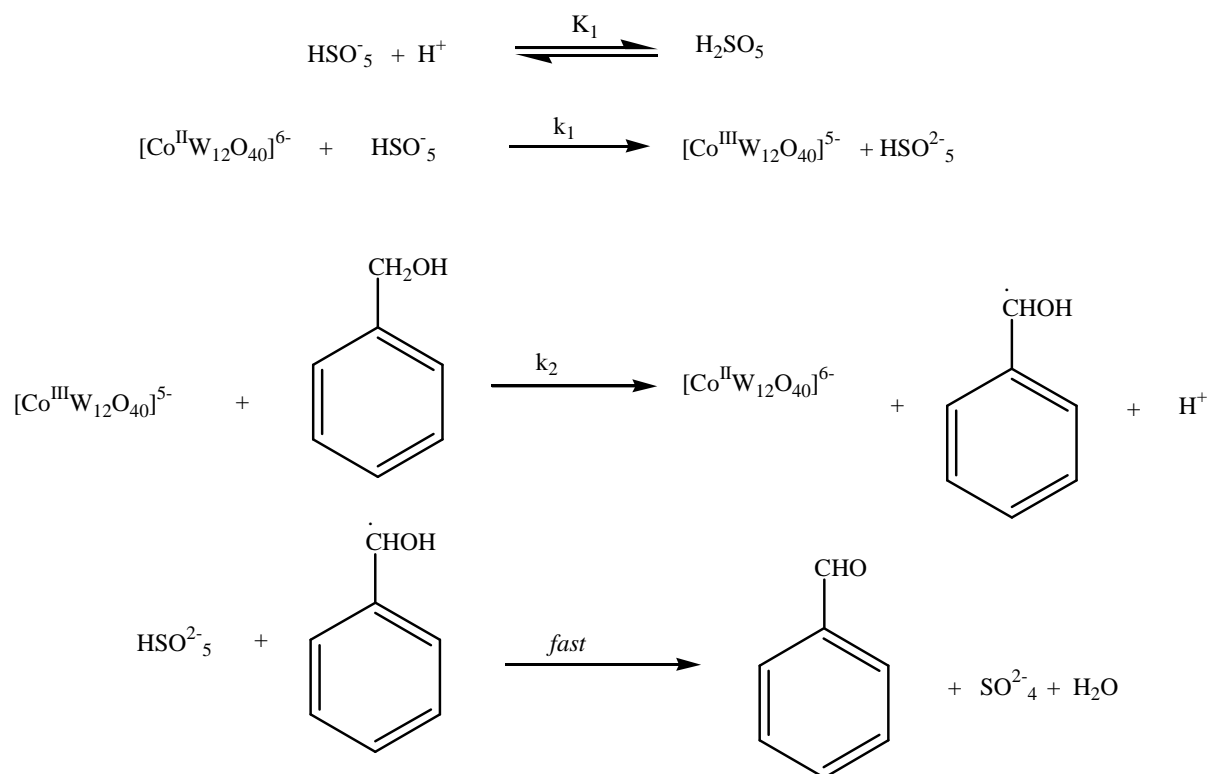
The effect of temperature was studied at 303, 308, 313 and 318K , keeping concentration of alcohol at 0.2 mol dm^{-3} , oxone at $2 \times 10^{-2} \text{ mol dm}^{-3}$ and catalyst at 4.0×10^{-4} . The activation parameters for $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ catalyzed benzyl alcohol oxidation by oxone were calculated and found as $\Delta H^{\ddagger} = 78.28 + 6 \text{ kJ mol}^{-1}$, $\Delta G^{\ddagger} = 75.7 + 5 \text{ kJ mol}^{-1}$ and $\Delta S^{\ddagger} = -116.39 + 3 \text{ J K}^{-1} \text{ mol}^{-1}$.

Uncatalyzed oxidation of the benzyl alcohol by oxone did not occur under the experimental conditions. Therefore, there was no contribution of the uncatalyzed reaction to the overall rate constant of the reaction. The order in oxidant and substrate were found to be unity each. The pseudo-first-order rate constants also increase linearly as the catalyst concentration increases showing first order dependence on the catalyst concentration also. The order in catalyst was also found to be unity as determined by log (pseudo-first-order rate constants) against log [catalyst] plots.

Since catalyst, 12-tungstocobaltate(II), do not undergo protonation as evidenced by spectroscopic studies⁹ and alcohol also do not undergo protonation, it is protonation of the oxidant which affects the rate of the reaction. Therefore involvement of a prior protonation equilibria is expected with unprotonated form of the reactant as the active specie. The oxidant, oxone, in aqueous solution exists as HSO_5^- and gets protonated.

Since the rate of reaction does not depend upon the concentration of either oxone or benzyl alcohol, the kinetic data 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 abstracts an electron from the benzyl alcohol to produce an benzyl alcohol-free radical and this free radical undergoes fast reaction with HSO_5^{2-} giving the product of reaction. The concentration of the catalyst used is of the order of 4.0×10^{-4} and that of the oxidant is very high, of the order 2.0×10^{-2} , making dependence of the overall reaction on oxidant concentration negligible. The effect of H^+ ion on the reaction also justifies earlier results^{3,4} considering HSO_5^- as the active oxidant species.

Therefore, the general mechanism of the $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ catalyzed oxidation of alcohols by oxone can be represented as,



According to scheme 1 the rate of reaction is given by,

$$\text{Rate} = k_2 [\text{B.A.}] [\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-} \quad (1)$$

Applying steady state principle to $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ we get,

$$[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-} = \frac{k_1 [\text{HSO}_5^-] [\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}}{K_2 [\text{B.A.}]} \quad (2)$$

Substituting equation (2) in (1), we get,

$$\begin{aligned} \text{rate} &= \frac{k_1 k_2 [\text{B.A.}] [\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-} [\text{HSO}_5^-]}{K_2 [\text{B.A.}]} \\ &= k_1 [\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-} [\text{HSO}_5^-] \end{aligned} \quad (3)$$

From equilibrium (1), the total concentration of oxidant would be

$$\begin{aligned} [\text{HSO}_5^-]_{\text{Total}} &= [\text{HSO}_5^-]_{\text{free}} + [\text{H}_2\text{SO}_5] \\ &= [\text{HSO}_5^-]_{\text{free}} + k_1 [\text{H}^+] [\text{HSO}_5^-]_{\text{free}} \\ &= [\text{HSO}_5^-]_{\text{free}} (1 + k_1 [\text{H}^+]) \\ \text{or } [\text{HSO}_5^-]_{\text{free}} &= \frac{[\text{HSO}_5^-]_{\text{Total}}}{1 + k_1 [\text{H}^+]} \end{aligned} \quad (4)$$

Substituting the value of $[\text{HSO}_5^-]_{\text{free}}$ in the rate equation (4), we get,

$$\text{Rate} = \frac{k_1 [\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-} [\text{HSO}_5^-]_{\text{Total}}}{1+k_1 [\text{H}^+]} \tag{5}$$

Rearranging equation (6) for pseudo-first-order rate constant k_{obs} , we have

$$k_{\text{obs}} = \text{rate}/[\text{HSO}_5^-]_{\text{Total}} = K_1 [\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-} / (1 + K_1 [\text{H}^+]) \tag{6}$$

The rate law 6 derived according to the above mechanism explains all the results obtained. The rate law 6 is independent of oxidant concentration and inversely dependent on the concentration of hydrogen ions. The catalyst, $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ used in the present study is converted into its oxidized form $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ and is an outer sphere reagent. There was no effect of ionic strength on the reaction. The decrease in the dielectric constant increases the rate of the reaction since the transition state is less solvated and also large in size it will be stabilized in the medium of higher permittivity¹¹. The value of entropy of activation also supports formation of such a transition state.

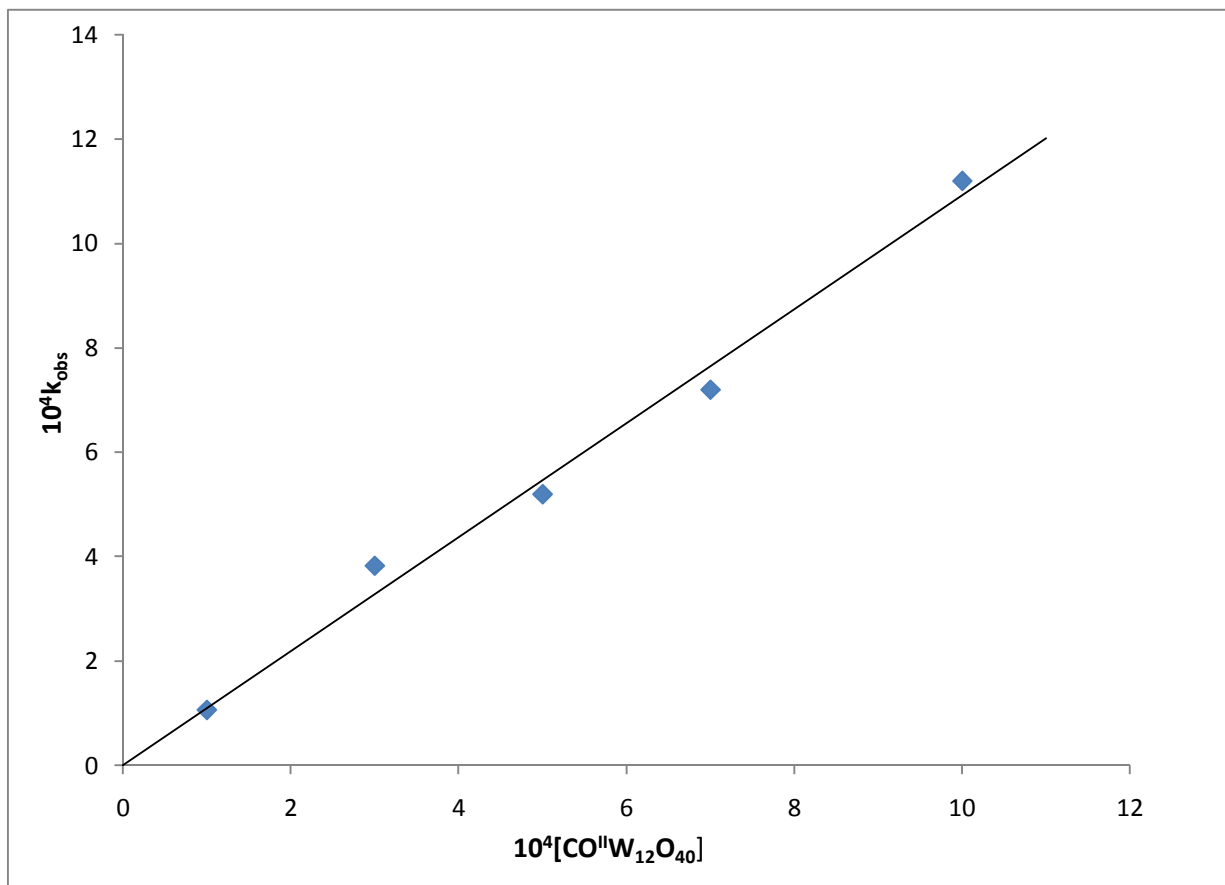


Table 1: Effect of reactants and catalyst concentration
 Benzyl alcohol = 0.2 mol dm⁻³ [Co^{II}W₁₂O₄₀]⁶⁻ = 4.0 × 10⁻⁴ mol dm⁻³
 oxone = 2.0 × 10⁻² mol dm⁻³ Temp. = 303K

[B.A] mol dm ⁻³	10 ² [oxone] mol dm ⁻³	10 ⁴ [Co ^{II} W ₁₂ O ₄₀] ⁶⁻ mol dm ⁻³	10 ⁴ sec ⁻¹
0.5	0.2	4.0	4.6
0.1	0.2	4.0	4.6
0.2	0.2	4.0	4.5
0.3	0.2	4.0	4.4
0.5	0.2	4.0	4.4
0.5	0.5	4.0	3.5
0.5	1.0	4.0	3.6
0.5	2.0	4.0	3.4
0.5	3.0	4.0	3.5
0.5	4.0	4.0	3.6
0.2	0.2	1.0	1.1
0.2	0.2	3.0	3.7
0.2	0.2	5.0	5.2
0.2	0.2	7.0	7.2
0.2	0.2	10.0	11.2

Figure 1 Effect of Catalyst (Conditions as in table 2)

Table 2: Effect of temperature and Thermodynamic Parameters on Benzyl alcohol oxidation

Benzyl alcohol = 0.2 mol dm^{-3} $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-} = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$
 oxone = $2.0 \times 10^{-2} \text{ mol dm}^{-3}$ Temp. = 303K

Temperature	$k \times 10^4 \text{ sec}^{-1}$
303	1.9
308	3.63
313	4.57
318	8.51

Thermodynamic parameters	E_a k J mole ⁻¹	ΔH k J mole ⁻¹	ΔS J mole ⁻¹	ΔG K J mole ⁻¹
Value	78.28	75.7	-116.39	73.44

CONCLUSION

The reaction between benzyl alcohol and oxone proceeds by free radical mechanism. The active species of oxone was found to be HSO_5^{2-} . The proposed mechanism is also supported by product analysis and kinetic study.

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