



Received: 02-12-2013

Accepted: 29-12-2013

ISSN: 2321-4902

Volume 1 Issue 4

Online Available at www.chemijournal.com

International Journal of Chemical Studies

Kinetic of Permanganetic Oxidation of Thiophene-2-aldehyde in acidic media

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Permanganetic oxidation of thiophene-2-aldehyde has been investigated at 25 °C using spectrophotometer under acidic condition. The effect of variation of substrate, oxidant and H₂SO₄ was studied under pseudo first order reaction conditions. The effect of different salts on oxidation of thiophene-2-aldehyde also was studied. The reaction was found to be first order with respect to oxidant; substrate and H₂SO₄. A suitable mechanism is suggested.

Keyword: Oxidation, thiophene-2-aldehyde, permanganate.

1. Introduction

The kinetics provides the useful information about the mechanism and rate of chemical reaction, which helps to run a chemical reaction successfully by a way of selecting optimum condition as to get maximum yield. The kinetic study also helps us to study the factors which influence the rate of reaction like temperature, pressure, substrate concentration, oxidant concentration, composition of reaction mixture and catalyst. The reaction kinetics plays a very important role in the investigation of the reaction mechanism. Oxidation of organic compound carried out by oxidising agent like potassium dichromate Cr (VI) ^[1, 2, 3]. The update literature survey shows that, though the considerable amount of work has been done on the oxidation of organic compounds ^[4, 5, 6, 7, 8] by potassium permagnate, but only a few studies is found on the kinetics of oxidation of aldehyde by potassium permagnate ^[9, 10]. The object of present investigation is to formulate the reaction mechanism from the data gathered from kinetic measurement. The present investigation reports the oxidation of thiophene-2-aldehyde by

potassium permanganate under pseudo first order conditions in acidic medium. The oxidation state of Mn in MnO₄⁻ is (VII). Therefore, it can be represented as Mn (VII) which is a powerful oxidizing agent and usually reduced to Mn (II). The result obtained shows that the direct oxidation is the only process occurring under the applied conditions of experiments.

2. Experimental

2.1 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 thiophene-2-aldehyde over, the oxidant at 25 °C. Requisite amount of solution of substrate, H₂SO₄, were equilibrated. A measured amount of KMnO₄ 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.

Thiophene-2-aldehyde (0.1M), KMnO₄ (0.2M), H₂SO₄ (1M) and water (total volume to 100 ml)

kept aside for 24 hours. The unconsumed KMnO_4 was determined spectrophotometrically and the product thiophene-2-aldehyde and was centered by TLC. The stoichiometry is determined to be 1:1.

3. Result & Discussion

3.1 Dependence of permanganate concentration

To study the effect of dependence of permanganate concentration. The concentration of KMnO_4 was varied from $1 \times 10^{-4} \text{M}$ to $9 \times 10^{-4} \text{M}$ 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 $\log [\text{KMnO}_4]$ verses time was made and pseudo first order rate constants were calculated.

The order of reaction was determined from $\log (\text{rate})$ verses $\log (C)$ thus shows that rate of reaction varies linearly with concentration of KMnO_4 . The graph between $K(\text{min})^{-1}$ & $[\text{KMnO}_4]$ gives good correlation ($r^2=0.892$) and the $\log (K)$ against $\log (C)$ gives ($r^2=0.931$).

3.2 Dependence of Substrate Concentration:-

The concentration of substrate was varied from 1×10^{-3} to $9 \times 10^{-3} \text{M}$ at fixed concentration of $[\text{KMnO}_4] = 1 \times 10^{-4} \text{M}$ & $[\text{H}_2\text{SO}_4] = 1 \text{M}$. The data obtained was used to calculate first order rate constant. From $\log (\text{rate})$ verses $\log (C)$ graph, the order was found to be close to one first order dependence on substrate. The graph between $K(\text{min})^{-1}$ & $[\text{substrate}]$ gives good correlation ($r^2=0.694$).

3.3 Dependence of Acid Concentration:-

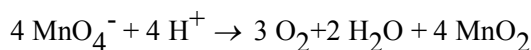
The hydrogen ion concentration dependence was studied by varying H_2SO_4 at fixed $[\text{KMnO}_4] = 1 \times 10^{-4} \text{M}$ & $[\text{Substrate}] = 1 \times 10^{-3}$. The pseudo first order rate constant were evaluated and the plot of these rate constant against $[\text{H}^+]$ shows direct proportionality. The graph between $K(\text{min})^{-1}$ & $[\text{H}_2\text{SO}_4]$ gives good correlation ($r^2=0.681$) and the $\log (K)$ against $\log (C)$ gives ($r^2=0.506$).

(Table 1)

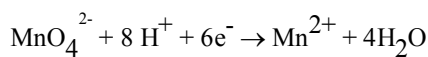
4. Effect of Salt

The rate of reaction was studied by adding salts while keeping constant concentration of $[\text{KMnO}_4]$, $[\text{Substrate}]$ and $[\text{H}_2\text{SO}_4]$ (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 an economically low cost material. It has high oxidation potential [$E^0=1.7\text{V}$], 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.

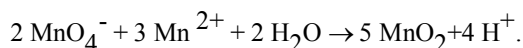
In acidic media, MnO_4^- gets converted into MnO_2



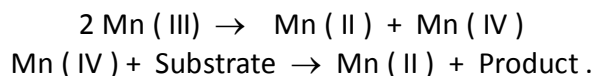
In acidic media, MnO_4^{2-} is converted to Mn^{2+}



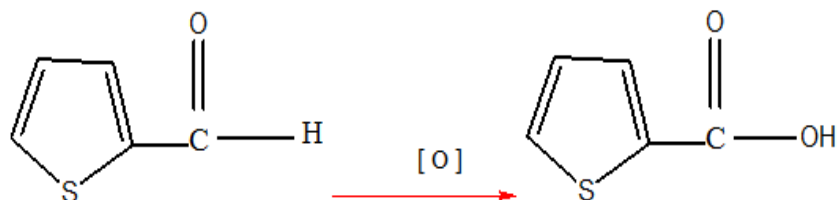
The Mn^{2+} may react with MnO_4^- and the product is



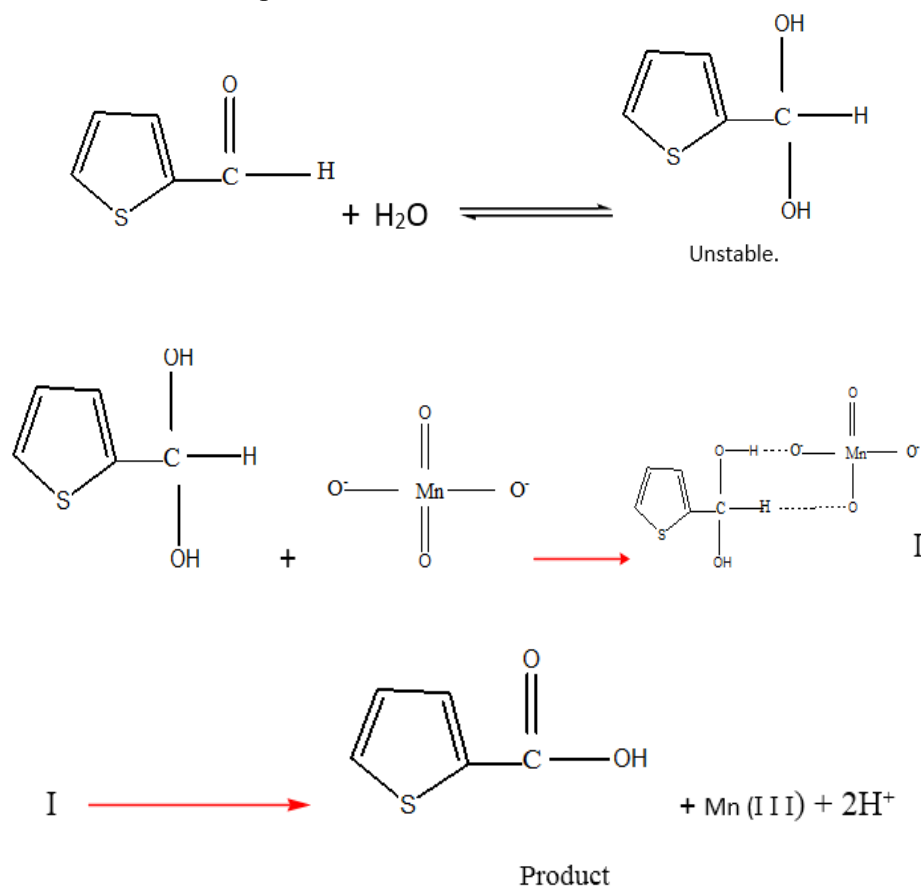
It is assumed that during the oxidation of aldehyde, positively charged species attack a lone pair of electron of the reductant at centre of high electron density. The formation of oxo-bridge in intermediate compound indicates the the oxygen passage of one electron from the substrate to bonded Mn^{+7} . 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 disproportionated product Mn(IV) instantaneously react with substrate giving final end product Mn^{+2} .



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).



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 °C

[thiophene-2-aldehyde] 10 ⁻³ M	[KMnO ₄] 10 ⁻⁴ M	[H ₂ SO ₄] M	K (min) ⁻¹
1	1	1	1.7741
1	2	1	1.8726
1	3	1	2.1541
1	4	1	2.3957
1	5	1	2.4677
1	6	1	2.3209
1	7	1	2.5877
1	8	1	2.6153
1	9	1	2.755
1	1	0.1	0.037125
1	1	0.2	0.021926
1	1	0.3	0.021147
1	1	0.4	0.022156
1	1	0.5	0.050804
1	1	0.6	0.06143
1	1	0.7	0.089722
1	1	0.8	0.091199
1	1	0.9	0.201632
1	1	1	2.0967
2	1	1	3.7606
3	1	1	2.6791
4	1	1	2.3886
5	1	1	3.1506
6	1	1	2.8769
7	1	1	6.0966
8	1	1	7.443
9	1	1	9.9351

Table 2: Effect of salts on reaction rate.

M [Salt]	KBr	KCl	KI	K ₂ SO ₄	AlCl ₃	MnSO ₄	CaCl ₂
1 X 10 ⁻²	0.077328	0.085715	0.085715	0.093347	0.054754	0.051819	0.109548
2 X 10 ⁻²	0.085024	0.069065	0.056151	0.105808	0.08679	0.033382	0.0933
3 X 10 ⁻²	0.07661	0.070362	0.052211	0.096116	0.102555	0.054664	0.121374
4 X 10 ⁻²	0.103474	0.087987	0.073976	0.078034	0.095649	0.039499	0.104194
5 X 10 ⁻²	0.260618	0.114622	0.07567	0.115443	0.103089	0.045247	0.117292
6 X 10 ⁻²	0.08999	0.102937	0.085251	0.091814	0.090456	0.050286	0.11559
7 X 10 ⁻²	0.146692	0.074794	0.080376	0.122943	0.100137	0.044216	0.101348
8 X 10 ⁻²	0.137462	0.108289	0.073409	0.108656	0.074015	0.040539	0.105981
9 X 10 ⁻²	0.064709	0.114016	0.115735	0.13813	0.163582	0.039213	0.081073

[Thiophene-2- Aldehyde]=1X10⁻³M, [H₂SO₄] = 1 M, [KMnO₄] =1 X10⁻⁴M, T =25 °C

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