

CORRELATION ANALYSES IN THE OXIDATION OF ALIPHATIC SECONDARY ALCOHOLS BY QUINOLINIUM DICHROMATE

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ABSTRACT

Some of the aliphatic secondary alcohols when subjected to oxidation by Quinolinium dichromate (QDC) in dimethyl-sulfoxide (DMSO) as a medium, leading to form a product as analogous ketones. The reaction is found to be in the order of unity in QDC. A Michaelis-Menten type of kinetics, i.e. fractional-order kinetics is observed concerning the secondary alcohols. All the reactions have shown the effect of hydrogen ions. The oxidation of deuterated benzhydrol (PhCDOHPh) showed a considerable kinetic isotope effect ($k_H/k_D = 5.65$ at 298 K). The effect of solvents was studied on the oxidation of 2-propanol (in 19 different organic solvents). The effect of solvents has been investigated after fitting the data in multiparametric equations of Taft's and Swain's. The polar and steric effects of the substituent are also analyzed. A hydride ion transfer mechanism is proposed for this reaction, which proceeds through chromate ester formation.

Keywords: Alcohols, Correlation Analysis, Dichromate, Kinetics, Mechanism, Oxidation

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INTRODUCTION

Synthetic organic chemistry is known to be selective oxidation of some organic compounds in nonaqueous solvents. Various chromium (VI) derivatives have been synthesized and reported in literature.¹⁻⁴ But they are insoluble in most of the nonaqueous solvents. To prevail over these barriers, various salts of Cr(VI) have been prepared and are very popular in synthetic organic chemistry as mild and selective oxidizing agents.¹⁻⁴ One of the compounds is Quinolinium dichromate (QDC)⁵ which has been used for the oxidation of alcohols to carbonyl compounds. It is a well-known fact that the mode of any oxidation reaction depends on the nature of the counter ion attached to the chromium species. We are always interested in oxidation kinetic and mechanistic studies of various organic functions by complexed Cr(VI) species. And several reports, by halochromates and dichromates have already been emanated⁶⁻¹⁰ from our group, in continuation of our previous work on a similar subject, we are going to report in the present MS the oxidation kinetics and mechanism of some aliphatic secondary alcohols by QDC in DMSO as a solvent.

Suitable mechanistic steps are proposed. The main objectives of the present study are to find out kinetic parameters and to evaluate the rate laws, the correlation analysis of the effect of structure over-reactivity and to postulate and propose a suitable mechanism for the oxidation process.

EXPERIMENTAL

Materials

All the alcohols used in the study are commercial (Fluka) and dried by a common procedure of anhydrous magnesium sulphate and then fractionally distilled. The recrystallization of benzhydrol was done ethyl alcohol. The oxidant QDC was synthesized by the method⁵ reported in the literature. The purity of QDC was checked by a iodometric method. Deuterated Benzhydrol (PhCDOHPh) was also prepared by a method reported earlier.⁹ Its isotopic purity was, as established by its n.m.r. spectra, was $96 \pm 4\%$.

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Because of the nonaqueous nature of the solvents used, p-toluenesulphonic acid (TsOH) was the source of hydrogen ions. All the other solvents were purified by their usual methods of purification.¹¹

Analyses of Products

The analysis of products was carried out under kinetic conditions i.e. with a large excess of the reactant over oxidant. In an experiment, 2-propanol (0.05 mol) and QDC (4.76 g, 0.01 mol) were made up, to 100 ml in DMSO and the reaction mixture was kept in dark for about 10 h to make sure that the reaction is complete. 200 ml saturated solution of 2,4-dinitrophenylhydrazine in 2 mol dm⁻³ HCl was used to treat that solution and kept 12 hrs in a refrigerator. The precipitated form of 2,4-dinitrophenylhydrazone (DNP) was filtered dried weighed recrystallized from ethyl alcohol and then again weighed. The yields of DNP before and after recrystallization were 2.46 g (86%) and 2.02 g (84%) respectively based on the consumptions of QDC. The DNP was found to be identical (m.p. and mixed m.p.) with the DNP of acetone. In similar experiments, with other alcohols, the yield of the DNP was in the range of 80-88% after recrystallization. The oxidation state of chromium in a completely reduced reaction mixture, determined by iodometric titrations was 3.95 ± 0.15 .

Kinetics Measurements

Reactions are done under pseudo-first-order reactions conditions by keeping an excess ($\times 10$ or more) of the alcohol on QDC. The solvent was DMSO otherwise it has been mentioned regarding the solvent. All reactions were carried out in flasks covered with dark paper from outside to avoid photochemical reactions if any. The reactions were carried out at a constant temperature and were followed up to 2 half-lives, by examining the lowering down in the concentration QDC spectrophotometrically at 361 nm. The pseudo-first-order rate constant, k_{obs} , was calculated by some least-squares plot of $\log [\text{QDC}]$ versus time. Duplicate runs showed that the rate constants were reproducible to within $\pm 5\%$.

RESULTS AND DISCUSSION

The experiments were done with all the reactant alcohols, but as the results were almost similar therefore only some of the data are presented here.

Stoichiometry

Secondary alcohols are oxidised by QDC to form consequent ketones. Reactions are represented as given below:



Rate Laws

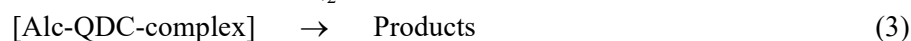
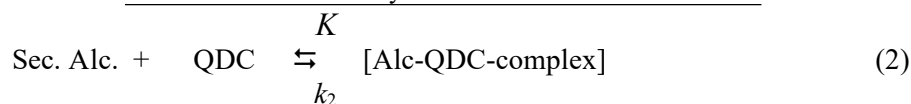
The reactions are of unit order w.r.t. QDC, and the pseudo-first-order rate constant, are not dependent on the starting concentrations of QDC. The rate of the reaction increases with an increment in concentrations of alcohols but not in a linear fashion as depicted by Table-1 and Fig.-1. The plot of $1/k_{\text{obs}}$ versus $1/[\text{Alcohol}]$ is linear ($r > 0.995$) with an intercept on the rate axis. Thus, fractional-order kinetics is observed w.r.t. the alcohol. It can be represented by the following mechanistic steps 2 & 3 and rate law 4.

Table-1: Values of k_{observed} of 2-propanol by QDC Rate Constant at 318 K

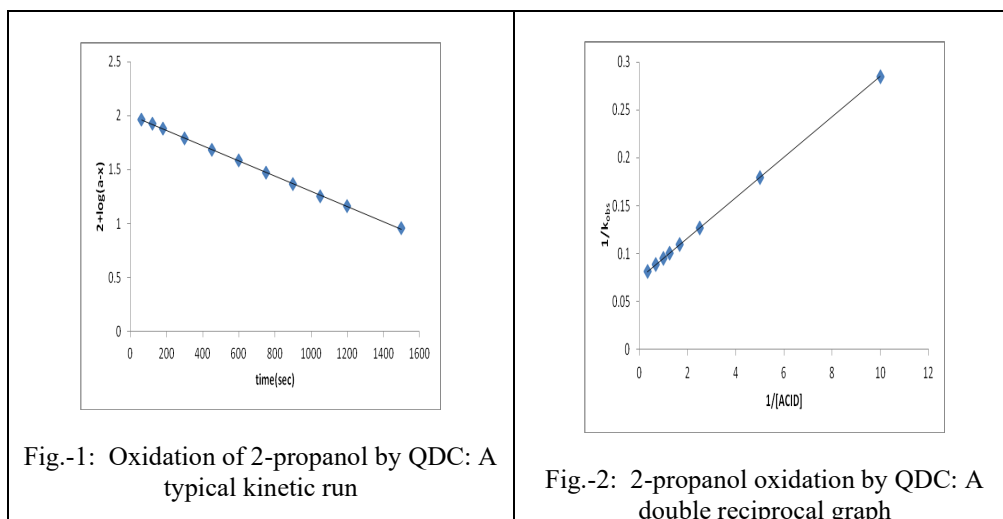
$10^3 [\text{QDC}]$ (mol dm ⁻³)	[2-Propanol] (mol dm ⁻³)	$10^4 k_{\text{obs}}$ (s ⁻¹)
1.00	0.10	3.51
1.00	0.20	5.57
1.00	0.40	7.88
1.00	0.60	9.15
1.00	0.80	9.95
1.00	1.00	10.5
1.00	1.50	11.3
1.00	3.00	12.3
2.00	0.20	5.76
4.00	0.20	5.31

6.00	0.20	5.85
8.00	0.20	5.49
1.00	0.40	7.92*

^acontained 0.001 M acrylonitrile



$$\text{Rate} = k_2 K [\text{Sec. Alc.}] [\text{QDC}] / (1 + K [\text{Sec. Alc.}]) \quad (4)$$



Reaction rates are dependent on reactant concentrations, which were studied at four diverse temperatures (288 to 318K). formation constants K and decomposition constants of the complex k_2 are also calculated. From these K and k_2 various thermodynamic and activation parameters are also evaluated, which are presented in tables two and three.

Table-2: Formation Constant and Thermodynamic Data of Alcohols – QDC Complexes

Alcohol	K (dm ³ mol ⁻¹)				$-\Delta H^*$	$-\Delta S^*$	$-\Delta G^*$
	288	298	308	318 K	(kJ mol ⁻¹)	(J mol ⁻¹ K ⁻¹)	(kJ mol ⁻¹)
Me	5.94	5.15	4.35	3.51	15.8±0.8	32±2	6.51±0.6
Et	5.58	4.80	3.96	3.18	16.7±0.7	36±2	6.32±0.6
n-Pr	6.03	5.25	4.41	3.63	15.4±0.6	30±2	6.55±0.5
i-Pr	6.13	5.35	4.51	3.72	15.2±0.6	29±2	6.60±0.5
i-Bu	5.76	4.96	4.16	3.35	16.2±0.7	33±2	6.41±0.6
Bu	5.85	5.06	4.25	3.42	16.0±0.8	33±2	6.46±0.6
ClCH ₂	5.67	4.88	4.05	3.26	16.5±0.7	35±2	6.36±0.6
MeOCH ₂	5.90	5.07	4.25	3.45	16.0±0.6	33±2	6.47±0.5
Ph	5.49	4.70	3.87	3.09	17.0±0.8	37±2	6.27±0.6
Benzhydrol	6.31	5.52	4.68	3.87	14.9±0.6	28±2	6.68±0.5
Benzhydrol- α -D	6.15	5.35	4.50	3.73	15.2±0.6	29±2	6.60±0.4

Presence of Free Radical Test

Polymerisation by vinyl chloride is done to check the presence of free radicals in the reaction. It was done in the inert atmosphere created by nitrogen. The absence of any free radical indicated that no operation of one electron oxidation process is in operation in this reaction. The experiments with BHT are also not positive in this reaction, is again indicating the non-operation of the free radical mechanism.

Kinetic Isotope Outcome

To ascertain the significance of breaking up the alpha C-H bond in the slow step, oxidation of deuterated benzhydrol is done with QDC, in which a considerable amount of primary kinetic isotope effect is observed. The data are presented in Table-2.

Table-3: Rate Constant and Activation Data of Sec.-Alc – QDC Complex

	$10^4 k_2 / (\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$				ΔH^*	$-\Delta S^*$	ΔG^*
Alcohol	288 K	298 K	308 K	318 K	(kJ mol ⁻¹)	(J mol ⁻¹ K ⁻¹)	(kJ mol ⁻¹)
Me	16.2	34.2	71.1	135	51.5±0.3	120±1	87.1±0.2
Et	27.0	54.9	108	198	48.2±0.1	127±1	85.9±0.1
n-Pr	45.9	88.2	162	279	43.4±0.2	139±0	84.7±0.2
i-Pr	73.8	135	243	405	40.9±0.3	144±1	83.7±0.2
i-Bu	117	207	351	540	36.5±0.6	155±2	82.7±0.5
Bu	51.3	97.2	180	306	42.9±0.3	140±1	84.5±0.3
ClCH ₂	0.36	0.96	2.34	5.31	65.8±0.3	102±1	96.0±0.3
MeOCH ₂	2.79	6.48	14.4	29.7	57.6±0.2	113±1	91.2±0.2
Ph	108	198	378	693	44.8±0.7	127±2	82.6±0.6
Benzhydrol	126	234	414	765	43.0±0.7	132±2	82.3±0.5
Benzhydrol- α -D	20.9	41.4	75.6	147	46.6±0.7	135±2	86.6±0.6
k_H/k_D	6.03	5.65	5.48	5.20			

Influence of Hydrogen Ions

Reactions are depending upon the concentration of acid, which is reflected in the rate and the relation is represented as $k_{\text{obs}} = a + b [\text{H}^+]$. Data of a and b, for 2-propanol, are $3.69 \pm 0.10 \times 10^{-3} \text{ s}^{-1}$ and $5.89 \pm 0.17 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ in that order ($r^2 = 0.9966$).

Table-4: Effect of Acidity on the Rate of Reaction

[QDC] = 0.001 mol dm ⁻³ ; [2-propanol] = 0.10 mol dm ⁻³ ; Temp. = 318 K						
[H ⁺]/mol dm ⁻³	0.10	0.20	0.40	0.60	0.80	1.00
$10^4 k_{\text{obs}}/\text{s}^{-1}$	4.14	5.04	6.12	7.11	8.37	9.63

Solvent Effect on Rate of Secondary Alcohol

Nineteen different solvents are used to find out the rate and solvent relationship. It is observed that values of K are not varying much as compared to k_2 values at 308K, which are represented in Table-5.

Table-5: Influence of Solvents on the Rate of Oxidation of 2-propanol by QDC at 308 K

Solvents	K (dm ⁻³ mol ⁻¹)	$10^4 k_{\text{obs}}$ (s ⁻¹)	Solvents	K (dm ⁻³ mol ⁻¹)	$10^4 k_{\text{obs}}$ (s ⁻¹)
CHCl ₃	5.86	34.7	C ₆ H ₅ CH ₃	5.04	10.7
1,2-C ₂ H ₄ Cl ₂	5.85	41.7	C ₆ H ₅ COCH ₃	5.89	58.9
CH ₂ Cl ₂	6.00	47.9	Tetrahydrofuran	5.85	18.6
DMSO	5.35	135	t-Butylalcohol.	5.69	17.4
CH ₃ COCH ₃	5.66	37.2	1,4 – C ₄ H ₈ O ₂	5.67	22.4
Dimethyl formamide	5.49	77.6	1,2- C ₄ H ₁₀ O ₂	5.55	12.0
C ₄ H ₈ O	6.03	27.5	Carbon Disulphide	5.77	6.46
Nitrobenzene	6.12	57.5	CH ₃ COOH	5.75	7.94
C ₆ H ₆	5.88	13.2	C ₂ H ₅ COOC ₂ H ₅	5.52	14.8
C ₆ H ₁₂	5.85	1.51			

Isokinetic Relationship

All the secondary alcohols under study are subjected to correlation analyses in terms of activation enthalpy and entropy ($r = 0.9748$). As per the study a compensation effect¹² is found under operation.

Data for the isokinetic temperature evaluated^{13,14} from this plot is 539 ± 35 K. whereas, as per Exner¹⁵, because of casual errors in experiments the data of enthalpy and entropy are found to be distracted, therefore an alternate method was suggested by Exner to calculate at two extreme temperatures taken into account the k observed values. A linear graph is obtained ($r^2 = 0.9991$; Fig.-3), the isokinetic temperature value is calculated by this Exner's graph is found 566 ± 40 K. this isokinetic relation indicated that all the reactants are going to oxidize with the similar mechanistic pathways and variation in rates is directed by enthalpy and entropy of activation.

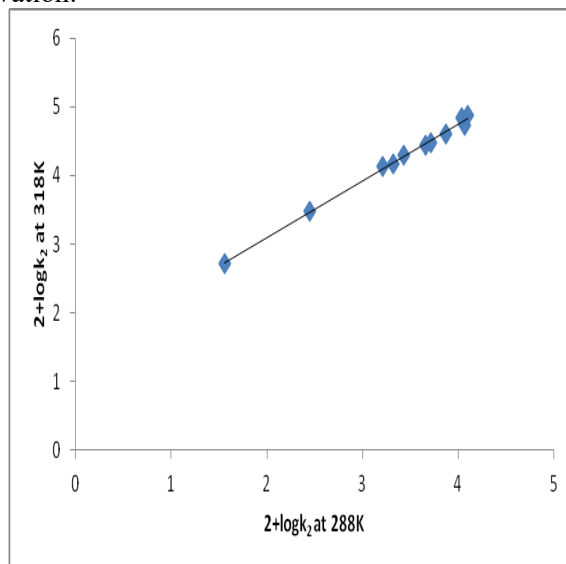


Fig.-3: Graph of Alcohol-QDC Complex by Exner Method of Isokinetic Relationship

Influence of Solvents

Kamlet and Taft¹⁶ model of solvent effect is applied to correlate the rate with LSER method. Carbon disulphide is not taken into the study as the whole series of solvent data are not available.

$$\log k_2 = A_0 + p\pi^* + b\beta + a\alpha \quad (3)$$

In this equation,

π^* denotes solvent polarity,

β denotes the hydrogen bond acceptor basicities

α denotes is the hydrogen bond donor acidity.

A_0 is the intercept term.

As a whole 12 solvents are having value of α is zero. The results, so obtained are summerised below as equation 4 to 7:

$$\log k_2 = -3.76 + 1.64 (\pm 0.19) \pi^* + 0.22 (\pm 0.15) \beta + 0.11 (\pm 0.15) \alpha \quad (4)$$

$$R^2 = 0.8775; \quad sd = 0.24; \quad n = 18; \quad \psi = 0.24$$

$$\log k_2 = -3.78 + 1.68 (\pm 0.18) \pi^* + 0.18 (\pm 0.14) \beta \quad (5)$$

$$R^2 = 0.8724; \quad sd = 0.17; \quad n = 18; \quad \psi = 0.38$$

$$\log k_2 = -3.75 + 1.72 (\pm 0.17) \pi^* \quad (6)$$

$$r^2 = 0.8591; \quad sd = 0.17; \quad n = 18; \quad \psi = 0.39$$

$$\log k_2 = -2.81 + 0.48 (\pm 0.36) \beta \quad (7)$$

$$r^2 = 0.0992; \quad sd = 0.44; \quad n = 18; \quad \psi = 0.98$$

In these equations n represents the data points and ψ is the Exner's mathematical value¹⁷.

Here 88% of data is explained by the tri-parametric equation of Kamlet¹⁶, whereas per the Exner¹⁷ this correlation is not good the mail role is played by solvent polarity, which explains almost 86% of the data point. Alpha and Beeta are not playing any significant rirole in it.

Therefore, the results are subjected to analyses by another model of cation and anion solvating concept are given by Swain's¹⁸ (8).

$$\log k_2 = aA + bB + C \quad (8)$$

In this equation

A is represented by anion-solvating power of the solvent

B the cation-solvating power.

C is the intercept term.

(A + B) is represented the solvent polarity.

As per the relation above, rates of oxidation are subjected to analyses with A, B separately and with A+B also.

$$\log k_2 = 0.68(\pm 0.05) A + 1.71 (\pm 0.03) B - 3.95 \quad (9)$$

$$R^2 = 0.9942; \text{ sd} = 0.04; n = 19; \psi = 0.08$$

$$\log k_2 = 0.44 (\pm 0.56) A - 2.78 \quad (10)$$

$$r^2 = 0.0343; \text{ sd} = 0.46; n = 19; \psi = 1.01$$

$$\log k_2 = 1.66 (\pm 0.12) B - 3.73 \quad (11)$$

$$r^2 = 0.9123; \text{ sd} = 0.14; n = 19; \psi = 0.30$$

$$\log k_2 = 1.37 \pm 0.13 (A + B) - 3.92 \quad (12)$$

$$r^2 = 0.8598; \text{ sd} = 0.17; n = 19; \psi = 0.38$$

Oxidation rates of 2-propanol are showing a very good correlation with Swain's model of solvent effect. Actually, cation solvating effect alone is explaining 91% of its results, which indicates that a major role is played by the cation solvating effect. Cation solvating effect is showing negligible influence. Solvent polarity is also playing its role and explains 86% of the results. Because of this specialty of solvent polarity, it was correlated with the relative permittivity of the medium. Though the graph plotted between rate and permittivity is non-linear. ($r^2 = 0.5541$; $\text{sd} = 0.31$; $\psi = 0.69$).

Reactivity and Correlation Analysis

There is no considerable co-relation is observed neither as a single parameter with Taft's¹⁹ σ^* and E_s data as shown in relation 13 and 14.

$$\log k_2 = -1.73 (\pm 0.16) \Sigma \sigma^* - 2.25 \quad (13)$$

$$r^2 = 0.9515; \text{ sd} = 0.19; n = 8; \psi = 0.24; T = 298 \text{ K}$$

$$\log k_2 = -1.32 (\pm 0.96) \Sigma E_s - 2.88 \quad (14)$$

$$r^2 = 0.2395; \text{ sd} = 0.74; n = 8; \psi = 0.93; T = 298 \text{ K}$$

Therefore, these rates are subjected to analyze with DSP equation of Pavelich-Taft's²⁰ (15).

$$\log k = \rho^* \Sigma \sigma^* + \delta \Sigma E_s + \log k_0 \quad (15)$$

Data for the substituent constant is available in the literature²⁰. It is observed that reaction constants are being negative and the correlation is also very good. Further σ^* and E_s are not having any linearity with the substituents under study.

Presence of negative $-\rho^*$ is the indication of a carbon center in slow step, which is lacking in electron density. Further, the negative values of $-\delta$ is showing that some steric acceleration is there in the reaction. It's because high ground state energy is available in highly crowded reactants. It was observed that crowding is not available neither in transition state nor in the ketone, product. Transition state energies are not having much difference therefore, steric acceleration is there. Fast rates of phenyl alcohols and benz-hydrol are because of the stabilization of electron less carbon center in the transition state created by phenyl group due to resonance effect.

Mechanistic Pathways

A large amount of kinetic isotope effect indicated the breaking of alpha C-H bond in the slow step. Substantial negative reaction constant (Polar) along with large kinetic isotope influence, is the signal of

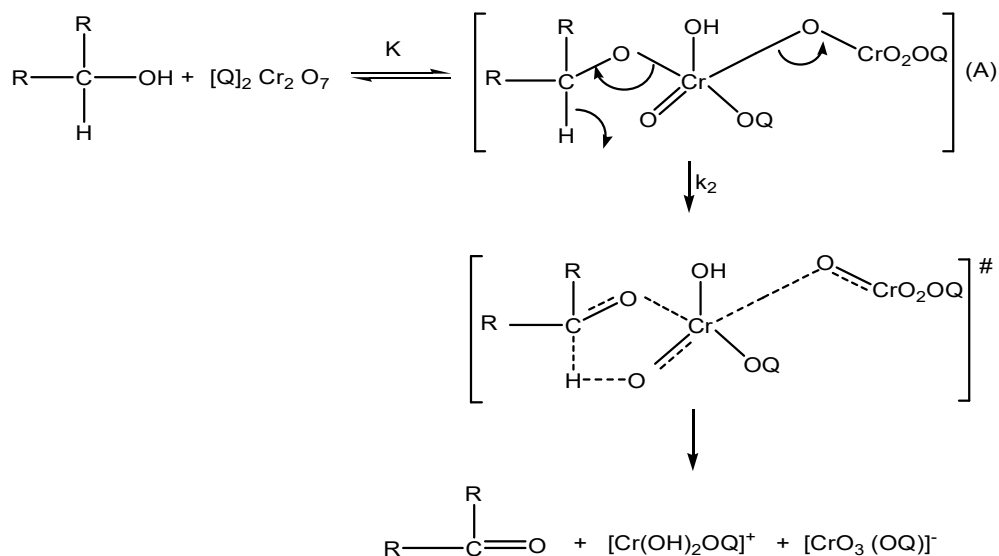
having a carbon center move towards to positive. Therefore, a transfer of hydride ion mechanistic pathway controlled by cation solvating powers of medium is postulated.

These reactions can continue either of the two path ways. One is a reaction that is bimolecular but acyclic. The second may engage a chromate ester transition state but cyclic. Kwart and Nickle²¹ resolved this problem by studying a dependence of isotope influence on the temperature of the reaction.

The results so observed for protio and duterio secondary alcohols are fit into the formula $k_H/k_D = A_H/A_D \exp(E_a/RT)$, which shows the corresponding property for transition state²²⁻²³, which is symmetrical, here the difference in activation energies k_H over k_D is zero energy difference for C-H and C-D bonds, which is almost equal to 4.5 kJ/mol; and these reactions are having almost the same frequency energy disparity in activation entropies. It has already been reported by Boardwell²⁴ that no one-step bimolecular process is not there in these reactions which having hydrogen transfer. It's obvious in this reaction also that hydrogen transfer through acyclic is not taking place.

The involvement of a linear hydrogen transfer²⁵ mechanism is significantly evidenced in concerted sigmatropic reactions. Similar evidence are provided by Littler²⁶ also, where the oxidation of alcohols by chromium six species is involving six electrons and forms a Huckel like structure which is evidenced which is permitted one process. Therefore, we propose that the ester intermediate is forming in the fast reaction step which is going to decompose in the rate-determining step through a symmetrical cyclic and planner transition state going to provide the product. On the basis of these mechanistic steps, we propose the following Schemes-1 and 2.

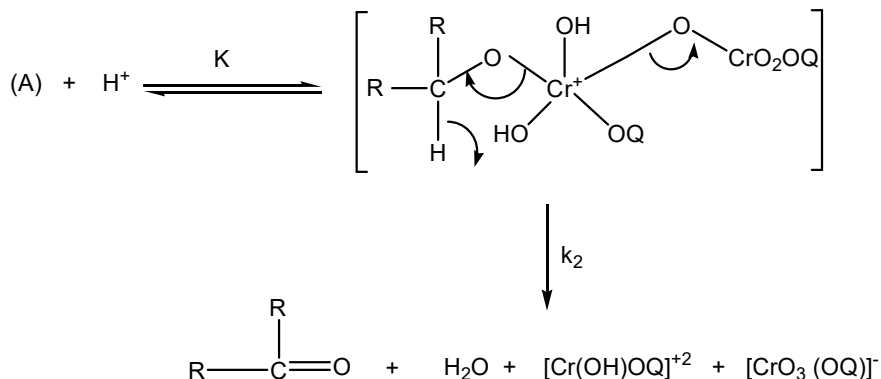
The proposed mechanism is also supported by the presence of -ve data values activation of entropies. Transition state is highly charged because of the transfer and the ends are hugely solvated. Therefore, a high quantity of solvent molecules is immobilized is resulting in a decrease in the entropy²⁷ values.



Acid-independent Path - Scheme - 1

Table-6: Dependency of Reaction Constants on Temperature

Temperature	$-\rho^*$	$-\delta$	r^2	Sd	ψ
288K	1.73±0.02	0.69±0.01	0.9999	0.003	0.02
298K	1.62±0.01	0.62±0.01	0.9998	0.012	0.02
308K	1.53±0.02	0.54±0.01	0.9989	0.006	0.04
318K	1.43±0.01	0.46±0.02	0.9999	0.006	0.01



Acid-dependent Path - Scheme - 2

CONCLUSION

In the present article, it is projected that reaction is proceeding through a hydride ion transfer mechanism through reductant to the oxidant via a chromate ester in the rate-determining step. An alpha C - H bond is a broken slow step. The reactive oxidizing species is QDC (both protonated and unprotonated).

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