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Mechanistic Study of Ruthenium (III) Catalyzed Oxidation of 4-methoxy benzyl alcohol by a Copper (III) periodate Complex in Aqueous alkaline medium

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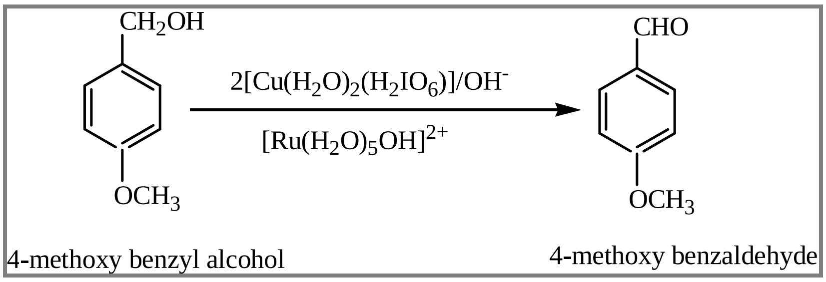
ABSTRACT

Ruthenium(III) chloride catalyzed oxidation of 4-methoxy benzyl alcohol by Copper(III) complex in aqueous alkaline medium at constant ionic strength of the medium was studied. Rate showed direct proportionality in oxidant, organic substrate, catalyst and hydroxyl ion concentrations while periodate ions, added externally, retard the reaction velocity. Increase in ionic strength of the medium has a positive effect on the rate. Thermodynamic parameters like energy of activation, free energy of activation, entropy of activation values were calculated. Oxidation products were identified with the help of IR and NMR spectral studies and on the basis of the experimental findings a probable mechanism was proposed which explains all the experimental findings. Comparatively simple, economical, less tedious and environmentally acceptable methodologies used in copper (III) oxidations have opened new avenues for the growth of oxidation chemistry.

Graphical Abstract



Keywords: Ruthenium(III) chloride, Alkaline Diperiodatocuprate(III), Catalysis.

INTRODUCTION

Apart from +2, copper can be found in 0, +1 and +3 oxidation states allowing it to act through one-electron or two-electron processes. Therefore, both radical and two-electro 4 methoxy benzaldehyde n bond-forming pathways via organometallic intermediates can occur. Further various oxidation states of copper associate well with a number of functional groups via Lewis acid interactions or π-coordination. These features confer a remarkably broad range of activities allowing copper to catalyze the oxidation and oxidative union of many substrates [1]. Tripositive copper was first reported in 1844 and history up to 1925 of compounds of Cu(III), has been reviewed by Vrtis [2]. Malaprade [3] succeeded in isolating sparingly soluble sodium diperiodatocuprate(III) ($Na_7[Cu(I0_6)_2]$). The works of Vrtis [2], Malaprade [3], and Malatesta [4] have established beyond doubt that Cu(II) may be oxidized by potassium persulfate to Cu(III) which is stabilized by coordination with a suitable anion like periodate or tellurate. In the recent past [5] some relatively stable copper(III) complexes have been prepared, viz., periodate, guanidine and tellurate complexes.

Increase in the velocity of reaction is ascribed to the generation of higher valent state species of metal ions like Ag^{+2} or Ag^{+3} and Mn^{+3} as active intermediates which help the course of reaction. Recently, attention has been directed towards the stabilization of such less common oxidation states of metal ions with suitable ligands to be used in the reaction as oxidants. Cu(III) periodate has been broadly used as an oxidant in the analysis of inorganic and organic compounds in aqueous alkaline media due to (i) the existence of copper in three different oxidation states (+1, +2 and +3), (ii) the reduction potential of $Cu^{3+/}Cu^{2+}$ couple being −1.8 V in alkaline solution [2, 6], (iii) absence of availability of other adaptable oxidizing agents in their stable form in alkaline media for quantitative analyses, and (iv) due to being a single electron transfer oxidant. Its active forms in alkaline media are known to be the diperiodatocuprate (III) (DPC) and monoperiodatocuprate (III) (MPC) complexes [7]. These forms have been exploited in the analysis of some organic compounds, particularly alcohols, amines and α-amino acids. They have also been used in the differential titration[8] of organic mixtures, in the estimation of the amounts of chromium, calcium and magnesium from their ores, and estimation of the amounts of antimony, arsenic and tin in their alloys. In the recent past DPC has been used to establish the reaction mechanism for the oxidation of some alcohols [9, 10] amines and α-amino acids as it is comparatively more stable than the ditelluratocuprate (III) and copper(III) hydroxide complexes [11]. In such reactions, Cu(III) acts as an electron abstracting agent, occurring either in a single step or through formation of an adduct with substrates in an equilibrium step prior to the redox reactions.

MATERIALS AND METHODS

All chemicals used were of reagent grade and double distilled water was used throughout the work. 4-methoxy benzyl alcohol was used as supplied without further purification. Stock solutions were prepared by dissolving the weighed samples in double distilled water. $RuCl_3$ (Johnson Matthey Chemicals) was dissolved in minimum amount of HCl and final strength of hydrochloric acid and ruthenium(III) chloride in stock solution were 3.0×10^{-2}M and 4.723×10^{-3} M respectively. To maintain the required alkalinity and constant ionic strength, aqueous solutions of KOH and KNO_3 respectively were employed.

Diperiodatocuprate(III), DPC, was prepared by the reported method [12] by oxidizing $CuSO_4 \cdot 5H_2O$ dissolved in aqueous alkaline medium. Copper sulphate (3.54 g), potassium metaperiodate (6.8 g), potassium persulphate (2.2 g) and KOH (9 g) were added to 250 cm^3 of water. Continuously stirred mixture was boiled on a hot plate till it becomes dark red. Heating was continued for further20-25 minutes to ensure completion of the reaction. The cooled mixture was filtered through a sintered glass crucible (G-4) and the filtrate was diluted to 250 cm^3 with distilled water. This solution, in the presence of periodate was found quite stable at room temperature, even for months. The complex was characterized by its UV-Visible spectrum, which displayed two noticeable broad absorption bands at 415 nm and 257 nm. The aqueous solution of copper (III) was standardized by both iodometric and gravimetric [13] methods. A periodate solution was obtained by dissolving a particular amount of potassium metaperiodate in hot water and put it for 24 h. Its concentration was ascertained iodometrically [14] at neutral pH maintained by phosphate buffer.

Kinetic measurements: Kinetic measurements were performed on a Systronic 20 D spectrophotometer. The reactions were studied at 20ºC ± 0.1ºC under first-order conditions where [4-methoxy benzyl alcohol] >> [DPC]. The reaction in the presence of catalyst Ru(III) was initiated by mixing DPC with the solution containing the calculated amount of KNO_3, KOH, KIO_4 and the catalyst ruthenium (III). Progress of the reaction was monitored spectrophotometrically (with the help of a Systronics 20 D spectrophotometer) by measuring the decrease in the absorbance of DPC at 415 nm at which other reactants do not interfere. The total concentrations of periodate and OH^- were calculated by adding the amounts of these ions present in DPC solution and that added additionally. First-order rate constants were determined from the log (absorbance) versus time plots. The plots were linear up to 70% completion of reaction under the range of [OH^-] used. The orders for various reactants were determined from the slopes of plots of log k versus respective concentration of species, by calculating the first order rate constant k_{obs} values for molar concentration of the reactant. k_{obs} values were calculated by dividing the rate values (-dc/dt) by the concentration of that particular reactant in the reaction mixture. In the case of [DPC] variation the rate values were calculated at a fixed initial time while in other cases these values were calculated at a fixed initial concentration of oxidant. Effect of variation of [KIO_4], [$CuSO_4$] and [KNO_3] on the rate was determined by adding these ions externally. Captions in the tables and graphs are the initial concentrations of the reactants.

Stoichiometry and product analysis: Stoichiometry of the reaction was studied by taking the oxidant in large excess compared to organic substrate to ensure complete oxidation of one mole of the organic substrate. Stoichiometry of the reaction was calculated by studying the reaction at different substrate:oxidant ratios. After ensuring the completion of the reaction the mixture was extracted three times with diethyl ether. After evaporating the solvent under reduced pressure the calculated amount of 2, 4-dinitrophenyl hydrazine solution was mixed to the extract. 4-methoxy benzaldehyde was found to be the product of oxidation in the case of 4-methoxy benzyl alcohol by the spot test methods [15] (F. Feigl, Spot Tests in Organic Chemistry, Elsevier, New York, 1960, 369 pp) and by taking IR

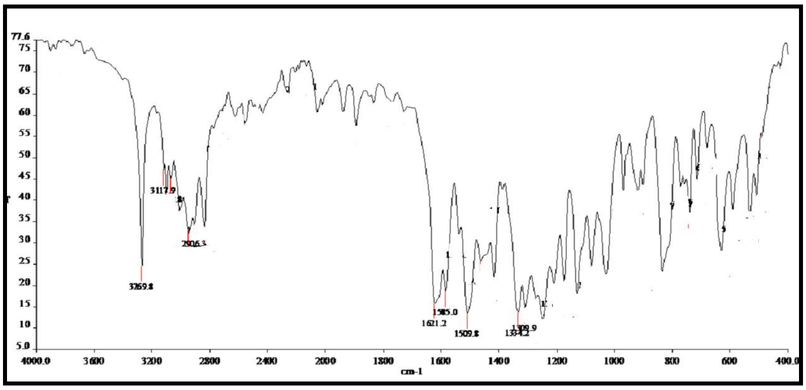


Figure 1. IR spectra of hydrazone of DNP of 4-methoxy benzaldebyde.

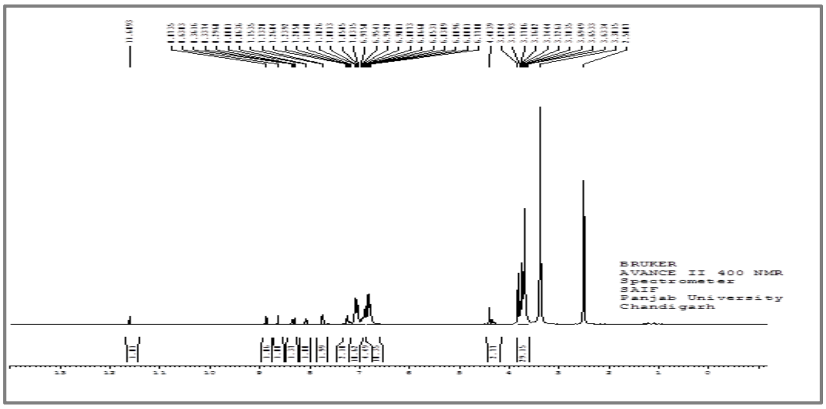


Figure 2. H^1 NMR of the DNP of 4 methoxy benzaldehyde.

(Perkin Elmer spectrum II (4000-400 cm^{-1}) by KBr pellet method figure 1) and NMR spectra (Bruker Avance II 400 NMR spectrometer; figure 2) of the products. Melting point of the DNP of the product was found to be 246ºC (reported m. p. of pure sample 254ºC). In case of hydrazone of 4-methoxy benzaldehyde IR spectra showed the peaks:υ_{max} 3269 cm^{-1} (N-H), υ_{max} 3117cm^{-1} (C-H aromatic str.) Υ_{max}2906 cm^{-1} (C-H str.), υ_{max}1585 cm^{-1} (N-H bending),υ_{max}1621cm^{-1} (C=N str.), υ_{max}1509cm^{-1} (NO asym. str.), υ_{max}1334cm^{-1} (NO sym.), υ_{max}1309 cm^{-1} (C-N str.). The NMR Signals were found at- δ 11.60 singlet (1H), δ 7-9 multiplet (8H). The results indicated 1:2 stoichiometry for the reaction.

RESULTS AND DISCUSSION

Reaction orders: Table 1 shows that –dc/dt values increase steadily with increasing [oxidant] in the beginning, reach to a maximum and beyond which further increase in [oxidant] starts decreasing the rate. First order rate constant values for molar concentration of oxidant are fairly constant in the beginning but start decreasing later on. On plotting –dc/dt values versus [DPC], straight line passing through the origin is obtained but after reaching to a maximum, it starts decreasing (Figure 3A). It shows that the reaction, only at low concentrations, shows direct proportionality w. r. to [oxidant]but after a certain point increase in [DPC] retards the rate. In case of 4-methoxy benzyl alcohol it was observed that the rate value increase proportionality with increasing concentration of organic substrate. Straight line passing through the origin was obtained on plotting graph between the rate values against [Organic substrate] indicating that order of the reaction is unity with respect to 4-methoxy benzyl alcohol (Figure 3B). Slope values of ~ 1.0 on plotting double logarithmic graphs between –dc/dt versus [organic substrate] and –dc/dt versus [oxidant] (at low concentrations), further confirm the results.

Table 1. Effects of variation of [DPC] and [4-methoxy benzyl alcohol] on the rate at 20ºC (μ = 0.2 M)

[DPC] × 10^4 M	-dc/dt × 10^6 M min^{-1}	k* × 10^3 M^{-1} min^{-1}	[4-methoxy benzyl alcohol] × 10^3 M	-dc/dt × 10^6 M min^{-1}	k* × 10^3 M^{-1} min^{-1}
0.9	0.28	3.20	1.5	0.45	0.60
1.8	0.57	3.17	3.0	0.94	0.62
2.5	0.75	3.00	5.0	1.69	0.67
3.5	1.10	3.14	7.5	2.35	0.62
5.0	1.25	2.50	10.0	3.12	0.62
6.0	1.66	2.76	15.0	4.58	0.61
7.5	1.09	1.45	-	-	-
9.0	0.80	0.88	-	-	-

[KOH] = 2.0 × 10^{-3} M, [$RuCl_3$] = 8.0 × 10^{-7} M, [KIO_4] = 1.0 × 10^{-5} M, [4-methoxy benzyl alcohol] = 5.0 × 10^{-3} M (for [DPC] variation), [DPC] = 5.0 × 10^{-4} M (for [4-methoxy benzyl alcohol] variation)

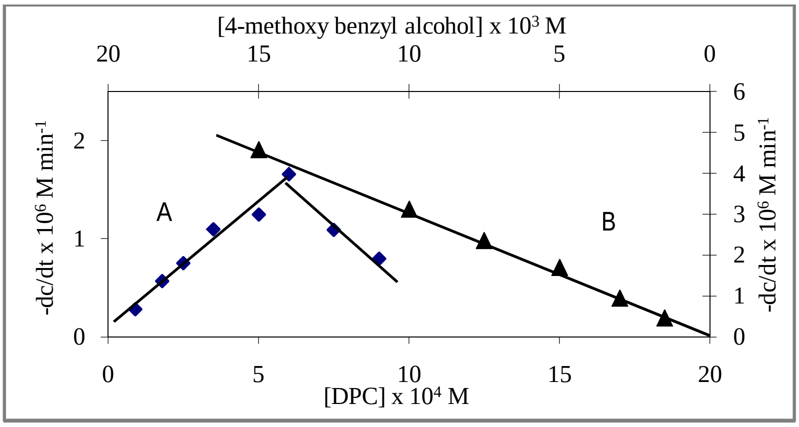


Figure 3. Effect of variation of [DPC] and [Organic substrate] on the rate at 20°C

On plotting –dc/dt values against [$RuCl_3$] and [KOH] both, straight lines passing through the origin were obtained. On plotting the double logarithmic graphs between log –dc/dt and log concentrations slope values of ~ 0.97 were obtained. Constancy in k* values in both the cases indicate that the reaction follows first order kinetics with respect to ruthenium(III) chloride and potassium hydroxide concentrations. Table 2 also indicates that rate of the reaction shows direct proportionality with respect to the concentrations of catalyst and hydroxyl ions both. This nature becomes clear from figure 4 (A and B) also in which effect of change of concentration of catalyst and KOH on the rate has been given.

Table 2. Effect of variation of [$RuCl_3$] and [KOH] on the rate at 20ºC

[$RuCl_3$] × 10^6 M	-dc/dt × 10^6 M min^{-1}	k^* × 10^3 M^{-1} min^{-1}	[KOH]×10^3 M	-dc/dt ×10^6 M min^{-1}	k^* × 10^3 M^{-1} min^{-1}
0.5	0.75	3.00	1.0	0.55	1.10
0.8	1.00	3.50	2.0	0.75	0.75
1.0	1.05	2.10	2.8	1.55	1.10
2.0	2.17	2.17	5.0	3.45	1.38
3.0	3.33	2.22	7.5	3.90	1.04
5.0	4.54	1.81	10.0	5.83	1.16

[DPC] = 5.0 × 10^{-4}M, [4-methoxy benzyl alcohol] = 5.0 × 10^{-3} M, [KIO_4] = 1.0 × 10^{-5} M, (μ = 0.2 M).
[KOH] = 2.0 × 10^{-3} M (for variation of [$RuCl_3$]; [$RuCl_3$] = 8.0 × 10^{-7} M (for variation of [KOH])

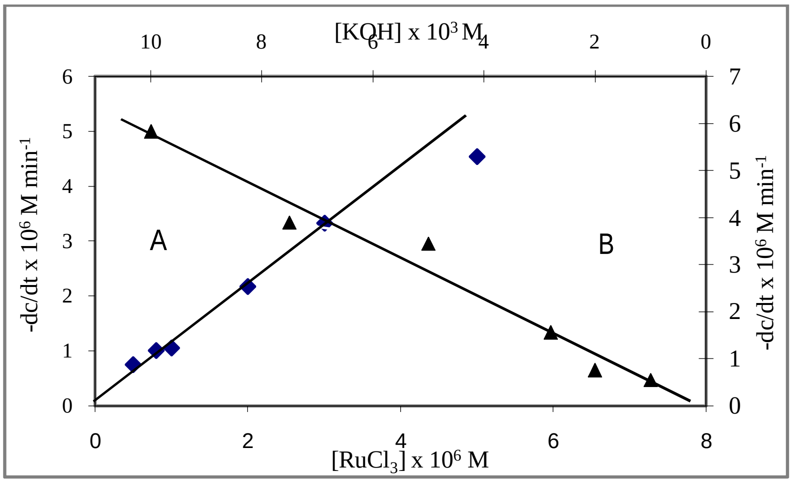


Figure 4. Effect of variation of [$RuCl_3$] and [KOH] on the rate at 20°C.

It is clear from the table 3 that the addition of potassium periodates ions retards the reaction velocity and –dc/dt values decreases with increasing concentrations of periodate ions. This nature is confirmed from figure 3also where –dc/dt values are plotted against the concentrations of periodate ions. To get an insight into the mechanistic aspect of reaction, that whether diperiodatocuprate (III), which is the oxidant in the present study, is reduced to copper(II) before the rate determining or not. To confirm this observation copper (II) ions were added externally into the reaction mixture (Table 3). It is observed that the external addition of copper (II) does not effect the reaction velocity indicating that the reduction diperiodatocuperate (III) in the reaction mixture takes place after the rate determining slow step. A number of experiments, with varying ionic strength of the medium with the help of potassium nitrate were carried out at constant concentrations of all the other reactants. It is clear from the table 3 that –dc/dt values increase with increasing ionic strength of the medium, indicating that increase in ionic strength of the medium has a positive effect on the reaction velocity. These results have been elaborated in figure 5 (A and B) also.

Table 3. Effect of variation of [KIO_4], [$CuSO_4$]and [KNO_3]on the rate at 20ºC

[KIO_4] × 10^5 M	-dc/dt × 10^6 M min^{-1}	[$CuSO_4$] × 10^3 M	-dc/dt × 10^6 M min^{-1}	[KNO_3]	-dc/dt × 10^6 M min^{-1}
1.0	1.05	0.9	1.14	0.20	1.13
3.0	0.93	1.0	1.44	0.25	1.76
5.0	0.68	1.5	1.16	0.30	2.00
6.0	0.56	2.0	1.20	0.40	2.53
8.0	0.49	3.0	1.14	0.50	3.12
10.0	0.34	5.4	1.38	0.70	3.44

[DPC] = 5.0 × 10^{-4}M, [4-methoxy benzyl alcohol] = 5.0 × 10^{-3} M, [$RuCl_3$] = 8.0 × 10^{-7} M, [KOH] = 2.0 × 10^{-3} M, μ = 0.2 M. [KIO_4] = 1.0 × 10^{-5} M (for the variation of [$CuSO_4$] and [KNO_3] only)

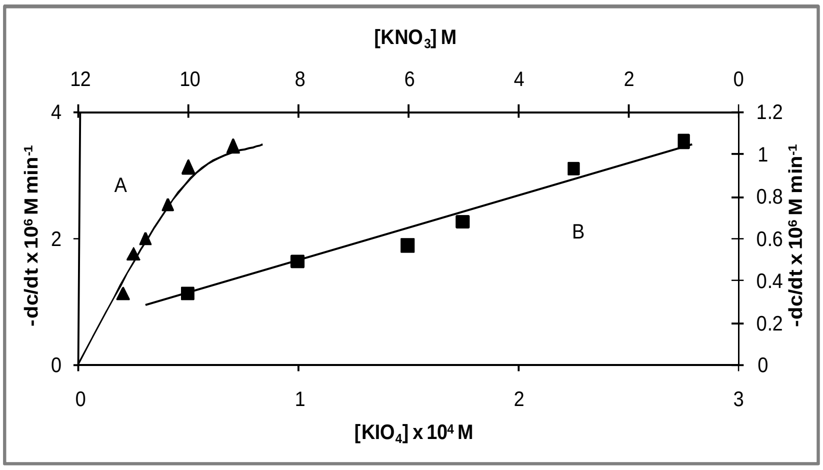


Figure 5. Effect of variation of [KIO4] on the rate at 20°C.

Mechanism: Water soluble DPC in alkaline medium exhibits an UV-Vis spectrum with two strong bands at 415 nm and 257 nm [16]. When solid $K_3H_3[Cu(IO_6)]4H_2O$ is dissolved in water it undergoes dissociation to have a complex ion[10]. In alkaline solution it may be present as $[Cu(HL)_2]^x$, $[CuL(HL)]^y$ and $[Cu(HL)]^z$, where HL contains an unlimited number of protons and L expresses the unprotonated periodate molecule in complex [17]. However, it is evident that periodate exists [18] as H_5IO_6, $H_4IO_6^-$, $H_3IO_6^{2-}$, $H_2IO_6^{3-}$ (eqn. (1 to 3) depending on the pH of the medium and total concentration of periodate. The bidentate ligands $H_3IO_6^{2-}$ and $H_3IO_6^{3-}$ satisfy the coordination number of Cu^{3+}. Similar structures of periodate complexes have been deduced for the Ni(IV) and Ag(III) periodate complexes[19, 20].

$$H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+ \quad (1)$$

$$H_4IO_6^- \rightleftharpoons H_3IO_6^{2-} + H^+ \quad (2)$$

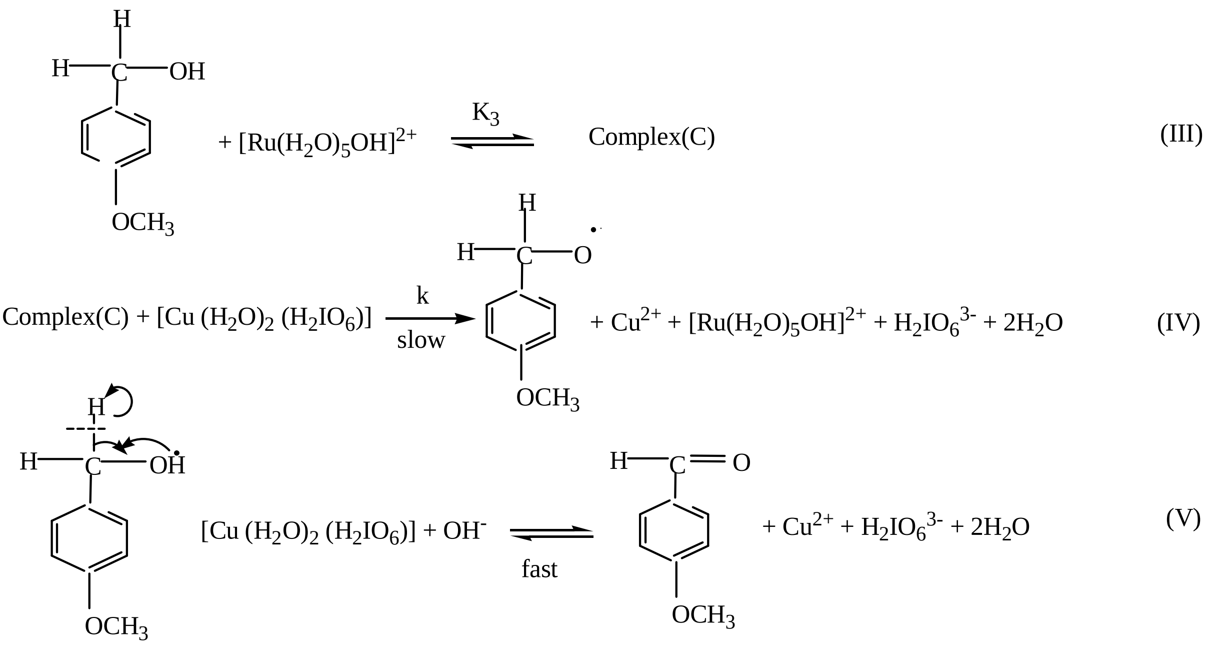
$$H_3IO_6^{2-} \rightleftharpoons H_2IO_6^{3-} + H^+ \quad (3)$$

In acidic medium active form of periodic acid is H_5IO_6 and in near neutral medium it exists as $H_4IO_6^-$. Since the present study was performed in alkaline medium, periodic acid is expected to be present in the forms $H_3IO_6^{2-}$ and $H_2IO_6^{3-}$. Dimeric form of periodate at higher concentrations has also been reported [21]. Decrease in the rate values at higher oxidant concentrations as observed in our case may be due to the formation of dimeric species. Hence in the light of the results obtained under the present investigation $Cu(OH)_2(H_3IO_6)]^-$ may be safely considered as the reactive species [22]. Ruthenium (III) chloride has been extensively used as a catalyst in several oxidation reduction reactions involving one or two equivalent oxidants [23, 24] both in acid as well as in alkali. In alkaline medium, ruthenium (III) is known to exist [25] as its hydroxylated species with general formula $[Ru(OH)_x(H_2O)_{6-x}]^{3-x}$ where x < 6 and variable, which depends on the pH of the medium. Considering the experimental conditions and pH of the present study $[Ru(H_2O)_5OH]^{2+}$has been considered as the reactive species of ruthenium(III) chloride[17].

Thus on the basis of the above discussion and the experimental findings following mechanism may be proposed for the oxidation of 4-methoxy benzyl alcohol

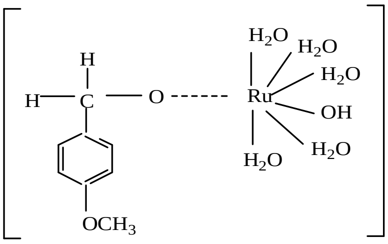
$$[Cu\,(H_3IO_6)_2]^- + OH^- \underset{}{\overset{K_1}{\rightleftharpoons}} [Cu\,(H_3IO_6)(H_2IO_6)]^{2-} + H_2O \qquad \text{(I)}$$

$$[Cu\,(H_3IO_6)(H_2IO_6)]^{2-} + 2\,H_2O \overset{K_2}{\rightleftharpoons} [Cu\,(H_2O)_2\,(H_2IO_6)] + H_3IO_6^{2-} \qquad \text{(II)}$$



Proposed mechanism for the oxidation of 4-methoxy benzyl alcohol

The probable structure of the complex is given as



From steps (I to III) of the mechanism

$$\text{Rate} = k\,[C] + [Cu\,(H_2O)_2\,(H_2IO_6)] \qquad (4)$$

$$[Cu\,(H_3IO_6)(H_2IO_6)]^{2-} = K_1\,[Cu\,(H_3IO_6)_2]^-\,[OH]^- \qquad (5)$$

$$[Cu\,(H_2O)_2\,(H_2IO_6)] = \frac{K_2\,[Cu\,(H_3IO_6)(H_2IO_6)]^{2-}}{[H_3IO_6{}^{2-}]} \qquad (6)$$

and

$$[C] = \frac{K_3\,[S][Ru(III)_T]}{1 + K_3\,[S]} \qquad (7)$$

On putting the values final rate expression may be given as

$$\text{Rate} = \frac{k\,K_1K_2K_3\,[Cu(H_3IO_6]^-\,[S]\,[Ru(III)]_T\,[OH]^-}{[H_3IO_6]^{2-}\,(1 + K_3\,[S]\,)} \qquad (8)$$

If 1 >>$K_3[S]$ then the final rate law reduces to

$$\text{Rate} = \frac{k\,K_1K_2K_3\,[Cu(H_3IO_6]^-\,[S]\,[Ru(III)]_T\,[OH]^-}{[H_3IO_6]^{2-}} \qquad (9)$$

This equation (9) explains all the experimental findings. Verification of the rate law can be done by rearranging eq. (9) and plotting the graphs between 1/rate Vs. $[H_3IO_6]^{2-}$ from where the values of rate constants can be calculated

$$\frac{1}{\text{Rate}} = \frac{[H_3IO_6]^{2-}}{k\,K_1K_2K_3\,[Cu(H_3IO_6]^-\,[S]\,[Ru(III)]_T\,[OH]^-} \qquad (10)$$

According to Equations 9 and 10 are in the form of straight lines and plots of 1/rate vs 1/[DPC], 1/rate Vs. 1/[S], 1/rate Vs. $1/[OH^-]$ and 1/rate Vs. [periodate] should give a straight line. With the help of the slope of straight line, $kk_1k_2k_3$ value was calculated which were found to be 2.71×10^{-2} M^{-3} min^{-1}, 3.35×10^{-3} $M^{-3}min^{-1}$,1.92×10^{-2} M^{-3} min^{-1} and 2.15×10^{-2} $M^{-3}min^{-1}$ respectively.

Table 4. Thermodynamic parameters and the rate constants

T (K)	$k \times 10^6$ min^{-1}
293	1.16
303	1.37
308	1.66
313	1.76
E_a (K Cal mol^{-1})	3.419
$\Delta S^\#$ (e. u)	-76.83
$\Delta F^\#$ (kcal mol^{-1})	23.28

[DPC] = 5.0×10^{-4}M, [4-methoxy benzyl alcohol] = 5.0×10^{-3} M, $[RuCl_3]$ = 8.0×10^{-7} M, [KOH] = 2.0×10^{-3} M, $[KIO_4]$ = 1.0×10^{-5} M, μ = 0.2 M

APPLICATION

It may be mentioned here that it is very interesting from the academic, industrial and biological point of views to study the oxidation of benzylic alcohols by using a newer one electron transfer oxidizing agent. Copper complexes have played a major role in oxidation chemistry as copper(III) is involved in many biological electron transfer reactions. Redox potential of Cu^{3+}/Cu^{2+} couple is reported to be

1.7 V and thus it can serve as a strong oxidizing agent like Fe(VI)/Fe(III) couple with redox potential of 2.2 V. Apart from the use of copper(III) as a green oxidant it has also been used for the removal of contaminants and antibiotics from the drinking water. The study is expected to be very important from the academic as well as from industrial and biological point of views.

CONCLUSION

To explore the possibility of using this metal ions as a homogeneous catalysis in the present work oxidation of 4-methoxy benzyl alcohol by alkaline diperiodatocuprate (III). Comparatively simple, economical, less tedious and environmentally acceptable methodologies used in copper(III) oxidation of 4-methoxy benzyl alcohol have opened new avenues for the growth of oxidation chemistry.

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