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Oxidation of Aliphatic Primary Alcohols by Pyridinium Dichromate: A Kinetic and Mechanistic Study

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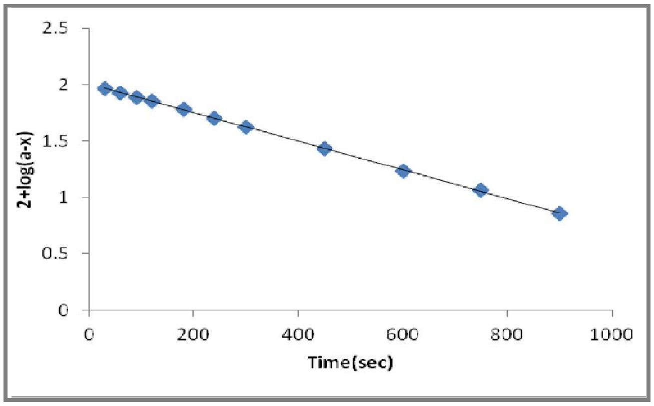
ABSTRACT

The oxidation of nine aliphatic primary alcohols by pyridinium dichromate (PDC) in dimethylsulphoxide leads to the formation of corresponding aldehydes. The reaction is first order with respect to PDC. Michaelis-Menten type kinetics is observed with respect to alcohols. The reaction is promoted by hydrogen ions; the hydrogen ion dependence has the form $k_{obs} = a + b\,[H^+]$*. The oxidation of* $[1, 1\text{-}^2H_2]$ *ethanol (*$MeCD_2OH$*) exhibits a substantial primary kinetic isotope effect (*$k_H/k_D = 5.67$ *at 298K). The reaction has been studied in nineteen different organic solvents. The solvent effect was analysed using Taft's and Swain's multiparametric equations. The rate of oxidation is susceptible to both polar and steric effects of the substituents. A suitable mechanism has been proposed.*

Graphical Abstract



Oxidation of Ethyl alcohol by PDC: A typical Kinetic Run.

Keywords: Alcohols, dichromate, pyridinium, kinetics, mechanism, oxidation.

INTRODUCTION

Salts of Cr(VI) have long been used as oxidizing reagents in synthetic organic chemistry. However, these salts are drastic and non-selective oxidants in nature. Further, they are insoluble in most of the organic solvents also. Thus miscibility is a problem. To overcome these limitations, a large number of organic derivatives of Cr(VI) have been prepared and used in synthetic organic syntheses as mild and selective oxidants in non-aqueous solvents [**1-4**]. One such compound is pyridinium dichromate (PDC) [**5**] used for the oxidation of alcohols to carbonyl compounds. It is known that the mode of oxidation depends on the nature of the counter-ion attached to the chromium anion. We have been interested in kinetic and mechanistic aspects of oxidation by complexed Cr(VI) species and several reports, by dichromates have already been reported [**6-10**]. Therefore, in continuation of our earlier work, we report here the kinetics and mechanism of oxidation of nine aliphatic primary alcohols by PDC in dimethylsulphoxide (DMSO) as solvent. The mechanistic aspects are discussed. The main aims of the present investigation are to (i) determine kinetic parameters and to evaluate the rate laws, (ii) to study the correlation analysis of effect of structure on reactivity and (iii) to postulate a suitable mechanism for the oxidation process.

MATERIALS AND METHODS

PDC was prepared by the reported method[5] and its purity was checked by an iodometric method. The procedures used for the purification of alcohols have been described earlier [**11**]. [1, 1-$^2H_2$]Ethanol ($MeCD_2OH$) was prepared by Kalpan's method [**12**]. Its isotopic purity, as ascertained by its NMR spectra, was 96±3%. Due to the non-aqueous nature of the medium, p-toluenesulphonic acid (TsOH) was used as a source of hydrogen ions. TsOH is a strong acid and in a polar medium like DMSO it is likely to be completely ionised. Solvents were purified by the usual method [**13**].

Product analysis: The product analysis was carried out under kinetic conditions. In a typical experiment, 2-propanol (0.05 mol) and PDC (3.76 g, 0.01 mol) were made up to 50 cm^3 in DMSO and kept in dark for *ca.* 15 hr to ensure the completion of the reaction. The solution was then treated with an excess (200 cm^3) of a saturated solution of 2, 4-dinitrophenylhydrazine in 2 mol dm^{-3} HCl and kept overnight in a refrigerator. The precipitated 2, 4-dinitrophenyl-hydrazone (DNP) was filtered off, dried, weighed, recrystallized from ethanol and weighed again. The yield of DNP before and after recrystallization was 1.90 g (87%) and 1.88 g (83%), respectively. The DNP was found identical (m.p. and mixed m.p.) with the DNP of acetaldehyde. Similar experiments with other alcohols led to the formation of DNP of the corresponding carbonyl compounds in yields ranging from 72 to 87%, after recrystallization. Iodometric determinations of the oxidation state of chromium in completely reduced reaction mixtures indicated that the oxidation state of the reduced chromium species was 3.90±0.10.

Kinetic Measurements: The reactions were followed under pseudo-first-order conditions by keeping a large excess (× 15 or greater) of the alcohol 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 361 nm for 80% of the reaction. The pseudo-first-order rate constants, k_{obs}, were evaluated from the linear ($r = 0.990 - 0.999$) plots of log [PDC] against time. Duplicate kinetic runs showed that the rate constants were reproducible to within ±3%. The second order rate constant, k_2, was evaluated from the relation $k_2=k_{obs}\,[\text{alcohol}]^{-1}$. Simple and multivariate linear regression analyses were carried out by the least-squares method on a personal computer.

RESULTS AND DISCUSSION

Stoichiometry: The oxidation of alcohols results in the formation of corresponding aldehydes. The overall reaction may be represented as equation (1).

$$3\ RCH_2OH + Cr_2O_7^{-2} + 8H^+ \longrightarrow 3\ RCHO + 7\ H_2O + 2Cr^{+3} \qquad (1)$$

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

$$\text{Alcohol} + \text{PDC} \overset{K}{\leftrightarrows} [\text{complex}] \qquad (2)$$

$$[\text{Complex}] \xrightarrow{k_2} \text{Products} \qquad (3)$$

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

Table 1. Rate constants for the oxidation of ethanol by PDC at 298 K.

10^3 [IDC] mol dm^{-3}	[Ethanol] mol dm^{-3}	$10^4\ k_{obs}s^{-1}$
1.00	0.10	4.32
1.00	0.20	6.43
1.00	0.40	8.52
1.00	0.60	9.55
1.00	0.80	10.2
1.00	1.00	10.6
1.00	1.50	11.2
1.00	3.00	11.8
2.00	0.20	6.34
4.00	0.20	6.21
6.00	0.20	6.57
8.00	0.20	6.03
1.00	0.40	8.82*

* contained 0.001 M acrylonitrile

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 (Figure 2). 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 2 and 3).

Test for free radical/Induced Polymerization of Acrylonitrile: The oxidation of alcohols, in an atmosphere of nitrogen, failed to induce polymerization of acrylonitrile. Further, the addition of acrylonitrile did not affect the rate. This indicates that a one-electron oxidation, giving rise to free radicals, is unlikely in the present reaction (Table 1). To 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.

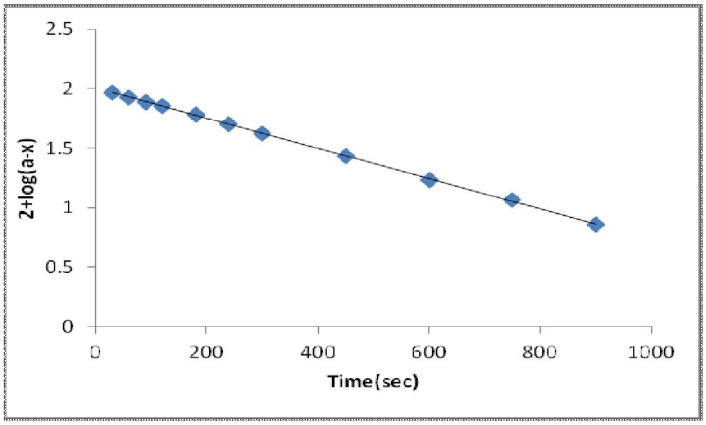


Figure 1. Oxidation of Ethyl alcohol by PDC: A typical Kinetic Run.

Table 2. Formation constants and thermodynamic parameters for the Alcohols – PDC complexes.

Alcohol	K ($dm^3 mol^{-1}$)				$-\Delta H^*$	$-\Delta S^*$	$-\Delta G^*$
	288 K	298 K	308 K	318 K	($kJ mol^{-1}$)	($J mol^{-1}K^{-1}$)	($kJ mol^{-1}$)
H	5.84	5.05	4.25	3.42	16.0±0.7	32±2	6.45±0.6
Me	6.10	5.22	4.50	3.67	15.2±0.6	29±2	6.57±0.5
Et	5.92	5.14	4.32	3.47	16.0±0.8	32±3	6.49±0.6
n-Pr	5.84	5.14	4.41	3.70	15.2±0.6	30±2	6.59±0.5
n-Bu	6.22	5.40	4.62	3.78	15.0±0.6	29±2	6.64±0.5
i-Pr	5.67	4.89	4.08	3.24	16.6±0.9	35±3	6.37±0.7
$ClCH_2$	5.50	4.68	3.87	3.05	17.4±0.8	38±3	6.26±0.6
$MeOCH_2$	5.75	4.95	4.14	3.35	16.1±0.7	33±2	6.41±0.5
t-Bu	5.94	5.15	4.30	3.55	15.6±0.6	31±2	6.50±0.5
$MeOCD_2OH$	5.89	5.04	4.23	3.42	16.2±0.6	33±2	6.46±0.5

Table 3. Rate constants and activation parameters for the Alcohols – PDC complexes.

Alcohol	$10^4 k_2 / (dm^3 mol^{-1} s^{-1})$				ΔH^*	$-\Delta S^*$	ΔG^*
	288 K	298 K	308 K	318 K	($kJ mol^{-1}$)	($J mol^{-1}K^{-1}$)	($kJ mol^{-1}$)
H	0.13	0.45	1.35	3.96	83.9±0.4	47±1	97.9±0.3
Me	5.67	12.6	28.8	61.2	58.1±0.6	106±2	89.5±0.5
Et	9.00	18.9	42.3	85.5	54.8±0.9	113±2	88.4±0.7
n-Pr	15.3	33.3	63.0	117	48.8±0.7	129±2	87.2±0.5
n-Bu	17.1	36.0	68.4	126	48.0±0.4	131±1	87.0±0.4
i-Pr	23.4	45.0	88.2	162	46.8±0.4	133±1	86.3±0.3
$ClCH_2$	0.18	0.54	1.44	3.69	74.0±0.3	79±1	97.4±0.2
$MeOCH_2$	1.17	2.88	7.20	16.2	64.5±0.5	97±2	93.1±0.4
t-Bu	207	315	495	720	29.4±0.4	175±1	81.5±0.3
$MeOCD_2OH$	0.94	2.22	5.33	12.0	62.3±0.6	106±2	93.8±0.5
k_H/k_D	6.03	5.67	5.40	5.10			

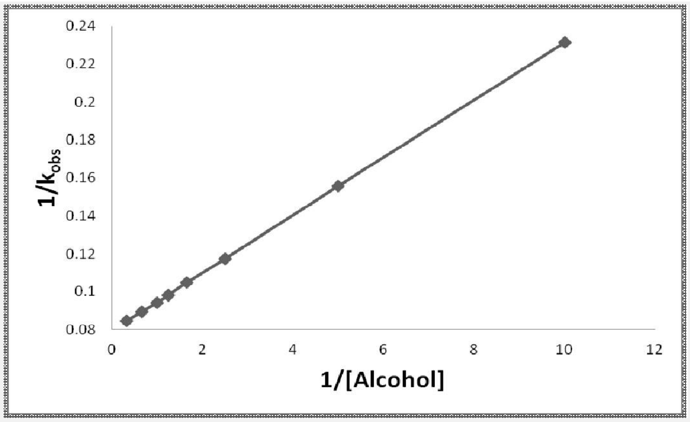


Figure 2. Oxidation of Alcohols by PDC: A double reciprocal plot.

Effect of Hydrogen Ions: The reaction is catalyzed by hydrogen ions (Table 4). The hydrogen-ion dependence has the following form equation (5). The values of *a* and *b*, for ethanol, are 3.97±0.13 × 10^{-4} s^{-1} and 7.55±0.21 ×10^{-4} mol^{-1} dm^3 s^{-1} respectively (r^2 = 0.9969).

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

Table 4. Dependence of the reaction rate on hydrogen–ion concentration.

[PDC] = 0.001 mol dm^{-3}; [Alcohol] = 0.10 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}	4.77	5.49	7.11	8.28	9.90	11.7

Kinetic Isotope Effect: To ascertain the importance of cleavage of the α–C–H bond in the rate-determining step, oxidation of [1, 1-$^2H_2$] ethanol was studied. The results showed the presence of a substantial primary kinetic isotope effect (Table 3).

Effect of Solvents: The oxidation of ethanol was studied in 19 different organic solvents. The choice of solvent was limited due to the solubility of PDC and its reaction with primary and secondary alcohols. There was no reaction with the solvents chosen. The kinetics was similar in all the solvents. The values of k_2 are recorded in table 5.

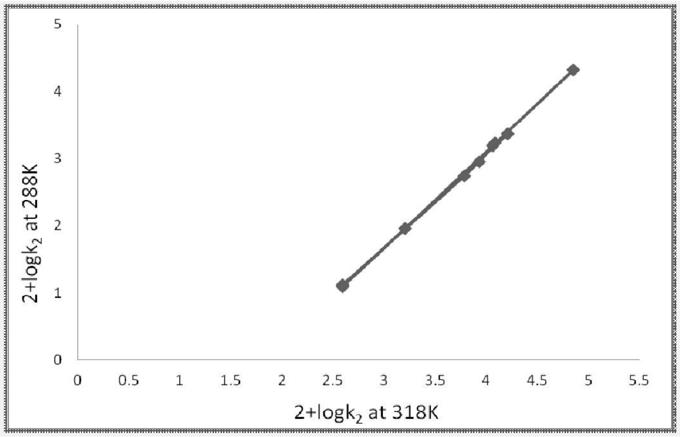
Table 5. Effect of solvents on the oxidation of alcohols by PDC at 298 K.

Solvents	K (dm^{-3} mol^{-1})	10^4 k_{obs} (s^{-1})	Solvents	K (dm^{-3} mol^{-1})	10^4 k_{obs} (s^{-1})
Chloroform	5.55	41.7	Toluene	4.99	12.0
1,2-Dichloroethane	5.63	47.9	Acetophenone	5.00	46.8
Dichloromethane	6.01	35.5	THF	5.15	20.9
DMSO	5.22	126	t-Butylalcohol	5.60	14.1
Acetone	5.79	39.8	1,4-Dioxane	5.81	20.9
DMF	5.91	57.8	1,2-Dimethoxyethane	5.45	10.2
Butanone	6.03	30.9	CS_2	6.00	4.68
Nitrobenzene	6.10	44.7	Acetic Acid	5.75	8.91
Benzene	5.66	14.8	Ethyl Acetate	5.85	13.5
Cyclohexane	5.89	1.29			

A satisfactory linear correlation (r=0.9925; temp. 441 ± 14) between the values the activation enthalpies and entropies of the oxidation of the nine aliphatic alcohols indicated the operation of compensation effect in this reaction [14]. The reaction also exhibited an excellent isokinetic effect, as determined by Exner's criterion [15]. An Exner's plot between log k_2 at 288K and at 318 K was linear (R= 0.9984; ψ = 0.09; slope = 0.7357 ± 0.0157) (Figure 3). The value of isokinetic temperature is 448±14 K. The linear isokinetic correlation implies that all the alcohols are oxidized by the same mechanism and the changes in rate are governed by the changes in both the enthalpy and entropy of the activation.

Solvent Effect: The rate constants of the oxidation, k_2, in eighteen solvents (CS_2 was not considered, as the complete range of solvent parameters was not available) did not yield any significant correlation in terms of the linear solvation energy relationship (LESR) of Kamlet and Taft [16] (6).

Figure 3. Exner's Isokinetic Relationship in the oxidation of Alcohols by PDC.



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

$$\log k_2 = -4.74 + 1.62\,(\pm 0.21)\,\pi^* + 0.12\,(\pm 0.17)\,\beta + 0.04\,(\pm 0.16)\,\alpha \qquad (7)$$
$$R^2 = 0.8404; \quad sd = 0.19; \quad n = 18; \quad \psi = 0.44$$

$$\log k_2 = -4.75 + 1.64\,(\pm 0.19)\,\pi^* + 0.11\,(\pm 0.16)\,\beta \qquad (8)$$
$$R^2 = 0.8397; \quad sd = 0.18; \quad n = 18; \quad \psi = 0.42$$

$$\log k_2 = -4.73 + 1.67\,(\pm 0.18)\,\pi^* \qquad (9)$$
$$R^2 = 0.8345; \quad sd = 0.18; \quad n = 18; \quad \psi = 0.42$$

$$\log k_2 = -2.80 + 0.40(\pm 0.36)\,\beta \qquad (10)$$
$$R^2 = 0.0727; \quad sd = 0.43; \quad n = 18; \quad \psi = 0.99$$

Here *n* is the number of data points and ψ is the Exner's statistical parameter [17].

Kamlet's [16] triparametric equation explains *ca.* 84% of the effect of solvent on the oxidation. However, by Exner's criterion [14] the correlation is not even satisfactory (cf. 7). The major contribution is of solvent polarity. It alone accounted for *ca.* 83% of the data. Both β and α play relatively minor roles.

The data on the solvent effect were analysed in terms of Swain's [18] equation (11) of cation- and anion-solvating concept of the solvents also.

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

Here A represents the anion-solvating power of the solvent and B the 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 eq. (12), separately with A and B and with (A + B).

$$\log k_2 = 0.75\ (\pm 0.06)\ A + 1.70\ (\pm 0.04)\ B - 3.99 \qquad (12)$$
$$R^2 = 0.9899;\ sd = 0.05;\ n = 19;\ \psi = 0.11$$

$$\log k_2 = 0.51\ (\pm 0.56)\ A - 2.82 \qquad (13)$$
$$R^2 = 0.0469;\ sd = 0.45;\ n = 19;\ \psi = 1.00$$

$$\log k_2 = 1.64\ (\pm 0.14)\ B - 3.74 \qquad (14)$$
$$R^2 = 0.8897;\ sd = 0.15;\ n = 19;\ \psi = 0.34$$

$$\log k_2 = 1.38 \pm 0.12\ (A + B) - 3.96 \qquad (15)$$
$$R^2 = 0.8774;\ sd = 0.16;\ n = 19;\ \psi = 0.36$$

Here *n* is the number of data points and ψ is the Exner's statistical parameter [17].

The rates of oxidation of ethanol in different solvents showed an excellent correlation in Swain's equation (cf. equation 12) with the cation-solvating power playing the major role. In fact, the cation-solvation alone account for *ca.* 89% of the data. The correlation with the anion-solvating power was very poor. The solvent polarity, represented by (A + B), also accounted for *ca.* 88% of the data. In view of the fact that solvent polarity is able to account for *ca.* 88% 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 ($r^2 = 0.4823$; sd = 0.15; $\psi = 0.34$).

Correlation Analysis of Reactivity: The rates of oxidation of the alcohols failed to yield any significant correlation separately with Taft's [20] σ^* and E_s values eqs. (16) and (17).

$$\log k_2 = -1.90\ (\pm 0.32)\ \Sigma\sigma^* - 2.69 \qquad (16)$$
$$R^2 = 0.8298;\ sd = 0.41;\ \psi = 0.44;\ n = 9$$

$$\log k_2 = -1.03\ (\pm 0.31)\ \Sigma E_s - 3.18 \qquad (17)$$
$$R^2 = 0.6185;\ sd = 0.62;\ \psi = 0.65;\ n = 9$$

The rates were, therefore, correlated in terms of Pavelich-Taft's [20] dual substituent-parameter (DSP) equation (18).

$$\log k_2 = \rho^* \sigma^* + \delta E_s + \log k_0 \qquad (18)$$

The values of substituent constants were obtained from the compilation by Wiberg [19]. The correlations are excellent; the reaction constants being negative (Table 6). There is no significant co linearity ($R^2 = 0.2322$) between σ^* and E_s values of the nine substituent's.

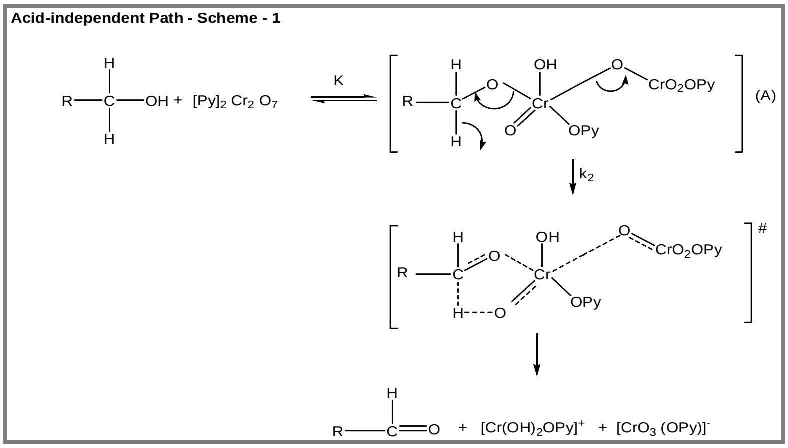
Table 6. Temperature dependence of reaction constants**.**

Temp. K^{-1}	$-\rho^*$	$-\delta$	r^2	Sd	ψ
288	1.58±0.01	0.70±0.01	0.9999	0.008	0.01
298	1.45±0.02	0.61±0.01	0.9997	0.020	0.02
308	1.35±0.01	0.54±0.01	0.9999	0.009	0.01
318	1.25±0.01	0.45±0.01	0.9998	0.011	0.02

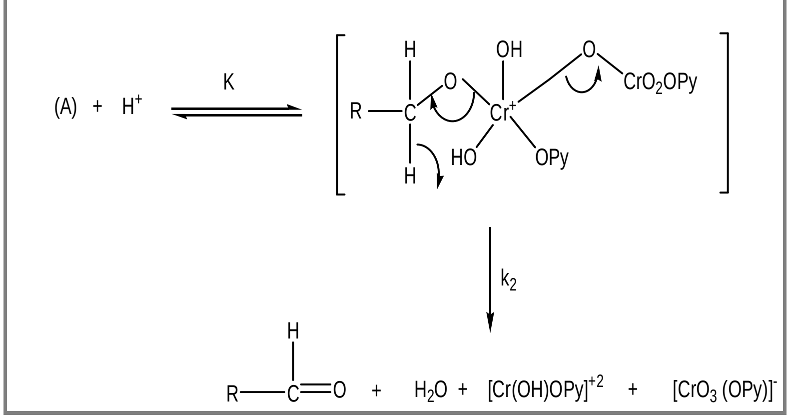
The negative polar reaction constant indicates an electron-deficient carbon centre in the transition state of the rate-determining step. The negative steric reaction constant shows a steric acceleration of the reaction. This may be explained on the basis of high ground state energy of the sterically 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 un-crowded alcohols do not differ much and steric acceleration, therefore, results.

Mechanism: The presence of a substantial primary kinetic isotope effect confirms the cleavage of an α-C-H bond in the rate-determining step. The large negative value of the polar reaction constant together with substantial deuterium isotope effect indicates that the transition state approaches a carbocation in character. Hence the transfer of hydride-ion from alcohol to the oxidant is suggested. The hydride-transfer mechanism is also supported by the major role of cation-solvating power of the solvents (Scheme 1).

Acid-independent Path - Scheme - 1



Acid-dependent Path - Scheme - 2



The hydride ion transfer may take place either by a cyclic process via an ester intermediate or by an acyclic one-step bimolecular process. This postulation is supported by an analysis of the temperature dependence of kinetic isotope effect. Kwart and Nickle[21] 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 deuterio-ethanols, fitted to the familiar expression $k_H/k_D = A_H/A_D$ $\exp(E_a/RT)$ [22-23] show a direct correspondence with the properties of a symmetrical transition state in which the activation energy difference (ΔE_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. The similar phenomena have also been observed earlier in the reactions of halochromates. Bordwell [24] 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 [25]. Littler [26] 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 step and then a disproportionation of the ester in a subsequent slow step via a cyclic concerted symmetrical transition state leading to the product (Scheme 1). The observed hydrogen-ion dependence can be explained by assuming a rapid reversible protonation of the chromate ester (A) with the protonated ester decomposing at a rate faster than (A) (Scheme 2).

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