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Oxidation of Cyclohexanol by Pyridinium Dichromate in Acidic Dioxan–Water Medium: A Kinetic Study

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Abstract

The oxidation of cyclohexanol by pyridiniumdichromatehas been studied by spectrophometrically in presence of perchloric acid, dioxan–water (30:70%) mixture in leads to the formation of cyclohexanone. The reaction is first order each in [PDC], [$HClO_4$] and [cyclohexanol]. The reaction rates were determined at different temperatures [25, 30, 35, 40 45, 50°C] and the activation parameters were calculated.

The reaction does not induce polymerization of acrylonitrile. With an increase in the amount of dioxane in its aqueous mixture perchoric acid, the rate increases. A suitable mechanism for the reaction was postulated.

Keywords: Kinetics, Michaelis–Menten, Oxidation Cyclohexanol Pyridiniumdichromate (PDC)

Introduction

Oxidants play an important role in synthesis of complex organic molecules in different reaction According to (Corey and Schmdt, Tetrahedron Lett., 399(1979)[1] Pyridinium dichromate being one of the most versatile available oxidizing agent and soluble in water and many organic solvent. conditions. oxidation of cyclohexanol play an important role in transformation in industrial chemistry. In this paper we study about Effect of PDC, Effect of substrate, solvent composition, ionicstrength, acrylonitrile and pyridine ect.

Objective of the study

The study of kinetics and mechanism of oxidation of organic compounds is a subject of considerable importance because this reaction plays an important role in chemical as well as natural life processes. Almost billion tons of organic compounds are decomposed by oxidation processes every day. Kinetics and mechanistic studies are most powerful methods for investigating any reaction mechanism in detail. It can be most help full in guiding operations and choosing optimum conditions of synthetic and analytical work. The oxidation of cyclohexanol is also important in chemical industries such as pesticides and medicines

Review of Literature

Oxidation of organic compounds is an important transformation in synthetic organic chemistry. Chromium (VI), in the form of chromic acid and metal dichromate is a versatile oxidant. Coreys reagent pyridinium chloro chromate (PCC)[1] was the first one reported. Its discovery has lead to an enhanced interest in filed of organic derivatives of chromium (VI) as oxidizing agent.a large number of worker reported related work such as sarrett identified the adduct of pyridine and chromium (VI) oxide (Collins reagent)[2] as a selective compound for the oxidation of primary and secondary alcohols to carbonyl compounds,Oxidation with chromium(VI) amines has two primary limitations. Operationally, the tarry byproducts of chromium oxidations cause reduced yields and product sequestration.[3] Benzyl alcohols and benzyl TBDMS[4] ethers were efficiently oxidized to the corresponding carbonyl compounds in high yield with periodic acid catalyzed by CrO_3 at low temperature (-78 °C). The oxidation procedure was highly functional group tolerant and very selective for the TBDMS group over the TBDPS groupDespite its selectivity, **G. E.; Beyler**[5].CrO_3-catalyzed oxidation of primary alcohols to carboxylic acids proceeds smoothly with only 1-2 mol % of CrO_3 and 2.5 equivalents of H_5IO_6 in wet MeCN to give the carboxylic acids in excellent yield. No significant racemization is observed for alcohols with adjacent chiral centers. Secondary alcohols are cleanly oxidized to ketones[5].A number of

reports on the oxidation of several substrates by pyridinium dichromate (PDC) are available in the literature like cycloalkanol in MeCN medium (giragia and kabalin)[6], α-hydroxy acids[7],oxime(palaniappan et.al)[8], organic sulphide (meenakshisundram et al.)[9], There seems to be no report on the oxidation of cyclohexanol by pyridiniumdichromate.Our literature survey reveals that the oxidation of cyclohexanol by different oxidants has received a limited attention so we are particularly interested to see the mechanism of the oxidation of cyclohexanol by pyridinium dichromate in acidic dioxan–water media.

Experimental

Materials

Required chemicals was used as supplied such as dioxin(SRL), $HClO_4$ and cyclohexanol (E. Merck India) and purity was checked by its boiling point .The water was double distilled used for preparing the solutions. Perchloric acid was prepared by diluting known volume of acid in water. The solution so prepared was standardized by titration with previously standardized sodium hydroxide using phenolphthalein as an indicator. Doubly distilled analytical grade dioxan was used as a source of solvent. And all other reagents used were of analytical grade with 99.9% purity.

Preparation of pyridinium dichromate

Pyridinium dichromate was prepared by the method describe by E.J.Corey and Shmidt[1]. To a stirred solution of CrO_3 in minimum quatity of water, cooled below 0^oC and then pyridine was added dropwise. The solution was cooled and kapt 4-5 hrs. Then the solution was diluted with aceton. The yellow organic solid was obtained which was filtered and washed with aceton, dried in vaccum and recrystallized from water and aceton.purity was checked by iodometrically, M.P.(154^oC)and by the UV –Vis IR $V_{,max}$ (KBr) =3250, 16660, 1500, 1340, 1210, 950, 870, $770cm^{-1}$ element analysis C= 32.047, H=2.613, N=7.426

Method

The rate measurements were carried out under first order conditions in the dioxan–water [30 (v/v) dioxan] solvent system at 313 K. The reaction was initiated by mixing thermally equilibrated solution of PDC and cyclohexanol in presence of perchloric acid also. The reaction was followed by monitoring the decrease in the absorbance of PDC at λ_{max} 350 nm in 1 cm cell placed in the thermostatted compartment of JASCO model 7800 UV/Vis spectrophotometer.The kinetic runs were followed for more than 80% completion of reaction and good first order kinetics was observed. First order rate constants k_{obs} were obtained from the slope of the plot of log (absorbance) versus time.

Stoichiometry and product analysis

Stoichiometery was ascertained by treating excess concentration of PDC with substrate in 10:1 ratio in presence of 0.5 mol H^+. The result revealed that 3 moles of cyclohexanol consume 2 moles of PDC and given by reaction.

$3\ RCH_2OH + 2Cr\ (VI) \rightarrow 3RCHO + 2\ Cr\ (III) + 6H^+$

1 mole of PDC

The productwas estimated in the above reaction mixture by taking 100 to 250 ml reaction mixture .it was treated with 2, 4-DNP allowed to stay for 6 to 8 hrs, the yellow precipitate was obtained .The precipitate was filtered, washed with cold water and dried. Than it was weighed and then moles of 2, 4-DNPcalculated, hence moles of aldehydes and Cr^{+3} (1.44:1) formed in reaction.

Results and discussion

Stability of pyridinium dichromate

To ascertain the stability of pyridinium dichromate in kinetic condition. We have studied the effect of pyridine on rate constants and spectra were taken at different time [H^+] up to 60^OC. There was no change in spectra and λ_{max} 350 nm .The spectra in same conditions were compared with that of solution contaning similar concentration of pyridine + chromic acid to PDC .PDC has different spectra than chromic acid + pyridine solutions. Based on these observations, we concluded that PDC was quite stable in acidic medium and in presence of dioxin and water medium during course of reaction.

Effect of PDC

It observed that at constant oncentration of [$HClO_4$], temperature and [cyclohexanol]. Plot of log [PDC] against time was linear indicating first order dependence of the rate on PDC. Furthermore, the rate constant did not change with change in concentration of pyridinium dichromate [Table 1].

Effect of substrate

Initial concentration of alcohol found to increase linearly with the increase in concentration of alcohols (1.0 to 8.0 M × 10^{-2}).The results of the effect of alcohol concentration on rate constant are summarized in (Table 1). A plot of log k_{obs} against log (cyclohexanol) gives a straight (Fig. 1) with slope =1 in cyclohexanol. The plot of $1\backslash k_{obs}$ vs. 1\ [cyclohexanol], (Fig. 3) gives straight line with passing through origin which is indicate that no complexes formation.

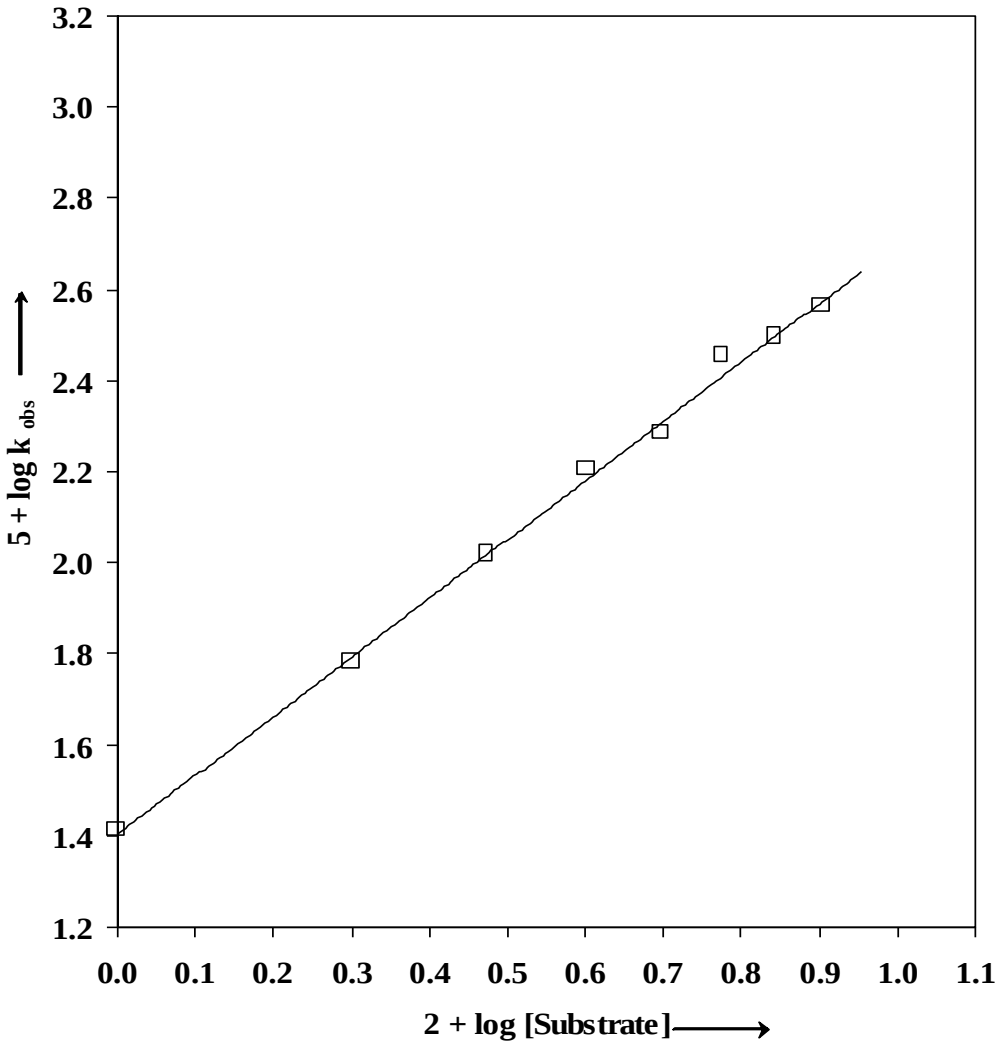
Figure -3.30

(c f Table - 3.14)

VARIATION OF RATE WITH SUBSTRATE CONCENTRATION

log k_{obs} v/s log [Substrate]

CYCLOHEXANOL



At constant PDC concentration, $[H^+]$ and temperature, first order rate constants calculated at different.

Table 1
Variation of Rate with PDC, Cyclohexanol, and Perchloric Acid Concentrations.

10^3x[PDC] Mol/dm^3	10^2x [cyclohexanol] Mol/dm^3	10x[H^+] Mol/dm^3	k_{obs}x10^5s^{-1}
0.2	4.0	5.0	69.64
0.3	4.0	5.0	68.89
0.4	4.0	5.0	68.48
0.5	4.0	5.0	69.89
0.6	4.0	5.0	69.89
1.0	4.0	5.0	69.41
2.0	4.0	5.0	69.41
0.4	1.0	5.0	11.23
0.4	2.0	5.0	31.25
0.4	3.0	5.0	58.36
0.4	4.0	5.0	69.64
0.4	5.0	5.0	83.65
0.4	6.0	5.0	136.20
0.4	7.0	5.0	156.56
0.4	8.0	5.0	231.36
0.4	4.0	2.0	1.67
0.4	4.0	4.0	2.91
0.4	4.0	6.0	6.03
0.4	4.0	8.0	9.13
0.4	4.0	10	12.04
0.4	4.0	20	22.00
0.4	4.0	30	30.10
0.4	4.0	40	44.20
0.4	4.0	50	70.30
0.4	4.0	60	82.50
0.4	4.0	70	101.00
0.4	4.0	80	126.00
0.4	4.0	90	153.00

Effect of Solvent Composition

Increase in the percentage of dioxane in solvent mixture (water and dioxane) rate of reaction increases, suggesting that a medium of low dielectric constant favors the oxidation rocesse in cyclohexanol. Plot log k_{obs} v/s (D-1)/ (2D+1)[10] gives straight line indicating absence of dipole-dipole interaction in rate determining step. Plot of log k_{obs} v/s reciprocal of dielectric constant (1/D) of the medium gives linear line with positive slope > 60, suggests the presence of either ion-ion or ion-dipole type interaction between oxidant and the substrate[11] but no change in rate by addition of ionic salts ruling out the possibility of ion-ion type interaction between reactants in rate determining step. Therefore, interactions in rate determining step are ion-dipole type. Positive slope indicate a reaction involving cation-dipole interaction in the rate-determining step.[12] Further, plots of log k_{obs} v/s mole fraction of water gives negative slopes indicating cation-dipole type interaction[13] Due to water (polar solvent), transition state is stabilized, as water molecule surrounds the transition state and hence less disproportion.

Table 2
Variation of Rate with Dioxin Water Medium

Dioxan:H_2O	k_{obs} x 10^5 s-^{1,}
10:90	32.66
20:80	54.87
30:70	61.98
40:60	68.69
50:50	76.98
60:40	84.69

Effect of Ionic Strength

At constant concentration of cyclohexanol, PDC, $HClO_4$ and other conditions are constant increase in concentration of ionic strength such as Na_2SO_4, $NaClO_4$. It has been observed that there was no significant on the rate. It prove that reaction may be ion and a molecule or between neutral molecule (Kabilan and ganapathy, 1989)[14].

Figure -3.40
(c f Table -3.16)

VARIATION OF RATE WITH SOLVENT COMPOSITION
log k_{obs} v/s 1/D

CYCLOHEXANOL

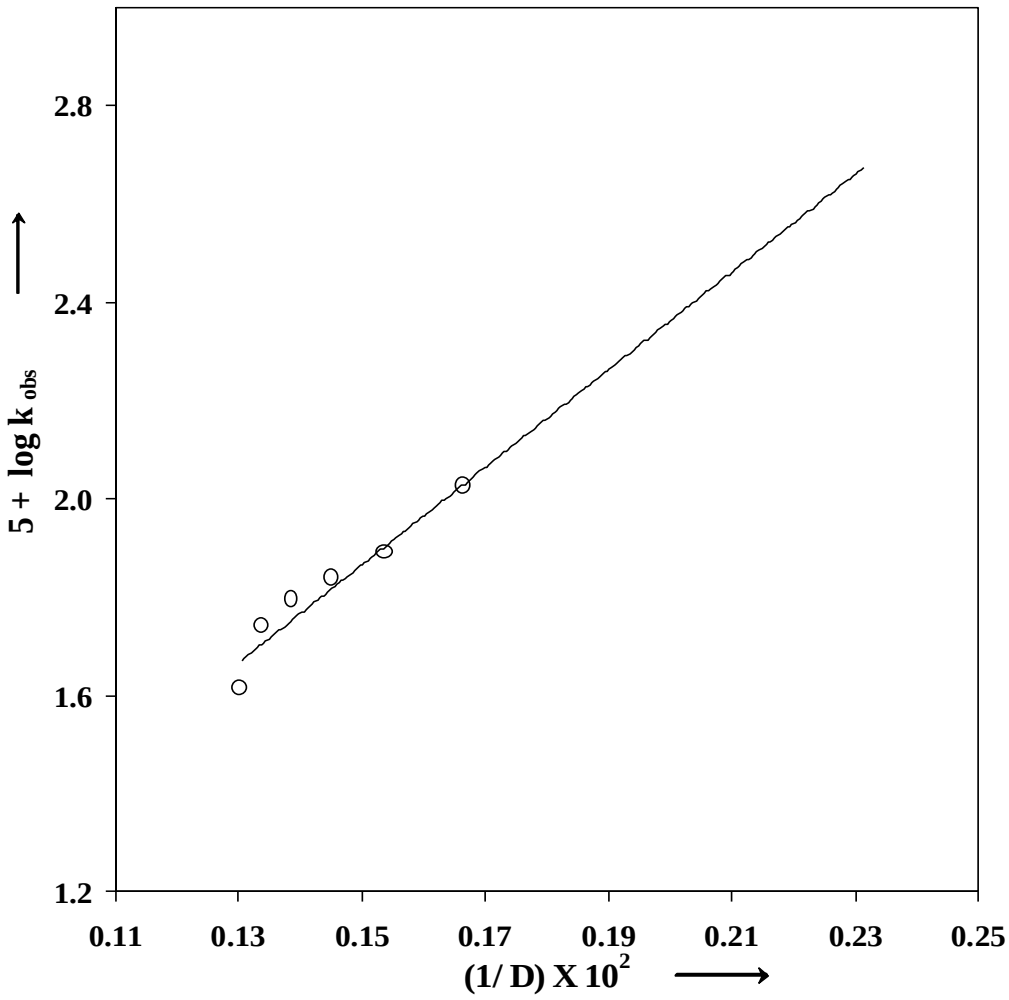


Figure -3.50
(c f Table -3.16)

VARIATION OF RATE WITH SOLVENT COMPOSITION
log k_{obs} v/s D-1/2D+1

CYCLOHEXANOL

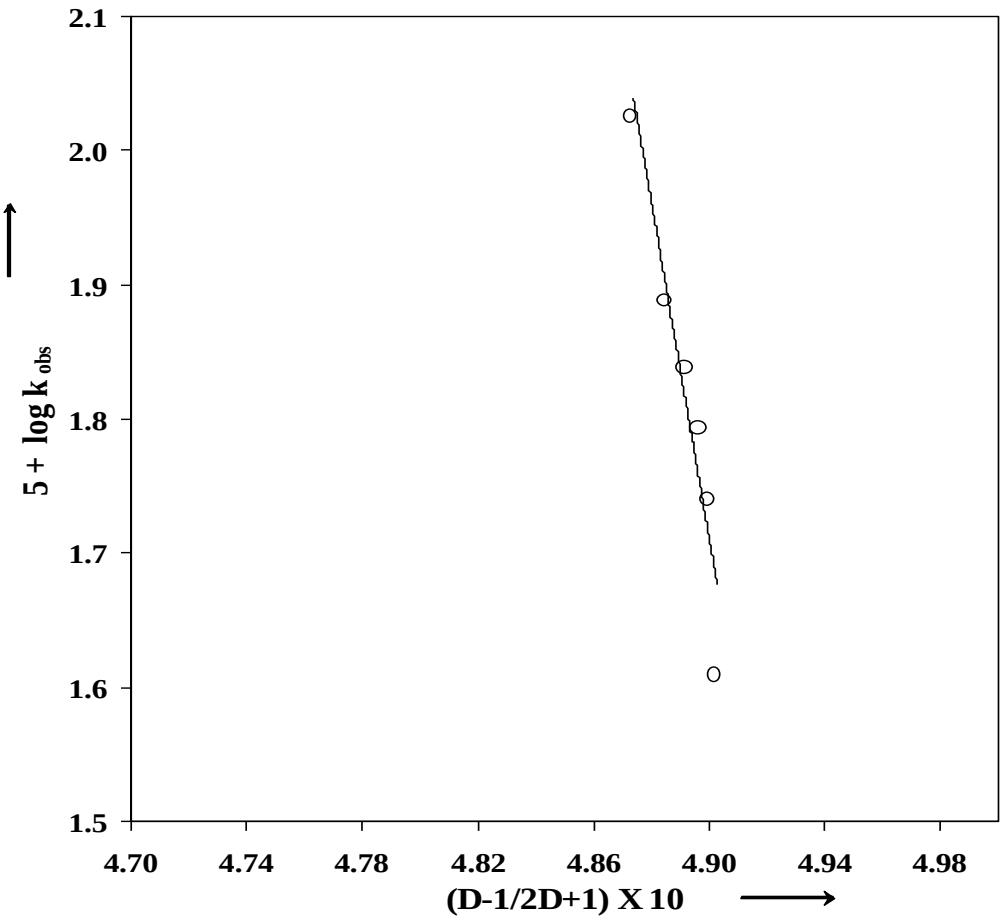


Table 3
Variarion of rate withsodium perchlorate (Na_2SO_4) concentration of cyclohexanol at 308K [cyclohexanol] = 4.0 × 10^{-2} M [$HClO_4$] 50 × 10^{-2} M [Temp] = 308 K [PDC] 4.0 × 10^{-3} M [Dioxane]=30%v/v

$[Na_2SO_4]\times10^3$mol/dm	1.0	2.0	3.0	5.0	6.0	8.0	9.0	11.0	13.0
$10^{-5}k_{obs}(s^{-1})$	69.64	68.98	69.52	69.09	70.01	69.25	68.98	69.45	68.22

Effect of Temperature

It was found that rate of oxidation increases with increase in temperature. In all the cases, a plot of log k_{obs}against 1/T (inverse of absolute temperature) is a linear line. This shows that Arrhenius equation is valid for these oxidations. The energy of activation ranges between 32-69 k J mol^{-1}. Energy of activation does not correspond to carbon-carbon fission in the decomposition of organic substrates by Cr (VI). Calculation of activation parameters showed that these reactions are not enthalpy controlled. Lowest energy of activation is not associated with highest rate or vice-versa. Glasston[15] has pointed out that if entropy of activation is large and positive, the reaction will be normal and fast but if it is negative, the reaction is slow. In this case, the negative values of entropy of activation come under a category of slow reactions. Negative values of entropy also suggest bimolecular reaction in the rate-determining step in the presence of water as a solvent and the involvement of a proton transfer during the rate-determining step.

Table 4 variation of rate with Temperature [Cyclohexanol] = 4.0 × 10^{-2}M [$HClO_4$] 50 × 10^{-2} M [Temp] = 308 K [PDC] 4.0 × 10^{-3} M [Dioxane] =30%v/v

Temperture (k) [1.0	303	308	313	318	323	328
$10^{-5}k_{obs}(s^{-1})$	69.64	73.03	110.96	132.00	164.10	192.36

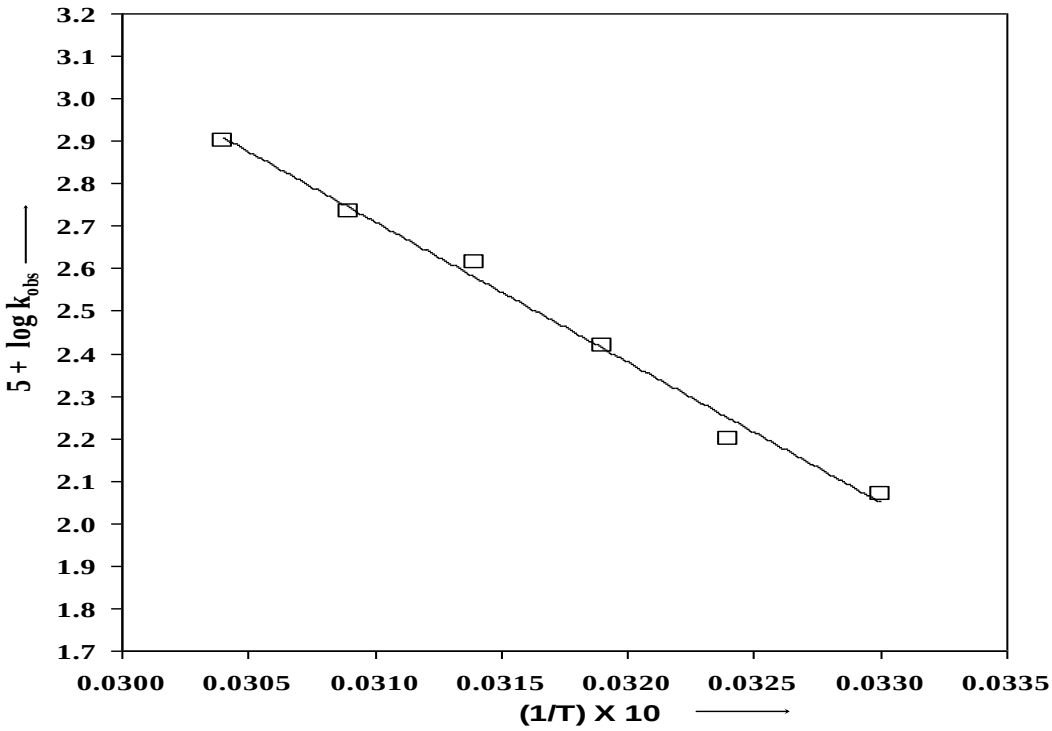
Table 5
Activation parameters

Parameters	ΔE^{a} (kJ mol^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (kJ mol^{-1})	$\Delta F^{\#}$ (kJ mol^{-1})
Values	69.15	9.51	-66.64	71.26

Figure -3.70
(c f Table -3.20)

VARIATION OF RATE WITH TEMPERATURE
log k_{obs} v/s 1/Temp.

CYCLO HEXANOL



Effect of Acrylonitrile and Pyridine

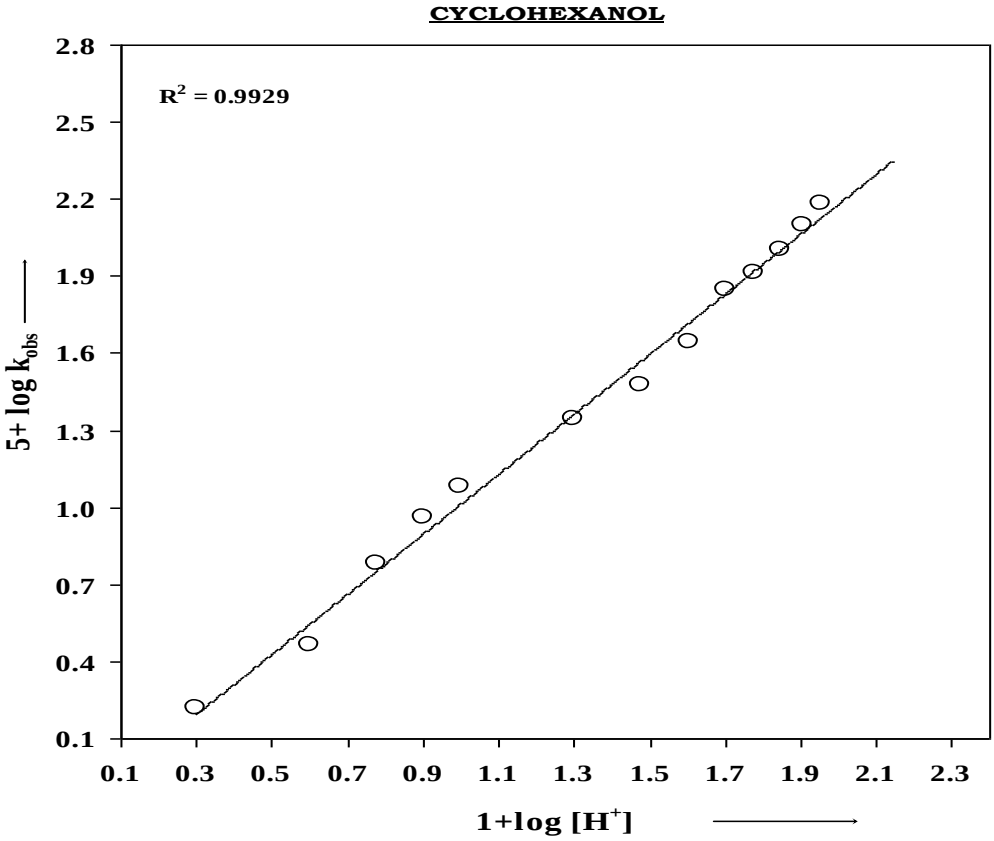
Involvement of radical mechanism is ruled out, as there is neither any decrease in rate in presence of stabilizer free acrylonitrile nor milky appearance under kinetic conditions. The rate of reaction does not change on addition of pyridine indicating thereby, the stability of PDC i.e. PDC is not hydrolyzed in the conditions understudy.

Effect of Perchloric Acid

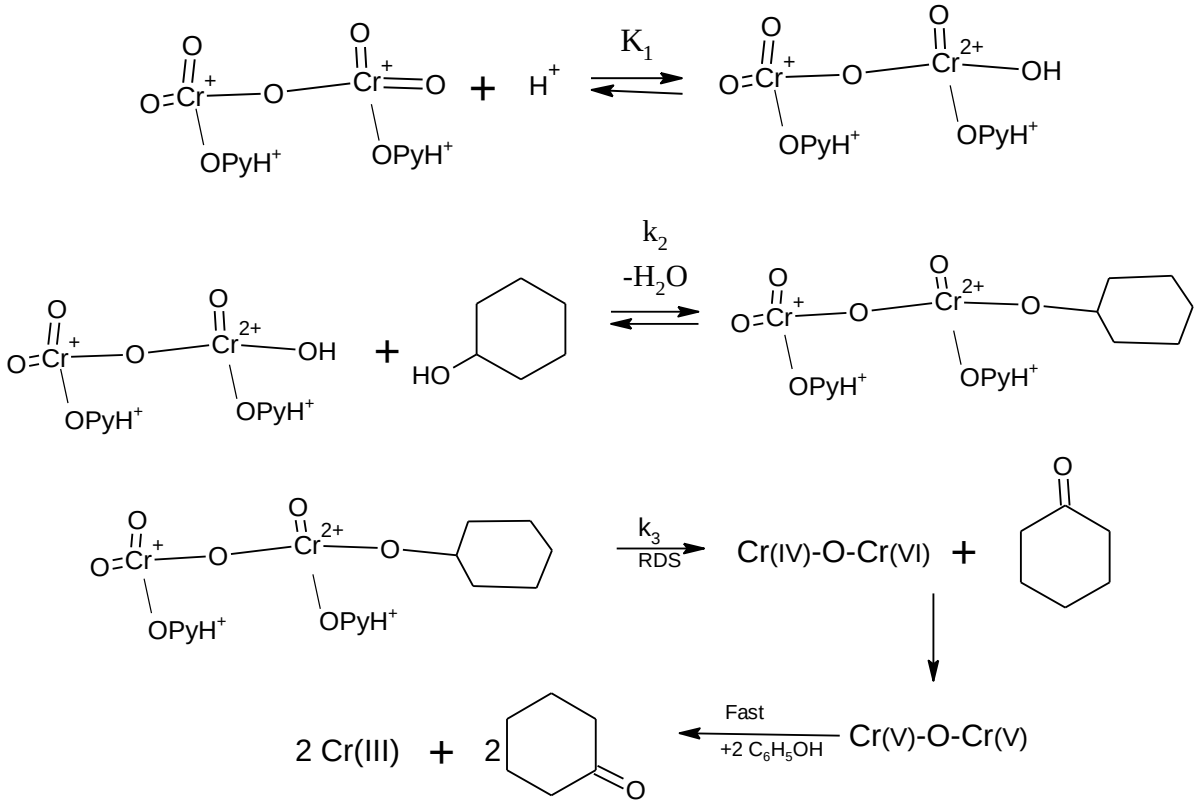
The rate of oxidation increases by increasing $[H^+]$ in the reaction.Logk_{obs} against log $[H^+]$ is a straight line in all the alcohols studied show first order dependence of $[H^+]$ on rate .This may be explained by considering protonated PDC as reactive species will be a better oxidizing agent than unprotonated as protonated species will aceept electrons easily from cyclohexanol and hence rate increases. To explain hydrogen ion catalysis in reaction various hypothesis like Zucker-Hammett,[16] Bunnett[17] and Bunnett-Olsen[18] were tested. In case of the alcohols studied, plot log k_{obs} v/s log $[H^+]$ is linear line with positive slope ≈1. Both plots of log k_{obs} against log $[H^+]$ and log k_{obs} v/s $-H_0$ are linear. Further, these plots (log k_1 v/s. H_0) produce an ideal unit slope ≈1. It follow Zucker-Hammett hypothesis. Applicability of Bunnett hypothesis[13] was also tested. Both plots log k_{obs}+ H_0 v/s log aH_2O and log k_{obs}-log $[H^+]$ v/s log aH_2O are linear with slope ω>3.3 and ω^*>-2.0 respectively. Futher these observations were calibrated by Bunnett-Olsen[19]in term of ϕ .Plot log k_1 –log $[H^+]$ against log$[H^+]$ + H_O are linear with slope range ϕ> + .58 suggesting that water is a proton abstracting agent and as a nucleophile in rate-determining step.

Figure-3.12
(c f Table -3.11)

VARIATION OF RATE WITH PERCHLORIC ACID CONCENTRATION
log k_{obs} v/s log $[H^+]$



Mechanism: - A Tentative Mechanism may be given as



Conclusion at room the reaction between cyclohexanol and PDC is veryb slow in the low concentration of perchloric acid in dioxin- water medium. The oxidation of cyclohexanol by PDC is first order with respect [PDC], cyclohexanol and [HClO4] The reaction was studied at different temperature the temperature range of 298-323K, Arrhenius eqation is valid. The negative value of entropy indicates the complex C is more ordered and reactant. The description of the mechanism is consistent with all experimental evidence.

Conclusion

Rate of reaction is increases with temperature and rate constant depend on concentration of hydrogen ion and concentration of cyclahexanol dioxin water composition all these factors are responsible for rate of reaction. It was found that rate of oxidation increases with increase in temperature. It is also found that at constant oncentration of [$HClO_4$], temperature and [cyclohexanol]. Plot of log [PDC] against time was linear indicating first order dependence of of the rate on PDC.

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