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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 mechanism of oxidation of ester by potassium permanganate in acid medium. In the present paper we reported the effect of oxidant ($KMnO_4$), 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: Dimethyl phthalate, Diethyl phthalate, Dibutyl phthalate, Ethyl formate, Isobutyl chloroformate

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, oxidatant 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 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 in moderately concentrate sulphuric acid 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 were of AR grade and was prepared and estimated by standard method. Esters are of Zobo Chem. Ltd. and the boiling point of both esters was confirmed. The ester were always freshly distilled before use for the kinetic measurement permagnate 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 permagnate solution.

The course of reaction was followed by measuring the absorbance (optical density) of unreacted permagnate ions 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 aldehydes were obtained in 90% yield as estimated from 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].

Results and discussion

Under the conditions [ester] > [$KMnO_4$] in 3.20 M. H_2SO_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 permagnate. This was also confirmed by verifying [$KMnO_4$] which did not show any change in Pseudo 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 increases in [H_2SO_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) unimoleculor 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 [Hx] that is the molecular concentration of an both the plots 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 propidlactone completing with A-1 mechanism. The reaction consistent with the A-2 process is hydrolysis of ester (A, B, C, and D & E) methyl chloroacetate ethyl loctoacetate and methyl formate. The addition 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 studied at different temperature like 283K, 293K, 303K, 313K, 323K and 333K. It is shown in table No.4, 5, 6, 7 and 8 and it is clear that as temperature increases rate constant increases (Table No. 4 [A] & 4 [B]). Thermodynamic parameters such as $\Delta H^{\#}$, $\Delta S^{\#}$, $\Delta G^{\#}$, E (ΔE) and A i.e. frequency factor were studies and given in table 2 and 3.

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 which generally proceeds through highly ionised transition state[13.]

It is well known that in acid solutions in addition to Mn (VII) Mn (III) and Mn (IV) is quite stable and a part of the oxidation might occur by these intermediate manganese ions. In some cases that Mn(III) and Mn (IV) were not the reactive species under the experimental conditions, was revealed by the fact that the reaction neither exhibited any induction period and nor the rate decreased by the addition of complexing agents like SO_4^{2-}, F^-, and $P_2O_7^-$. 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 $\log k^I$ Vs -Ho was linear (fig. 1C) . This may probably be due to the formation of HMnO4 species, a more powerful oxidant according to the equilibrium.

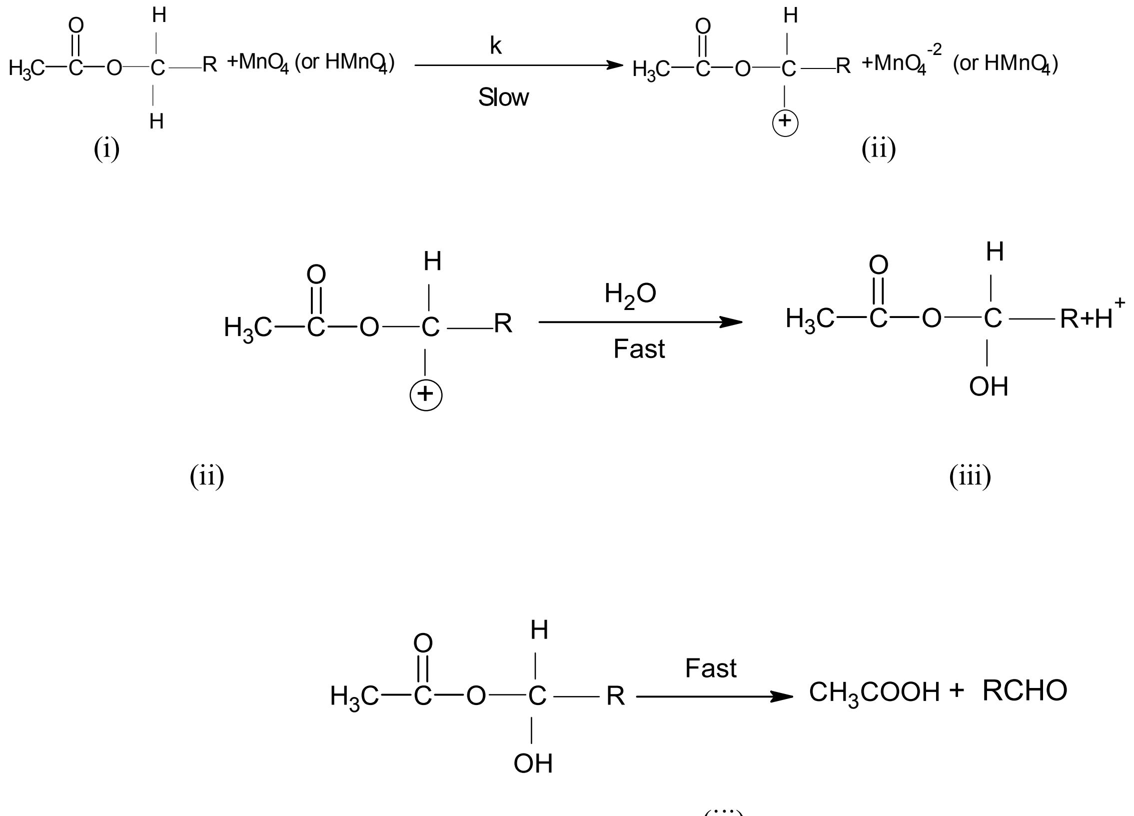
$$H^{7} + MnO_4 \rightleftharpoons HMnO_4$$

This point has been also confirmed by previous reseachers. 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 $10k^I$ Vs log [H_2So_4] and $\log k^I$ Vs Ho indicates that the reactions are acid catalyed, but none of the above plots gives an ideal slope for unity. In view of the departure from the ideal behaviour, applicability of Bunnett's hypotheis was tested. A plot of $\log k^I$ Vs Ho

Vs log a H20 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 per Bunnett's, while the hydrolysis rate was 3.3x10^{-5} liter mol^{-1} sec^{-1} under identical condition, from this it is clear that the direct oxidation is the only process occurring under the experimental conditions used.

A probable mechanism (scheme -1) in which MnO_4^- or $HMnO_4$ attacks the alcohol moiety of the ester is consider explaining the observed kinetic result.



Compound (III) being highly unstable disproportionate to give acetic acid and the corresponding aldehyde.
The rate law can be expressed by equation (1)

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

This type of hydride ion transfer process has been proposed in the oxidation of aldehyde, formic acid, ethers, alcohols etc. by permagnate 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 2 and 3). 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 K value, due to steric effect. In case of ethyl formate and isobutyl chloroformate the rate of reaction is more in later case even though there is presence of electron with drawing group $\overline{Cl}$. The electron donating isobutyl group predominating as well as the isobutyl group is having more oxidation centre hence the rate of reaction is more in isobutyl chloroformate than the ethyl formate. It is interesting to know that the rate of oxidation depends on inductive effect in case of ethyl chloroacetate and ethyl cyanoacetate the rate of ethyl chloroacetate is more than the cyanoacetate, this is because of electronegativity of $\overline{Cl}$ and $\overline{CN}$. $\overline{CN}$ group is more electronegative i.e. more electron withdrawing than $\overline{Cl}$, hence the rate of reaction is retarded because of more electronegative $\overline{CN}$ group.

Table No.1 Shows effect of oxidant ($KMnO_4$)

Sr.No.	Name of Ester	[$KMnO_4$] x 10^{-4} M	kx10^{-2}/min
1	Dimethyl phthalate	**4.2**	**1.15**
2	Diethyl phthalate	**4.5**	**0.74**
3	Dibutyl phthalate	**4.5**	**0.80**
4	Ethyl formate	**4.7**	**2.5**
5	Isobutyl chloroformate	**4.76**	**0.97**

[Ester] = 4.7x10^{-7}m Temp = 30^{O}c λ max = 520 nm

Table No- 2, Effects of ester on oxidation of ethyl chloroacetate.

Sr. No.	Name of Ester	[Ester] x 10^{-3}	log [Sub]	k x 10^{-2}/min	logk
1	Dimethyl phthalate	**4.2**	-2.3	1.048	$\bar{2}.02$
2	Diethyl phthalate	**4.5**	-2.34	1.03	$\bar{2}.01$
3	Dibutyl phthalate	**4.5**	-2.34	0.92	$\bar{3}.96$
4	Ethyl formate	**4.7**	-2.32	2.42	$\bar{2}.3848$
5	Isobutyl chloroformate	**4.76**	-2.32	1.83	$\bar{2}.2624$

[$KMnO_4$] = 4.7x10^{-4}m Temp = 30^{O}c λ max = 520 nm

Table No. 3 Effect of variation of concentration of acid on oxidation of esters.

Sr. No.	Name of Ester	[H_2SO_4]	Log [H_2SO_4]	Log a w	Ho	K x 10^{-2}/ min	Log K	Ho+LogK
1	Dimethyl phthalate	1.25	0.096	-0.023	-0.3	1.036	2.015	-2.315
2	Diethyl phthalate	0.857	1.93	0.014	0.05	0.8060	$\bar{3}.90$	-3.8583
3	Dibutyl phthalate	1.63	0.2121	-0.033	-0.5	0.8636	3.9363	-4.4363
4	Ethyl formate	200	0.3010	0.045	-0.85	2.303	$\bar{2}.3622$	-3.2122
5	Isobutyl chloroformate	2.34	0.36	0.05	-0.99	1.43	$\bar{2}.158$	-3.148

[$KMnO_4$] = 4.7x10^{-4}m
[H_2SO_4] = 0.857 M Temp = 30^{O}c λ max = 520 nm

Table No- 4, Effect of temperature on reaction rate dimethyl phthalate

$T^{O}k$	$1/T x 10^{-3}$	$k x 10^{-2}$/min	logK	LogA	A	E J/mole	Δ H≠ J/mole	Δ G≠J/mole	Δ S≠ J^{-1}/$mole^{-1}$
283	3.53	0.8060	$\bar{3}.9063$	1.1180	$0.718 x 10^{-1}$	8297.09	5944.23	23976.99	-63.72
293	3.41	0.8521	$\bar{3}.9304$	1.0004	$03979 x 10^{-1}$	8297.09	5861.09	24894.37	-64.96
303	3.30	0.9672	$\bar{3}.9855$	0.8940	$9.513 x 10^{-1}$	8297.09	5777.95	25779.16	-66.96
313	3.19	1.151	$\bar{2}.0610$	1.5143	$7.112 x 10^{-1}$	8297.09	5694.81	22383.97	-53.32
323	3.09	1.312	$\bar{2}.1179$	1.4036	$6.059 x 10^{-1}$	8297.09	5611.67	15236.91	-25.81
333	3.00	1.84	$\bar{2}.2648$	1.3518	$5.462 x 10^{-1}$	8297.09	5528.53	23793.58	-54.83

$[KMnO_4] = 4.7x10^{-4}$m
[Dimethyl phthalate] = $4.7X10^{-3}$ M

Table No- 5, Effect of temperature on reaction rate diethyl phthalate

$T^{O}k$	$1/T x 10^{-3}$	$k x 10^{-2}$/min	logK	LogA	A	E J/mole	Δ H≠ J/mole	Δ G≠J/mole	Δ S≠ J^{-1}/$mole^{-1}$
283	3.53	0.8060	$\bar{3}.9063$	2.4746	$6.763 x 10^{-1}$	11488.28	9135.45	25266.41	-57.27
293	3.41	0.9212	$\bar{3}.9658$	2.3142	$4.972 x 10^{-1}$	11488.28	9052.28	22683.22	-46.52
303	3.30	0.9822	$\bar{3}.9921$	2.1524	$1.829 x 10^{-1}$	11488.28	8969.14	25634.14	-55.70
313	3.19	1.082	$\bar{2}.0342$	2.7235	$8.594 x 10^{-1}$	11488.28	8886.00	22488.98	-43.46
323	3.09	1.151	$\bar{2}.0610$	2.5927	$7.728 x 10^{-1}$	11488.28	8802.86	23257.11	-44.85
333	3.00	1.266	$\bar{2}.1024$	1.7644	8.833	11488.28	8719.72	23944.48	-45.75

$[KMnO_4] = 4.7x10^{-4}$m
[Diethyl phthalate] = $4.7X10^{-3}$ M

Table No. 6 , Effect of temperature on reaction rate dibutyl phthalate

$T^{O}k$	$1/Tx1^{-3}$	k x 10^{-2}/min	logK	LogA	A J/Mole	E J/mole	Δ H≠ J/mole	Δ G≠J/mole	Δ S≠ $J^{-1}/mole^{-1}$
283	3.53	0.5757	$\bar{3}.7601$	6.5266	7.212 x 10^{6}	2.1061.85	18708.99	24074.67	-18.96
293	3.41	0.7484	$\bar{3}.8741$	6.2341	3.694 x 10^{6}	21061.85	16625.85	22434.85	-13.00
303	3.30	0.8235	$\bar{3}.9163$	5.9524	9.788 x 10^{5}	21061.85	18542.71	25045.09	-21.46
313	3.19	0.9212	$\bar{3}.9643$	5.6917	8.399 x 10^{5}	21061.85	18459.57	25880.08	-23.71
323	3.09	1.312	$\bar{2}.1179$	6.1089	2.276 x 10^{6}	21061.85	18376.43	22426.85	-12.64
333	3.00	1.727	$\bar{2}.2372$	5.9572	9.810 X 10^{5}	21061.85	14685.9	20227.02	-16.64

$[KMnO_4] = 4.7x10^{-4}m$
[Dibutyl phthalate] = 4.7 x 10^{-3} M

Table No. 7, Effect of temperature on reaction rate ethyl formate

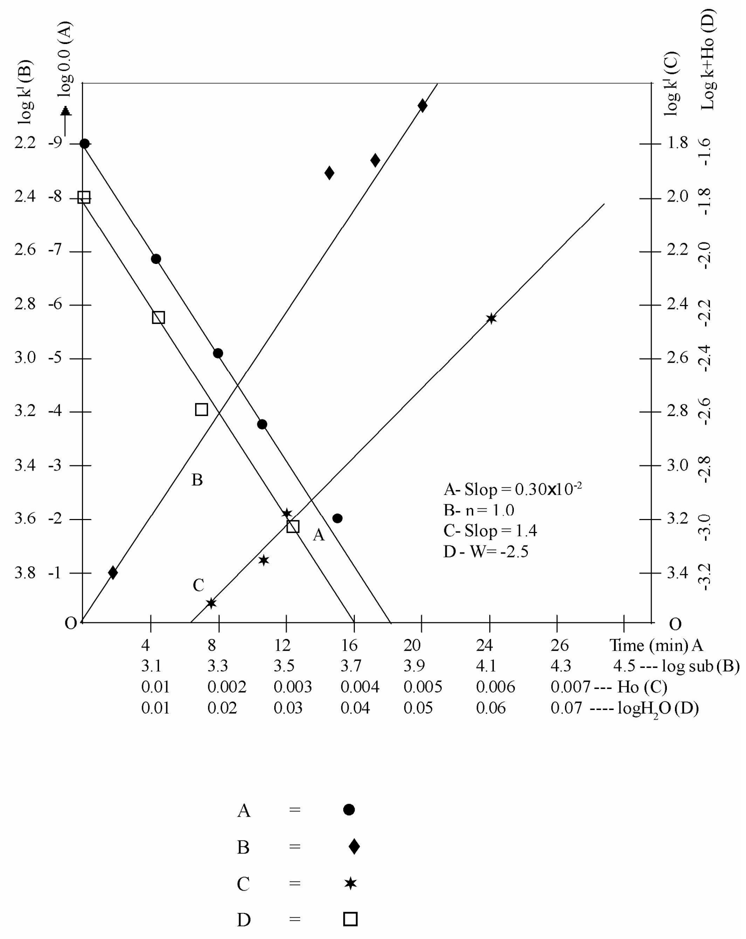
$T^{O}k$	$1/Tx10^{-3}$	k x 10^{-2}/min	logK	LogA	A J/Mole	E J/mole	Δ H≠ J/mole	Δ G≠ J/mole	Δ S≠ $J^{-1}/mole^{-1}$
283	3.53	0.5757	$\bar{3}.2397$	5.6486	8.119 x 10^{4}	19147.14	167194.28	9150.45	-27.01
293	3.41	0.6909	$\bar{3}.1605$	5.3706	5.689 x 10^{4}	19147.14	16711.14	8055.92	-29.54
303	3.30	0.9212	$\bar{3}.9642$	5.1004	1.7 x 10^{5}	19147.14	16628.00	6874.43	-32.19
313	3.19	1.151	$\bar{2}.9383$	5.8262	9.170 x 10^{4}	19147.14	16544.86	11558.77	-15.93
323	3.09	1.451	$\bar{2}.1616$	5.5982	7.768 x 10^{4}	19147.14	16461.72	10618.65	-18.09
333	3.00	1.842	$\bar{2}.2652$	5.3528	5.475 X 10^{4}	19147.14	16378.58	9478.82	-20.72

(ACETIC ACID = 4.25 M)
$[KMnO_4] = 4.7x10^{-4}m$

Table No. 8, Effect of temperature on reaction rate isobutylchloroformate

$T^{O}k$	$1/Tx1^{-3}$	$k \times 10^{-2}$/min	logK	LogA	A J/Mole	E J/mole	Δ H≠ J/mole	Δ G≠ J/mole	Δ S≠ J^{-1}/$mole^{-1}$
283	3.53	0.5181	$\bar{3}.7143$	7.7473	8.77×10^{6}	22976.57	20623.71	17301.29	-11.74
293	3.41	0.6909	$\bar{3}.8394$	7.0169	2.27×10^{5}	22976.57	20540.57	16128.07	-15.06
303	3.30	0.7484	$\bar{3}.8742$	6.6905	8.38×10^{5}	22976.57	20457.43	14942.83	-18.21
313	3.19	0.8520	$\bar{3}.9304$	6.4175	6.20×10^{5}	22976.57	20374.29	13951.53	-20.52
323	3.09	13.381	$\bar{2}.1402$	6.8878	9.48×10^{5}	22976.57	20291.15	17486.14	-08.87
333	3.00	1.612	$\bar{2}.2073$	8.2992	4.75×10^{7}	22976.57	20208.01	16545.5	-11.07

(ACETIC ACID = 4.25 M)[$KMnO_4$] = 4.7×10^{-4}m
[Isobutyl Chloroformate] = 4.7×10^{-3}M



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