ORIGINAL ARTICLE

KINETICS AND MECHANISM OF OXIDATION OF α-HYDROXY ACIDS BY PIPERAZINIUM DICHROMATE (PIDC)

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ABSTRACT

Piperaziniumdichromate(PIDC) is a selective oxidant and has been used in the oxidation of number of organic compounds. The reactions of piperazinium dichromate with α-hydroxy acids such as mandelic, lactic and glycolic acids has been studied in the presence 100% H_2O medium at a temperature of $35\pm0.2°C$.The reaction is first order with respect to PIDC, hydroxy acids and [H+] and the reaction is catalyzed by hydrogen ions. The reaction rate increased remarkably with the increase in the concentration of perchloric acid. The rate is increases with decreasing the concentration of Mn(II).The reaction rate were determined at different temparatures and the activation parameters computed. A suitable mechanism has been proposed.

Keywords: PDC, α-hydroxy acids, Oxidation, Perchloric acid

1.INTRODUCTION

Kinetics and oxidation of various compounds like alcohols, aldehydes, ketones, hydroxyl acids etc,.With oxidants likeMn(II), Cr(VI), V(V), and Th(III). Oxidation reactions are very important in nature and in organic synthesis. Among the most important oxidants is chromium(VI) which may play a significant role in the chemistry of vanillin in the environment due to the mutagenic and carcinogenic activity of chromium. Chromium exists in both trivalent, Cr(III), and hexavalent, Cr(VI), species in aqueous solutions and the two oxidation states are identified by various physical/chemical behavior and toxicity. Chromium(VI) compounds are very dangerous for biological systems, but those of chromium(III) are relatively non-toxic[1]. Chromium(VI) is employed for oxidation of organic compounds and it is reduced to lower oxidation states[2]. The chemistry of Cr(V) and Cr(IV) as intermediate species which may be formed during reduction of chromium(VI) were attracted many researchers because of their involvement in the mechanism of Cr–induced cancers[3]. The Cr(VI) compounds have proved themselves as effective oxidants since they give different reactive specie during oxidation. A lot of work has been done employing the different Cr(VI) oxidants. The oxidation of α-hydroxy acids such as mandelic acid, lactic acid, glycolic acid by various oxidant have been tudied.[4-6].The study of oxidation reactions through elucidation of their mechanisms and the investigation of reaction kinetics deal with the study of change in concentration of the components of the reaction system in gas phase, as well as Liquid phase, with the passage time. piperazinium dichromate is non hygroscopic and the oxidative coupling of thiols to disulphides by piperazinium dichromate have been studied by Mavassagh et al[7] . Kinetics and oxidation of number of hydroxyl acids by various oxidants have been studied[8-12].The present work concern the higly reactive oxidant PIDC oxidation of α-hydroxy acids of mandelic, lactic and glycolic acids in water medium.

2.MATERIALS AND METHODS

Preparation of piperazinium dichromate (PIDC)

Chromium(VI) (4.6g, 0.046 mole) in 5 ml of water was added in portions to piperazine(2g, 0.0233 mole) in 10 ml of water at room temperature and the mixture stirred for 5 minutes. The bright orange solid formed was filtered under suction and washed with acetone (2 x 10 ml) and then water (10 ml). The filterate was air dried to afford 6.8g (96%)of piperazinium dichromate.

Kinetic measurements

All kinetic measurements were carried out An Evolution 60 Thermo spectrophotometer fitted with recording and thermostating arrangement was used to follow the rate of the reaction. The progress of the reaction was followed at 365 nm by monitoring the decreases of Cr (IV) in free α-hydroxy acids and 501nm by monitoring the changes in absorbance. The required [α-hydrox acids], [HClO4], and [PIDC] were premixed in a reaction vessel, thermostated in an oil bath, andPIDC solution (thermally equilibrated at 323K) was then added prior to the absorbance measurements. The reaction was started by adding the oxidant to the mixture. A stopwatch was started when half of the oxidant had been delivered. Fixed amount of the reaction mixtures were removed at definite intervals and the unreacted PIDC was estimated iodometrically. The kinetic investigations were carried out under pseudo- first order conditions. Keeping the substrate concentration always in excess.

Stoichiometric Analysis

Kinetic measurements of the oxidation of α-hydroxy acids were carried out under pseudo first order conditions. The stoichiometric studies for the oxidation of α-hydroxy acids by PIDC were carried out with the oxidant in excess. After nine half-lives when the reaction was nearing completion, the concentration of unreacted was determined spectrophotometrically.

3.RESULTS AND DISCUSSION

The oxidation of some *α*-hydroxy acids like mandelic, lactic and glycolic acids by PIDC have been conducted in 100% water medium at 303 K, under pseudo first order conditions and the result obtained were discussed. The comparative study of piperazinium dichromate oxidation of α-hydroxy acids may be throw light on the mechanistic aspect of the reaction.

The reaction between PIDC with α-hydroxy acids in water medium , the specific rates calculated are nearly the same, pointing to first order

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dependence of PIDC concentration. Also graphs of logarithm PIDC concentration *versus* time are linear and from the slopes, the specific rates calculated agree with those calculated using integrated first order option.As the specific rates are nearly the same , the rate of the reaction depends upon first order of [PIDC].The rate is given as

-d[Cr(VI) = k1[Cr(VI)]   --------------------(1)

From the Table 1 for the oxidation of PIDC of α-hydroxy acids like mandelic, lactic and glycolic acids has been made in water medium under pseudo-first order conditions.T herate of the reaction increases with increasing the concentration of substrate. The slope of nearly unity is obtained from the linear graph of logarithm of specific rates (k^1 is s^{-1}) versus log α-hydroxy acids in each case suggesting first order dependence of rate on α-hydroxy acids. The oxidation rate of mandelic acid is faster comparative to lactic and glycolic acids this is due to stabilization of intermediate may probably be the reason for this behavior.

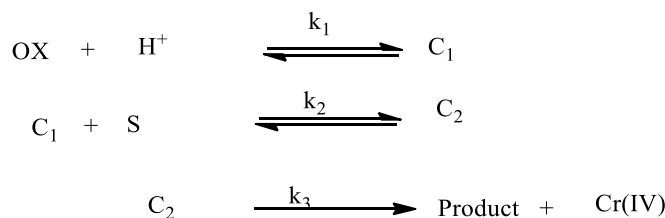-d[Cr(VI)   = k2[Cr(VI)] [α-hydroxy acids] -------------(2)

Table 1 Kinetic data for the oxidation of α-hydroxy acids by PIDC

α-hydroxy acids	[Compound] $\times 10^3$ (mol dm^{-3})	$10^4 k_1$ (s^{-1})	$10^2 k_2$ ((mol^{-1} dm^{-3}s^{-1}))
Mandelic acid	0.50	3.33	6.66
	1.00	6.62	6.62
	1.50	8.25	6.60
	2.00	9.91	6.65
	2.50	13.51	6.65
Lactic acid	0.50	2.61	5.22
	1.00	5.24	5.24
	1.50	6.52	5.21
	2.00	7.83	5.22
	2.50	10.40	5.20
Glycolic acid	0.50	0,92	1.84
	1.00	1.82	1.82
	1.50	2.28	1.82
	2.00	2.78	1.85
	2.50	3.74	1.87

[HClO$_4$] = 1.00 mol dm^{-3} Temparature = 35±0.2°C   Medium = 100% H$_2$O

The PIDC oxidation of α-hydroxy acids is an acid catalysed reaction and the effect of HClO$_4$ concentration on the rate of PIDC oxidation has been studied in the concentration range0.309 to 1.00 mol dm-3 at constant ionic strength (Table 2) with increasing HClO$_4$ concentration. The rate of PIDC oxidation increases proportionately and a graph of logarithm of specific rate versus logarithm of HClO$_4$ concentration is linear with slope nearly equal to unity .This is an acid catalyzed reaction and the order with respect to [H+] is unity. This shows that the rate determining step, in the presence of an acid, involves protonated Cr(VI).By varying the Mn(II) and keeping the other factors constant , the rate of the reaction decrease with increase in the concentration of Mn(II). Indicating that the reaction involves Cr(IV) as intermediate.This decrease in rate of addition of Mn(II), the rate of reaction showing the involvement of two electron change in the rate determining step.

Effect of Temperature

The kinetics of oxidation of hydroxy acids was studied at four different temperatures *viz*., 303 to 318 K.using the Eyring relationship by the method of least square and presented in Table 2. The various thermodynamic parameters are calculated that shows the reaction may be bimolecular.The kinetics and the stoichiometric results with product analysis are obtained in the piperazinium dichromate induced electron transfer in α-hydroxy acids. The rate of PIDC oxidation of mandelic, lactic and glycolic acid depends on the first power of Cr(VI)concentration.The rate of the reaction depends on the first power of concentration of α-hydroxy acids.Of the three acids mandelic acid reacts faster than lactic and glycolic acids. Based on the above results the following mechanism is proposedfor Cr(VI) oxidation of mandelic acid.

$$OX + H^+ \underset{}{\overset{k_1}{\rightleftharpoons}} C_1$$

$$C_1 + S \underset{}{\overset{k_2}{\rightleftharpoons}} C_2$$

$$C_2 \xrightarrow{k_3} Product + Cr(IV)$$

$$Rate = k_3 [C_2]$$

$$[C_1] = K_1 [OX][H^+]$$

$$[C_2] = K_2 [S][C_1]$$

$$[C_2] = K_1 K_2 [OX][S][H^+]$$

$$Rate = K_1 K_2 k_3 [OX][S][H^+]$$

$$Rate = k[OX][S][H^+] [k = K_1 K_2 k_3]$$

Table 2 Activation parameters in the oxidation of α-hydroxy acids by PIDC

α-hydroxy acids	$10^4 k_1$ (s^{-1})				$\Delta H \neq$ (kJ mol^{-1})	$-\Delta S \neq$ (Jmol-1K^{-1})	$\Delta G \neq$ (kJ mol^{-1})
	303K	308K	313K	318K			
Mandelic acid	5.29	6.62	8.48	10.60	35.63	192.29	92.81
Lactic acid	3.85	5.24	7.45	9.44	45.64	140.62	89.65
Glycolic acid	1.45	1.82	2.32	2.96	38.94	154.12	88.23

[HClO$_4$] = 1.00 $\times 10^{-3}$ mol dm^{-3} [α-hydroxy acids] = 1.00 $\times 10^{-2}$ mol dm^{-3} [PIDC] = 1.00 $\times 10^{-3}$ mol dm^{-3}

4.CONCLUSION

The kinetics and mechanism of oxidation of α-hydroxy acids by PIDC in aqueous HClO4 medium is followed under different experimental condition and temperature. The reaction follows first order with respeact to PIDC. The order with respect to α-hydroxy acids and [H+] are unity. The oxidation rate of mandelic acid is faster to lactic and glycolic acids.The rate was followed at four different temperature viz .,303, 308, 313 and 318 K and rates were measured and the thermodynamic parameters were calculated. The reaction was characterized by a low enthalpy of activation and negative entropy of activation is due to extensive solvation of transition state over the reactant. piperazinium dichromate oxidizes α-hydroxy acids to the respective keto acids, such a transition state can be envisaged only when the C-H bond occurs in the slow step with hydride ion transfer.

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