OXIDATION OF PHENOL BY PYRAZINIUM CHLOROCHROMATE

K.Anbarasu and K.K.Ilavenil*

Department of Chemistry,

Arignar Anna Govt. Arts College,

Bharathidasan University, Trichy, Musiri-621 211, Tamilnadu, India,

ABSTRACT

Kinetic measurements and oxidation mechanism of phenol by pyrazinium chlorochromate (PzCC) catalysed by perchloric acid has been studied. The main yield of the product of oxidation was benzoquinone. The reaction obeyed first order with respect to [PzCC] and fractional order with respect to [phenol] and [H$^+$]. The rate constant of the reaction decreased with the increase in [O].The temperature effect was studied at 293K, 303K, 313K and 323K and thermodynamic parameters ($\Delta H^{\#}$, $\Delta G^{\#}$, E_a and -$\Delta S^{\#}$) were evaluated using Eyrings plot. Based on these evidences a plausible mechanism of oxidation of phenol is proposed.

Keywords—Oxidation, phenol, pyrazinium chlorochromate, kinetics, mechanism.

I. INTRODUCTION

The Cr based compounds are extensively employed and they are very potential for the oxidation of alcohol to carbonyl groups [1-3]. Several chromium (VI) reagents which are highly specific in their action have been synthesised. Depending on the nature of the reactants, solvent, catalyst and temperature the transfer of electrons from the chromium (VI) compounds vary. Of the variety of synthetic organic chromium reagents the most significant and steroselective reagents are quinolinium chlorochromate [4], potassium chlorochromate [5], pyridinium fluorochromate [6], pyrazinium dichromate [7], pyridinium dichromate [8]. The rate of oxidation is found to be high in presence of acid catalysed reaction. In the case of acid sensitive groups, the chromium (VI) reagents are less significant due to the low pH and aqueous condition of the medium. The kinetic measurement and oxidation mechanism of phenol have been reported by several investigators [9-12]. This paper reveals the oxidation using pyrazinium chlorochromate.

II. EXPERIMENTAL

Reagents

Pyrazinium chlorochromate ($C_4N_2H_5CrO_3Cl$) was prepard by the literature method [13]. The orange coloured solid was obtained and the melting point was found to be 147.5 °C. It is nearer to the reported value. Phenol was purchased from Sigma Aldrich of AnalaR grade. Doubly distilled water was used throughout the experiment. Glacial acetic acid was refluxed over CrO_3 and acetic anhydride. The fraction obtained between 116 to 118°C was collected in a brown bottle.

Kinetic measurements

The kinetic studies were carried using Colorimeter at wavelength (470nm), of make Elico CL-63 Photometer. Pseudo-first order conditions were maintained throughout the reaction, where [Phenols] > [PzCC]. Phenol, perchloric acid and solvent aqueous acetic acid (60:40% (v/v)) was maintained in a thermostat. The reactions were initiated by the required addition of pyrazinium chlorochromate (PzCC). The reaction progress was monitored for every one minute and the unreacted oxidant was determined by Colorimetric method. Correlation analysis was done using Micro cal origin software.

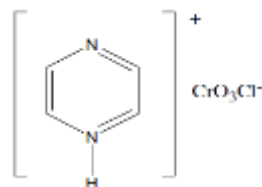### Structure of Pyrazinium chlorochromate (PzCC)

Figure 1. Structure of Pyrazinium chlorochromate

Stoichiometry

The stoichiometry of the reaction was determined by adding large amount of oxidant over the substrate. The estimation of unreacted PzCC confirmed that one mole of phenol consumed two moles of PzCC.

Product Analysis

The substrate phenol, perchloric acid, aqueous acetic acid and excess of oxidant (PzCC) was added and taken in a beaker and the mixture was warmed and left undisturbed for three days. A dark brown coloured precipitate was obtained and it was extracted with $CHCl_3$ and dried over anhydrous Na_2SO_4. The solid benzoquinone was obtained after the slow evaporation of the $CHCl_3$ layer. The solid benzoquinone was evidenced by the Infra Red spectra using potassium bromide pellet.

III. RESULT AND DISCUSSION

Kinetic measurements of oxidation of phenols by PzCC were reported at different concentration of the reactants. The reactions were maintained in a thermostat and preceded in aqueous acetic acid medium.

Oxidant effect on the reaction rate

The rate of the reaction decreases with increase in the concentration of pyrazinium chlorochromate, due to the presence of chromium as acidic chromate [14]. The correlation for the plot of log absorbance versus time was linear(Fig.2). The rate of the reaction was calculated from the slope and followed first order kinetics .
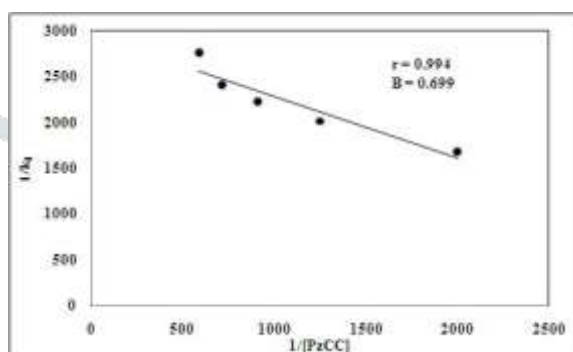

Figure 2. Plot of $1/k_1$ versus $1/[PzCC]$

Substrate effect on the reaction rate

The concentration of the substrate phenol was varied and the rate constant of the reaction increased as shown in the table. The plot of log k_1 versus log [S] found to be linear with r = 0.997, B = 0.553(Fig.3). The constant value confirms the order to be fractional in the case of [S].
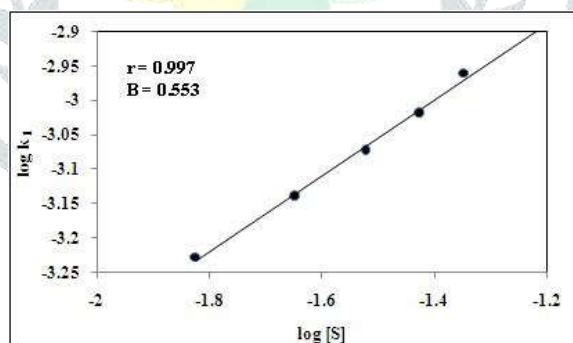

Figure 3. Plot of log k_1 versus log[S]

Effect of acidity

The acidity of the reaction was evaluated by increasing the concentration of perchloric acid $[H^+]$. The rate of the reaction increased [15] from 2.71×10^{-4} to 19.21×10^{-4} s^{-1} shown in the Table 1. The order of the reaction was found to be r = 0.993, B = 2.30 from the plot of log k_1 versus log $[H^+]$ respectively (Fig.4). The reaction is acid catalysed since the slope of [acid] fractional.
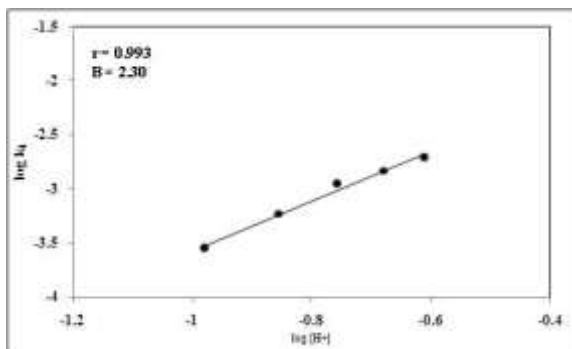
Figure 4. Plot of log k_1 versus log [H$^+$]

Ionic strength of the reaction medium

The addition of sodium perchlorate (NaClO$_4$) of various concentrations showed no variation in the rate of the reaction and it was evidenced by the participation of ion and neutral molecule in the slow step (Rate determining step). Free radical mechanism was not observed on the addition of acrylonitrile(CH$_2$=CH-CN or C$_3$H$_3$N). Further the addition of manganous sulphate decreased the rate constant of the reaction which implies the transfer of two electrons in the oxidation [16]

Dielectric effect of the medium

The plot of log k_1 versus 1/ D (dielectric constant) showed linearity (Fig.5) with a positive slope value(r = 0.998, B = +11.94). From this we can conclude that the chromium (VI) species in the protonated state is involved in the rate determining step. This may be due to the interaction between ion and neutral molecule [17].
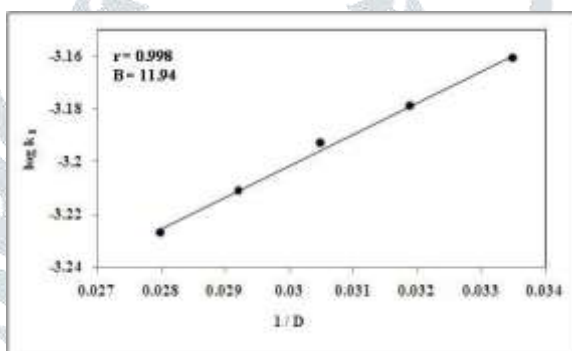
Figure 5. Plot of log k_1 versus 1/D

Effect of Temperature

The oxidation was subjected to different temperature viz., 293K to 323K without varying other parameters. The rate of the reaction increased as the temperature was raised (Fig.6). The activation and thermodynamic parameters were evaluated using Eyring's least square method [18-19].
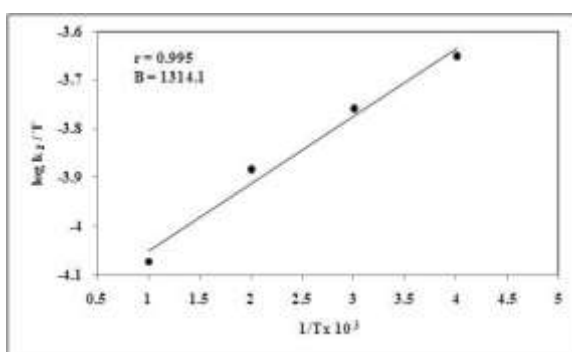

Figure 6. Plot of log k_2/T versus 1/T

Table 1. Rate data for the oxidation of phenol by PzCC at 303K

[PzCC]10^3(mol dm^{-3})	Phenol]10^2(mol dm^{-3})	H+]10^1(mol dm^{-3})	AcOH : H$_2$O(v/v)	k$_{obs}$ 10^4 (s^{-1})
0.5 – 1.7	1.50	0.14	60:40	5.93 – 3.62
0.5	1.50 – 4.50	0.14	60:40	5.93 – 10.99
0.5	1.50	2.5 – 2.1	60:40	2.79 – 19.21
0.5	1.50	0.14	60:40 – 68:32	5.93 – 6.90

AcOH:H$_2$O = 60:40 *(v/v)*

Table 2. Rate data for the oxidation of phenol by PzCC

Temperature K	[NaClO$_4$] 10^4 (mol dm $^{-3}$)	[MnSO$_4$] 10^4 (mol dm $^{-3}$)	k$_1$ 10^4 (s^{-1})
293 - 323	-	-	3.73 – 10.81
303	0.00 – 24.0	-	5.93 – 6.04
303	-	0.00 – 24.0	5.93 – 4.75

[PzCC] = 0.5 x 10^{-3}mol dm^{-3}; [Phenol] = 1.5 x 10^{-2}mol dm $^{-3}$; [H$^+$] = 0.14 x 10^{-1} mol dm $^{-3}$

Reaction mechanism
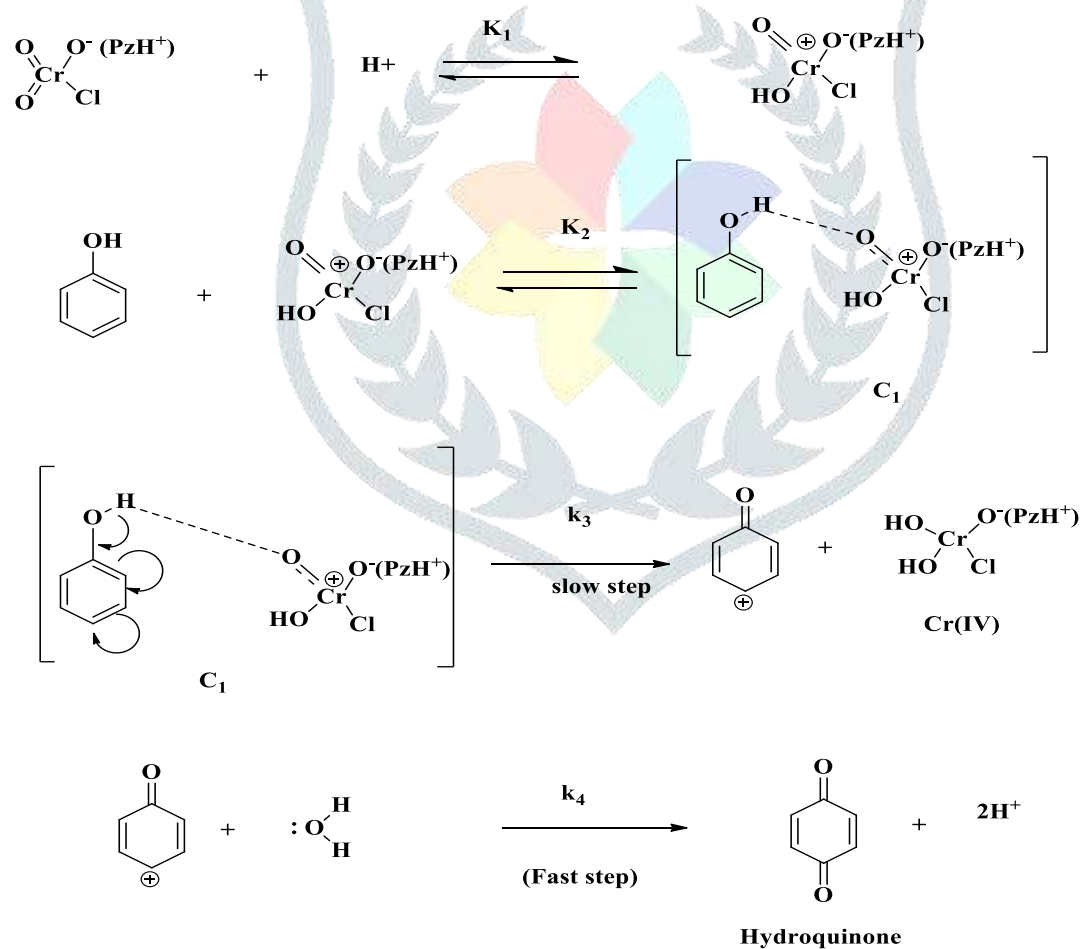
Rate law

$$\text{Rate} = \frac{-d[PzCC]}{dt} = k_3 \,[complex]$$

$$= \frac{k_3 \, K_2 \, [S] \, [C_1]}{1 + K_2 \, [S]}$$

$$= \frac{k_3 \, K_2 \, K_1 [S] \, [PzCC][H^+]}{(1 + K_2[S])(1 + K_1 \, [H^+])}$$

$$= \frac{k_3 \, K_2 \, K_1 [S] \, [PzCC][H^+]}{1 + K_2[S] + K_1 \, [H^+]}$$

IV. CONCLUSION

The kinetics and oxidation of phenol by pyrazinium chlorochromate in 60% aqueous CH_3COOH was reported at 303K in a thermostat. The reaction kinetics followed fractional order for [S], [acid] and first order for [O]. The addition of polymer acrylonitrile did not show any precipitate and hence free radical formation was not evidenced. Two electron transfer was reported for the change in the concentration of manganous sulphate. Based on this investigation a suitable mechanistic pathway has been proposed with rate law. The product obtained for the oxidation of phenol was the corresponding benzoquinone and the thermodynamic and activation parameters were calculated from Eyring's relation ($\Delta H^{\#} = 10.92 KJmol^{-1}$; $\Delta S^{\#} = -193.97$ $JK^{-1}mol^{-1}$; $\Delta G^{\#} = 69.69$ $KJmol^{-1}$; $E_a = 13.44 KJmol^{-1}$)

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