



## Oxidation of Cyclicketones by Benzyltriethylammonium Chlorochromate by 1,10- Phenanthroline as Catalyst-Kinetic and Mechanistic Study

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### ABSTRACT

The catalytic activity of 1, 10-phenanthroline (phen) in Cr(VI) oxidation of phenols has been studied in 40% 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 kinetics of the oxidation of cyclicketones by benzyltriethylammonium chlorochromate(BTEACC), in aqueous acetic acid medium have been reported. The rate shows first order dependence in [BTEACC] and fractional order with respect to [substrate] , [H<sup>+</sup>] and [phen]. The order of reactivity for the cyclicketones has been observed. The proposed mechanism involves acid catalyzed enolisation of cyclicketones in the slow and rate determining step, followed by its fast interaction with BTEACC giving corresponding 1,2-diketones as final products. Thermodynamic parameters have been computed by studying the reaction at different temperatures.

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

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### INTRODUCTION

Organic halochromates have been used as mild and selective oxidizing reagents in Synthetic Organic Chemistry[1,2]. Benzyltriethylammonium chlorochromate (BTEACC) is one such compound used for the oxidation of organic substrates[3,4,5]. Since there exists an equilibrium between the keto form and the enol form of ketones, different views have been expressed on either the keto form[6] of the enol form[7] undergoing reactions with different oxidants.

We report here the kinetics and mechanism of oxidation of cyclicketones by BTEACC in aqueous acetic acid and 1, 10 – phenanthroline (phen) as a catalyst. The correlation between structure and reactivity which would help to decipher the mechanism of the oxidation of cyclicketones.

### EXPERIMENTAL SECTION

Cyclopentanone and cyclohexanone [E.Merck] were used after distillation. Cycloheptanone and cyclooctanone [Fluka] were used after distillation and recrystallisation respectively. BTEACC was prepared by the reported method[8]. Solvents were purified by the usual procedure[9] and all the chemicals and reagents were of analytical grade.

**KINETIC MEASUREMENT****Stoichiometry**

A number of reaction mixtures containing excess of BTEACC at least twice the concentration of cyclohexanone in the presence of perchloric acid were kept at room temperature for sufficient length of time. The estimation of unreacted BTEACC showed that one mole of substrate consumed two moles of the oxidant.

**Product Analysis**

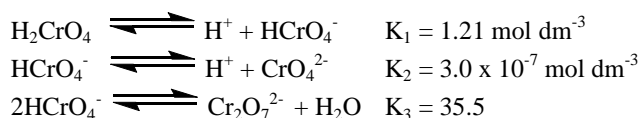
The reaction mixture from the actual kinetic run after sufficient length of time was extracted with chloroform and dried over anhydrous sodium sulphate. The chloroform layer was then evaporated in a hot water bath to get the solid product 1, 2 – cyclohexanedione which was confirmed by the spot test [10].

**RESULTS AND DISCUSSION**

The oxidation of cycloketones by BTEACC leads to the formation of corresponding diketones. BTEACC undergoes a two electron change [11,12]. The reactions were found to be first order with respect to oxidant. Further, the pseudo first – order rate constant does not depend on the initial [BTEACC]. The reaction rate increases linearly with an increase in the [cyclohexanone]. The increase in the percentage of  $H^+$  and acetic acid increases the rate of the reaction. The added  $Mn^{2+}$  ion retards the rate of the reaction and  $Al^{3+}$  ions has increases the rate of the reaction.

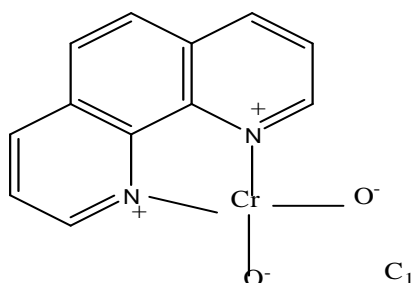
**Mechanism and Rate law**

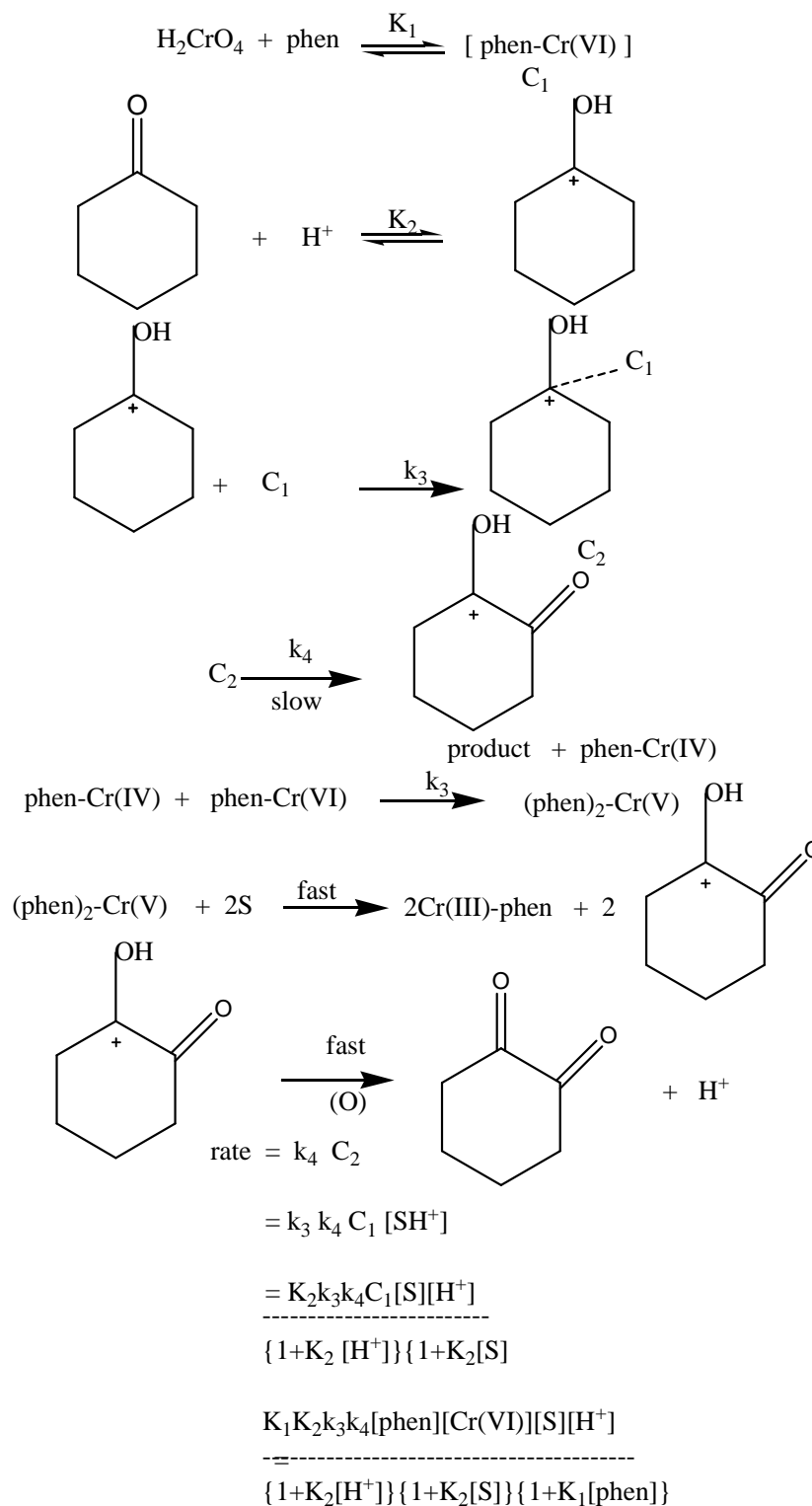
The oxidation by Cr(VI) will vary with nature of the Cr(VI) species used and solvent will play an important role on the rate of the reaction. In aqueous solution and in the absence of other ions the following equilibria are existing.



Here the dimerization equilibrium is of considerable importance. In water the dichromate ion will be Predominating species only at the concentrations greater than about  $0.05 \text{ mol dm}^{-3}$ . In this case as the concentration of Cr(VI) is lesser than  $0.05 \text{ mol dm}^{-3}$ , the monomeric form predominates and the active oxidizing species is  $HCrO_4^-$  and at higher acidity, the reverse reaction of the first equilibrium process is predominating. The reaction is acid catalysed one.

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. It has been reported that the phen complexes are more stable than the bipyridyl complexes. Quite likely, the complexing agents stabilize the end products, chromium (III), and hence accelerate the whole of the reaction [13]. 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 the facile formation of Cr(VI)-phen complex in acid solutions. This is similar to the view reported in the Cr(V) oxidation of sulphides and cycloketones in the presence of picolinic acid[14]. The reactive nucleophile Cr(VI)-phen complex ( $C_1$ ) has been reported in the oxidation of anisole by chromic acid[15]. Based on the available kinetic data can be rationalized by following mechanistic scheme 1.





scheme-1

The rate of oxidation of cyclooctanone, cyclohexanone, cycloheptanone and cyclopentanone have been studied at four different temperatures viz., 303K, 313K, 323K and 333K. The activation parameters are calculated using Eyring's

plot [16] and the values are given in (Table- 3 ).The negative value of the entropy of activation ( $\Delta S^\ddagger$ ) suggest extensive solvation of the transition state over the reactants.

More generally, if the Hammett equation is valid at a given temperature, the condition for it validity at any other temperature is a linear relationship between enthalpies called isokinetic relationship.

$$\Delta H^\ddagger = \Delta H_o^\ddagger + \beta \Delta S^\ddagger$$

$\Delta H_o^\ddagger$  is the enthalpy of activation, when  $\Delta S^\ddagger = 0$  and usually has no physical significance and  $\beta$  is the isokinetic temperature( $\beta=350\text{K}$ ). A plot of  $\Delta H^\ddagger$  versus  $\Delta S^\ddagger$  gave a straight line with good correlation coefficient ( $r = 0.999$ )(Fig 1).

The Exner plot[17] of  $5+\log k_{1(313\text{K})}$  versus  $5+\log k_{1(303\text{K})}$  gave straight lines with  $r = 0.996$ (Fig 2). Such a good correlation indicates that all the substituents show a common mechanism.

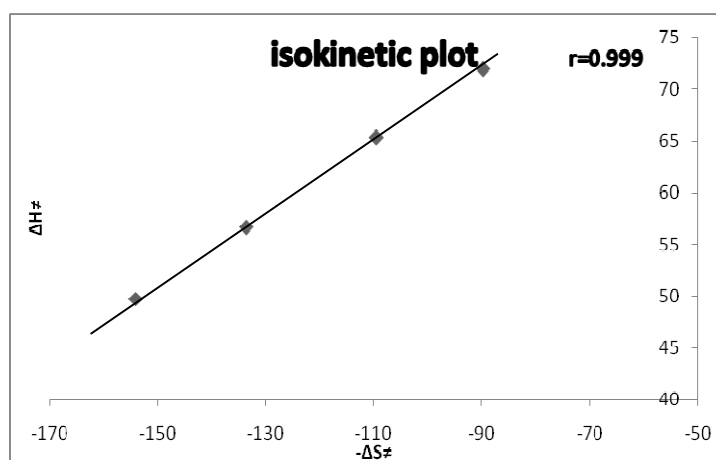


Fig 1.  $\Delta H^\ddagger$  Vs.  $-\Delta S^\ddagger$

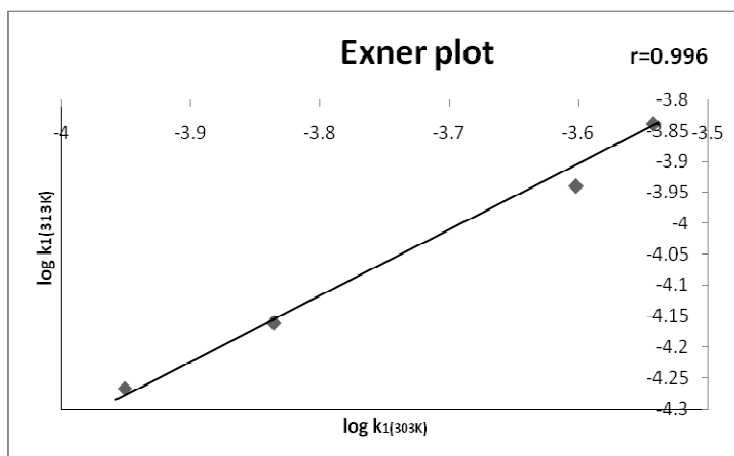


Fig 2.  $5+\log k_{1(313\text{K})}$  Vs.  $5+\log k_{1(303\text{K})}$

To have an idea about, the order with respect to each of the substrate has been studied at 313K and results are given in Table 4. It is interesting to note that cyclohexanone, cyclooctanone, cycloheptanone and cyclopentanone shows a fractional order dependence on the reaction rate.

**Effect of structure on the reactivity of cyclicketones**

The rate data shows the order of reactivity of cyclicketones: cyclohexanone > cyclooctanone > cyclopentanone > cycloheptanone. This would become more relevant and meaningful only when conformational aspects were taken into consideration.

In its chair form, cyclohexanone would owe its unique stability to the fact that each of its energy components would be a minimum. A more favoured model would be a form with only four carbon atoms planar, which would be similar to the half-chair cyclohexene in shape [18]. This form would be the direct intermediate conformation between the chair form and the twist-boat form, all of  $C_{2v}$  symmetry. The interconversion of chair to twist-boat takes place by a rotation of one bond around the 2-fold axis. Since this is the most economical route for boat-chair conversion, it is probably also the most economical pathway for deformations of the six-membered cycloalkanone. Hence, the reactivity of cyclohexanone would be the highest among the cycloalkanones.

Cyclooctane has  $C_{2v}$  symmetry, resulting in a particular type of deformed crown structure [19,20]. There appear to be three different kinds of axial positions and three different kinds of equatorial positions, indicating that cyclooctanone is a mixture of six conformations (some possibly in negligible amounts). In cyclooctanone, the oxygen is compressed by the hydrogen atoms at C1 and C5 and there is no significant relief of this compression when cyclooctanone is subjected to oxidation. Hence, the rate of oxidation of cyclooctanone would be slower than that for cyclohexanone.

The lower reactivity of cyclopentanone was due to the existence of cyclopentanone in the half-chair form (stable conformation) having greater symmetry [21].

For cycloheptanone, there were two forms that could be interconverted through major deformation of bond angles from tetrahedral. These two plane-symmetrical forms were the chair form and the boat form. However, both forms would be flexible with respect to their bond angles and may undergo pseudorotation. The chair form has a H-H repulsion across the axial C3-positions, which may be relieved by pseudorotation. In the boat form, the half-cycle position provided minimum repulsion energy. This form has a 2-fold symmetry axis, called the twist-chair conformation [22]. This would low reactivity of cycloheptanone when subjected to oxidation.

**Table 1 – Effect of [cyclohexanone], [oxidant],  $[H^+]$  and [catalyst] on the reaction rate at 313K.**

[oxidant] $\times 10^3$ mol dm <sup>-3</sup>	[cyclohexanone] $\times 10^2$ mol dm <sup>-3</sup>	$[H^+] \times 10^2$ mol dm <sup>-3</sup>	[catalyst] $\times 10^3$ mol dm <sup>-3</sup>	$k_r \times 10^4$ s <sup>-1</sup>
0.50	1.50	3.75	1.25	2.87
1.00	1.50	3.75	1.25	2.87
1.50	1.50	3.75	1.25	2.88
2.00	1.50	3.75	1.25	2.86
2.50	1.50	3.75	1.25	2.84
1.00	1.00	3.75	1.25	2.56
1.00	1.50	3.75	1.25	2.87
1.00	2.00	3.75	1.25	3.15
1.00	2.50	3.75	1.25	3.48
1.00	3.00	3.75	1.25	3.82
1.00	1.50	2.75	1.25	2.24
1.00	1.50	3.25	1.25	2.53
1.00	1.50	3.75	1.25	2.87
1.00	1.50	4.25	1.25	3.28
1.00	1.50	4.75	1.25	3.44
1.00	1.50	3.75	0.75	2.26
1.00	1.50	3.75	1.25	2.87
1.00	1.50	3.75	1.75	3.58
1.00	1.50	3.75	2.25	4.40
1.00	1.50	3.75	2.75	5.03

**Table 2- Effect of solvent,  $[Mn^{2+}]$  and  $[Al^{3+}]$  on the reaction rate at 313K**  
 $[substrate]= 1.50 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[oxidant]= 1.00 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[H^+]= 3.75 \times 10^{-2} \text{ mol dm}^{-3}$   
 $[catalyst] = 1.25 \times 10^{-3} \text{ mol dm}^{-3}$

$[Mn^{2+}] \times 10^3$ $\text{mol dm}^{-3}$	$[Al^{3+}] \times 10^3$ $\text{mol dm}^{-3}$	% acetic acid (v/v)	$k_1 \times 10^4$ $\text{s}^{-1}$
0.00	-	-	2.87
1.50	-	-	2.62
2.00	-	-	2.31
2.50	-	-	1.93
3.00	-	-	1.60
-	0.00	-	2.87
-	1.50	-	3.18
-	2.00	-	3.56
-	2.50	-	3.88
-	3.00	-	4.23
-	-	35	2.87
-	-	40	3.16
-	-	45	3.32
-	-	50	3.80
-	-	55	4.01

**Table 3-Effect of temperature and activation parameters for oxidation of cyclicketones**

$[substrate]= 1.50 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[oxidant]= 1.00 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[H^+]= 3.75 \times 10^{-2} \text{ mol dm}^{-3}$   
 $[catalyst] = 1.25 \times 10^{-3} \text{ mol dm}^{-3}$

substrate	order	$k_1 \times 10^4 \text{ s}^{-1}$				$\Delta H^\ddagger$ $\text{kJmol}^{-1}$	$-\Delta S^\ddagger$ $\text{JK}^{-1} \text{mol}^{-1}$	$\Delta G^\ddagger$ $\text{kJmol}^{-1}$	r
		303 K	313K	323K	333K				
Cyclopentanone	0.35	1.45	2.87	5.97	9.26	49.69	154.30	97.99	0.994
Cyclohexanone	0.31	1.05	2.50	5.62	8.56	56.35	134.59	98.48	0.989
Cycloheptanone	0.49	0.69	1.46	3.90	7.49	66.23	106.22	99.48	0.990
Cyclooctanone	0.52	0.54	1.12	3.68	7.25	72.46	88.01	100.01	0.991

Supporting arguments for the observed order of reactivity for cyclicketones [ $C_6 > C_8 > C_5 > C_7$  (ring size)] could be based on the following considerations:

- i) I-strain in these rings. The concept of I-strain has been involved to explain the relative ease with which a change in the bond hybridization ( $sp^2$  to  $sp^3$ ) takes place in these ring compounds[23]. The change may refer to the formation of a transition state or of a product leading to a kinetic effect or a thermodynamic effect, respectively. In the rate-determining step of the reaction, one of the ring-carbon atoms changes from the  $sp^2$  to the  $sp^3$  state of hybridization. The relative ease of such a change in the state of hybridization is in the order (ring size):  $C_6 > C_8 > C_5 > C_7$ [24].
- ii) cyclohexanone is essentially free of strain. The strain due to eclipsing of the carbonyl oxygen by the equatorial hydrogen atoms at C2 and C6 appears to be relieved when the hybridization of the carbonyl oxygen is changed from  $sp^2$  to  $sp^3$ .
- iii) the higher reactivity of cyclohexanone is due to the terminal hydrogen of the nearly strainless puckered  $(CH_2)_4$  residue, fulfilling the stereochemical requirement for hyperconjugation with the cyclic  $C=C$  groups better than the terminal hydrogen of the nearly flat  $(CH_2)_3$  residue in cyclopentanone does[25].

## CONCLUSION

The oxidation of cyclicketones by BTEACC in the presence of phen in aqueous acetic acid medium leads to formation of complex, which finally gives products. The reaction follows pseudo-first order kinetics. The order of The order of reactivity for the cyclicketones was  $C_6 > C_8 > C_5 > C_7$  (ring size) have been observed. The negative value of  $\Delta S^\ddagger$  provided support for the formation of the activated complex in the slow step. The constancy of  $\Delta G^\ddagger$  values indicates that a similar mechanism is operative in the oxidation of cyclicketones by BTEACC. The mechanism proposed for this oxidation kinetics is in accordance with observed kinetic facts.

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