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KINETIC OF PERMAGNETIC OXIDATION OF PYRIDINE-3-CARBOXALDEHYDE IN ACIDIC MEDIA

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ABSTRACT

Permagnetic oxidation of pyridine-3-carboxaldehyde has been investigated at 25°C 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-3-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 also suggested.

Key words: Permagnetic oxidation, Pyridine-3-carboxaldehyde, Acidic media.

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-3-carboxaldehyde 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

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*Author for correspondence; E-mail: mazahar_64@rediffmail.com performed under pseudo first order conditions with excess of the pyridine-3-carboxaldehyde over, the oxidant at 25°C. 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-3-carboxaldehyde (0.1 M), $KMnO_4$ (0.2 M), H_2SO_4 (1 M) and water (total volume to 100 mL) kept aside for 24 hours. The unconsumed $KMnO_4$ was determined spectrophotometrically and the product pyridine-3-carboxaldehyde and was centired by TLC. The stochiometry is determined to be 1 : 1.

RESULTS AND DISCUSSION

Dependence of permanganate concentration

To study the effect of dependence of permanganate concentration. The concentration of $KMnO_4$ was varied from 1 x 10^{-4} M to 9 x 10^{-4} M keeping constant concentration of other reaction ingredients such as substrate and acid. Since 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 $KMnO_4$.

Dependence of substrate concentration

The concentration of substrate was varied from 1 x 10^{-3} to 9 x 10^{-3} M at fixed concentration of [$KMnO_4$] = 1 x 10^{-4} M and [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

Dependence of acid concentration

The hydrogen ion concentration dependence was studied by varying H_2SO_4 at fixed [$KMnO_4$] = 1 x 10^{-4} M and [Substrate] = 1 x 10^{-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 $(min)^{-1}$ and [H_2SO_4] gives good correlation (r^2 = 0.959) and the log K against log C gives (r^2 = 0.852) (Table 1).

Table 1: Effect of varying concentration of reactants at 25°C

[Pyridine-3-carboxaldehyde]·10^{-3} M	[$KMnO_4$]·10^{-4} M	[H_2SO_4]·M	k $(min)^{-1}$
1.0	1.0	1	2.7575
1.0	2.0	1	2.2653
1.0	3.0	1	1.917
1.0	4.0	1	1.8584
1.0	5.0	1	1.9116
1.0	6.0	1	1.9421
1.0	7.0	1	1.8055
1.0	8.0	1	1.7612
1.0	9.0	1	1.7363
1.0	1.0	0.1	0.024044
1.0	1.0	0.2	0.025427
1.0	1.0	0.3	0.02633
1.0	1.0	0.4	0.029592
1.0	1.0	0.5	0.028254
1.0	1.0	0.6	0.032959
1.0	1.0	0.7	0.035389
1.0	1.0	0.8	0.037469
1.0	1.0	0.9	0.039112
1.0	1.0	1	1.6587
2.0	1.0	1	1.8139
3.0	1.0	1	1.9854
4.0	1.0	1	1.9914
5.0	1.0	1	2.1304
6.0	1.0	1	2.159
7.0	1.0	1	2.4164
8.0	1.0	1	2.5072
9.0	1.0	1	2.8152

Effect of salt

The rate of reaction was studied by adding salts while keeping constant concentration of [$KMnO_4$], [Substrate] and [H_2SO_4] (Table 2). The result reveals that there is no regular trend for rate constant with change in concentration of added salt.

Table 2: Effect of salts on reaction rate

[Salt] M	KBr	KCl	KI	K_2SO_4	$AlCl_3$	$MnSO_4$	$CaCl_2$
1×10^{-2}	0.097066	0.031266	0.035994	0.024838	0.027368	0.029968	0.028649
2×10^{-2}	0.117904	0.022051	0.037526	0.018393	0.021226	0.014195	0.052213
3×10^{-2}	0.178595	0.023113	0.034099	0.023115	0.022861	0.024786	0.044033
4×10^{-2}	0.119441	0.029786	0.038132	0.01845	0.020815	0.019651	0.019861
5×10^{-2}	0.128968	0.021543	0.049289	0.015698	0.020377	0.052566	0.024393
6×10^{-2}	0.07625	0.017174	0.060382	0.016054	0.019012	0.034125	0.023299
7×10^{-2}	0.115923	0.020112	0.04216	0.020174	0.018565	0.036781	0.051318
8×10^{-2}	0.167582	0.019191	0.04216	0.025036	0.015498	0.045563	0.079492
9×10^{-2}	0.221292	0.015236	0.128475	0.026471	0.011592	0.059004	0.050036

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

$KMnO_4$ is selected as an oxidizing agent for our present study because; it is a economically low cost material. It has high oxidation potential [E0 = 1.7 V], 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

$4\ MnO_4^- + 4\ H^+ \longrightarrow 3\ O_2 + 2\ H_2O + 4\ MnO_2$

In acidic media, MnO_4^{2-} is converted to Mn^{2+++}

$MnO_4^{2-} + 8\ H+ + 6\ e^- \longrightarrow Mn^{2+} + 4\ H_2O$

The Mn^{2+} may react with MnO_4^- and the product is MnO_2.

$2\ MnO_4^- + 3\ Mn\ 2^+ + 2\ H_2O \longrightarrow 5\ MnO_2 + 4\ H^+$

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.

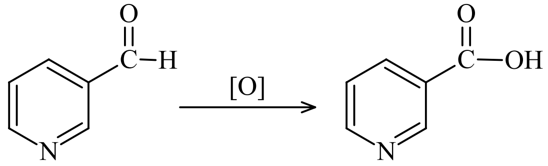
The formation of oxo-bridge in intermediate compound indicates the the oxygen passage of one electron from the substrate to bonded Mn^{+7}.

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}.

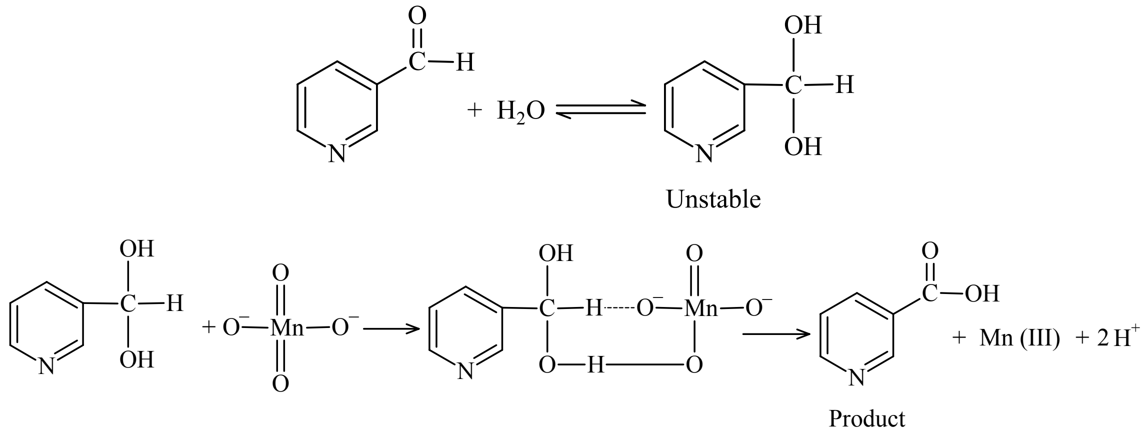
$$2\text{ Mn (III)} \longrightarrow \text{Mn (II)} + \text{Mn (IV)}$$

$$\text{Mn (IV)} + \text{Substrate} \longrightarrow \text{Mn (II)} + \text{Product}$$

Considering the following steps the kinetic expression can be given -



The probable mechanism can be depicted as –



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

$$2\text{ Mn (III)} \rightarrow \text{Mn (II)} + \text{Mn (IV)}$$

The Mn (IV) obtained further reacts with substrate to give final product. The mechanism involved oxo-bridge formation and abstraction of hydrogen from substrate.

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