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Research Article

KINETIC AND MECHANISTIC STUDY OF OXIDATION OF ESTER BY $K_2Cr_2O_7$

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ABSTRACT

In present investigation we are studied the kinetics and mechanism of oxidation of ester by potassium dichromate in acid medium. In the present paper we reported the effect of oxidant K2Cr2O7 , 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, as temperature increases rate of the reaction also increases.

Keywords: $K_2Cr_2O_7$, Ethyl butyrate, 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) [1-3]. Various chromium (VI) containing compounds like 2-2[1] bipyridinium chlorochromate, pyridinium chromate1, benzimidazolium finorochromate have been used to carry out the kinetics and mechanism of various organic compounds. Kinetics of substituted esters studies.

The update literature survey shows that, though the considerable amount of work has been done on the oxidation of organic compounds[4-8,15] 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 ethyl butyrate. The kinetic of oxidation of ester by potassium dichromate in moderately concentrate chromic acid medium has been investigated.

The rate law:

$$\frac{-d[Cr(VI)]}{dt} = k\,(Ester)[Cr_2O_7]_{total}$$

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 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 both esters was confirmed.

The ethyl butyrate 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 permanganate 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. Chromic 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] > [$K_2Cr_2O_7$] in 3.20 M. Chromic Acid. The plot of log absorbance (O.D.) Vs time were linear indicating the first order dependence of rate on [$K_2Cr_2O_7$] Oxidation of esters depends on the concentration of potassium dichromate. This was also confirmed by verifying [$K_2Cr_2O_7$] 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 [ester] (Table 2). The rate of reaction increases with increases in Concentration of Chromic Acid. Table 3.

Table 1: Shows effect of oxidant ($K_2Cr_2O_7$)

Sr. No	[$K_2Cr_2O_7$] x 10^4 M	kx10^2/min
	B	B
1	3.60	1.650
2	2.90	1.610
3	2.50	1.580
4	2.10	1.620
5	1.40	1.590
6	1.09	1.633

[Ethyl butyrate] = 4.7x10^{-7}m; Temp = 30^0c; λ max = 520 nm

Table 2: (Oxdation of Ethyl Butyrate) Effect of ethyl butyrate

Sr.No.	[Ester] x 10^3	log [Sub]	k x 10^2/min	log [k]
1	1.30	-2.8861	1.189	-1.9248
2	1.80	-2.7448	1.398	-1.8544
3	2.70	-2.5687	1.400	-1.8538
4	3.10	-2.0976	1.425	-1.8461
5	3.60	-2.4430	1.450	-1.8386
6	4.50	-2.3468	1.190	-1.7169

Table 3: Effect of various concentration of acid

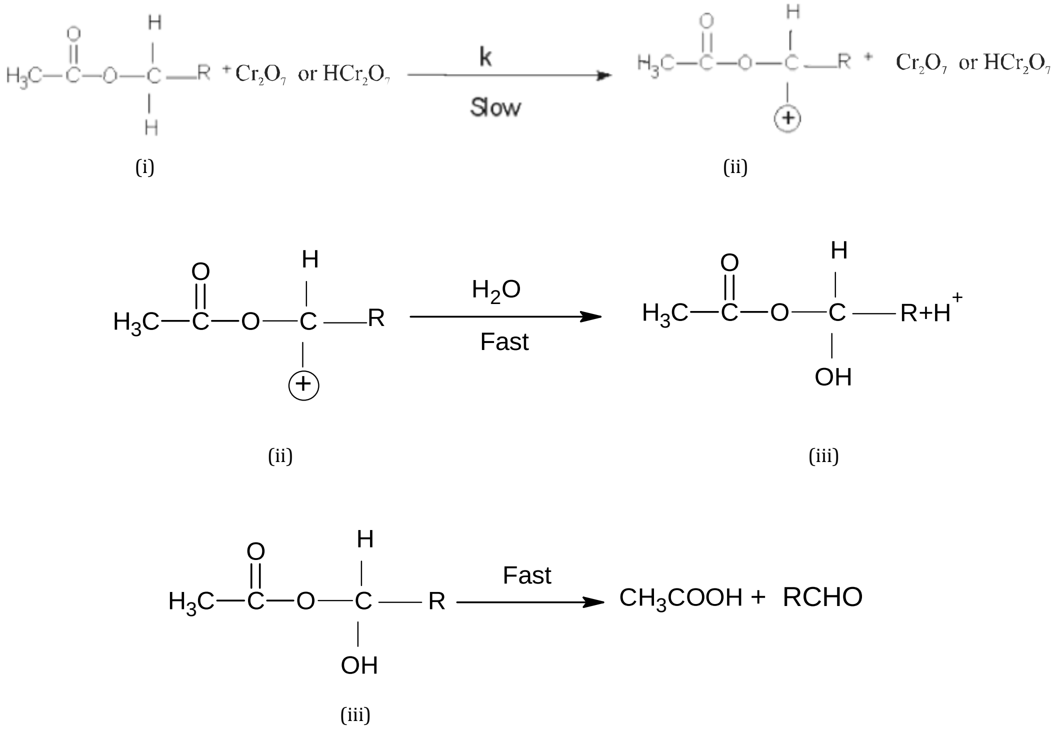
$[H_2SO_4]$	Log $[H_2SO_4]$	Log a w	Ho	K x 10^{-2}/ min	Log K	Ho+LogK
2.80	-3.5529	-0.0700	0.70	1.80	-3.744	-3.044
3.00	-3.5229	-0.0550	0.65	2.00	-3.698	-3.048
3.30	-3.4815	-0.0425	-0.10	2.50	-3.602	-3.702
3.50	-3.4560	-0.0325	-0.45	3.00	-3.522	-3.972
3.80	-3.4203	-0.0200	-0.20	3.50	-3.455	-3.655
4.00	-3.3980	-0.0150	0.08	4.00	-3.397	-3.312
4.20	-3.3768	-0.0110	0.02	4.40	-3.356	-3.336

ETHYL BUTYRATE; $[K_2Cr_2O_7] = 4.7\times10^{-4}$m; $[H_2SO_4] = 0.857$ M; Temp = 30^oc; λ max = 520 nm

Table 4: Effect of temperature on reaction rate

T^ok	$1/T\times10^{-3}$	k x 10^{-2}/min	logK	LogA	A	E J/mole	Δ H# J/mole	Δ G# J/mole	Δ S# J/mole
298	3.36	0.86	-2.863	14.8	1.170	18443	15966	82036	-221
303	3.30	1.28	-1.892	19.8	1.288	18443	15925	82418	-219
308	3.25	1.39	-1.854	18.8	1.274	18443	15883	83557	-219
313	3.19	1.75	-1.756	20.9	1.321	18443	15842	84329	-218
318	3.14	1.87	-1.738	19.5	1.292	18443	15800	85560	-219
323	3.10	2.76	-1.558	26.6	1.425	18443	15758	85795	-216

$[K_2Cr_2O_7] = 4.7\times10^{-4}$m; [ETHYL BUTYRATE] = $4.7\mathrm{X}10^{-3}$ M



The reaction consistent with the A-2 process is hydrolysis of ester ethyl butyrate. 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 $K_2Cr_2O_7$.

The effect of temperature was also studied at different temperature like 283K, 293K, 303K, 313K, 323K and 333K. It is shown in table.4 and it is clear that as temperature increases rate constant increases. Thermodynamic parameters such asΔ H ,ΔS ,$\Delta\Gamma$, ΔE and A i.e. frequency factor were studied.

A probable mechanism (scheme -1) in which Cr_2O_7 or HCr_2O_7attacks the alcohol moiety of the ester is considers explaining the observed kinetic result.

Compound (III) being highly unstable disproportionate to give Chromic Acid and the corresponding aldehyde.

The rate law can be expressed by equation (1)

$$\frac{-d[Cr(VI)]}{dt} = k\,(Ester)[Cr_2O_7]_{total} \quad \text{---- (2)}$$

This type of hydride ion transfer process has been proposed in the oxidation of aldehyde, formic acid, ethers, alcohols etc. by potassium dichromate 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

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