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Kinetics and Mechanism of the Oxidation of Some α-Hydroxy Acids by Pyridinium Dichromate

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ABSTRACT

The oxidation of glycolic, lactic, and malic and a few substituted mandelic acids by pyridinium dichromate (PDC) in dimethylsulphoxide (DMSO) lead to the formation of corresponding oxoacids. The reaction is first order each in PDC. Michaelis-Menten type of kinetics is observed with respect to the hydroxy acids. Reaction is failed to induce the polymerisation of acrylonitrile. The oxidation of α-deuteriomandelic acid shows the presence of a primary kinetic isotope effect (k_H/k_D = 5.79 at 298 K). The reaction does not exhibit the solvent isotope effect. The reaction is catalysed by the hydrogen ions. The hydrogen ion dependence has the form: $k_{obs} = a + b [H^+]$. Oxidation of p-methyl mandelic acid has been studied in 19 different organic solvents. The solvent effect has been analysed by using Kamlet's and Swain's multiparametric equations. A mechanism involving a hydride ion transfer via a chromate ester is proposed.

Keywords: Correlation analysis, dichromate, hydroxy acids, kinetics, mechanism, oxidation.

INTRODUCTION

Mild and selective oxidation of organic compounds under non-aqueous conditions is an important reaction in synthetic organic chemistry. For this a number of different chromium (VI) derivatives have been reported [1-4]. Pyridinium dichromate (PDC) is also one such compound used for the oxidation of aliphatic primary, secondary alcohols and aldehydes also [5]. We have been interested in the kinetic and mechanistic aspects of the oxidation by complexed Cr (VI) species and a few studies have already been reported [6-10]. The report on the oxidation of hydroxy acids by PDC is not available, therefore, it was of interest to investigate the kinetics of the oxidation of some α-hydroxy acids by PDC in DMSO. A suitable mechanism has also been postulated.

MATERIALS AND METHODS

Materials: The hydroxy acids were commercial products of the highest purity available and were used as such. The preparation and specification of the substituted mandelic acids have been described earlier [11]. PDC was prepared by reported method[5] and its purity was checked by an iodometric method. α-Deuteriomandelic acid (PhCD (OH) COOH or DMA) was prepared by the method of Kemp and Waters

[12]. Its isotopic purity, ascertained by NMR spectra, was 95 ± 4%. Due the non-aqueous nature of the solvent, toluene p-sulphonic acid (TsOH) was used as a source of hydrogen ions. Solvents were purified by their usual methods [13].

Product analysis: Product analyses were carried out under kinetic conditions i.e., with an excess of the reductant over PDC. In a typical experiment mandelic acid (7.6 g, 0.05mol) and PDC (3.76 g, 0.01mol) were dissolved in 100 ml of DMSO and was allowed to stand in dark for ≈ 24 h to ensure the completion of the reaction. It was then treated with an excess (250 ml) of a freshly prepared saturated solution of 2,4-dinitrophenylhydrazine in 2 mol dm^{-3} HCl and kept overnight in a refrigerator. The precipitated 2,4-dinitrophenyl-hydrozone (DNP) was filtered off, dried, weighed, recrystallised from ethanol and weighed again. The product was identical (mp and mixed mp) to an authentic sample of DNP of phenylglyoxylic acid. Similar experiments with the other hydroxy acids yielded the DNP of the corresponding oxoacids in 78 to 90% yields, after recrystallization. The oxidation state of chromium in completely reduced reaction mixtures, determined by an Iodometric method, was 3.90 ± 0.10.

Kinetic measurements: The pseudo-first order conditions were attained by keeping a large excess (× 15 or greater) of the hydroxy acid over PDC. The temperature was kept constant to ±0.1 K. The solvent was DMSO, unless specified otherwise. The reactions were followed by monitoring the decrease in the concentration of PDC spectrophotometrically at 350 nm for up to 80% of the reaction. No other reactant or product has any significant absorption at this wavelength. The pseudo-first order rate constants, k_{obs}, were computed from the linear least square plots of log [PDC] versus time. Duplicate kinetic runs showed that the rates were reproducible within ±3%. The second order rate constants, k_2, were calculated from the relation: $k_2 = k_{obs}$/[hydroxy acid]. All experiments, other than those for studying the effect of hydrogen ions, were carried out in the absence of TsOH.

RESULTS AND DISCUSSION

The rate and other experimental data were obtained for all the hydroxy acids studied. Since the results were similar, only representative data are reproduced here.

Stoichiometry: The oxidation of hydroxy acids resulted in the formation of the corresponding oxoacids. Product analysis and stoichiometric determinations indicated that the overall reaction could be written as below (1).

$$ArCH(OH)COOH + Cr_2O_7^{-2} + 12H^+ \longrightarrow ArCOCOOH + 7H_2O + 2Cr^{+3} \quad (1)$$

Rate Laws: The reactions are of first order with respect to PDC. Figure1 depict a typical kinetic run. Further, the pseudo-first order rate constant, k_{obs} is independent of the initial concentration of IFC. The reaction rate increases with increase in the concentration of the hydroxy acid but not linearly (Table 1). A plot of $1/k_{obs}$ against 1/[Hydroxy acid] is linear ($r > 0.995$) with an intercept on the rate-ordinate (Figure 2). Thus, Michaelis-Menten type kinetics are observed with respect to the hydroxy acid. This leads to the postulation of following overall mechanism (2) and (3) and rate law (4).

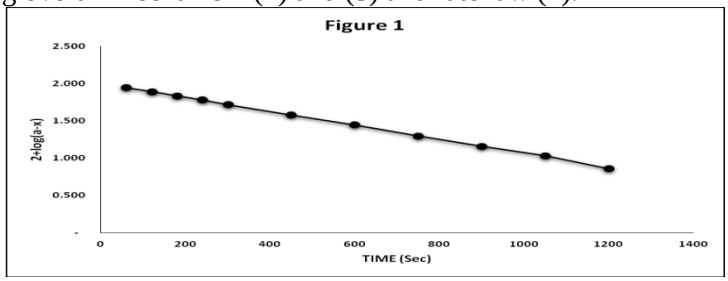


Figure 1. Oxidation of Mandelic by PDC: A typical Kinetic Run

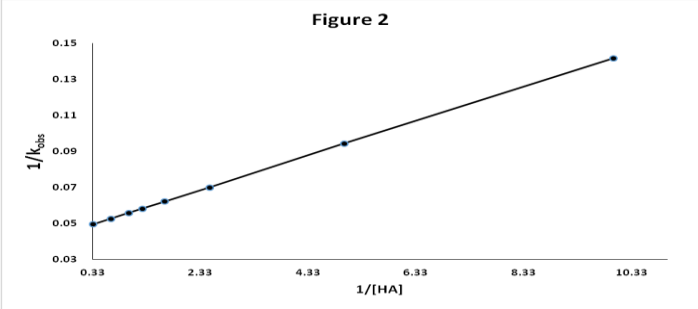


Figure 2. Oxidation of hydroxy acids by PDC: A double reciprocal plot

Table 1. Rate constants for the oxidation of mandelic acid by PDC at 308 K

10^3 [PDC] / mol dm^{-3}	[HA] / mol dm^{-3}	10^4 k_{obs} / s^{-1}
1.00	0.10	7.06
1.00	0.20	10.6
1.00	0.40	14.3
1.00	0.60	16.1
1.00	0.80	17.2
1.00	1.00	17.9
1.00	1.50	19.0
1.00	3.00	20.2
2.00	0.20	11.7
4.00	0.20	10.1
6.00	0.20	11.1
8.00	0.20	9.98
1.00	0.40	15.3[*]

[a] contained 0.001 M acrylonitrile

$$\text{Hydroxy Acid} + \text{PDC} \overset{K}{\leftrightarrows} [\text{complex}] \quad (2)$$

$$[\text{complex}] \xrightarrow{k_2} \text{Products} \quad (3)$$

$$\text{Rate} = k_2 K [\text{HA}] [\text{PDC}] / (1 + K [\text{HA}]) \quad (4)$$

The dependence of reaction rate on the reductant concentration was studied at different temperatures and the values of K and k_2 were evaluated from the double reciprocal plots. The thermodynamic parameters of the complex formation and activation parameters of the decomposition of the complexes were calculated from the values of K and k_2 respectively at different temperatures (Tables 3 and 4).

Table 3: Formation constants for the decomposition of PDC−hydroxy acid complexes and thermodynamic parameters

R	K / (dm^3 mol^{-1}) 288 K	298 K	308 K	318 K	$-\Delta H^*$ (kJ mol^{-1})	$-\Delta S^*$ (J $mol^{-1}K^{-1}$)	$-\Delta G^*$ (kJ mol^{-1})
H	6.50	5.71	4.86	4.05	14.5±0.6	26±2	6.76±0.5
p-F	5.88	5.05	4.25	3.42	16.1±0.7	33±2	6.46±0.6

p-Cl	5.72	4.90	4.14	3.26	16.6±0.9	35±3	6.39±0.7
p-Br	6.03	5.24	4.41	3.60	15.5±0.7	31±2	6.55±0.5
p-Me	6.57	5.75	4.93	4.15	14.1±0.5	25±1	6.79±0.4
p-Pr^i	5.77	4.95	4.13	3.35	16.2±0.6	34±2	6.41±0.5
p-OMe	5.58	4.75	3.95	3.13	17.0±0.8	37±2	6.31±0.6
m-Cl	6.39	5.55	4.73	3.98	14.5±0.4	27±1	6.71±0.3
m-NO_2	6.30	5.47	4.67	3.87	14.8±0.5	28±2	6.67±0.4
p-NO_2	6.12	5.33	4.52	3.71	15.1±0.6	29±2	6.59±0.5
GA	5.94	5.15	4.33	3.52	15.7±0.7	31±2	6.50±0.5
LA	5.85	5.03	4.26	3.40	16.1±0.8	33±3	6.45±0.6
MLA	6.01	5.22	4.40	3.56	15.7±0.7	31±2	6.54±0.6
DMA	6.45	5.67	4.85	4.05	14.3±0.6	26±2	6.75±0.4

Induced polymerisation of acrylonitrile: The oxidation of hydroxy acids, by PDC, in an atmosphere of nitrogen failed to induce the polymerisation of acrylonitrile. Further, addition of acrylonitrile had no effect on the rate (Table 1). We further confirm the absence of free radicals in the reaction pathway, the reaction was carried out in the presence of 0.05 mol dm^{-3} of 2,6-di-t-butyl-4-methylphenol (butylated hydroxytoluene or BHT). It was observed that BHT was recovered unchanged, almost quantitatively.

Effect of acidity: Reaction is catalysed by hydrogen ions. p– Toluene sulphonic acid (TsOH) was used as a source of hydrogen ions. The hydrogen ion dependence has the following form (Table 2).

$$k_{obs} = a + b[H^+] \quad (5)$$

The values of a and b, for p-methyl mandelic acid, are $6.59\pm0.19\times10^{-4}$ s^{-1} and $12.1\pm0.32\times10^{-4}$ mol^{-1} dm^3 s^{-1} respectively ($r^2 = 0.9973$).

Table 2. Effect of hydrogen ion concentration on the oxidation of mandelic acid by PDC

[PDC] = 0.001 mol dm^{-3};	[HA] = 1.0 mol dm^{-3};				Temp. = 298 K	
$[H^+]$/mol dm^{-3}	0.10	0.20	0.40	0.60	0.80	1.00
10^4 k_{obs}/s^{-1}	7.83	9.00	11.7	13.5	16.2	18.9

Kinetic isotope effect: To ascertain the importance of the cleavage of the C-H bond in the rate-determining step, the oxidation of α-deuteriomandelic acid (DMA) was studied. Results showed the presence of a substantial primary kinetic isotope effect (Table 4). The value of k_H/k_D is 5.79 at 298 K.

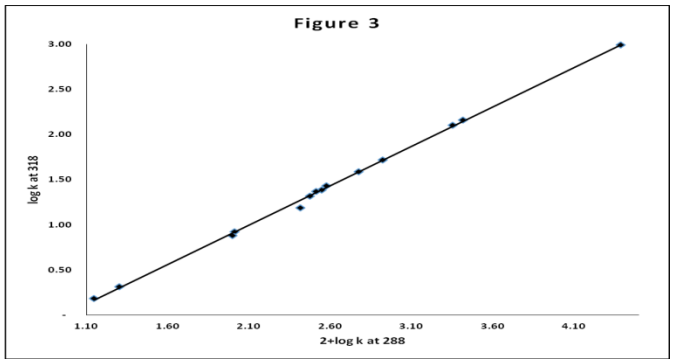


Figure 3. Exner's Isokinetic Relationship in the oxidation of Hydroxyacids by PDCC

Table 4. Rate constants and activation parameters for the oxidation of hydroxy acid by PDC

R	$10^4 k_2$ / (dm^3 mol^{-1} s^{-1})				ΔH^*	$-\Delta S^*$	ΔG^*
	288 K	298 K	308 K	318 K	(kJ mol^{-1})	(J $mol^{-1}K^{-1}$)	(kJ mol^{-1})
H	5.94	11.7	21.6	38.7	45.0±0.1	151±1	89.8±0.1
p-F	8.37	16.2	29.7	52.2	43.9±0.2	152±1	88.9±0.1
p-Cl	3.51	47.11	13.5	24.3	46.6±0.2	150±1	91.0±0.2
p-Br	2.97	5.94	11.7	20.7	47.0±0.4	149±1	91.4±0.3
p-Me	26.1	48.6	83.7	144	40.6±0.3	154±1	86.3±0.2
p-Pr^i	22.5	41.4	73.8	126	41.2±0.1	153±1	86.6±0.1
p-OMe	143	405	648	981	33.0±0.3	162±1	81.0±0.3
m-Cl	1.02	2.16	4.32	8.37	50.8±0.1	145±1	93.9±0.1
m-NO_2	0.20	0.45	0.99	2.07	56.8±0.3	138±1	97.8±0.2
p-NO_2	0.14	0.36	0.73	1.53	57.0±1.0	138±4	98.5±1.0
GA	2.61	4.68	8.37	15.3	42.3±0.8	167±3	92.0±0.6
LA	3.78	7.29	14.4	27.0	47.5±0.5	146±2	90.8±0.4
MLA	3.24	6.30	12.6	23.4	47.9±0.5	146±2	91.2±0.4
DMA	0.99	2.02	4.01	7.58	49.2±0.1	151±1	94.1±0.1
k_H/k_D	6.00	5.79	5.39	5.11			

Effect of solvents: The rate of oxidation of mandelic acid was determined in nineteen different organic solvents. The choice of the solvents was limited by the solubility of PDC and reaction with primary and secondary alcohols. There was no noticeable reaction with the solvents chosen. The kinetics was similar in all the solvents. The values of k_2 at 298 K are recorded in Table 5.

Table 5. Effect of solvents on the oxidation of mandelic acid by PDC at 298 K

Solvents	K (dm^{-3} mol^{-1})	10^5 k_{obs} (s^{-1})	Solvents	K (dm^{-3} mol^{-1})	10^5 k_{obs} (s^{-1})
Chloroform	6.03	41.7	Toluene	4.89	14.8
1,2-Dichloroethane	5.85	51.3	Acetophenone	4.90	50.1
Dichloromethane	6.12	39.8	THF	5.31	24.5
DMSO	4.41	117	t-Butylalcohol	5.67	15.8
Acetone	4.65	43.6	1,4-Dioxane	4.95	22.4
DMF	5.72	61.6	1,2-Dimethoxyethane	5.77	12.6
Butanone	5.55	34.7	CS_2	4.86	7.08
Nitrobenzene	5.80	47.9	Acetic Acid	4.69	7.94
Benzene	6.01	18.2	Ethyl Acetate	5.87	19.5
Cyclohexane	6.39	2.29			

Table 6. Temperature dependence of the reaction constant

Temp./ K	$-\rho^*$	r^2	Sd	ψ
288	2.07±0.01	0.9999	0.006	0.02
298	1.97±0.01	0.9998	0.011	0.01

308	1.89±0.01	0.9999	0.005	0.01
318	1.80±0.02	0.9989	0.005	0.03

The entropy and enthalpy of activation of the oxidation of ten substituted mendalic acids are linearly related (r^2 = 0.9948), indicating the operation of compensation effect in this reaction [14]. The value of isokinetic temperature evaluated [15, 16] from this plot is 1011±36 K. The correlation was tested and found genuine by Exner's' criterion [17]. The isokinetic temperature, calculated from Exner's plot of log k_2 at 288 K *versus* log k_2 at 318 K (r^2 = 0.9998) is 1024±151 K. A linear isokinetic relationship is necessary condition for the validity of linear free energy relationship, which suggests that all the hydroxy acids are oxidised by the same mechanism.

Solvent effect: The rate constants of oxidation, k_2, in eighteen solvents (CS_2 was not considered, as the complete range of solvent parameters was not available) were correlated in terms of the linear solvation energy relationship (6) of Kamlet *et al.*[18].

$$\log k_2 = A_0 + p\pi^* + b\beta + a\alpha \quad (6)$$

In this equation π^* represents the solvent polarity, β the hydrogen bond acceptor basicities and α is the hydrogen bond donor acidity. A_0 is the intercept term. It may be mentioned here that out of the 18 solvents, 12 have a value of zero forα. The results of correlation analyses in terms of (6), a biparametric equation involving π^* and β, and separately with π^* and β are given-

$$\log k_2 = -3.52 + (1.39 \pm 0.19)\pi^* + (0.12 \pm 0.16)\beta - (0.17 \pm 0.15)\alpha \quad (7)$$
$$R^2 = 0.8355;\ sd = 0.17;\ n = 18;\ \Psi = 0.48$$
$$\log k_2 = -3.56 + (1.45 \pm 0.18)\pi^* + (0.07 \pm 0.15)\beta \quad (8)$$
$$R^2 = 0.8203;\ sd = 0.17;\ n = 18;\ \Psi = 0.45$$
$$\log k_2 = -3.55 + (1.47 \pm 0.17)\pi^* \quad (9)$$
$$r^2 = 0.8179;\ sd = 0.17;\ n = 18;\ \Psi = 0.44$$
$$\log k_2 = -2.72 + (0.33 \pm 0.32)\beta \quad (10)C$$
$$r^2 = 0.0603;\ sd = 0.39;\ n = 18;\ \Psi = 0.99$$

Where *n* is the number of data points and Ψ is the Exner's statistical parameter [19].

Kamlet's [18] triparametric equation explains *ca.* 84% of the effect of solvent on the oxidation. However, by Exner's criterion the correlation is not even satisfactory (cf. 7). The major contribution is of solvent polarity. It alone accounted for *ca.* 82% of the data. Both β and α play relatively minor roles.

The data on the solvent effect were analysed in terms of Swain's equation [20] of cation- and anion-solvating concept of the solvents also (11).

$$\log k_2 = aA + bB + C \quad (11)$$

Here A and B represent the anion-solvating and cation-solvating power. C is the intercept term. (A + B) is postulated to represent the solvent polarity. The rates in different solvents were analysed in terms of (11), separately with A and B and with (A + B).

$$\log k_2 = (0.47 \pm 0.03)A + (1.74 \pm 0.02)B - 3.77 \quad (12)$$
$$R^2 = 0.9974;\ sd = 0.02;\ n = 19;\ \Psi = 0.05$$
$$\log k_2 = 0.25(\pm 0.50)A - 2.69 \quad (13)$$
$$r^2 = 0.0144;\ sd = 0.41;\ n = 19;\ \Psi = 1.02$$
$$\log k_2 = 1.49\ (\pm 0.09)B - 3.59 \quad (14)$$

$$\begin{aligned} r^2 &= 0.9438;\ \text{sd} = 0.10;\ n = 19;\quad \Psi = 0.24 \\ \log k_2 &= 1.17\pm0.14\,(\text{A} + \text{B}) - 3.71 \\ r^2 &= 0.8109;\ \text{sd} = 0.18;\ n = 19;\quad \Psi = 0.45 \end{aligned} \qquad (15)$$

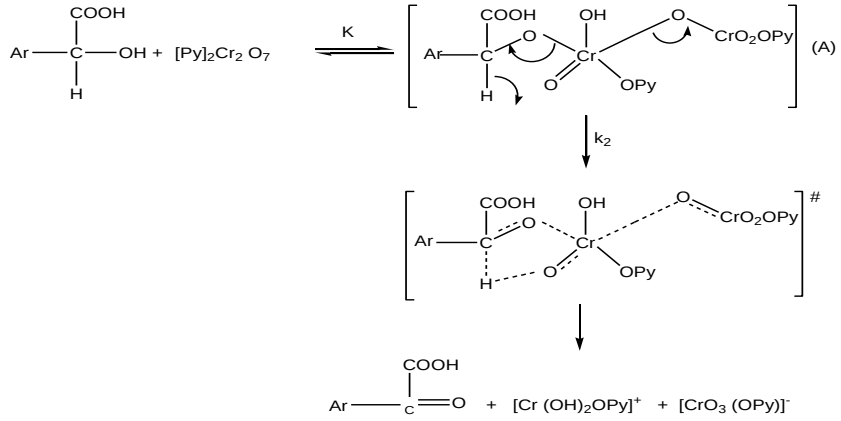
The rates of oxidation of mandelic acid in different solvents showed an excellent correlation in Swain's equation (cf. 12) with the cation-solvating power playing the major role. In fact, the cation-solvation alone accounts for *ca* 99% of the data. The correlation with the anion-solvating power was very poor. The solvent polarity, represented by (A + B), also accounted for *ca.* 81 % of the data. In view of the fact that solvent polarity is able to account for *ca.* 81 % of the data, an attempt was made to correlate the rate with the relative permittivity of the solvent. However, a plot of log k_2 against the inverse of the relative permittivity is not linear (r^2 = 0.4949; sd = 0.29; Ψ = 0.73).

Correlation analysis of reactivity: The reaction rates of hydroxy acids were correlated with Hammett's σ values but did not yield very significant correlation. Though the rates of oxidation of substituted mendalic acids correlated well with Brown's σ^+ values [21], the reaction constant is being negative (Table 5). The large negative reaction constants and correlation with σ^+ values indicate a carbocationic reaction centre in the transition state.

Mechanism: Absence of any effect of added acrylonitrile on the reaction discounts the possibility of a one-electron oxidation, leading to the formation of free radicals. The presence of a substantial kinetic isotope effect in the oxidation of mandelic acid confirms the cleavage of the α-C-H bond in the rate-determining step. The large negative reaction constant (–2.08 at 298 K) together with the excellent correlation with Brown's σ^+ values [21] point to a highly electron-deficient carbon centre in the transition state. The transition state thus approaches a carbocation in character. This is supported by the solvent effect also. Greater role played by the cation-solvating power of the solvents supported the postulation of a carbocationic transition state. Therefore, the correlation analysis of substituent and solvent effects on the oxidation of mandelic acid supports the mechanism involving a hydride-ion transfer via a chromate ester.
Kwart and Nickle [22] have shown that a study of the dependence of the kinetic isotope effect on temperature can be gainfully employed to resolve this problem. The data for protio- and deuteriomandelic acids, fitted to the familiar expression $k_H/k_D = A_H/A_D \exp(E_a/RT)$ [23,24] show a direct correspondence with the properties of a symmetrical transition state in which the activation energy difference (E_a) for k_H/k_D is equal to the zero-point energy difference for the respective C-H and C-D bonds (≈ 4.5 kJ/mol) and the frequency factors and the entropies of activation of the respective reactions are nearly equal.

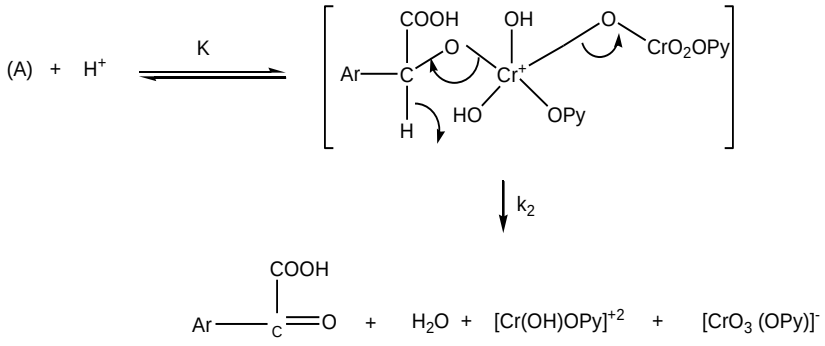
Bordwell[25] has documented a very cogent evidence against the occurrence of concerted one-step biomolecular processes by hydrogen transfer and it is evident that in the present studies also the hydrogen transfer does not occur by an acyclic biomolecular process. It is well established that intrinsically concerted sigmatropic reactions, characterized by transfer of hydrogen in a cyclic transition state, are the only truly symmetrical processes involving a linear hydrogen transfer [26]. Littler [27] has also shown that a cyclic hydride transfer, in the oxidation of alcohols by Cr(VI), involves six electrons and, being a Huckel-type system, is an allowed process. Thus the overall mechanism is proposed to involve the formation of a chromate ester in a fast pre-equilibrium and then a decomposition of the ester in a subsequent slow step via a cyclic concerted symmetrical transition state leading to the product (Scheme 1and 2). The observed negative value of entropy of activation also supports a polar transition state.
The observed negative entropy of activation also supports it. As the charge separation takes place, the charged ends become highly solvated. This results in an immobilization of a large number of solvent molecules, reflected in the loss of entropy [28].

Acid-independent Path (Scheme -1)



Scheme-1

Acid-dependent Path (Scheme - 2)



Scheme 2

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