PERMANGNATIC OXIDATION OF ETHYL-2- CLOROACTOTACETATE : A KINETIC AND MECHANISTIC STUDY .

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Abstract

Oxidation of ethyl-2-Chloroacetoacetate in aqueous acidic medium has been carried out, the reaction shows first order in oxidant and pseudo first order with substrate. The rate of oxidation increases with increase in concentration of acid where as also the rate of reaction increases with increase temperature and there is no effect and of solvent on oxidation. The thermodynamic parameters have been studied mathematically based on all the kinetic data a possible operative mechanism has been shown to it and a suitable rate low has been derived.

CH_3-CO-CH-$COOC_2H_5$
| Cl

Keywords : ethyl 2-Chloroacetoacetate, Kinetics, oxidation, mechanism, thermodynamic parameters.

Introduction :

The paramagnet ion (MnO^-_4) oxidize a great variety of substances and it find extensive applications in organic synthesis. Among the various organic compounds employed in oxidative studies esters ethyl-2-Chloroacetoacetate attractive substrate in terms of their availability and easy to oxiditive property. These compounds readily undergoes oxidation with various oxidant. Kinetic studies constitute important source of mechanistic information about reaction.

During the oxidation by permangnate it is evident that the Mn(VII) in permagnate is reduced to various oxidation states in acid, alkaline and neutral media. The mechanism by which this multivalent oxidant oxidise a substrate depends not only on the substrate but also on medium used for the study in strongly alkaline medium the stable reduction product is the magnate ion, MnO_4^{-2} requires ap^H range 12-13^{PH} below which the system becomes distributed and the reaction will proceed. Further to give a reduced product of oxidant as Mn(IV) which slowly develops yellow turbidity[1].

Oxidation reaction by Potassium permanganate are 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 oxidising agent like potassium dichromate Cr (VI)[2-4] The update literature survey shows that, though the considerable amount of work has been done on the oxidation of organic compounds[5to13] by potassium permagnate, but only a few studies is found on the kinetics of oxidation of ester by potassium permagnate[14,15]. The object of present investigation is to formulate the reaction mechanism from the date 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 dimethyle phthalate, dicthyl phthalate, dibutyl phthalate, ethyl formate, isobuty chloroformate. the kinetic of oxidation of ester by potassium permagnet in moderately concentrate sulphuric and medium has been investigated.The rate law

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

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

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 postassium 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 esters was confirmed. The ester were always freshly distilled before used for the kinetic measurement permagnate and sulphuric acid solution were taken in two different flasks and covered with black cloth and placed in a thermostal 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 spectrophotomer. 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 [16]. 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

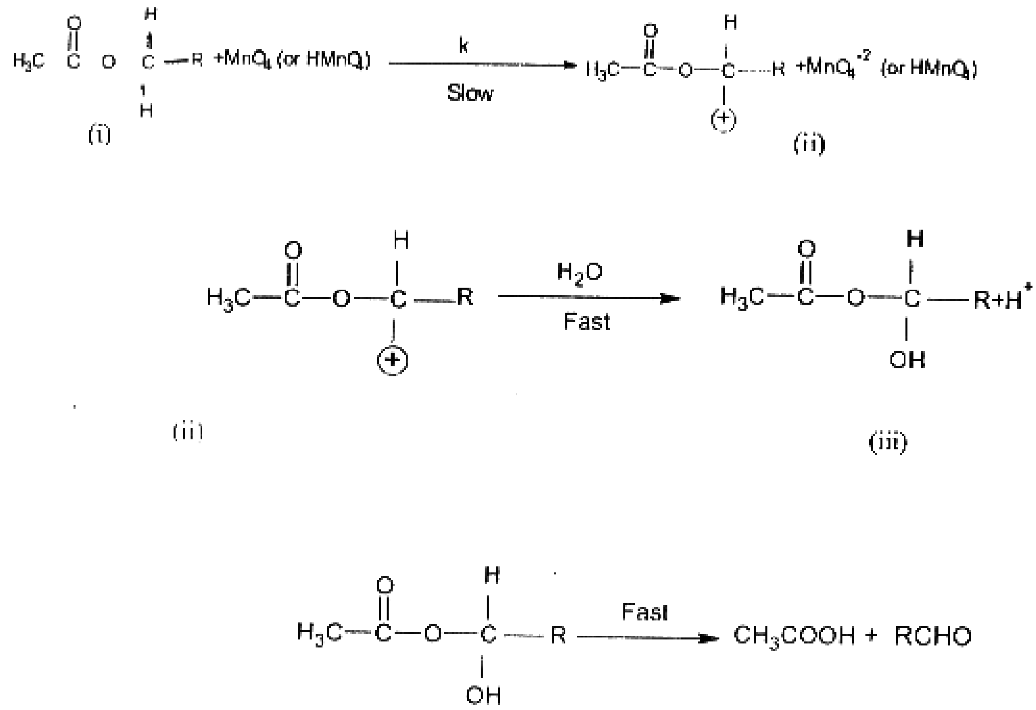
Under the conditions [ester] > [$KMnO_4$] in 3.20 M. H_2SO_4. The plot of log absorbance (O.D.) Vs time were linear indicating the first order dependence of rate on [$KMnO_4$). (fig has not shown) A Oxidation of esters depends on the concentration of potassium permagnate. This was also confirmed by verifying [$KMnO_4$] 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] (Table 2). The rate of reaction increases with increases in [H_2SO_4]. (Table No.3)

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. It is clear that as temperature increases rate constant increases (Table No. 4). Thermodynamic parameters such as □ $H^\#$ □ $S^\#$□ $G^{\#,}$ E □ E and A i.e. frequency factor were studies and given in

The negative values of entropy of activation shows that the intermediate transition state is rigid the relatively small values of □ H and □ S are consistent with the reaction generally proceeds through highly ionised transition state[17].

$$H^7 + MnO_4 ® HMnO_4$$

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 $HMnO_4$. 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 $10K^1$ Vs log [H_2SO_4] and $\log K^1$ Vs Ho (fig has not shown) 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 $\log K^1$ Vs Ho Vs log H20 was linear (fig has not shown) and the slop 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 3.2×10^{-5} liter mol^{-1} sec^{-1} under identical condition, from this it is



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

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

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[18].

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 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.

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 with drawing group $C\bar{l}$.

Acknowledgement

One of the author (Sayyed Husain) is very much thankful to UGC, New Delhi for its financial assistance of Major Research Project File No. 39-816/2010 (SR) dated 11th Jan. 2011.

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