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Kinetics and correlation analysis of reactivity in the oxidation of aliphatic primary alcohols by isoquinolinium dichromate in non-aqueous medium



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Keywords: Kinetics Alcohols Oxidation Correlation Mechanism IQDC	Mild oxidation in dimethyl sulfoxide (DMSO) medium by isoquinolinium dichromate (IQDC) of aliphatic primary alcohols produces corresponding carbonyl compounds. A Michaelis-Menten kind kinetics noticed as for alcohols while unit dependency on rate observed as for IQDC. At non-identical temperatures the formation constants and the rates of decomposition of alcohol-IQDC complexes have been evaluated. Thermodynamic parameters and activation parameters for formation of the complex and break down of the complexes have been determined respectively. The oxidation process accelerates with increase in proton concentration. An α -C-H bond fisson in the rate-controlling step suggested by the deuterium isotope effect. For oxidation of ethanol, $k_{\rm H}/k_{\rm D} = 5.82$ at 293 K, was observed. The oxidation rates have been evaluated in 19 organic solvents and greater role of solvating power of the cation is observed. Depended on the kinetic parameters, solvent effect analysis and the outcome of thermodynamic parameters, a mechanism in which rate-controlling break down of the complex is suggested, to give the resulting product through hydride-ion transfer with a cyclic transition state.

1. Introduction

In synthetic organic chemistry, under non-aqueous medium particular oxidation of organic compounds is a significant conversion. Due to this reason various Cr(VI) complexes have been documented [1,2]. Isoquinolinium dichromate [IQDC, $(C_9H_7NH^+)_2Cr_2O_7^2$] is a complex of Cr(VI), reported in 1998 [3]. Since IQDC is neither light sensitive nor hygroscopic, thus, it is stored easily and more stable rather than other derivatives of Cr(VI). Conversion of primary and secondary alcohols by IQDC to their respective carbonyl compounds with 60 to 90% yield is well documented³. We get focused on mechanistic investigations with kinetic aspects of the oxidation by IQDC. A study of literature appears that there is no work reported on the oxidation kinetics of aliphatic primary alcohols by IQDC. Here we investigate the oxidation kinetics of aliphatic primary alcohols by IQDC in solvent DMSO.

2. Materials and methods

From the described procedure [3] oxidant IQDC was composed and its IR spectrum (KBr) showed bands at 930, 875, 765 and 730 $\rm cm^{-1}$ which are the properties of dichromate-ion. Its immaculateness was checked iodometrically. The alcohols were commercial products and

were purified by usual methods. $[1,1-^{2}H_{2}]$ Ethanol was formed by the described procedure [4] and its purity was 92.4% which is determined by proton NMR spectra. Purification of solvents was determined by the described methods [5]. Amongst the solvents, CS_{2} is a combustible and toxic liquid in the midst of solvents, and as resource of hydrogen ions TsOH was utilized. The standard alkali solution was used for standardization of TsOH solution.

Product analysis: Under kinetic conditions *i.e.* excess of alcohol over oxidant, product analyses were executed. In this experiment, ethanol (0.5 mol), TsOH (0.1 mol), and IQDC (0.02 mol) in DMSO were compose to 100 ml and it was then left in absence of light for a day to make sure the reaction accomplishment. The solution with 200 ml of 2,4-dinitrophenylhydrazine (saturated) solution in 2 M hydrochloric acid was then reacted by above solution and kept in a chiller for whole night, and obtained product corresponding hydrazone was percolated, parched, weighed and with ethyl alcohol recrystallized it and again weighed. The formation of 2,4-dinitrophenylhydrazone (DNP), previously and subsequently recrystallization was 6.05 g (90%) and 5.44 g (81%) correspondingly. It was perceived analogus identical (mixed mp and mp) to an authentic sample of DNP of acetaldehyde. Similar experiment was repeated with other alcohols the yield of DNP of the related aldehyde later recrystallization was around 78–85%.

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Table 1

Stoichiometry data for the oxidation by IQDC of ethanol.

10 ³ [IQDC] (mol dm ⁻³)	10^3 [Ethanol] (mol dm ⁻³)	10 ³ [Unused IQDC] (mol dm ⁻³)	[Ethanol] [Used up IQDC]
10.0	2.0	8.74	1.55
10.0	4.0	7.30	1.48
10.0	6.0	6.03	1.51
			Mean = 1.51 ± 0.03

 Table 2

 Rate data at 313 K for alcohols oxidation by IQDC.

10 ³ [IQDC] (mol	[Alcohol] (mol	10 [H ⁺] (mol	$10^3 k_{obs}(s^{-1})$		
dm ⁻³)	dm ⁻³)	dm ⁻³)	ethanol	n- propanol	
1.0	0.05	2.0	5.4	11.69	
1.0	0.1	2.0	7.9	16.73	
1.0	0.2	2.0	10.3	21.32	
1.0	0.3	2.0	11.4	23.47	
1.0	0.4	2.0	12.1	24.7	
1.0	0.6	2.0	12.8	26.1	
1.0	1.0	2.0	13.6	27.3	
0.5	0.6	2.0	12.96	26.31	
0.8	0.6	2.0	12.6	25.95	
1.5	0.6	2.0	12.4	26.05	
2.0	0.6	2.0	13.2	26.2	
5.0	0.6	2.0	13.04	25.83	
1.0	1.0	2.0	13.42 ^a	27.51 ^a	

Stoichiometry: The oxidation of alcohols prompts the development of relating oxoacids. For stoichiometry determination, IQDC (0.05 mol) and alcohol (0.002 mol) in DMSO were composed to 200 ml with 1.0 M TsOH. To ensure the completion of the reaction the solution was kept as it

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is for a day. Spectrophotometrically at 370 nm the residual IQDC was measured. Various observations indicate that 3 mol of alcohols react with 2 mol of IQDC at non-identical alcohol concentrations. The outcomes with ethanol are shown in Table 1. IQDC is reduced to Cr(III) and participating in the reaction as a 3-electron oxidant.

Kinetic measurements: The pseudo-first-order state were executed for all kinetic runs at constant temperature (\pm 0.1), by sustaining over abundance of alcohols (15 fold or greater) on IQDC. DMSO was used as solvent in the reaction, unless specified. The progress of reaction up to 75% was studied by monitoring the consumption of IQDC at 370 nm. In this investigation for all concentrations Beer's law is applicable. A graphic between log [IQDC] and time was linear with $r^2 > 0.99$ and velocity constant (k_{obs}) was obtained from it and for more than two runs replicability $\pm 3\%$ was observed. In correlation analyses coefficient of determination (R^2 or r^2), Exner's parameter [6] (ψ) and standard deviation (sd) was used.

3. Results

The stoichiometric ratios, Δ [Alcohols]/ Δ [IQDC], confirmed the following overall reactions for the oxidation of alcohols respectively.

$$3RCH_2OH + 2Cr_2O_7^{-2} + 22H^+ \rightarrow 3RCHO + 2Cr^{+6} + 2Cr^{+3} + 14H_2O \quad (1)$$

3.1. Test for free radical

Oxidations of alcohols by IQDC, under nitrogen ambience, the acrylonitrile induce polymerization was not observed. No considerable IQDC consumption, in absence of alcohols, was noticed. The oxidation rate was unaffected on acrylonitrile addition (Table 1). For additional confirmation of the absence of one electron oxidation during course of the



Fig. 1. A plot of $(10^3 k_{obs})$ against [Alcohol] at 313 K [TsOH] = 0.2 mol dm⁻³; [IQDC] = 0.001 mol dm⁻³.



Fig. 2. A plot of $1/(10^3 k_{obs})$ against 1/[Alcohol] at 313 K [TsOH] = 0.2 mol dm⁻³; [IQDC] = 0.001 mol dm⁻³.

Table 3	
RCH ₂ OH-IQDC complex formation constants and their parameters of thermodynamics in	DMSO.

Alcohol (R)	$K^{\#}$ (mol ⁻¹ dm	3)			$\Delta H_{\rm f}$	ΔS_{f}	$\Delta G_{\rm f}$
	293 K	303 K	313 K	323 K	kJ mol ⁻¹	$J \text{ mol}^{-1} \text{ K}^{-1}$	kJ mol $^{-1}$
Н	22.3	16.3	12.9	11.2	-20.67 ± 1.2	-37 ± 3.8	-9.79 ± 0.9
Me	22.1	15.8	11.6	10.05	-23.6 ± 1.4	-47 ± 4.6	-9.3 ± 1.1
Et	24.8	16.9	13.2	10.8	-24.14 ± 1.3	-48 ± 4.1	-9.98 ± 1.0
Pr	24.5	18.1	12.8	10.6	-25.03 ± 1	-51 ± 3.2	-10 ± 0.78
Bu	23.9	16.3	12.1	9.9	-25.7 ± 1.3	-54 ± 3.9	-9.88 ± 0.94
Pr ⁱ	24.9	17.2	12.3	10.1	-26.5 ± 1.2	-56 ± 3.8	-9.9 ± 0.92
ClCH ₂	21.2	14.8	11.8	9.5	-23.28 ± 1	-46 ± 3.2	-9.6 ± 0.8
MeOCH ₂	22.7	14.9	12.1	10.9	-20.9 ± 0.5	-38 ± 1.8	-9.84 ± 0.4
Bu ^t	23.2	15.7	11.2	9.3	-26.8 ± 1.4	-58 ± 4.6	-9.8 ± 1.1
MeCD ₂ OH	22.8	16.5	13.5	11.0	-21.32 ± 0.8	-39 ± 2.8	-9.85 ± 0.7

reaction, the reaction was executed with $0.005 \text{ mol dm}^{-3}$ of butylated hydroxytoluene (BHT). The BHT did not show any considerable change and observed nearly quantitatively.

3.2. Rate laws

In this oxidation reactions unit dependency exhibited as for BIDC

therefore graphic was straight line ($r^2 > 0.996$) between logarithms of [IQDC] and time. The k_{obs} (pseudo-first-order velocity constant) do not alter appreciably on IQDC beginning concentration (Table 2). The fractional dependency (0<order<1) was observed for alcohols (Table 2). In Fig. 1, a graphic between k_{obs} and [Alcohol] is exhibited. The curvature of the plots leading towards a lower level reveals the development of a complex. Double reciprocal graphic between $1/k_{obs}$ and 1/[Alcohol] was

Table 4

RCH ₂ OH-IQDC comple	x decomposition	constants and their	parameters	of activation	in DMSO
			+		

Alcohol (R)	$10^3 k_2 (s^{-1})$				ΔH^*	ΔS^*	ΔG^{\star}
	293 K	303 K	313 K	323 K	kJ mol ⁻¹	$J \text{ mol}^{-1} \text{ K}^{-1}$	kJ mol $^{-1}$
Н	0.0074	0.022	0.068	0.18	81.7 ± 0.8	-65 ± 2.7	100 ± 0.6
Me	3.2	6.8	14.7	31.1	$\textbf{57.2} \pm \textbf{0.8}$	-98 ± 2.7	$\textbf{86.2}\pm\textbf{0.6}$
Et	6.65	13.6	29.4	58.6	54.9 ± 0.8	-100 ± 2.5	84.5 ± 0.6
Pr	16.4	32.2	63.6	125	$\textbf{50.7} \pm \textbf{0.7}$	-107 ± 2.4	$\textbf{82.4}\pm\textbf{0.6}$
Bu	19.3	37.2	73.2	147	49.5 ± 2.7	-110 ± 8.8	82. ±2.1
Pr ⁱ	33.5	63	119.1	230	$\textbf{47.9} \pm \textbf{0.9}$	-110 ± 3	80.6 ± 0.7
ClCH ₂	0.024	0.064	0.186	0.48	76.5 ± 1.1	-73 ± 3.7	98.1 ± 0.9
MeOCH ₂	0.35	0.82	1.97	4.54	64.8 ± 0.8	-91 ± 2.7	91.7 ± 0.6
Bu ^t	1172	1830	2960	4596	33.5 ± 0.6	-130 ± 1.8	72 ± 0.4
MeCD ₂ OH	0.55	1.28	2.92	6.45	62.06 ± 0.5	-96 ± 1.5	90.5 ± 0.4
$k_{\rm H}/k_{\rm D}$	5.82	5.31	5.03	4.82			

Table 5

Rate	of	reaction	reliance	on	concentration	of	hydrogen-ion
[IQDC]	= 0.0	001 mol dm	⁻³ , [Alcoho] = 0.	5 mol dm ⁻³ at 31	3 K.	

[TsOH] (mol dm ⁻³)	0.1	0.2	0.4	0.6	1.0	1.5
ethanol, $10^3 k_{obs}$ (s ⁻¹)	8.1	13.6	25.2	31.2	39.9	46.4
n-propanol, $10^3 k_{obs}$ (s ⁻¹)	18.4	29.5	45.6	51.8	60.6	66.3

straight line with positive intercept (Fig. 2). Hence, for all Alcohols, a Michaelis-Menten kind kinetics was noticed. This suggests the existence of following rate law and mechanism:

$$Alcohol + IQDC \rightleftharpoons [Complex]$$
(2)

$$[\text{Complex}] \xrightarrow{k_2}{\rightarrow} \text{Product}$$
 (3)

$$Rate = k_2 K^{\#}[Alcohol][IQDC]_t / (1 + K^{\#}[Alcohol])$$
(4)

Or,

$$1 / (\text{Rate} / [\text{IQDC}]_{t}) = 1 / k_{\text{obs}} = 1 / k_2 K^{\#}[\text{Alcohol}] + 1 / k_2$$
(5)

Here, $[IQDC]_t = [IQDC] + [Complex]$

At non-identical temperatures, the k_{obs} dependency on alcohol concentrations were calculated and using eq. (5), k_2 and $K^{\#}$ values with the help of double reciprocal graphic, were determined. For establishment of complex, the thermodynamic parameters (Table 3) and breaking down of them, the activation parameters (Table 4) were determined at nonidentical temperatures, from k_2 and $K^{\#}$ values respectively.

3.3. Kinetic isotope effect

The oxidation of $[1,1-{}^{2}H_{2}]$ ethanol was analyzed with IQDC for established the significance of α -C–H bond fission in the rate-controlling pathway. The findings (Table 3) revealed that complex formation constants of ethanol and deuterated ethanol are nearly close but decomposition rates of them (Table 4) indicated a deuterium isotope effect ($k_{\rm H}/k_{\rm D}$ = 5.82 at 293 K). Primary kinetic isotope effect value was found similar in case of benzyl alcohol oxidation by BIDC [7]. Further, in

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present study, the value of $k_{\rm H}/k_{\rm D}$, increases with decrease in temperature.

3.4. Effect of hydrogen-ion concentration

The rates of oxidation of alcohols are catalyzed by hydrogen-ion concentration (Table 5). A graphic between log k_{obs} and log [H⁺] is straight line with positive slope which is less than one. This suggests the dependency with hydrogen-ion concentration on rate is between zero to one. Thus, a graphic between $1/k_{obs}$ and 1/[H⁺] was undertaken and with positive intercept a straight line was obtained (Fig. 3). No particular reaction was observed without toluene *p*-sulphonic acid (TsOH).

3.5. Solvent effect

Nineteen organic solvents were used to study the oxidation of alcohols by IQDC. The reaction of IQDC with 1° and 2° alcohols and reactant's solubility restricted the solvent's selectivity. No reaction was observed

Table 6

Solvent's effect at 313 K on the ethanol oxidation of by IQDC.

Solvent	$K^{\#} (\mathrm{mol}^{-1}\mathrm{dm}^3)$	$10^{3}k_{2} (s^{-1})$
Chloroform	12.1	4.28
Carbon disulfide	10.6	0.83
1,2-Dichloroethane	11.3	5.36
Dichloromethane	12.4	5.12
DMSO	11.6	14.7
Acetone	10.8	4.92
DMF	11.5	8.34
Butanone	11.1	3.70
Nitrobenzene	11.0	6.18
Benzene	10.2	1.94
Cyclohexane	12.3	0.23
Toluene	11.8	1.57
Ethyl acetate	10.3	2.05
Acetophenone	12.2	6.79
Tetrahydrofurane	10.8	2.68
tert-Butyl alcohol	11.9	1.84
1,4-Dioxane	12.0	2.73
1,2-Dimethoxy ethane	11.7	1.46
Acetic acid	11.1	0.72



Fig. 3. A plot of $1/(10^3 k_{obs})$ against $1/[H^+]$ at 313 K [Alcohol] = 0.2 mol dm⁻³; [IQDC] = 0.001 mol dm⁻³.

with the selected solvents. The kinetics was nearly same with these solvents. In Table 6, corresponding $K^{\#}$ and k_2 values are mentioned.

4. Discussion

The enthalpies and entropies of the oxidation of nine alcohols revealed adequate correlation ($r^2 = 0.9979$) with an isokinetic temperature 750.14 ± 1.8 K. The correlation was checked and observed authentic with Exner's criterion [8]. The Exner's graphic between the values of log k_2 at 293 K and at 323 K, for the nine alcohols, was linear (slope = 0.8504 ± 2.03 , $r^2 = 0.9999$) and value of isokinetic temperature was 773 ± 17 K. The two values showed perfect agreement. For validity of linear free energy relationships⁸, a linear isokinetic relationship is an essential requirement. It specifies that all the reactions which are correlated, oxidized through common mechanism.

Protonated oxidant (IQDCH⁺) appears to be an ionic compound. In our reaction ambience the nature of IQDC is determined at 313 K with conductivity measurements. Low conductivity of DMSO and insignificant variation in conductivity value due to the inclusion of IQDC in DMSO was observed; therefore IQDC does not break up as isoquinolinium and dichromate ions thus IQDC remain non-ionised in our reaction system. The rate of oxidation does not alters on addition of isoquinolinium ion, also favours the postulation that IQDC remain as non-ionised.

It is observed, after protonation IQDC **(X)** produce a protonated Cr(VI) species **(Y)** which is active electrophile and stronger oxidant (eq. **(6)**). Thus, oxidation process through IQDC depends upon proton concentration.

$$(\operatorname{IQOH})_{2}\operatorname{Cr}_{2}\operatorname{O}_{5} + \operatorname{H}^{+\overset{K_{1}}{\rightleftharpoons}}(\operatorname{IQOH})_{2}\operatorname{OCr}(\operatorname{OH})\operatorname{OCrO}_{2}$$
(6)

Here, BI represents benzimidazole. Further, effect of proton concentration on rate could be expressed as -

$$1/k_{obs} = a + b / [H^+]$$
 (7)

Generation of a protonated Cr(VI) complex has been before suggested in the reactions of other Cr(VI) complexes [9,10]. Magnified reactivity obtained due to the internal electron transfer from hydroxy acid to IQDC which promotes by the protonation of IQDC. Further, hydrogen ion dependency shows fast equilibrium amid (X) and (Y), magnitude of equilibrium constant, K_1 , is less and at higher concentrations of [H⁺] the reaction remains incomplete because at higher hydrogen ion concentration no leveling of velocity constants occurred. No astounding oxidation noticed without TsOH recommends that just the protonated IQDC (Y) carries on like an oxidizing species. In oxidation of MA by BIDC similar kind of hydrogen-ion dependency observed [11].

4.1. Solvent effect

The described data in Table 6 represents that with change in solvent the rate constant (k_2), varies considerably though equilibrium constant($K^{\#}$), is quite insensible. Similar kind of oxidation kinetics observed in aliphatic primary alcohols oxidation by BIDC [12]. Hence, k_2 for the breakdown of complexes, in 18 solvents (CS₂ has not been studied because the absolute range of solvent parameters are unavailable), have been associated regarding linear solvation energy relationship (LSER) of Kamlet et al. [13]. Irrelevant correlations were observed.

Regarding to the Swain's [14] eq. (8), data of solvent effect had been studied where A, B and (A + B) denotes the solvating power of anion, solvating power of cation and polarity of solvent respectively and intercept term denoted by C.

$$\log k = aA + bB + C \tag{8}$$

In respect of Swain's eq. (8) the conclusion of the correlation studies, separately with A, B and (A + B) are described as:

Table 7

Correlation of the rates of oxidation of alcohols in terms of Pavelich- Taft equation.

T (K)	ρ*	δ	R ²	sd	Ψ	n
293	-2.30 ± 0.01	-1.21 ± 0.02	0.9998	0.0042	0.016	9
303	-2.19 ± 0.02	-1.14 ± 0.03	0.9999	0.0041	0.011	9
313	-2.07 ± 0.02	-1.08 ± 0.01	0.9999	0.0094	0.011	9
323	-1.97 ± 0.01	-1.03 ± 0.01	0.9998	0.0089	0.016	9

n = number of data points.

log $k_2 = 0.42 \pm 0.01 \text{ A} + 1.65 \pm 0.03 \text{ B} - 3.75$	(9)
$R^2{=}0.9999,sd{=}0.003,n{=}19,\psi{=}0.01,T{=}313K$	
log $k_2 = 0.18 \pm 0.54$ A - 2.61	(10)
$r^2 = 0.0068$, $sd = 0.44$, $n = 19$, $\psi = 1.02$, $T = 313$ K	

$$\log k_2 = 1.62 \pm 0.07 \text{ B} - 3.61 \tag{11}$$

$$r^2 = 0.9654$$
, sd = 0.08, n = 19, $\psi = 0.19$, T = 313 K

$$\log k_2 = 1.24 \pm 0.16 \,(A+B) - 3.71 \tag{12}$$

 $r^2 = 0.7861$, sd = 0.20, n = 19, $\psi = 0.47$, T = 313 K

The observed results of solvent effect revealed a perfect correlation regarding Swain's equation with both solvating power of cation- and anion-participating with perceived effect of solvent. Although, the contribution of solvating power of cation is greater, it alone contributes for 96.54% of the data. (A + B), represents the polarity of the solvent, explains 78.61% of the data. Relative permittivities of the solvents were correlated with the data by considering that 78.61% of the data is contributed by polarity of the solvent. The above mentioned data was correlated with the Kirkwood function, $(\varepsilon-1)/(2\varepsilon+1)$, here ' ε ' is dielectric constant of the medium. A graphic between log k_2 and Kirkwood function, though, It is not linear ($r^2 = 0.4758$). This showed that the relative permittivity and polarity of solvent do not represent the same solvent characteristics, defined by Swain et al. [14].

4.2. Correlation analysis of reactivity

Preliminary computation showed that the rate constants (k_2) of the oxidation of alcohols do not reveal acceptable correlation either with the Taft polar (σ^*) or steric substituent (E_s) parameters separately [15].

$$\log k_2 = (-2.86 \pm 0.57) \,\sigma^* - 1.47$$

$$r^2 = 0.7799$$
, $sd = 0.73$, $n = 9$, $\psi = 0.50$, $T = 313$ K (13)

$$\log k_2 = (-1.68 \pm 0.44) \,\mathrm{E_s} - 2.24$$

$$r^2 = 0.6792$$
, $sd = 0.88$, $n = 9$, $\psi = 0.60$, $T = 313$ K (14)

Therefore, the rates were evaluated in terms of dual substituentparameter (DSP) equation (eq. (15)) of Palvelich and Taft [15].

$$\log k_2 = \rho^* \, \sigma^* + \delta \, E_s + \log k_o \tag{15}$$

The observed correlation was excellent with negative reaction constants (Table 7). A steric acceleration is indicated by negative steric reaction constant of the reaction. This may be described based on large ground state energy of the sterically crowded alcohols. Since the crowding is relieved in the product aldehyde as well as in the transition state leading to it, the transition state energies of the crowded and noncrowded alcohols do not vary much and a steric acceleration, therefore, results.



Scheme 1. Mechanism for the oxidation of aliphatic primary alcohol by IQDC.

4.3. Mechanism

Considering about the non attendance of any impact of acrylonitrile the reaction rate it is unfavoured that oxidation by one-electron is operative in the present reaction. BHT is a perfect trapping reagent for free radicals [16]. The acid-catalysis is considered as earlier IQDC protonation to produce IQDCH⁺(Y). The major role of solvating power of cation supports it. In a fast dynamic-equilibrium development of a 1:1 complex (Z) recommended by the Michaelis-Menten kind kinetics in the context of alcohols. Nucleophilic attack of –OH group of alcohol on BIDCH⁺ (Y) results in the origination of the complex C(Scheme 1). The process of oxidation increases by the electron-donating methyl groups and this is reflected by the reactivity increasing power. It shows that in the formation of complex the availability of electron in –OH group expands. It is noticed that the complexes of normal and $[1,1-^{2}H_{2}]$ ethanol have formation constants which are nearly equal, however a primary

kinetic isotope impact indicated by the rate of decomposition and it suggests that in the rate controlling step the α -C-H bond is broken. The end product (aldehyde) in Scheme 1 obtained from the complex (**Z**), due to the hydride-ion shifting from alcohol to IQDC and mechanism of shifting of this hydride-ion further supports that solvating power of cation have major role. A carbocationic nature accessed by a polar transition status is postulated in oxidation process. It was noticed that the oxidation of benzyl alcohols by BIDC [7] is also followed the similar mechanism. However, the generation of a centre of carbonium ion is suggested in the controlled step in few reports on primary alcohol's oxidation [17,18].

Transfer of a hydride-ion may occur either by an acyclic process or *via* a chromate ester. Kwart and Nickle [19] developed a method to study of the temperature reliance of the kinetic isotope effect, revealed that a concerted cyclic mechanism precedes loss of hydrogen. The results for ordinary and deuterited-alcohols have been expressed in a familiar manner-

$$(k_{\rm H}/k_{\rm D}) = (A_{\rm H}/A_{\rm D}) \exp\left(-\Delta E_a / RT\right)$$
(16)

The difference of activation energy for $k_{\rm H}/k_{\rm D}$ is *ca*. 4.89 kJ mol⁻¹ which concluded by final results agrees that the activation entropy (ΔS^*) and zero-point energy gap for both C-D and C-H bonds (ca. 4.86 kJ mol⁻¹) are almost same in the present reaction. It is directly agrees with a symmetrical transition state properties [20,21]. Previously, similar kind of results has been noticed in alcohol's oxidation by butyltriphenyl-phosphonium dichromate (BTPPD) [22]. Bordwell [23] has specified strong facts beside the phenomenon of bimolecular concerted process of hydrogen shifting completed in one-step. In the present reaction system this is strongly recommended that the shifting of hydrogen does not undergo through an acyclic bimolecular course of action. This symmetrical process is really sigmatropic a reaction in which direct transfer of hydrogen is involved in which a cyclic transition state shifting is specified [24]. Afterwards, two electrons transfer in a cyclic scheme was the next in this reaction. In the oxidation of alcohols by IQDC concerned with six electrons which resembles with Hückel's $(4n+2)\pi$ system, is a permitted process [25]. Hence, it is presumed that hydride-ion transfer occurring through a cyclic transition state in alcohol's oxidation by IODC.

Described mechanism in Scheme 1 is based on the experimental findings. In suggested mechanism (Scheme 1) the rate law could be discussed below. Cr(VI) can be determined on applying the equilibrium condition,

$$-d[Cr(VI)] / dt = k_2[Z] = k_2 K_1 K_2 [Alcohol][H^+][Cr(VI)]$$
(17)

or,
$$-d[Cr(VI)] / dt = \frac{k_2 K_1 K_2 [Cr(VI)]_{t} [H^+] [Alcohol]}{1 + K_1 K_2 [H^+] [Alcohol]}$$

or,

$$k_{obs} = \frac{k_2 K_1 K_2 [\mathrm{H}^+] [\mathrm{Alcohol}]}{1 + K_1 K_2 [\mathrm{H}^+] [\mathrm{Alcohol}]}$$
(18)

Here, $[Cr(VI)]_t = [Cr(VI)] + [Z]$, here K_1 is low and produced [Y] which get react with alcohol.

or,
$$1/k_{obs} = 1/k_2 K_1 K_2$$
 [H⁺] [Alcohol] + $1/k_2$ (19)

The reaction system is well characterized by equation (18) or (19). With the help of equations (5) and (19), we have $K^{\#} = K_1 K_2 [H^+]$.

The observed loss of entropy $(-\Delta S)$ of activation favors proposed mechanism. In the transition state, two ends become extremely solvated when the charge segregation occurs and this leads to stabilization of large number of solvent molecules, which appears as entropy loss. The effect of solvent also accounts by loss of entropy.

In the beginning oxidation state of Chromium metal reduced from Cr(VI) to Cr(IV) and expected to react with another Cr(VI) to produced

Cr(V). In a fast step this Cr(V) species ultimately produces Cr(III) species. This pattern of reactions in oxidations by Cr(VI) is markedly established [26].

It is interesting here to compare the findings of the oxidation of the existing reaction with the results of oxidation of alcohols by other Cr(VI) complexes viz. quinolium dichromate (QDC) [27], BIDC [12], BTPPD [22]. The oxidation kinetics of alcohols by QDC and in present reaction exhibited the Michaelis-Menten type kinetics with respect to alcohols suggesting the formation of an intermediate in pre-equilibrium and its subsequent disproportionation in the rate-controlling step. However, with BIDC and BTPPD, the order of reaction with respect to alcohol is found to be two. The oxidation of alcohols by BTPPD and BIDC suggested also involving the formation of an intermediate ester, but the second order dependence on alcohol concentration can be explained by assuming that the equilibrium constant of the formation of an intermediate is very small and not reflected in the rate laws. All four reactions exhibited a primary kinetic isotope effect confirming the fission of the α -C-H bond in rate-controlling step. An analysis of the temperature dependence of the kinetic isotope effect indicated the presence of a symmetrical cyclic transition state in all the four oxidation reactions. The oxidation of alcohols catalyzed by hydrogen-ion, but the dependence is of first order in case of QDC where as second order for the oxidation by BTPPD and BIDC. Fractional order dependency on [H⁺] is observed in the present reaction. Therefore protonated oxidants are reactive oxidizing species in the oxidation by QDC and IQDC while doubly protonated for BIDC and BTPPD. The mechanism of the oxidation of alcohol by BIDC was similar with that of BTPPD except that BTPPD is postulated to get dissociated to give dichromate ion which on protonation acts as reactive oxidizing species. The BIDC is postulated to exist as undissociated under our reaction condition. Though, the data are not conclusive, it appears that the oxidation process relies on state of the reaction and character of the oxidant.

5. Conclusions

The oxidation of alcohols by IQDC in DMSO resulted in the formation of corresponding aldehyde. The reaction is catalyzed by hydrogen ion and protonated IQDC is proposed to be the reactive oxidizing species. Michaelis-Menten type kinetics observed with alcohols and first order dependency observed as for IQDC. An α -C-H bond fission is indicated in rate controlling step. An excellent correlation between rate constants and duel substituent parameters (polar and steric) is observed, the reaction constants being negative. A mechanism taking in the rate-controlling oxidative breakdown of complex through a hydride-ion transfer from alcohol to oxidant to give end product is suggested.

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