



## Oxidation of cyclic ketones by alkaline hexacyanoferrate(III) catalyzed by rhodium(III)

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### ABSTRACT

The kinetics of the reaction between cyclopentanone and cyclohexanone with hexacyanoferrate(III) ion catalyzed by rhodium(III) chloride in alkaline medium has been investigated at four temperatures. The data show that the reaction follows first order kinetics with respect to hydroxide ion and cyclic ketone concentrations while the rate shows direct proportionality with respect to low concentrations of hexacyanoferrate(III) ion, which tends to become zeroth order at higher [oxidant]. Increase in rhodium(III) chloride concentrations increases the rate in the beginning but after reaching to a maximum further increase in catalyst concentration retards the rate, thus showing a peculiar nature. In both cases, decrease in rate after a fixed maximum is attributed to a particular pH of the medium below which un-reactive species of catalyst retards the velocity. Change in pH of the medium shows that decreasing pH decreases the rate with breaks at specific points. Increase in ionic strength of the medium has a positive effect, while increase in hexacyanoferrate(II) decreases the reaction velocity. Various thermodynamic parameters were calculated.

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### 1. Introduction

Main drawback with cerium(IV) lies in the fact that it can be used in the acidic medium only. Oxidation by iron(III) in the form of various complexes has received much attention presumably due to its cheap availability, less complexity involved in the estimation and its ability to act in acidic and alkaline medium both. Iron(VI) has gained great attention as an environment friendly oxidant and coagulant for water and wastewater treatment [1,2]. The oxidation potential of the couple  $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$  ( $-0.45\text{ V}$ ) makes it possible to use it as a moderate oxidizing agent. Studies [3] with alkaline hexacyanoferrate(III) showed that ferricyanide directly abstracts an electron from the anion of the organic substrate. Singh et al. [4,5] also have suggested that an electron is directly transferred to ferricyanide in the oxidation of aldehydes and ketones without the formation of complex. Later on some workers [6,7] have reported that the oxidation proceeds *via* complex formation between the anion of the diol and hexacyanoferrate(III) ion. This difference in mechanism shown by alkaline hexacyanoferrate(III) in the oxidation of organic compound and to see the catalytic efficiency of rhodium(III) chloride under homogeneous conditions, prompted us

to study the kinetics of oxidation of cyclopentanone and cyclohexanone by alkaline hexacyanoferrate(III).

### 2. Experimental

Potassium ferricyanide (BDH), sodium hydroxide, sulphuric acid, ferroin (E. Merck), cyclopentanone and cyclohexanone (Fluka A.G.) were used as supplied without further purification by preparing their solutions in doubly distilled water. Cerium(IV) sulphate (Loba Chemie Industral Co.), prepared by dissolving the sample in 1:1 sulphuric acid, was titrated against a standard solution of ferrous ammonium sulphate, using ferroin as an internal indicator. All other chemicals used were either Analar or chemically pure substances. Progress of the reaction was measured (constant temperature  $\pm 0.1\text{ }^\circ\text{C}$ ) at different intervals of time by estimating the amount of ferrocyanide ions produced at different intervals of time, with the help of a standard solution of ceric sulphate using ferroin as an internal indicator. In all kinetic runs organic substrate was in excess.

#### 2.1. Determination of kinetics

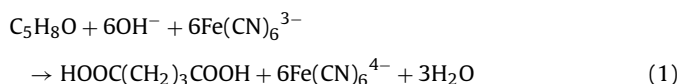
Rate of the reaction ( $-\text{dc}/\text{dt}$ ) was obtained by calculating the initial slopes of the graphs plotted between the residual concentrations of hexacyanoferrate(III) in the reaction mixture versus time. Order of the reaction with respect to various reactants was confirmed by plotting graphs between  $-\text{dc}/\text{dt}$  or  $k_{\text{obs}}$  values against the

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concentration of that particular reactant, by calculating slopes of the double logarithmic graphs between the rate and concentration of reactant, by plotting first order graphs between  $\log [K_3Fe(CN)_6]$  versus time, by calculating the first order rate constant  $k_{obs}$  values for molar concentration of the reactant ( $k_{obs}$  was obtained by dividing the rate values ( $-dc/dt$ ) by the concentration of that particular reactant in the reaction mixture. In case of oxidant variation  $-dc/dt$  values were calculated at a fixed initial time while in other cases, these values were calculated at a fixed initial concentration of the oxidant. Effect of [hexacyanoferrate(II)] and  $Cl^-$  ions on the reaction velocity was studied by adding the ions externally. Effect of the change of pH of the medium on the rate was studied with the help of perchloric acid at constant concentrations of all other reactants. Captions in the tables and graphs are the initial concentrations of the reactants.

## 2.2. Product study and stoichiometry

Stoichiometry of the reaction was studied by taking hexacyanoferrate(III) in large excess compared to the organic substrate in different ratios to ensure complete oxidation of the organic substrate. Total amount of hexacyanoferrate(III) consumed by 1 mol of organic substrate for its complete oxidation was determined. In both the cases, formation of dicarboxylic acids was confirmed by the spot test method [8] and chromatographic technique [9]. Product of the reaction was also confirmed by extracting the reaction mixture with ether (3 ml  $\times$  15 ml). IR spectra of the organic phase showed peaks at  $1639\text{ cm}^{-1}$  and  $1634\text{ cm}^{-1}$  (C=O stretching (asymmetric) of sodium salt of organic acid and  $1450\text{ cm}^{-1}$  and  $1475\text{ cm}^{-1}$  (weak C=O stretching symmetric) of the carboxylate anion for cyclopentanone and cyclohexanone respectively. It is known [10] that C=O stretching (asymmetric) peak of organic acids (generally found from 1725 to 1700) shifts to  $1650\text{--}1550\text{ cm}^{-1}$ , when the acid is present in the form of its sodium salt, while the weak peak corresponding to C=O stretching (symmetric) of the carboxylate anion shifts near  $1400\text{ cm}^{-1}$ . Stoichiometry of the reaction, e.g. for cyclopentanone may be given by Eq. (1)

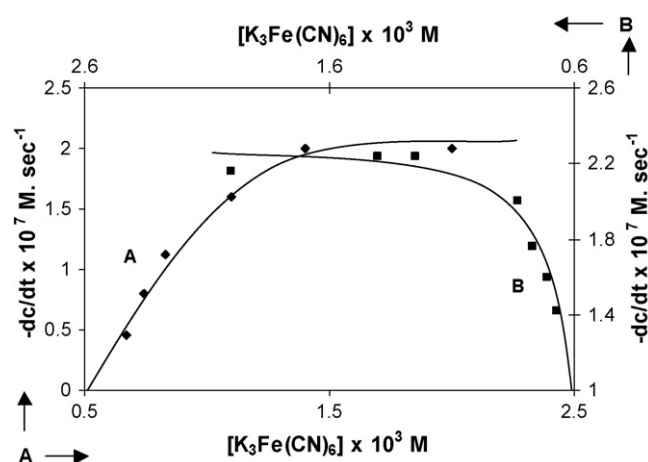


## 3. Results

Table 1 shows that  $-dc/dt$  values increase steadily with increasing [oxidant] but the increase is not prominent at higher concentrations of the oxidant. First order rate constant values for molar concentration of oxidant are fairly constant in the beginning but start decreasing later on (Table 1). On plotting  $-dc/dt$  values versus [hexacyanoferrate(III)], straight lines passing through the origin were obtained in the beginning while the lines become parallel to x-axis at higher concentrations of the oxidant (Fig. 1). Similar trend

**Table 1**  
Effect of variation of [hexacyanoferrate(III)] on the rate at 30 °C. A: cyclopentanone; B: cyclohexanone.

| [K <sub>3</sub> Fe(CN) <sub>6</sub> ] $\times 10^3$ M | $-dc/dt \times 10^7$ M s <sup>-1</sup> |      | $k_{obs}$ ( $-dc/dt/[K_3Fe(CN)_6] \times 10^4$ s <sup>-1</sup> ) |      |
|---|--|------|--|------|
|   | (A)                                    | (B)  | (A)  | (B)  |
| 0.67  | 0.46                                   | 1.42 | 0.69   | 2.12 |
| 0.71  | –                                      | 1.60 | –  | 2.25 |
| 0.74  | 0.80                                   | –    | 1.08   | –    |
| 0.77  | –                                      | 1.76 | –  | 2.28 |
| 0.83  | 1.12                                   | 2.00 | 1.35   | 2.41 |
| 1.10  | 1.60                                   | –    | 1.45   | –    |
| 1.25  | –                                      | 2.24 | –  | 1.79 |
| 1.40  | 2.00                                   | 2.24 | 1.43   | 1.60 |
| 2.00  | 2.00                                   | 2.16 | 1.00   | 1.08 |



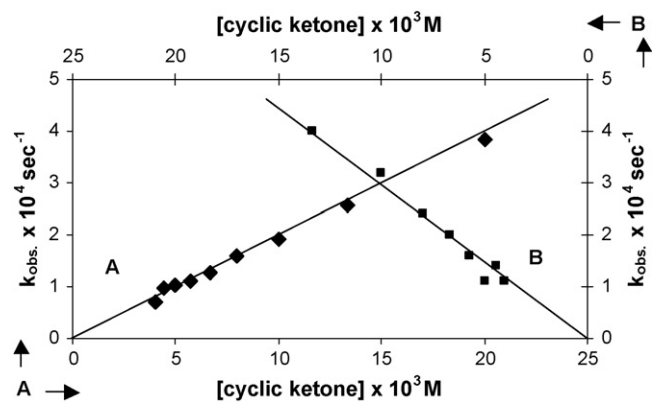
**Fig. 1.** Effect of variation of [K<sub>3</sub>Fe(CN)<sub>6</sub>] on the rate at 30 °C. (A) [NaOH]= $5.00 \times 10^{-3}$  M, [cyclopentanone]= $10.00 \times 10^{-3}$  M, [RhCl<sub>3</sub>]= $1.90 \times 10^{-5}$  M. (B) [NaOH]= $5.00 \times 10^{-3}$  M, [cyclohexanone]= $6.70 \times 10^{-3}$  M, [RhCl<sub>3</sub>]= $1.90 \times 10^{-5}$  M. Foot note (concentrations are the initial concentration of reactants).

was obtained in case of both cyclic ketones. From these evidences it is clear that the reaction shows first order dependence on ferricyanide at low concentrations, while the rate becomes independent of concentration at higher [hexacyanoferrate(III)].

On plotting double logarithmic graphs between  $-dc/dt$  versus [cyclic ketone] slope values of 1.14 and 1.20 were obtained for cyclopentanone and cyclohexanone respectively. The second order rate constant  $k_2$  values in Table 2 are fairly constant. These facts confirm that rate of the reaction shows direct proportionality w.r.o. [organic substrate]. This result can further be confirmed by plotting  $k_{obs}$  values versus [ketone], where straight lines passing through the origin are obtained for both the ketones (Fig. 2). In the case of variation of  $[OH^-]$  slope values of 0.94 and 1.18 were obtained on plotting double logarithmic graphs between rate versus  $[OH^-]$  for cyclopentanone and cyclohexanone respectively. The second order rate constant  $k_2$  values in Table 3 are fairly constant. These facts confirm that rate of the reaction shows direct proportionality w.r.o.  $[OH^-]$ . This result can further be confirmed by plotting  $k_{obs}$  values versus  $[OH^-]$ , where straight lines passing through the origin are obtained for both the ketones (Fig. 3). Trend in the rate values for various concentrations of rhodium(III) chloride in Table 4 show a specific nature. It was observed that the rate values increase proportionately with increasing catalyst concentrations in the beginning but after reaching to a maximum, the values start decreasing with increasing catalyst concentrations. The second order rate constants  $k_2$  values remain constant in the beginning but start decreasing later on. Confirmation of this nature comes from the graph between  $k_{obs}$  values versus  $[RhCl_3]$  in which rate values increase proportionately in the beginning reach to a maximum and beyond which

**Table 2**  
Effect of variation of [cyclic ketone] on the rate at 30 °C. A: cyclopentanone; B: cyclohexanone.

| [Cyclic ketone] $\times 10^3$ M | $k_{obs} \times 10^4$ s <sup>-1</sup> |      | $k_2$ ( $k_{obs}/[\text{cyclic ketone}] \times 10^2$ M <sup>-1</sup> s <sup>-1</sup> ) |      |
|---------------------------------|---------------------------------------|------|--|------|
|                                 | (A)                                   | (B)  | (A)  | (B)  |
| 4.00                            | 0.71                                  | 1.12 | 1.77   | 2.80 |
| 4.44                            | 0.96                                  | 1.40 | 2.16   | 3.15 |
| 5.00                            | 1.02                                  | 1.12 | 2.04   | 2.24 |
| 5.70                            | 1.12                                  | 1.60 | 1.96   | 2.81 |
| 6.70                            | 1.28                                  | 2.00 | 1.91   | 2.98 |
| 8.00                            | 1.60                                  | 2.40 | 2.00   | 3.00 |
| 10.00                           | 1.92                                  | 3.20 | 1.92   | 3.20 |
| 13.33                           | 2.56                                  | 4.00 | 1.92   | 3.00 |
| 20.00                           | 3.84                                  | –    | 1.92   | –    |

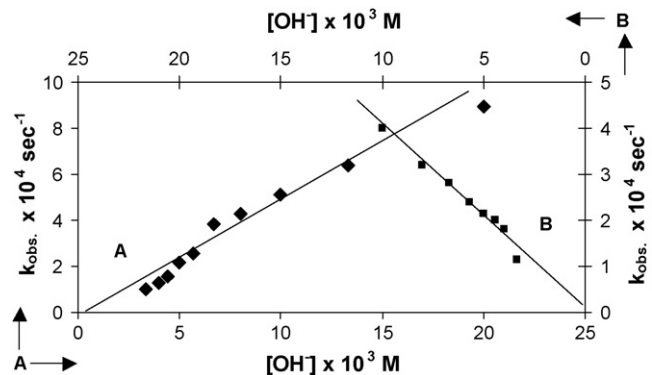


**Fig. 2.** Effect of variation of [organic substrate] on the rate at 30°C. (A)  $[K_3Fe(CN)_6]=1.25 \times 10^{-3}$  M,  $[NaOH]=5.00 \times 10^{-3}$  M,  $[RhCl_3]=1.90 \times 10^{-5}$  M. (B)  $[K_3Fe(CN)_6]=1.00 \times 10^{-3}$  M,  $[NaOH]=5.00 \times 10^{-3}$  M,  $[RhCl_3]=1.90 \times 10^{-5}$  M. Foot note (concentrations are the initial concentration of reactants).

**Table 3**  
Effect of variation of  $[OH^-]$  on the rate at 30°C. A: cyclopentanone; B: cyclohexanone.

| $[NaOH] \times 10^3$ M | $k_{obs} \times 10^4$ s <sup>-1</sup> |      | $k_2 \times 10^2$ M <sup>-1</sup> min <sup>-1</sup> |      |
|------------------------|---------------------------------------|------|---|------|
|                        | (A)                                   | (B)  | (A)   | (B)  |
| 3.33                   | 1.02                                  | 1.13 | 3.06  | 3.39 |
| 4.00                   | 1.28                                  | 1.80 | 3.20  | 4.50 |
| 4.40                   | 1.56                                  | 2.00 | 3.54  | 4.54 |
| 5.00                   | 2.14                                  | 2.13 | 4.28  | 4.26 |
| 5.70                   | 2.56                                  | 2.40 | 4.49  | 4.21 |
| 6.70                   | 3.84                                  | 2.80 | 5.73  | 4.18 |
| 8.00                   | 4.26                                  | 3.20 | 5.32  | 4.00 |
| 10.00                  | 5.12                                  | 4.00 | 5.12  | 4.00 |
| 13.33                  | 6.40                                  | –    | 4.81  | –    |
| 20.00                  | 8.96                                  | –    | 4.48  | –    |

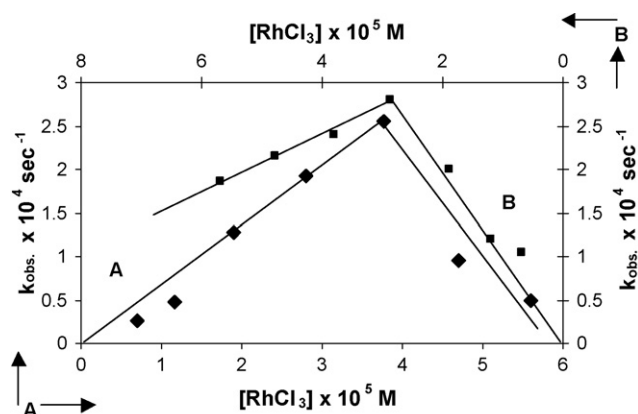
further increase in catalyst concentration decreases the rate (Fig. 4). Interestingly the maximum in the graph comes in the vicinity of a fixed point (i.e.  $3.75 \times 10^{-5}$  M) in both the cases. These results indicate that the reaction follows first order kinetics in the beginning but after reaching to a maximum, increase in concentration shows a retarding effect on the rate. Change in pH of the medium was studied by changing  $[H^+]$ . As change in hydrochloric acid in the reaction mixture, in which the catalyst was prepared, will also change concentration of chloride ions, therefore pH of the medium was changed with the help of perchloric acid in the reaction mixture and thus keeping all other concentrations including  $[Cl^-]$  in the reaction mixture constant (Table 5). It was observed that in the



**Fig. 3.** Effect of variation of  $[OH^-]$  on the rate at 30°C. (A)  $[K_3Fe(CN)_6]=1.25 \times 10^{-3}$  M,  $[cyclopentanone]=10.0 \times 10^{-3}$  M,  $[RhCl_3]=1.90 \times 10^{-5}$  M. (B)  $[K_3Fe(CN)_6]=1.00 \times 10^{-3}$  M,  $[cyclohexanone]=6.70 \times 10^{-3}$  M,  $[RhCl_3]=1.90 \times 10^{-5}$  M. Foot note (concentrations are the initial concentration of reactants).

**Table 4**  
Effect of variation of  $[RhCl_3]$  on the rate at 30°C. A: cyclopentanone; B: cyclohexanone.

| $[RhCl_3] \times 10^5$ M | $k_{obs} \times 10^4$ s <sup>-1</sup> |      | $k_2$ M <sup>-1</sup> min <sup>-1</sup> |       |
|--------------------------|---------------------------------------|------|---|-------|
|                          | (A)                                   | (B)  | (A)                                     | (B)   |
| 0.70                     | 0.26                                  | 1.04 | 3.66                                    | 14.86 |
| 1.17                     | 0.48                                  | –    | 4.10                                    | –     |
| 1.20                     | –                                     | 1.20 | –                                       | 10.00 |
| 1.90                     | 1.28                                  | 2.00 | 6.74                                    | 10.53 |
| 2.80                     | 1.92                                  | –    | 6.86                                    | –     |
| 2.87                     | –                                     | 2.80 | –                                       | 9.76  |
| 3.76                     | 2.56                                  | –    | 6.80                                    | –     |
| 3.80                     | –                                     | 2.40 | –                                       | 6.32  |
| 4.70                     | 0.96                                  | –    | 2.04                                    | –     |
| 4.78                     | –                                     | 2.16 | –                                       | 4.52  |
| 5.60                     | 0.50                                  | –    | 0.90                                    | –     |
| 5.70                     | –                                     | 1.86 | –                                       | 3.26  |

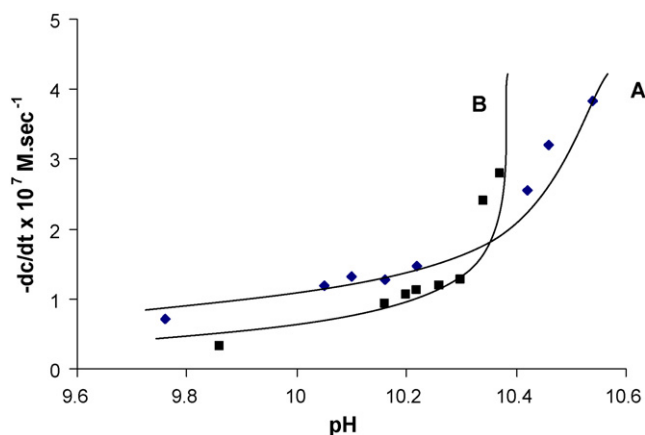


**Fig. 4.** Effect of variation of [rhodium(III) chloride] on the rate at 30°C. (A)  $[K_3Fe(CN)_6]=1.25 \times 10^{-3}$  M,  $[cyclopentanone]=10.0 \times 10^{-3}$  M,  $[NaOH]=5.00 \times 10^{-3}$  M. (B)  $[K_3Fe(CN)_6]=1.00 \times 10^{-3}$  M,  $[cyclohexanone]=6.70 \times 10^{-3}$  M,  $[NaOH]=5.00 \times 10^{-3}$  M. (concentrations are the initial concentration of reactants).

low pH range, increase in rate with increasing pH is not prominent but steep rise in rate values is observed in the vicinity of pH  $\sim 10.2$ – $10.4$  (Fig. 5). This range corresponds to the pH of the reaction mixture at which different variations were performed. Effect of change of ferrocyanide ion concentration on the rate by changing the concentration of externally added hexacyanoferrate(II) was studied to see whether the ferricyanide is reduced before the rate determining step or not. It was observed that change in externally added hexacyanoferrate(II) affects the reaction velocity in a

**Table 5**  
Effect of variation of pH of the medium on the rate at 30°C. A: cyclopentanone; B: cyclohexanone.

| pH    | $-dc/dt \times 10^7$ M s <sup>-1</sup> |      |
|-------|--|------|
|       | (A)                                    | (B)  |
| 9.76  | 0.72                                   | –    |
| 9.86  | –                                      | 0.32 |
| 10.05 | 1.20                                   | –    |
| 10.10 | 1.31                                   | –    |
| 10.16 | 1.27                                   | 0.92 |
| 10.20 | –                                      | 1.06 |
| 10.22 | 1.48                                   | 1.13 |
| 10.26 | –                                      | 1.20 |
| 10.30 | –                                      | 1.28 |
| 10.34 | –                                      | 2.40 |
| 10.37 | –                                      | 2.80 |
| 10.42 | 2.56                                   | –    |
| 10.46 | 3.20                                   | –    |
| 10.54 | 3.83                                   | –    |



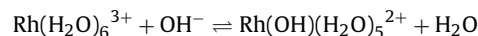
**Fig. 5.** Effect of variation of pH of the medium on the rate at 30°C. (A)  $[K_3Fe(CN)_6]=1.25 \times 10^{-3}$  M, [cyclopentanone]= $10.0 \times 10^{-3}$  M,  $[NaOH]=5.00 \times 10^{-3}$  M,  $[RhCl_3]=1.90 \times 10^{-5}$  M. (B)  $[K_3Fe(CN)_6]=1.00 \times 10^{-3}$  M, [cyclohexanone]= $6.70 \times 10^{-3}$  M,  $[NaOH]=5.00 \times 10^{-3}$  M,  $[RhCl_3]=1.90 \times 10^{-5}$  M. Foot note (concentrations are the initial concentration of reactants).

negative manner and the rate values ( $-dc/dt$ ) decrease from 4.0 to  $1.6 (\times 10^{-7} \text{ M s}^{-1})$  on changing [hexacyanoferrate(II)] from 0.67 to  $2.00 (\times 10^{-3} \text{ M})$ , when the oxidant, organic substrate, sodium hydroxide were 1.25, 10.0,  $5.00 (\times 10^{-3} \text{ M})$  and rhodium(III) chloride concentration was  $1.90 \times 10^{-5} \text{ M}$  for cyclopentanone. The rate values decreased from 2.4 to  $1.6 (\times 10^{-7} \text{ M s}^{-1})$  on changing [hexacyanoferrate(II)] from 0.67 to  $2.00 (\times 10^{-3} \text{ M})$  when the oxidant, organic substrate and sodium hydroxide concentrations were 1.25, 6.70,  $5.00 (\times 10^{-3} \text{ M})$  and rhodium(III) chloride concentration was  $1.90 \times 10^{-5} \text{ M}$  for cyclohexanone. Effect of change of chloride ion concentration (and hence the ionic strength of the medium) on the reaction velocity was also studied and it was observed that addition of externally added standard solution of potassium chloride in the reaction mixture accelerates the rate. The rate values increased from  $3.20$  to  $9.60 (\times 10^{-7} \text{ M s}^{-1})$  on increasing ionic strength of the medium from 0.02 to 0.10 M, when oxidant, organic substrate, alkali

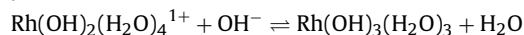
concentrations were 1.25, 10.00,  $5.00 (\times 10^{-3} \text{ M})$  and the catalyst concentration was  $1.90 \times 10^{-5} \text{ M}$ .

#### 4. Reactive species of rhodium(III) chloride

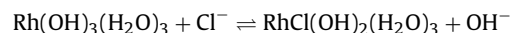
It has been reported that the aqua ion  $[Rh(H_2O)_6]^{3+}$  is quite stable and exchange between first sphere  $H_2O$  protons and bulk water is highly pH dependent [11]. It has also been reported that rhodium trichloride when dissolved in hydrochloric acid gives  $RhCl_3(H_2O)_3$  species in aqueous medium. It is also known that its water solution is extensively hydrolyzed [12]. Between the species  $RhCl_6^{3-}$  which is obtained in excess of hydrochloric acid and  $Rh(H_2O)_6^{3+}$  which is formed on boiling aqueous solutions of rhodium trichloride, there are several intermediate species. Equilibrium between various species may be shown as:



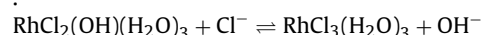
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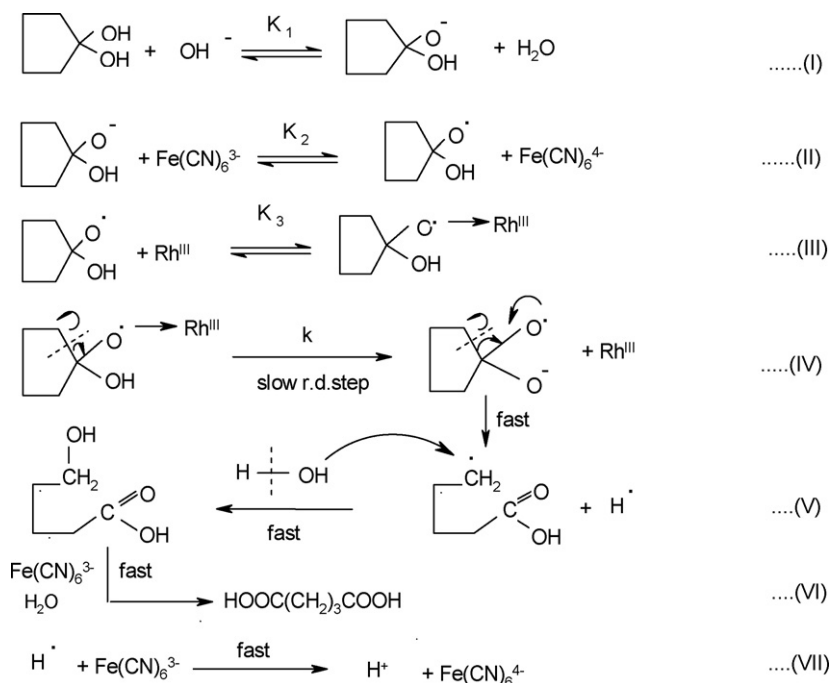
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It has also been reported [13] that in limited HCl,  $RhCl_3(H_2O)_3$  species is formed while in excess HCl,  $(RhCl_6)^{3-}$  species is obtained. Thornton and Firtz [14] revealed the existence of only one complex,  $[RhCl_5(H_2O)]^{2-}$ , in 40% HCl. While Trimerbaev and co-worker [15] has reported two more species  $[RhCl_4(H_2O)_2]^-$  and  $[RhCl_3(OH)(H_2O)_2]^-$  due to hydrolysis on diluting the solutions. It has also been reported that in hydrochloric acid solutions at pH 1.0–5.3 the fraction of a cationic rhodium form decreases and uncharged complex becomes the dominating species along with the formation of two negatively charged chloro complexes [16]. It has been shown that the greater the content of cationic complexed species of rhodium in solution, greater is the catalytic action. Present study



**Scheme 1.** Proposed steps in the oxidation of cyclopentanone by heacyanoferrate(III) in aqueous alkaline medium in the presence of rhodium(III) chloride.

was performed in alkaline medium in which it was not possible to decrease the pH of the medium beyond a certain level. Steep change in the rate values in the range of pH 10.2–10.4 in case of both organic substrates clearly supports the view that existence of the reactive species of rhodium is pH dependent.

## 5. Mechanism

According to Scheme 1, anion of ketone, formed in steps I of the mechanism react with ferricyanide to give the radical. Ferricyanide is reduced to ferrocyanide. At this stage presence of rhodium only facilitates the breaking of C–C bond. Due to this attraction of rhodium, electron slightly shifts away making the oxygen atom electron deficient, which enhances the breaking of C–C bond and the intermediate is quickly oxidized to alcohol and finally to

dicarboxylic acid. It seems that the function of rhodium is only to facilitate the breaking of bond because it is regenerated as such without change in its oxidation state.

## 6. Discussion

In the present study positive effect of  $\text{Cl}^-$  ions was observed while on increasing the concentration of catalyst the rate starts decreasing after reaching to a maximum. These two results collectively indicate that retarding nature shown by the catalyst is not due to the increase in chloride ion concentrations in the reaction mixture, because increase in  $\text{KCl}$  or  $\text{RhCl}_3$  both will increase chloride ions in the reaction mixture. As catalyst was prepared in hydrochloric acid it seems to be the pH of the medium, which has a retarding effect on the reaction rate. Increase in the concentration of catalyst decreases pH of the medium and the maximum rate in catalyst variation was always found in the vicinity of a fixed point ( $3.75 \times 10^{-5} \text{ M}$ ) in both the cases. This clearly shows that when pH of the medium drops to a certain level some un-reactive species of catalyst is formed which starts retarding the reaction. To further confirm the probable change in the species of the catalyst study was extended to see the effect of change of pH of the medium keeping all other concentrations constant. Fig. 5 clearly shows that decreasing pH of the medium decreases the rate. In case of both ketones steep fall in the rate values is obtained in the range when pH is decreased from 10.4 to 10.2. Interestingly this range of pH corresponds to the range of pH in which the present study was performed. Thus, on the basis of above discussion, positive effect of chloride ions on the reaction velocity, as well as pH of the medium in which the present study was performed we can safely assume that  $\text{Rh}(\text{OH})_3(\text{H}_2\text{O})_3$  is the reactive species of rhodium trichloride in our case which has been considered by other workers [17,18] also in alkaline medium. Conversion of the reactive species into  $\text{RhCl}_3(\text{H}_2\text{O})_3$  species with decreasing pH, has a negative effect on the catalytic action. Thus, on the basis of the above discussion path given in Scheme 1, may be proposed for the oxidation of cyclic ketones. Existence of aldehydes [4,5] in the hydrated form is well documented. Position of equilibrium and stability depend on the structure of hydrates and the groups attached with carbonyl carbon. In case of cyclopentanones formation of hydrates relieves some of the internal strain (I-strain) [19]. Change in ring strain in cyclic ketones and eclipsing and transannular strain in rings of seven to eleven members, effects the rates due to transformation of tetrahedral to trigonal carbon or vice versa [20]. Although, the possibility of formation of doubly negative anion has been reported [21] and

also in the Cannizzaro reaction [22] In the uncatalyzed oxidation of cyclic ketones we also have reported the existence of cyclic ketones in their hydrated form in alkaline medium [23,24] which was supported by the second order kinetics in hydroxyl ion concentrations. In the present study it appears that in comparatively low concentration of hydroxyl ions and in the presence of rhodium(III) chloride, formation of double negative ion does not take place and the order with respect to hydroxyl ions remain unity through out the course of the reaction.

## 7. Derivation of rate law

Value of complex  $\text{C}_2$  may be calculated by considering equilibrium in steps I and II of the Scheme 1 and putting this value in step III of the mechanism, after rearrangement, the final rate law in terms of decreasing concentrations of hexacyanoferrate(III) can be given as-

$$-\frac{d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = \frac{kK_1K_2K_3[\text{Fe}(\text{CN})_6^{3-}][\text{S}]_T[\text{OH}^-][\text{Rh}^{\text{III}}]}{[\text{Fe}(\text{CN})_6^{4-}][\text{H}_2\text{O}] + K_1[\text{OH}^-] + K_1K_2[\text{OH}^-][\text{Fe}(\text{CN})_6^{3-}](1 + K_3[\text{Rh}^{\text{III}}])} \quad (3)$$

Under our experimental conditions inequality  $[\text{H}_2\text{O}] \gg K_1[\text{OH}^-]$  and  $1 \gg K_3[\text{Rh}^{\text{III}}]$ , may be considered valid and the Eq. (3) reduces to

$$-\frac{d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = \frac{kK_1K_2K_3[\text{Fe}(\text{CN})_6^{3-}][\text{S}]_T[\text{OH}^-][\text{Rh}^{\text{III}}]}{[\text{Fe}(\text{CN})_6^{4-}][\text{H}_2\text{O}] + K_1K_2[\text{OH}^-][\text{Fe}(\text{CN})_6^{3-}]} \quad (4)$$

This rate law clearly explains first order kinetics with respect to organic substrate and rhodium(III) chloride concentrations. Nature shown by hexacyanoferrate(III) and the retarding nature given by the hexacyanoferrate(II) are also quite clear. However, this rate law predicts zero order kinetics at higher  $\text{OH}^-$  ion concentrations, which was not observed in the present study. This may be due to the reason that the study at still higher concentrations of  $\text{OH}^-$  ions could not be performed because the rate becomes too fast to be measured properly. Although first order kinetics with respect to rhodium(III) at its low concentrations is well explained by this equation but retarding nature shown by the catalyst at its higher concentrations is not explained, for which a valid reason that pH of the medium retards the rate at higher catalyst concentrations has already been discussed in Section 6. Eq. (4) may also be written in the form

$$\frac{1}{-d[\text{Fe}(\text{CN})_6^{3-}]} = \frac{[\text{Fe}(\text{CN})_6^{4-}]}{kK_1K_2K_3[\text{Fe}(\text{CN})_6^{3-}][\text{S}]_T[\text{OH}^-][\text{Rh}^{\text{III}}]} + \frac{1}{kK_3[\text{Rh}^{\text{III}}][\text{S}]_T} \quad (5)$$

From this equation graph between  $1/\text{rate}$  versus  $1/[\text{Fe}(\text{CN})_6^{3-}]$  was plotted. Straight line with positive intercept on y-axis further supports the rate law (3) and the proposed mechanism. With the help of the slope of this straight line  $kK_1K_2K_3$  values were calculated and were found to be 2.01 and  $10.52 (\times 10^9 \text{ M}^{-3} \text{ min}^{-1})$  for cyclopentanone and cyclohexanone respectively. Inability to detect free radical in the present system may be as the free radical formed is probably fast oxidized with alkaline ferricyanide to intermediate product, which undergoes further oxidation to acid. In most of the oxidation reactions ferricyanide resembles the copper(II), which involves free radical formation and its rapid oxidation [25–28]. The ferricyanide–ferrocyanide system which has higher redox potential than  $\text{Cu}(\text{II})\text{--Cu}(\text{I})$ , substantiates better possibility of the rapid oxidation of the free radicals with ferricyanide. The alkaline medium and the rapid oxidation of the free radical may completely mask the polymerization test. Sometimes free radicals are themselves oxidized under the experimental conditions and the test fails for free radicals.

The kinetic measurements were extended at four temperatures. The energy of activation for cyclopentanone and cyclohexanone comes out to be 8.25 and 8.98 (kJ mol<sup>-1</sup>), respectively. The entropy of activation was found to be -45.62 and 45.45 (JK<sup>-1</sup> mol<sup>-1</sup>), consistent with a reaction involving two negatively charged ions. Free energy of activation values were found to be 22.07 and 22.75 (kJ mol<sup>-1</sup>). Radical mechanism in the oxidation of thiols by ferricyanide has been supported by other workers also [29]. To further check the possibility of hydration of ferricyanide in alkaline medium spectra of ferricyanide alone and after mixing various amounts of alkali were taken in which no detectable change was observed [24]. This again indicates that probably Scheme 1 is operative in the present system.

## 8. Conclusion

The present study shows that the catalytic activity of rhodium(III) chloride mainly depends on the pH of the medium. The reactive species of catalyst, which exists at higher pH of the medium starts converting into the un-reactive species, thus retarding the rate if pH of the medium decreases to a certain level. The study also indicates that hexacyanoferrate(III) oxidizes the cyclic ketones by abstracting the electron before the rate determining step and no complex formation takes place between the oxidant and the organic substrate.

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