Ruthenium (III) catalyzed oxidation of hexamine by alkaline permanganate: A kinetic and mechanistic approach

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Abstract:

The kinetics of Ruthenium (III) (Ru(III)) catalyzed oxidation of hexamine by permanganate in alkaline medium at constant ionic strength (0.80mol dm^{-3}) has been studied spectrophotometrically. The reaction between hexamine and [MnO^{4-}] in 1:2 stoichiometry [Hexamine: MnO^{4-}]. The reaction showed first order kinetics in permanganate concentration and apparent less than unit order dependence in hexamine and inverse fractional order in alkali concentrations and unit order dependence on catalyst (Ru(III)). Effect of added products, ionic strength and dielectric constant of the reaction medium have been investigated. The main products were identified by spot test and IR studies. A mechanism involving the formation of a complex between hexamine and permanganate has been proposed. The active species of oxidant is [MnO^{4-}]. The reaction constants involved in the mechanism were evaluated. The activation parameters were computed with respect to the slow step of the mechanism and discussed.

Introduction

Permanganate is widely used as an oxidizing agent in synthetic as well as in analytical chemistry, and also as a disinfectant. The permanganate reactions are governed by the pH of the medium. Among the six oxidation states of manganese (+2 to +7), Permanganate, manganese (VII) is the most potent oxidation state in acid as well as in alkaline medium. The manganese chemistry

involved in these multistep redox reactions provides an important source of information as the manganese intermediates are relatively easy to identify when they have sufficiently long life times, oxidation states of the intermediates permit useful conclusions to be drawn as to the possible reaction mechanism, including the nature of intermediates. Oxidation by permanganate ion is applied extensively in organic syntheses[1–7] especially since the advent of phase transfer catalysis[3,4,6]. Kinetic studies are important sources of mechanistic information on the reactions, as demonstrated by the results referring to unsaturated acids both in aqueous [1,3,7] and non aqueous media[8]. During the oxidation, it is evident that permanganate is reduced to various oxidation states in acidic, alkaline and neutral media. Furthermore, the mechanism by which the multivalent oxidant oxidizes a substrate depends not only on the substrate but also on the medium [9] used for the study. In strongly alkaline medium, the stable reduction product[10,11] of the permanganate ion is manganate ion, MnO_4^{2-}. No mechanistic information is available to distinguish between a direct one-electron reduction to manganese(VI) and a mechanism, in which a hypomanganate is formed in a two-electron reduction followed by rapid oxidation of the hypomanganate ion[12].

Hexamethylenetetramine(hexamine) is used as corrosion inhibitor for steel, cross linking agent for phenolic resins, manufacturing explosive compounds, fuel tablet for camping stoves. The oxidation of hexamine by quinolinium dichromate in acid medium has been studied[13] and the uncatalysed reaction between permanganate and hexamine has been reported[14].

A microscopic amount of ruthenium(III) is sufficient to catalyse the reaction in the alkaline medium and a variety of mechanisms are possible. Ruthenium(III) acts as a efficient catalyst in many redox reactions, particularly in an alkaline medium[15]. The catalysis mechanism can be quite complicated, due to the formation of different intermediate complexes, free radicals and different oxidation states of ruthenium. The kinetics of fast reactions between ruthenate (VII), RuO_4^- , and manganate(VI), i.e. MnO_4^{2-} , have been studied[16]; the reaction is presumed to proceed via an outer-sphere mechanism. The rapid exchange between MnO_4^{2-} and MnO_4^- has been studied in detail by a variety of techniques[17].

The literature survey reveals that there are no reports on mechanistic studies of ruthenium(III) catalysed oxidation of hexamine by alkaline permanganate. Thus in order to explore the mechanism of oxidation and to know the active species of oxidant, reductant, and catalyst species in such media and to arrive at plausible mechanism.

Experimental

A Stock solution of hexamine (Merk), was prepared by dissolving the appropriate amount of sample in doubly distilled H_2O. The solution of potassium permanganate (BDH) was prepared and standardised against oxalic acid[18]. Potassium manganate solution was prepared as described by Carrington and Symons[19] as follows: an aqueous solution of potassium manganate was heated to boiling> $100\ ^0 C$ in 8.0 mol dm^{-3} KOH solution until it turned green. The solid potassium manganate, which formed on cooling, was recrystallised from KOH solution. Using the required amount of recrystallised sample, a stock solution was standardised by measuring the absorbance using UV-Visible spectrophotometer at 608 nm ($\varepsilon =1530 \pm 20$ dm^3 mol^{-1} cm^{-1}).

The ruthenium(III) solution was prepared by dissolving a known weight of $RuCl_3$ (S.D. Co., fine chemicals) in $HClO_4$ (0.20 mol/ dm^3). Mercury was added to the ruthenium (III) solution to reduce any ruthenium(IV) formed during the preparation of the ruthenium(III) stock solution was kept for a day. The ruthenium(III) concentration was assayed by EDTA titration[20]. All other reagents were of analytical grade and their solutions were prepared by dissolving the requisite amount of the samples in doubly distilled H_2O. Sodium hudroxide and potassium nitrate were used to provide the required alkalinity and to maintain the ionic strength respectively.

A regression analysis of experimental data, in order to obtain the regression coefficient (r) and the standard deviation (S), of points from the regression line, was performed with computer Core2 Duo Processor.

All kinetic measurements were performed under pseudo first order conditions with [hexamine] being at least thirty-fold molar excess over [MnO_4^-] ion at constant ionic strength (0.80 mol dm^{-3}). The reaction was initiated by mixing previously thermos tatted solutions of MnO_4^-, ruthenium(III) and hexamine, which also contained the necessary quantities of NaOH and KNO_3. The

temperature was maintained at 27 ± 0.1 ^{0}C. The course of reaction was followed by monitoring the decrease in absorbance of MnO^-_4 in the 1 cm quartz cell UV-Visible spectrophotometer at its absorption maximum of 608 nm, as a function of time. Earlier it was verified that negligible interference occurs from other reagents at this wavelength. The application of Beer's law to permanganate at 608nm had been verified, giving (literature $\varepsilon = 1530 \pm 20$ dm^3 mol^{-1} cm^{-1})[10]. The first order rate constants, k_{obs} were evaluated by plots of log $[A_t-A_\infty]$ versus time. Where, A_t refers to absorbance at any time t and A_∞ at infinite time, The first order plots in almost all cases were linear to 80% completion of the reaction and kc values were reproducible within $\pm 10\%$.

During the course of measurements, the solution changed from violet to blue and then to green. The spectrum of the green solution was identical to that of MnO^{2-}_4. It is probable that the blue originated from the violet of Permanganate and the green of the manganate, excluding the accumulation of hypomanganate.

The effect of dissolved oxygen on the reaction rate was checked by preparing the mixture and following the reaction in an atmosphere of dinitrogen. No significant difference between the results obtained under the nitrogen and in the presence of air was observed. In view of the ubiquitous contamination of basic solutions by carbonate, the effect of carbonate on the reaction was also studied. Added carbonate had no effect on the reaction rate. Nevertheless as a precaution, fresh solutions were used when conducting kinetic experiments. In view of the modest concentration of alkali used in the reaction medium, attention was also given to the effect of the surface of the reaction vessel on the kinetics. The use of polythene or acrylic ware and quartz or polyacrylate cells gave the same results, indicating that the surface does not have any significant effect on the rate.

RESULTS AND DISCUSSION

The reaction mixtures containing an excess of permanganate over hexamine, in 0.08 mol mol dm^{-3} NaOH at a constant ionic strength of 0.50 mol dm^{-3} were allowed to react for ca. 4 h at 27 ± 0.1 ^{0}C under an inert atmosphere. After completion of the reaction, solid KI was added following acidification by H_2SO_4 (10%), and then remaining permanganate was assayed spectrophotometrically by measuring the absorbance at 608 nm.

The reaction products were identified as formaldehyde and Oxime by their spot tests[21 a,b] and manganate by its visible spectrum.

The products formaldehyde and oxime were obtained when the product analysis was carried under pseudo first order conditions for hexamine. A test for corresponding acid was negative, so, it is concluded that the stoichiometry of the reaction under kinetic study is 1:2 as shown in below equation.
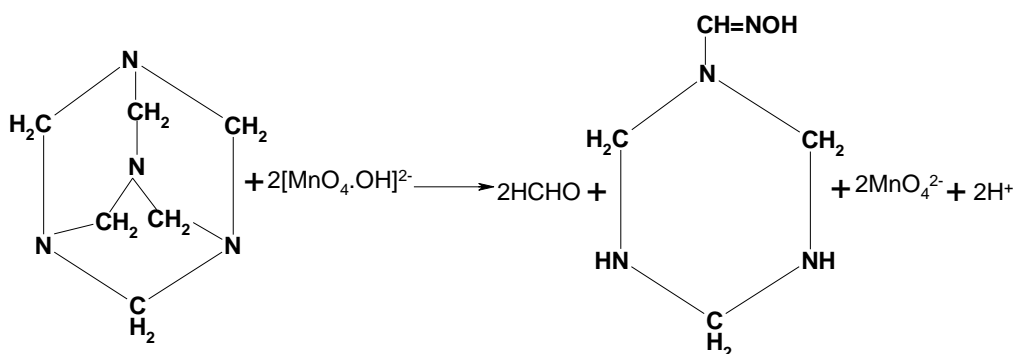
Such type of products were also obtained in previous work [22] on the oxidation hexamine by H_2O_2. It was also observed that the formaldehyde and oxime does not undergo further oxidation under the present kinetic conditions.

As the reduction of permanganate by hexamine in alkaline medium proceeds with a measurable rate in the absence of ruthenium (III), the catalysed reaction is understood to occur in parallel paths with contributions from both catalysed and uncatalysed paths. Thus,the total rate constant(k_T) is equal to the sum of the rate constants of the catalysed (k_c) and uncatalysed (k_u) reactions, so $kc = k_T - k_u$.Hence the reaction orders have been determined from the slopes of log k_c versus log(concentration) plots by varying the concentrations of hexamine, ruthenium(III) and alkali in turn while keeping the others constant.

The oxidant (potassium permanganate) concentration was varied in the range of 0.5×10^{-4} to 5.0×10^{-4} mol dm^{-3} keeping all others conditions constant Linearity of the plots of log [MnO$_4^-$] versus time, for different initial concentrations of MnO$_4^-$ indicates the order in MnO$_4^-$ was unity(r > 0.9964,

r < 0.021), This fact was also confirmed by varying $[MnO_4^-]$ which did not show any change in pseudo-first order constants, kc. (Table)

The substrates, hexamine were varied in the range of 1.0×10^{-3} to 10.0×10^{-3} mol dm^{-3} at 27 ^{0}C, keeping all other reactant concentrations and conditions constant (Table)The rate constant, kc increased with increase in concentration of hexamine, indicating a less than unit order dependence on the substrate concentration.

The alkali, $[OH^-]$ was varied in the range of 0.03 to 0.3 mol dm^{-3} at 27^{0}c, keeping all other reactant concentrations and conditions constant (Table- 1). The rate constants increases with the increase in [alkali], the order with respect to $[OH^-]$ was found to be less than unity.

The ruthenium (III) concentration was varied over the 1.0×10^{-6} to $\cdot$ 10×10^{-6} moldm^{-3} (Table 1)at constant concentration of permanganate, hexamine, alkali and at constant ionic strength of 0.8 mol dm^{-3}.The order with respect to ruthenium was found to be unity.

The effect of initially added reaction products such as formaldehyde and manganate(Mn(VI)) in the form of potassium manganate were studied in the concentration range of 1.0×10^{-5} to 1.0×10^{-4} mol dm^{-3},keeping all other reactant concentrations constant. It was found that the added products had negligible effect on the rate of reaction.

The effect of ionic strength was studied by varying the potassium nitrate concentration from 0.08 to 0.80 mol dm^{-3} at constant concentrations of permanganate, hexamine, alkali and ruthenium(III)(Table 1   ). It was found that the rate constants,k_c increased with increase in the concentration of potassium nitrate. The plot of log k_c versus $I^{1/2}$ was linear with positive slope .r > 0.9989, r <0.031).

To test the free radical intervension, the reaction mixture containing acrylonitrile was kept for 2 h in an inert atmosphere. On diluting the reaction mixture with methanol, a precipitate was obtained, indicating the intervention of free radicals in the reaction. The blank experiments of either permanganate or hexamine with acrylonitrile alone did not induce polymerization under the same conditions as those induced with reaction mixture. Intially added acrylonitrile decreases the rate indicatig the free radical intervention, which is the case in earlier work[24].

The reaction rate was measured at four different temperatures with varying [OH⁻] and [hexamine], keeping other conditions constant. The rate was found to increase with increasing temperature. The rate constants, k of the slow step of Scheme 1 were obtained from the intercept of the plots of $[RuIII]/k_c$ versus $1/[OH^-]$ (r > 0.9880, r < 0.0241) at four different temperatures. The values of $k \times 10^{-3} \, s^{-1}$ were 6.471, 6.988, 7.454, 8.200 at 27,32,37,42^{0}C respectively. From these data the values of $Ea, \Delta H^\#$, and $\Delta S^\#$ are obtained as $12.16\pm0.5, 09.60\pm0.8$ and $-33.39\pm0.9 (JK^{-1}mol^{-1})$ respectively. The experimental results can be accommodated in Scheme 1 as given below.
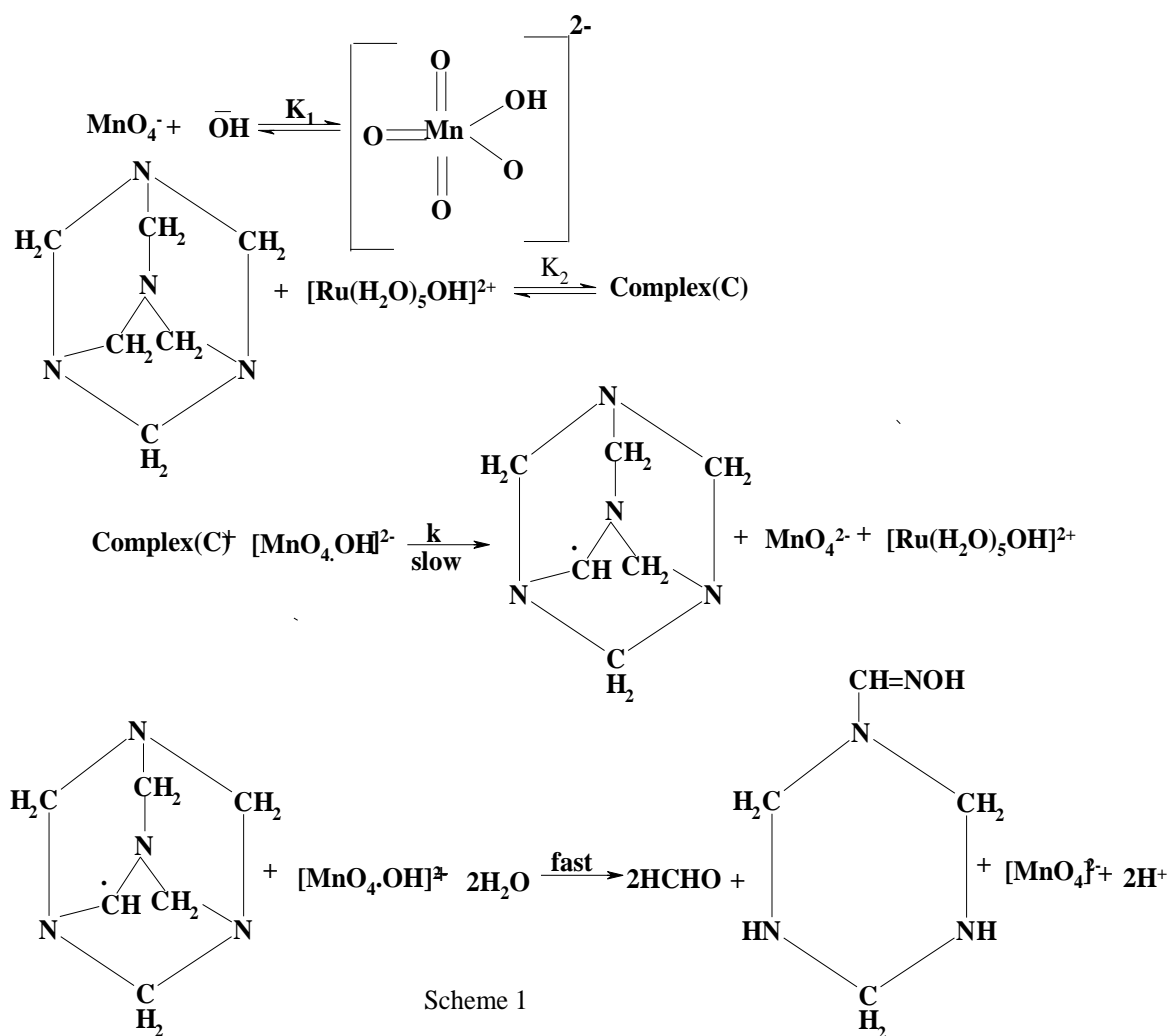
Scheme 1

The evidence for complex formation is obtained by kinetic studies (i.e., from the Michaelis-Menten plot). The plot of [Ru(III)]/k_c versus 1/[hexamine] is linear with an non zero intercept. Such type of substrate-catalyst complex formation has been reported previously[28].

The mechanism is also supported by moderate values of activation parameters. A negative value of $\Delta S^{\#}$ suggests that the intermediate complex is more ordered than the reactants. The observed modest enthalpy of activation, and relatively low value of the entropy of activation and higher rate constant for the slow step of the mechanism, indicate that oxidation presumably occurs by an inner-sphere mechanism. This conclusion is supported by earlier work[29].

The permanganate oxidation of hexamine in aqueous alkaline medium proceeds at a measurable rate in the absence of ruthenium(III) catalyst. Hence, in the presence of catalyst the reaction is understood to occur parallel path with contribution from the uncatalysed paths. Thus,the total rate constants(k_T) is equal to the sum of the rate constants of the catalysed (k_c) and uncatalysed (k_u) reactions.

Since scheme 1 is in accordance with generally well accepted principle of non complementary oxidations taking place in a sequence of one-electron steps, the reaction would involve a radical intermediate. Since permanganate is a one electron oxidant in alkaline medium, the reaction between substrate and oxidant would give rise to a radical intermediate. A Free radical scavenging experiment revealed such a possibility. This type of radical intervention in the oxidation of hexamine has also been observed earlier work[24].

[Ru(III)]/k_c versus 1/[OH⁻] be linear (Fig 1) From the slopes and intercepts of such plots,the values of K_1,K_2 and k,were found to be 8.67 ± 0.58 dm^3 mol^{-1},218.31 ± 0.08 dm^3 mol^{-1} and $(6.47 \pm 0.2) \times 10^3$ dm^3 mol⁻s^{-1},respectively.Using these values, the rate constants under different experimental conditions were calculated by equation(8). and compared with experimental data Experimental and calculated values agreed reasonably well supporting the assumptions of scheme 1.The value of K_1 is in good agreement with earlier work[14]. The difference in the activation parameters for the catalysed and uncatalysed reactions[14] explains the catalytic effect on the reaction. The catalyst ruthenium(III) forms the complex with hexamine, which shows more reducing property than hexamine itself. Hence,

the catalyst Ru(III) lowers the energy of activation,i.e.,it provides an alternative pathway with lower activation parameters for the reaction.

It becomes apparent that in carrying out this reaction the role of pH in a reaction medium is crucial. It is also noteworthy that under the conditions studied the reaction occurs in two successive one-electron reductions rather than two-electron in a single step (Scheme 1). The description of the mechanism is consistent with all the experimental evidence including both kinetic and product studies.

Effect of variation of$[MnO_4^-]$,[hexamine], [Ru(III)] and [OH$^-$] on Ru(III) catalysed oxidation of hexamine by KMnO$_4$ in aqueous alkaline medium at 27 ^{0}C and I = 0.80 mol dm^{-3},

$[MnO4^-]X10^4$	$[Hex]x10^3$	$[OH^-]$	$[Ru^{III}]x10^6$	k_Tx10^3,s^{-1}	k_ux10^3,s^{-1}	$k_cx10^2,s-1$	
						Expt.	Calc.
0.5	6.0	0.08	5.0	8.72	1.51	7.21	7.51
1.0	6.0	0.08	5.0	8.76	1.53	7.23	7.51
2.0	6.0	0.08	5.0	8.74	1.50	7.24	7.51
3.0	6.0	0.08	5.0	8.70	1.50	7.25	7.51
5.0	6.0	0.08	5.0	8.78	1.52	7.26	7.51
2.0	1.0	0.08	5.0	3.00	0.60	2.40	2.37
2.0	4.0	0.08	5.0	6.60	1.20	5.40	6.17
2.0	6.0	0.08	5.0	8.74	1.50	7.24	7.51
2.0	8.0	0.08	5.0	9.86	1.70	8.16	8.42
2.0	10.0	0.08	5.0	15.08	2.96	12.18	9.09
2.0	6.0	0.03	5.0	4.51	0.91	3.60	3.78
2.0	6.0	0.05	5.0	6.97	1.24	5.72	5.55
2.0	6.0	0.08	5.0	8.74	1.50	7.24	7.51
2.0	6.0	0.10	5.0	10.54	2.11	8.43	8.50
2.0	6.0	0.30	5.0	16.50	4.50	12.00	13.25
2.0	6.0	0.08	1.0	1.80	0.30	1.50	1.50
2.0	6.0	0.08	3.0	5.37	0.96	4.40	4.50
2.0	6.0	0.08	5.0	8.74	1.50	7.24	7.51
2.0	6.0	0.08	8.0	14.22	2.42	11.80	12.00
2.0	6.0	0.08	10.0	17.91	3.20	14.90	15.03

Error:10 ± 5%
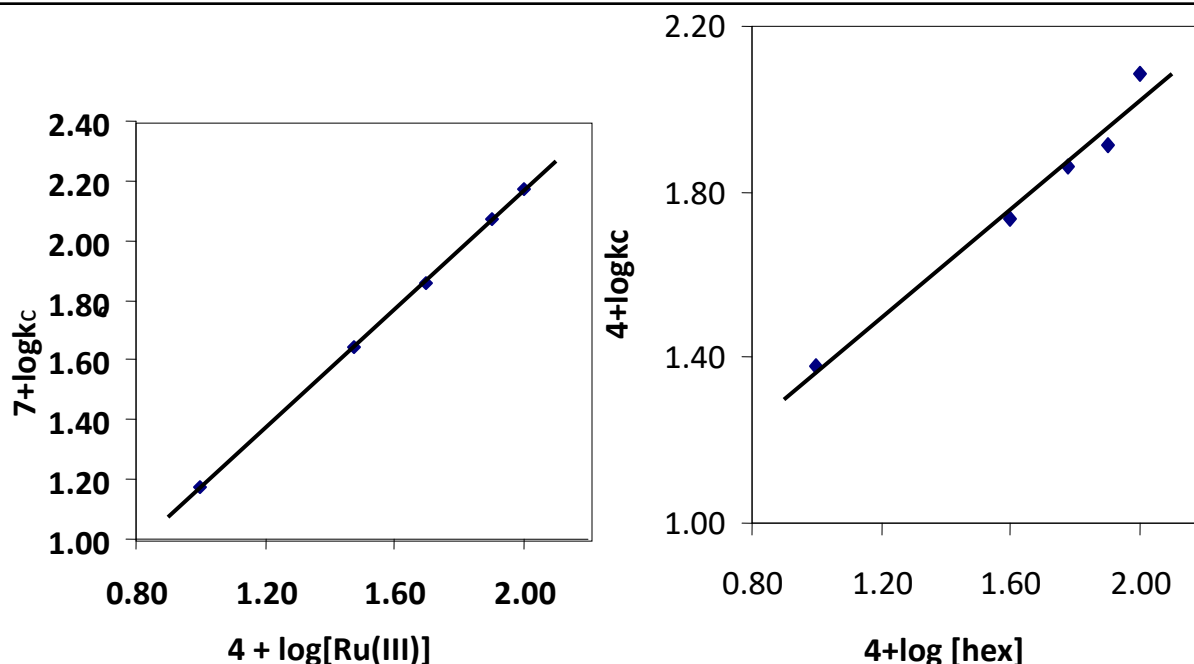
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Appendix-1 & 2 ----

Given below

APPENDIX-1

Schme 1 leads to the rate law as follows,

$$\text{Rate} = \frac{d[MnO_4^-]}{d} = k\,[C]\,[MnO_4.OH]^{2-}$$

$$= kK_2[Ru(III)]_f[Hex]_f\,K_1[OH^-][MnO_4^-]$$

$$= kK_2[Ru(III)]_f[Hex]_f\,K_1[OH^-][MnO_4^-]$$

$$= kK_1K_2[Ru(III)]_f[Hex]_f\,[OH^-]_f[MnO_4^-]_f \qquad (1)$$

The total $[MnO_4^-]$ is given by,(where t aand f stands for total and

$$[MnO_4^-]_t = [MnO_4^-]_f + [MnO_4^-][OH^-]_f$$

$$= [MnO_4^-]_f + K_1[MnO_4^-][OH^-]_f$$

$$= [MnO_4^-]_f + K_1[MnO_4^-][OH^-]_f$$

$$[MnO_4^-]_t = [MnO_4^-]_f\,\{1+K_1[OH^-]_f$$

Therefore

$$[MnO_4^-]_f = \frac{[MnO_4^-]_t}{1+K_1[OH^-]} \qquad (2)$$

Similarly,

$$[Hex]_f = [Hex]_f + [C]$$

$$= [Hex]f + K_2[Hex]_f[Ru(III)]_f$$

$$= [Hex]_f\{1 + K_2[Ru(III)]_f$$

Similarly,

$$[OH^-]_t = [OH^-]_f + [MnO_4.OH]^{2-}$$

$$= [OH^-]_f + K_1[OH^-]_f\,[MnO_4^-]_f$$

$$= [OH^-]_f\,\{1+K_1\,[MnO_4^-]_f$$

Therefore,

$$[OH^-]_f = \frac{[OH^-]_t}{1+K_1[MnO_4^-]_f} \qquad [75] \qquad (4)$$

APPENDIX-2

Similarly

$[Ru(III$ $= [Ru(H_2O)_5OH]^{2+}_f + [Complex]$

$= [Ru(H_2O)_5OH]^{2+}_f$

$[Ru(III)]$ $= [Ru(H_2O)_5OH]^{2+}_f \{1+K_2 [Hex]_f\}$

Theref

$[[Ru(II$ $\dfrac{\quad\quad}{1+}$ (5

Substituting equation (2),(3),(4),and (5) in equation

$$\text{Rate}_{ } \quad \frac{kK_1K_2 [Hex]_f[OH^-][Ru(III)]_f [MnO_4^-]}{\{(1+ K_1[OH^-](1+ K_2[Ru(III)])(1 + K_1[MnO_4^-}} \quad (6$$

In view of the low concentration of catalasyt and oxidant used the terms $(1+ K_2[Ru(III)])$

And $(1 + K_1[MnO_4^-])$ are neglected.

$$\text{Rate}_{ } - \frac{kK_1K_2 [Hex]_f[OH^-][Ru(III)]_f [MnO_4^-]}{\{(1+ K_1[OH^-}} \quad (7$$

Equation (7) becomes equation (8)

$$k_c = \frac{\text{Rate}}{[\text{Mn}} - \frac{kK_1K_2 [Hex] [OH^-}{\{(1+ K_1K_2 K_2[Hex][OH^-]+ K_2Hex]+ K_2[MnO_4} \quad (8$$

The above equation (8) can be rearranged to the following form (9),which is used for the

$$\frac{[Ru(III}{k} = \frac{1}{kK_1K_2[OH^-][H} - \frac{1}{kK_2[Hex} - \frac{1}{kK_1[OH^-} + \frac{1}{k} \quad (9$$

Order with respect to [Ru(III)] on the ruthenium(III) catalysed permanganate oxidation of hexamine in aqueous alkaline medium at 27 ^{0}C(Conditions as in Table 1).