



Oxidation of Ethyl 3-chloropropionate by KMnO_4 : A kinetic and mechanistic study

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ABSTRACT

Kinetic deals with rate of reaction and mechanism gives us how molecules forms, this we have studied the kinetics and mechanism of oxidation of ethyl 3 - Chloropropionate. ($\text{CH}_3\text{-CH-COOC}_2\text{H}_5$). We have studied the different parameters like effect of variation concentration of substrate, oxidant acid, and temperature with the help of oxidising agent KMnO_4 which shows the reaction is first order with respect to oxidant and substrate. As the concentration of acid increases rate of reaction also increase and temperature also show same trend i.e. as temperature increase rate of reaction also increase. © 2012 Trade Science Inc. - INDIA

KEYWORDS

Ethyl 3-chloropropionate;
Kinetics;
Oxidation mechanism;
Thermodynamic parameters.

INTRODUCTION

Oxidation reaction by Potassium permanganate is of considerable academic and technological importance because of variable oxidation state of potassium (k).

The Kinetics provides the useful information about the mechanism and rate of chemical reaction, which helps to run a Oxidation of organic compound carried out by oxidizing agent like potassium dichromate Cr (VI)^[1-3]. The update literature survey shows that, though the considerable amount of work has been done on the oxidation of organic compounds^[4-8, 15-18] by potassium permanganate, but only a few studies is found on the kinetics of oxidation of ester by potassium permanganate^[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 permanganate in moderately concentrate sulphuric and medium has been investigated.

The rate law

$$\frac{-d[\text{Mn(VII)}]}{dt} = k(\text{Ester})[\text{MnO}_4]_{\text{total}}$$

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

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Although the considerable amount of work has been carried out on organic compounds by update literature survey shows that few work has been on ester that is why we have planned to carry out the work of ester i.e. ethyl 3-chloropropionate by KMnO_4 .

MATERIAL AND METHODS

All the chemicals used were of AR grade, specially potassium permanganate used were of AR grade and was prepared and estimated by standard method. Esters are of Zobo Chem. Ltd., and the boiling point of esters was confirmed. The ester were always freshly distilled before used 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 permanganate ions from time to time at 520 nm using Carl-Zeiss spectrophotometer. The reaction was followed upto 70 to 85% completion and the product was identified as acid i.e. acetic acid and aldehyde by 2, 4 DNP tests^[11]. The aldehydes were obtained in 90% yield as estimated from their 2,4 DNP derivative. The addition of mercuric chloride to reaction system did not induce the precipitation of mercuric chloride showing that no free radicals are formed in the system^[12].

RESULTS AND DISCUSSION

Under the conditions $[\text{ester}] > [\text{KMnO}_4]$ in 3.20 M. H_2SO_4 . The plot of log absorbance (O.D.) Vs time were linear (Not shown) indicating the first order dependence of rate on $[\text{KMnO}_4]$. An Oxidation of esters depends on the concentration of potassium permanganate. This was also confirmed by verifying $[\text{KMnO}_4]$ which did not show any change in Pseudo First order constant (k^1) value (TABLE 1). The reaction was also found to be first order in $[\text{ester}]$ (TABLE 2). The rate of reaction increases with increases in $[\text{H}_2\text{SO}_4]$.

TABLE 1 : Effect of variation of concentration of KMnO_4 [Ethyl 3 - chloropropionate] = 4.7×10^{-7} Temperature : 30°C $\lambda_{\text{max}} = 520 \text{ nm}$

Sr. No.	$[\text{KMnO}_4] \times 10^{-4} \text{ M}$	$\text{K} \times 10^{-2}/\text{min}$
1	3.012	0.7905
2	3.418	0.9125
3	3.56	1.012
4	4.11	0.85
5	4.21	1.01

TABLE 2 : Effect of variation of concentration of ethyl-3-chloropropionate

Sr.No.	$[\text{Ester}] \times 10^{-3}$	Log [Sub]	$\text{K} \times 10^{-2}/\text{min}$	Log k^1
1	3.012	-2.4502	0.5252	$\bar{3}.5601$
2	3.256	-2.4156	0.6219	$\bar{3}.6381$
3	3.346	-2.3828	0.7205	$\bar{3}.7282$
4	3.828	-2.3446	0.7819	$\bar{3}.8212$
5	4.120	2.2812	0.8215	$\bar{3}.8865$
6	4.560	2.3682	0.9212	$\bar{3}.9643$

TABLE 3 : Effect of variation of concentration of acid on oxidation

$[\text{KMnO}_4] = 437 \times 10^{-4} \text{ m}$ $[\text{H}_2\text{SO}_4] = 0.857 \text{ M}$
Temperature : $\lambda_{\text{max}} = 520 \text{ nm}$

Sr. No.	Log $[\text{H}_2\text{SO}_4]$	Log aw	Ho	$k \times 10^{-2}/\text{min}$	LogK	Ho ⁻¹ LogK
1	0.439	1.6424	-	-	0.5152	$\bar{3}.7601$ $\bar{3}.7601$
2	0.857	1.932	0.012	0.04	0.6215	$\bar{3}.8192$ $\bar{3}.8592$
3	1.25	0.096	0.018	+0.03	0.6559	$\bar{3}.8212$ $\bar{3}.8512$
4	1.63	0.212	0.024	0.05	0.9282	$\bar{3}.9212$ $\bar{3}.9712$
5	2.00	0.301	0.030	0.75	1.021	$\bar{2}.018$ $\bar{1}.772$
6	2.34	0.369	0.045	0.82	1.125	$\bar{2}.050$ $\bar{2}.87$

(TABLE 3).

The effect of temperature was also studied at different temperature like 283K, 293K, 303K, 313K, 323K and 333K. It is clear that as temperature increases rate constant increases (TABLE 4). Thermodynamic parameters such as ΔH^\ddagger , ΔS^\ddagger , ΔG^\ddagger , E , ΔE and an i.e. frequency factor were studies.

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

TABLE 4: Effect of temperature on reaction rate.

[KMnO₄] = 4.7 x 10⁻⁴ m[Ethyl 3-chloropropionate] = 4.7 x 10⁻³ m

Tic	1/T x 10 ⁻³	K x 10 ⁻² /min	logK	A	E J/Mole	ΔH≠J/Mole	ΔG≠J/Mole	ΔS≠J/Mole
283	3.53x10 ⁻³	0.5153	$\bar{3.7601}$	8.12 x 10 ³	14220.11	11982.78	24012.81	-40.12
393	3.41	0.69	$\bar{3.83}$	6.62 x 10 ³	14220.11	11725.72	24980.12	-41.21
303	3.30	0.73	$\bar{3.86}$	6.00 x 10 ³	14220.11	11682.68	25240.81	-42.18
313	3.19	0.98	$\bar{2.01}$	8.82 x 10 ³	14220.10	11621.62	25892.12	-41.00
323	3.09	0.6212	$\bar{3.70}$	9.12 x 10 ³	14220.11	11582.54	27512.62	-44.36
333	3.00	0.63	$\bar{3.80}$	8.12 x 10 ³	14220.11	11452.42	28.25.82	-48.12

H⁷+MnO₄®HMnO₄

This point has been also confirmed by previous researchers. Hence Mn (VII) could be considered as the reactive specie and this probably exists to a certain extent as HMnO₄.

As the acid concentration is increased the formation of HMnO₄ is favored and hence increases the oxidation may be assumed to be taking place by Mn (VII) in the form of either MnO₄⁻ or HMnO₄ or both depending on the acid concentration. The linear plot of 10K¹ Vs log [H₂SO₄] and logK¹ Vs Ho indicates that the reactions are acid catalyzed (not shown), but none of the above plots gives an ideal slope for unity. In view of the departure from the ideal behavior, applicability of Bunnett's hypothesis was tested. A plot of logK¹ Vs Ho Vs log H₂O was linear (not shown) and the slope was found to be -2.5. This value indicates non-involvement of water molecule in the rate determining steps as per Bunnett's, while the hydrolysis rate was 3.2x10⁻⁵ liter mol⁻¹ sec⁻¹ under identical condition, from this it is compound (III) being highly un-

stable disproportionate to give acetic acid and the corresponding aldehyde. The rate law can be expressed by equation 1

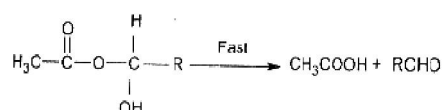
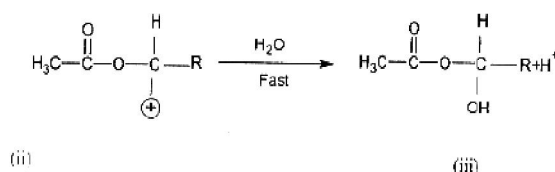
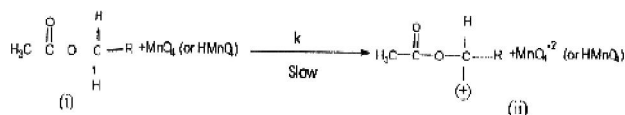
$$\frac{-d[\text{Mn(VII)}]}{dt} = K(\text{Ester})[\text{MnO}_4]_{\text{total}}$$

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 solutions^[14].

The effect of temperature on reaction rate was studied which shows the increase in reaction rate with increase in temperature (TABLE 4). The rate of oxidation in case of dimethyl phthalate, diethyl phthalate, and dibutylphthalate, the rate of reaction as the number of alkyl group increases there is decrease is clear that the direct oxidation is the only process occurring under the experimental conditions used.

A probable mechanism (Scheme 1) in which MnO₄⁻ or HMnO₄ attacks the alcohol moiety of the ester is considered explaining the observed kinetic result.

K value, due to steric effect In case of ethyl 3-chloropropionate and the rate of reaction is more though there is presence of electron withdrawing group Cl⁻.

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