OXIDATION OF CYCLOHEXANONE BY PIPERIDINIUM CHLOROCHROMATE – A KINETIC MECHANISTIC ASPECT

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ABSTRACT

The kinetics of oxidation of cyclohexanone by piperidinium chlorochromate (PipCC) has been studied 50% acetic acid-water (v/v) medium. The reaction shows first order with respect to cyclohexanone and piperidinium chlorochromate. The reaction is simply acid catalysed and medium of low dielectric constant helps the reaction. It has negligible effect on the reaction rate while increasing the ionic strength. The reaction does not follow the polymerization with acrylonitrile. The rate of reaction decreases with change in the concentration of manganous sulphate. The thermodynamic and activation parameters have been calculated using Eyring's equation from the plot log k_2/T against $1/T$. From the obtained kinetic observations, a plausible mechanism has been proposed and suitable rate law is derived.

Key words: Kinetics, Mechanism, Cyclohexanone, Piperidinium chlorochromate, Thermodynamic parameters.

1. INTRODUCTION

Many ketones are cyclic in nature. The simplest class have the formula $(CH_2)_nCO$, where *n* varies from 2 for cyclopropanone to the teens. Cyclohexanone, a symmetrical cyclic ketone, is an important intermediate in the production of nylon. Isophorone is derived from acetone, it is an unsaturated, asymmetrical ketone that is the precursor to other polymers. Chromium (VI) (Cr^{+6}) are powerful oxidizing agent for the oxidation of varieties of organic compounds [1]. Cr (VI) reagents have been proved to be versatile reagents capable of oxidising almost all the oxidisable

organic functional groups [2-4]. The chromates and dichromates ions are strong oxidizing agents at low pH. So, the oxidation reaction favors in presence of acid medium.

Kinetics of oxidation of cyclohexanone has been studied using several mild chromium (VI) compounds [5-8]. Piperidinium chlorochromate is one of the chromium (VI) mild oxidising agents [9]. Kinetics of oxidation of some organic substrates [10-13] by piperidinium chlorochromate has also been reported. The present work involves the kinetic study of oxidation of cyclohexanone with piperidinium chlorochromate in the presence of perchloric acid.

2. EXPERIMENTAL

2.1. Materials and Methods

Piperidinium chlorochromate was prepared by a known procedure [9]. The ice-cooled solution of chromium trioxide was (5 g, 0.05 mol) dissolved in 9.2 ml of 6 M hydrochloric acid. 4.2 ml of piperidine was added in small portions with constant stirring. The resulting solution was kept in an ice bath for about 6 h. The yellowish orange complex so formed was filtered and dried in vacuo. The structure of   piperidinium chlorochromate was confirmed by spectral studies. Purity of piperidinium chlorochromate was checked by estimated iodometrically. The structure of piperidinium chlorochromate was given below,
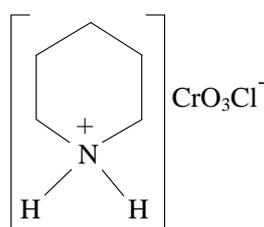
Figure 1. Structure of Piperidinium Chlorochromate

The cyclohexanone (Sigma Aldrich) was of the highest purity available and used as such in the reaction kinetic study. Acetic acid was refluxed over chromium trioxide for 6 h and then

fractionated [14]. All other chemicals used were of AnalaR grade. Only double distilled water used throughout the experiment. The reaction mixture was homogeneous throughout the course of the reaction.

2.2. Kinetic Measurements

The kinetics of oxidation of cyclohexanone by piperidinium chlorochromate was carried out in 50% aqueous acetic acid medium. The concentration of cyclohexanone was maintained in large excess concentration than the oxidant to attain pseudo-first order conditions. The absorbance was studied using colorimeter at 470 nm, Elico CL-63 Photometer. The temperature was controlled using thermostat (ROYAL) to an accuracy of ± 0.5 ^{o}C. The oxidation process was started by adding piperidinium chlorochromate at 303 K. 78% completion of reaction was carried and the rate constants were determined using linear regression method using Microcal origin software. The results were reproducible with in $\pm 2\%$ error.

2.3. Stoichiometry and Product Analysis

The stoichiometry of the reaction [piperidinium chlorochromate] : [cyclohexanone] was determined by taking excess of [piperidinium chlorochromate] over [cyclohexanone] and allowing the reaction to go for completion. After sufficient length of time, all the cyclohexanone had completely reacted with piperidinium chlorochromate leaving behind the unreacted piperidinium chlorochromate. The unreacted piperidinium chlorochromate was estimated by iodometrically. The stoichiometry between cyclohexanone and piperidinium chlorochromate was found to be 1:1.

The reaction mixture containing cyclohexanone (0.1 M) in acetic acid and piperidinium chlorochromate (0.1 M) in water was added and the medium was maintained using perchloric acid. After 48 h, the reaction mixture was extracted with ether and dried over anhydrous sodium sulphate. The ethereal layer was washed with water several times and kept on a water bath for

ether evaporation and cooled to get the product. The producs of oxidation of cyclohexanone was found to be 2-hydroxy cyclohexanone. It was confirmed by spot test [15] spectral studies.

3. RESULTS AND DISCUSSION

The kinetics of oxidation of cyclohexanone was studied in 50% aqueous acetic acid medium in presence of perchloric acid at 303 K.

3.1. Effect of Varying [Cyclohexanone]

The rate of reaction was increased steadily with increase in the concentration of cyclohexanone in Table 1. The linear plot of log k_1 *against* log [s] (Figure 2) with a slope (1.186) of unity and r = 0.994, it clearly indicates that the reaction has unit order dependence on the concentration of cyclohexanone.
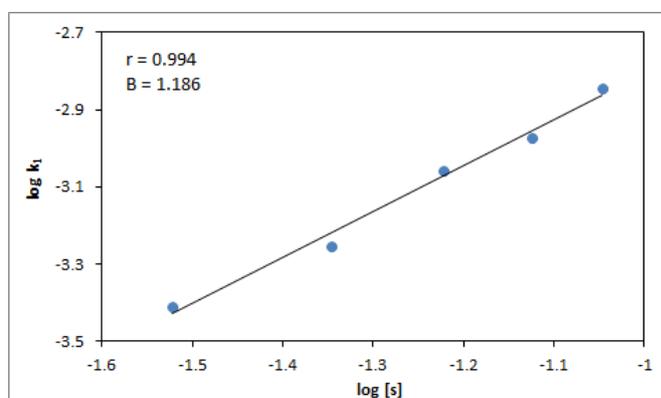
Figure 2. Plot of log k_1 *against* log [s]

3.2. Effect of Varying [PipCC]

The oxidation of cyclohexanone by PipCC was investigated at several concentrations of oxidant [PipCC], the [cyclohexanone], [$HClO_4$], AcOH, water and temperature remains constant. The plot of log absorbance *against* time was linear indicating first order dependence of the reaction on [PipCC]. The pseudo-first order rate constants k_1 (Table 1) were calculated from the

linear square fit (r = 0.990). The rate of the reaction decreased with increase in the concentration of oxidant [16-17] in Table 1. It is attributed to the decrease in effective concentration of Cr (VI) species in the reaction medium.

3.3. Effect of [Perchloric Acid]

The effect of added H^+ ion on the pseudo-first order rate constant was studied by adding perchloric acid in the region of 0.8 – 2.4 M. The rate of reaction increased with increase the concentration of perchloric acid (Table 1). The plot of log k_1 *against* log $[H^+]$ gave a straight line (Figure 3) with slope 1.346 (r = 0.991) indicating that the protonated species of the oxidant in the effective nature. It can be concluded that the reaction is simply an acid catalyzed one [18].
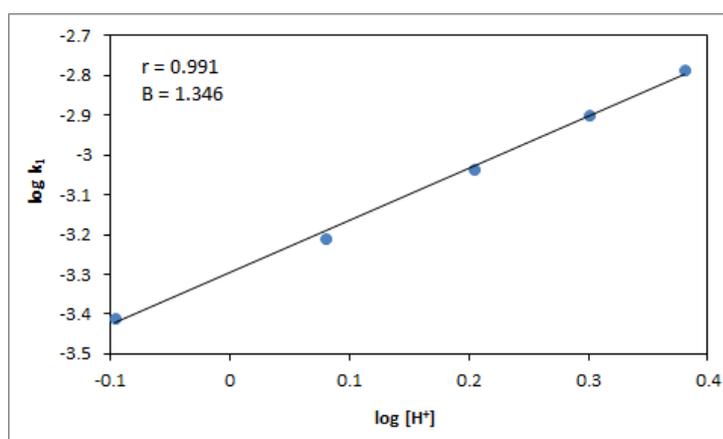

Figure 3. Plot of log k_1 *against* log $[H^+]$

Table 1. Rate Data for the Oxidation of Cyclohexanone by Piperidinium Chlorochromate in 50% Acetic acid Medium at 303 K

[Cyclohexanone] 10^2 (mol dm^{-3})	[PipCC] 10^3 (mol dm^{-3})	$[H^+]$ (mol dm^{-3})	k_1 10^4 (s^{-1})
3.0	2.0	0.8	3.903
4.5	2.0	0.8	5.556
6.0	2.0	0.8	8.707
7.5	2.0	0.8	10.604

9.0	2.0	0.8	14.315
3.0	2.0	0.8	3.903
3.0	3.0	0.8	3.652
3.0	4.0	0.8	3.362
3.0	5.0	0.8	2.754
3.0	6.0	0.8	2.413
3.0	2.0	0.8	3.903
3.0	2.0	1.2	6.194
3.0	2.0	1.6	9.204
3.0	2.0	2.0	12.560
3.0	2.0	2.4	16.444

AcOH:Water (v/v) = 50:50

3.4. Effect of Ionic Strength and Solvent Composition

The reaction was carried out at different initial concentrations of sodium perchlorate while the other variables were kept constant. Increase in ionic strength of the medium by adding sodium perchlorate has no effect on the reaction rate (Table 2) indicating the involvement of ion and neutral molecule in the rate-determining step. The reaction was carried out at five different percentages of acetic acid-water mixtures while all other factors were constant. The rate of reaction increased with increase in the percentage of acetic acid (Table 2). The plot of log k_1 *against* 1/D was found to be linear (r= 0.997) with positive slope (+ 22.21). This might be probably due to ion-dipole interaction [19-20] in the rate determining step.

3.5.Test for Free Radical Reaction

The reaction mixture when allowed to stand acrylonitrile does not induce polymerization. It suggests that the absence of free radical pathway of this oxidation reaction mechanism.

3.6. Effect of varying [MnSO$_4$]

The rate of reaction decreases with increase in the concentration of manganous sulphate [21]. Thus, it is conceivable that the reaction involves a two electron transfer process. The reaction rates are listed in table 2.

Table 2. Rate Data for the Oxidation of Cyclohexanone by Piperidinium Chlorochromate at 303 K

[NaClO$_4$] 10^3 (*mol dm^{-3}*)	AcOH:Water (*v/v*)	[MnSO$_4$] 10^3 (*mol dm^{-3}*)	k$_1$ 10^4 (*s^{-1}*)
0.0	50:50	-	3.903
2.0	50:50	-	3.708
4.0	50:50	-	3.804
6.0	50:50	-	3.954
8.0	50:50	-	3.885
-	40:60	-	3.296
-	45:55	-	3.639
-	50:50	-	3.903
-	55:45	-	4.355
-	60:40	-	5.070
-	50:50	0.0	3.903
-	50:50	2.0	3.023
-	50:50	4.0	2.952
-	50:50	6.0	2.715
-	50:50	8.0	2.585

[Cyclohexanone] = 3.0 x 10^{-2} *mol dm^{-3}*   [PipCC] = 2.0 x 10^{-3} *mol dm^{-3}*   [H$^+$] = 0.8 *mol dm^{-3}*

3.7. Effect of Temperature

The rate constants were measured at four different temperatures viz., 303, 308, 313 and 318 K while maintaining the concentration of substrate, oxidant and [H$^+$] as constant. The thermodynamic and activation parameters have been calculated from the plot of log k$_2$/T *versus* 1/T (Figure 4) using the Eyring's equation [22-23] (Table 3).
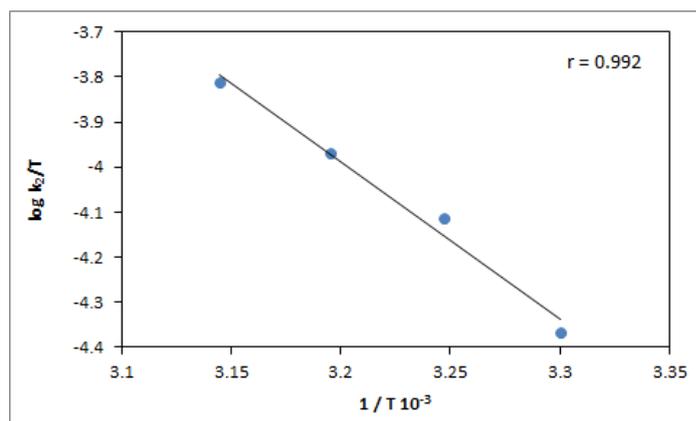
Figure 4. Plot of log k₂/T *against* 1/T

Table 3. Effect of Temperature for the Oxidation of Cyclohexanone by Piperidinium Chlorochromate in 50% Aqueous Aceticacid Medium

Temperature (*K*)	$k_1 \, 10^4$ (s^{-1})	Thermodynamic and Activation Parameters
303	3.903	$\Delta H^{\#} = 29.06 \, kJ \, mol^{-1}$
308	7.134	$\Delta S^{\#} = -137.77 \, kJ \, mol^{-1}$
313	10.129	$\Delta G^{\#} = 70.78 \, kJ \, mol^{-1}$ at 303 K
318	14.721	$E_a = 31.58 \, kJ \, mol^{-1}$ at 303 K

[Cyclohexanone] = 3.0 x 10^{-2} *mol dm*$^{-3}$ [PipCC] = 2.0 x 10^{-3} *mol dm*$^{-3}$ [H$^+$] = 0.8 *mol dm*$^{-3}$

3.8. Mechanism and Rate Law

The cyclohexanone was oxidized by piperidinium chlorochromate to give 2-hydroxy cyclohexanone in the presence of perchloric acid. The reaction shows first order with respect to oxidant, substrate and fractional order with respect to hydrogen ion concentration. But, it was merely acid catalyzed one. In this case, the concentration of oxidant was attributed to the decrease in effective concentration of Cr (VI) species in the reaction medium. The retardation of the rate by the addition of manganous sulphate confirms that a two electron transfer process was involved in the reaction. From these interpretations, the following mechanism (Scheme 1) was proposed and suitable rate law was derived.
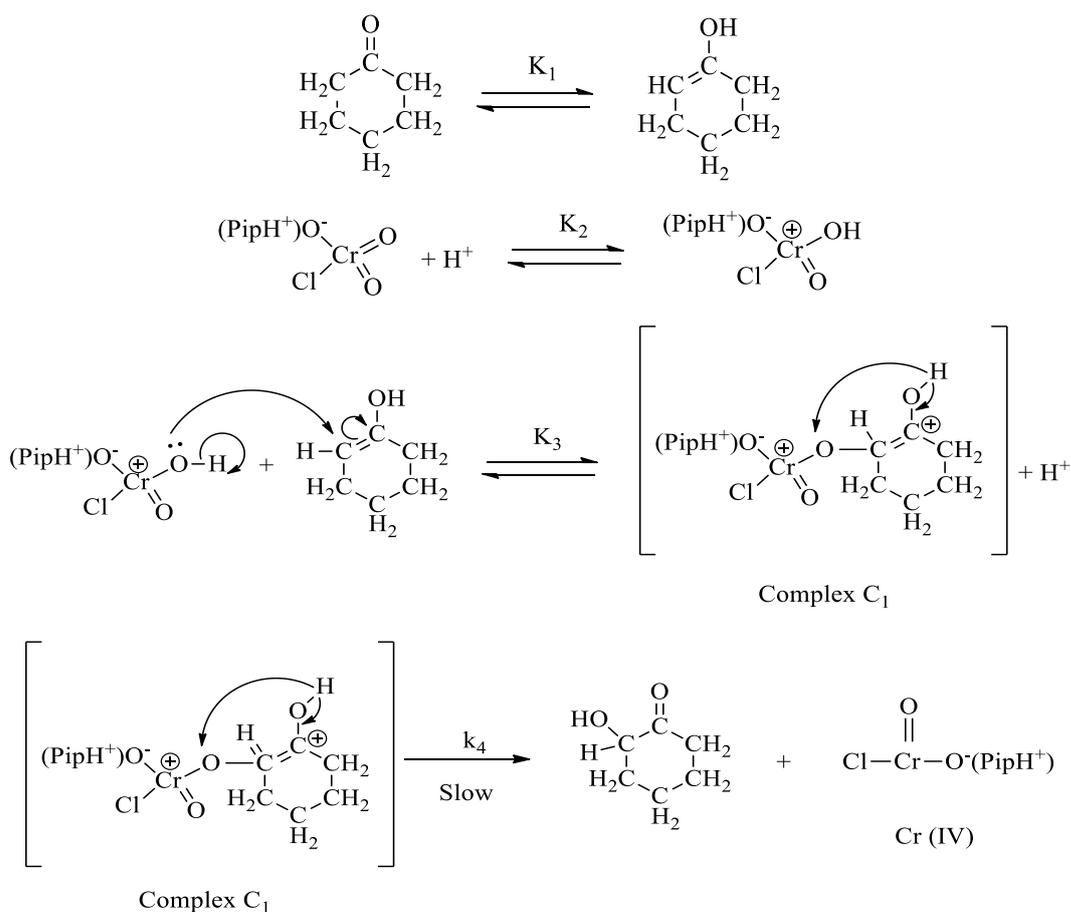
Scheme 1. Mechanism for the Oxidation of Cyclohexanone by Piperidinium Chlorochromate

$$\text{Rate} = k_4 \, [\text{Product}]$$

$$= k_4 K_3 [\text{PipCCH}^+] \, [\text{S*}]$$

$$= \frac{k_4 K_3 K_2 [\text{PipCC}] \, [\text{H}^+] \, [\text{S*}]}{1 + K_2 [\text{H}^+]}$$

$$= \frac{k_4 K_3 K_2 K_1 [\text{PipCC}] \, [\text{H}^+] \, [\text{S}]}{1 + K_2 [\text{H}^+]}$$

S* indicates resonance structure of substrate

The proposed mechanism and the suitable rate law support all the observations made including the effect of solvent polarity and the negative entropy of activation.

4. CONCLUSION

The oxidation of cyclohexanone by piperidinium chlorochromate in aqueous acetic acid medium leads to the formation of a complex giving 2-hydroxy cyclohexanone as the final product. The reactions were followed under pseudo-first order kinetics. The activated complex was formed as rigid due to the negative $\Delta S^{\#}$ values. The proposed mechanism and rate law for this oxidation kinetics in accordance with the observed kinetic data.

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