Ru(III) Catalysed Oxidation of (+) - (R)- Pantothenic Acid by Aqueous Alkaline $KMNO_4$: A Kinetic and mechanistic Approach

Adarsha J.R, Shailasree S, Surekha M*, Heney T.P and S.T.Nandibewoor
Global Academy of Technology, Sri Sairam College of Engineering

Department of Studies in Chemistry,
The Oxford College of Engineering, Bangalore-68, India

Abstract:

The Ru (III) catalysed oxidation of (+) - (R) – Pantothenic acid (PA) by permanganate in aqueous alkaline medium at constant ionic strength of 0.15 mol dm^{-3} has been studied by using UV-Visible spectrophotometer. The catalysed oxidation of substrate was found to occur via substrate- catalyst complex formation in equilibrium step followed by the interaction of oxidant species and a complex in a slow step to yield the products with regeneration of catalyst. The reaction constants of individual steps of the reaction mechanism have been computed and are used to regenerate rate constants. The activation parameters were calculated with respect to the slow step of the proposed mechanism. There is a good agreement between the observed and calculated rate constants under the different experimental conditions.

Keywords: Ruthenium catalyst; Pantothenic Acid ; Alkaline Permanganate; Oxidation; Kinetics.

INTRODUCTION

Oxidation by permanganate ion finds extensive applications in organic syntheses [1-7], specially since the arrival of phase–transfer catalysis [3,4,6], which permits the use of solvents like dichloromethane and benzene. Kinetic studies are important sources of mechanistic information on the reactions, as demonstrated by results referring to unsaturated acids in both aqueous [1, 3-7] and non-aqueous media [8].

In strongly alkaline medium, the stable reduction product [9] of permanganate ion is manganate ion (MnO_4^{2-}). To distinguish between a direct one electron reduction to Mn(VI) or prior formation of hypomanganate at two electron step followed by a fast reaction, no mechanistic information is available [10,11].

The manganese chemistry involved in these multistep redox reactions is an important source of information. As the manganese intermediates are relatively easy to identify when they have sufficiently long life times. The oxidation states of the intermediates allow useful conclusions to the promising reaction mechanism including the nature of the intermediates.

The substrate, Pantothenic acid (PA) is in the form of its calcium salts has been used successfully in treating the paralysis of the gastrointestinal tract after surgery, which causes the accumulation of gas and severe abdominal pain. The substrate functions as part of glucose carrier system to facilitate absorption through the intestinal mucosa, as a chick antidermatitis factor and also for promoting the growth of yeast and bacteria.

Ru(III) acts as [12] as an efficient catalyst in many redox reactions and the use of $RuCl_3$ as a homogeneous catalyst in both acid and alkaline media is of interest. Though the mechanism of catalysis dependence on the nature of substrate, oxidant, and other experimental conditions, it has been shown that metal ions act as catalysts by one of different paths

like formation of complex with reactants or free radicals etc.

Although some work on the oxidation of organic [10] and inorganic [11] substrates by permanganate in aqueous alkaline medium has been carried out. However, there is no report in the literature on the mechanistic studies of Ru(III) catalyzed oxidation of pantothenic acid in such media. The continuation of work in our laboratory [13] on alkaline permanganate oxidation is to explore the mechanism in strongly alkaline medium by selecting pantothenic acid as a substrate for the oxidation. The present study deals with the title reaction to investigate the redox chemistry of permanganate and to arrive at a plausible mechanism.

EXPERIMENTAL

Materials

Stock solutions of pantothenic acid (PA) (s.d fine chemicals) and potassium permanganate (BDH) were prepared by dissolving the appropriate amounts of sample in doubly distilled water. The stock solution of potassium permanganate was standardized against oxalic acid [14]. Potassium permanganate was prepared as described by Carring and Symons [15]. The solution was standardize by measuring the absorbance using Hitachi Model 150-20 Spectrophotometer with a 1cm cell at $ë_{max}$ = 608 nm (^{a} = 1530 + 20 dm^{-3} mol^{-1} cm^{-1}). A stock solution of Ru(III) was prepared by dissolving $RuCl_3$ (S.D Fine Chemicals) in 0.2 mol dm^3 HCl. The concentration was determined by EDTA titration [16]. Mercury was added and kept for a day to convert any Ru(IV) formed into Ru(III) during the preparation of solution.

All other reagents were of analytical grade and their solutions were prepared by dissolving required amounts of the samples in doubly distilled water. NaOH and $NaClO_4$ were used to provide the required alkalinity and to maintain the ionic strength respectively.

Kinetic measurements

All kinetic measurements were performed under pseudo-first order conditions with pantothenic acid (PA) in at least ten-fold excess over permanganate ion at a constant ionic strength of 0.20 mol dm^{-3} the reaction was initiated by mixing previously thermostated solutions of MnO_4^- and pantothenic acid, which also contained the essential quantities of NaOH and $NaClO_4$ to maintain the required alkalinity and ionic strength respectively. The temperature was maintained at 25 ± 0.1 ^{0}C. The course of reaction was followed by monitoring the decrease in absorbance of MnO_4^- in a 1cm quartz cell of a Hitachi model 150-20 Spectrophotometer at 526 nm as a function of time.. The application of Beers law to permanganate at 526 nm had upto 70% completion of the reaction and rate constant values were reproducible within ± 5%.

During the course of the reaction the colour of the solution changed from violet to blue and further to green. The UV- Vis spectrum of the green solution was identical with that of MnO_4^{2-}. The blue colour is originated from violet of permanganate and green from manganate excluding the accumulation of hypomanganate. The formation of Mn(VI) was also evidenced by (Fig.1), where the absorbance of Mn (VII) decreases at 526 nm and that of Mn(VI) increase at 608nm during the course of reaction. The effect of dissolved oxygen on the rate of the reaction was checked by preparing reaction mixture and following the reaction in an atmosphere of N_2. No significant difference between the results obtained under N_2 and in presence of air was observed. The effect of carbonate on the reaction was also studied and added carbonate had no effect on the reaction rate. However, fresh solutions were used while conducting the experiment. Regression analysis of experimental data to obtain regression coefficient 'r' and 's' the standard deviation of points from the regression line was performed with PC Pentium computer.

Stoichiometry

The reaction mixture containing the excess permanganate concentration over pantothenic acid and Ru(III) was mixed in the presence of 0.05 mol dm^3 NaOH at a constant ionic strength of 0.20 mol dm^3 and allowed to react for about 8 hours 25 ± 0.1 ^{0}C. The remaining permanganate was then analyzed with UV-Visible Spectrophotometer. The results indicated that four moles of MnO_4 consumed by one mole of pantothenic acid, according to Eq. (1).

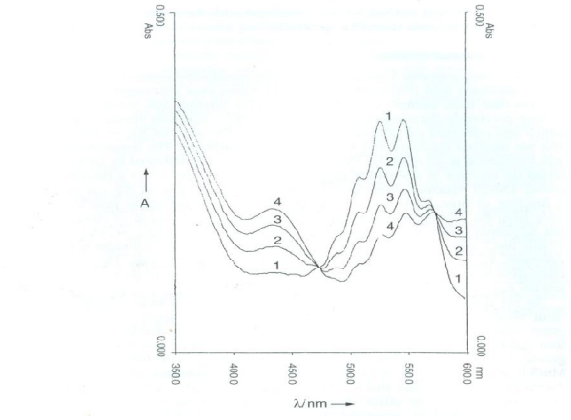


Fig.1. Spectral changes in the oxidation of pantothenic acid by alkaline permanganate with $[MnO_4^-]$= 2.0 x 10^{-4}, [PA] = 2.0 x 10^{-3}, $[OH^-]$ = 0.05, I= 0.20 mol dm^{-3} and Ru(III) = 3x 10^{-5} 25^0C with scanning time interval of one minute.

The reaction products were eluted with solvent diethylether and organic products were submitted to spot test [17] and chromatographic analysis [18] which revealed the presence of aldehyde (2, 2-dimethyl-3-hydroxypropanaldehyde). The aldehyde was also confirmed by its IR spectrum [19] which showed the band at 3463-3431cm^{-1} for OH stretching and 1727-1730cm^1 for C=O stretching respectively, whereas the band at 2925-2930 cm^{-1} is due to aldehydic stretching. The product CO_2 was qualitatively detected [20] by bubbling N_2 gas through the acidified reaction mixture and passing the liberated gas through a tube containing lime water and manganate was identified by its spectrum. Another product â- alanine was also identified by a known test. It was further observed that the aldehyde does not undergo further oxidation under the present kinetic conditions.

RESULTS AND DISCUSSION

Reaction order

The reaction orders were determined from the slopes of log $k-_{obs}$ versus log [concentration] plots by varying the concentration of oxidant, reductant, catalyst and alkali, while keeping others constant. The potassium permanganate concentration was varied in the range of 0.5 X 10^{-4} to 5.0 X10^{-4} mol dm^3 and the linearity of plots of log $c(MnO_4)$ versus time (r > 0.9989, s d" 0.032) indicated a reaction order in $c(MnO_4^-)$ as unity. This was also confirmed by varying the $c(MnO_4)$, which did not show any change in pseudo-first-order rate constants k_c (Table 1). The substrate [pantothenic acid] was varied in the range of 5.0 X 10^{-4} to 5.0 X 10^{-3} mol dm^3 at 25^0C keeping all other reactant concentrations and conditions constant. The reaction order in [pantothenic acid] was found to be less than unity (0.68) (Table 1).

Effect of initially added products

The initially added product such as manganate, ammonia and aldehyde did not have any significant effect on the rate of the reaction.

Effect of alkali

The effect of alkali on the reaction was studied at constant concentration of pantothenic acid and potassium permanganate and keeping a constant ionic strength of 0.20 mol dm^{3-} at 25 ^{0}C. The rate constant increased with increase in alkali indicating an apparent less than unit order dependence on [alkali] (Table 1).

Effect of ionic strength and solvent polarity

The ionic strength was studied by varying the sodium perchlorate concentration in the reaction medium. The ionic strength of the reaction medium was varied from 0.05 to 0.30 mol dm^{-3} at constant concentrations of permanganate, pantothenic acid, alkali and catalyst. It was found that the rate constant increased with the increase in concentration of $NaClO_4$ and the plot of log k_{obs} versus "I was linear with (r > 0.9389, s< 0.014) the positive slope (Fig.2).

The relative permittivity ($^a{}_Y$) effect was studied by varying the t-butyl alcohol- water content in the reaction mixture with all other conditions being maintain constant. Attempts to measure the relative permittivity were not successful. However, they were computed from the values of pure liquids as given in earlier work [21]. There was no reaction of the solvent with the oxidant under the experimental conditions used. The rate constant, k_{obs} increased with decrease in the dielectric constant of the medium.

Table 1. Effect of [PA], [MnO_4^-], [OH^-] and Ru(III) catalysed oxidation of pantothenic acid by permanganate in aqueous alkaline medium at 25^0 C (I = 0.20 mol dm^{-3}).

$[MnO_4^-]x10^{-4}$	$[PA]x10^3$	$K_T \times 10^3 (s^{-1})$		$K_U \times 10^3 (s^{-1})$		$K_c \times 10^3 (s^{-1})$	
$mol_{dm}-3$	mol $_{dm}-3$	Exptl*	Calc*	Exptl*	Calc*	Exptl*	Calc*
0.5	2.0	6.38	6.44	3.68	3.70	2.70	2.75
1.0	2.0	6.40	6.45	3.65	3.70	2.75	2.75
2.0	2.0	6.49	6.46	3.69	3.70	2.80	2.76
3.0	2.0	6.49	6.46	3.67	3.70	2.85	2.76
5.0	2.0	6.53	6.44	3.68	3.70	2.82	2.76
2.0	0.5	1.73	1.67	1.00	0.97	0.73	0.70
2.0	1.0	3.0	3.23	1.80	1.91	1.20	1.32
2.0	2.0	6.6	6.62	3.70	3.70	2.90	2.92
2.0	3.0	9.78	9.80	5.39	5.38	4.40	4.42
2.0	5.0	15.5	18.99	8.00	8.44	7.50	7.55

***experimental and calculated**

The plot of log k_{obs} *versus* $1/^a_Y$ was linear (Fig.2) (r > 0.9994, s d" 0.081).

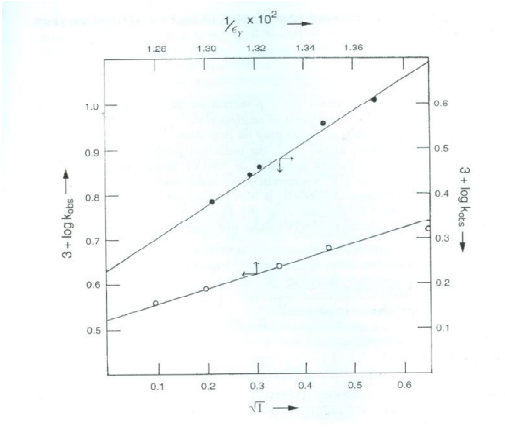


Fig.2. Plots of log k_c VS. $I^{1/2}$ and log k_c VS. $1/^a_Y$

Polymerization study

To test the intervention of free radicals the reaction mixture was mixed with acrylonitrile monomer and kept for 24 hours in an inert atmosphere. On diluting with methanol, a appearance of white precipitate indicating the intervention of free radicals in the reaction.

Effect of Catalyst

The ruthenium concentration was varied in the series of 1.0 to 10.0 x 10^{-5} mol dm^{-3} range and the linearity of plots of log [Ru(III)] vs log k_{obs} with unit slopes showed the order of the reaction was one. The uncatalysed reaction is negligible compared to catalysed reaction under the conditions used for this study

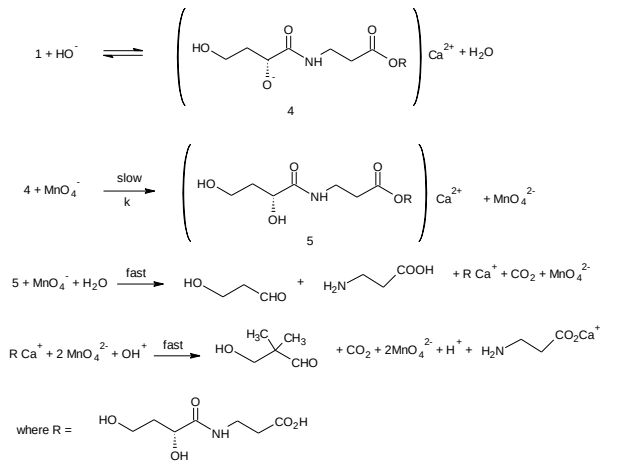
Table 2. Thermodynamic activation parameters for the Ru(III) catalysed oxidation of pantothenic acid by alkaline permanganate with respect to slow step of scheme 1.

$[MnO_4^-] = 2.0 \times 10^{-4}$, [PAN] = 2.0×10^{-3}, $[OH^-] = 0.05$, $[Ru(III)] = 3.0 \times 10^{-5}$, I = 0.20 mol dm^{-3}

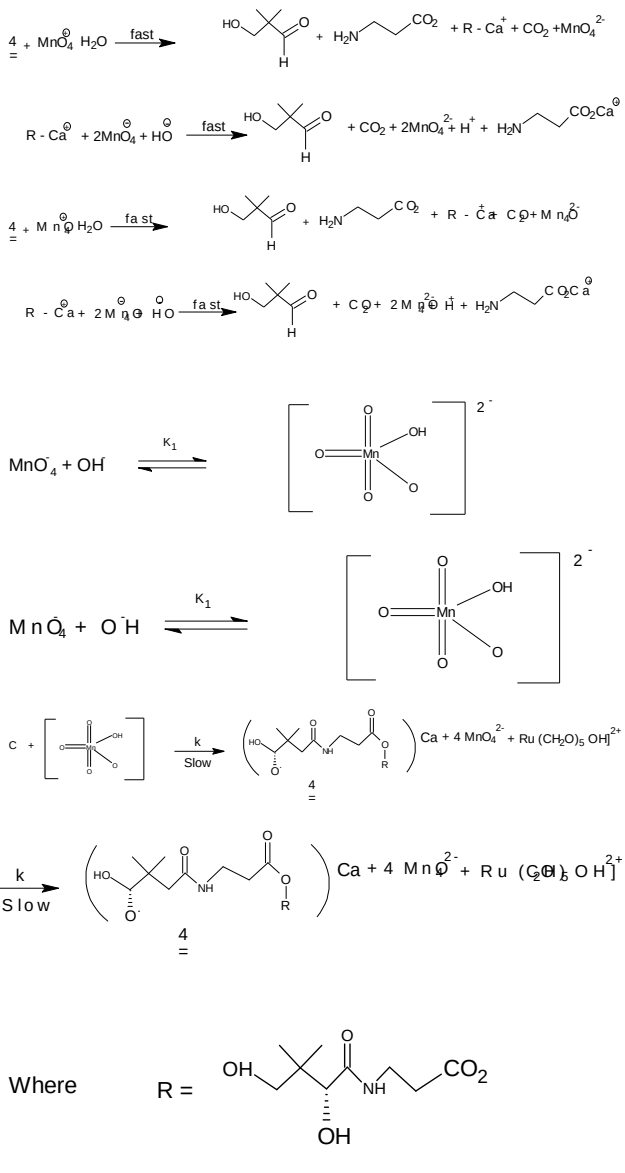
Activation parameters	Uncatalysed values	Catalysed values
Ea (kJ mol^{-1})	55 ± 3	46.86 ± 3
LogA	8.6 ± 0.4	6.46 ± 0.4
$\Delta H^{\#}$ (kJ mol^{-1})	53 ± 3	46.86 ± 3
$\Delta G^{\#}$ (kJ mol^{-1})	57 ± 3	47.24 ± 3
$\Delta S^{\#}$ (kJ mol^{-1})	-15 ± 0.8	-15 ± 0.8

Discussion

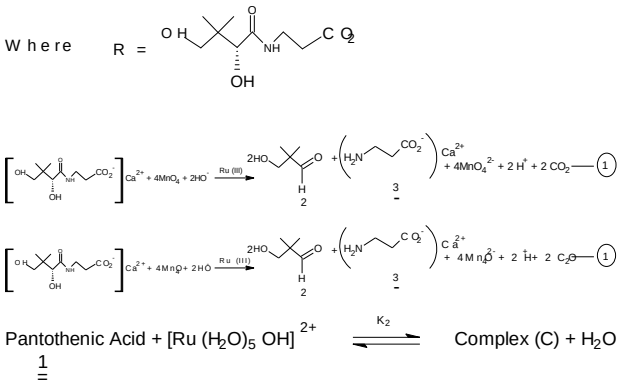
The permanganate ion, MnO_4^- is a powerful oxidant in aqueous alkaline medium. As it exhibits a multitude of oxidation states, the stoichiometric results and pH of the reaction media play an important role. Under the present experimental conditions at pH > 12, the reduction product of Mn (VII), i.e., Mn (VI) is stable and further reduction of Mn(VI) might be stopped [11]. Diode – array rapid scan UV / Vis spectrophotometric studies have shown that at pH > 12, the product of Mn (VII) is Mn(VI) and no further reduction was observed as reported by Simandi *et al* [9]. However, on prolonged standing Mn(VI) is slowly reduced to Mn(IV) under our experimental conditions. The reaction between pantothenic acid, catalyst and permanganate in alkaline medium has a stoichiometry of 1: 4 with less than unit order dependence on both alkali and pantothenic acid concentrations and a first order dependence on the $[MnO_4^-]$ and catalyst. No effect of the added products such as aldehyde was observed. The results suggest that the alkali first reacts with pantothenic acid to form its anion species with deprotonation which explains the base catalysis,



Scheme 1



Where R =



Where R =

The anionic species reacts with one molecule of oxidant i.e., permanganate to form the free radical of pantothenic acid in a slow step which is further followed by subsequent fast steps to yield the reaction products as shown in scheme 1. This is in accordance with the generally well accepted principle of non-complementary oxidations taking place in sequence of one- electron steps, the reaction between the substrate and oxidant would afford a radial intermediate. A free radical scavenging experiment revealed such a possibility. This type of radial intermediate has also been observed in earlier work [22] on the alkaline permanganate oxidations of various organic substrates.

The thermodynamic parameters [23] for the equilibrium step I of **scheme 1** and activation parameters for the rate limiting step II in scheme 1 could be evaluated as follows: Hydroxide ion concentration (as in Table 1) was varied at several temperatures and values of K were determined at each temperature. The values of K obtained are 27, 38, 50, and 70 mol dm^{-3} at 25, 30, 35, and 40 ^{0}C respectively. A Vant's Hoff plot was made for the variation of K with the temperature (i.e., log K versus 1 /T), and values of the enthalpy of the reaction ÄH, entropy of reaction ÄS and free energy of reaction ÄG were calculated as 38.93 kJ mol^{-1}, - 62.58 JK^{-1} mol^{-1} and 57.25 kJ mol^{-1}, respectively. An Arrhenius plot of log k versus 1/ T yield the activation parameters for the rate limiting step in scheme 1(Table 2). A comparison of the values supports the fact that reaction before the rate determining steps is fairly rapid has less activation energy.

Scheme 1 leads to the following rate law:

$$Rate = \frac{d\left[MnO_4^-\right]}{dt} = \frac{kK\,[PA]\,[OH\text{-}]_T\,[MnO4\text{-}]\,[Ru(III)]_T}{1+K\,[OH\text{-}]+K^2\,[PA]\,[OH\text{-}]+K[PA]} \quad (2)$$

Thus, (2) can be rearranged to the following form, which is used for the verification of rate law:

$$\frac{Rate}{\left[MnO_4^-\right]} = k_c = \frac{kK\,[PA]\,[OH\text{-}]_T\,[Ru(III)]_T}{1+K\,[OH\text{-}]+K^2\,[PA]\,[OH\text{-}]+K\,[PA]} \quad (3)$$

$$Ru(III)/\,k_c = \frac{1}{kK\,[PA]\,([OH\text{-}]_T - [PI])} + \frac{1}{k\,([OH\text{-}]_T - [PI])} + \frac{1}{k\,[PA]} + \frac{K}{k\,[PA]}$$

$$= \frac{1}{k\,[PA]}\left\{\frac{1}{K[OH\text{-}]}+1\right\} + \frac{1}{K[OH\text{-}]} + \frac{K}{k} \quad (5)$$

According to Eq. (5), the plots of Ru(III) / k_c versus 1 / [PA] and Ru(III)/ k_c versus 1 / [OH^-] were obtained (Fig. 3 & 4). The slopes and intercepts of such plots lead to the values of k and K at 25 ^{0}C as 2.7 ± 0.2 dm^3 $mol^{-1}s^{-1}$ and 30 ± 2 mol dm^{-3} respectively. Using these values, rate constants under different experimental conditions were calculated and compared with experimental data (Table 1). There is a reasonable agreement between them, which supports scheme 1.

Effect of temperature

The rate constant, k, of the slow step of scheme 3 were obtained from the intercept of the plots of $1/k_c$ versus 1/[OH^-] at different temperatures and used to calculate the activation parameters (Table 2). The values of k (s^{-1}) are (2.5 ± 0.2), (3.3 ± 0.2), (4.8 ± 0.3 and (5.5 ± 0.3) at 25, 30, 35 and 40^{0}C respectively. The activation parameters corresponding to these constants were evaluated from the plots of log k vs 1/T (Table 2).

The effect of increasing ionic strength on the rate qualitatively explains the reaction between the two negatively charged ions with Ru(III) as shown in scheme 1. The effect of solvent on the reaction kinetics has been described in detail in the earlier literature [24-28]. For the limiting case of a zero angle approach between two dipoles or an ion–dipole system. Amis has shown that a plot of log k_c vs $1/^{a}_{Y}$

gives a straight line with a negative slope for a reaction between a negative ion and a dipole or two dipoles, and with a positive slope for a ion and dipole interaction. In the present study, an increase in rate with decrease in the dielectric constant of the medium was observed, which cannot be explained by Amiss theory [29], the presence of positive ion is unlikely in the alkaline medium employed. Applying the born equation, Laidler and Eyring derived the equation

$$Lnk = lnk_0 + \frac{NZ^2e^2}{RT}\left(\frac{1}{r} - \frac{1}{r^*}\right)2^a_y \quad (6)$$

Where k_o is the rate constant in a medium of infinite dielectric constant and r and r^* refer to the radius of the reacting species and activated complex respectively. It can be seen from Eq. (6) that the rate should be greater in a medium of lower dielectric constant when $r > r^*$. There is a possibility of intramolecular hydrogen bonding that could stabilize the transition state, increasing the size of activated complex by attracting solvent molecules due to solvent effect. The fairly high positive values of $\Delta H^{\#}$, and $\Delta G^{\#}$, (Table 2) also indicate that the transition state is highly solvated which results in an increase in the size of transition state. It is likely that $r > r^*$ for pantothenic acid, thus explaining the experimental observations. Hence one can expect intramolecular hydrogen bonding is common [30] for molecules having COOH and NH_2, COOH and OH groups, etc. The moderate values of $\Delta H^{\#}$ and $\Delta S^{\#}$ were both favorable for electron- transfer processes. The negative values of $\Delta S^{\#}$ within the range of radial reactions have been ascribed [31] to the nature of electron pairing and electron unpairing processes. The difference in the activation parameters for the catalysed and uncatalysed reactions [32] explains the catalytic effect on the reaction. The reaction path is altered by lowering the energy of activation in the presence of catalyst Ru(III).

It is interesting to note that the oxidant species [MnO^-_4] required a pH >12, below which the system becomes apparent that in carrying out this reaction. It is also noteworthy that under the conditions studied, the reaction occurs in two successive one electron reduction (Scheme 1) rather than two electron reduction in a single step. Ru(III) is known to be an efficient catalyst especially in alkaline medium, which catalyses the reaction with a measurable velocity at a concentration of 10^{-6} mol dm^{-3}.

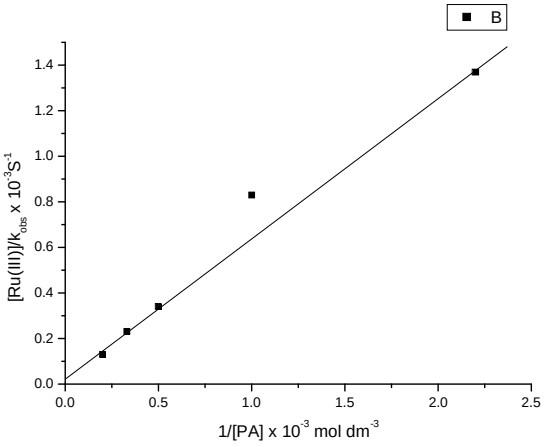


Fig- 3: Plot of Ru(III)/ k_c versus 1 / [PA] Conditions as in Table 1)

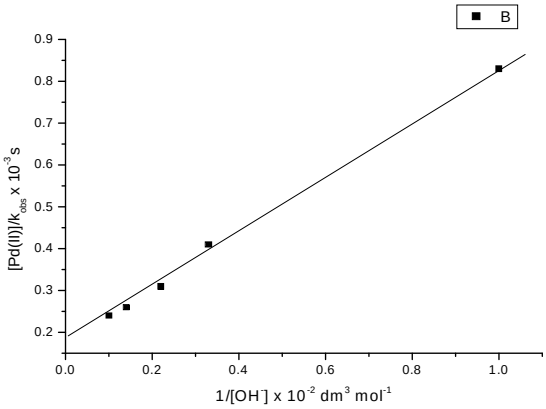


Fig- 4: Plot of Ru(III)/ k_c versus 1 / [OH^-] Conditions as in Table 1)

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