Kinetics and mechanism of oxidation of aliphatic alcohols by oxone catalyzed by Keggin type 12-tungstocobaltate(II)

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The oxidation of various aliphatic alcohols by oxone catalyzed by Keggin type $[\text{Co}^{III}\text{W}_{12}\text{O}_{40}]^{6-}$ has been studied in a buffer medium of pH=4. The reaction proceeds by the oxidation of $[\text{Co}^{IV}\text{W}_{12}\text{O}_{40}]^{6-}$ to $[\text{Co}^{V}\text{W}_{12}\text{O}_{40}]^{5-}$ by oxone which then oxidizes the alcohol in a rate determining step generating alcohol free radical. The reaction is accelerated by increase in the pH of the solution due to the protonation equilibria of the oxidant. The reaction between oxone and $[\text{Co}^{II}\text{W}_{12}\text{O}_{40}]^{6-}$ has also been studied and is found to proceed in two one-electron steps, involving formation of $\text{HSO}_5^-$ free radical in a slow first step followed by its reaction with reductant in a fast step. The reaction rate is inhibited by the $[\text{H}^+]$ due to protonation equilibria of $\text{HSO}_5^-$ which is the active species. 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 determined for both the reactions support the proposed mechanisms.

Peroxo compounds like peroxydisulphate, perborate, peroxomonosulphate and organic peroxides are economically and environmentally preferred for oxidation of organic compounds than conventional metal ion oxidants. But under ordinary conditions, oxidation by these reagents is slow and requires various metal ions as catalysts. The preliminary step of a catalyzed path is oxidation of the metal ion to its higher oxidation state which then effects the oxidation of the substrate. Such catalysis is more feasible if the redox potential of the metal ion is about 1.0 V. Therefore, the metal ions having redox potential higher than 1.0 V can be reduced considerably by using different complexing agents. Transition metal substituted heteropolymetolates exhibit such diverse chemical and electrochemical properties which makes them attractive for catalytic and electrocatalytic applications. These attributes include stability under highly oxidizing conditions, availability of a variety of transition metal ions which can be incorporated into heteropolymetolate structure, reversible oxidation and reduction of the incorporated metal ion and the ability to modify the formal redox potentials. It has long been known that tungsten and molybdenum compounds and their polyoxometalates are efficient catalysts for oxidations by peroxo compounds. Therefore, understanding and utilization of polyoxometalates in synthetic organic chemistry is of importance. In continuation of our earlier work involving polyoxometalates, herein we report the kinetics of oxidation of aliphatic alcohols by oxone in presence of Keggin type 12-tungstocobaltate(II).

Materials and Methods
Reagent grade chemicals and doubly distilled H$_2$O were used throughout. The cobalt complexes $[\text{Co}^{III}\text{W}_{12}\text{O}_{40}]^{6-}$ and $[\text{Co}^{II}\text{W}_{12}\text{O}_{40}]^{6-}$ were prepared by literature method and standardized spectrophotometrically (at 388 nm for $[\text{Co}^{III}\text{W}_{12}\text{O}_{40}]^{6-}$ and at 624 nm for $[\text{Co}^{II}\text{W}_{12}\text{O}_{40}]^{6-}$ respectively) using an Elico SL 159 UV-vis spectrophotometer. The solutions of oxone(Lancaster) were freshly prepared and standardised iodometrically. The ionic strength was maintained using Na$_2$SO$_4$ and in order to vary hydrogen ion concentration, H$_2$SO$_4$ (BDH) was used. The buffer solutions were prepared by using sodium acetate-acetic acid solutions. The solutions of alcohols (Merck) were prepared by dissolving the required quantities in water.

Kinetic procedure
The reactions were studied under pseudo-first-order conditions keeping large excess of alcohol over oxone and the unreacted oxidant was determined iodimetrically. The pseudo-first-order rate constants were obtained from linear $(r>0.956)$ log [oxone] against time plots. The reaction between 12-tungstocobaltate(II) and oxone was followed by
measuring the absorbance of $[\text{Co}^{II}\text{W}_{12}\text{O}_{40}]^{6-}$ at 624 nm under pseudo-first-order condition keeping large excess of oxidant over the reductant. Beer's law was tested earlier for $[\text{Co}^{II}\text{W}_{12}\text{O}_{40}]^{6-}$ between the concentration of $1.0 \times 10^{-2}$ to $5.0 \times 10^{-3}$ mol dm$^{-3}$ ($e_{624} = 180 \pm 2$ dm$^{-1}$ cm$^{-1}$) under the experimental conditions. The pseudo-first-order rate constants ($r > 0.966$) were determined from linear log $[\text{Co}^{II}\text{W}_{12}\text{O}_{40}]^{6-}$ versus time plots and the rate constants were reproducible within $\pm 6\%$.

Results and Discussion

The alcohol (2.2 mmol) and oxone (1 mmol) were taken in a buffer of $pH=4$ and the catalyst $[\text{Co}^{II}\text{W}_{12}\text{O}_{40}]^{6-}$ (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 and GC. After completion of the reaction, the resulting solution was extracted with dichloromethane. The combined organic layer was washed with a solution of NaHCO$_3$ and dried over MgSO$_4$. The organic solution was then filtered and concentrated to obtain the crude carbonyl compound. The melting points of the 2,4 DNP derivatives agree well with the literature values in the case of all alcohols studied. The stoichiometry for the reaction between $[\text{Co}^{II}\text{W}_{12}\text{O}_{40}]^{6-}$ and oxone was studied by keeping the concentration of $[\text{Co}^{II}\text{W}_{12}\text{O}_{40}]^{6-}$ ($1.0 \times 10^{-2}$ mol dm$^{-3}$) constant and varying the oxone concentration from 0.5 to $3.0 \times 10^{-2}$ mol dm$^{-3}$ in 0.2 mol dm$^{-3}$ H$_2$SO$_4$. The reactants were mixed and the concentration of $[\text{Co}^{II}\text{W}_{12}\text{O}_{40}]^{6-}$ was determined spectrophotometrically after 24 h at 624 nm. The stoichiometry was found to be 2 moles of $[\text{Co}^{II}\text{W}_{12}\text{O}_{40}]^{6-}$ per mole of oxone.

Uncatalysed oxidation of the alcohols by oxone did not occur under the experimental conditions. Therefore, there was no contribution of the uncatalysed reaction to the overall rate constant of the reaction. There was no effect of oxone and alcohols on the pseudo-first-order rate constant of the reaction (Tables 1 & 2), whereas the pseudo-first-order rate constants increased with increase in concentration of the catalyst (Fig. 1). For reaction between $[\text{Co}^{II}\text{W}_{12}\text{O}_{40}]^{6-}$ and oxone, the pseudo-first order plots

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**Table 1**—Effect of alcohol on oxidation of aliphatic alcohols by oxone catalyzed by 12-tungstocobaltate(II).

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<th>[Alcohol] (mol dm$^{-3}$)</th>
<th>MeOH</th>
<th>EtOH</th>
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<th>i-PrOH</th>
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<th>i-BuOH</th>
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<td>1.50</td>
<td>1.80</td>
<td>1.70</td>
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**Table 2**—Effect of oxone on oxidation of aliphatic alcohols by oxone catalyzed by 12-tungstocobaltate(II).

<table>
<thead>
<tr>
<th>[Oxone] (mol dm$^{-3}$)</th>
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<th>i-PrOH</th>
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<th>i-BuOH</th>
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were found to be linear and the pseudo-first order rate constants were found to be constant as [CoIII(W12O40)]6 varies (Table 3) between the concentration range of 3.35 \times 10^{-4} and 3.35 \times 10^{-3} mol dm^{-3} indicating the order in reactant to be unity. Pseudo-first order rate constants were found to increase as the concentration of oxidant increased from 5.0 \times 10^{-3} to 6.0 \times 10^{-2} mol dm^{-3} (Table 3). The order in oxone was found to be unity as determined by the log-log plot of \(k_{obs}\) against [oxone]. There was no effect of the added products \(SO_4^{2-}\) and [CoIII(W12O40)]6 on the reaction.

Since the [CoIII(W12O40)]6 catalysed oxidation of alcohols by oxone was found to be retarded by hydrogen ion concentration and oxone itself produces proton in solution, the study was carried out in acetic acid - sodium acetate buffer medium. The effect of pH was studied between 3.3 and 4.6 and the reaction was found to be accelerated by increase in the pH (Fig. 2). In the case of reaction between [CoIII(W12O40)]6 and oxone, the effect of hydrogen ions was studied in order to understand the nature of reactant species present in the solution. The concentration of [H+] was varied between 0.02 and 0.2 mol dm^{-3} at an ionic strength of 0.3 mol dm^{-3} (Table 3). The increase in hydrogen ion concentration decreases the rate of reaction and the order in hydrogen ion concentration was found to be -0.6 as determined from the plot of log \(k_{obs}\) versus log [H+]. The [H+] was calculated using the dissociation constants of sulphuric acid.

The effects of the ionic strength and solvent polarity were studied for the reaction between [CoIII(W12O40)]6 and oxone only as the oxidation of alcohols were studied in a buffer medium. The effect of ionic strength, solvent polarity and temperature was studied keeping [CoIII(W12O40)]6, [oxone], and sulphuric acid constant at 3.35 \times 10^{-4}, 1.0 \times 10^{-3} and 0.2 mol dm^{-3} respectively, while NaClO4 and acetic acid were used to vary the ionic strength and solvent polarity respectively. The reaction rate increases as the ionic strength decreases (from 0.2 to 0.5 mol dm^{-3}) and the percentage of acetic acid increases (from 0 to 60 vol. %). The relative permittivities of the reaction mixtures were computed from the values of the pure solvents, and the plot of log \(k_{obs}\) versus 1/\(D\) was found to be linear with a positive slope.

The effect of temperature was studied at 25, 30, 35 and 40°C and the activation parameters for [CoIII(W12O40)]6 catalysed alcohol oxidations by oxone were calculated (Table 4). The effect of temperature for the [CoIII(W12O40)]6 oxidation by oxone was studied at 25, 30, 35 and 40°C and the rate constants obtained were 3.5 \times 10^{-5}, 5.4 \times 10^{-5}, 7.7 \times 10^{-5} and 10.7 \times 10^{-5} s^{-1} respectively. The activation parameters \(\Delta H^\#\) and \(\Delta S^\#\) were found to be 43.8 \pm 3 kJ mol^{-1} and -177.2 \pm 4 JK^{-1} mol^{-1} respectively.

**Mechanism of reaction between [CoIII(W12O40)]6 and oxone**

The kinetic data obtained for [CoIII(W12O40)]6 catalyzed oxidation of alcohols by oxone indicate that
the reaction is independent of concentration of alcohol and oxone. Therefore, the catalyzed path is initiated by the reaction between \([\text{Co}^{III}\text{W}_{12}\text{O}_{40}]^{6-}\) and oxone generating \([\text{Co}^{II}\text{W}_{12}\text{O}_{40}]^{5-}\), which then oxidizes the alcohol. Therefore, the reaction between \([\text{Co}^{II}\text{W}_{12}\text{O}_{40}]^{6-}\) and oxone was studied in detail in order to understand the mechanism and the reactive species of the reactants.

Oxidation of one-electron reductants by oxone, peroxomonomosulphate, involves formation of the sulphate\(^{12,13}\) free radical. In the present study, the oxidation of the Co(II) complex, \([\text{Co}^{III}\text{W}_{12}\text{O}_{40}]^{6-}\), a well-known outer-sphere reductant, proceeds in two single electron transfer steps. The first step would be a slow electron transfer from reductant to the oxidant with the formation of HSO\(_3^\cdot\) free radical as evidenced by first order dependence of the reaction on both the reactants. The plot of \(k_{obs}\) against [oxone] was linear and the second order rate constants \(k_{obs}/[\text{oxone}]\) were also found to be fairly constant indicating that there is no formation of a precursor complex between the reactants. Since, there was no effect of both the products on the reaction, no reversible equilibrium is involved in the reaction. Further, HSO\(_3^\cdot\) free radical formed in the slow first step reacts rapidly with another reductant molecule. The negative dependence of the reaction on the concentration of hydrogen ions may be understood to be due to the protonation equilibrium of oxone only, as \([\text{Co}^{III}\text{W}_{12}\text{O}_{40}]^{6-}\) does not involve\(^{11}\) any such equilibrium. In acidic solutions, first dissociation constant of H\(_2\)SO\(_4\) was taken as equal to that of sulphuric acid while the second dissociation\(^{14}\) has a very low value. Under the conditions of the present study, the predominant species of the oxidant would be HSO\(_3^\cdot\) and its further dissociation occurs to a negligible extent. Considering the HSO\(_3^\cdot\) as the active species the decrease in the rate of the reaction as the [H\(^+\)] increases can be explained due to its protonation. The mechanism to account for the results obtained above can be represented as in Scheme 1 with corresponding rate law by Eq. 1 and the expression for the pseudo-first order rate constant by Eq. 2.

\[
\text{HSO}_3^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{SO}_4
\]

\[\begin{align*}
[\text{Co}^{II}\text{W}_{12}\text{O}_{40}]^{6-} + \text{HSO}_3^- & \rightarrow [\text{Co}^{II}\text{W}_{12}\text{O}_{40}]^{5-} + \text{HSO}_4^- \\
[\text{Co}^{II}\text{W}_{12}\text{O}_{40}]^{5-} + \text{HSO}_4^- & \rightarrow [\text{Co}^{II}\text{W}_{12}\text{O}_{40}]^{4-} + \text{SO}_4^{2-} + \text{H}_2\text{O}
\end{align*}\]

Scheme 1

Rate = \(k_1 [\text{H}_2\text{SO}_4] [\text{Co}^{III}\text{W}_{12}\text{O}_{40}]^{6-}\) \(\quad \ldots (1)\)

\(k_{obs} = k_1 K_1 [\text{H}_2\text{SO}_4] / (K_1 + [\text{H}^+])\) \(\quad \ldots (2)\)

Equation 2 was derived by applying Michaelis-Menten treatment to the dissociation of H\(_2\)SO\(_4\) and verified by plotting [H\(_2\)SO\(_4\)]/\(k_{obs}\) against [H\(^+\)] which was found to be linear with an intercept. From the slope and intercept of the plot, the values of \(k_1\) and \(K_1\) were calculated as \(3.3 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\) and \(2.5 \times 10^{-2} \text{ mol} \text{ dm}^{-3}\) respectively. These values were used to calculate the pseudo-first order rate constants and there is good agreement between the observed and the calculated values (Table 3).

The effect of ionic strength may be due to the prior equilibrium between the charged ions of the opposite kind as shown in Scheme 1. Increase in the acetic acid content in the reaction medium leads to an increase in the reaction rate and the plot of log \(k_i\) versus \(1/D\), where \(D\) is the relative permittivity, is linear with a positive slope. Formation of an inner-sphere complex between the central Co(II) ion and the oxidant species is unlikely because it is completely shielded by a shell of W\(_6\) octahedra. Therefore, formation of an outer-sphere complex by the replacement of one of

<table>
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\(Ea\) kJ mol\(^{-1}\)
- 67.7 \pm 3
- 71.8 \pm 4

\(\Delta H^\circ\) kJ mol\(^{-1}\)
- 61.3 \pm 3
- 65.1 \pm 4

\(\Delta S^\circ\) J mol\(^{-1}\)K\(^{-1}\)
- 80.8 \pm 4
- 67.6 \pm 4

Table 4—Effect of temperature on oxidation of aliphatic alcohols by oxone catalyzed by 12-tungstocobaltate(II).

\([\text{Alcohol}] = 0.3 \text{ mol dm}^{-3}, [\text{Oxone}] = 3.0 \times 10^{-2} \text{ mol dm}^{-3}, [\text{Co}^{III}\text{W}_{12}\text{O}_{40}]^{6-} = 4.0 \times 10^{-5} \text{ mol dm}^{-3}, \text{pH} = 4.0\)
the water molecules of hydration is the more probable transition state. Since the probable transition state is less solvated and is also larger in size it will be more stabilized in the medium of higher relative permittivity as observed. Decrease in the value of entropy of activation also supports formation of such a transition state.

Mechanism of $[\text{Co}^{II} \text{W}_{12} \text{O}_{40}]^{6-}$ catalyzed oxidation of alcohols by oxone

Since the rate of the reaction does not depend upon the concentration of either oxone or alcohol and there is no significant variation in the values of pseudo-first order rate constants even when the nature of alcohol is changed. This indicates that the initiation of the reaction is due to the interaction of oxidant and the catalyst, $[\text{Co}^{II} \text{W}_{12} \text{O}_{40}]^{6-}$. The detailed study of the mechanism reaction between oxidant and the catalyst was found to involve two single-electron transfer steps (Scheme 1) with HSO$_5^-$ as the oxidant species. In the $[\text{Co}^{II} \text{W}_{12} \text{O}_{40}]^{6-}$ catalyzed alcohol oxidation also, the reaction proceeds with the generation of $[\text{Co}^{III} \text{W}_{12} \text{O}_{40}]^{5-}$ in the slow step which then abstracts an electron from 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 HSO$_5^-$ 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 $[\text{Co}^{III} \text{W}_{12} \text{O}_{40}]^{5-}$ catalyzed oxidation of alcohols by oxone can be represented as in Scheme 2 and the corresponding rate law as in Eq. 3. Since concentration of oxidant is very high, in comparison

$$[\text{Co}^{II} \text{W}_{12} \text{O}_{40}]^{6-} + \text{HSO}_5^- \xrightarrow{k_1} [\text{Co}^{II} \text{W}_{12} \text{O}_{40}]^{5-} + \text{HSO}_4^-$$

$$[\text{Co}^{III} \text{W}_{12} \text{O}_{40}]^{5-} + \text{RCH}_2\text{OH} \xrightarrow{k_2} [\text{Co}^{III} \text{W}_{12} \text{O}_{40}]^{5-} + \text{RCHO} + \text{SO}_4^- + \text{H}_2\text{O}$$

**Scheme 2**

$$k_{obs} = k_2 K_1 [\text{Co}^{III} \text{W}_{12} \text{O}_{40}]^{5-} / [\text{HSO}_5^-][K_1 + [\text{H}^+]] \quad \ldots (3)$$

$$k_{obs} = k_2 K_1 [\text{Co}^{III} \text{W}_{12} \text{O}_{40}]^{5-}/(K_1 + [\text{H}^+]) \quad \ldots (4)$$

with catalyst, Eq. 3 can be simplified to Eq. 4. The rate law 4 derived according to the mechanism of Scheme 2 explains all the results obtained. The rate law 4 is independent of oxidant and alcohol concentration and inversely dependent on the concentration of hydrogen ions. The catalyst, $[\text{Co}^{II} \text{W}_{12} \text{O}_{40}]^{6-}$ used in the present study is converted into its oxidized form $[\text{Co}^{III} \text{W}_{12} \text{O}_{40}]^{5-}$ and is an outer sphere reagent. Therefore, irrespective of the nature of alcohol the interaction between alcohol group and the catalyst in the transition state formed would be the same, making the rate of the reaction independent of nature of the alcohol. The Exner’s plot of log $k_{obs}$ (298 K) against log $k_{obs}(313 K)$ was linear ($r > 0.965$) and isokinetic plot of $\Delta H^\circ$ against $\Delta S^\circ$ was also found to be linear ($r > 0.987$) with isokinetic temperature of 264 K supporting the above conclusions. The probable transition state for the oxidized catalyst form and alcohol may be as given below.

$$\text{OH} \quad \begin{array}{c}
\text{[R}_1\text{R}_2\text{C} && \\ \\
\text{H} && \\ \\
\text{O} \end{array} \quad \text{WCo}^{III} \quad \text{f}^-$

Acknowledgement

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References