

Oxidation of Cyclic Alcohols by Hexacyanoferrate(III) in Alkaline Medium in the Presence of Rhodium(III) Chloride as a Homogeneous Catalyst

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Abstract: Un-catalyzed oxidation of cyclic alcohols viz. cyclopentanol and cyclohexanol by hexacyanoferrate(III) in aqueous alkaline medium does not proceed to measurable extent even after 98 hr. Addition of traces of RhCl₃, used as a homogeneous catalyst accelerates the reaction resulting in the formation of corresponding dicarboxylic acids. Correlating this result with previously reported results in the un-catalyzed oxidation of cyclopentanone to dicarboxylic acid indicates that hexacyanoferrate(III) in alkaline medium is incapable to oxidize cyclopentanol. Addition of catalyst initiates the initial conversion of cyclic alcohol into cyclic ketone which in turn is oxidized to dicarboxylic acid. Rate follows direct proportionality at low concentrations of catalyst, reaching to a maximum with increasing catalyst concentrations but further increase in RhCl₃ concentration retards the reaction velocity. As the amount of catalyst is increased in the reaction mixture it also increases the amount of hydrochloric acid in which RhCl₃ was prepared, resulting in the decrease in pH of the medium. At a particular pH, reactive species of catalyst Rh(OH)₃(H₂O)₃, converts into the un-reactive RhCl₃(H₂O)₃ and thus the reaction velocity decreases. Rate of the reaction shows first order kinetics in [OH⁻] and [cyclic alcohol], but it is one changing to zero order in oxidant concentrations. Increase in chloride ions and hexacyanoferrate(II) concentrations respectively increases and decreases the reaction velocity. Entropy, free energy and enthalpy values were calculated.

Keywords: Cyclic alcohols, alkaline hexacyanoferrate(III), rhodium(III) chloride, catalyst.

1. INTRODUCTION

Various oxidation states of iron from +3 to +6 have gained much attention as environmental friendly oxidants. Coagulating power of hypervalent iron species viz. Fe(IV), Fe(V) and Fe(VI) has recently been used for removing various impurities from contaminated water [1, 2]. Oxidation potential of ferricyanide/ferrocyanide couple is -0.45 V and thus ferricyanide has extensively been used as a moderate oxidant. Electrode potentials are normally pH dependent for anions whose protons are involved in the oxidation/reduction equation, thus the reduction potential of [Fe(CN)₆]³⁻/[Fe(CN)₆]⁴⁻ couple does not depend on pH of the medium. Many workers have reported [3] that electron is directly abstracted from the anion formed by the organic substrate. Aldehydes and ketones [4, 5] are oxidized by ferricyanide by direct transfer of electron without forming the complex. While hexacyanoferrate(III) forms complex with anion of organic substrate in case of diols [6, 7]. Direct transfer of electron from organic substrate to hexacyanoferrate(III) has been supported by us in our previous studies [8, 9]. Due to the conflicting observations it is desirable to come at a definite conclusion regarding the mode of oxidation of organic substrates having different functional groups by hexacyanoferrate(III) in alkaline medium and to find out the efficiency of RhCl₃ under homogeneous conditions. Thus the present work was carried out by studying the oxidation of

cyclopentanol and cyclohexanol by hexacyanoferrate(III) in aqueous alkaline medium catalyzed by rhodium(III) chloride.

2. EXPERIMENTAL

2.1. Materials and Methodology

Solution of cerium(IV) sulfate (Loba Chemie Industralanal Co) was prepared by dissolving the salt in diluted sulfuric acid (50%) and was standardized by titrating the solution with a standard ferrous ammonium sulfate solution using ferroin as an internal indicator. Potassium hexacyanoferrate(III) (BDH), NaOH, sulfuric acid, ferroin, (E. Merck), cyclopentanol and cyclohexanol (Fluka A.G.) were used as supplied. Other chemicals were of the highest grade pure chemicals. Solution of rhodium(III) chloride was prepared by dissolving the salt potassium hexachlororhodate (III) in minimum amount of HCl. Final strengths of catalyst and acid were 2.31×10^{-3} M and 5.58×10^{-2} M respectively. Temperature of the reaction mixture was kept constant with an accuracy of $\pm 0.1^\circ$ C. Reactions were followed by estimating the amount of hexacyanoferrate(II) produced in the reaction mixture at various time intervals. This was done by adding aliquots to a fixed amount of ferrous ammonium sulfate and then estimating excess ferrous ammonium sulfate with the help of a standard solution of ceric sulfate. Ferroin was used as an internal indicator. Due to excess of organic substrate compared to the oxidant in all the kinetic runs, reported orders of the reaction are with respect to the oxidant concentrations.

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2.2. Kinetic Determinations

Rate of the reaction ($-dc/dt$) was calculated from the slopes of the graphs plotted between the remaining concentration of oxidant versus time. Orders of the reaction with respect to various reactants were confirmed by various possible methods. Initial rates were calculated at a fixed time or concentration as the case may be. Potassium hexacyanoferrate(II) and chloride ions were added externally to study their effect on the reaction velocity. Tables and graphs show the concentrations of the reactants at the start of the reaction.

3. RESULTS

3.1. Product Study and Stoichiometry

Stoichiometry of the reaction was determined by calculating the number of moles of oxidant required to completely oxidize one mole of organic substrate. For this purpose ratio of the oxidant and organic substrate was changed and complete oxidation of organic substrate was ensured. It was observed that eight moles of oxidant were required for the complete oxidation of one mole of organic substrate. Final oxidation products were found to be dicarboxylic acids in case of both the organic substrates. Products of oxidation were confirmed by the spot test methods [10] and chromatographic technique [11] both. To determine the product of reaction under the experimental conditions, the reaction mixture was left at 30 °C till the yellowish colour of hexacyanoferrate(III) disappears completely. Now the reaction mixture was extracted with ether (3 x 15 ml). IR peaks at 1632 cm^{-1} and 1638 cm^{-1} (C=O stretching (asymmetric)) showed the presence of sodium salt of organic acid. Presence of the carboxylate anion of cyclopentanol and cyclohexanol was confirmed by the peaks at 1435 cm^{-1} and 1440 cm^{-1} (weak C=O stretching symmetric) respectively. Formation of sodium salt of organic acid shifts C=O (st. Asym) and weak C=O (str. Sym.) peaks from 1725-1700 to 1650-1550 cm^{-1} and near 1400 cm^{-1} [12]. Equation (1) shows stoichiometry of the reaction for cyclopentanol.



3.2. Reaction Orders

In both cases plotting of graph between the rate and concentration of oxidant gives a straight line passing through the origin at low concentrations becoming parallel to y-axis at higher concentrations of oxidant (Fig. 1). This confirms that order of the reaction is one at low concentrations which tends to become zero order at higher oxidant concentrations. After a fair constancy, gradual decrease in the first order rate constant (k_{obs}) values at higher concentrations of oxidant along with the steady increase in $-dc/dt$ values with increasing [oxidant] at low concentrations diminishes at higher oxidant concentrations (Table 1). Diminishing of reaction velocity at higher oxidant concentrations is less prominent in case of cyclohexanol because the reaction could not be studied at still higher concentrations of cyclohexanol. The trend in rate values becomes clear if we see the trend in rate values in light of rate constant values.

These facts collectively support that order of the reaction is one at low concentrations which tends to become zero order at higher oxidant concentrations.

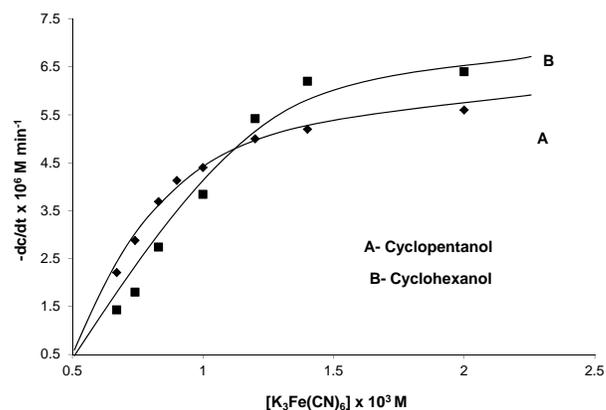


Fig. (1). Effect of variation of [oxidant] on the rate at 30 °C. A- [NaOH] = 6.70×10^{-3} M, [cyclopentanol] = 10.00×10^{-3} M, [RhCl₃] = 1.90×10^{-5} M. B- [NaOH] = 6.70×10^{-3} M, [cyclohexanol] = 10.00×10^{-3} M, [RhCl₃] = 1.90×10^{-5} M. Captions are same for Table 1.

In case of cyclopentanol and cyclohexanol both it was observed that the rate values increase proportionately with increasing concentrations of organic substrates and on plotting graph between rate values against organic substrate concentrations straight lines passing through the origin were obtained (Fig. 2). This indicates that order of the reaction is unity with respect to organic substrate in both the cases. Fair constancy obtained in the second order rate constants k_2 values up to the end of the variation (Table 2), slope values of 1.03 and 1.17 on plotting double logarithmic graphs between $-dc/dt$ versus [cyclic alcohol] further confirm the reaction follows first order kinetics with respect to organic substrate concentrations.

After an initial increase k_{obs} values start decreasing at higher concentrations of RhCl₃. The second order rate

Table 1 Effect of Variation of [Oxidant] on the Rate at 30 °C

A-Cyclopentanol; B- Cyclohexanol

[K ₃ Fe(CN) ₆] × 10 ³ M	-dc/dt × 10 ⁶ M min ⁻¹		k _{obs} × 10 ³ min ⁻¹	
	A	B	A	B
0.67	2.21	1.43	3.30	2.13
0.74	2.88	1.80	3.89	2.43
0.83	3.69	2.74	4.44	3.30
0.90	4.13	-	4.59	-
1.00	4.40	3.84	4.40	3.84
1.25	5.00	5.42	4.00	4.34
1.40	5.20	6.20	3.71	4.43
2.00	5.60	6.40	2.80	3.20

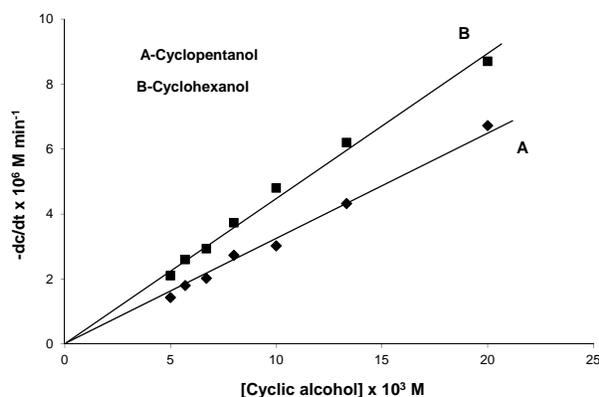


Fig. (2). Effect of change of [cyclic alcohol] on the rate at 30 °C. A- $[K_3Fe(CN)_6] = 1.25 \times 10^{-3}$ M, $[NaOH] = 6.70 \times 10^{-3}$ M, $[RhCl_3] = 1.90 \times 10^{-5}$ M. B- $[K_3Fe(CN)_6] = 1.25 \times 10^{-3}$ M, $[NaOH] = 6.70 \times 10^{-3}$ M, $[RhCl_3] = 1.90 \times 10^{-5}$ M. Captions are same for Table 2.

Table 2 Effect of Change of [Cyclic Alcohol] on the Rate at 30°C

A- Cyclopentanol; B- Cyclohexanol

[Cyclic Alcohol $\times 10^3$ M]	$k_{obs} \times 10^3 \text{ min}^{-1}$		$k_2 (k_{obs}/[\text{Cyclic Alcohol}]) \text{ M}^{-1} \text{ min}^{-1}$	
	(A)	(B)	(A)	(B)
5.00	1.15	1.68	0.23	0.34
5.70	1.44	2.08	0.25	0.36
6.70	1.62	2.35	0.24	0.35
8.00	2.19	2.99	0.27	0.37
10.00	2.42	3.84	0.24	0.38
13.33	3.46	4.96	0.26	0.37
20.00	5.38	6.96	0.27	0.35

constants k_2 values show constancy at low catalyst concentrations but start decreasing at higher concentrations of catalyst (Table 3). Nature of the reaction with changing catalyst concentrations becomes clear on plotting rate values against the concentration of catalyst (Fig. 3) in which direct proportionality of the reaction velocity with respect to low catalyst concentrations can be clearly seen. Opposite trend of the reaction i.e. decrease in the rate with increasing catalyst concentration in the later part shows a peculiar nature. It is important to note that behaviour of the catalyst changes when concentration of catalyst in the reaction mixture comes in the vicinity of 3.75×10^{-5} M. $RhCl_3$ was prepared in hydrochloric acid, thus increasing concentration of catalyst will increase acidity of the reaction mixture resulting in the decrease in pH of the medium. pH of the reaction mixture starts decreasing with increasing catalyst concentration and becomes 10.2 to 10.4 (in both the cases) when concentration of catalyst reaches to 3.75×10^{-5} M. It may be mentioned that different variations in the study were performed in this range of pH.

Slope values of 0.96 and 1.06 on plotting graphs between log rate versus log $[OH^-]$ in the case of cyclopentanol and

cyclohexanol respectively and the constant second order rate constant k_2 values in Table 4 indicate that rate of the reaction shows direct proportionality with respect to the concentration of hydroxyl ions. Straight lines passing through the origin (Fig. 4) on plotting $-dc/dt$ values versus $[OH^-]$ confirm the findings in case of both the alcohols.

Table 3 Effect of Variation of [Catalyst] on the Rate at 30°C

A- Cyclopentanol; B- Cyclohexanol

$[RhCl_3] \times 10^5$ M	$k_{obs} \times 10^3 \text{ min}^{-1}$		$k_2 (k_{obs}/[RhCl_3]) \times 10^{-2} \text{ M}^{-1} \text{ min}^{-1}$	
	(A)	(B)	(A)	(B)
0.70	-	1.68	-	2.40
1.17	1.15	3.34	0.98	2.86
1.90	1.92	4.22	1.01	2.22
2.80	2.54	6.88	0.91	2.46
3.76	3.49	8.83	0.93	2.35
4.70	1.92	5.44	0.41	1.15
5.60	0.96	2.19	0.17	0.39

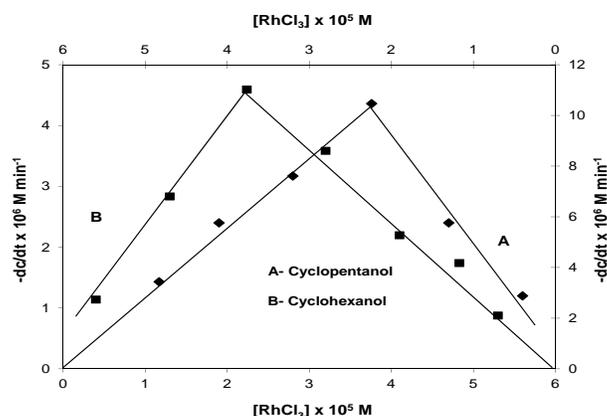


Fig. (3). Effect of variation of [catalyst] on the rate at 30°C. A- $[K_3Fe(CN)_6] = 1.25 \times 10^{-3}$ M, [cyclopentanol] = 10.00×10^{-3} M, $[NaOH] = 6.70 \times 10^{-3}$ M. B- $[K_3Fe(CN)_6] = 1.25 \times 10^{-3}$ M, [cyclohexanol] = 10.00×10^{-3} M, $[NaOH] = 6.70 \times 10^{-3}$ M. Captions are same for Table 3.

Table 4 Effect of Change of $[OH^-]$ on the Rate at 30°C

A- Cyclopentanol; B- Cyclohexanol

$[NaOH] \times 10^3$ M	$k_{obs} \times 10^3 \text{ min}^{-1}$		$k_2 (k_{obs}/[NaOH]) \text{ M}^{-1} \text{ min}^{-1}$	
	(A)	(B)	(A)	(B)
5.00	1.26	-	0.25	-
5.70	-	3.84	-	0.67
6.70	1.77	4.22	0.26	0.63
8.00	2.30	4.61	0.29	0.58
10.00	2.72	6.42	0.27	0.64
13.33	3.38	9.60	0.25	0.72
20.00	5.10	13.44	0.25	0.67

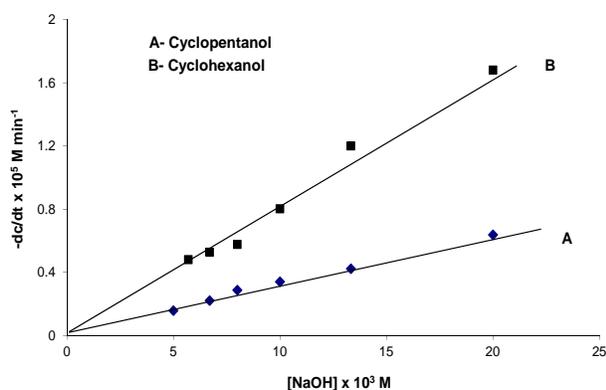


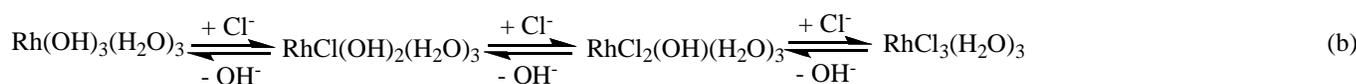
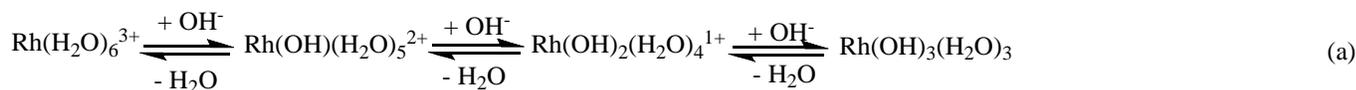
Fig. (4). Effect of change of $[\text{OH}^-]$ on the rate at 30°C . A- $[\text{K}_3\text{Fe}(\text{CN})_6] = 1.25 \times 10^{-3} \text{ M}$, $[\text{cyclopentanol}] = 10.00 \times 10^{-3} \text{ M}$, $[\text{RhCl}_3] = 1.90 \times 10^{-5} \text{ M}$. B- $[\text{K}_3\text{Fe}(\text{CN})_6] = 1.25 \times 10^{-3} \text{ M}$, $[\text{cyclohexanol}] = 10.00 \times 10^{-3} \text{ M}$, $[\text{RhCl}_3] = 1.90 \times 10^{-5} \text{ M}$. Captions are same for Table 4.

Reaction velocity decreases from 5.62 to 2.06 ($\times 10^{-6} \text{ M min}^{-1}$) on changing the concentration of ferrocyanide from 0.67 to 2.00 ($\times 10^{-3} \text{ M}$) when organic substrate and sodium hydroxide concentrations were 10.0 and 6.70 ($\times 10^{-3} \text{ M}$) respectively in case of cyclopentanol; similarly the rate values decrease from 5.28 to 1.34 ($\times 10^{-6} \text{ M min}^{-1}$) on changing [hexacyanoferrate(II)] from 0.67 to 2.00 ($\times 10^{-3} \text{ M}$) when organic substrate and sodium hydroxide concentrations were 6.70 and 6.70 ($\times 10^{-3} \text{ M}$) respectively for cyclohexanol. In both the cases oxidant concentration was $1.25 \times 10^{-3} \text{ M}$ and the catalyst concentration was $1.90 \times 10^{-5} \text{ M}$. On the basis of common ion effect decrease in reaction velocity on increasing the concentration of externally added hexacyanoferrate(II) shows that prior presence of hexacyanoferrate(II) ions in the reaction mixture slows down step II of the mechanism in which hexacyanoferrate(II) is produced and thus the rate of reaction is decreased. This result clearly indicates that reduction of ferricyanide ion takes place before the slow step in the mechanism. Effect of change of ionic strength of the medium was studied with the help of KCl. Addition of chloride ions in the reaction mixture increases the rate to a great extent. Increase in rate on increasing ionic strength of the medium indicates that reaction is taking place in between the similarly charged ions. An increase in the rate values from 0.72 to 1.28 ($\times 10^{-5} \text{ M min}^{-1}$) on increasing ionic strength of the medium from 0.04 to 0.12 M was observed when oxidant, organic substrate, alkali concentrations were 1.25 , 10.00 , 6.70 ($\times 10^{-3} \text{ M}$) and the catalyst concentration was $1.90 \times 10^{-5} \text{ M}$.

4. DISCUSSION

4.1. Reactive Species of Rhodium(III) Chloride

On boiling aqueous solutions of rhodium trichloride, stable $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$ species is obtained in which pH



determines the exchange between first sphere H_2O protons and bulk water [13]. Rhodium trichloride is extensively hydrolyzed in aqueous solution [14]. When hydrochloric acid is in excess, RhCl_6^{3-} gives $\text{RhCl}_3(\text{H}_2\text{O})_3$ species. Between $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$ and $\text{RhCl}_3(\text{H}_2\text{O})_3$ intermediate species remain in equilibrium as shown in equilibrium (a) and (b):

In dilute hydrochloric acid (40%) rhodium remains in the form of $[\text{RhCl}_5(\text{H}_2\text{O})]^{2-}$ [15] but on diluting the solution formation of $[\text{RhCl}_4(\text{H}_2\text{O})_2]^-$ and $[\text{RhCl}_3(\text{OH})(\text{H}_2\text{O})_2]^-$ species also takes place [16]. Cationic form of rhodium is responsible for the catalytic activity the fraction of which decreases from pH 1.0 to 5.3 (in HCl) and fraction of the uncharged species increases. In this range of pH, two chloro complexes having negative charge are also formed [17]. Alkaline medium in the present study limited our efforts to decrease pH of the medium beyond a certain limit. Maximum rate in the present study was found in the pH range of 10.2 to 10.4 beyond which rate starts decreasing in case of both organic substrates. Interestingly this range of pH corresponds to the range in which different variations were performed in the present study. Increasing concentration of rhodium(III) chloride in the reaction mixture increases the concentration of HCl also in which the catalyst was prepared. Thus, increasing catalyst concentration increases both H^+ and Cl^- ions concentrations in the reaction mixture. Increased H^+ ions decrease pH of the medium while increased Cl^- ions may shift equilibrium (b) towards the right hand side. Shifting of equilibrium (b) towards the right hand side simply by increasing chloride ion concentration in the reaction mixture is contrary to our experimental results because externally added chloride ions have a positive effect on the rate. This clearly indicates that the shifting of equilibrium (b) towards the right hand side takes place only below a particular pH of the medium which is the governing factor for conversion of reactive species of the catalyst into the un-reactive species. Thus, catalytic effect of rhodium trichloride is highly pH dependent which is due to the conversion of reactive species into the un-reactive species.

4.2. Mechanism

According to the proposed path of oxidation in Scheme 1 alkoxide ion obtained from cyclic alcohol in alkaline medium is oxidized by hexacyanoferrate(III) resulting in the formation of radical. Attraction of electron towards rhodium results in an unstable complex which dissociates in the slow step ultimately giving rise to the cyclic ketone by quick rearrangement of bonds. Probably the slight attraction of electron towards rhodium causes electron deficiency on the oxygen atom which enhances homolytic fission of C-H bond. Complete transfer of electron to rhodium may be difficult thus oxidation state of rhodium may not change and in that case it will be generated in its original form in the subsequent step along with the generation of hydrogen

radical [8, 9], which may be quickly oxidized to H^+ ion by ferricyanide ion. On the other hand in case of the complete transfer of electron, oxidation state of rhodium may decrease giving rise to Rh(II) species and in this case H^+ ion is generated in step IV of the mechanism. Rhodium(II) species in the next step may give rise to original Rh(III) species by utilizing one ferricyanide ion. In both the cases fast oxidation takes place and under our laboratory conditions it is not possible to clearly identify the separate steps. Further either of the condition will not affect the final rate law and also stoichiometry of the reaction. As previously reported by us in the un-catalyzed oxidation of cyclopentanone by alkaline hexacyanoferrate(III), it was found that the cyclic ketone is oxidized to dicarboxylic acid by consuming six ferricyanide ions [18,19]. Suggested path of oxidation in Scheme 1, evidenced by stoichiometry of the reaction (eq. 1) in the present case consumption of 8 molecules of oxidant compared to 6 molecules in the un-catalyzed oxidation of cyclopentanone [18] indicates consumption of two ferricyanide ions in the conversion of cyclopentanol to cyclopentanone. Intermediate cyclic ketone by taking six more ferricyanide molecules ultimately converts into the dicarboxylic acid, the presence of which was confirmed by spectral studies of the reaction mixture. To check the course of reaction if rhodium is removed from the system, the reaction was studied under similar concentrations of all other reactants in the absence of rhodium(III) and change in absorbance of ferricyanide was recorded. It was observed that absorbance of the solution remains constant (λ_{max} 420 nm, 1.307 ± 0.019) even after 98 hr. This eliminates the possibility that the electron available on the radical in step III

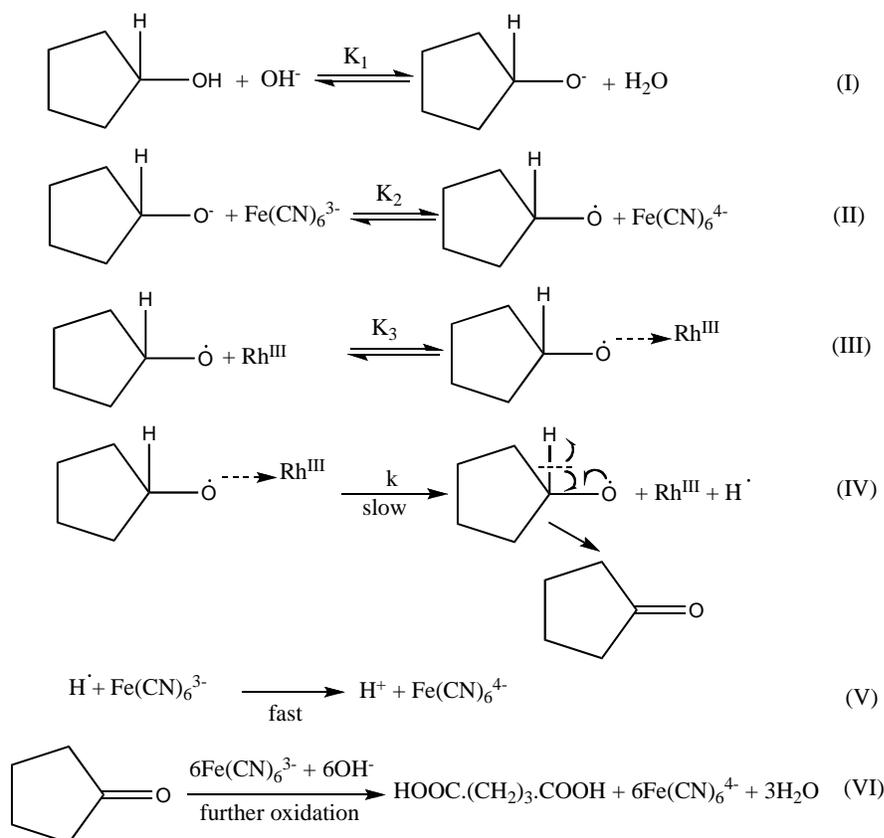
(Scheme 2) may be taken up by ferricyanide in the absence of rhodium(III). Moreover, the only alternative to convert alkoxide ion into ketone will be its oxidation by two ferricyanide ions in the absence of rhodium(III), as shown in Scheme 2. Under these conditions the order with respect to ferricyanide will come out to be two as given in eq.(2), which is contrary to the experimental results obtained in our case in which first order tending to become zeroth order was obtained. Scheme 2 leads to final rate law as given in eq. (2) by which nature shown by the reaction on changing the concentration of hexacyanoferrate(II) cannot be explained.

$$\text{Rate} = -\frac{d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = \frac{kK_1[\text{Fe}(\text{CN})_6^{3-}]^2[\text{S}][\text{OH}^-]}{[\text{H}_2\text{O}]} \quad (2)$$

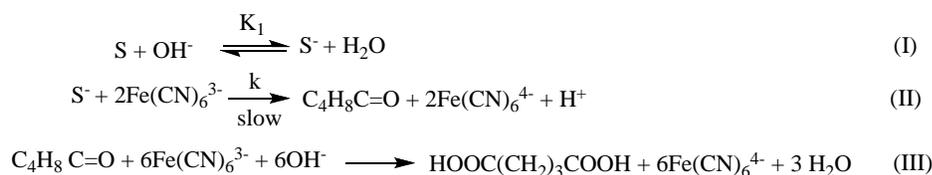
Thus, the probable route of conversion of cyclic alcohol to corresponding dicarboxylic acid *via* cyclic ketones as an intermediate may be given as in Scheme 1. Rate constants for the un-catalyzed oxidation of cyclopentanone to dicarboxylic acid reported by previously by us [19] were found to be in the range of $10^4 \text{ M}^{-3} \text{ min}^{-1}$ compared to the present case in which rate constant for conversion of cyclopentanol to dicarboxylic acid was obtained in the range of $10^7 \text{ M}^{-3} \text{ min}^{-1}$.

4.3. Derivation of Rate Law

As the catalyst rhodium(III) was prepared in hydrochloric acid therefore its increasing amount in the reaction mixture although may increase chloride ion concentration but will certainly decrease pH of the medium. In the light of accelerating effect of chloride ions on the reaction rate,



Scheme 1. Proposed mechanism for rhodium(III) catalyzed oxidation of cyclopentanol by aqueous alkaline hexacyanoferrate(III)



Scheme 2. Probable steps in the oxidation of cyclopentanol by heacyanoferrate(III) in aqueous alkaline medium in the absence of rhodium(III) chloride.

increase in chloride ions cannot be the reason for decreasing rate with increasing catalyst concentrations. Thus, decrease in pH of the medium must be responsible for decrease in the reaction velocity at higher concentrations of catalyst. This fact gains ground on the basis of experimental findings in which it was observed that rate of the reaction starts decreasing abruptly when pH of the reaction mixture comes in the vicinity of a fixed point (3.75×10^{-5} M) in the case of both organic substrates. It may be possible that decrease in pH increases the percentage of some un-reactive species of catalyst which results in the decrease in reaction velocity. Under similar conditions in the oxidation of cyclic ketones [9], it has been observed that decrease in pH from 10.4 to 10.2 results in the steep fall in the rate values. It may be pointed out that the present study also was performed in this range of pH. Thus we can safely assume that $\text{Rh}(\text{OH})_3(\text{H}_2\text{O})_3$ is the reactive species of rhodium trichloride in alkaline medium which has been considered by other workers [20,21] also. Rate decreases due to the conversion of reactive $\text{Rh}(\text{OH})_3(\text{H}_2\text{O})_3$ species into the unreactive $\text{RhCl}_3(\text{H}_2\text{O})_3$ species. Formation of alkoxide ion has been reported in a number of studies in alkaline medium [22-24]. It has also

$$[\text{S}]_{\text{T}} = [\text{S}] + [\text{S}^-] + [\text{S}^*] + [\text{C}] \quad (4)$$

Concentrations of [S], [S⁻] and [S^{*}] may be given from equilibrium I to III respectively

$$[\text{S}] = \frac{[\text{S}^-][\text{H}_2\text{O}]}{K_1[\text{OH}^-]} \quad (5)$$

$$[\text{S}^-] = \frac{[\text{S}][\text{Fe}(\text{CN})_6^{4-}]}{K_2[\text{Fe}(\text{CN})_6^{3-}]} \quad (6)$$

$$[\text{S}^*] = \frac{[\text{C}]}{K_3[\text{Rh}(\text{III})]} \quad (7)$$

Concentration of [S^{*}], in terms of [C] may be calculated by substituting the value of [S⁻] from eq. (7) into eq. (6) and the value of [S⁻] thus obtained may be substituted in eq. (5) for getting the value of [S] in terms of [C]. Now putting the values of [S], [S⁻] and [S^{*}] in terms of [C], in eq. (4), total

$$[\text{C}] = \frac{K_1 K_2 K_3 [\text{Fe}(\text{CN})_6^{3-}] [\text{Rh}^{\text{III}}] [\text{OH}^-] [\text{S}]_{\text{T}}}{[\text{Fe}(\text{CN})_6^{4-}] \{ [\text{H}_2\text{O}] + K_1 [\text{OH}^-] \} + K_1 K_2 [\text{Fe}(\text{CN})_6^{3-}] [\text{OH}^-] \{ 1 + K_3 [\text{Rh}^{\text{III}}] \}} \quad (8)$$

Final rate law from step (IV) of the mechanism can now be given as

$$-\frac{d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = \frac{k K_1 K_2 K_3 [\text{Fe}(\text{CN})_6^{3-}] [\text{S}]_{\text{T}} [\text{OH}^-] [\text{Rh}^{\text{III}}]}{[\text{Fe}(\text{CN})_6^{4-}] \{ [\text{H}_2\text{O}] + K_1 [\text{OH}^-] \} + K_1 K_2 [\text{OH}^-] [\text{Fe}(\text{CN})_6^{3-}] \{ 1 + K_3 [\text{Rh}^{\text{III}}] \}} \quad (9)$$

been suggested [25,26] that alkoxide ion is one of the reacting species which is formed by the ionization of alcohols during their oxidation by permanganate in alkaline medium.



Thus, oxidation path of cyclopentanol (Scheme 1) may be proposed on the basis of discussion and the experimental findings given above.

According to Scheme 1 total concentration of substrate ([S]_T) may be given as

$$-\frac{d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = \frac{k K_1 K_2 K_3 [\text{Fe}(\text{CN})_6^{3-}] [\text{S}]_{\text{T}} [\text{OH}^-] [\text{Rh}^{\text{III}}]}{[\text{Fe}(\text{CN})_6^{4-}] [\text{H}_2\text{O}] + K_1 K_2 [\text{OH}^-] [\text{Fe}(\text{CN})_6^{3-}]} \quad (10)$$

concentration of [C] may be given as

Present study was performed in aqueous medium thus the inequality $[\text{H}_2\text{O}] \gg K_1 [\text{OH}^-]$ stands valid and at low concentrations of catalyst the second condition, $1 \gg K_3 [\text{Rh}(\text{III})]$, may also be considered valid. With these two assumptions equation (9) reduces to

According to rate law (10) rate of the reaction should follow direct proportionality with respect to organic substrate up to its many fold variation in concentrations which is consistent with the experimental findings. First order kinetics shown by the oxidant at its low concentrations tending to become zero order at higher concentrations and retarding effect shown by hexacyanoferrate(II) on the

reaction velocity is also explained. Direct proportionality of the reaction with respect to low concentrations of catalyst is also explained. However, this rate law fails to explain the nature shown by OH⁻ ions and rhodium(III) at their higher concentrations. Zero order kinetics with respect to hydroxyl ions at their higher concentrations as shown by equation (10) was not observed experimentally in the present study. Probable reason for this discrepancy may be that the study at still higher concentrations could not be performed because rate of the reaction becomes too fast to be measured in a proper way. According to equation (10) rate of the reaction should show direct proportionality even at higher concentrations of the catalyst. This discrepancy is due to the decrease in pH of the medium on increasing catalyst concentrations which affects the reaction velocity in a negative manner and has been discussed in detail in section 6. On reversing equation (10) we get

$$\frac{1}{d[\text{Fe}(\text{CN})_6^{3-}]} = \frac{[\text{Fe}(\text{CN})_6^{4-}]}{kK_1K_2K_3[\text{Fe}(\text{CN})_6^{3-}][\text{S}]_T[\text{OH}^-][\text{Rh}^{\text{III}}]} + \frac{1}{kK_3[\text{Rh}^{\text{III}}][\text{S}]_T} \quad (11)$$

Equation (11) is in the form of a straight line equation and a plot of 1/rate versus 1/[Fe(CN)₆³⁻] should give a straight line with positive intercept at y-axis which is obtained experimentally also and supports the rate law (10) and the proposed mechanism. With the help of the slope of straight line, kK₁K₂K₃ values were calculated which were found to be 1.21 and 6.31 (× 10⁷ M⁻³ min⁻¹) for cyclopentanol and cyclohexanol respectively. Free radicals could not be detected in the present system probably due to their fast oxidation to intermediate product with alkaline hexacyanoferrate(III). Free radicals formed in copper(II) oxidation are quickly oxidized. Ferricyanide-ferrocyanide system has many similarities with Cu(II)-Cu(I) system [27-29] with higher redox potential. Higher redox potential of ferrocyanide-ferrocyanide system helps in quick oxidation of radicals. Test for the free radicals may be completely masked due to rapid oxidation, alkaline medium and self oxidation of free radicals under experimental conditions. Energy of activation (ΔE[#]), entropy of activation (ΔS[#]) and Free energy of activation (ΔF[#]) values were calculated by performing the reactions at four different temperatures. These values for cyclopentanol and cyclohexanol come out to be 21.29 and 22.80 (kJ mol⁻¹); -43.70 and -43.55 (JK⁻¹ mol⁻¹) and 34.53 and 35.99 (kJ mol⁻¹) respectively. Possibility of hydration of ferricyanide in alkaline medium was ruled out as there was no detectable change in the spectra of ferricyanide [18] was observed after mixing various amounts of alkali. Previously reported uncatalyzed oxidation of cyclopentanone into dicarboxylic acid when considered in the light that in the absence of rhodium(III) chloride cyclic alcohol is not oxidized shows that ferricyanide is not capable to extract electron from the radical. Thus it can be safely assumed that Scheme 1 is operative in the present system.

5. CONCLUSION

Present study shows that the conversion of cyclopentanol and cyclohexanol to the intermediate cyclic ketones by aqueous alkaline solution of ferricyanide takes place only in the presence of rhodium(III) chloride probably by facilitating the breaking of C-H bond. Further oxidation of the

intermediate cyclic ketone to dicarboxylic acid may take place in the presence as well as in the absence of rhodium. Fraction of active species of rhodium(III) chloride strongly depends on the pH of the medium. Formation of un-reactive species at higher concentrations of catalyst decreases pH of the medium which in turn decreases rate of the reaction. The study also indicates that electron from the organic substrate is directly transferred to hexacyanoferrate(III) without the formation of complex.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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