

Structure Reactivity in the Oxidation of Cyclic Ketones by Quinolinium Dichromate

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The kinetics of oxidation of cyclic ketones *viz.*, cyclopentanone, cyclohexanone, cycloheptanone and cyclooctanone with quinolinium dichromate has been studied in 60 % acetic acid-water medium. The reaction shows first order dependence with respect to both oxidant and substrate. The reaction exhibits dual behaviour with respect to $[H^+]$ *i.e.*, unit order dependence at lower $[H^+]$ and greater than one at higher $[H^+]$. The rate of the reaction decreases with increase in the dielectric constant of the medium. The retardation of the rate by the addition of Mn^{2+} ions confirms that a two electron transfer process is involved in the reaction. A relationship has been observed between ring size and reactivity of the cyclic ketones. The order of reactivity has been rationalized.

Key Words: Kinetics, Oxidation, Cyclic ketones, Quinolinium dichromate, Activation parameters.

INTRODUCTION

Quinolinium dichromate [QDC, $(C_9H_7NH^+)_2 Cr_2O_7^{2-}$], one of the Cr(VI) compound, is reported to be a neutral and mild oxidant for selective oxidation¹. Kinetics of oxidation of some organic substrates by quinolinium dichromate has already been reported²⁻¹⁰. The kinetics of oxidation of cyclic ketones by pyridinium fluorochromate¹¹, quinolinium dichromate¹² and quinolinium fluorochromate¹³ have been studied. The Bayer's strain theory or I-strain theory has explained the difference in the reactivity. This paper presents the kinetic features of the oxidation of cyclic ketones by QDC in perchloric acid medium is to ascertain the nature and the order of reactivity of these compounds under the given kinetic conditions.

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EXPERIMENTAL

Quinolinium dichromate was prepared by the reported method¹ and its purity was checked by spectral analysis. Infrared spectrum (KBr) gave bands at 930, 875, 765 and 730 cm^{-1} , characteristic of the dichromate ion. All the cyclic ketones (Fluka) were used after distillation and recrystallization, respectively. Acetic acid (E-Merck) was distilled and the fraction distilling at 116 °C was used. All other chemicals used were of AR grade. The solutions were prepared in triple distilled water.

Kinetic measurements: The reaction was carried out under pseudo-first order conditions ($[\text{Cycl}] \gg [\text{QDC}]$) in glacial acetic acid containing perchloric acid medium. The kinetic measurements were carried out spectrophotometrically in a thermostated cell compartment of Jasco UVIDECS-340 spectrophotometer at 350 nm. The pseudo-first order rate constants (k_{obs}) were evaluated from the linear plots of $\log [\text{absorbance}]$ vs. time by the least squares method and were reproducible within $\pm 2\%$.

Stoichiometry and product analysis: The stoichiometry of the reaction was determined for a number of reaction mixtures containing at least a threefold excess of oxidant over the substrate. The estimation indicated that one mole of the oxidant reacted with one mole of the substrate.

The reaction mixture from the actual kinetic run after sufficient length of time was extracted with ether and dried over anhydrous sodium sulphate. The ether was removed by warming and the product obtained was found to be adipic acid (m.p. 155 °C). Infrared spectrum (KBr) gave bands at 2952, 1724, 1462, 1428, 1408, 1278, 1193, 926, 734 cm^{-1} .

RESULTS AND DISCUSSION

The order of the reaction with respect to QDC was found to be unity as shown by the linearity of \log absorbance vs. time plots, over 70 % of the reaction. But the first order rate constant (k_1) decreases as $[\text{QDC}]$ increases. The plot of $1/k_1$ vs. $[\text{QDC}]$ is linear; such observations have been reported by several authors¹⁴. This may be due to that condition only a smaller portion of the total Cr(VI) is in the form of acid chromate ion which is the effective oxidant¹⁵. The reaction was found to be first order in substrate as evidenced by the unit slope of the plot of $\log k_1$ vs. $\log [\text{Cycl}]$. It was further well demonstrated by the constancy of the specific reaction rate constant k_1 by the [substrate] (Table-1).

The reaction was studied by varying the concentrations of sodium perchlorate and keeping all other factors constant. The rate constant was decreased with increase in the ionic strength of the medium indicating that the reaction is in between ions of oppositely charged particles in the rate determining step. The rate of the reaction increases with an increase in the concentration of perchloric acid, suggesting that the protonated species of

TABLE-1
EFFECT OF CONCENTRATION OF REACTANTS OF
REACTION RATES AT 308 K
[H⁺] = 10.0 × 10⁻¹ mol dm⁻³, 60 % AcOH-H₂O (v/v)

10 ² [Cyclohexanone] (mol dm ⁻³)	10 ⁴ [QDC] (mol dm ⁻³)	10 ⁴ k ₁ (s ⁻¹)	10 ³ k ₂ = k ₁ /[S] (l mol ⁻¹ s ⁻¹)
12	3	6.59	—
12	4	6.45	—
12	5	6.26	—
12	6	6.02	—
12	8	5.48	—
12	10	5.06	—
4	5	2.08	5.20
8	5	4.19	5.24
12	5	6.26	5.22
16	5	8.35	5.22
20	5	10.46	5.23
24	5	12.51	5.21

the reactant is involved in the slow step and the reaction is an acid-catalyzed. It is also interesting to note that here the order with respect to [H⁺] is unity at the lower [H⁺] ion (2.5 × 10⁻¹–7.5 × 10⁻¹ mol dm⁻³) and at higher [H⁺] ion (10.0 × 10⁻¹–15.0 × 10⁻¹ mol dm⁻³) the order is greater than unity (Fig. 1, Table-2).

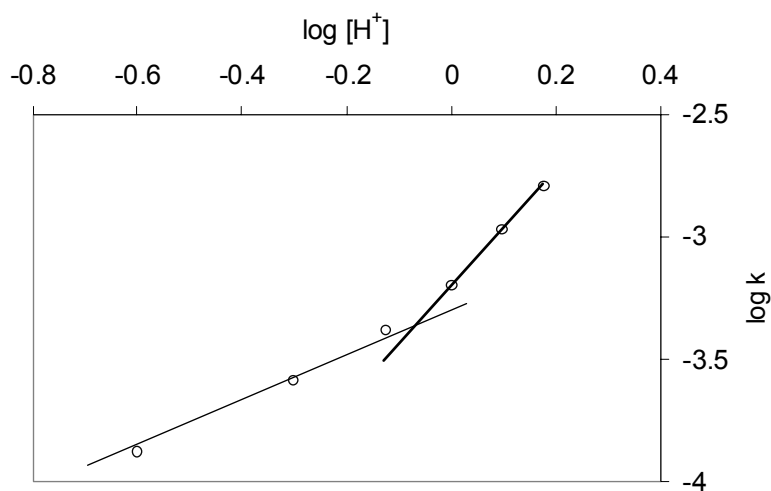


Fig. 1. Plot of log [H⁺] vs. log k

TABLE-2
EFFECT OF VARYING IONIC STRENGTH AND $[H^+]$ ON THE RATE
OF OXIDATION AT 308 K
[Cyclohexanone] = $12.0 \times 10^{-2} \text{ mol dm}^{-3}$, [QDC] = $5.0 \times 10^{-4} \text{ mol dm}^{-3}$,
60 % AcOH-H₂O (v/v)

$10^2 [NaClO_4]$ (mol dm ⁻³)	$10^4 k_1$ (s ⁻¹)	$10^1 [HClO_4]$ (mol dm ⁻³)	$10^4 k_1$ (s ⁻¹)
0.00	6.26	2.50	1.31
1.08	5.98	5.00	2.55
2.16	5.56	7.50	4.16
3.24	5.47	10.00	6.26
4.32	4.95	12.50	10.68
5.40	4.72	15.00	16.11

The effect of variation of solvent composition on the pseudo-first order rate constant was also studied. The rate was found to increase when the per cent content of acetic acid (*i.e.*, lowering of dielectric constant) increases. A plot of log k_1 vs. inverse of dielectric constant is linear with a positive slope suggesting an interaction between a positive ion and a dipole. This confirms the involvement of protonated Cr(VI) species in the rate-determining step¹⁶ (Table-3).

TABLE-3
EFFECT OF CONCENTRATION OF SOLVENT ON
REACTION RATES AT 308 K
[Cyclohexanone] = $12.0 \times 10^{-2} \text{ mol dm}^{-3}$, [QDC] = $5.0 \times 10^{-4} \text{ mol dm}^{-3}$,
[H⁺] = $10.0 \times 10^{-1} \text{ mol dm}^{-3}$

AcOH-H ₂ O (% v/v)	40	50	55	60	65	70
Dielectric constant	63.40	56.00	50.80	45.50	42.00	38.50
$10^4 k_1$ (s ⁻¹)	3.62	4.52	5.22	6.26	7.38	9.02

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 Mn²⁺ ions retarded the reaction rate showing the two-electron transfer process in the reaction (Table-4).

TABLE-4
EFFECT OF CONCENTRATION OF MANGANOUS
SULPHATE OF REACTION RATES AT 308 K
[Cyclohexanone] = $12.0 \times 10^{-2} \text{ mol dm}^{-3}$, [QDC] = $5.0 \times 10^{-4} \text{ mol dm}^{-3}$,
[H⁺] = $10.0 \times 10^{-1} \text{ mol dm}^{-3}$, 60 % AcOH-H₂O (v/v)

$10^2 [MnSO_4]$ (mol dm ⁻³)	0.00	1.50	3.00	4.00	6.00	7.00
$10^4 k_1$ (s ⁻¹)	6.26	5.06	4.75	4.65	4.33	4.03

To have an idea about the order with respect to each of the cyclic ketones, the order with respect to each of the substrates has been studied at 308 K and the results are given in Table-5. It is interesting to note that the order with respect to cyclopentanone was found to be fractional whereas the order with respect to cycloheptanone, cyclooctanone was found to be unity. The rate constant was measured at five different temperatures and the activation parameters have been determined. The activation parameters have been computed from a plot of $\ln k_2/T$ vs. $1/T$ using Eyring's equation (Table-5).

TABLE-5
EFFECT OF VARYING SUBSTRATES AND ACTIVATION PARAMETERS
FOR THE OXIDATION OF CYCLIC KETONES WITH QDC

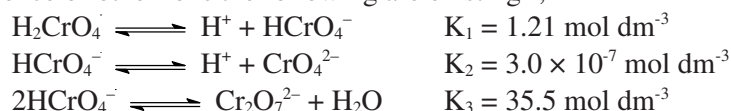
Cyclic ketones	Order	$k_1 \cdot 10^4$ (s ⁻¹)					ΔH^\ddagger (kJ mol ⁻¹)	$-\Delta S^\ddagger$ (JK ⁻¹ mol ⁻¹)
		303 K	308 K	313 K	318 K	323 K		
Cyclopentanone	0.50	1.01	1.42	2.18	3.86	5.09	54.36	124.65
Cyclohexanone	1.00	4.41	6.26	8.78	12.68	16.84	52.54	118.42
Cycloheptanone	1.00	1.89	2.67	3.99	5.33	7.54	53.72	121.53
Cyclooctanone	1.00	12.96	17.99	25.11	33.99	46.22	49.17	120.56

$\Delta G^\ddagger = 89 \pm 3$ kJ mol⁻¹ at 308 K, $E_a = 54 \pm 3$ kJ mol⁻¹ at 308 K

The fairly high values of enthalpy of activation (ΔH^\ddagger), free energy activation (ΔG^\ddagger) and energy of activation (E_a) indicate that the transition state is highly solvated. The negative values of the entropy of activation (ΔS^\ddagger) suggest extensive solvation of the transition state over the reactants. It also reveals that the rate determining state is less disorderly oriented relative to the reactants. As (ΔH^\ddagger) and (ΔS^\ddagger) do not vary linearly no isokinetic relationship is observed. This indicates the absence of enthalpy-entropy compensation effect¹⁷. The linear Exner¹⁸ plots ($r = 0.999$) favours a similar mechanism in all the cyclic ketones.

Mechanism and rate law

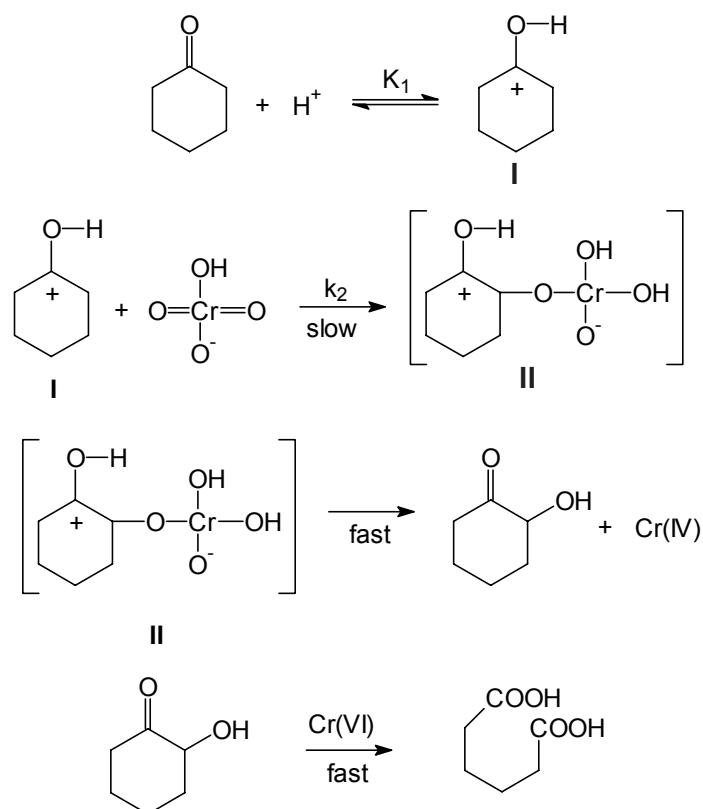
It is clear that reaction is first order dependence on oxidant and substrate and dual behaviour with respect to $[H^+]$ *i.e.*, unit order dependence in the lower acid concentration and higher than one in the higher acid concentration. The oxidation by Cr(VI) is varying with the nature of the Cr(VI) species used and the solvent. In aqueous solution and in the absence of other ions the following are existing¹⁹,



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 mol dm^{-3} . In this case as the concentration of Cr(VI) is lesser than 0.05 mol dm^{-3} , the monomeric form predominates and the active oxidizing species is HCrO_4^- and at the higher acidity, the reverse reaction of the first equilibrium process is predominating.

When the $[\text{H}^+]$ is low, the reaction shows first order dependence on $[\text{H}^+]$. Under those conditions only the cyclic ketones would be protonated as given in the following **Scheme-I**. Hence the rate law when $[\text{H}^+] \ll 1.0 \text{ mol dm}^{-3}$ can be derived as follows,

$$\begin{aligned} \text{Rate} &= -d[\text{Cr(VI)}]/dt = k_2 [\text{cyclohexanone H}^+] [\text{HCrO}_4^-] \\ &= K_1 k_2 [\text{cyclohexanone}] [\text{H}^+] [\text{HCrO}_4^-] \end{aligned}$$



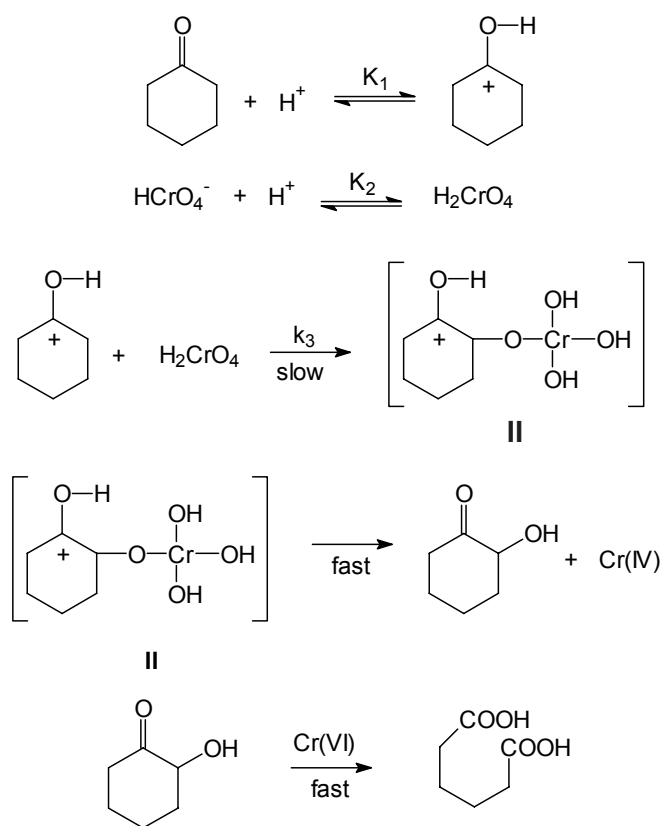
In the case of 7- and 5- membered rings the rate of protonation is also comparatively slow and steps 1 and 2 would be simultaneously slow and rate determining steps. Hence the rate law can be given by invoking the steady-state approximation for 1 as,

$$k_{\text{obs}} = K_1 k_2 [\text{S}] [\text{H}^+] / 1 + K_1 [\text{S}]$$

This clearly shows the fractional order dependence on the substrate. At higher acid concentration when $[\text{H}^+] > 1.0 \text{ mol dm}^{-3}$ the following mechanism can be given (**Scheme-II**) *i.e.*, in this scheme both oxidant and substrate are protonated first followed by the interaction of these two protonated species.

Hence the rate law when $[\text{H}^+] \gg 1.0 \text{ mol dm}^{-3}$ becomes

$$k_{\text{obs}} = K_1 K_2 k_3 [\text{S}] [\text{H}^+]^2$$



Scheme-II

The rate law clearly indicates the higher order of dependence on $[\text{H}^+]$ *i.e.*, it is greater than one. The proposed mechanism (**Scheme-I**) is supported by the fact that in the acid medium the mode of preferential attack is only on the keto form and not on the enol form has already been well established in the study of oxidation of cyclanones by vanadium(V)²⁰. Under these conditions as the initial rate of consumption of oxidant was always of first order, the rates of oxidation of intermediate products cannot be kinetically significant²¹.

Structure and reactivity: From the above results the reactivity amongst cyclic ketones is found to be:

cyclooctanone > cyclohexanone > cycloheptanone > cyclopentanone

The order observed shows that even membered cyclic ketones (C₆ and C₈) react much faster than the odd membered ketones (C₅ and C₇). It is interesting to recall the similar differences noticed between the infrared spectra of the even and odd membered ketones. For even membered ketones, the spectrum changes suddenly at the melting point, while in the rest of temperature range only slight changes are observed. For odd membered ring ketones the spectrum also changes, not at the melting point but at a transition point which lies lower than the melting point. The change in spectrum may be attributed to the possible disappearance of one or more conformations at a given temperature.

The higher reactivity of cyclooctanone is attributed to its existence in the crown form which has lower symmetry where as 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. The higher rates of cyclohexanone and cyclooctanone are due to largest I-strain involved during *sp*³ to *sp*² change. Therefore it can be concluded that as the symmetry order increases the reactivity decreases in the oxidation of cyclic ketones by quinolinium dichromate.

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