Kinetics and Oxidation mechanism of Organic substrate 2-iso propyl-5-methyl cyclohexanol by isonicotinium Dichromate (INDC)

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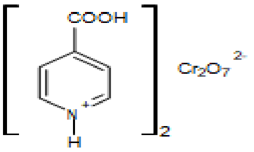
Abstract

Isoicotinium dichromate is oxidises hydroxy group into carbonyl group. INDC is derivedfrom pyridine 4- carboxalic acid The kinetic oxidation of menthol Show's first order reaction with respect to oxidant.Substrate and perchloric acid. The reaction rate increases with decreases in the dielectric constant. The consequence of oxidation are the corresponding menthone. The $\Delta H^{\#}$ and $\Delta S^{\#}$ were delibrated by Temprature effect.

Introduction

In recent years a variety of chromium (VI) complexes have been prepared and least to be an effective oxidants. INDC is the one of them. It is mild, reactive reagents for the oxidation of organic compounds freely soluble in water.



The literature Survey reveals that very less number of kinetic works has been substantially doneso for using INDC as an oxidant. The kinetics of oxidation of some Substituted Phenyl methyl sulfides by INDCwas studied by karunakaran et al[1]. In the similar may, kalavathy[2] requested a kinetic study of the co- oxidation of benzoldehydes and oxalic acid by using Isonicotinium dichromate(VI) Complex Convertion of alcohol into carboxyl compounds[3,4]. The oxidation of furfural have been standard by INDC[5]. The Kinetics of the oxidation of dibenzalacetone (DBA) by Isonicotinium Dichromote (INDC in acidic and water medium Catalysed by 1,10, phenonthroline has been studied. The reaction show fractional order dependence with respect to$[H^+]$[6]. The kinetic oxidation of 2-iso propyl-5-methyl cyclohexanol by INDC inaqueous acetic acid has not been reported.

EXPERIMENTAL

Materials:

The menthol used were purified by distillation[8] and their m.p. is 250^0. Isonicotinium dichromate prepared by procedure described in literature and its purity was checked by melting point. TLC and Iodometric method. The reaction products menthone were characterized by Spectral and estimated as their 2,4, dinitro phenyl hydrazones.

Kinetic measurement:

The kinetic measurements were studied at 303K for oxidation of 2-iso propyl-5-methyl cyclohexanol known volume of substrate water perchloric acid were mixed and kinetic measurements were carried out lodometrically. The kinetic investication carried out under pseudo first order conditions and rate constant were calculated Graphically.

Stoichiometry:

The reaction mixture containing excess of the Isonicotinium dichromate over 2-iso propyl-5- methyl cyclohexanol was kept at room temperature for sufficient length of lime under the conditions employed for the kinetic runs. Estimation of unchanged INDC showed of that 1mole of 2-iso propyl-5-methyl cyclohexanol consumed 1mol of INDC.

Product Analysis:

1mole 2-iso propyl-5-methyl cyclohexanol was allowed to react with 1mol of INDC under condition of Kinetic measurements. The mixture was neutralized with sodium bicarbonate Solution and extracted, with ether. The ether was evaporated and residue was crystallized several times from aqueous ethanol and the product was identified by IR spectrum.

Result and discussion:

Coordination complexes of chromium can be used successfully for the conversion of hydroxyl into carbonyl groups in cyclic alcohols. The kinetics and mechanism of oxidation of cyclic alcohol by INDC has been Studied under different conditions with view to Understand the reaction mechanism.

The reaction was carried out under pseudo - first order conditions in the presence of peschlosse perchloric acid - water (50 : 50) as a solvent at 303K . The result were summarised and discussed is the subsequent pages.

The rate constant of the reaction were calculated when the reaction were examined by varying the concentration of INDC and keeping all other reactants remains constants. The reaction show first order kinetics indicated by the plot of log time versus time From the plot pseudo first order rate constant kobs were ovulated, according to the first order equation by the method of least squared.(r=0.996)

The reactions were carried out at various initial concentration of (2-iso propyl-5-methyl cyclohexanol) which was always excess and keeping the concentrations of other reactants as constant at 303K. The reaction was found to be first order dependence, because the plot of log kobs Versus [2- iso propyl-5-methyl cyclohexanol] . gave the slope very close to Unity (B=1.03 ;r=0.998; sd=0.02)

<u>Table-1 KINETIC OXIDATION OF 2-ISO PROPYL-5-METHYL CYCLOHEXANOL</u>

Effect of variation of [INDC], [2-iso propyl-5-methyl cyclohexanol],[HClO4] and solvent composition Temperature on the reaction rate,

[INDC] =0.30X 10^{-2}mol dm^{-3} , [2-iso propyl-5-methyl cyclohexanol] =1.5x 10^{-2}mol dm^{-3} [HClO4]=0.75X 10^{-2}mol dm^{-3} AcOH : H20 (1:1 v/v)

DC] X10^{-2} mol dm^{-3}	**so propyl-5- methyl cyclohexanol] x 10^{-2}mol dm^{-3}**	**lO4] X10^{-4} mol dm^{-3}**	**AcOH : H20 (1:1 v/v)**	**x 10^{-4}S-1**
0.20	1.5	0.75	50:50	8.75
0.25	1.5	0.75	50:50	8.81
0.30	1.5	0.75	50:50	8.90
0.35	1.5	0.75	50:50	8.96
0.40	1.5	0.75	50:50	8.99
0.30	1.0	0.75	50:50	7.65
0.30	1.5	0.75	50:50	8.90
0.30	2.0	0.75	50:50	10.05
0.30	2.5	0.75	50:50	11.24
0.30	3.0	0.75	50:50	12.45
0.30	1.5	0.25	50:50	7.50
0.30	1.5	0.5	50:50	8.90
0.30	1.5	0.75	50:50	9.65
0.30	1.5	0.10	50:50	10.85
0.30	1.5	1.25	50:50	11.75
0.30	1.5	0.75	40-60	7.85
0.30	1.5	0.75	50-50	8.90
0.30	1.5	0.75	60-40	9.85
0.30	1.5	0.75	70-30	10.84
0.30	1.5	0.75	80-20	11.92

By changing the concentration of HClO4 the rates are measured. The increasing concentration of perchloric acid enhance the rate off reaction and evidenced by the plot of logk Vs log[H^{+}] Shows first order kinetics (B=0.65)(r=0.996; sd=0.01) .

The rate of the reaction were studied by alternating composition of acidic and keeping all other reactant concentration constant. The observed rate constants were tabulated, from the observed results, it is concluded that the rate of the reaction increases with increasing percentage of acetic acid - water mixture. It shows ion dipole interaction[9] plays as Vital rate in the mechanistic pathways.

Effect of sodim perchlorate, acrylonitille, and Mn^{2+}:

The reactions were carried out at Various ionic strength by Vary (NaClO4) and keeping the other factors constant to it has been observed that the addition of perchlorate ion has no significant effect on thereaction rates[10] (Table-3). Indicating that the reaction may be between ion and a neutral molecule as between neutral Species in the rate determining step.

Effect of variation of [MnSO4] [NaClO4] and [Acrylonitrile] on the reaction rates.

[INDC] =0.30 X 10^{-2}mol dm^{-3} [2-iso propyl-5-methyl cyclohexanol] =1.5x 10^{-2}mol dm^{-3}

[HClO4]= 0.75X 10^{-2}mol dm^{-3} ACOH : H20 (1:1 v/v)

Table-2

Temperature = 303 K

[Mnso4] X 10^4 Mol dm^{-3}	[NaClO4] X 10^4 Mol dm^{-3}	[Acrylonitrile] X 10^4 Mol dm^{-3}	kobs x 10^4 S-1
0.0	-	-	9.36
4.5	-	-	9.45
9.0	-	-	9.85
13.5	-	-	10.10
18.0	-	-	10.48
-	0	-	9.36
-	0.57	-	9.47
-	1.14	-	9.48
-	1.71	-	9.43
-	2.28	-	9.51
-	-	0	9.36
-		9.1	9.33
-	-	18.1	9.32
-	-	27.2	9.29
-	-	36.2	9.28

No polymerization was observed with acrylonitrile. Also addition of acrylonirile produced to change in the rate values indicating the absence of free radicals during the reaction (Table-2). The rate constant were measure at different concentrations of Mn(II) (Tabe-2). addition of Mn^{2+} inssscreases the rate of the reaction showing the involvement of the electron transformation in the rate determining step[11].

Effect of temperature on the reaction rule's

The reaction rates at four different temperatures Viz 298, 302, 308, 313 (Table-3) with an accurancy of ± 0.lk. From Iyring plot lnk_2/T Vs 1/T) (fig 1) (r=0.977 ; sd=0.670). The activation parameters $\Delta H^{\#}$ and $\Delta S^{\#}$ were delibrated from the slops and intercept calculated of the plot. When the temperature increases from 298 to 318K, the rate of reaction here increases and these reaction rate identified by high negative value of entropy formed.

Indicate that the Solvents molecules are energetically oriented around the ions, which result in theloss of entropy[12], the effect being larger in non-polar solvents.

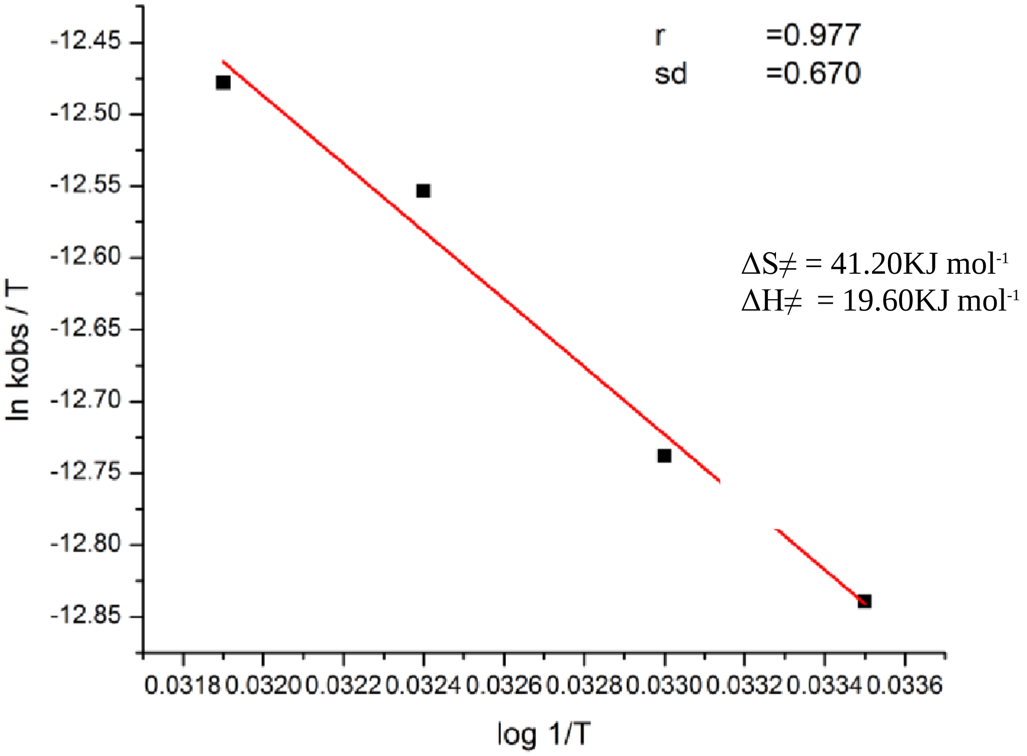


Fig-1

This can firms that, the decrease of polarity of medium results in increase of the entropy values andthe number of unfound molecules in the solution increases[13].

TABLE-3

S. No.	Substate	Temperature (K)	10^4Kobs S^{-1}
1	2-iso propyl-5-methyl cyclohexanol	298	7.26
2		303	9.36
3		305	10.36
4		308	11.36

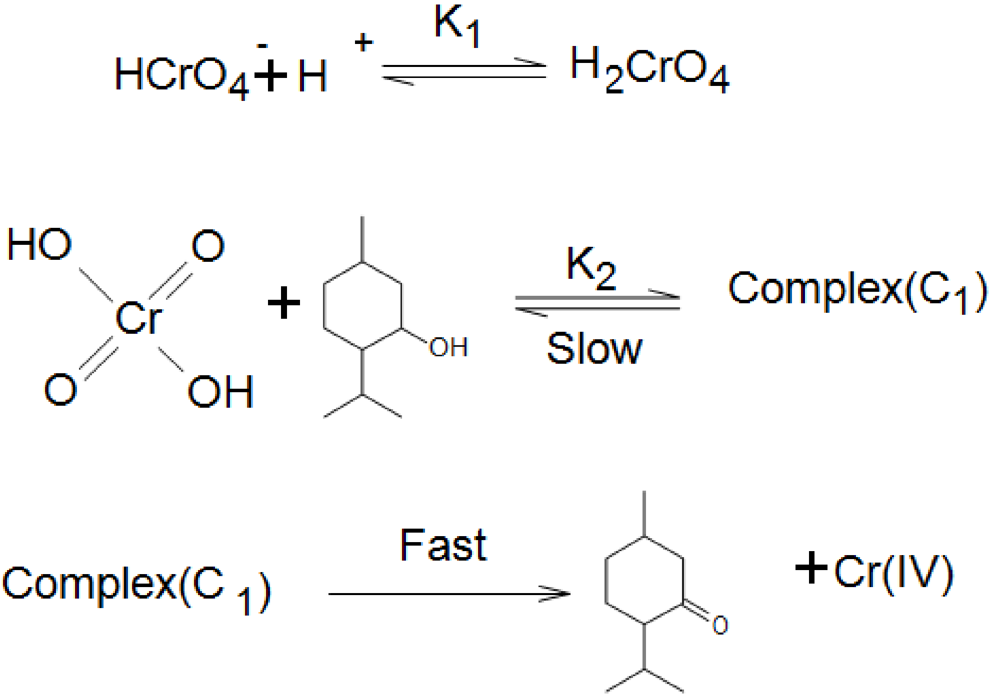
Mechanism and rate law

Under the experimental conditions employed in the present study menthol to menthone. Based on the above kinetic observations, the reaction showed first under dependence on (INDC) and (ClO_4)(Substrate).

The rate of reaction increase with decrease into dielectric constant of the medium. The addition of$NaClO_4$ does not affect the rate of the reaction. During the addition of Mn^{2+} rate of the reaction decreases that may be due to the formation of Cr(VI) in the slow step.

Moreover, the reaction did not include polymerization of acrylonitrile indicating the absence of freeradical pathway.

In aqueous medium the oxidant will give $HCrO_4^-$ is the active oxidant in Cr(VI) oxidation reaction[14].Based on the above facts, the following mechanism is proposed for the oxidation of menthol by INDC.



The rate law for above mechanismRate = k2 [S] [H2CrO4]

= k2k1[S] [H+] [$HCrO_4^-$]

Kobs =k2k1[S] [H^+]

Where[S] = 2-iso propyl-5-methyl cyclohexanol

Conclusion:

We conclude that, The oxidation reaction between the oxidant Isonicotinium Dichromate and 2-iso propyl-5-methyl cyclohexanol was found to be first order, with respect to [S] [Oxi] and [H^+]. The consequence oxidation was corresponding carbonyl compound. The suitable mechanism was proposed.

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