KINETIC OF PERMAGNETIC
PYRIDINE - 2- CARBOXALDEHYDE IN ACIDIC MEDIA

Najwa Abdul aziz Saeed Awn, Maqdoom Farooqui[a], S.B.Pakhare[a] and Mazhar Farooqui
[a]Post graduate and research center, Maulana Azad College Aurangabad

ABSTRACT

Paramagnetic oxidation of pyridine-2- carboxaldehyde has been investigated at 25^0C using spectrophotometer under acidic condition. The effect of variation of substrate, oxidant and H_2SO_4 was studied under pseudo first order reaction conditions.The effect of different salts on oxidation of pyridine -2- carboxaldehyde also was studied.The reaction was found to be first order with respect to oxidant ; substrate and H_2SO_4.A suitable mechanism is suggested.

INTRODUCTION:-

A survey of recent literature on kinetic study reveals that there is a lot of scope for the systematic study of oxidation processes involving various oxidants 1-4. There are various systems reported in the literature such as oxidation of pyridoxine by Mn (III); oxidation of aldehyde by Cr(VI), acid permanganate; N-Bromoacetamide, Os(VII) pyridinium hydrobromide and bis 2,2 (bi pyridyl), Cu(II) Permanganate, etc 5-8 .The present investigation reports the oxidation of pyridine-2-carbox aldehyde by potassium permanganate under pseudo first order conditions in acidic medium.The oxidation state of Mn in MnO_4^- is (VII). Therefore, it can be represented as Mn (VII) which is a powerful oxidizing agent and usually reduced to Mn (II).

EXPERIMENTAL :-

Material and Methods :- All chemical used for kinetic study were of A.R. grade. Kinetic investigations were performed under pseudo first order conditions with excess of the pyridine-2-carboxaldehyde over, the oxidant at 25^0C. Requisite amount of solution of substrate, H_2SO_4, were equilibrated. A measured amount of $KMnO_4$ was added to the reaction mixture with stirring. The time of initiation of the reaction was recorded when half of the contents of pipette

were released.The solution was taken in a cuvette and absorbance was measured at 526 nm using double beam spectrophotometer.

Pyridine -2-carboxaldehyde(0.1M) , $KMnO_4$ (0.2M) , H_2SO_4 (1M) and water (total volume to 100 ml) kept aside for 24 hours. The unconsumed $KMnO_4$ was determined spectrophotometrically and the product pyridine-2-carboxaldehyde and was centered by T.L.C.The stochiometry is determined to be 1:1.

RESULT & DISCUSSION :-

1) Dependence of permanganate concentration:- To study the effect of dependence of permanganate concentration. The concentration of $KMnO_4$ was varied from 1×10^{-4} M to 9×10^{-4} M keeping constant concentration of other reaction ingredients such as substrate and acid. Since the reaction has been studied under pseudo first order condition. A plot of log $[KMnO_4]$ verses time was made and pseudo first order rate constants were calculated.

The order of reaction was determined from log (<rate>) verses log (<C>) thus shows that rate of reaction varies linearly with concentration of $KMnO_4$. The graph between $K(min)^{-1}$ & $[KMnO_4]$ gives good correlation ($r^2 = 0.800$) and the log (K) against log <C> gives ($r^2 = 0.906$).

2) Dependence of Substrate Concentration:- The concentration of substrate was varied from 1×10^{-3} to 9×10^{-3} M at fixed concentration of $[KMnO_4] = 1 \times 10^{-4}$ M & $[H_2SO_4] = 1$ M. The data obtained was used to calculate first order rate constant. From log (<rate>) verses log (<C>) graph , the order was found to be close to one first order dependence on substrate.The graph between $K(min)^{-1}$ & [substrate] gives good correlation ($r^2 = 0.857$) and the log (K) against log <C> gives ($r^2 = 0.765$) .

**3) Dependence of Acid Concentration:-** The hydrogen ion concentration dependence was studied by varying H_2SO_4 atfixed $[KMnO_4] = 1 \times 10^{-4}$ M & $[Substrate] = 1 \times 10^{-3}$. The pseudo first order rate constant were evaluated and the plot of these rate constant against $[H^+]$ shows

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direct proportionality. The graph between $K(min)^{-1}$ & $[H_2SO_4]$ gives good correlation (r^2=0.748) and the log (K) against log <C> gives (r^2=0.613). (Table 1)

4) Effect of Salt:- The rate of reaction was studied by adding salts while keeping constant concentration of $[KMnO_4]$, [Substrate] and $[H2SO_4]$ (Table 2). The result reveals that there is no regular trend for rate constant with change in concentration of added salt. $KMnO_4$ is selected as an oxidizing agent for our present study because; it is a economically low cost material. It has high oxidation potential $[E^0$=1.7V], it can oxidize wide variety of substances and it is effective over wide range of PH . There are various oxidation states of Mn like (+II, + III, +IV, +V, +VI and + VII). Hence it become very complicated to find out the exact species involved in it.
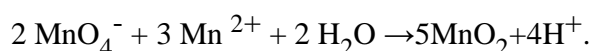
In acidic media, MnO_4^- gets converted into MnO_2

$$4MnO_4^- + 4H^+ \rightarrow 3\ O_2 + 2H_2O + 4\ MnO_2$$
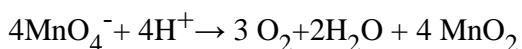
In acidic media, MnO_4^{2-} is converted to Mn^{2+}

$$MnO_4^{2-} + 8\ H^+ + 6e^- \rightarrow Mn^{2+} + 4H_2O$$
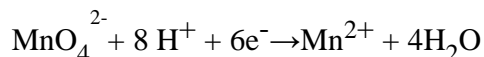
The Mn^{2+} may react with MnO_4^- and the product is MnO_2.

$$2\ MnO_4^- + 3\ Mn^{2+} + 2\ H_2O \rightarrow 5MnO_2 + 4H^+.$$
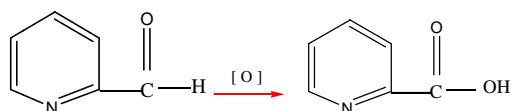
It is assumed that during the oxidation of aldehyde, positively charged species attack a lone pair of electron of the reductant at centre of high electron density.

The formation of oxo-bridge in intermediate compound indicates the the oxygen passage of one electron from the substrate to bonded Mn^{+7}.This bridge due to protonation, rupture and gives Mn^{+3} species. Since the solution does not indicate any presence of Mn (III) or precipitated MnO_2 it is quite logical to state that Mn (III) react or its dispropenated product Mn (IV) instantaneously react with substrate giving final end product Mn^{+2}.

$$2\ Mn\ (\ III) \rightarrow\ Mn\ (\ II\ ) +\ Mn\ (\ IV\ )$$

$$Mn\ (\ IV\ ) +\ Substrate \rightarrow Mn\ (\ II\ ) +\ Product$$

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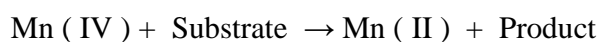
Considering the following steps the kinetic expression can be given ,

The probable mechanism can be depicted as:-
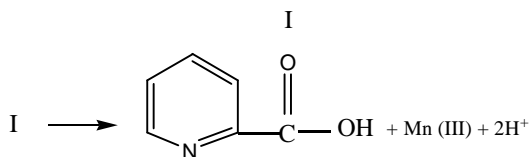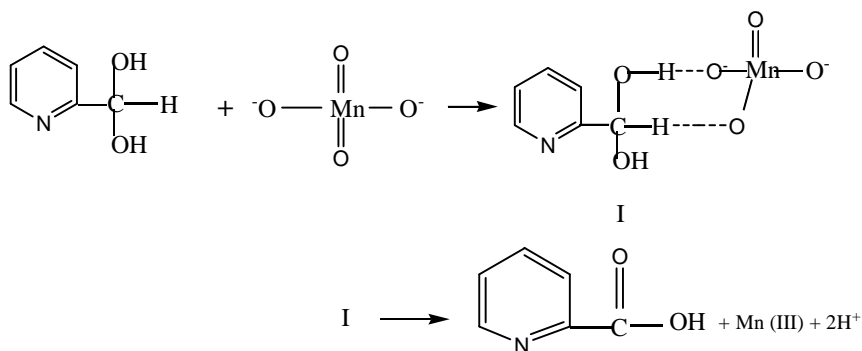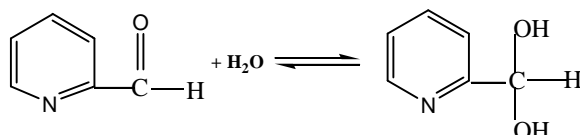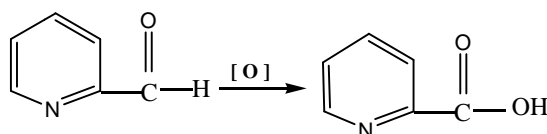
Product.

The Mn (III) undergoes disproportionation to give final Mn(II).

$$2\,Mn(\,III\,) \rightarrow Mn(\,II) + Mn(IV)$$

The Mn (IV) obtained further reacts with substrate to give final product. The mechanism

involved oxo-bridge formation and abstraction of hydrogen from substrate.

Table 1: Effect of varying concentration of reactants at 25^0C

[Pyridine-2-carbox aldehyde] 10^{-3} M	[KMnO$_4$] 10^{-4} M	[H$_2$SO$_4$] M	K (min)$^{-1}$
1	1	1	3.4608
1	2	1	2.834
1	3	1	2.7233
1	4	1	2.7348
1	5	1	2.7168
1	6	1	2.4569
1	7	1	2.4202
1	8	1	2.4541
1	9	1	2.2131
1	1	0.1	0.025454
1	1	0.2	0.027019
1	1	0.3	0.027052
1	1	0.4	0.027742
1	1	0.5	0.027652
1	1	0.6	0.02796
1	1	0.7	0.029053
1	1	0.8	0.030952
1	1	0.9	0.03558
1	1	1	2.4429
2	1	1	2.9532
3	1	1	2.973
4	1	1	3.0747
5	1	1	3.3565
6	1	1	3.9421
7	1	1	3.9102
8	1	1	5.631
9	1	1	5.9044

Table 2: Effect of salts on reaction rate:

M [Salt]	KBr	KCl	KI	K$_2$SO$_4$	ALCl$_3$	MnSO$_4$	CaCl$_2$
1×10^{-2}	0.065202	0.044831	0.013406	0.065265	0.022718	0.040017	0.035677
2×10^{-2}	0.054375	0.030115	0.029206	0.082036	0.031506	0.034809	0.032151
3×10^{-2}	0.035567	0.031025	0.046582	0.035547	0.034724	0.039414	0.035655
4×10^{-2}	0.028933	0.053048	0.01623	0.038235	0.030095	0.037877	0.035821
5×10^{-2}	0.047756	0.030116	0.023756	0.035505	0.027635	0.039668	0.034875
6×10^{-2}	0.051334	0.052637	0.020191	0.04498	0.020666	0.054921	0.037883

7×10^{-2}	0.044697	0.045717	0.020782	0.043122	0.027202	0.044983	0.037039
8×10^{-2}	0.061335	0.074515	0.020692	0.059124	0.023508	0.060169	0.037146
9×10^{-2}	0.094503	0.038261	0.015225	0.05913	0.023799	0.049566	0.048899

[Pyridine-2-carbox aldehyde] = 1×10^{-3} M, [H_2SO_4] = 1M, [$KMnO_4$] = 1×10^{-4}M , T =25^0C

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