STRONG ACID CATALYZED OXIDATION OF α -HYDROXY ACID (GLYCOLIC ACID) BY CHROMIC ACID; A KINETIC AND MECHANISTIC APPROACH

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ABSTRACT

Strong acid (Sulphuric Acid) catalyzed oxidation of α – hydroxy acid (Glycolic Acid) by Chromic Acid have been studied with spectrophotometerically at the temperature 300K.The rate of reaction is catalyzed with the increase in the concentration of strong acid. The reaction is first order with respect to Chromic Acid, α – Hydroxy Acid and $[H^+]$. Reaction is catalyzed by Hydrogen ions. Oxidation products of Glycolic Acid are identified. Kinetic parameters such as catalytic constant, temperature coefficient are calculated. A suitable mechanism is proposed.

Keywords; Kinetics, Oxidation, α – Hydroxy acid, Chromic Acid, Sulphuric Acid, Glycolic Acid

1. INTRODUCTION:

Chromium exists usually in both trivalent Cr(III) and hexavalent Cr(VI) forms in aqueous systems. These two oxidation states are characterized by notable difference in chemical,physical behavior and toxicity. Trivalent chromium is readily precipitated on a variety of inorganic and organic surfaces. Hexavalent Chromium Cr (VI) is established as a versatile oxidant for many types of substrates varying from metal ions to naturally occurring organic compounds. Hexavalent Chromium as chromate or dichromate is highly soluble in water and is reported to be highly toxic. A variety of compounds containing hexavalent Chromium have proved to be versatile reagent capable of oxidizing almost every oxidiasable functional group. Chromic Acid is more efficient for quantitative oxidation of several organic substrates and has certain advantages over similar oxidizing agents in term of the amount of oxidant and solvent required, short reaction time and high end products.

Glycolic Acid is a α-hydroxy acid and a class of chemical compounds that consist of a carboxylic acid substituted with a hydroxy group on the adjacent carbon and having formula $HOCH_2CO_2H$. Glycolic Acid is also known as Hydroacetic Acid or Hydroxyacetic Acid. It is a simple and smallest α- hydroxy acid . Glycolic Acid is well known for its important role in dermatology and cosmetic industry, being used as inhibitor of harmful oxidation, biochemical process. Now a day's important research is going on in order to develop new materials based on biodegradable polymers derived from Glycolic Acid that can be used reconstruction of biological tissues and in organic transplantation. Glycolic Acid is found in some sugar-crops.

2. MATERIALS AND METHOD:

All the chemicals were of A R grade Glycolic Acid $HOCH_2COOH$ (Merck), CrO_3 (Qualigens), Sulphuric Acid (H_2SO_4) (Merck) and others all chemicals were used of highest purity available commercially. Solutions were prepared in double distilled water. Solutions of oxidant and reaction mixtures containing known quantities of substrates, Glycolic Acid, H_2SO_4, H_2CrO_4 and other necessary solutions were separately thermostated. The reaction was initiated by mixing the requisite amounts of the oxidant with the reaction mixture. Progress of the reaction was monitored by following the rate disappearance of Cr (VI) by spectrophotometer.

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PRODUCT ANALYSIS

Product analysis was carried out under kinetics conditions i.e. with excess of the .Under the kinetics conditions, the results show that $HOCH_2COOH$ react with H_2Cr0_4 (CrO_3+H_2O) to form an intermediate compound. Intermediate compound finally decompose slowly to give reaction products, HCOOH and CO_2. $HOCH_2COOH$ initially produces Glyoxylic Acid which subsequently is oxidized to HCOOH. The products of the oxidation of Glycolic Acid by Chromic Acid in presence of H_2SO_4 are confirmed by Fiegl spot test[1] and other usual tests.

The Kinetic equation proposed for this reaction is given below;

$$\frac{-\ d[\,Cr\ (VI)\,]}{dt} = K\,[Cr\ (VI)][\,Glycolic\ Acid][H^+]$$

In the oxidation of $HOCH_2COOH$ by Chromic Acid in presence of strong acid i.e. H_2SO_4 some of the kinetic runs performed by keeping the concentration of H_2CrO_4 and $HOCH_2COOH$ constant at 4.20 X 10^{-3} M and 2.50 X 10^{-2} M respectively while the concentration of H_2SO_4 had varied from1.25 x 10^{-2} M to 6.25.x 10^{-2} M respectively. The average value of catalytic constant is determined and found to be order of the 1.4975.Values of rate constant and catalytic constants of various kinetics runs are given below in Table No.01 and Temperature coefficient of various reaction mixtures in Table No.02

Table No-01

S. No	Concentration of H_2SO_4(M)	Rate Constant K x 10^{-3} min^{-1}	H^+ concentration x10^{-2}at 300K	Catalytic Constant x 10^{-1}
1.	0.00 x10^{-2}	1.9604	1.023	-
2.	1.25 x10^{-2}	5.3492	2.455	1.3804
3.	2.50 x10^{-2}	6.0436	2.754	1.4826
4.	3.75 x10^{-2}	6.3460	2.884	1.5207
5.	5.00 x10^{-2}	6.7011	3.090	1.5342
6.	6.25.x10^{-2}	7.2568	3.311	1.5694

Table No-02

S. No	Concentration of H_2SO_4 (M)	Rate constants Kx10^{-3}at 300K	Rate constants Kx10^{-3} at 310K	Rate constants Kx10^{-3} at 320K	pH values at 300K	Temperature Coefficient	
						k_{310} / k_{300}	k_{320} / k_{310}
1.	0.00 x10^{-2}	1.9604	3.8816	7.5692	1.99	1.98	1.93
2.	1.25 x10^{-2}	5.3492	10.5379	17.2822	1.61	1.97	1.94
3.	2.50 x10^{-2}	6.0436	11.7850	23.0986	1.56	1.95	1.96
4.	3.75 x10^{-2}	6.3460	12.5651	24.6276	1.54	1.98	1.96
5.	5.00 x10^{-2}	6.7011	13.0001	25.6103	1.51	1.94	1.97
6.	6.25.x10^{-2}	7.1568	14.0273	27.3534	1.48	1.96	1.95

RESULTS AND DISCUSSION:

Rate of the reaction is increases as increase in the concentration of Sulphuric Acid. Effect of H_2SO_4 as a positive catalyst is explained on the basis of Shpitalsky[11] "Classical" theory of intermediate compound formation. Numerous observations have led to two important generalizations in the field of catalysis.

First, the decrease of energy of activation as the most pronounced manifestation of the activity of the catalyst.

Second, especially for homogeneous catalysis in the solutions, the concept of proportionality between the reaction rate and the concentration of the catalyst. These propositions lead of necessity to the conclusion that Sulphuric Acid participates in the reaction forming certain unstable intermediate compounds or complexes and thus make it possible for the reaction to proceed along a more energetically favorable pathway.

In the presence and absence of H_2SO_4 under the experimental conditions the rate of disappearance of Chromium Cr (VI) shows a first order dependence on Cr (VI) and also one with respect to hydrogen ion concentration. On the basis of table no.2, it is clear that the temperature coefficient is fairly constant as it is

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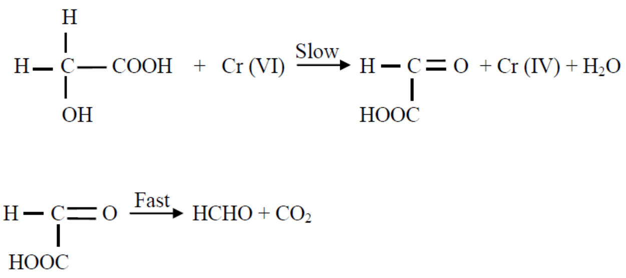
equal to 2, so the temperature effect is purely thermal.

PROPOSED MECHANISM

$$CrO_3 + H_2O = H_2CrO_4$$

$$H_2CrO4 \rightleftharpoons H^+ + HCrO_4^-$$



$$Cr(IV) + Cr(IV) \longrightarrow Cr(V) + Cr(III)$$

$$HCHO + Cr(V) \xrightarrow{O} HCOOH + Cr(III)$$

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