Research Article

Kinetics and Mechanism of the Oxidative Cleavage of Cyclic Ketones by Nicotinium Dichromate – Catalysed by 1,10-Phenonthroline

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ABSTRACT

The kinetics of the oxidation of cyclic ketones by nicotinium dichromate (NDC), in acetonitrile medium, catalysed by 1,10-phenonthroline has been investigated. The order of reactivity for the cyclic ketones was $C_8 > C_6 > C_7 > C_5$. The reaction shows fractional order dependence with respect to [substrate] and [H^+] and first order dependence with respect to [oxidant]. Activation parameters have been evaluated and a suitable mechanism has been proposed.

Keywords: Kinetics, oxidation, cyclic ketones, NDC, perchloric acid, water.

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INTRODUCTION

Selective oxidation of organic compounds under aqueous [1] and non-aqueous [2] conditions is an important transformation in synthetic organic chemistry. Chromium compounds especially Cr(VI) reagents have been proved to be versatile reagents and capable of oxidizing almost all the oxidisable organic functional groups [3,4]

Nicotinium dichromate (NDC) a complex of Nicotinic acid & chromium trioxide is reported to be more versatile oxidant **[3-8]**. Now, we report the kinetics and mechanism of oxidation of cyclic ketones by NDC in the presence of 1,10–phenanthroline (Phen). Extensive kinetics and mechanistic studies on oxidation of organic compounds with chromium reagents revealed that such reaction ordinarily involves three – electron change where by Cr (VI) species are reduced to Cr (III). The objective of the present study is to ascertain the reaction pathway especially with respect to chromium.

EXPERIMENTAL SECTION

Materials
All chemicals used were of 'AnalaR'grade (Fluka). Triply distilled water was used for the preparation of solutions. NDC is prepared by improved method of Corey & Suggs **[9]** described by Agarwal. The yellow orange solid which is collected on a sintered glass funnel dried for 1h in vacuum and m.p. $(215 – 217^0C)$ was checked. NDC solution was prepared by dissolving the known amount of this compound in water and standardized iodometrically using starch as indicator.

Kinetic measurement
The reaction was carried out under pseudo-first order conditions by maintaining a large excess of cyclic ketones over Cr(VI). The mixture was homogeneous throughout the course of the reaction. The reaction was followed titrimetrically. The rate constants were evaluated from log (titre) versus time plots. All rate constants are average of two or more determinations.

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Stoichiometry
Reaction mixture containing an excess of the oxidant over cyclohexanone were kept at room temperature in the presence of 1,10-phenanthroline as a catalyst for 24 h. Estimation of unchanged oxidant showed that 3 mol of cyclohexanone consumed 2 mol of oxidant. The product 1,2–cyclohexane dione was identified by IR&UV spectra.

RESULTS AND DISCUSSION

Effect of oxidant and substrate concentration on reaction rate
The oxidation of cyclohexanone by NDC was investigated at several concentrations of oxidant [NDC] (Table 1) and the [substrate]. The plot of log titre versus time was linear indicating the first order dependence on [NDC]. The values of pseudo-first order rate constant k_1 were evaluated from the plot of log titre versus time following least square method (Fig. 1). The plot of log k_1 versus log [substrate] is a straight line in all the cases with slope respectively for cyclohexanone (0.23), cyclopentanone (0.56) (Fig.2), cycloheptanone (0.41) and cyclooctanone (0.48).

Table – 1 Effect of reactants on the reaction rate of oxidation of cyclohexanone at 303K

[S] x 10^2 mol dm^{-3}	[OX] x 10^3 mol dm^{-3}	[Cat] x 10^2 mol dm^{-3}	[H$^+$] x 10^1 mol dm^{-3}	k_1 x 10^5 s^{-1}
2.0	1.0	1.0	6.0	6.10
3.0	1.0	1.0	6.0	6.90
4.0	1.0	1.0	6.0	7.18
5.0	1.0	1.0	6.0	7.58
3.0	0.5	1.0	6.0	6.90
3.0	1.0	1.0	6.0	6.90
3.0	1.5	1.0	6.0	6.92
3.0	2.0	1.0	6.0	6.91
3.0	1.0	1.0	3.0	5.89
3.0	1.0	1.0	6.0	6.90
3.0	1.0	1.0	9.0	7.38
3.0	1.0	1.0	12.0	7.68
3.0	1.0	0.5	6.0	5.55
3.0	1.0	1.0	6.0	6.90
3.0	1.0	1.5	6.0	7.53
3.0	1.0	2.0	6.0	8.51

Effect of [H$^+$] and catalyst concentration on reaction rate
The rate constants were found to increase with increase in [H$^+$] as shown in Table 1 and the plot of log k_1 against log [H$^+$] gave a straight line with the slope less than one. The reaction rate were also measured at the different initial concentration of 1,10-phenonthroline and the rate constant was found to increase with the concentration of 1,10-phenonthroline. The plot of log k_1 versus log [catalyst] was linear with the slope less than one.

Table – 2 Variation of rate with Substrate concentration at 303K
[OX] = 1.0 x 10^{-3} mol dm^{-3} [H$^+$] = 6.0 x 10^{-1} mol dm^{-3}
[Phen] = 1.0 x 10^{-2} mol dm^{-3} Acetonitrile-H$_2$O =73-27% (v/v)

[Substrate] ×10^2 mol dm^{-3}	$k_1 \times 10^5$ sec^{-1}			
	Cyclopentanone	Cyclohexanone	Cycloheptanone	Cyclooctanone
2.0	3.91	6.10	4.58	8.01
3.0	5.06	6.90	5.49	9.57
4.0	5.78	7.18	6.01	11.20
5.0	6.58	7.58	6.72	13.56
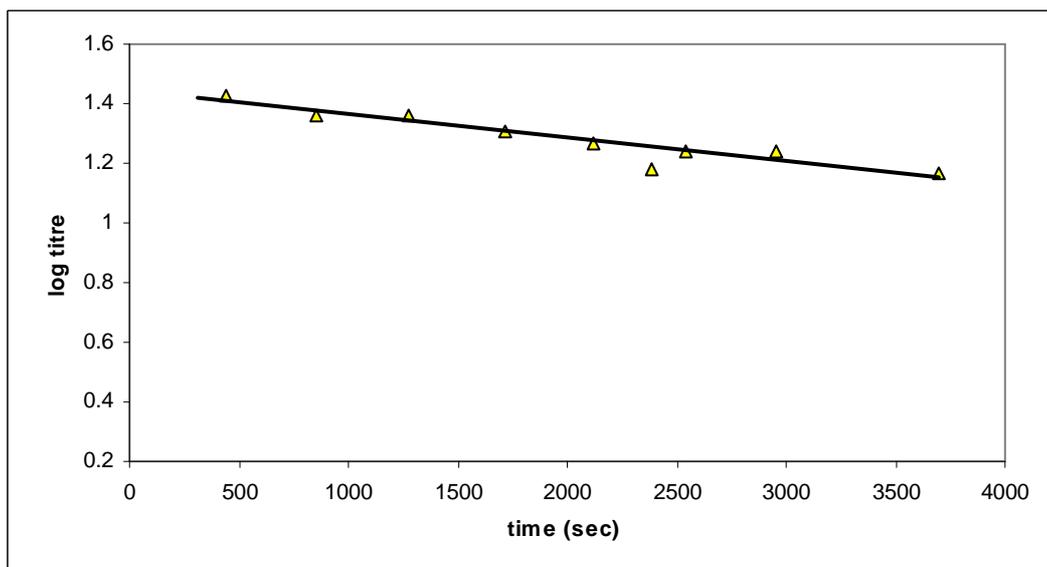
Fig.1 log titre versus time (sec)
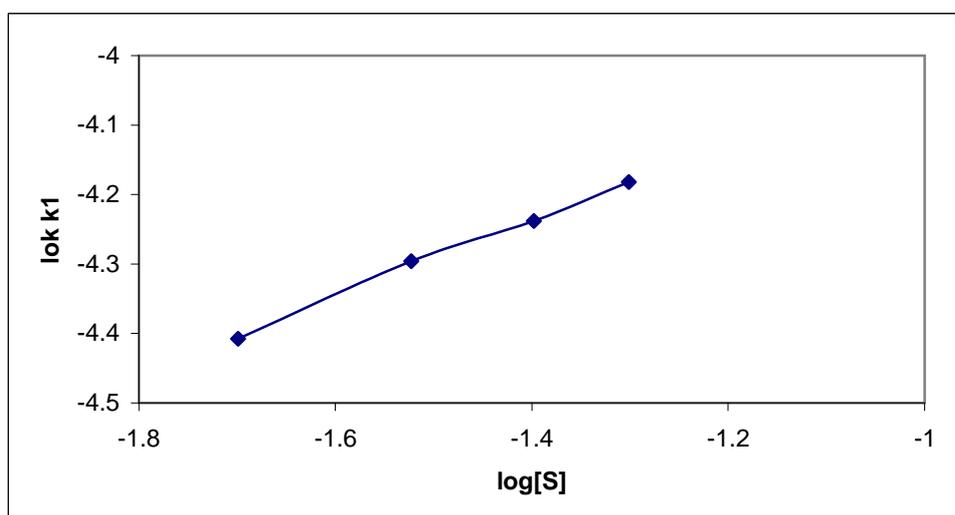
Fig.2 log k_1 versus log[S]

Table – 3 Effect of Mn^{2+}, Al^{3+} and $NaClO_4$ on the reaction rate of cyclohexanone at 303 K
[S]=3x10^{-2} mol dm^{-3}, [OX]=1x10^{-3} mol dm^{-3}, [Cat]=1x10^{-2} mol dm^{-3}, [H$^+$]=6x10^{-1} mol dm^{-3}

[Mn^{2+}] mol dm^{-3}	[Al^{3+}] mol dm^{-3}	[$NaClO_4$] mol dm^{-3}	$k \times 10^5 s^{-1}$
0.5	-	-	6.86
1.0	-	-	6.72
1.5	-	-	6.68
2.0	-	-	6.60
-	0.5	-	6.83
-	1.0	-	6.42
-	1.5	-	6.12
-	2.0	-	6.01
-	-	0.5	6.92
-	-	1.0	6.98
-	-	1.5	7.23
-	-	2.0	7.27

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Effect of Mn^{2+}, Al^{3+} and $NaClO_4$ on the reaction rate of cyclohexanone
To analyze the number of electrons involved in the oxidation process, the reaction rate was followed by varying the concentration of acrylonitrile, $[Mn^{2+}]$, $[Al^{3+}]$. The added acrylonitrile has no effect on reaction rate, indicating absence of free radical pathway. Depressed reactivity observed in the presence of Mn^{2+} clearly indicated the involvement of intermediate valence states of Chromium, particularly Cr (IV). With the increase in the concentration of Al^{3+} the rate of reaction decreases indicating the 3 electron transfer in the reaction.

Effect of Temperature
Kinetics of oxidation of cyclohexanones and other cyclic ketones by NDC was carried out under pseudo-first order conditions. From a series of kinetic runs the rate constants k_1 were estimated for some cyclic ketones at three different temperatures, viz. 303, 313 and 323 K. The thermodynamic parameters were calculated using the Eyring's plot (Fig.3) and the values are given in the Table 4 (r = 0.990).

Table – 4 Rate constant and activation parameters of cycloalkanones

$[S] = 3.0 \times 10^{-2} mol\ dm^{-3}$ $[OX] = 1.0 \times 10^{-3} mol\ dm^{-3}$
$[Phen] = 1.0 \times 10^{-2} mol\ dm^{-3}$ $[H^+] = 6.0 \times 10^{-1} mol\ dm^{-3}$
Acetonitrile - H_2O = 73-27% (v/v)

Cycloalkanone	$k_1 \times 10^5\ S^{-1}$			$(\Delta H^{\#})$ kJmol^{-1}	$(\Delta G^{\#})$ (303K) kJmol^{-1}	-$(\Delta S^{\#})$ Jmol^{-1}	r
	303 K	313 K	323 K				
Cyclopentanone	5.06	9.08	14.92	41.54	99.17	190.21	0.99
Cyclohexanone	6. 90	13.18	23.44	48.03	98.45	166.39	0.99
Cycloheptanone	5.49	10.56	17.82	45.21	98.93	177.31	0.99
Cyclooctanone	9.57	17.69	31.72	46.39	97.60	169.01	0.99

The fairly high values of enthalpy of activation ($\Delta H^{\#}$), free energy of activation ($\Delta G^{\#}$), and energy of activation (E_a) indicate that the transition state is highly solvated. The negative values of the entropy of activation ($\Delta S^{\#}$) suggest extensive solvation of the transition state over the reactants. It also reveals that the rate-determining step is less disorderly oriented relative to the reactants. As $\Delta H^{\#}$ and $\Delta S^{\#}$ do not vary linearly, no isokinetic relationship is observed. This indicates the absence of enthalpy entropy compensation effect [10].

Exner [11] criticized the validity of such a linear correlation between $\Delta H^{\#}$ and $\Delta S^{\#}$, as these quantities are dependent on each other. When the measurements at two different temperatures have been made, the data can be analyzed by the following equation.

$$\log (k_1)_{T2} = a + b \log(k_1)_{T1} \text{ where } T_2 > T_1$$

The plots of log k_{obs} (313 K) versus log k_{obs} (303 K) (r = 0.997) and log k_{obs} (323 K) versus log k_{obs} (303 K) give straight lines with r = 0.991 (Fig.4). Such a good correlation indicates that all the substituents follow a common mechanism of oxidation.
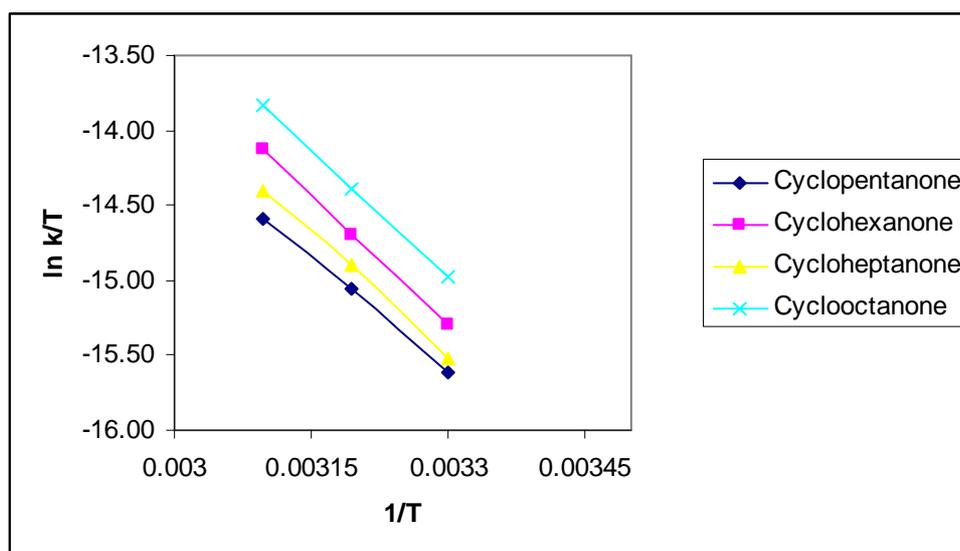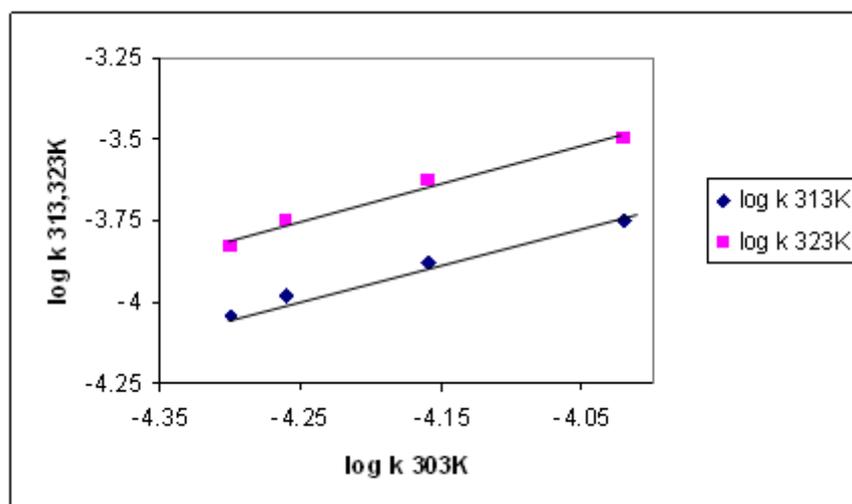

Fig.3 The Eyring's Plot

Fig.4 The Exner Plot

Mechanism and rate law

It is believed that the catalytic activity of complex 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 bi-pyridyl complexes. Quite likely, the complex agents stabilize the end products, chromium(III), and hence accelerate the whole of the reaction [12,13,14]. Addition of Phen and its binding to the Cr(VI) would presumably change the redox potential of the chromium oxidant, the protonation of cyclohexanone which has been already reported. Substantial acid catalytic activity in the present study can be attributed to facile formation of Cr(VI)-Phen complex in acidic solutions. This is similar to the view reported in the chromium (V) oxidation of sulphides in the presence of picolinilic acid [15]. The reactive nucleophile Cr(VI)-Phen complex, C_1 has been reported in the oxidation of anisole by chromic acid [16]. The rate constants were measured at 303, 313 and 323 K.
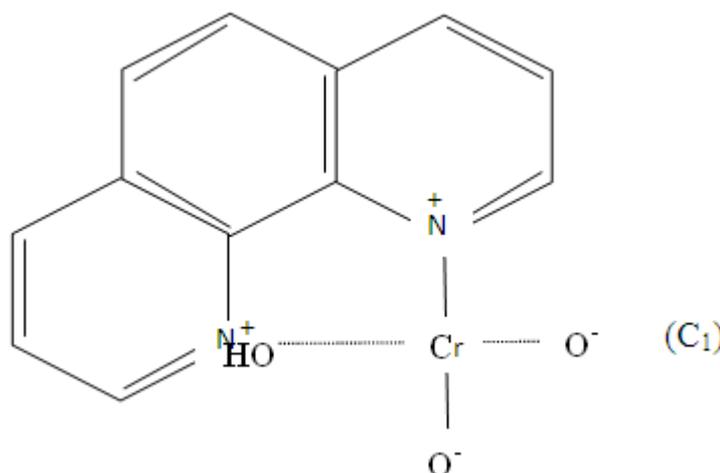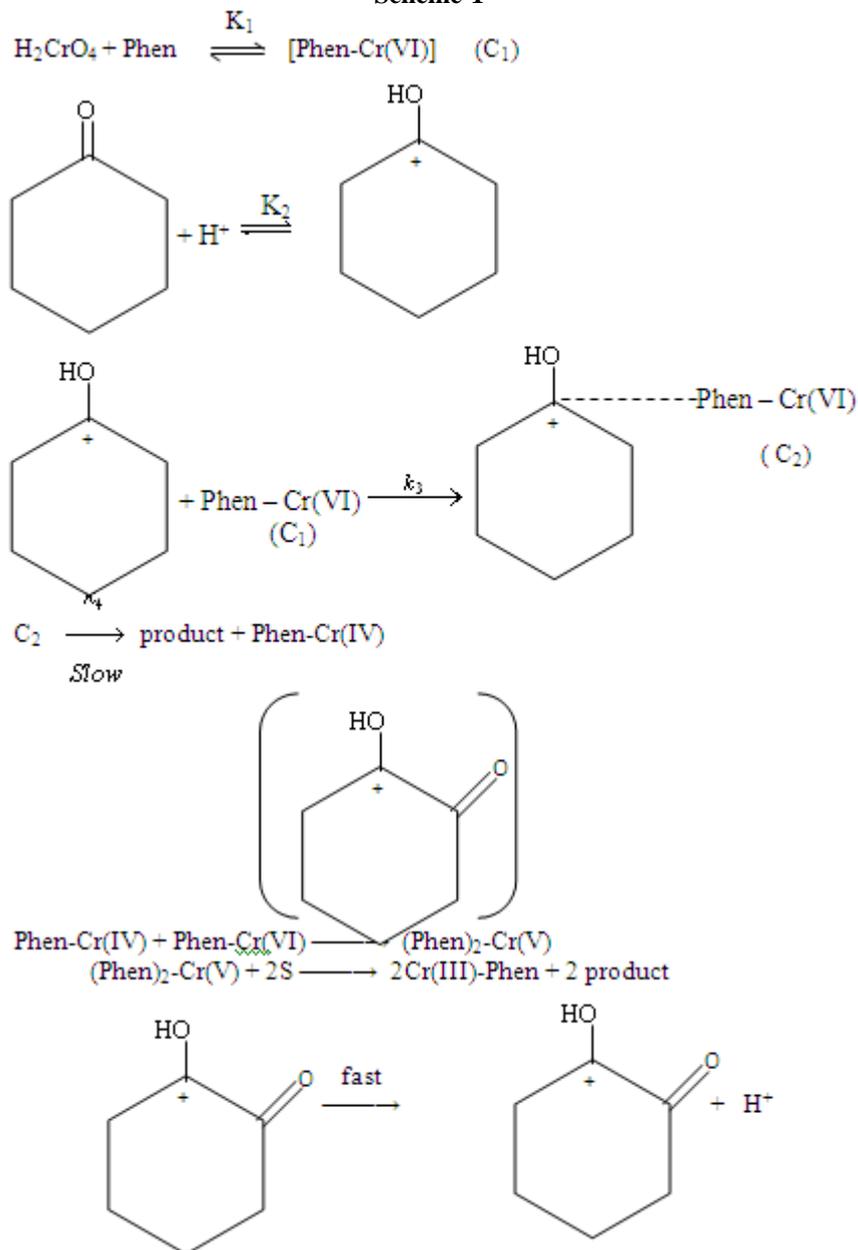

The available kinetic data can be rationalized by the following mechanistic scheme (scheme –1)

$$\text{rate} = k_4 C_2$$

$$= k_4 k_3 [\text{phen-Cr(VI)} \, [\text{SH}^+]$$

$$= \frac{K_2 k_3 k_4 \, [\text{Phen-Cr(IV)}][\text{S}][\text{H}^+]}{\{1+K_2 \, [\text{s}]\} \, \{1 + K_2 \, [\text{H}^+]\}}$$

$$= \frac{K_1 K_2 k_3 k_4 \, [\text{Phen}] \, [\text{Cr(IV)}] \, [\text{S}] \, [\text{H}^+]}{[1+K_1 \, [\text{Phen}] \, [1+K_2 \, [\text{s}]] \, [1 + K_2 \, [\text{H}^+]]}$$

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$$K_{obs} = \frac{K_1 K_2 k_3 k_4 \,[Phen]\,[Cr(IV)]\,[S]\,[H^+]}{\{[1 + K_1\,[Phen] + K_2\,[s] + K_2\,[H^+]]\}}$$

$$K_{obs} = K_1 K_2 k_3 k_4$$

Scheme-1

DISCUSSION

The kinetic data of oxidation of the above cyclic ketones were analyzed with a view to study the effect of ring size on reactivity. In general, the order of reactivity of cyclic compounds may be two types. In some cases the order of reactivity increases with increasing size of the ring as noticed in the oxidation of cyclic alcohols by acid bromate [17] and hexacyanoferrate (III). In this case the order of reactivity of various cyclanols is **5> 6 > 7 > 8**, which is in conformity with the Bayer's strain theory. During the oxidation of these cyclanols the hydroxyl carbon atom is undergoing change in hybridization from **Sp^3 to Sp^2** to form the cyclic ketones, i.e. the four to three. The strain which is developed during this conversion is released as the ring size is increased. Hence, here the order of reactivity increases with the size of the ring; on the other hand, the reactivity of enolisation of cyclanones [18,19] in acid medium as the function of ring size is **6 > 8 > 5 > 7.** This is in accordance with I-strain hypothesis. I-strain is that change in internal strain which results from change in co-ordination number of a ring atom involved in a chemical reaction.

The five- and seven-member rings are appreciably strained, primarily as a result of the torsional forces about C-C single bond. It is proposed that the introduction of an atom with preferred 120^0 angle leads to a decrease in internal strain. Therefore, I-strain will favour the reactions involving changes in coordination number from four to five or four to three and oppose reactions involving covalency change from three to four.

The reactions involving a change in co-ordination number from three to four are strongly favoured in six-ring compounds relative to five- and seven-ring derivative, because the cyclohexane ring with six tetrahedral carbon atoms is highly symmetrical and stable. Moreover hydrogen-hydrogen repulsions are reduced to a minimum in the chair form as a result of fully staggered constellation remitted by this form. Enlargement of one of the ring (C-C-C) angles will decrease the symmetry, decrease the puckering and increase the hydrogen-hydrogen repulsions. The increase in the angle will lead to an increase in internal strain (positive strain). Therefore, in cyclehexanone derivative I-strain will oppose the reaction involving a change in covalency of a ring atom from either four to five or four to three. Conversely in these compounds a change in covalency of a ring atom from three to four will involve a decrease in internal strain (negative strain) and will be strongly favoured.

In the present study the order reactively among the cyclic ketones is the following: Cyclooctanone > Cyclohexanone > Cycloheptanone > Cyclopentanone.

The order observed shows that even-member cyclic ketones (C_8 and C_6) react much faster than the odd-member ketones (C_7 and C_5). It is interesting to recall the similar differences noticed between the spectra of the even-and odd-member ketones. For even-member ketones, the spectrum changes suddenly at the melting point while in the rest of the temperature range only slight changes are observed.

For odd-member ring ketones the spectrum also changes not at the melting point but at the transition point which lies lower than the melting point. The change in spectrum may be attributed to the possible disappearance of one or more conformation at a given temperature. It is generally presumed that the most favoured conformation of cyclopentanone is the twist chair [20,21] which is responsible for the lowest rate of oxidation. Similarly the lower reactivity of cyclopentanone can be attributed to the existence of cyclopentanone in the half chair form (stable conformation) which has greater symmetry. However, the reactivity of medium-sized rings are known to alternate as evidenced from the process involving **sp3-sp2** conversions such as solvolysis of cycloalkyl chloride, acetolysis of cycloalkyl bromides with lithium potassium iodide [22].

Strictly speaking the observed reactivity of a series of medium sized cyclic derivatives depends mainly on their conformations.

CONCLUSION

In the present study the higher reactivity of cyclooctanone is attributed to its existence in the crown form which has lower symmetry whereas the cyclohexanone exists in the chair form, cycloheptanone in the twist chair form and cyclopentanone in the half chair form (stable conformation) which has greater symmetry. Therefore, it can be safely argued that as the symmetry order increases the reactivity of oxidation of cyclic ketones by NDC decreases (or) in other words, it can be concluded that higher the order of symmetry, lower the rate of reactivity.

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