KINETICS AND MECHANISTIC OXIDATION OF 3-ETHOXY-4-HYDROXYBENZALDEHYDE USING POTASSIUM PERMANGANATE

Siddharth B. Pakhare[1], Milind Ubale[2], Jaishree Gawai[3] and Mazahar Farooqui[4],*

[1]Post Graduate & Research Centre, Maulana Azad College, Aurangabad, India
[2]Vasantrao Naik College, Aurangabad, India
[3]Jawaharlal Nehru Engineering College, Aurangabad, India
[4]Dr. Rafiq Zakaria College for Women, Aurangabad, India
*E-mail: mazahar_64@rediffmail.com

ABSTRACT

Permagnetic oxidation of 3-Ethoxy-4-Hydroxybenzaldehyde has been studied at different temperatures using spectrophotometer under acidic conditions. The effect of variation of substrate (3-E-4-HB), oxidant (KMnO$_4$) and H$_2$SO$_4$ was studied under pseudo first order reaction conditions. The effect of different salts on oxidation of 3-E-4-HB was also studied. The reaction was found to be first order with respect to oxidant, substrate and H$_2$SO$_4$. A suitable mechanism is also suggested for the oxidation reaction.
Keywords: 3-Ethoxy-4-Hydroxybenzaldehyde (3-E-4-HB)

INTRODUCTION

A survey of most recent literature on kinetic study reveals that there is a lots of scope for the study of oxidation process involving various oxidants.[1-4] There are different system reported in the literature such as oxidation of 3-E-4HB by Mn(III): oxidation of aldehyde by Cr(VI), acid permanganate, N-Bromoacetamide, Os(VII) pyridinium hydrobromide and bis 2,2 (bipyridyl), Cu(II) permanganate.[5-8] The Potassium Permagnate is used widely used as oxidizing agent.[9-14]

The present investigation reports that the oxidation of 3-Ethoxy-4-Hydroxybenzaldehyde by KMnO$_4$ under pseudo first order condition 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 the chemicals used for this kinetic study were of A.R. Grade. Kinetic investigations were performed under pseudo first order conditions with excess of 3-E-4HB over, the oxidant at 25^{0}C to 45^{0}C. Required amount of solution of substrate, H$_2$SO$_4$ were equilibrated. A measured amount of KMnO$_4$ was added to the reaction mixture with constant stirring. The time of initiation of the reaction was recorded when half of the content of pipette were released. The solution was taken in a cuvette and absorbance was measured at 526nm using double beam spectrophotometer SL 210.

3-E-4HB (0.001M), KMnO$_4$ (0.0002M) and H$_2$SO$_4$ (1M) and water volume 100ml kept a side for 24hrs. The unconsumed KMnO$_4$ was determined spectrophotometrically and the product 3-Ethoxy-4-Hydroxybenzoic acid was verified by TLC. The stochiometry is determined to be 1:1.

Product Analysis

Product study was made under acidic condition in benzaldehyde. Keeping concentration of KMnO$_4$ in excess over benzaldehyde. The two solutions were mixed and sulphuric acid was also added. The reaction mixture was set aside for about 24hr. to ensure completion of the reaction. The reaction mixture was then evaporated and extracted with ether. The ether layer was washed with water many times. The ether layer was than kept as a water bath for the

evaporation of ether and cooled in ice-bath to obtain the product. The product was dissolved in benzene and a TLC analysis was done with substituted benzoic acid and respective benzaldehyde as references. Only one spot corresponding to respective benzoic acid was obtained. Formation of benzoic acid was further confirmed by mixing the product with pure benzoic acid and noting that there was no change in the melting point.

RESULTS AND DISCUSSION

Effect of variation of potassium permanganate (KMnO$_4$) concentration

To study the effect of variation of KMnO$_4$ concentration, the experimental sets were prepared in which concentration of KMnO$_4$ was varied from 1×10^{-3} to 9×10^{-3} M keeping constant concentration of 3-Ethoxy-4-Hydroxybenzaldehyde (3-E-4-HB) and H$_2$SO$_4$ (Sulphuric acid). As the reaction has been studied under pseudo first order condition using equation -

$$K = \frac{2.303}{t} \log \frac{a}{a-x}$$

(1)

Which was modified as-?

$$k = \frac{2.303}{t} \log \frac{(OD)_\infty - (OD)_0}{(OD)_\infty - (OD)_t}$$

(2)

Pseudo first order rate constants were calculated.

When initial rate is plotted against concentration of KMnO$_4$ the trend line has been found to be almost straight with negative slope indicating first order reaction at low concentration of KMnO$_4$. This has been further confirmed when log [KMnO$_4$] versus log [FOR] is plotted. Hence the reaction under pseudo first order rate depends on the concentration of oxidant. Secondly, from the obtained results, it is clear that pseudo first order rate constant decrease with increase in concentration of potassium permanganate.

Table-1: Effect of Variation of concentration of KMnO$_4$ on initial rate and rate constant of 3-Ethoxy-4-Hydroxybenzaldehyde

S. No.	[KMnO$_4$] (M)	Initial Rate (10^{-4} x mol/lit/sec)	log (FOR)	Rate constant (k) (sec^{-1})
1	1×10^3	4.3874	2.0012	0.0862
2	2×10^{-3}	4.9923	2.3841	0.0841
3	3×10^{-3}	3.9218	2.5815	0.0821
4	4×10^{-3}	3.0017	2.9812	0.0733
5	5×10^{-3}	3.1295	2.1774	0.0619
6	6×10^{-3}	2.4883	2.0241	0.0582
7	7×10^{-3}	4.9831	2.3876	0.0478
8	8×10^{-3}	5.1267	2.1182	0.0402
9	9×10^{-3}	5.8312	2.3912	0.0390

Table-2: Average rate determination of oxidation of 3-Ethoxy-4-Hydroxybenzaldehyde

Time (s)	O.D.	10^5 Conc. (mole/lit)	10^5 <c>	10^5 Δ c	Δ t	10^8 <rate> mol/lit/sec	log <c>	Log <rate>
0	0.486	23.9056	-	-	-	-	-	-
3	0.483	23.7580	23.8318	0.1476	3	49.1884	1.3772	1.6919
6	0.48	23.6104	23.6842	0.1476	3	49.1884	1.3745	1.6919
9	0.476	23.4137	23.5121	0.1968	3	65.5845	1.3713	1.8168
12	0.473	23.2661	23.3399	0.1476	3	49.1884	1.3681	1.6919
15	0.47	23.1185	23.1923	0.1476	3	49.1884	1.3653	1.6919
18	0.468	23.0202	23.0694	0.0984	3	32.7923	1.3630	1.5158
21	0.465	22.8726	22.9464	0.1476	3	49.1884	1.3607	1.6919
24	0.462	22.7250	22.7988	0.1476	3	49.1884	1.3579	1.6919
27	0.46	22.6267	22.6758	0.0984	3	32.7923	1.3556	1.5158
30	0.456	22.4299	22.5283	0.1968	3	65.5845	1.3527	1.8168

33	0.451	22.1840	22.3069	0.2459	3	81.9807	1.3484	1.9137
36	0.447	21.9872	22.0856	0.1968	3	65.5845	1.3441	1.8168
39	0.441	21.6921	21.8396	0.2951	3	98.3768	1.3392	1.9929
42	0.437	21.4953	21.5937	0.1968	3	65.5845	1.3343	1.8168
45	0.431	21.2002	21.3478	0.2951	3	98.3768	1.3294	1.9929
48	0.432	21.2494	21.2248	0.0492	3	16.3961	1.3268	1.9929
51	0.429	21.1018	21.1756	0.1476	3	49.1884	1.3258	1.6919
54	0.426	20.9543	21.0280	0.1476	3	49.1884	1.3228	1.6919
57	0.422	20.7575	20.8559	0.1968	3	65.5845	1.3192	1.8168
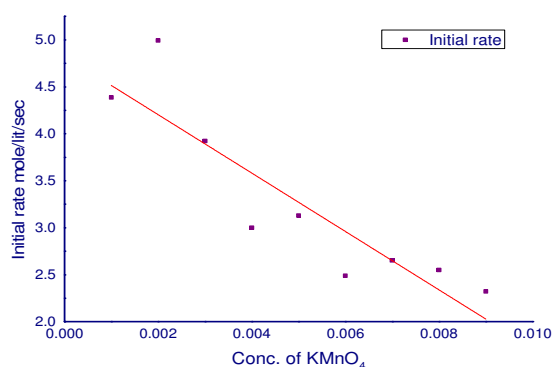
Fig.-1: Variation of Conc. of KMnO$_4$ Vs Initial rate at constant [3-E-4-HB] = 1x10^{-3}
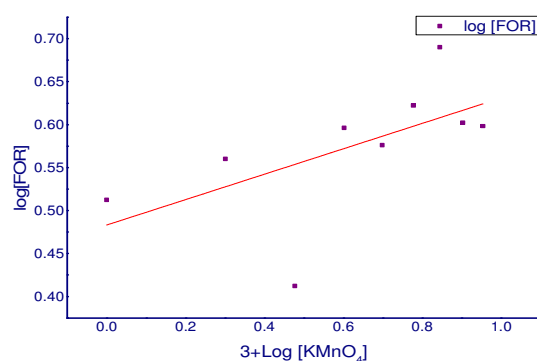

Fig.-2: Variation of conc. of KMnO$_4$ Vs log [FOR] at constant [3-E-4-HB]

Effect of variation of 3-Ethoxy-4-Hydroxybenzaldehyde concentration
To study the effect of variation of concentration of substrate, the sets were prepared in which the concentration of 3-E-4-HB was varied from 1 x 10^{-3} to   9 x 10^{-3} M, keeping constant concentration of [KMnO$_4$] = 7 x10^{-4} M, [H$_2$SO$_4$] = 2 x10^{-1} M. As the reaction has been studied under pseudo first order condition pseudo first order rate constants were calculated. It is clear that pseudo first order rate constants were found decrease with increases with concentration of [3-E-4-HB] in irregular way. When initial rate is plotted against concentration of 3-E-4-HB, the trend line is linear with positive slope. When log [FOR] versus log [3-E-4-HB] is plotted it confirms the fractional order of reaction. Hence the reaction under pseudo first order rate depends on the concentration of substrate.

Table-3: Effect of Variation in concentration of 3-Ethoxy-4-Hydroxybenzaldehyde on initial rate and rate constant

S. No.	[3-E-4-HB] (M)	Initial Rate (10^{-4} x mol/lit/sec)	log (FOR)	Rate constant (k) (sec^{-1})
1	1 x 10^{-3}	3.1022	0.5124	0.0812
2	2 x 10^{-3}	3.2913	0.5602	0.0846
3	3 x 10^{-3}	2.9120	0.4124	0.0795
4	4 x 10^{-3}	3.9089	0.5962	0.0761
5	5 x 10^{-3}	3.7853	0.5761	0.0820
6	6 x 10^{-3}	4.8212	0.6223	0.0711
7	7 x 10^{-3}	4.0123	0.6900	0.0702
8	8 x 10^{-3}	4.1712	0.6023	0.0612
9	9 x 10^{-3}	3.8912	0.5983	0.0593

Effect of variation of H$_2$SO$_4$ concentration
To study the effect of variation of concentration of sulphuric acid (H$_2$SO$_4$), in the experimental sets the concentration of H$_2$SO$_4$ is varied from 2 x 10^{-2} to 9 x 10^{-2} M, keeping constant concentration i.e. [3-E-4-HB]= 1 x 10^{-4} and [KMnO$_4$] = 1 x 10^{-4}M. As the reaction has been studied under pseudo first order condition for varying [H$_2$SO$_4$] was made and pseudo first order rate constants were calculated. It is clear from that pseudo first order rate constants decreases with

change in concentration of H_2SO_4 confirming the first order dependence with respect to acid. Hence the reaction under pseudo order rate depends on the concentration of acid. The average rate determination data confirm that the order with respect to acid concentration is unity.
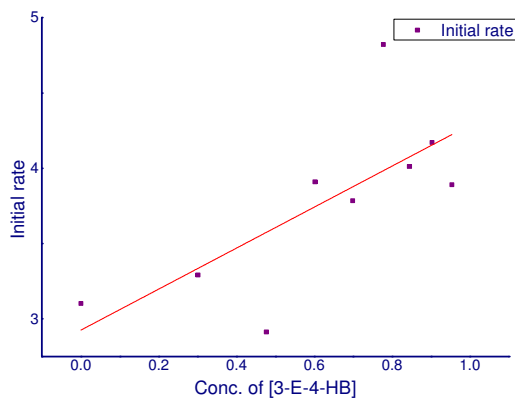

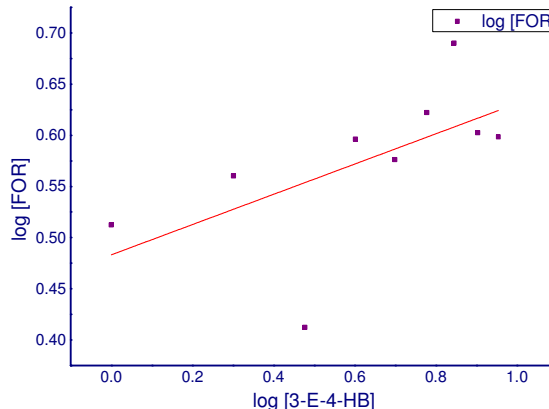Fig.-3: Variation of Conc. of 3-E-4-HB Vs initial rate

Fig.-4: Variation of Conc. of 3-E-4-HB Vs log [FOR]

Table-4: Effect of Variation in concentration of H_2SO_4 on initial rate and rate constant of
[3-E-4-HB] oxidation

[$KMnO_4$]=1 x 10^{-4} [3-E-4-HB] = 1 x 10^{-4} [H_2SO_4] = 1 M

S. No.	[H_2SO_4] (M)	Initial Rate (10^{-4} x mol/lit/sec)	log (FOR)	Rate constant (k) (sec^{-1})
1	0.02	5.1242	3.1211	0.0817
2	0.04	3.2791	3.1013	0.0931
3	0.6	3.5126	2.9542	0.0827
4	0.08	3.7812	2.7612	0.0802
5	0.10	4.0012	2.5117	0.0711
6	0.12	3.9831	3.0135	0.0798
7	0.14	3.5673	2.9120	0.0743
8	0.16	3.0135	2.3141	0.0612
9	0.18	4.0023	2.8691	0.0699

Table-5: Average rate determination of oxidation of 3-Ethoxy-4-Hydroxybenzaldehyde
[3-E-4-HB] = 5 x 10^{-3} [$KMnO_4$] = 7 x 10^{-4}M   [H_2SO_4] = 1M

Time (s)	O.D.	10^{-5} Conc. (mole/lit)	10^{-5}< c >	10^{-5} Δc	Δt	10^{-8} <rate> mole/lit/sec	log <c >	log <rate>
0	0.392	19.2818						
3	0.39	19.1835	19.2327	0.0984	3	32.7923	1.2840	1.5158
6	0.389	19.1343	19.1589	0.0492	3	16.3961	1.2824	1.2147
9	0.387	19.0359	19.0851	0.0984	3	32.7923	1.2807	1.5158
12	0.385	18.9375	18.9867	0.0984	3	32.7923	1.2784	1.5158
15	0.381	18.7408	18.8392	0.1968	3	65.5845	1.2751	1.8168
18	0.378	18.5932	18.6670	0.1476	3	49.1884	1.2711	1.6919
21	0.375	18.4456	18.5194	0.1476	3	49.1884	1.2676	1.6919
24	0.373	18.3473	18.3965	0.0984	3	32.7923	1.2647	1.5158
27	0.371	18.2489	18.2981	0.0984	3	32.7923	1.2624	1.5158
30	0.369	18.1505	18.1997	0.0984	3	32.7923	1.2601	1.5158

33	0.365	17.9538	18.0521	0.1968	3	65.5845	1.2565	1.8168
36	0.362	17.8062	17.8800	0.1476	3	49.1884	1.2524	1.6919
39	0.36	17.7078	17.7570	0.0984	3	32.7923	1.2494	1.5158
42	0.358	17.6094	17.6586	0.0984	3	32.7923	1.2470	1.5158
45	0.355	17.4619	17.5357	0.1476	3	49.1884	1.2439	1.6919
48	0.353	17.3635	17.4127	0.0984	3	32.7923	1.2409	1.5158
51	0.35	17.2159	17.2897	0.1476	3	49.1884	1.2378	1.6919
54	0.348	17.1176	17.1667	0.0984	3	32.7923	1.2347	1.5158
57	0.345	16.9700	17.0438	0.1476	3	49.1884	1.2316	1.6919
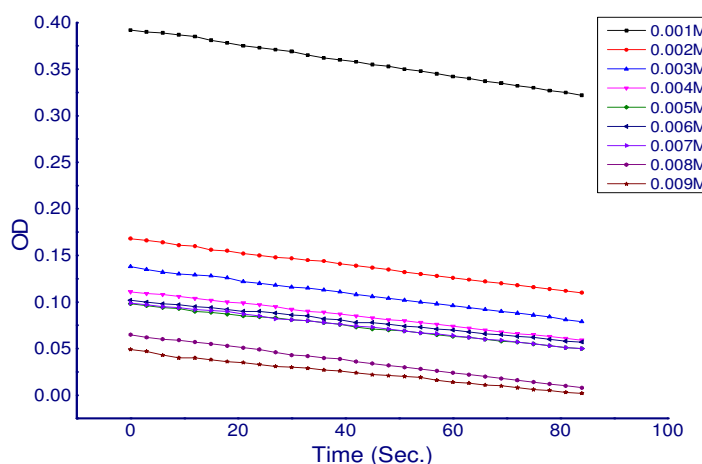
Fig.-5: Effect of variation of [H$_2$SO$_4$] Effect of variation of temperature

The effect of temperature was studied keeping constant concentration of all reactants such as [KMnO$_4$] = 7 x 10^{-4} M, [3-E-4-HB] = 5 x 10^{-3} M and [H$_2$SO$_4$] = 8 x 10^{-2} M. The temperature variation was done in the range of 25 to 45° C. The energy of activation was calculated by plotting graph between log k verses 1/T, a straight line was obtained. The temperature dependence on a number of reactions can be depicted by an equation. The modest enthalpy of activation and higher rate constant of slow step indicate that the oxidation presumably occurs by an inner sphere mechanism. The free energy change (ΔG) enthalpy changes (ΔH) and entropy change (ΔS) was determined.

The energy of activation was found to be -1712.19 J/mole. This activation energy was used to calculate the enthalpy of activation (ΔH) using equation-

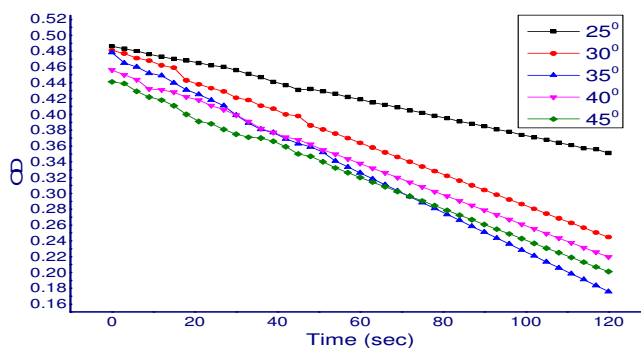$$\Delta H = \Delta E - RT$$

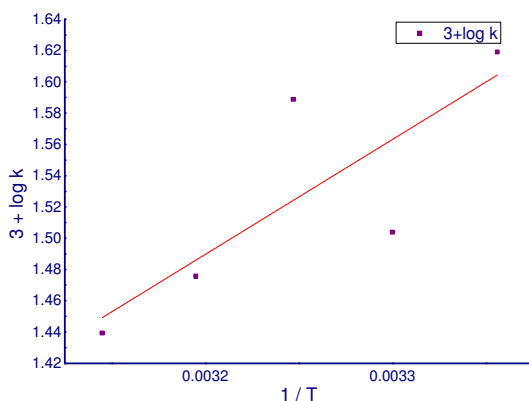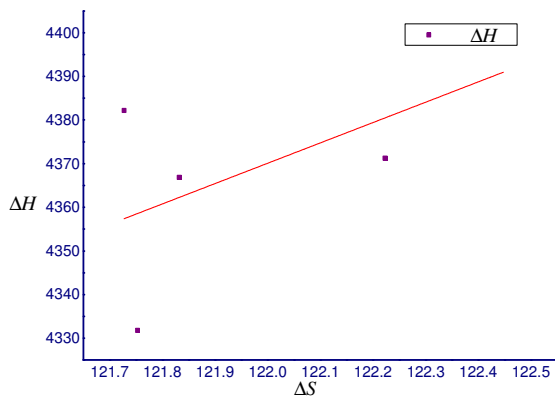Fig.-6: Effect of temperature

Fig.-7: 3+log K Vs 1 / T

Fig.-8: ΔS Vs ΔH

Table-6: Effect of Temperature on Kinetics of permanganate Oxidation of 3-Ethoxy-4-Hydroxybenzaldehyde in acidic media

Rate k	t^0C	T K	1 / T	3+logk
0.0416	25	298	0.003356	1.619093
0.0319	30	303	0.003300	1.503791
0.0388	35	308	0.003247	1.588832
0.0299	40	313	0.003195	1.475671
0.0275	45	318	0.003145	1.439333

Table-7: Effect of Temperature on Kinetics of permanganate Oxidation of 3-Ethoxy-4-Hydroxybenzaldehyde in acidic media
$[KMnO_4]=7 \times 10^{-4}$ M [3-E-4-HB]= 5×10^{-3} M $[H_2SO_4]=8 \times 10^{-2}$M
Activation Energy = -1712.19 J/mole

S. No.	temp K	ΔH(J/mole)	ΔS (J/mole)	ΔG (J/mole)
01	298	-4189.76	-122.50	32315.75
02	303	-4231.33	-121.77	32663.52
03	308	-4272.90	-122.24	33377.80
04	313	-4314.47	-121.83	33819.08
05	318	-4356.04	-121.73	34355.07
Average		-4272.90	-122.01	33306.24

The value of (ΔH) decreases with increase in temperature; which is obvious. The average (ΔH) was found to be -4272.90 J/mole with a range –4189.76 to –4356.04 J/mole. From this, we calculated entropy of activation using formula-

$$K = \frac{K_B}{T} e^{\frac{\Delta Ea^{\#}}{RT}} e^{\frac{\Delta S^{\#}}{R}}$$

(3)

Where *k*= pseudo first order rate constant
k_B = Boltzmann constant
T = Temperature

There was no regular trend of entropy change it varies from –122.50 to –121.73 J/mole. The average entropy of activation was found to be -122.01 J/mole which is negative and indicates that the transition state is highly organized

due to loss of number of degrees of freedom. The average free energy (ΔG) was then calculated using (ΔH) and (ΔS) as per the equation-

$$\Delta G = \Delta H - T\Delta S \tag{4}$$

It was observed that (ΔG) increases with increase in temperature. The average (ΔG) was found to be 33306.24 J/mole, and changes from 32315.75 to 34355.07 J/mole. A plot of (ΔH) verses (ΔS) is linear which is followed by this equation-

$$(\Delta H) = \beta \, \Delta S \tag{5}$$

Where β is called isokinetic temperature, for 3-E-4-HB it was — 46.62748 K

Effect of variation of salts

To study the effect of variation of salts, the concentration of salts was varied from 1 x 10^{-2} to 9 x 10^{-2} M, keeping constant concentration of reactants such as [KMnO$_4$] = 7 x 10^{-4} M, [3-E-4-HB] = 5 x 10^{-3} M, [H$_2$SO$_4$] = 8 x 10^{-2} M. These results are given in the table. 1.5.1. From the obtained results, it is clear that pseudo first order rate constant k_{obs} increases with the increase in concentration of salts. A plot of log k_{obs} vs $\sqrt{\mu}$, according to extended Bronsted Debye-Huckel equation was found to be linear with positive slopes (MgCl$_2$ and Ca(NO$_3$)$_2$) indicating positive salt effect. On the other hand pseudo first order rate constant decreased with increase in concentration of salts. A plot of log k_{obs} versus $\sqrt{\mu}$ was found to be linear with negative slopes (KBr, KI, KCl, K$_2$SO$_4$, CaCl$_2$, AlCl$_3$ and MnSO$_4$) indicating negative salt effect.
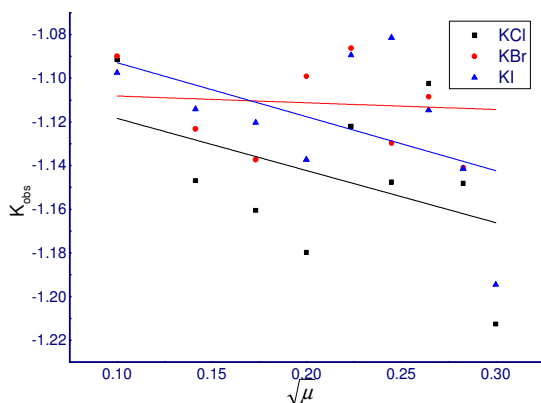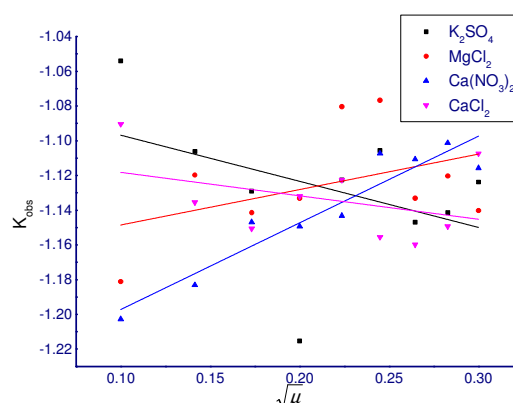

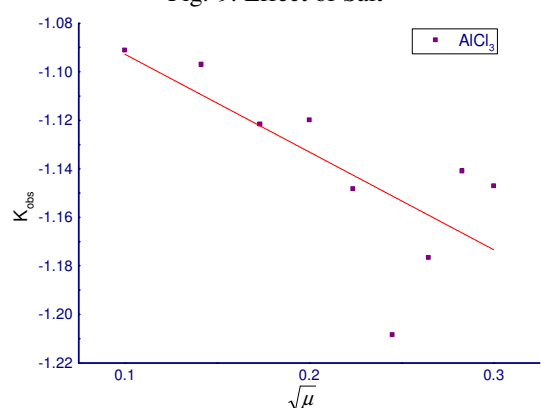Fig.-9: Effect of Salt
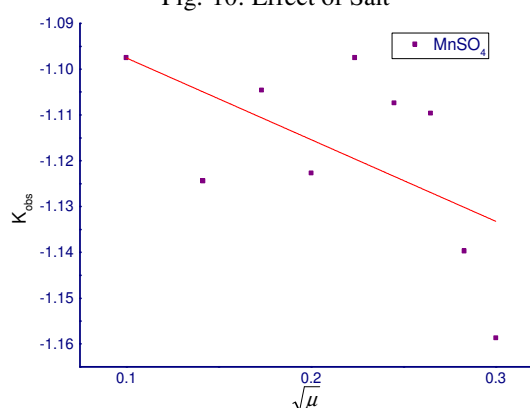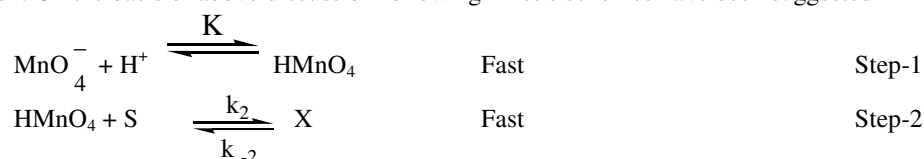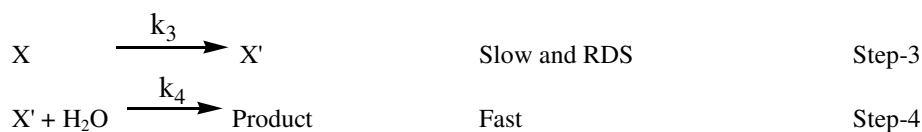

Fig.-10: Effect of Salt

Fig.-11: Effect of Salt

Fig.-12: Effect of Salt

Kinetic expression: On the basis of above discussion following kinetic schemes have been suggested-

$$MnO_4^- + H^+ \underset{}{\overset{K}{\rightleftharpoons}} HMnO_4 \qquad \text{Fast} \qquad\qquad \text{Step-1}$$

$$HMnO_4 + S \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} X \qquad \text{Fast} \qquad\qquad \text{Step-2}$$

$$X \xrightarrow{k_3} X' \qquad \text{Slow and RDS} \qquad \text{Step-3}$$

$$X' + H_2O \xrightarrow{k_4} \text{Product} \qquad \text{Fast} \qquad \text{Step-4}$$

Where S is a substrate X, X' are intermediate species since third step is rate determining step.

$$\text{Rate} = k_3 [X] \qquad (6)$$

Applying steady state approximation to X,

$$K_2 [HMnO_4] [S] - k_{-2}[X] - k_3[X] = 0$$

$$K_{-2} [X] + k_3[X] = k_2 [HMnO_4] [S] \qquad (7)$$

Applying Law of mass action to first step,

$$K = \frac{[HMnO_4]}{[MnO_4^-][H^+]}$$

$$\therefore [HMnO_4] = k[MnO_4^-][H^+] \qquad (8)$$

Substituting equation-8 in 7,

$$[X](k_{-2} + k_3) = Kk_2[MnO_4^-][H^+][S]$$

$$[X] = \frac{Kk_2[MnO_4^-][H^+][S]}{k_{-2} + K_3} \qquad (9)$$

Substituting equation-9 in equation-6,

$$\therefore \text{Rate} = \frac{Kk_3k_2[MnO_4^-][S][H^+]}{k_{-2} + k_3} \qquad (10)$$

If the concentration of acid and substrate is kept constant than-

$$\text{Rate} = k_{obs}\left[MnO_4^-\right] \qquad (11)$$

Where

$$k_{obs} = \frac{Kk_3k_2[H^+][S]}{k_{-2} + k_3}$$

Hence the graph of k_{obs} against concentration of acid $[H^+]$ is a straight line which confirms that the present model is for kinetics. The reaction rates observed allows us to assume that protonated MnO_4 i.e. $HMnO_4$ as a active oxidising species involved.[15]
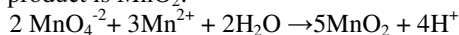
Table-8: Effect of added Salt on first order rate constant
$[KMnO_4]=7\times10^{-4}$ M [3-E-4-HB]= 5×10^{-3} M $[H_2SO_4]=8\times10^{-2}$M

Conc. Of salts (M)	Rate constant (k), S^{-1}								
	KCl	KBr	KI	K$_2$SO$_4$	MgCl$_2$	Ca(NO$_3$)$_2$	CaCl$_2$	AlCl$_3$	MnSO$_4$
0.01	0.0521	0.0307	0.0425	0.0436	0.0433	0.0553	0.0412	0.0408	0.0392
0.02	0.0498	0.0298	0.0413	0.0412	0.0471	0.0538	0.0401	0.0403	0.0417
0.03	0.0472	0.0273	0.0405	0.0428	0.0412	0.0512	0.0388	0.0404	0.0423
0.04	0.0463	0.0264	0.0399	0.0398	0.0392	0.0501	0.0415	0.0463	0.0443
0.05	0.0454	0.0251	0.0388	0.0374	0.0381	0.0533	0.0421	0.0469	0.0465
0.06	0.0411	0.0388	0.0375	0.0332	0.0373	0.0539	0.0429	0.0492	0.0418
0.07	0.0397	0.0263	0.0384	0.0311	0.0380	0.0545	0.0438	0.0471	0.0465
0.08	0.0372	0.0372	0.0298	0.0278	0.0388	0.0558	0.0447	0.0402	0.0419
0.09	0.0368	0.0358	0.0307	0.0257	0.0378	0.0541	0.0417	0.0513	0.0448

$KMnO_4$ is selected as an oxidizing agent for this study because it is an 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 is complicated to find out the exact species[16] involved in it. In acidic media $MnO_4^- + 4 H^+ + 3O_2 \rightarrow 2H_2O + 4MnO_2$ even MnO_4^{-2} is converted to Mn^{+2}.

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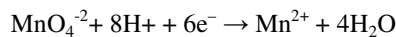
The Mn^{2+} may react with MnO_4^{-2} and the product is MnO_2.

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

It is assumed that during oxidation of aldehyde positively change species attack a lone pair of electron of the reductant at centre of high electron density.[17]

The formation of oxo-bridge in intermediate compound indicates the oxygen passage of one electron from the substrate bonded to Mn^{+7}. This bridge due to protonation, rupture and give Mn^{+3} species. Since the solution dies not indicate any presence of Mn(III) is precipitated MnO_2 it is quite logical to state that Mn(III) react or its disproportionated product Mn(IV) instantaneously react with substrate giving final product Mn^{+2}.[18-19]

$$2Mn (III) \rightarrow Mn (II) + Mn (IV)$$
$$Mn (IV) + substrate \rightarrow Mn (II) + product$$
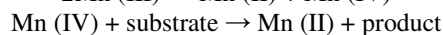
Considering the following step in the reaction is as-
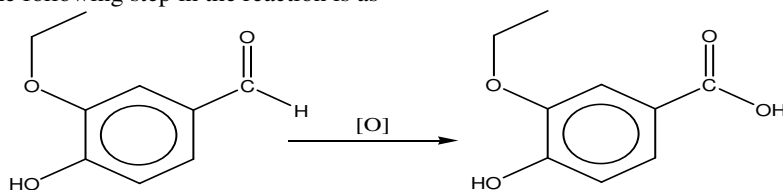
And the mechanism can be depicted as-
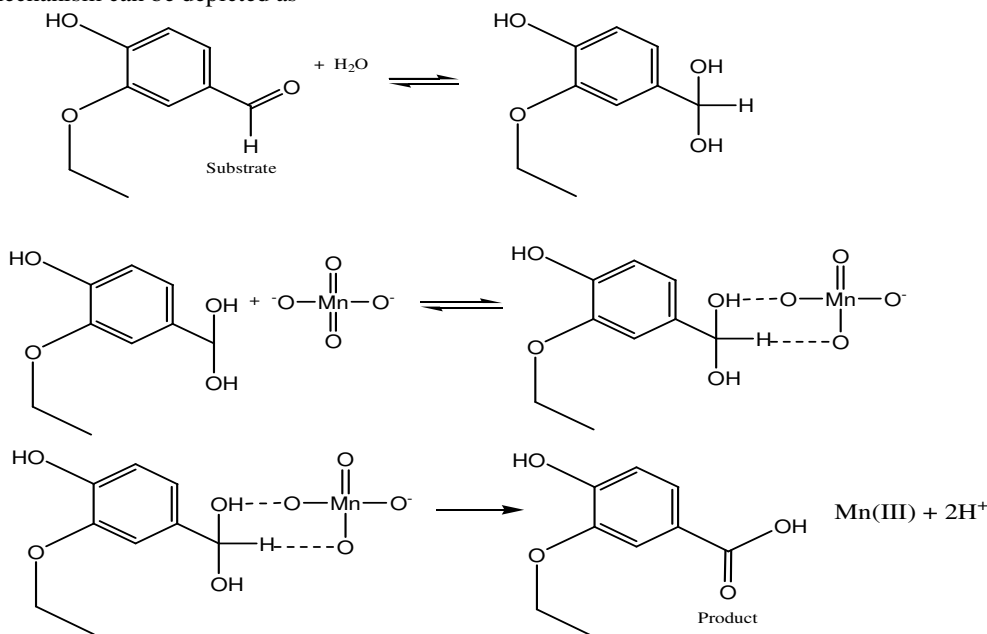
Scheme-1

REFERENCES

1. Sayyed Hussain S., Mazhar Farooqui, Gaikwad Digambar, *Int. J. Chem. Tech. Res.,* **2(1)**, 242(2010).
2. Sayyed Hussain, B.R. Agrawal, S.B. Pakhare, Mazahar Farooqui, *Int. J. Chem. Res.,* **2**, (2011).
3. I.A. Zaafarany, K.S. Khairou, R.M. Hassan, *J. Mol. Catal. A: Chem.,* **302**, 112(2009).
4. Bhagwansing Dobhal, Mazahar Farooqui and Milind Ubale, *Int. J Chem. Tech. Res.,* **2(1)**, 443(2010).

5. Abdo Taher, Mazahar Farooqui and Maqdoom Farooqui, *Int. J. of Green and Herbal Chem.,* **1(2)**, 203 (2012)
6. Vimal Soni, R.S. Sindal, Raj N. Mehrotra, *Chimica Acta,* **360**, 3141(2007).
7. Ibrahim A. Darwish, *Analytica Chimica Acta,* **551**, 222(2005).
8. Virender K. Sharma, *Coordination Chemistry Reviews,* **257**, 495(2013).
9. Alsediq A. Obeid, *Rasayan Journal of Chemistry*, **2(4)**, 786(2009).
10. Syed Asif, Syed Sultan, Syed Abed and Mazahar Farooqui, *Rasayan J. Chem.,* **3(2)**, 232 (2010).
11. M. Komal Reddy, Narmeta Bhasker and K. Raghava Raju, *Rasayan J. Chem.,* **2(1)**, 108(2009).
12. G. Sailaja and R. Ramachandra Murthy, *Rasayan J. Chem.,* **3(2)**, 321(2010).
13. Goutam K. Ghosh and Sankar Chandra Moi, *Rasayan J. Chem.,* **2(4)**, 924(2009).
14. Brijesh Pare, Anjali Soni and V.W. Bhagwat, *Rasayan J. Chem.,* **1(2)**, 413(2008)
15. H.V. Rajeshwari, K.S. Byadagi, S.T. Nandibewoor and S.A. Chimatadar, *J. Chem. Eng. & Mat. Sci.*, **3(5)**, 65(2012).
16. Alexandra Csavdari and Ioan Baldea, *Studia Universitatis Babes-Bolyai, Chemia*, **LII**, 1, (2007).
17. A.A. Osunlaja, S.O. Idris and J.F. Iyun, *Arch. Appl. Sci. Res.*, **4(2)**, 772(2012).
18. S.P. Deraniyagala and T.N.T. Premasiri, *Vidyodaya J. of Sci.*, **159**, 8149(1999).
19. S. Udhayavani and K. Surbamani, *Acta Chim. Pharm. Indica*: **2(4)**, 213(2012).

[RJC-1233/2015]