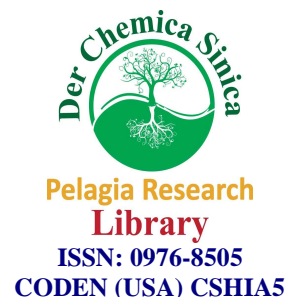




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### Reactivity of phenol towards benzyltriethylammonium chlorochromate oxidation in the presence of 1, 10-phenanthroline as catalyst

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#### ABSTRACT

The catalytic activity of 1, 10-phenanthroline (phen) in Cr(VI) oxidation of phenol has been studied in 60% acetic acid medium. The Cr(VI) phen complex is believed to be the probable electrophile in the catalyzed oxidation. The catalytic activity is quite likely to shift the redox potential of the oxidant. The reaction shows first order with respect to substrate, catalyst, oxidant and H<sup>+</sup>. Increase in acidity as well as increase in the dielectric constant increases the rate of the reaction. The added acrylonitrile has no effect on the reaction rate indirectly indicating the absence of free radical mechanism.

**Keywords:** Kinetics, Phenol, Oxidation, 1, 10-phenanthroline, Benzyltriethylammonium chlorochromate.

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#### INTRODUCTION

Benzyltriethylammonium chlorochromate (BTEACC) is reported to be a neutral and mild oxidant for selective oxidation[1]. The kinetics of oxidation of some organic substrates by BTEACC have already been reported[2-4]. Extensive kinetic and mechanistic studies on oxidation of organic compounds by chromium reagents has revealed that such reactions ordinarily involve a three electron change, whereby Cr(VI) species are reduced to Cr(III)[ 5-7]. The present work deals with the kinetics and mechanism of oxidation of phenol by BTEACC in acid medium in the presence of phen. The mechanistic aspects are also discussed.

#### MATERIALS AND METHODS

##### Materials

Phen [E-Merck] was used as such. BTEACC was prepared by the method reported by Corey and Schmidt[8]. Acetic acid was refluxed over chromium trioxide for 8 hours and then fractionated[9]. All other chemicals used were of AnalaR grade.

##### Kinetic measurement

Kinetics runs were all performed under pseudo-first order conditions of a large excess of substrate over the oxidant. The reaction was carried out in a glass stoppered purex boiling tube whose outer surface was blackened to eliminate photochemical effects. The mixture was homogeneous throughout the course of the reaction. The titrimetric

procedure of Wiberg and Mill was followed for the estimation of unreacted Cr(VI)[10]. The rate constants were evaluated from log (titre value) vs. time plots. All rate constants reported in the study are the average of two or more determinations.

### Stoichiometry and product analysis

Reaction mixtures containing an excess of the oxidant over phenol were kept in a thermostat in the presence of H<sup>+</sup> and phen for 24 hours. Estimation of unchanged oxidant showed that one mole of phenol consumes one mole of oxidant confirming the stoichiometry of the reaction as 1:1. The reaction mixture from actual kinetic run with excess of oxidant after slight warming was kept for two days and extracted with chloroform and dried over anhydrous sodium sulphate. The chloroform layer was then evaporated and the solid on analysis through IR spectra was found to be p-benzoquinone.

## RESULTS AND DISCUSSION

The order with respect to oxidant was found to be one as evidenced by the linear plot of log (titre value) vs. time. The decrease in the rate observed with the increase in the concentration of the oxidant is attributed to the decrease in effective concentration of Cr(VI) species in the reaction medium. The reaction shows first order with respect to substrate as evidenced by the plot of log k vs. log substrate concentration with slope 0.92 (r = 0.997)(Fig.1). The rate constants were found to increase with increase in the concentration of [phen] (Table 3). The order with respect to catalyst was found to be first order as evidenced by the plot of log k versus log [catalyst] which was linear with slope 0.89 (r = 0.993) (Fig.3)

**Table 1-Effect of [substrate], [oxidant] and [H<sup>+</sup>] on the reaction rate at 313K**

60 % (v/v) acetic acid-water, [catalyst] = 1.25 X 10<sup>-2</sup> mol<sup>-2</sup>

[substrate] X 10 <sup>3</sup> mol dm <sup>-3</sup>	[oxidant] X 10 <sup>3</sup> mol dm <sup>-3</sup>	[H <sup>+</sup> ] X 10 <sup>3</sup> mol dm <sup>-3</sup>	k <sub>1</sub> X 10 <sup>4</sup> s <sup>-1</sup>
1.5	1.00	9.50	2.64
2.0	1.00	9.50	3.26
2.5	1.00	9.50	4.11
3.0	1.00	9.50	4.97
3.5	1.00	9.50	5.60
2.50	0.5	9.50	4.08
2.50	1.0	9.50	4.11
2.50	1.5	9.50	4.14
2.50	2.0	9.50	4.16
2.50	2.5	9.50	4.17
2.50	1.00	8.5	3.61
2.50	1.00	9.0	3.82
2.50	1.00	9.5	4.11
2.50	1.00	10.0	4.23
2.50	1.00	10.5	4.55

There was no appreciable change in the rate with change of ionic strength indicating the involvement of a neutral molecule in the rate determining step. Studying the reaction rate various initial [H<sup>+</sup>], keeping [oxidant], [substrate] and temperature constant, it was found that the rate of the reaction increases with increasing [H<sup>+</sup>] (Table 1 & Fig.2). The observation indicates participation of perchloric acid on the rate determining step and order has been found to be one. The variation in the dielectric constant of the medium changed the rate of the reaction appreciably (Table 3 & Fig.3). The reaction mixture, when allowed to stand with acrylonitrile, does not induce polymerization suggesting the absence of free radical mechanism. On the other hand, the addition of Mn<sup>2+</sup> ions retards the rate of the reaction and the addition of Al<sup>3+</sup> ion increase the reaction rate (Table 2).

### Effect of Temperature

The reaction was studied at five different temperature and the activation parameters are calculated (Table 4 & Fig.4).

**Table 2-Effect of  $[\text{Mn}^{2+}]$  and  $[\text{Al}^{3+}]$  on  $\text{NaClO}_4$  on the reaction rate at 313K**

$[\text{substrate}] = 2.50 \times 10^{-2} \text{ mol dm}^{-3}$ ;  $[\text{oxidant}] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $[\text{H}^+] = 9.50 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $[\text{phen}] = 1.25 \times 10^{-3} \text{ mol dm}^{-3}$

$[\text{Mn}^{2+}] \times 10^3$ $\text{mol dm}^{-3}$	$[\text{Al}^{3+}] \times 10^3$ $\text{mol dm}^{-3}$	$[\text{NaClO}_4] \times 10^3$ $\text{mol dm}^{-3}$	$k_1 \times 10^4$ $\text{s}^{-1}$
0.00	-	-	4.11
0.50	-	-	3.92
1.00	-	-	3.62
1.50	-	-	2.23
2.00	-	-	0.91
-	0.00	-	4.11
-	0.50	-	5.06
-	1.00	-	6.20
-	1.50	-	6.98
-	2.00	-	8.02
-	-	0.00	4.11
-	-	0.50	4.15
-	-	1.00	4.17
-	-	1.50	4.23
-	-	2.00	4.19

**Table 3-Effect of  $[\text{phen}]$  and  $[\text{acetic acid}]$  on the reaction rate at 313K**

$[\text{substrate}] = 2.50 \times 10^{-2} \text{ mol dm}^{-3}$ ;  $[\text{oxidant}] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $[\text{H}^+] = 9.50 \times 10^{-3} \text{ mol dm}^{-3}$

$[\text{phen}] \times 10^2 \text{ mol dm}^{-3}$	% acetic acid(v/v)	$k_1 \times 10^4 \text{ s}^{-1}$
1.00	60	3.05
1.25	60	4.11
1.50	60	4.77
1.75	60	5.89
2.00	60	6.99
1.25	40	0.32
1.25	50	1.06
1.25	60	4.11
1.25	70	5.92
1.25	80	7.01

**Table 4-Effect of Temperature**

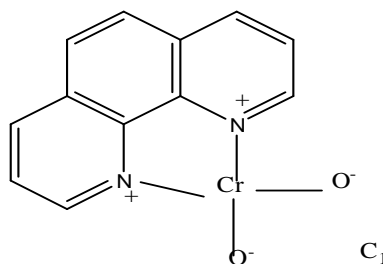
$[\text{Substrate}] = 2.50 \times 10^{-2} \text{ mol dm}^{-3}$ ;  $[\text{oxidant}] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $[\text{H}^+] = 9.50 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $[\text{phen}] = 1.25 \times 10^{-3} \text{ mol dm}^{-3}$ ; 60%(v/v) acetic acid-40%water

Temperature(K)	$k_1 \times 10^4 \text{ s}^{-1}$
303	2.85
313	4.11
323	5.96
333	7.45

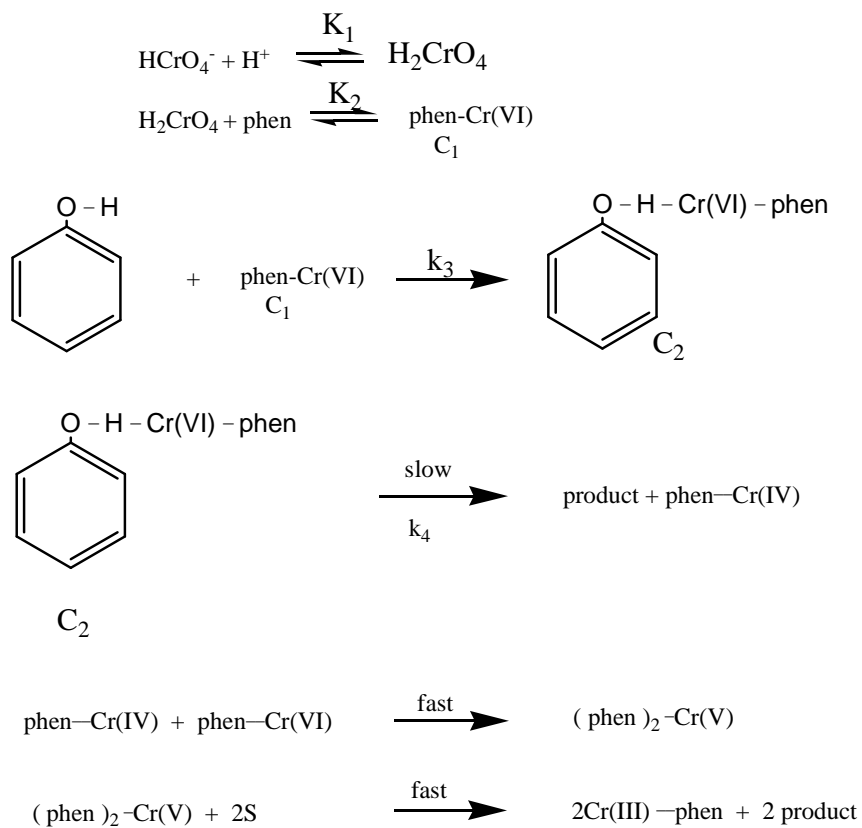
$$\Delta H^\ddagger = 24.53 \text{ k J mol}^{-1}; \Delta S^\ddagger = -231.91 \text{ J K}^{-1} \text{ mol}^{-1}; \Delta G^\ddagger = 97.12 \text{ k J mol}^{-1}$$

**Mechanism and Rate law**

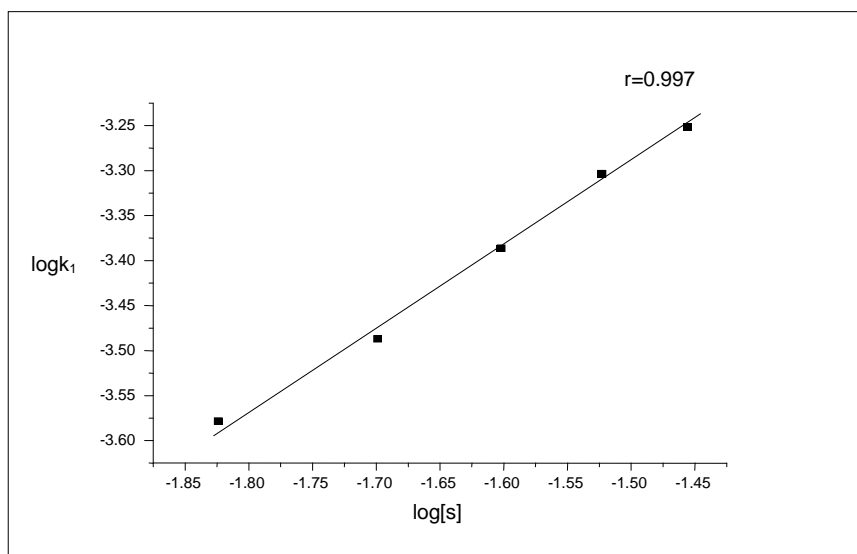
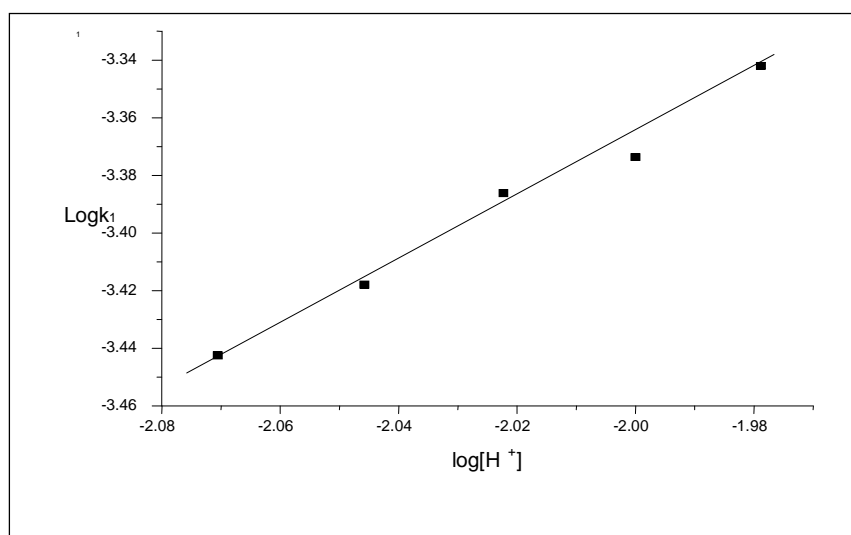
It is believed that the catalytic activity of complexing agents such as 2, 2'-bipyridyl and phen depends on their ability to stabilize intermediate chromium valence states[11-13]. It has been reported that phen complexes are more stable than bipyridyl complexes. Quite likely, the complexing agents stabilize the end products, chromium (III), and hence accelerate the whole of the reaction. Addition of phen at its binding to the Cr(VI) would presumably change the redox potential of chromium oxidant. Substantial acid catalytic activity in the present study can be attributed to facile formation of Cr (VI)-phen complex in acid solutions. This is a similar to the view reported in the Cr(VI) oxidation of sulphides and cyclicketones in the presence of picolinic acid[14,15]. The reactive nucleophile Cr (VI)-phen complex (C1) has been reported[16] in the oxidation of anisole by chromic acid.

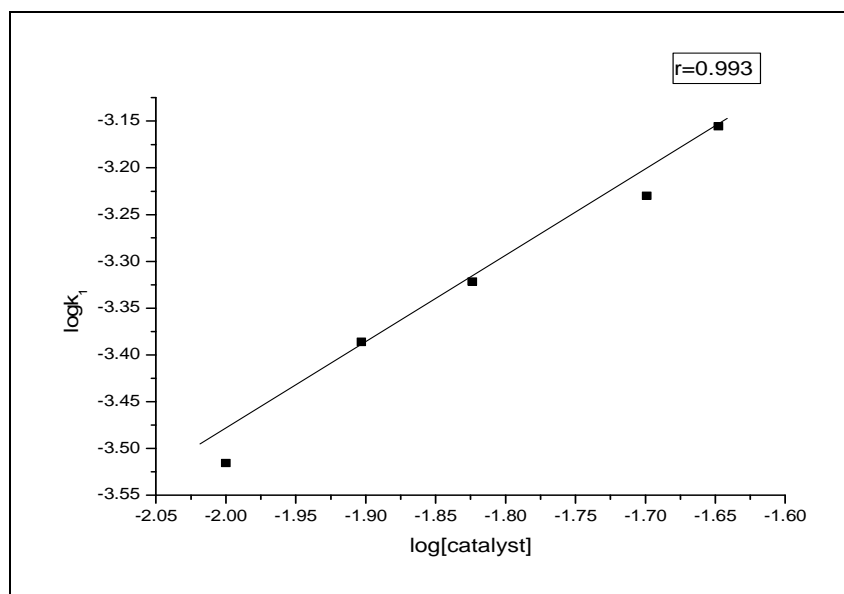
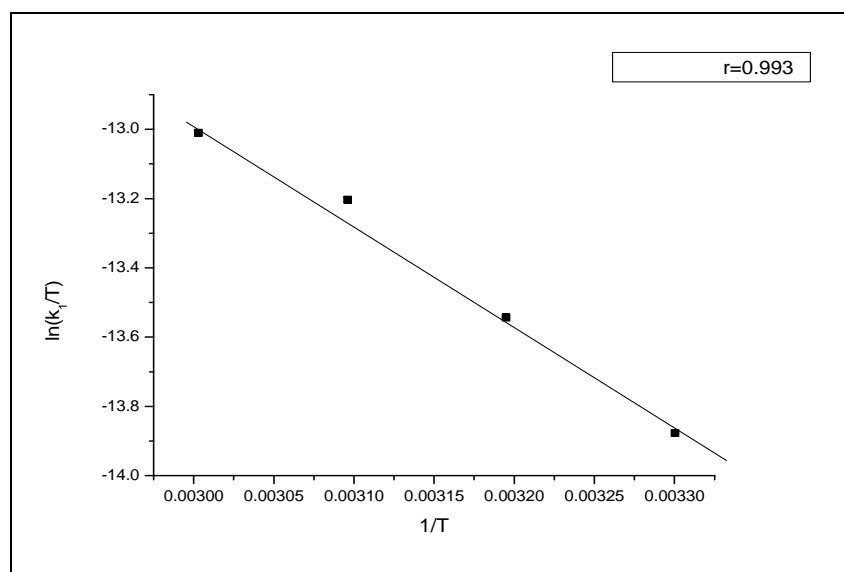


The available kinetic data can be rationalized by the following mechanistic scheme.



$$\begin{aligned} \text{Rate} &= k_4 \text{C}_2 \\ &= k_3 k_4 \text{C}_1 [\text{S}] \\ &= K_2 k_3 k_4 [\text{S}] [\text{Cr(VI)}] [\text{phen}] \\ &= K_1 K_2 k_3 k_4 [\text{S}] [\text{Cr(VI)}] [\text{H}^+] [\text{phen}] \end{aligned}$$

**Fig.1-Effect of [Substrate]****Fig.2-Effect of  $[H^+]$**

**Fig.3-Effect of [phen]****Fig.4-Effect of Temperature**

### CONCLUSION

The oxidation of phenol by BTEACC in the presence of phen in aqueous acetic acid medium leads to formation of complex and it finally gives products. The negative value of  $\Delta S^\ddagger$  provided support for the formation of the activated complex in the slow step. The reaction follows simple order kinetics. The mechanism proposed for this oxidation kinetics is in accordance with observed kinetic facts.

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