KINETIC OF PERMAGNETIC
PYRIDINE - 2- CARBOXALDEHYDE IN ACIDIC MEDIA

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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

Journal of Medicinal Chemistry and Drug Discovery
ISSN: 2347-9027
Special Issue
Analytical Chemistry Teachers And Researchers Association
National Convention/Seminar
18 January 2015

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 &

Journal of Medicinal Chemistry and Drug Discovery
ISSN: 2347-9027
Special Issue
Analytical Chemistry Teachers And Researchers
Association
National Convention/Seminar
18 January 2015

$[H_2SO_4]$=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 x 10^{-4} M & [Substrate] = $1x10^{-3}$. The pseudo first order rate constant were evaluated and the plot of these rate constant against $[H^+]$ shows 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.
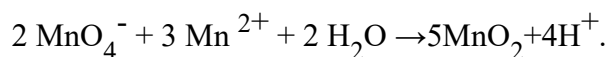
In acidic media, MnO_4^- gets converted into MnO_2

$$4MnO4^- + 4H^+ \rightarrow 3\ O_2 + 2H_2O + 4\ MnO_2$$
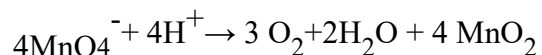
In acidic media, MnO_4^{2-} is converted to Mn^{2+}

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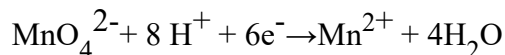
The Mn^{2+} may react with MnO_4^- and the product is MnO_2.

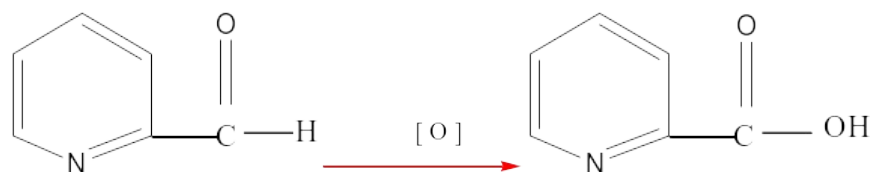$$2\ MnO_4^- + 3\ Mn^{2+} + 2\ H_2O \rightarrow 5MnO_2 + 4H^+.$$

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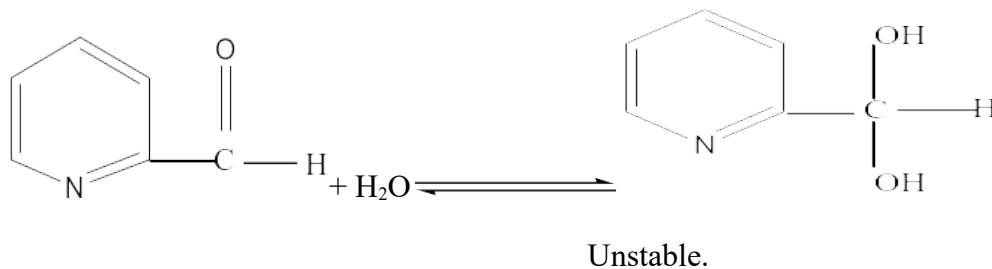
The formation of oxo-bridge in intermediate compound indicates the the oxygen passage of one electron from the substrate to bonded Mn^{+7}. This bridge due to protonation , rupture and gives Mn^{+3} species. Since the solution does not indicate any presence of Mn(III) or precipitated MnO_2 it is quite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

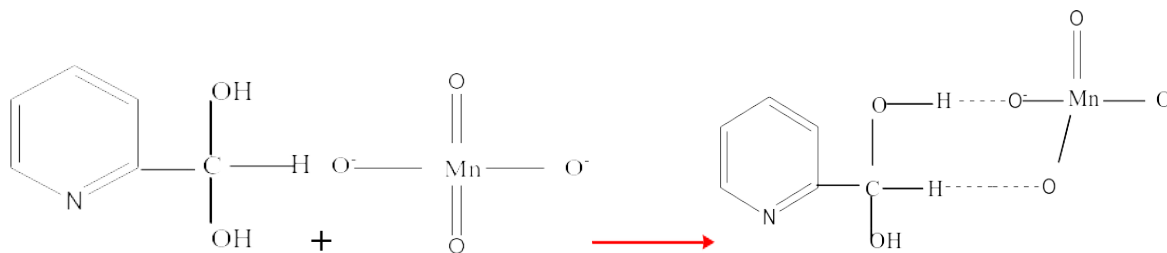$$2\ Mn\ (\ III) \rightarrow Mn\ (\ II\ ) + Mn\ (\ IV\ )$$

$$Mn\ (\ IV\ ) + Substrate \rightarrow Mn\ (\ II\ ) + Product\ .$$
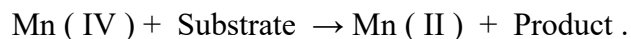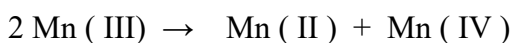
Considering the following steps the kinetic expression can be given ,

The probable mechanism can be depicted as:-

Unstable.

Journal of Medicinal Chemistry and Drug Discovery
ISSN: 2347-9027
Special Issue
Analytical Chemistry Teachers And Researchers
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National Convention/Seminar
18 January 2015

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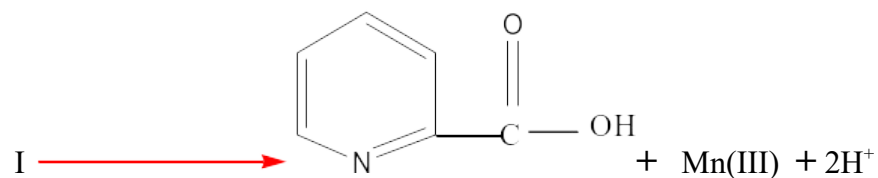
Product.

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.

Journal of Medicinal Chemistry and Drug Discovery
ISSN: 2347-9027
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18 January 2015

[pyridine-2-carboxaldehyde] 10^{-3} M	[KMnO4] 10^{-4} M	[H2SO4] 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 1. Effect of varying concentration of reactants at 25^0C

Table2. Effect of salts on reaction rate

M[Salt]	KBr	KCl	KI	K_2SO_4	$ALCl_3$	$MnSO_4$	$CaCl_2$
1×10^{-2}	0.065202	0.044831	0.013406	0.064265	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] = 1 M ,   [$KMnO_4$]=1×10^{-4}M, T =25 ^{0}C

References

1) Sayyed Hussain S., Mazhar Farooqui, Gaikwad Digambar KINETIC AND MECHANISTIC STUDY OF OXIDATION OF ESTER BY $KMnO_4$.
International Journal of ChemTech Research. 2,(1) 242-249, 2010.

2)SAYYED HUSSAIN, B R AGRAWAL, S B PAKHARE, MAZAHAR FAROOQUI .
KINETIC AND MECHANISTIC STUDY OF OXIDATION OF ESTER BY
K2Cr2O7 .International Journal of Chemistry Research
(2), 2011.

3)I.A. Zaafarany, K.S. Khairou, R.M. Hassan,
Acid-catalysis of chromic acid oxidation of kappa-carrageenan polysaccharidein aqueous
perchlorate solutions.
Journal of Molecular Catalysis A: Chemical 302 (2009) 112–118.

4)Bhagwansing Dobhal, Mazahar Farooqui and Milind UbaleKinetics of Permagnetic oxidation
of 4-hydroxy Benzaldehyde in acidic media
2, (1)443-446, Jan-Mar 2010.

5) Abdo Taher, Mazahar Farooqui and Maqdoom Farooqui. Kinetic and Equilibrium Studies of
Adsorption of Acetic Acid on Low Cost Material.
International Journal of Green and Herbal Chemistry. 2012;1.(2) 203-207..

6) Vimal Soni, R.S. Sindal, Raj N. Mehrotra *Kinetics and mechanism of the oxidation of oxalic
acid by tetrachloroaurate(III) ionInorganica
 Chimica Acta 360 (2007) 3141–314.

7) Ibrahim A. Darwish. Kinetic spectrophotometric methods for determination
of trimetazidine dihydrochloride   .Analytica Chimica Acta 551 (2005) 222–231.

8) Virender K. Sharma . Ferrate(VI) and ferrate(V) oxidation of organic compounds: Kinetics
and mechanism
Coordination Chemistry Reviews 257 (2013) 495– 510.
9) Bin Xu, Nai-yun Gao, Hefa Cheng, Chen-yan Hu, Sheng-ji Xia,
Xiao-feng Sun, XuejiaoWang, Shaogui Yang .   Ametryn degradation by aqueous chlorine:
Kinetics and reaction influences.Journal of Hazardous Materials 169 (2009) 586–592.

10) Manu Mehrotra, Vimal Soni, Raj N. Mehrotra .Oxidation of S(IV) by the
dodecatungstocobaltate(III) ion over an extended pH range using acetic acid–acetate buffer:
Different kinetics, oxidation product and mechanism. Polyhedron 27 (2008) 609–616.

11) Manu Mehrotra, Raj N. Mehrotra. The oxidation of carbohydrazide by the 12-
tungstocobaltate(III) ion in acidic medium: Kinetics and mechanism
Polyhedron 27 (2008) 1989–1994.

Journal of Medicinal Chemistry and Drug Discovery
ISSN: 2347-9027
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