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OXIDATION OF PHENOL BY QUINOLINIUM CHLOROCHROMATE IN AQUEOUS ACETIC ACID MEDIUM

Dr. S. K. Periyasamy* **and Mr. M Satham Hussain**

PG& Research Department of Chemistry, Jamal Mohamed College (Autonomous), Tiruchirappalli, 620 020, Tamilnadu, India.

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***Correspondence for Author**
Dr. S. K. Periyasamy
PG& Research Department of Chemistry, Jamal Mohamed College (Autonomous), Tiruchirappalli, 620 020, Tamilnadu, India.

ABSTRACT

The kinetics of oxidation of Phenol by quinolinium Chlorochromate (QCC) in aqueous acetic acid leads to the formation of quinone. The reaction is first order with respect to both aniline and QCC and is catalyzed by hydrogen ion. The hydrogen-ion dependence has the form: $k_{obs} = a+b\,[H^+]$. The rate of oxidation decreases with increasing dielectric constant of solvent, indicating the presence of an ion-dipole interaction. The reaction does not induced the polymerization of acrylonitrile. The retardation of the rate by the addition of Mn^{2+} ions confirms that a two electron transfer process is involved in the reaction. The reaction rates have been determined at different temperatures and the activation parameters have been calculated. From the above observation kinetic results a suitable mechanism has been proposed.

KEYWORDS: Kinetics, Oxidation, Quinolinium Chlorochromate, Phenol, Acid catalyst, Activation Parameters.

INTRODUCTION

Halochromates have been used as mild and selective oxidizing reagent in synthetic organic chemistry. A variety of compounds containing chromium(VI) have proved to be versatile reagents capable of oxidizing almost every oxidizing functional group. The kinetics and mechanism of oxidation of Cr(VI) has been well studied, chromic acid being one of the most versatile available oxidizing reagents, reacting with diverse substrates. The development of newer chromium(VI) reagents for the oxidation of organic substrates continues to be of interest. A number of new chromium containing compounds like pyridinium bromochromate[1], quinolinium chlorochromate[2], 2,2'-bipyridinium chlorochromate[3],

pyridinium fluorochromate[4], quinolinium fluorochromate[5], quinolinium bromochromate[6], quinolinium dichromate[7], pyridinium fluorochromate[8], imadazolium fluorochromate[9] have been used to study the kinetics and mechanism of oxidation of various organic compounds. However, most of the reagents developed so far suffer from at least one of the drawbacks such as high acidity, photosensitivity, instability, hygroscopicity, low selectivity, long reaction time and need for large excess of reagent. To overcome these disadvantages, we have synthesized Quinolinium chlorochromate (QCC) as a new mild, efficient and stable reagent which is able to work as both an oxidizing agent.

Quinolinium chlorochromate is a mild and selective oxidant. Quinolinium chlorochromate[10] is a stable reagent originally introduced as an oxidizing agent for alcohol is used in synthetic organic chemistry.[11-16]

The kinetic mechanistic aspects of oxidation reactions by QCC reports are available in the literature[17- 22] The kinetics of oxidation of Phenols by various oxidizing reagents have been well studied.[23-25] Phenol is so inexpensive that it attracts many small-scale uses. It once was widely used as an antiseptic, especially as carbolic soap. It is a component of industrial paint strippers used in the aviation industry for the removal of epoxy, polyurethane and other chemically resistant coatings. Phenol derivatives are also used in the preparation of cosmetics including sunscreens, hair colorings, and skin lightening preparations.

Structure of Quinolinium chlorochromate

EXPERIMENTAL

Materials and methods

All the chemicals used were analytical grade. Phenol was used after vacuum distillation. Double distilled water was used for all purposes.

Preparation of Quinolinium Chlorochromate [QCC]

Chromium trioxide (7 g) was dissolved in 8 ml of water in a e beaker and 11 ml of 40% hydrochloric acid were added with stirring at room temperature. A clear orange red solution was formed and 9 ml of quinoline were added drop-wise with stirring. The mixture was heated on a water bath for about 15 min, then cooled to room temperature and allowed to stand for 1 h. The bright yellow crystalline quinolinium chloroochromate was isolated by

filtration. It was recrystallized from water and dried in vacuo for about 2 h. The compound melted at (128 °C)[lit m.p 127-130 °C][26] and further analysed through spectral studies.

Acetic acid

The procedure followed for the purification of acetic acid was essentially similar to that of Weissberger[27] Glacial acetic acid (AR) 2 litre was partially frozen and about one litre of the liquid was removed. The residue was melted and refluxed with chromium trioxide (30 g) for 4 h and fractionally distilled. The portion distilling between 116-118 °C was collected, partially frozen and about half of the acid was discarded as liquid. The remaining residue was melted and fractionated again after treating with chromium trioxide (30 g). The fraction boiling at 116-118 °C was collected and kept in brown bottles.

Kinetic measurements

The kinetic experiments were conducted in aqueous acetic acid (50% V/V) at 313K. The reaction mixture consisted of Phenol = 4.50×10^{-2} mol dm^{-3} , QCC=1.00×10^{-3} mol dm^{-3} and H_2SO_4 = 3.00×10^{-1} mol dm^{-3}.The temperature was maintained constant within ± 0.2º.

The reaction was carried out under pseudo- first order conditions by maintaining the substrate concentration in excess of quinolinium chlorochromate. Known volumes of substrate, water and acetic acid were mixed to bring the percentage of acetic acid to the desired value and thermostated. The reaction was started by adding the oxidant to the mixture and aliquots were removed at definite time intervals and the decrease in [QCC] by digital photoelectric colorimeter at 470nm.The reactions were followed up to 70% completion. The rate constants were obtained from the slope of the plot of log absorbance versus time by the least square method. The results were reproducible within ±1.

Stoichiometry

The kinetics of reaction was to establish the stoichiometry of the reaction and identify any side reactions. The stoichiometry of the reaction [QCC]:[Phenol] was determined by taking excess of [QCC] over [Phenol] and allowing the reaction to go for completion. After sufficient length of time, all the substrate has completely reacted to quinolinium chlorochromate leaving behind the unreacted quinolinium chlorochromate. The unreacted quinolinium chlorochromate was estimated iodometrically. The estimation of unreacted

quinolinium chlorochromate showed that one mole of substrate consumed by one mole of oxidant. The stoichiometry between phenol and QCC was found to be 1:1.

Product analysis

The reaction mixture containing Phenol (0.045 M) in acetic acid and QCC (0.001M) in acetic acid was added and the medium was maintained using sulphuric acid. Then the reaction mixture was slightly warmed and was kept aside for about 48 h for the completion of reaction. After 48 h, the reaction mixture was extracted with ether and dried over anhydrous sodium sulphate. The ethereal layer was washed with water several times and kept on a water bath for ether evaporation and cooled to get the product. Para benzoquinone was identified as product.

The product 1, 4 benzoquinone was identified by its physical constant (m.p.113 $^{\circ}$ C) and was confirmed through IR-spectral data and further confirmed by mass spectrum

RESULTS AND DISCUSSION

Effect of varying the Oxidant

The reaction was investigated with varying concentrations of QCC at constant Phenol and sulphuric acid concentrations. The reaction was found to be first order with respect to the oxidant as evidenced by the linear plot of plot of log absorbance *versus* time (Fig.1) and also from the constancy of the first order rate constant in (Table 1).

Effect of varying the Substrate Phenol

The reaction was carried out by varying the concentration of Phenol keeping the other variables constant. The rate of reaction increased with increase in the concentration of Phenol and the plot of log k_1 *versus* log [Substrate] gave a straight line with a slope of unity (Fig 2) showing a first order dependence on the substrate. (Table 2).

Effect of varying the ionic strength

The reaction was studied with varying concentration of sodium sulphate and keeping the other variables constant. The results indicate that ionic strength has negligible effect on the reaction rate, which confirmed the participation of an ion and neutral molecule in the rate determining step[28](Table -3).

Effect of varying the hydrogen ion concentration

The reaction was followed with different concentration of hydrogen ion keeping the concentration of quinolinium chlorochromate and substrate constant. The rate has been found to increase with increase in concentration of H^+ . A plot of log k_1 *versus* log $[H^+]$ give a straight line (Fig 4) with a slope of 1.30 (r = 0.992) . Since the plot of log k_1 *versus* log $[H^+]$ did not give an ideal slope of unity. It is not possible to take the order with respect to $[H^+]$ as one and it can be concluded that the reaction is simply an acid catalyzed one.[29] (Table 4).

Effect of varying the solvent composition

The reaction rate was measured at different acetic acid -water mixtures. It was observed that an increase in the percentage of acetic acid considerably increased in the rate of the reaction. The plot of log k_1 *versus* D^{-1} gave a straight line with a positive slope (Fig 5) suggests the involvement of an ion –dipole interaction in the rate determining step[30-32] (Table 5).

Effect of added acrylonitrile

The added acrylonitrile has no effect on the reaction mixture indicating the absence of free radical mechanism, no turbidity was obtained.

Effect of varying the manganous sulphate

The reaction was carried out with the varying concentrations of Mn^{2+} ions keeping all the other factors constant The added Mn^{2+} ions has decreased the rate of the reaction. It indicates that two electron process may be involved in the reaction[31-35] (Table 6)

Effect of varying the temperature

The reaction has been studied at six different temperatures keeping all other factors constant. The thermodynamic parameters have been calculated from the least square procedure of a linear plot of ln(k_2/T) *versus* 1/T (Fig.6) using Eyring's equation.[36,37]

$\Delta H^{\#}$ = 12.89 $kJmol^{-1}$
$\Delta S^{\#}$ = -166.81 $JK\text{-}1mol^{-1}$
$\Delta G^{\#}$ = 65.01 $kJmol^{-1}$
Ea = 15.49 $kJmol^{-1}$

Mechanism and Rate law

From the above observation it is clear that the reaction is showing first order with respect to QCC and Phenol . The oxidation by Cr(VI) will vary with the nature of the Cr(VI) species used

and the solvent will play an important role on the rate of the reaction. In aqueous solution and in the absence of other ions the following are existing,[38]

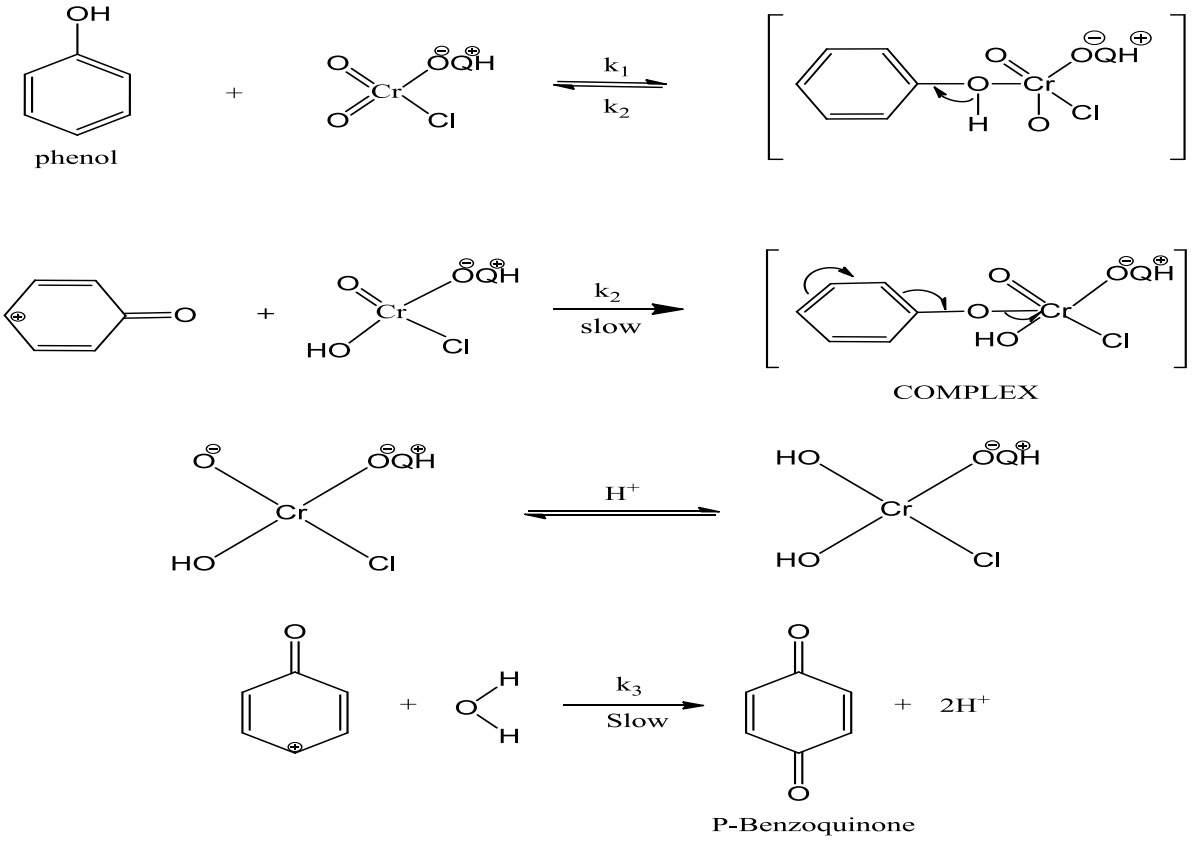
(i) $H_2CrO_4 \rightleftharpoons H^+ + HCrO_4^-$ $K_1 = 1.21\ mol\ dm^{-3}$

(ii) $HCrO_4^- \rightleftharpoons H^+ + CrO_4^{2-}$ $K_2 = 3.0\times 10^{-2}\ mol\ dm^{-3}$

(iii) $2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$ $K_d = 35.5$

Here the dimerisation equilibrium is of considerable importance. In water the dichromate ion will be predominating species only at the concentrations greater than about 0.05 *mol dm*$^{-3}$. In this case as the concentration of Cr(VI) is less than 0.05 *mol dm*$^{-3}$. The monomeric form predominates and the active oxidising species is $HCrO_4^-$. The reaction is acid catalysed one. The rate increased with decrease in the dielectric constant of the medium and increase in ionic strength has negligible effect on the rate. The reaction did not induce polymerization of acrylonitrile indicating the absence of free radical path way. The retardation of the rate by addition of Mn^{2+} ions confirmed that a two electron transfer process is involved in the reaction. Based on the above facts the following mechanism was proposed (Scheme 1).

Mechanism and Rate law



Scheme1: Probable mechanism of oxidation of Phenol by Quinolinium chlorochromate.

Rate law

The above mechanism leads to the following rate law.

Rate = $k_1\ k_2\ k_3$ [Phenol] [QCC] [H^+]

Table-1- Effect of varying the Oxidant

[QCC]× 10^{-3} *mol dm*$^{-3}$	**$k_1\times10^4$ *s*$^{-1}$**
0.50	16.41
1.00	16.40
1.50	16.42
2.0	16.41
2.50	16.40
3.00	16.44

[Phenol] = 4.5×10^{-2} *moldm*$^{-3}$ AcOH-H_2O = 50:50(%)

[H^+] = 3.0×10^{-1} *moldm*$^{-3}$ Temperature = 313K

Table-2- Effect of varying the Substrate phenol

[Phenol] ×10^2 *mol dm*$^{-3}$	**$k_1\times10^4$ *s*$^{-1}$**
3.00	12.00
4.50	16.40
6.00	22.38
7.50	27.54
9.00	33.11
10.50	36.30

[QCC] = 1.00×10^{-3} *moldm*$^{-3}$ AcOH-H_2O = 50:50(%)

[H^+] = 3.0×10^{-1} *moldm*$^{-3}$ Temperature = 313K

Table-3- Effect of varying the ionic strength

[Na_2SO_4] ×10^4 *mol dm*$^{-3}$	**$k_1\times10^4$ *s*$^{-1}$**
0.00	16.40
0.50	16.42
1.00	16.41
1.50	16.43
2.00	16.44
2.50	16.46

[QCC] = 1.00×10^{-3} *moldm*$^{-3}$ [H^+] = 3.0×10^{-1} *moldm*$^{-3}$

AcOH-H_2O = 50:50(%) [Phenol] = 4.5×10^{-2} *moldm*$^{-3}$

Temperature = 313K

Table-4- Effect of varying the hydrogen ion concentration

$[H^+]$ $\times 10^1$ *mol dm*$^{-3}$	$k_1 \times 10^4$ s^{-1}
1.5	5.01
3.00	16.40
4.50	25.70
6.00	36.30
7.50	43.65
9.00	53.70

[QCC] = 1.00×10^{-3} *moldm*$^{-3}$ AcOH-H_2O = 50:50(%)

[Phenol] = 4.5×10^{-1} *moldm*$^{-3}$ Temperature = 313K

Table -5 - Effect of varying the solvent composition

AcOH-H_2O %(v/v)	E	k_1 10^4 s^{-1}
40-60	50.46	15.48
50-50	43.08	16.40
60-40	35.69	21.87
70-30	28.31	23.44
80-20	20.92	38.01
90-10	13.53	74.13

[QCC] = 1.00×10^{-3} *moldm*$^{-3}$ $[H^+]$ = 1.0×10^{-2} *moldm*$^{-3}$

[Phenol] = 3.0×10^{-2} *moldm*$^{-3}$ Temperature = 313K

Table-6- Effect of varying the manganous sulphate

$[MnSO_4]$ $\times 10^4$ *mol dm*$^{-3}$	$k_1 \times 10^4$ s^{-1}
0.00	16.40
0.50	16.38
1.00	16.35
1.50	16.31
2.00	16.25
2.50	16.19

[QCC] = 1.00×10^{-3} *moldm*$^{-3}$ $[H^+]$ = 3.0×10^{-1} *moldm*$^{-3}$

AcOH-H_2O = 50:50(%) [Phenol] = 4.5×10^{-2} *moldm*$^{-3}$

Temperature = 313K

Table-7- Effect of varying the temperature

Temperature K	$k_1 10^4$ s^{-1}
303	13.53
308	14.85
313	16.40
318	17.55
323	19.65
328	21.90

[QCC] = 1.00×10^{-3} *moldm*$^{-3}$ $[H^+]$ = 3.0×10^{-1} *moldm*$^{-3}$

[Phenol] = 4.5×10^{-2} *moldm*$^{-3}$ AcOH-H_2O = 50:50(%)

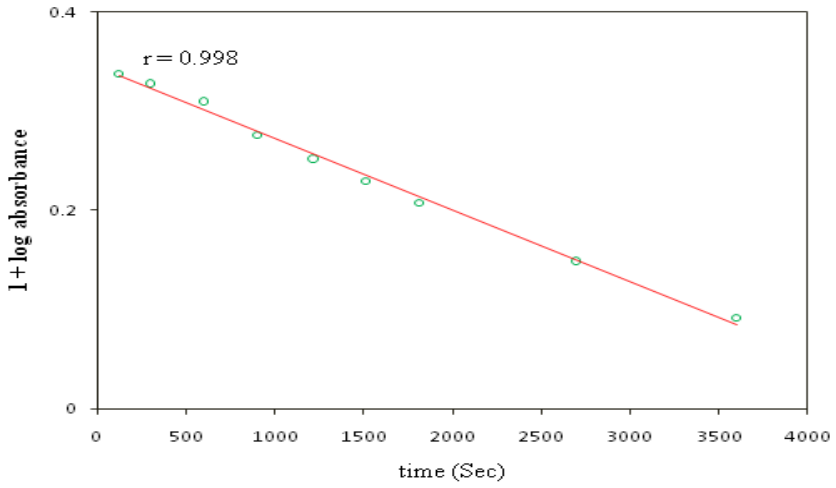


fig:1 plot of log absorbance vs time

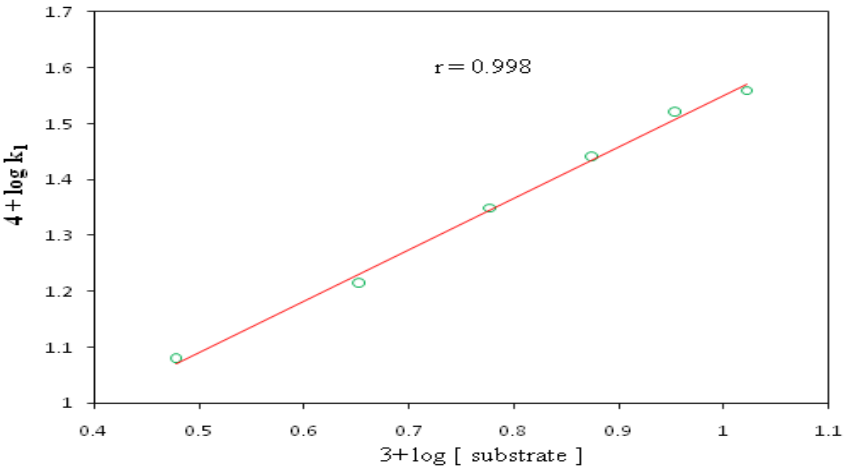


fig:2 plot log k1 vs log of [substrate]

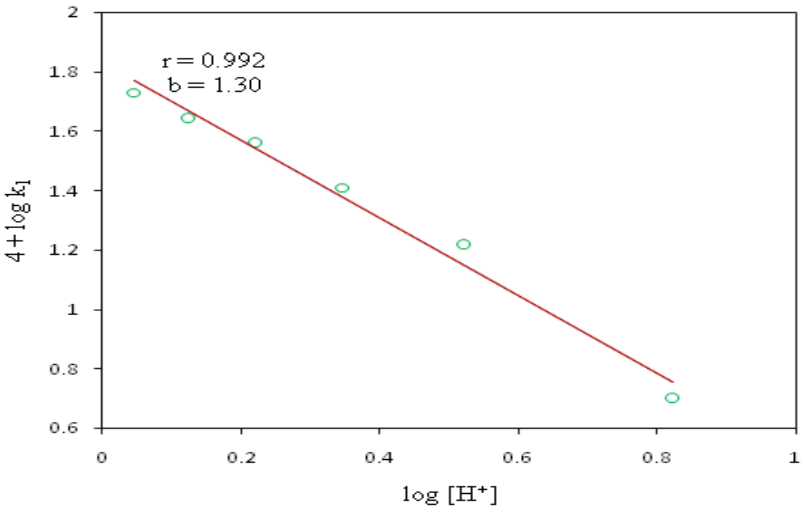


Fig .4 Plot of log k_1 *versus* log $[H^+]$

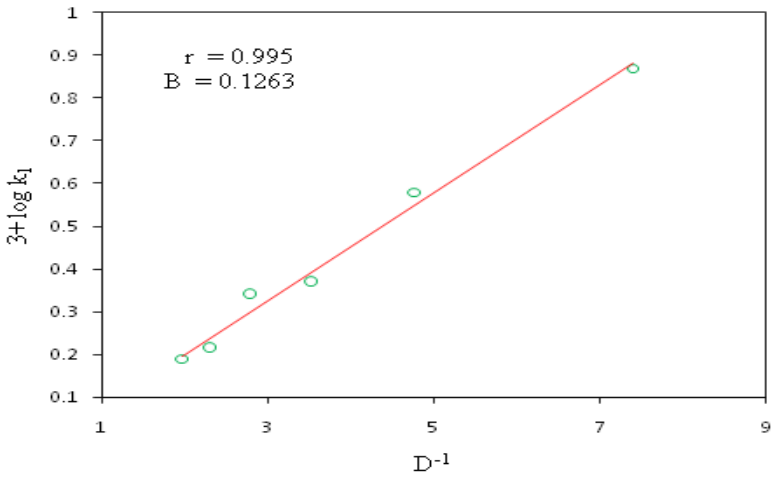


Fig.5 Plot of log k_1 *versus* D^{-1}

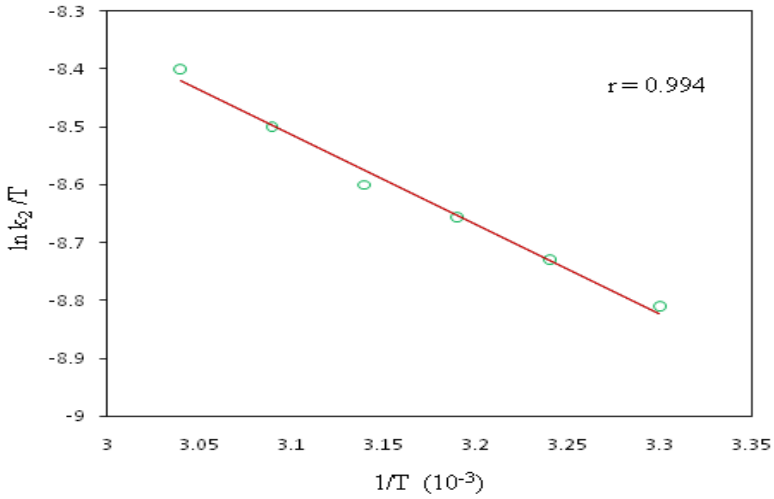


Fig.6 Plot of lnk_2/T *versus* 1/T

CONCLUSION

In this paper we have reported the detail mechanism of the Phenol by Quinolinium chlorochromate. The reaction is first order with recpect to oxidant and Phenol. The reaction is acid catalysed by hydrogen ion concentration. The oxidation of phenol yield by para benzoquinone. For this purpose deep understanding of the mechanism of the process of phenol is needed. The negative value of $\Delta S^{\#}$ provided support for the formation of the activated complex in the slow step.

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