Kinetics of Oxidation of 1-(4-Chlorobenzyl)-4-piperidiamine by Potassium Permanganate in Aqueous Alkaline Medium

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ABSTRACT

The Kinetics of oxidation of 1-(4-Chlorobenzyl)-4-piperidiamine by $KMnO_4$ in aqueous alkaline medium was studied spectrophotometrically at constant ionic strength 0.01 mol/dm^3. The reaction exhibits 1:3 stoichiometry. The reaction is pseudo first order with respect to Oxidant, first order with respect to reductant and fractional order with respect to medium. The activation parameters E_a (kJ/mol), $\Delta H^{\#}$ (kJ/mol), $\Delta S^{\#}$ (J/K/mol) and $\Delta G^{\#}$ (kJ/mol) for the slow step were calculated. Effect of ionic strength and dielectric constant of medium has been studied. Rate constant of rate determining step was calculated and a suitable mechanism has been proposed.

1. INTRODUCTION

Permanganate is a unique, widely used oxidizing agent in neutral, alkaline and acid medium [1]in synthetic and analytical chemistry [2] due to its several advantages as an analytical reagent e.g. vividly coloured, strong, serving as its own indicator.

In general potassium permanganate is a powerful oxidant in aqueous alkaline medium. It is interesting because manganese exhibits variable oxidation state from +2 to +7. In strong alkaline medium, the stable reduction product[4,5,6] is the manganate ion, MnO_4^{2-}.

No mechanistic information is available to distinguish between direct one-electron reduction to Mn (VI) and one in which a hypomanganate is formed in a two-electron step followed by rapid reaction[7].

Permanganates ions oxidize a greater variety of substrates and find extensive applications in organic synthesis[8-14] especially after the advent of phase transfer catalysis , which permits the use of solvents such as methylene chloride and benzene. Kinetic studies constitute an important source of mechanistic information on the reaction, as demonstrated by results referring to unsaturated acids in both aqueous and non-aqueous media[15].

The permanganate oxidation of large biological molecule such as nucleic acid[16,17], protein[18], thymine[19], uracil[20] and several amino acid[21-26] have already been reported. This paper presents how manganese shows the change of various oxidation states during the course of the reaction. The product of the reaction have been isolated and characterized. Possible mechanism of the reaction has been suggested. Solvent effect on such reaction has been studied. The potassium permanganate in alkaline medium exists as $MnO_4(OH)^{2-}$ species[24]. The active species reacts with the substrate and forms an intermediate complex and the complex decompose into product.

In the present study the kinetics of oxidation of compound 1-(4-Chlorobenzyl)-4-piperidiamine (Figure(1)) has been studied in alkaline medium. Piperidiamine Drugs used to prevent Nausea or Vomiting.
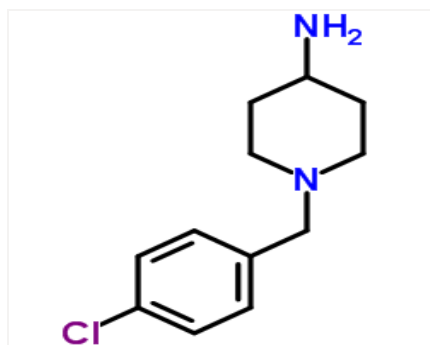
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Figure (1): Structure of 1-(4-Chlorobenzyl)-4-piperidiamine

EXPERIMENTAL

2. MATERIALS AND METHODS

2.1. Materials and reagents used

All Chemicals and reagents used were analytical reagent grade and solutions were prepared using double distilled water, free from dissolved oxygen. Potassium permanganate was prepared by the requisite amount of salt in doubly distilled water. The solution was standardized by measuring the absorbance using UV-visible spectrophotometer at 525 nm.

1-(4-Chlorobenzyl)-4-piperidiamine was prepared by dissolving requisite amount of sample in 1ml NaOH and diluted using distilled water. NaOH, KNO_3 were also prepared in doubly distilled water and standardized by standard methods Vogel book reference[27]. Absorbance was recorded on Systronic UV-Vis Spectrophotometer at wave length 525 nm.

2.2. Kinetic Studies

The kinetics of oxidation of 1-(4-Chlorobenzyl)-4-piperidiamine was studied spectrophotometrically under pseudo-first order conditions with [1-(4-Chlorobenzyl)-4-piperidiamine] : [$KMnO_4$] > 10:1 at constant ionic strength (I = 0.1 mol dm^{-3}). The [1-(4-Chlorobenzyl)-4-piperidiamine] was varied from 5×10^{-4} to 4.5×10^{-3} mol dm^{-3} and [OH^-] was varied from 2.5×10^{-3} to 0.02 mol dm^{-3}.

The application of Beer's law for permanganate at 525 nm had earlier been verified[27], giving $\varepsilon = 2389 \pm 50$ dm^3 mol^{-1} cm^{-1} (Literature10 $\varepsilon = 2400$ dm^{-3} mol^{-1} cm^{-1}) as a function of time.

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The reaction kinetics was followed by monitoring disappearance of Mn (VII) at λ_{max} = 525nm using conventional Systronics UV-VIS spectrophotometer equipped with a thermostatic bath for temperature control with an accuracy of $\pm$ 0.1^{o}C. The pseudo-first order rate constant (k_{obs}) were evaluated from the slope of linear plots of logA versus time(s).

The orders for various species were determined from the slopes of plots of log k_{obs} versus respective log concentration of substrate, permanganate and sodium hydroxide and in turn while keeping all other concentrations and conditions constant.

3. RESULTS

3.1. Stoichiometry and product analysis

Different sets of the reaction mixture containing different amounts of reactants [MnO_4^-] > [1-(4-Chlorobenzyl)-4-piperidiamine] at constant [OH^-] = 0.1mol dm^{-3} and constant ionic strength (I=0.1mol dm^{-3}) were allowed to react for 24hrs. The remaining MnO_4^- was analyzed spectrophotometrically. The results showed that three moles of MnO_4^- reacted with one mole of 1-(4-Chlorobenzyl)-4-piperidiamine. From the above stoichiometric study it is calculated that the stoichiometry of the reaction is as shown below.
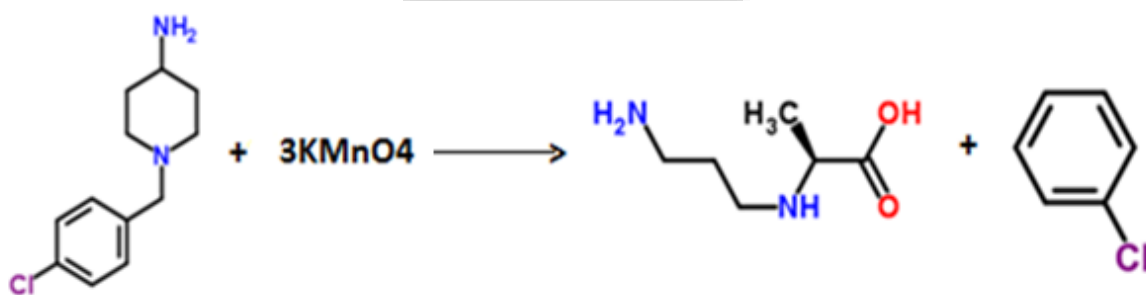
In order to get the reaction product 0.0015mol $KMnO_4$ and 0.01mol of 1-(4-Chlorobenzyl)-4-piperidiamine were mixed in a container and [OH^-] was kept at 0.01mol dm^{-3}. The reaction mixture was allowed to stand about 24hrs at 298K for completion of the reaction. The product was identified by LC-MS. **The peak at 112 indicates the presence of chlorobenzene and the peak near to 147 confirms the product as L-Alanine, N-(2-aminomethylethyl)-carboxylic acid.**

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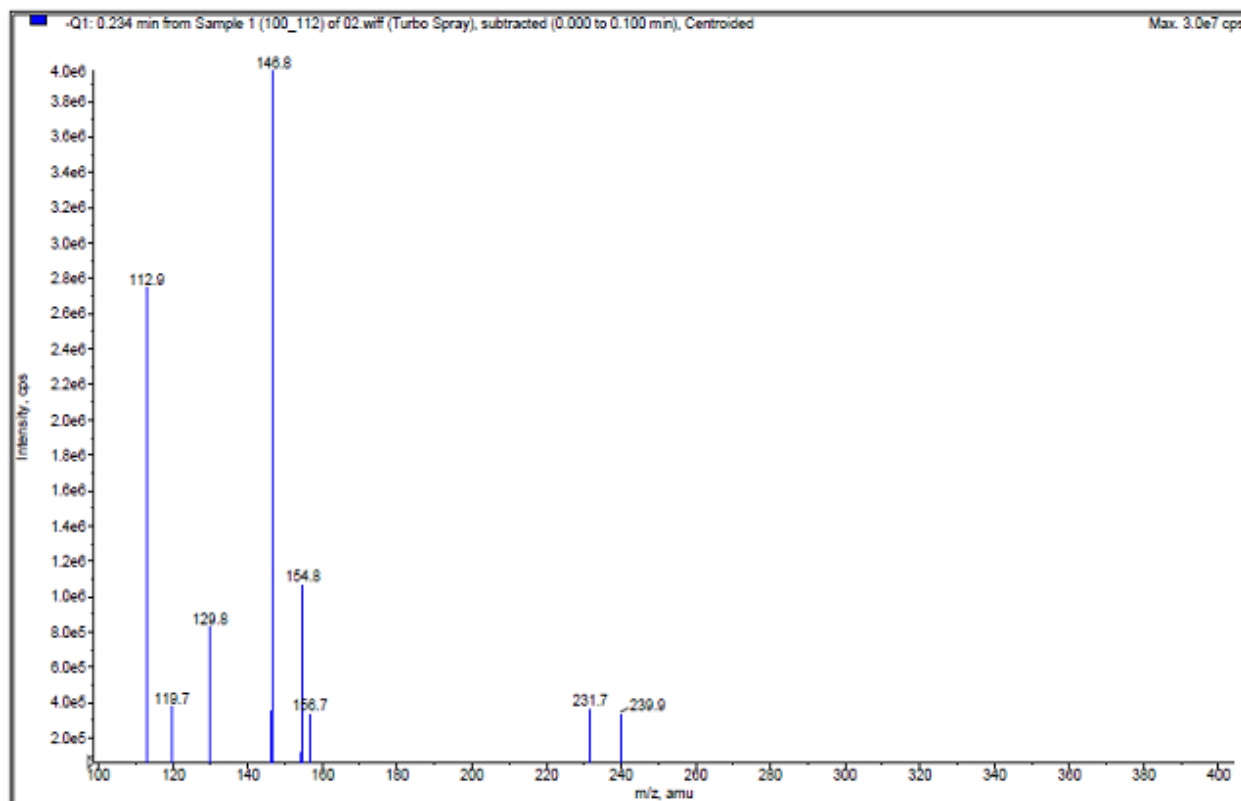
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Figure (2): LC-MS for the product analysis. The peak at 112 indicates the presence of chlorobenzene and the peak near to 147 confirms the product as L-Alanine, N-(2-aminomethylethyl)-carboxylic acid.

3.2. Reaction Order

The electron transfer reaction between 1-(4-Chlorobenzyl)-4-piperidiamine and alkaline Mn(VII) has been studied over the range 5×10^{-4} to 4.5×10^{-3} mol dm^{-3} and 5×10^{-5} to 4.5×10^{-4} mol dm^{-3} respectively; [OH$^-$] in the range of 2.5×10^{-3} to 0.02 mol dm^{-3}; temperature from 298K to 318K and I=2.5×10^{-3} to 0.03 mol dm^{-3}.

The reaction order were determined using the slopes of log k_{obs} versus log[MnO$_4^-$] plots by varying the concentrations of the reductant and OH$^-$ while keeping other factors constant. With constant concentrations of 1-(4-Chlorobenzyl)-4-piperidiamine 2.5×10^{-3} mol dm^{-3} and alkali 0.01 mol dm^{-3} and ionic strength 0.01 mol dm^{-3}, the permanganate concentration varied from 5×10^{-5} to 4.5×10^{-4} mol dm^{-3}. The linearity of plots of log (absorbance) versus time, for different concentrations of permanganate indicates that the order in Mn (VII) is unity (Fig:1). The 1-(4-

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Chlorobenzyl)-4-piperidiamine concentration was varied from 5×10^{-4} to 4.5×10^{-3} mol dm^{-3} at constant alkali and permanganate concentrations and constant ionic strength of 0.01mol dm^{-3} at 298K. The k_{obs} values increased with an increase in 1-(4-Chlorobenzyl)-4-piperidiamine over the concentration range

3.2.1. Effect of potassium permanganate

The concentration of potassium permanganate was varied from 5×10^{-5} to 4.5×10^{-4} mol dm^{-3} at fixed concentration of other reactants. A plot of initial rates versus concentration of potassium permanganate showed the first order dependence with the oxidant.(Figure : 3) The constant values of k (Table 1) indicate the unit order with respect to KMnO$_4$.

3.2.2. Effect of 1-(4-Chlorobenzyl)-4-piperidiamine

The concentration of 1-(4-Chlorobenzyl)-4-piperidiamine was varied from 5×10^{-4} to 4.5×10^{-3} mol dm^{-3} at fixed concentration of other reactants. A plot of initial rates versus concentration of 1-(4-Chorobenzyl)-4-piperidiamine shows the fractional order dependence with substrate.
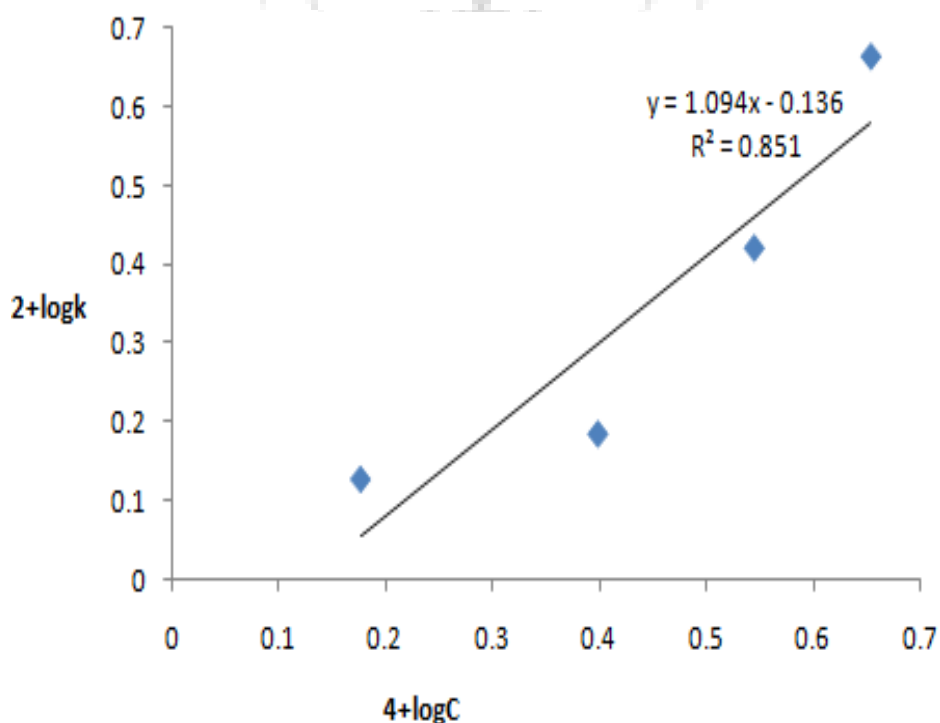

Figure (3)

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3.2.3. Effect of NaOH

The concentration of sodium hydroxide was varied from 2.5×10^{-3} moldm^{-3} to 0.02 moldm^{-3} by keeping all other reactant concentrations constant. There was an increase in rate with NaOH concentration. A plot of initial rates versus concentration of sodium hydroxide shows the fractional order dependence with sodium hydroxide.

3.2.4. Effect of Temperature

The reaction rates are studied at four different temperatures 298K, 303K, 308K, 313K and 318K under varying concentrations of KMnO$_4$ and the substrate The rate constants (k) of the slow step of the reaction mechanism were obtained from the slopes of graph plotted between log A versus time. Rate of reactions increases with increase of temperature.
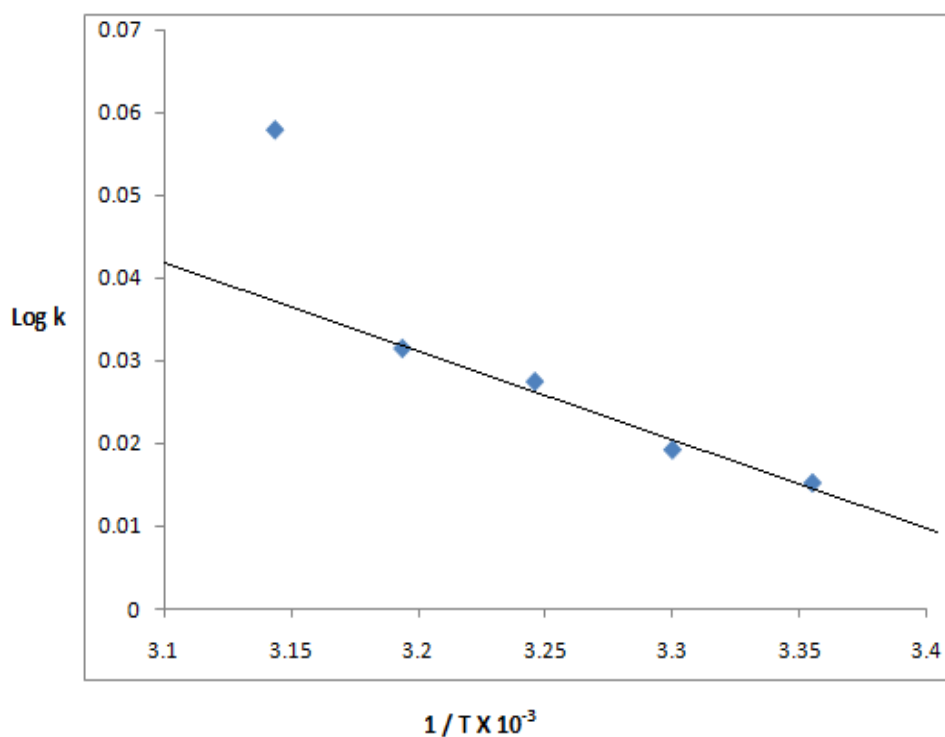

Figure (4): A plot of log k against 1/T (K^{-1}) for the calculation of activation parameters.

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3.2.5 Effect of KNO₃

The concentration of KNO_3 was varied from 2.5×10^{-3} moldm^{-3} to 0.03 mol dm^{-3} by keeping all other reactant concentrations constant. A plot of initial rates versus concentration of KNO_3 has shown the fractional order dependence with substrate.

Table (I): Effect of 1-(4-Chlorobenzyl)-4-piperidiamine, [KMnO₄], [OH⁻] on reaction rate at Temperature = 25 ± 0.1ºC, μ=0.01 mol dm⁻³.

[KMnO₄] x 10⁻⁴ (mol dm⁻³)	1-(4-Chloro benzyl)-4-piperidiamine x 10⁻³ (mol dm⁻³)	[OH⁻] x 10⁻¹ (mol dm⁻³)	[NO³⁻] x 10⁻² (mol dm⁻³)	k_{obs}	k_{cal}
0. 5	2.5	0.1	0.1	0.0123	0.0110
1.5	2.5	0.1	0.1	0.0134	0.0180
2.5	2.5	0.1	0.1	0.0153	0.0192
3.5	2.5	0.1	0.1	0.0263	0.0199
4.5	2.5	0.1	0.1	0.0460	0.0399
2.5	0.5	0.1	0.1	0.0333	0.005
2.5	1.5	0.1	0.1	0.0355	0.015
2.5	2.5	0.1	0.1	0.0153	0.023
2.5	3.5	0.1	0.1	0.0143	0.0305
2.5	4.5	0.1	0.1	0.0115	0.0369
2.5	2.5	0.025	0.1	0.0066	0.0067
2.5	2.5	0.05	0.1	0.0120	0.0128
2.5	2.5	0.1	0.1	0.0153	0.023
2.5	2.5	0.15	0.1	0.0230	0.0322
2.5	2.5	0.2	0.1	0.4318	0.0398
2.5	2.5	0.1	0.25	0.0418	0.0390
2.5	2.5	0.1	0.5	0.0230	0.02
2.5	2.5	0.1	1	0.0153	0.0191
2.5	2.5	0.1	2	0.0085	0.011
2.5	2.5	0.1	3	0.0080	0.009

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Table (II): Rate Constant with respect to Temperature for oxidation of 1-(4-Chlorobenzyl)-4-piperidiamine by KMnO₄ in aqueous alkaline medium
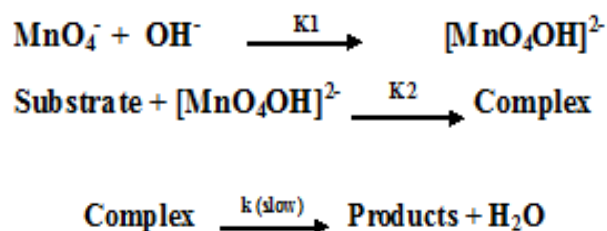
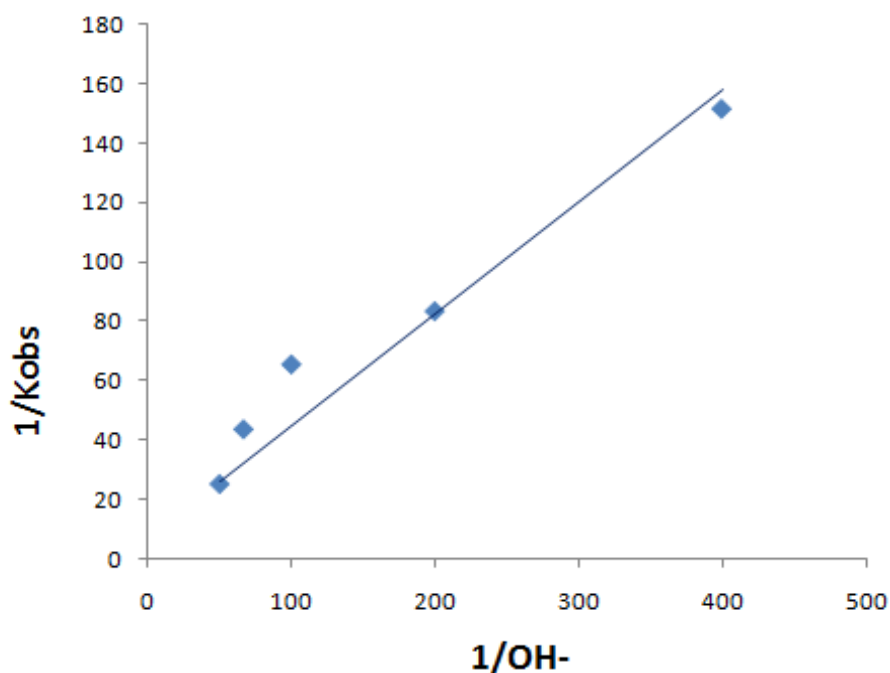| Temperature in (K)	$k \times 10^{-2}(s^{-1})$
298	1.53
328	1.93
308	2.75
313	3.15
318	5.78

Table (III): The Activation Parameters for oxidation of 1-(4-Chlorobenzyl)-4-piperidiamine by KMnO₄ in aqueous alkaline medium

Parameters	Values
E_a (kJ/mol)	19.74
$\Delta H^{\#}$ (kJmol^{-1})	2457.76
$\Delta S^{\#}$ (J K^{-1}mol^{-1})	-185.8
$\Delta G^{\#}$ (kJmol^{-1})	83.384

Activation parameters (E_a, $\Delta H^{\#}$, $\Delta S^{\#}$ and $\Delta G^{\#}$) and thermodynamic quantities for the oxidation of 1-(4-Chlorobenzyl)-4-piperidiamine using potassium permanganate in alkaline medium with respect to slow step of scheme-I are listed in Table III (Figure: 4).

Scheme-I:

$$MnO_4^- + OH^- \xrightarrow{K1} [MnO_4OH]^{2-}$$

$$Substrate + [MnO_4OH]^{2-} \xrightarrow{K2} Complex$$

$$Complex \xrightarrow{k\,(slow)} Products + H_2O$$

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Verification of rate law for oxidation of 1-(4-Chlorobenzyl)-4-piperidiamine by KMnO₄ in aqueous alkaline medium.

The rate law was verified by plotting $1/K_{obs}$ Versus $1/OH^-$. From the slopes of graph we calculated K_1K_2 value. And from the intercept k was found out. Thus by substituting the values of K_1K_2 and k in the rate equation the rate constant k values are calculated.

$$Rate = k \, [Complex]$$

$$= kK_2 \, [Substrate] \, [MnO_4OH]^{2-}$$

$$= kK_1K_2 \, [Substrate] \, [MnO_4^-] \, [OH^-] \qquad\qquad \text{-------------- (1)}$$

$$[MnO_4]_T = [MnO_4]_f + K_2[Substrate] \, [MnO_4OH]^{2-}$$

$$= [MnO_4^-]_f + K_1K_2[Substrate] \, [MnO_4^-] \, [OH^-]$$

$$= [MnO_4^-]_f \, \{1+K_1K_2[Substrate] \, [OH^-]\}$$

$$[MnO_4]_f = [MnO_4]_T \, / \, 1+K_1K_2 \, [Substrate] \, [OH^-]$$

$$[OH^-]_T = [OH^-]_f + [MnO_4OH]^{2-} + [Complex]$$

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$$= [OH^-]_f + K1[MnO_4^-] [OH^-] + K2[Substrate] [MnO_4OH]^{2-}$$

$$= [OH^-]_f + K1[MnO_4^-] [OH^-] + K1 K2 [Substrate] [MnO_4^-] [OH^-]$$

$$= [OH^-]_f \{1 + K1 [MnO_4^-] + K1 K2 [Substrate] [MnO_4^-]\}$$

$$[OH^-]_f = [OH^-]_T / 1 + K1[MnO_4^-] + K1 K2[Substrate] [MnO_4^-]$$

$$[OH^-]_f = [OH^-]_T \quad \text{since [Substrate]} \gg [MnO_4^-]$$

Substituting in equation (1)

$$\text{Rate} = kK1K2 [Substrate] [MnO_4^-] [OH^-] / 1 + K1 K2 [Substrate] [OH^-]$$

This is the rate law

$$kobs = kK1K2 [Substrate] [MnO_4^-] [OH^-] / 1 + K1 K2 [Substrate] [OH^-]$$

$$1 \ 1 / kobs = 1 / kK1K2 [Substrate] [OH^-] + 1 / k$$

DISCUSSIONS

Permanganate ion is powerful oxidizing agent in aqueous alkaline medium. It exhibits many oxidation states. The PH & stoichiometry of the reaction plays important roles. At PH> 12 reaction product is Mn (VII)) and it is stable and further reduction of Mn (VII) may be stopped. The reaction between 1-(4-Chlorobenzyl)-4-piperidiamine in alkaline medium has been studied. The stochiometry of the reaction is found to be 1:3. The oxidant has first order & the substrate & alkali has fractional order dependence. The added products have no effect on the rate of reaction. The order less than unity in OH^- indicates the formation of alkali permanganate species $MnO_4(OH)^{2-}$ from permanganate in a prior equilibrium step[24]. Formation of $MnO_4(OH)^{2-}$ is further supported by Michaeils Menton plot (Figure (4)) which is linear with positive intercept. The $MnO_4(OH)^{2-}$ react with substrate to form intermediate complex which further reacts with one mole of alkali permanganate species in slow step to form the products. The activation parameters were calculated. The moderate values favours the electron transfer processes. The ionic strength has no effect indicates the involvement of neutral species at rate determining step.

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