Kinetic and Mechanistic Study of Oxidation of Ester By KMnO$_4$

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ABSTRACT

In present investigation we are studied the kinetics and mechansim of oxidation of ester by potassium permanganate in acid medium. In the present paper we reported the effect of oxidant (kM$_n$O$_4$), effect of substrate (ester), effect of sulphuric acid and effect of temperature on oxidation of ester. The reaction is first order with respect to oxidant and substrate.

Key words: KM$_n$O$_4$, Ethyl Chloroacetate, Oxidation, kinetics, Mechanism.

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[4,5,6,7,8,15]

by potassium permagnate, but only a few studies is found on the kinetics of oxidation of ester by potassium permagnate[9,10.] The object of present investigation is to formulate the reaction mechanism from the data gathered from kinetic measurement. It is found that the oxidation of ester occurs by two ways, hydrolysis followed by the oxidation of alcohol, direct oxidation of esters. But no conclusive evidence was provided in support of either of the two pathways, hence it is decided to undertake the systematic investigation kinetic of dimethyl phthalate, diethyl phthalate, dibutyl phthalate, ethyl formate, isobutyl chloroformate. The kinetic of oxidation of ester by potassium permagnet permagent in moderately concentrate sulphuric acid is the only process occurring under the applied conditions of experiments. medium has been investigated .

The rate law

$$\frac{-d[Mn(VII)]}{dt} = k \ (Ester)[MnO_4]_{total}$$

The result obtained shows that the direct oxidation is the only process occurring under the applied conditions of experiments.

MATERIAL AND METHODS

All the chemicals used were of AR grade, specially potassium permagnate used of AR grade and was prepared and estimated by standard method. Esters are of Lobo chem. Ltd. And the boiling point of both esters was confirmed. The ester were always freshly distilled before use for the kinetic measurement permanganate and sulphuric acid

solution were taken in two different flasks and covered with black cloth and placed in a thermostat for 1 hour to attain constant temperature by both the flask. In order to prevent the hydrolysis, required volume of given ester was directly added to acid solution with micro pipette just before mixing it with permanganate solution.

The course of reaction was followed by measuring the absorbance (Optical density) of unreacted permagnate ion from time to time at 520 nm using Carl-Zeiss spectrophotometer. The reaction were followed upto 70 to 85% completion and the product were identified as acid i.e. acetic acid and aldehyde by 2,4, DNP test[11]. The aldehaydes were obtained in 90% yield as estimated form their 2.4 DNP derivative. The addition of mercuric chloride to the reaction system did not induce the precipitation of mercuric chloride showing that no free radicals are formed in the system [12].

(i)

(ii)

(ii)

(iii)

(iii)
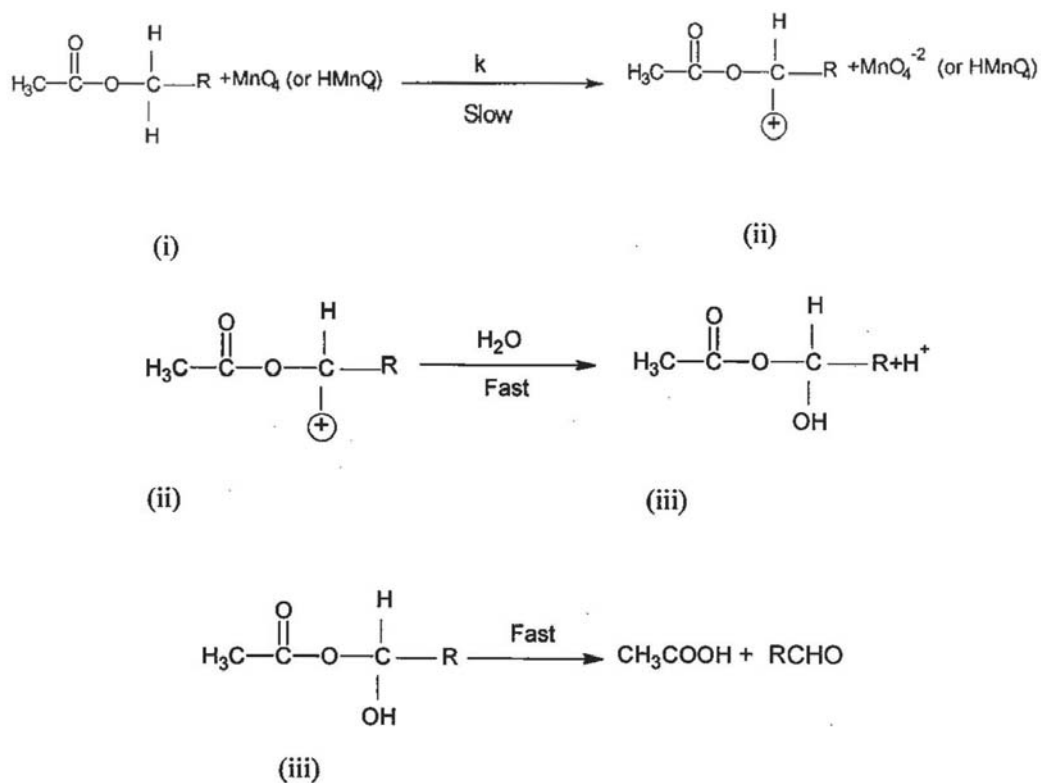
RESULTS AND DISCUSSION

Under the conditions (Ester) > (KMnO$_4$) in 3.20 M. H$_2$SO$_4$. The plot of log absorbance (O.D.) Vs time were linear indicating the first order dependence of rate on (KMnO$_4$) Fig. 1, A Oxidation of esters depends on the concentration of potassium permanganate. This was also confirmed by verifying (KMnO$_4$) which did not show any change in Pesudo First order constant (k^1) Value (Table No. 1.) The reaction was also found to be first order in (ester) Fig. 1B (Table 2 (A). The rate of reaction increases with increase in (H$_2$SO$_4$) Table No. 3.

Zucker and Hammett proposed that for acid catalysed reaction in strong acid the rate correlates with Ho of activated complex does not contain a water molecule. For (A-1) unimolecular mechanism the rate is correlated with Hammett acidity function Ho and a linear plot between log Kabs Vs Ho is obtained. The A-2 mechanism (Ingold's terminology) gives correlation with H$^+$ ion and a linear plot is obtained between log Kabs against log Kabs against log (Hx) that is the molecular concentration of an both that gives unit slope. This hypothesis is called Zuckker – Hammett hypothesis, hold good for large number of reaction. For example hydrolysis of benzylidene diacetate, ethyl acetate and propylacetate completing with A-1 mechanism. The reaction consistent with the A-2 process is hydrolysis of ester ethyl chloroacetate. The addition of sulphate and pyrophosphate ions has negligible effect on the rate. For reactions in solution the nature of sulphate and pyrophosphate ions has negligible effect on the rate. For reactions in solution the nature of solvent plays an important role which has been discussed in detail by Aims. In present investigation, effect of solvent could not be studies because of reactivity of solvent such as alcohols, ketones, dioxine, etc with KMnO$_4$.

The effect of temperature was also studies at different temperature like 283K, 293K, 303K, 313K and 333K. It is shown in table No. 1,2,3,4 and it is clear that as temperature increases rate constant increases (Table 4.) Thermodynamic parameters such as $\Delta H^\#$, $\Delta S^\#$, $\Delta G^\#$, E ($\Delta E^\#$) and A i.e. frequency factor were studies and given in table 2 and 3.

The negative values of entropy of activation show that the intermediate transition state is rigid the relatively small values of ΔH and ΔS are consistent with the reaction which generally proceeds through highly ionised transition state[13].

It is well know that in acid solution in addition to Mn (VII) Mn (III) and (IV) is quite stable and part of the oxidation might occur not the reactive species under the experimental conditions, was revealed by the fact that the reaction neither exhibited any induction period and nor the the rate decreased by the addition of complexing agents like SO$_4^{2-}$, F$^-$, and P$_2$O$_7^-$. The absence of such a behavior clearly indicates that Mn (VII) is probably the only reactive specie present in the system in the oxidation of esters.

The plot of logk^1 Vs-Ho was linear (fig. 1C). This may probably be due to the formation of HMnO$_4$ species, a more powerful oxidant according to the equilibrium .

$$H^7 + MnO_4^- \rightarrow HMnO_4$$
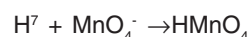
This point has been also confirmed by previous researcher. Hence Mn(VII) could be considered as the reactive specie and this probably exists to a certain extent as HMnO$_4$.

As the acid concentration is increased the formation of HMnO$_4$ is favoured and hence increases the oxidation may be assumed to be taking place by Mn (VII) in the form of either *MnO$_4^-$* *or HMnO$_4$ or* both depending on the acid concentration. The linear plot of logk^1 Vs log (H$_2$So$_4$) and logk^1 Vs Ho indicates that the reactions are acid catalyed, but none of the above plots gives and ideal slope for unity. In view of the departure from the ideal behavior, applicability of Bunnett's hypotheis was tested. A plot of logk^1 Vs Ho Vs log a H2O was linear (fig. 1D) and the slope was found to be -2.5. This value indicates non-involvement of water molecule in the rate determining steps as pet Bunnett's, while the hydrolysis rate was 3.3 X 10^{-5} liter mol^{-1} sec^{-1} under indentical condition, form this it is clear that the direct oxidation is clear that the direct oxidation is the only process occurring under the experimental conditions used.

Table 1: Shows effect of oxidant (KMnO$_4$)

[Ethyle chloroacetate] = 4.7 × 10^{-7}m

Temp = 30°   λ max = 520 nm

S. No	[KMnO$_4$]×10^{-4}M	K×10^{-2}/min
1.	3.125	0.8060
2.	3.529	1.036
3.	3.88	1.036
4.	4.21	0.92
5.	4.5	1.03
6.	4.76	1.15
7.	5.0	1.036
8.	5.21	1.036

A probable mechanism (Scheme – 1) in which MnO$_4^-$ or HMnO$_4$ attacks the alcohol moiety of the ester is considered explaining the observed kinetic result.

Compound (III) being highly unstable disproportionate to give acetic acid the corresponding aldehyde.

The rate law can be expressed by equation (1)

$$...(1)$$

Table 2: Effects of substrate (ester) on oxidation
[oxidation of Ethyle chloroacetate]

[KMnO$_4$] = 4.7 × 10^{-4}m

Temp = 30°C   λmax = 520 nm

S. No	[Ester]×10^{-3}	log [Sub]	k×10^{-2}/min	logk^1
1	3.125	-2.5052	0.5757	$\bar{3}$.7601
2.	3.529	-2.4524	0.6909	.8394
3.	3.888	-2.4103	0.8060	.9063
4.	4.210	-2.3758	0.8870	.9499
5.	4.5	-2.3468	0.9020	.9552
6.	4.76	2.3224	0.9212	.9643
7.	5.00	-2.3011	1.151	.0610
8.	5.21	-2.2826	1.1820	.0726

$$-\frac{d\,[Mn(VII)]}{dt} = K\,(ester)\,(MnO_4)\,Total \text{-------1}$$

Table 3: Effect of variation of Conc. of acid on oxidation
(Oxidation of ethyl cyanoacetate)

[KMnO$_4$] = 4.7 × 10^{-4}m   [H$_2$SO$_4$] = 0.857 M

Temp = 30°C   λmax = 520 nm

[H$_2$SO$_4$]	log [H$_2$SO$_4$]	Log a w	Ho	K × 10^{-2}/min	Log K	Ho+LogK
0.439	1.6424	-	-	0.5757	.7601	
0.857	1.9329	0.014	0.05	0.6909	.8394	-3.7894
1.25	0.0969	-0.023	-0.3	0.6909	.8674	-4.1674
1.63	0.2121	0.033	-0.5	1.036	.0153	-2.5153
2.00	0.3010	-0.045	-0.85	1.125	.0511	-2.9011
2.34	0.3692	-0575	-0.99	1.381	.1401	-3.1301

Table 4: Effect of Temperature on reaction rate

Ethyl Chloroacetate

T°k	$[KMnO_4]$ = 4.7 x 10^{-4}m						[Ethyl Chloroacetate] = 4.7 x 10^{-3} M		
	1/T x 10^{-3}	k x 10^{-2}/min	log K	log A	A	E J/mole	ΔH# J/mole	ΔG# J/mole	ΔS# J/mole
283	3.53 x 10^{-3}	0.575	3.7601	3.6784	8.314 x 10^3	14360.35	12007.49	24071.78	-42.63
293	3.41	0.6909	3.8394	3.4867	6.8725 x 10^3	14360.35	11924.35	24910.11	-44.32
303	3.30	0.7363	3.8674	2.4018	6.040 x 10^2	14360.35	11841.21	25839.81	-46.20
313	3.19	1.036	2.0153	3.8226	9.151 x 10^3	14360.35	11758.06	22515.51	-34.36
323	3.09	0.6448	3.8014	2.9392	9.727 x 10^2	14360.35	11674.93	27740.95	-49.79
333	3.00	0.6333	3.8016	2.6930	8.407 x 10^2	14360.35	11591.79	29207.49	-52.90

This type of hydride ion transfer process has been proposed in the oxidation of aldehyde, formic acid, ethers, alcohols etc. by permanganate in moderately concentrated acid solution [14].

The effect of temperature on reaction rate was studied which shows the increase in reaction rate with Increase in temperature.
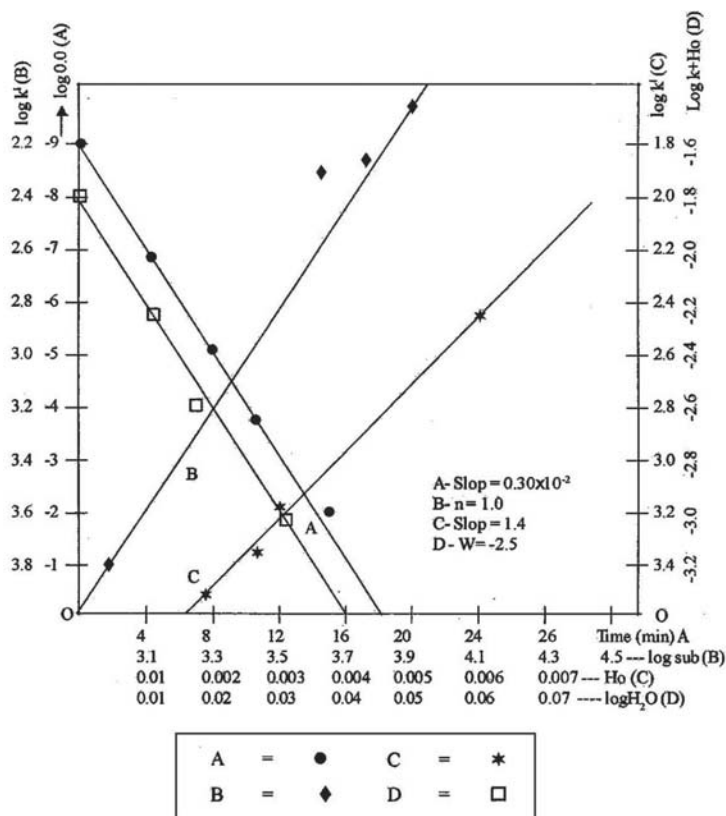
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