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MECHANISM OF GLYCOLIC ACID TOWARDS PIPERIDINIUM CHLOROCHROMATE OXIDATION

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ABSTRACT

The kinetics of oxidation of glycolic acid with piperidinium chlorochromate (PipCC) has been studied in aqueous acetic acid medium. The reaction order is one with respect to oxidant, substrate and fractional order with respect to hydrogen ion concentration. Decrease in dielectric constant of the medium increases the rate of reaction. No appreciable change in the rate is observed by increasing the ionic strength of the medium. The reaction does not induce the polymerization of acrylonitrile. From the kinetic data obtained, the activation parameters have been calculated and plausible mechanism has been proposed. A suitable rate law is derived.

Keywords: kinetics, oxidation, parameters, piperidinium chlorochromate

INTRODUCTION

A great variety of new chromium(VI) oxidant together with special reaction conditions have been developed for the chemospecific, regiospecific and stereospecific oxidative generation of functional groups in highly sensitive systems. Recently some neutral or almost neutral chromium (VI) reagents have been developed to effective oxidations under mild conditions. Piperidinium chlorochromate is found to be a mild selective reagent for the oxidation of alcohols to the corresponding carbonyl compounds[1]. The oxidation of α-hydroxy acids by various chromium compounds have also been studied extensively[2-11]. Our present work involves the kinetic study of oxidation of glycolic acid with piperidinium chlorochromate in the presence of perchloric acid.

EXPERIMENTAL

Materials and Methods

Piperidinium chlorochromate was prepared by literature method[1] and its purity was checked by determining chromium (VI) concentration iodometrically. Glycolic acid (Aldrich) was used extra pure variety and the melting point is 69.5°C (literature value 70°C). All other chemicals were used of AnalaR grade. Double distilled water can be used for throughout the work.

Kinetic Measurements

The reaction was carried out under pseudo first order conditions and keeping the substrate always in excess. The reactions were followed by monitoring the decrease in absorption of PipCC at 470 nm employing a UV-visible spectrophotometer[12]. Computations of rate constants were made from the plot of log absorbance versus time. All the rate constants were reproducible with ± 3% error which is given in Table-1.

Stoichiometry and Product Analysis

The stoichiometric runs were carried out in presence of excess of PipCC at 35^{0}C reveal that one mole of oxidant was consumed by one mole of the substrate. The keto acid was formed as the oxidation product *ie*., detected by the characteristic test[13].

$$\text{HCHOHCOOH} + \text{Cr (VI)} \longrightarrow \text{HCOCOOH} + 2\text{H}^+ + 2\ \text{Cr (IV)}$$

The same experimental condition was used for the kinetic determination; solutions of oxidant (0.1 mol), glycolic acid (0.1 mol) and perchloric acid (0.1 mol) were mixed and kept under nitrogen atmosphere for 24 for completion of the reaction. The main product obtained was found to be the corresponding carbonyl compounds. The oxidation product was detected by the characteristics spot test[13].

RESULTS AND DISCUSSION

The kinetics of oxidation of glycolic acid by PipCC was investigated at several initial concentrations of the reactants. The oxidation of glycolic acid by PipCC proceeds smoothly at 313K in 50% acetic acid-water medium. The reaction was found to be first order with respect to PipCC as evidenced by a linear plot of log absorbance versus time. But the rate of reaction is decreased with increase the concentration of oxidant[14-16], the plot of [PipCC] versus 1/k_1 which is also linear (Fig.-1). The rate of reaction is increased with increase the concentration of substrate, the reaction was found to be first order with respect to substrate as evidenced by the unit slope (r = 0.998) of the plot of log k_1 versus log [substrate]. It was further well demonstrated by the constancy of the specific reaction rate constant k_2. ie., k_1/[substrate]. Table-1.

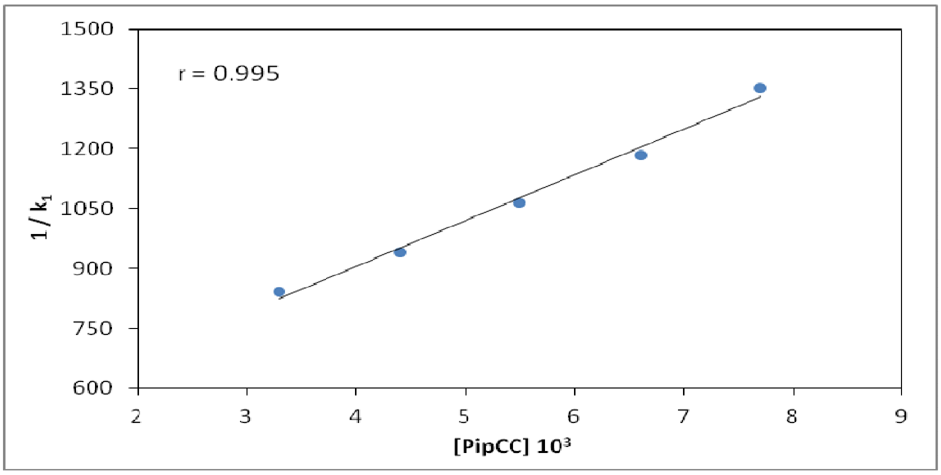


Fig.-1: Plot of 1/k_1 *versus* [PipCC]

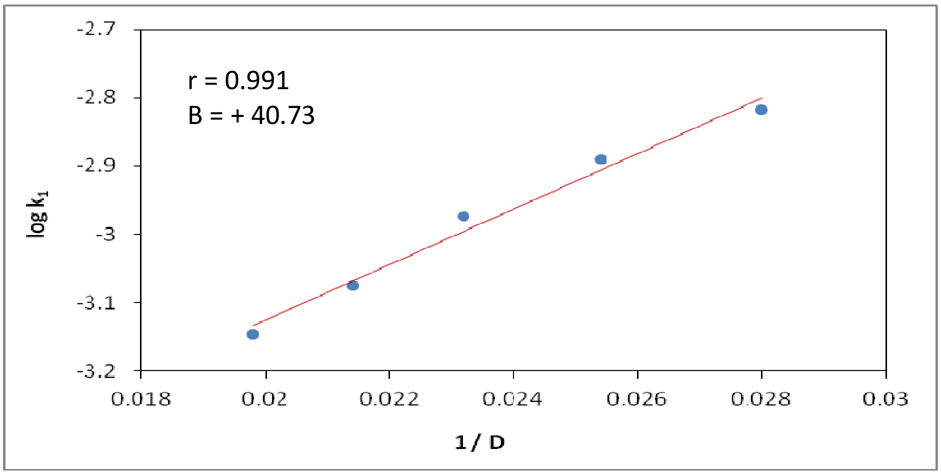


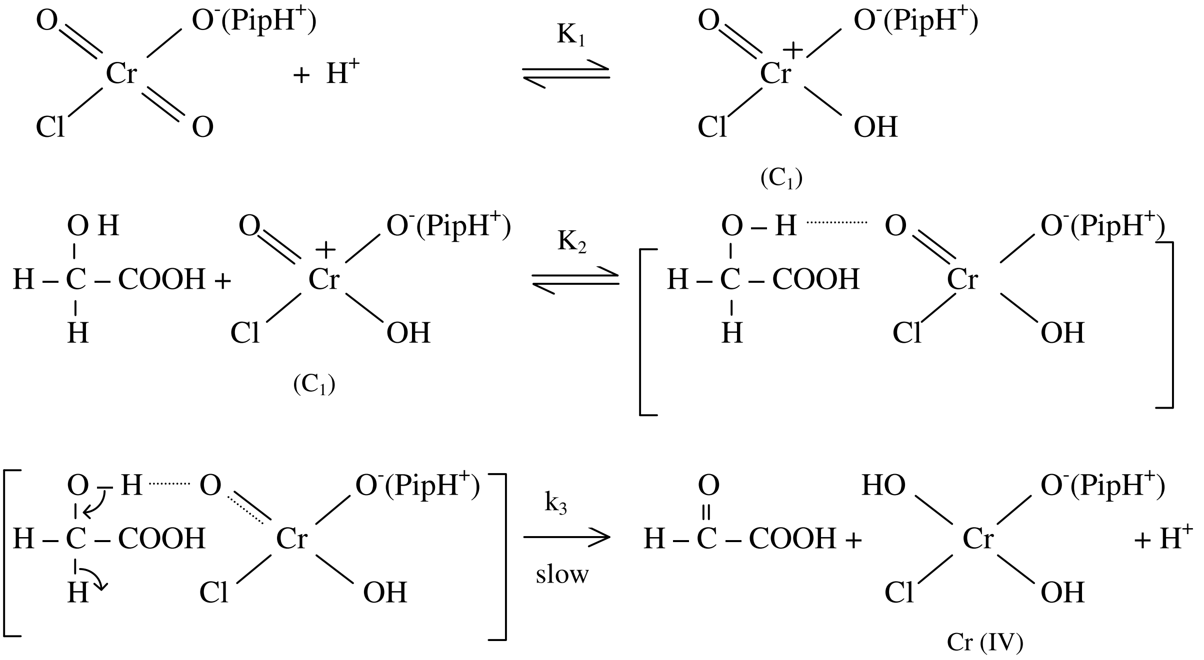
Fig.-2: Plot of log k_1 *versus* 1/D*

*If the AcOH: Water 50:50(*v/v*), D = (50x6.15+50x80)/100. Where, 6.15 is the dielectric constant for Acetic acid and 80 is the dielectric constant for water

At constant concentrations of the reactants, the reaction rate increased with increase in the concentration of the hydrogen ion. But the plot of log k_1 versus log $[H^+]$ was found to be linear with a fractional slope indicating fractional order dependence with respect to hydrogen ion concentration. Increase in ionic strength of the medium by adding sodium perchlorate has no effect on the reaction rate indicating the involvement of ion neutral molecule in the rate determining step[17]. The rate of oxidation increases with the increase in percentage of acetic acid. It is well known that as the polarity of the solvent decreases, the rate of oxidation increases. The plot of log k_1 versus D^{-1} is linear (Fig.-2) with positive slope (B = +40.73) implying the reactive species in acid medium to be a positively charged one[18] and this provides convincing evidence that PipCC is protonated. At constant concentrations of the reactants, the reaction was followed by varying acrylonitrile, [manganous sulphate] while acrylonitrile has no effect, manganous sulphate retarded the reaction rate considerably indicating a two electron transfer mechanism. (Table-3). The rate constants were measured at five different temperatures and activation parameters have been calculated from a plot of log k_2 versus T^{-1} using the Eyring's equation (Table-4). The low E_a and $\Delta H^{\#}$ values supported the proposed concerted mechanism. The negative values of the entropies of activation ($\Delta S^{\#}$) suggested that the transition state formed was considerable rigid, resulting in a reduction in the degree of freedom of the molecules.

Mechanism and Rate law

The reaction shows first order with respect to [PipCC], [substrate] and fractional order with respect to $[H^+]$. Increase in ionic strength of the medium by adding sodium perchlorate has no effect on the reaction rate indicating the involvement of an ion and neutral molecule in the rate determining step. The rate of reaction is increased with increase the percentage of the medium. No polymerization was observed with acrylonitrile, indicating the absence of free radicals during the reaction. The retardation of the rate by the addition of Mn^{2+} ion confirms that a two electron transfer process is involved in the reaction. Based on the above facts, the following mechanism was proposed (Scheme -1).



Where, K_1 and K_2 are the equilibrium rate constants and k_3 is the rate determining step of the reaction.

Scheme-1

Table-1: Rate Constants for the Oxidation of Glycolic Acid by PipCC at 313 K

[PipCC] 10^3 (*mol dm^{-3}*)	[Glycolic Acid] 10^2 (*mol dm^{-3}*)	k_1 10^4 (*s^{-1}*)	k_2 (*s^{-1} mol^{-1} dm^3*)
3.3	7.5	11.87	-
4.4	7.5	10.62	-
5.5	7.5	9.38	-
6.6	7.5	8.44	-
7.7	7.5	7.39	-
4.4	5.0	7.01	0.140
4.4	7.5	10.62	0.141
4.4	10.0	14.32	0.143
4.4	12.5	17.78	0.142
4.4	15.0	21.25	0.141
[H^+] = 6.8 x 10^{-2}*mol dm^{-3}*	AcOH : H_2O = 50 : 50 (*v/v*)		

Table-2: Rate Constants for the Oxidation of Glycolic Acid by PipCC at 313 K

[H^+] 10^2 (*mol dm^{-3}*)	AcOH : H_2O (*v/v*)	k_1 10^4 (*s^{-1}*)
3.4	50:50	7.96
6.8	50:50	10.62
10.2	50:50	13.21
13.6	50:50	16.44
17.0	50:50	19.81
6.8	40:60	7.14
6.8	45:55	8.42
6.8	50:50	10.62
6.8	55:45	12.88
6.8	60:40	15.19
[PipCC] = 4.4 x 10^{-3}*mol dm^{-3}*	[Glycolic Acid] = 7.5 x 10^{-2}*mol dm^{-3}*	

Table-3: Rate Constants for the Oxidation of Glycolic Acid by PipCC at 313 K

[$NaClO_4$] 10^3 (*mol dm^{-3}*)	[$MnSO_4$] 10^2 (*mol dm^{-3}*)	k_1 10^4 (*s^{-1}*)
0.00	-	10.62
5.01	-	10.42
10.02	-	10.24
15.03	-	10.44
20.04	-	10.36
-	0.00	10.62
-	2.02	8.10
-	4.04	8.02
-	6.06	8.24
-	8.08	8.14
[PipCC] = 4.4 x 10^{-3}*mol dm^{-3}* [H^+] = 6.8 x 10^{-2}*mol dm^{-3}*	[Glycolic Acid] = 7.5 x 10^{-2} *mol dm^{-3}* AcOH : H_2O = 50 : 50 (*v/v*)	

Rate Law

$$\begin{aligned}\text{Rate} &= k_3\,[\text{Product}]\\ &= k_3K_2\,[C_1]\,[S]\end{aligned}$$

$$\frac{-d\,[\mathrm{PipCC}]}{dt} = \frac{k_3K_2K_1\,[S]\,[O]\,[H^+]}{1 + K_1[H^+]}$$

$$= \frac{k_3K_2K_1\,[S]\,[H^+]}{1 + K_1[H^+]}$$

Table-4: Rate Constants and Activation Parameters for the Oxidation of Glycolic Acid with PipCC

Substrate	Order w.r.t. Substrate	$k_1\ 10^4\ (s^{-1})$					$\Delta H^{\#}$ $(kJmol^{-1})$	$-\Delta S^{\#}$ $(JK^{-1}mol^{-1})$	$\Delta G^{\#}$ $(kJmol^{-1})$	E_a $(kJmol^{-1})$	r at 313K
		303K	308K	313K	318K	323K					
Glycolic Acid	1.14	6.82	8.07	10.62	12.64	14.34	12.50±0.3	185.57±2	70.58±0.8	15.10±0.4	0.992

[PipCC] = 4.4 x 10^{-3}*mol dm*$^{-3}$ [Glycolic Acid] = 7.5 x 10^{-2}*mol dm*$^{-3}$ [H^+] = 6.8 x 10^{-2}*mol dm*$^{-3}$ AcOH : H_2O = 50 : 50 (*v/v*)

CONCLUSION

This study investigated the mechanism of oxidation of glycolic acid by piperidinium chlorochromate. The order of reaction is one with respect to oxidant, substrate and fractional order with respect to hydrogen ion concentration was also determined. From the kinetic data obtained, the activation parameters have been calculated using Eyring's equation. A suitable rate law also derived.

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