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Kinetics and Mechanism of Oxidation of Cyclic Ketones by Chloramine-T in Acid Medium.

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ABSTRACT

Kinetics of oxidation of cyclo pentanone, cyclo hexanone, cyclo heptanone and cyclo octanone by Chloramine-T (CAT) in the acid medium using aqueous acetic acid as solvent has been taken up in order to find out the nature of the reactive species and mechanism of the reaction. Under conditions $[\text{cyclic ketones}] \gg [\text{CAT}]$, the rate of oxidation exhibited pseudo first order dependence in $[\text{CAT}]$ as seen from linearity of plot of $\log a/a-x$ vs time. The rate increases with increase in substrate. The order in $[\text{Sub}]$ was found to be one from plot of $\log K^1$ vs $\log [\text{cyclic ketone}]$, $[\text{H}^+]$ was found to be fractional one. Solvent and salt effects were not considerable. The effect of toluene sulphonamide was negligible. No polymerisation was observed with added acrylamide. Suitable mechanism has been suggested and rate law consistent with experimental findings has been derived.

Keywords: Chloramine-T (CAT), cyclic ketones, pseudo first order, toluene sulphonamide, polymerization, mechanism & rate law

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INTRODUCTION

The study of redox reactions involving oxidation is of great importance as it helps in understanding biochemical transformations, industrial processes and other applications like construction of rockets, space crafts etc. The kinetics of oxidation of cycloalkanones in the presence of CAT has been the subject of many investigations.

In the current study, oxidation of cyclic ketones by CAT was carried out. Generally ketonic group shows some resistance towards oxidation. However cyclic ketones such as cyclo pentanone, cyclo hexanone, cyclo heptanone and cyclo octanone undergo oxidation with considerable ease. The ring strain may be the reason because of which they exhibit tendency to undergo oxidation. Many reports of oxidation of these compounds are seen in literature [1-10].

The reactive species of ketone in these studies depend largely on experimental condition. However it may not be possible sometimes to say why particular species enol/enolate or free ketone is reactive species. Preliminary investigation showed that cyclic ketones are oxidized by CAT with considerable ease. Hence with an objective of ascertaining reactive species and suggesting a mechanism for the oxidation, a systematic kinetic study in the temperature range 300- 320 K was carried out.

EXPERIMENTAL

Chloramine-T (E- merck) was standardized iodometrically [11] and preserved in a black coated standard flasks to prevent its photochemical decomposition [12]. Cyclo pentanone, cyclo hexanone, cyclo heptanone and cyclo octanone were of Fluka (puriss) grade. Acetic acid was distilled by standard procedure. All the chemicals used were of analar grade. All solutions were prepared fresh in doubly distilled water.

The stoichiometric experiments were repeated by taking excess [cyclic ketone] over CAT. Unreacted ketone was determined as 2, 4- DNP to calculate stoichiometry of reaction.

The products of cyclic ketones were identified as corresponding 1, 2- hydroxyl ketones. After the completion of reaction, the solution was extracted with ether. Then subjected to fractionation gave a solid which on recrystallization from ethanol gave a white product which was characterized by IR spectrum.

Kinetic Measurements

The reactions were carried out under pseudo first order conditions keeping [cyclic ketone] more than [CAT]. In a typical kinetic run the appropriate amounts of cyclic ketones, HCl, NaClO₄, acetic acid were mixed in a standard black coated reaction vessel equilibrated thermally at desired temperature. Appropriate volume of CAT, which was preequilibrated at the same temperature, was poured into reaction vessel to initiate the reaction. The progress of the reaction was followed by estimating the unreacted CAT iodometrically. The pseudo first order rate constants k , computed by least square method were reproducible within $\pm 3\%$

RESULTS AND DISCUSSIONS

Kinetics of oxidation of cyclic ketones by CAT:

Kinetic features

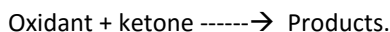
1. The products of oxidation were identified as hydroxyl ketones from their characteristic spot tests.
2. Stoichiometric studies were carried out taking excess [CAT] and analyzing unreacted CAT at the end of 72 hrs. in separate experiments, the cyclic ketone was taken in excess quantity and the unreacted ketone is isolated as 2,4- DNP derivative. This study indicated that 1 mole of substrate is consuming 2 moles of CAT.
3. Under conditions [CAT] \ll [substrate] the plots of $\log a/(a-x)$ vs time were linear indicating first order in [CAT]. The slope of above plot yielded pseudo first order rate constant (K). The K^1 values did not change on changing CAT confirming first order in [CAT]. The results are shown in Table –1 and plot is shown in Fig-1A

4. At constant [CAT], [H⁺] and temperature the rate of oxidation increased linearly with increasing [S]. The order in [S] from the plots of log K¹ vs log [s] was found to be one (Table-2) and plot is shown in Fig-1B.
5. Michaelis-Menton plot of 1/K¹ vs 1/[S] was found to be linear passing through origin indicating absence of complex formation.(Fig-1C)
6. At constant [CAT], [S] and temperature the rate of oxidation increased with increasing [H⁺] from the plot log K¹ vs log [H⁺] was found to be fractional one. The results are shown in Table-3 and plot is shown in Fig-1IA
7. Solvent effect studies were carried out using aquo acetic acid medium. It is observed that rate of oxidation decreased with increasing dielectric constant of the medium.
8. Added TSA and Cl⁻ have no effect on rate of oxidation
9. Salts such as NaClO₄, Na₂SO₄ did not influence the rate of oxidation.
10. No polymerization was observed when acryl amide or acrylonitrile is added to deaerated reaction mixture indicating absence of free radicals in the reaction path.
11. The reactions are conducted at four different temperatures to calculate activation energy and other parameters. The results are shown in Table-4

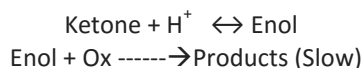
DISCUSSION

The nonzero or finite order in [S] indicates that H₂OCl⁺ or HOCl may not be reactive species of CAT. The acid effect can be explained by the formation of (RNH₂Cl⁺). Solvent effect studies indicate a reaction between positive ion and neutral molecule in the rate determining step. Hence the two species must be ketone and RNH₂Cl⁺. However ketone in acid medium will be present in keto or enol forms. The reactive species of ketone can be determined from kinetic data by comparing with the enolization rates.

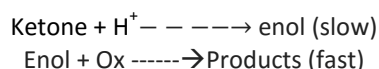
a) If rate of oxidation is higher, then direct reaction between free ketone and oxidant is possible.



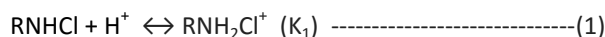
b) If the rate of enolization > rate of oxidation and order in oxidant is unity the oxidation can be written as



c) If the rate of enolization < rate of oxidation and order in oxidant is zero the oxidation can be written as



In the present study the order in [Ox] was found to be one as the plot of log a/a-x vs time was perfectly linear and the rates of oxidation of cyclic ketones were found to be in the order 10⁻⁸. The rates of enolizations of all cyclic ketones determined by iodination method were found to be in the order of 10⁻⁶ to 10⁻⁵ which are very much higher than rate of oxidation of present study. Hence it may be concluded that enol must be reacting with oxidant in the slow step. From the above discussion a plausible mechanism for the oxidation of cyclic ketones by CAT can be written as



From the above mechanism the rate law in the terms of disappearance of CAT can be written as

$$\frac{d[\text{CAT}]}{dt} = K_3 [\text{enol}] [\text{RNH}_2\text{Cl}^+] \text{-----(5)}$$

$$[\text{RNH}_2\text{Cl}^+] = \frac{K_1 [\text{RNHCl}] [\text{H}^+]}{1 + K_1 [\text{H}^+]}$$

Ketone concentration can be taken as enol as more and more ketone is converted to enol as it is converted into products.

$$\frac{d[\text{CAT}]}{dt} = \frac{K_1 K_3 [\text{RNHCl}] [\text{ketone}] [\text{H}^+]}{1 + K_1 [\text{H}^+]} \text{-----(6)}$$

$$[\text{RNHCl}] = [\text{CAT}]$$

$$\frac{d[\text{CAT}]}{dt} = \frac{K_1 K [\text{CAT}] [\text{ketone}] [\text{H}^+]}{1 + K_1 [\text{H}^+]} \text{-----(7)}$$

$$K^1 = \frac{K_3 K_1 [\text{ketone}] [\text{H}^+]}{1 + K_1 [\text{H}^+]} \text{-----(8)}$$

The above rate law explains all experimental observations. The above equation (8) envisages a linear plot between $1/K^1$ vs $1/[\text{H}^+]$. In fact such plots were realized in all ketones chosen confirming the derived rate law to be correct. The results are given in Figure-II B.

Table-1: Order of [CAT] in CAT-Cyclohexanone reaction

[CAT] = $1.25 \times 10^{-3} \text{ mol dm}^{-3}$; [CHN] = 0.1 mol dm^{-3} ; [H⁺] = 0.1 mol dm^{-3} ; Temp = 27°C ; ACOH = 10% v/v

Time min	(a-x)	Log a/(a-x)	$10^4 K/\text{sec}^{-1} = 2.303/t \log a/(a-x)$
0	15.5	-	-
2	14.3	0.034	6.52
4	13.1	0.073	7.01
6	12.1	0.107	6.87
8	11.2	0.141	6.77
10	10.3	0.177	6.81
12	9.5	0.212	6.80
15	8.5	0.260	6.67
30	6.95	0.348	6.68

Average $K_1 = 6.76 \times 10^{-4} \text{ sec}^{-1}$ (Fig-IA)

Table-2: Effect of [S] on K_1 and search for complex formation in CAT-CHN reaction.

[CAT] = $1.25 \times 10^{-3} \text{ mol dm}^{-3}$; [H⁺] = 0.1 mol dm^{-3} ; Temp = 27°C ; ACOH = 10% v/v

$10 [\text{CHN}] / \text{mol cm}^{-3}$	$10^4 K^1 / \text{sec}^{-1}$	$2 + \log [\text{CHN}]$	$4 + \log K^1$	$1 / 100X K^1$	$1 / [\text{CHN}]$
1.0	6.72	1.00	0.8273	14.88	10
2.00	13.5	1.301	1.130	7.40	5
4.0	27.2	1.602	1.434	3.67	2.5
8.0	54.5	1.903	1.736	1.83	1.25
10.0	67.4	2.000	1.828	1.48	1.0
15.0	100.8	2.176	2.176	1.00	0.666

The observed order of reactivities was found to be cyclohexanone > cyclooctanone > cyclopentanone > cycloheptanone. The ease of formation of these compounds is also in the same order as above. Cyclohexanone forms enol readily and much of it will be present in enol form. Hence cyclohexanone is more reactive. The tendency of these compounds to form enol is decreasing in the order as shown above. Therefore rates of oxidation are decreasing. This also confirms the assumption that enol is reactive species in the present

study. Bimolecular rate constants (K^{11}) at four different temperatures along with activation parameters are listed in Table-4. An examination of data reveals that the reaction with highest rate is having lowest enthalpy controlled nature of the reactions. Constancy in ΔG^\ddagger values indicate similar mechanism to be operative in all the substrates chosen.

Table 3: Effect of [H+] on K1 in CAT-CHN Reaction.

[CAT]= 1.25×10^{-3} mol dm⁻³; [CHN]=0.1 mol dm⁻³; Temp=27°C; ACOH=10% v/v

$10 [H^+]$ /mol cm ⁻³	$10^4 K^1$ /sec ⁻¹	$2 + \log [H^+]$	$4 + \log K^1$	$1/[H^+] \times 10$	$1/10 K^1$
1.00	6.72	1.00	0.827	100	14.88
2.00	10.75	1.301	1.031	50	9.30
4.00	17.2	1.602	1.235	25	5.81
8.00	27.5	1.903	1.439	12.5	3.63
10.0	38.4	2.000	1.584	10	2.60

Table 4: Activation Parameters of CAT-Cyclic ketone reactions at 27°C

Substrate	$10 K^{11}$ (dm ³ mole ⁻¹ sec ⁻¹) T(K)				Ea KJ mole ⁻¹	ΔH^\ddagger KJ mole ⁻¹	ΔG^\ddagger KJ mole ⁻¹	$-\Delta S^\ddagger$ JK ⁻¹ mole ⁻¹
	300	310	315	320				
Cyclohexanone	6.72	14.2	20.5	28.8	58.4	55.9	85.9	100
Cyclooctanone	4.10	9.87	14.7	21.6	64.7	62.2	87.0	82.9
Cyclopentanone	1.15	2.81	4.3	6.4	68.9	66.4	90.3	79.6
Cycloheptanone	0.599	1.55	2.44	3.78	73.4	70.9	91.9	69.9

Figure I

A) Order in [CAT] in CAT- cyclohexanone reaction
Plot of $\log a / (a-x)$ versus time

B) Order in [cyclohexanone] in CAT-cyclohexanone reaction
Plot of $\log K^1$ versus $\log [\text{cyclohexanone}]$

C) Search for complex formation in CAT- Cyclohexanone reaction
Plot of $1/K^1$ versus $1/[\text{cyclohexanone}]$

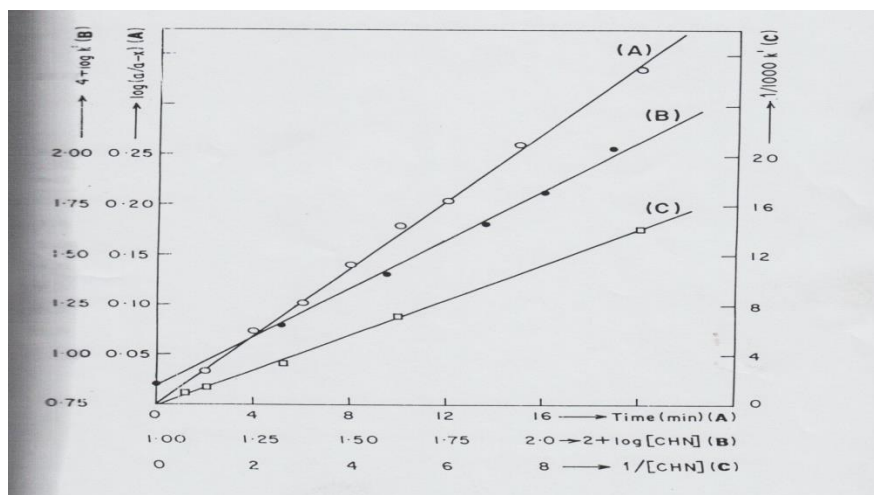


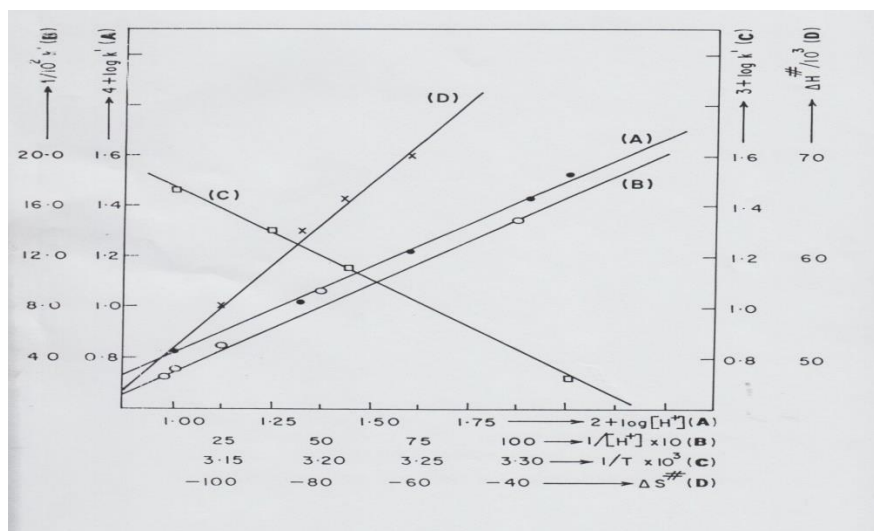
Figure II

A) Order in $[H^+]$ in CAT- cyclohexanone reaction
Plot of $\log K^1$ versus $\log [H^+]$

B) Verification of rate law in CAT- cyclohexanone reaction
Plot of $1/K^1$ versus $1/[H^+]$

C) Effect of temperature on K^1 in CAT- cyclohexanone reaction
plot of $\log K^1$ versus $1/T$

D) Isokinetic temperature
Plot of ΔH^\ddagger versus ΔS^\ddagger



CONCLUSIONS

Under conditions $[\text{cyclic ketones}] \gg [\text{CAT}]$, the rate of oxidation exhibited pseudo first order dependence in $[\text{CAT}]$ as seen from linearity of plot of $\log a/a-x$ vs time. The rate increases with increase in substrate. The observed order of reactivities was found to be cyclohexanone > cyclo octanone > cyclopentanone > cycloheptanone. The enol content of these compounds also decreases in the same order. This also confirms the assumption that enol is reactive species in the present study.

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