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KINETIC AND MECHANISM OF RUTHENIUM (III) CATALYZED OXIDATION OF 4-(3-HYDROXY PHENYL AMINO)-4-OXO BUTANOIC ACID BY HEXACYANOFERRATE (III) IN AQUEOUS ALKALINE MEDIUM

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ABSTRACT

The kinetics and mechanism of hexacyanoferrate (HCF(III)) oxidation of 4-(3-hydroxy phenyl amino)-4-oxo butanoic acid (4-Oxo acid) in aqueous alkaline medium has been studied at 26 ± 0.1°C in presence of ruthenium (III) catalyst. The reaction shows first order dependence in each [HCF (III)] and [Ru (III)], zero order dependence in [4-Oxo acid] and fractional order dependence in [OH^-]. Variation of ionic strength by the addition of KNO_3 has no significant effect on the rate. The stoichiometry of the reaction is found to be 1:4 and the main oxidative products are N-(4-hydroxyphenyl) formamide and malonic acid. A mechanism involving formation of complex has been proposed and the active species of ruthenium (III) is understood as $[Ru(H_2O)_5(OH)]^{2+}$. The reaction constants involved in the different steps of mechanism are calculated. Activation parameters with respect to slow step of the mechanism are calculated and tabulated. The rate constant of catalyzed reaction is found to be 0.184×10^{-2} s^{-1}.

Key words: Hexacyanoferrate (III), Kinetics, Mechanism, Ruthenium (III), Oxidation, 4-(3-hydroxy phenyl amino)-4-oxo butanoic acid.

INTRODUCTION

4-Oxo acids are interesting substrates comparing to other organic compounds in terms of their enolization. Generally, in 4-Oxo acids, two carbon atoms separates the carboxyl and carbonyl groups and hence they behave both as acids and as oxo compounds without the direct influence of other group. These compounds readily undergo oxidation

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with various oxidants, unlike their corresponding carboxylic acids, and various mechanisms have been proposed[1-5].

In present work, we have discussed oxidation of substituted oxo acid viz. 4-(3-hydroxy phenyl amino)-4-oxo butanoic acid as shown in Fig. 1, catalyzed by ruthenium(III) in aqueous alkaline medium. Oxidation of organic compounds by hexacyanoferrate (III) is generally slow. However, trace amounts of transition metals such as Osmium (VIII)[4], Ruthenium (III)[5] and Iridium (III)[6] are normally used to catalyze many such oxidations.

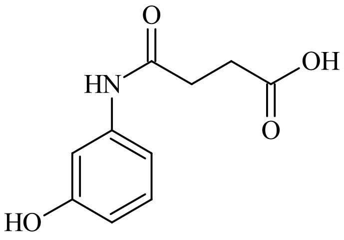


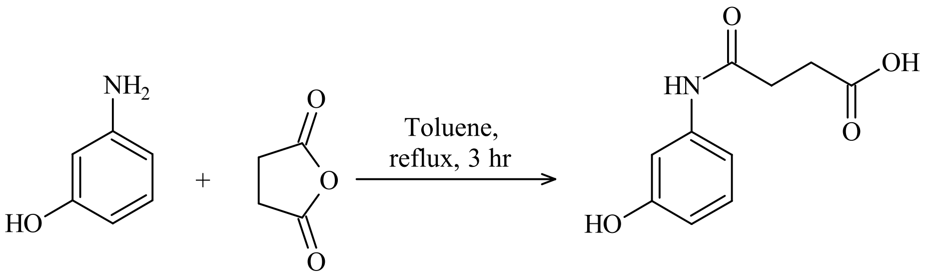
Fig. 1: 4-(3-hydroxy phenyl amino)-4-oxo butanoic acid

Ruthenium (III) chloride has been extensively used as catalyst in many redox reactions involving one or two equivalent oxidants[7-10] both in acid as well as in alkaline medium. Ru (III) has d^5 electronic configuration and forms stable cationic, anionic and neutral complexes. Aqueous solution of $RuCl_3$ is existed as its chloride complexes i.e. $[Ru(H_2O)_5Cl]^{2+}$, $[Ru(H_2O)_4Cl_2]^{+}$, $[Ru(H_2O)Cl_4]^{-}$ and $[RuCl_6]^{3-}$ in addition to its aqueousspecies as $[Ru(H_2O)_6]^{3+}$. In alkaline medium, ruthenium (III) is known to exist as its hydroxylated species[11,12] with general formula $[Ru(OH)_X(H_2O)_{6-X}]^{3-X}$ where $X < 6$ and variable which is depending upon the $[OH^-]$ used. Under present experimental condition where $[OH^-] > [Ru\ (III)]$. It is mainly existed as $[Ru(H_2O)_5(OH)]^{2+}$ as shown in Eq. 1.

EXPERIMENTAL

Materials and reagents

All chemicals used were of reagent grade. 4-(3-hydroxy phenyl amino)-4-oxo butanoic acid was synthesized (Succinic anhydride (0.01 M) was taken in toluene and heated to get clear solution. To this solution, 3-amino phenol in toluene (0.01 M) was added drop wise and heating was continued for 1 hr. Completion of reaction was monitored by TLC, obtained precipitate was filtered under vacuum, dried to give 4-(3-hydroxy phenyl amino)-4-oxo butanoic acid as white solid, which was crystallized by using aqueous ethanol and its purity was checked by its melting point).



3-Aminophenol Succinic anhydride 4-(3-Hydroxy phenyl amino)-4-oxo butanoic acid

Ruthenium(III) solution was prepared by dissolving known mass of $RuCl_3$ (S.d.fine-Chem) in 0.2 moldm^{-3} HCl. Mercury was added to ruthenium(III) solution to reduce any ruthenium(IV) formed during the preparation of ruthenium(III) stock solution and kept for about 24 hrs. Its concentration was ascertained by EDTA titration[13].

NaOH, KNO_3, Hexacyanoferrrate (III) (Merck) were of analytical reagent grade and were used as received. Spectrophotometer (Systronics Double beam 2203 smart) was used for absorption studies. Identification of products in the reaction was performed using LC-MS as shown in Fig. 2 and qualitative analysis[14].

Kinetic measurements

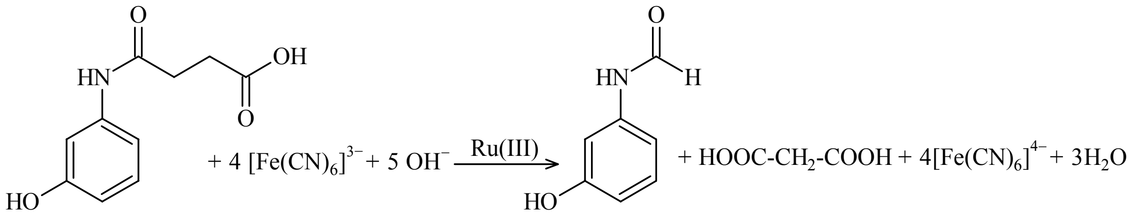
Reaction of 4-Oxo acid with HCF (III) was studied under pseudo first order condition where the [4-oxo acid] is ten times greater than [HCF (III)] at $26 \pm 0.1^{o}C$. The reaction was initiated by mixing HCF (III) to 4-Oxo acid containing required amount of NaOH, Ru (III) and KNO_3. The progress of reaction was observed spectrophotometrically by measuring decrease in absorbance of HCF (III) at 420 nm wavelength. Graphs of log [HCF (III)] versus time were plotted for pseudo first order reaction linear upto 85% completion of reaction and the rate constants (k_{obs}) were calculated.

RESULTS AND DISCUSSION

Stoichiometry and product analysis

Stoichiometry of the reaction was determined by equilibrating reaction mixture of various [HCF (III)] and [4-Oxo acid] at $26^{o}C$ for 24 hrs, keeping all other reagents constant. The unreacted hexacyanoferrate was estimated spectophotometrically at 420 nm, which reveals that one mole of 4-Oxo acid requires four moles of HCF (III) for oxidation.

The oxidative products were identified as N-(4-hydroxyphenyl) formamide, which gives molecular ion peak at 137 MHz as shown in Fig. 2 and malonic acid is identified by its melting point (135°C) and with its characteristic spot test through conversion into barbituric acid[14].



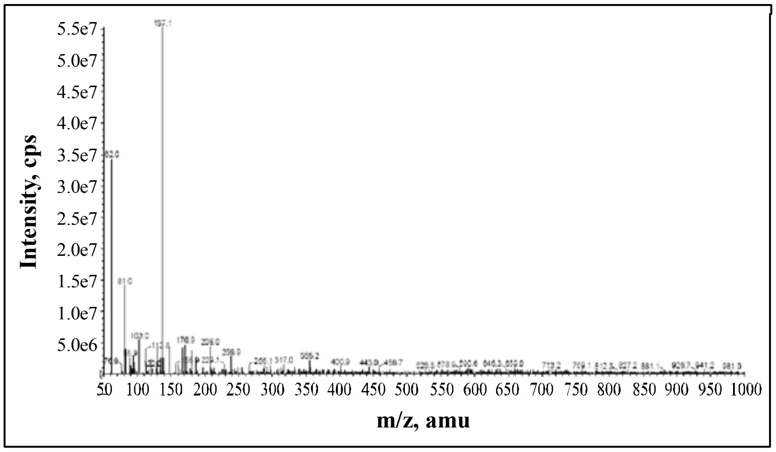


Fig. 2: LC-MS Spectra of product

Table 1: Effect of concentration of HCF (III), 4-Oxo acid, KNO_3 and Ru (III) on the rate of reaction [Temp. 26 ± 0.1°C]

[HCF] × 10^{-3} (mol dm^{-3})	[4-Oxo acid] × 10^{-2} (mol dm^{-3})	[Ru(III)] × 10^{-4} (mol dm^{-3})	[NaOH] (mol dm^{-3})	[KNO_3] (mol dm^{-3})	k_{obs} × 10^{-2} s^{-1}	K_{cal} × 10^{-2} (s^{-1})
0.25	1.25	1.25	0.1	0.01	0.118	0.216
0.75	1.25	1.25	0.1	0.01	0.166	0.216
1.25	1.25	1.25	0.1	0.01	0.184	0.216
1.75	1.25	1.25	0.1	0.01	0.201	0.216
2.25	1.25	1.25	0.1	0.01	0.214	0.216
1.25	0.25	1.25	0.1	0.01	0.186	0.216

Cont…

[HCF] × 10^{-3} (mol dm^{-3})	[4-Oxo acid] × 10^{-2} (mol dm^{-3})	[Ru(III)] × 10^{-4} (mol dm^{-3})	[NaOH] (mol dm^{-3})	[KNO_3] (mol dm^{-3})	k_{obs} × 10^{-2} s^{-1}	K_{cal} × 10^{-2} (s^{-1})
1.25	0.75	1.25	0.1	0.01	0.194	0.216
1.25	1.25	1.25	0.1	0.01	0.184	0.216
1.25	1.75	1.25	0.1	0.01	0.189	0.216
1.25	2.25	1.25	0.1	0.01	0.207	0.216
1.25	1.25	0.25	0.1	0.01	0.053	0.043
1.25	1.25	0.75	0.1	0.01	0.084	0.129
1.25	1.25	1.25	0.1	0.01	0.184	0.216
1.25	1.25	1.75	0.1	0.01	0.248	0.302
1.25	1.25	2.25	0.1	0.01	0.346	0.389
1.25	1.25	1.25	0.025	0.01	0.087	0.088
1.25	1.25	1.25	0.05	0.01	0.142	0.146
1.25	1.25	1.25	0.1	0.01	0.184	0.216
1.25	1.25	1.25	0.2	0.01	0.287	0.285
1.25	1.25	1.25	0.3	0.01	0.337	0.318
1.25	1.25	1.25	0.1	0.0025	0.202	0.216
1.25	1.25	1.25	0.1	0.005	0.207	0.216
1.25	1.25	1.25	0.1	0.01	0.184	0.216
1.25	1.25	1.25	0.1	0.02	0.194	0.216
1.25	1.25	1.25	0.1	0.03	0.201	0.216

Reaction order

HCF (III) dependence

The concentration of HCF(III) was varied from 0.25 × 10^{-3} to 2.25 × 10^{-3} moldm^{-3} at fixed concentration of 4-Oxo acid (1.25 × 10^{-2} moldm^{-3}), Ru(III) (1.25 × 10^{-4} moldm^{-3}), KNO_3 (0.01 moldm^{-3}) and OH^- (0.1 moldm^{-3}). A plot of log OD of HCF (III) versus time (sec) result in straight line, which is linear upto 80% completion of reaction as shown in Fig. 3, hence the reaction is first order with respect to oxidant.

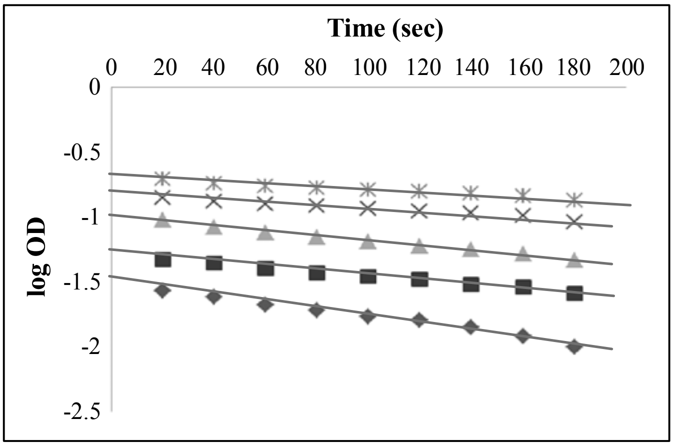


Fig. 3: A graph of log OD versus time (sec) shows first order with respect to hexacyanoferrate (III)

4-Oxo acid dependence

The concentration of 4-Oxo acid was varied from 0.25×10^{-2} to 2.25×10^{-2} moldm^{-3} at fixed concentration of HCF(III) (1.25×10^{-3} moldm^{-3}), Ru(III) (1.25×10^{-4} moldm^{-3}), KNO_3 (0.01 moldm^{-3}) and OH^- (0.1 moldm^{-3}). The pseudo-first order plots for the various concentrations of 4-Oxo acid were also linear with non-variation in the slopes which indicates that the rate of reaction was independent upon the [4-Oxo acid]. Hence, the order in 4-Oxo acid is zero in the concentration range 0.25×10^{-2} to 2.25×10^{-2} moldm^{-3} as shown in Table 1.

OH^- dependence

The reaction was carried out by varying the concentration of $[OH^-]$ from 0.025 to 0.3 moldm^{-3} atfixed concentration of HCF (III) (1.25×10^{-3} moldm^{-3}), 4-Oxo acid (1.25×10^{-2} moldm^{-3}), Ru (III) (1.25×10^{-4} moldm^{-3}) and KNO_3 (0.01 moldm^{-3}). The rate constants of the reaction were found to increase with increase in $[OH^-]$ as shown in Table 1. A plot of log k_{obs} versus log $[OH^-]$ was linear with a slope of 0.5, suggesting that reaction to be fractional order with respect to $[OH^-]$ as shown in Fig. 4.

Ru (III) dependence

The reaction was performed by varying concentration of Ru (III) from 0.25×10^{-4} moldm^{-3} to 2.25×10^{-4} moldm^{-3} at fixed concentration of HCF (III) (1.25×10^{-3} moldm^{-3}), OH^- (0.1 moldm^{-3}), 4-Oxo acid (1.25×10^{-2} moldm^{-}3) and KNO_3 (0.01 moldm^{-3}). The rate of reaction increased linearly with increase in concentration of Ru (III) as shown in Table 1 and also plot of log k_{obs} versus log [Ru (III)] indicates unit order dependence as shown in Fig. 5.

NO_3^- dependence

Ionic strength of the reaction was studied by varying concentration of KNO_3 from 0.0025 to 0.03 $moldm^{-3}$ at fixed concentration of HCF (III) (1.25×10^{-3} $moldm^{-3}$), 4-Oxo acid (1.25×10^{-2} $moldm^{-3}$), Ru (III) (1.25×10^{-4} $moldm^{-3}$) and OH^- (0.1 $moldm^{-3}$). From rate constant values as shown in Table 1 which clearly indicates, concentration of KNO_3 has no significant effect on reaction rate. The negligible effect of ionic strength in the reaction might be due the presence of various ions in reaction as shown in **Scheme 1**.

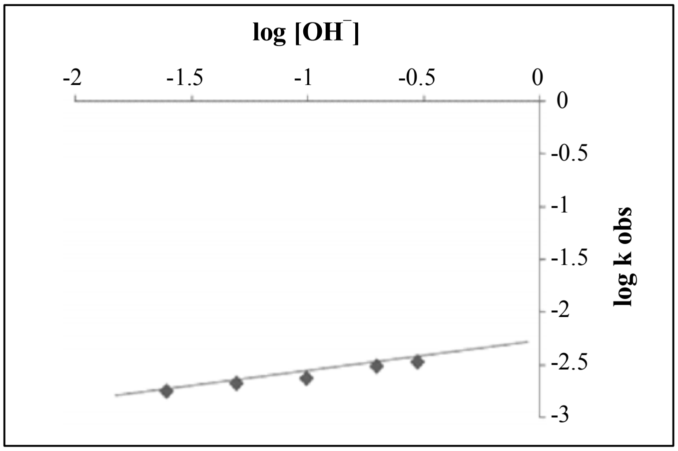


Fig. 4: A graph of log k_{obs} versus log $[OH^-]$ shows fractional order with respect to $[OH^-]$

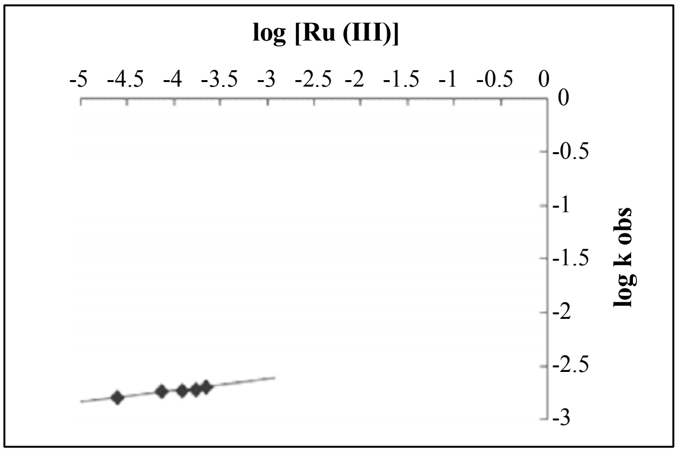


Fig. 5: A graph of log k_{obs} versus log [Ru(III)] Shows first order with respect to [Ru(III)

Test for free radicals

Involvement of free radical during oxidation of 4-Oxo acid by HCF (III) was studied by adding acrylonitrile[15,16] followed by dilution with methanol resulted in non-preceptible precipitation, which clearly indicates reaction is free from intervention of free radical.

Effect of temperature

Effect of temperature on reaction rate was studied at different temperatures (299, 303, 308, 313 and 318 K) at constant reaction condition and observed that the rate of reaction increased with increase in temperature as shown in Table 2. The Arrhenius plot of log k versus 1/T gives straight line as shown in Fig. 6. From the slope and intercept, the experimental energy of activation E_a and the frequency factor $\log_{10}A$ were calculated. The activation parameters $\Delta H^{\#}$, $\Delta S^{\#}$ and $\Delta G^{\#}$ were calculated and tabulated in Table 3.

Table 2: Effect of temperature on the rate of oxidation of 4-Oxo acid by hexacyanoferrate (III) in aqueous alkaline medium

Temp. (K)	$k_{obs} \times 10^{-2}$ (s^{-1})
299	0.184
303	0.262
308	0.371
313	0.547
318	0.729

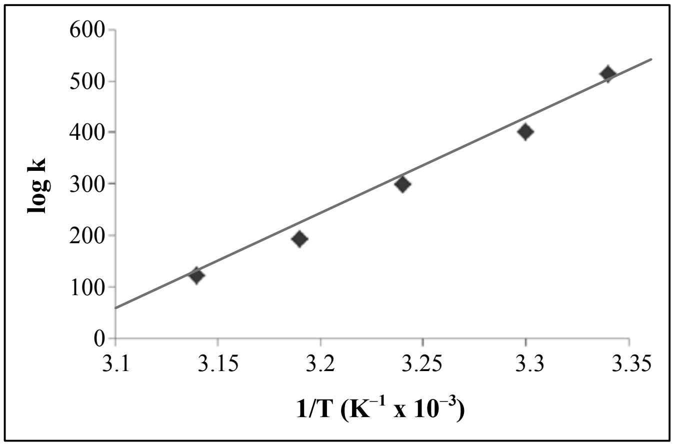


Fig. 6: A graph of log k versus 1/T (K^{-1}) (Arrhenius plot) for the calculation of activation parameters

The mechanism of reaction is written by considering unit order dependence each in [Ru (III)] and [HCF (III)], fractional order in [OH^-] and independent of rate of [4-Oxo acid]. The unit order dependence both in oxidant and catalyst reveals that reaction follows outer sphere mechanism.

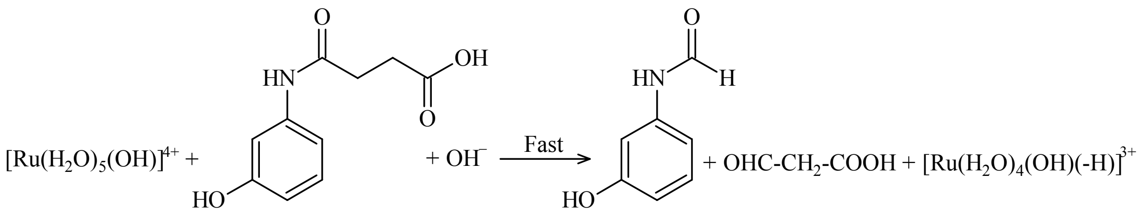
Table 3: Activation parameters of oxidation of 4-Oxo acid by Hexacyanoferrate (III) in aqueous alkaline medium

Activation parameters	Values
E_a (KJ/ mol)	67.25
$\Delta H^\#$ (KJ/mol)	64.76
$\Delta S^\#$ (J/K/mol)	-406.2
$\Delta G^\#$ (kJ/mol)	61.38
$\log_{10}A$	18.2

$$[Ru(H_2O)_6]^{3+} + OH^- \overset{k_1}{\rightleftharpoons} [Ru(H_2O)_5(OH)]^{2+} + H_2O \qquad ...(1)$$

$$[Ru(H_2O)_5(OH)]^{2+} + [Fe(CN)_6]^{3-} \xrightarrow{k,\ Slow} [Ru(H_2O)_5(OH)]^{3+} + [Fe(CN)_6]^{4-}$$

$$[Ru(H_2O)_5(OH)]^{3+} + [Fe(CN)_6]^{3-} \xrightarrow{Fast} Ru(H_2O)_5(OH)]^{4+} + [Fe(CN)_6]^{4-}$$



Scheme 1

$$[Ru(H_2O)_4(OH)(–H)]^{3+} + OH^- \xrightarrow{Fast} [Ru(H_2O)_5(OH)]^{2+}$$

$$[Ru(H_2O)_5(OH)]^{2+} + 2[Fe(CN)_6]^{3-} \xrightarrow{Fast} [Ru(H_2O)_5(OH)]^{4+} + 2[Fe(CN)_6]^{4-}$$

Cont...

$$\mathrm{OHC{-}CH_2{-}COOH + [Ru(H_2O)_5(OH)]^{4+} + OH^- \xrightarrow{Fast} HOOC{-}CH_2{-}COOH + [Ru(H_2O)_4(OH)(-H)]^{3+} + H_2O}$$

$$\mathrm{[Ru(H_2O)_4(OH)(-H)]^{3+} + OH^- \xrightarrow{Fast} [Ru(H_2O)_5(OH)]^{2+} + H_2O}$$

Scheme 2

Because of presence of intermediate in **Scheme 1**, rate law can be written by considering **Scheme 2**,

$$-d[Fe(CN)_6]^{3-}/dt = k\,[Fe(CN)_6]^{3-}\,[Ru(H_2O)_5(OH)]^{2+} \quad ...(2)$$

$$= kK_1\,[Ru(H_2O)_6]_f^{3+}\,[Fe(CN)_6]_f^{3-}\,[OH^-]_f \quad ...(3)$$

However, $[Ru(III)]_T = [Ru(H_2O)_6]_f^{3+}\,[Ru(H_2O)_5(OH)]_f^{2+}$

The other species of Ru(III) complexes like $[Ru(H_2O)_5Cl]^{2+}$, $[Ru(H_2O)_4Cl_2]^+$, $[Ru(H_2O)Cl_4]^-$ and $[RuCl_6]^{3-}$ are neglected and equation [2] can be written as –

$$[Ru\,(III)]_T = [Ru(H_2O)_6]_f^{3+} + K_1[Ru(H_2O)_6]_f^{3+}\,[OH^-]_f$$

$$[Ru\,(H_2O)_6]_f^{3+} = [Ru\,(III)]_T / 1+ K_1[OH^-]_f \quad ...(4)$$

By substituting equation (4) in equation (3), we get –

$$Rate = -d[Fe(CN)_6]^{3-}/dt = kK_1\,[Fe(CN)_6]_f^3[Ru\,(III)]_T[OH^-]_T /1+ K_1[OH^-]_f \quad ….(5)$$

The subscripts ‘f’ and ‘T’ are neglected for the verification of rate law

$$k_{obs} = kK_1\,[Ru\,(III)][OH^-]/1+ K_1[OH^-] \quad …(6)$$

$$1/k_{obs} = 1/kK_1\,[Ru\,(III)][OH^-] + 1/k\,[Ru\,(III)] \quad …(7)$$

Equation (7) is verified by plotting Ru (III)/k_{obs} versus 1/$[OH^-]$ a**s** shown in Fig. 7, from the slope and intercept of plot, reaction constants k and K_1 are calculated and the values are found tobe 33.33 and 10.83, respectively. These constants are used to calculate ‘k_{cal}’ under different experimental conditions and were found to be in close agreement with experimental results represented in Table 1.

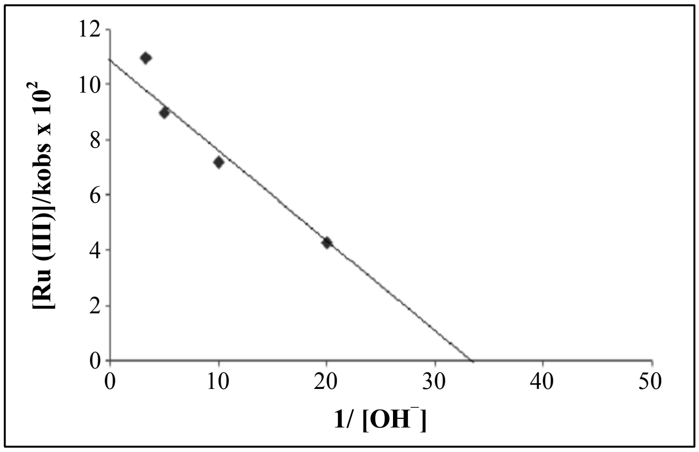


Fig. 7: A graph of [Ru (III)] /k_{obs} versus 1/[OH^-] for the verification of rate law

CONCLUSION

Ru(III) catalyzed oxidation of 4-(3-hydroxy phenyl amino)-4-oxo butanoic acid by alkaline hexacyanoferrate(III) is found to be first order with respect to HCF(III) and Ru(III), fractional order with respect to NaOH and independent of concentration of reductant. The moderate values of $\Delta H^{\#}$ and $\Delta S^{\#}$ are favorable for electron transfer reaction. The value of $\Delta H^{\#}$ was due to energy of solution changes in the transition state. Intermediate complex is more ordered than the reactants[17]. Hydroxyl ion place a crucible role during the formation of active species of ruthenium $[Ru(H_2O)_5(OH)]^{2+}$. Although a number of spectrophotometric methods are available for the oxidation of 4-Oxo acids, the present method suggests easy routine for the synthesis of carboxylic acids.

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