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Correlation Analysis of Reactivity in the Oxidation of some Vicinal and Non-vicinal Diols by Picolinium Chlorochromate

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Abstract:
The kinetics of oxidation of four vicinal, four non-vicinal diols by picolinium chlorochromate (PICC) have been studied in dimethylsulphoxide (DMSO). The main product of oxidation is the corresponding hydroxycarbonyl compound. The reaction is first order in PICC. Michaelies-Menten type of kinetics is observed with respect to the diols. The reaction is catalysed by hydrogen ions. The hydrogen ion dependence has the form: $k_{obs} = a + b[H^+]$. The oxidation of [1,1,2,2-$^2H_4$] ethanediol exhibits a substantial primary kinetic isotope effect (k_H/k_D = 5.76 at 298 K). The reaction has been studied in nineteen different organic solvents and the solvent effect has been analysed using Taft's and Swain's multiparametric equations. The temperature dependence of the kinetic isotope effect indicates the presence of a symmetrical transition state in the rate-determining step. A suitable mechanism has been proposed.

Keywords: *Correlation analysis, diols, halochromate, kinetics, mechanism, oxidation*

Introduction

Inorganic salts of Cr(VI) are well known oxidants for the organic compounds. However these salts are rather drastic and non-selective oxidants. Further, they are insoluble in most organic solvents. Thus miscibility is a problem. To overcome these limitations, a large number of organic derivatives of Cr(VI) have been prepared and used in organic synthesis as mild and selective oxidants in non-aqueous solvents[1-5]. One of such compounds is picolinium chlorochromate (PICC), reported by reported method.[6] We have been interested in the kinetic and mechanistic aspects of the oxidation by complex salts of Cr(VI) and several reports on halochromates have already reported from our laboratory[7-10]. There seems to be no report on the oxidation aspects of diols using picolinium chlorochromate (PICC). Therefore, it was of interest to investigate the kinetics of the oxidation of some vicinal and non-vicinal diols by PICC in DMSO. A suitable mechanism has also been postulated.

Materials and Methods

Materials: The diols (BDH or Fluka) were distilled under reduced pressure before use. PICC was prepared by the reported method[6]. [1,1,2,2-$^2H_4$]Ethanediol (DED) was prepared by reducing diethyl oxalate with lithium aluminium deuteride[11]. Its isotopic purity,

determined by its NMR spectrum, was 95±4%. Due to the non-aqueous nature of the medium, toluene-p-sulphonic acid (TsOH) was used as a source of hydrogen ions. TsOH is a strong acid and in a polar solvent like DMSO, it is likely to be completely ionized.

Product analysis: Product analysis was carried out under kinetic conditions. In a typical experiment, ethanediol (0.1 mol) and PICC (0.01 mol) were taken in DMSO (100 ml) and the mixture was allowed to stand in the dark for ca. 10 h to ensure completion of the reaction. Most of the solvent was removed under reduced pressure and residue treated overnight with an excess (250 ml) of a saturated solution of 2,4-dinitrophenylhydrazine in 2 mol dm^{-3} HCl. The precipitated 2,4-dinitrophenyl hydrazone(DNP) was filtered off, dried, recrystallized from ethanol and weighed. The product was found identical (m.p. and mixed m.p.) with an authentic sample of DNP of hydroxyethanal. The oxidation state of chromium in completely reduced reaction mixture determined by an iodometric method is 3.95±0.15.

Kinetic measurements: The reactions were followed under pseudo-first order conditions keeping a large excess (x 15 or greater) of the diols over PICC. The temperature was kept constant to ±0.1K. The solvent was DMSO, unless specified otherwise. The reactions were followed by monitoring the decrease in the concentration of PICC spectro photometrically at 354 nm for up to 80% of the reaction. No other reactant or product has any significant absorption at this wave-length. The pseudo-first order rate constants, k_{obs}, were evaluated from the linear (r = 0.995 - 0.999) plots of log [PICC] against time. Duplicate kinetic runs showed that the rate constants were reproducible to within ±4%. All experiments, other than those for studying the effect of hydrogen ions, were carried out in the absence of TsOH.

Results and Discussion

Stoichiometry: The homogeneity of the DNP derivatives indicated the formation of only one product in each case. Under our reaction conditions, therefore, there is no observable oxidation of the second hydroxy group. This may be due to the presence of a large excess of the diol over PICC. The overall reaction may, therefore, be written as equation (1).

$$HOCH_2–CH_2OH + O_2CrClO^-PicH^+ \longrightarrow HOCH_2–CHO + H_2O + OCrClO^-PicH^+ \quad (1)$$

PICC undergoes a two-electron change. This is in accord with the earlier observations with structurally similar halochromates. It has already been proved earlier also that both pyridinium fluorochromate (PFC)[12] and pyridinium chlorochromate (PCC)[13] act as two electron oxidants and are reduced to chromium (IV) species, by determining the oxidation state of chromium by magnetic succeptibility, ESR and IR studies.

Kinetic Dependence: The reactions are of first order with respect to PICC. Further, the pseudo-first order rate constant, k_{obs} is independent of the initial concentration of PICC. Figure 1 depict a typical kinetic run.The reaction rate increases with increase in the concentration of the diols but not linearly (Table 1). A plot of $1/k_{obs}$ against 1/[Diol] 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 diol. This leads to the postulation of following overall mechanism (2) and (3) and rate law (4).

Table 1. Rate constants for the oxidation of propan-1,2-diol by PICC at 298 K

10^3 [PICC]	[Diol]	10^4 k_{obs}
(mol dm^{-3})	(mol dm^{-3})	(mol dm^{-3})
1.0	0.10	6.33
1.0	0.20	9.36
1.0	0.40	12.3
1.0	0.60	13.8
1.0	0.80	14.6
1.0	1.00	15.2
1.0	1.50	16.0
1.0	3.00	17.0
2.0	0.40	12.6
4.0	0.40	11.7
6.0	0.40	12.0
8.0	0.40	11.3
1.0	0.20	9.27*

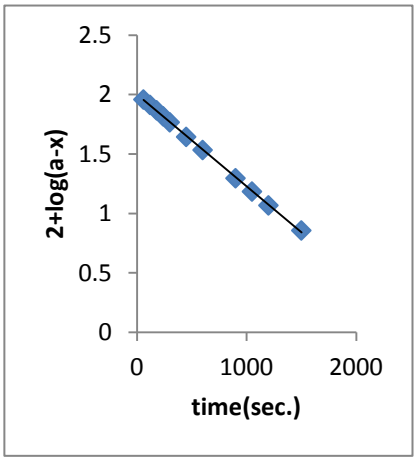

Fig. 1. Oxidation of Propane-1,2-diol by PICC: A typical Kinetic Run

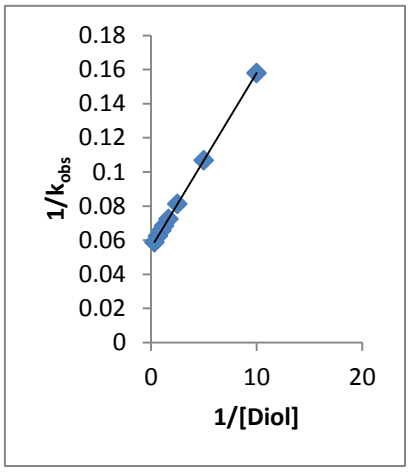

Fig. 2. Oxidation of Propane-1,2-diol by PICC: A double reciprocal plot

$$\text{Diol} + \text{PICC} \underset{}{\overset{K}{\leftrightarrows}} [\text{complex}] \quad (2)$$

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

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

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 2 and 3).

Table 2. Rate constants for the decomposition of PICC–Diol complexes and activation parameters

$10^4\ k_2$ / ($dm^3\ mol^{-1}\ s^{-1}$)					ΔH^*	$-\Delta S^*$	ΔG^*
Diols	288 K	298 K	308 K	318 K	(kJ mol^{-1})	(J $mol^{-1}K^{-1}$)	(kJ mol^{-1})
Ethane-1,2	1.62	4.32	10.8	26.1	67.9±0.3	82±1	92.2±0.2
Propan-1,2	7.65	18.0	40.5	90.0	59.9±0.4	97±1	88.6±0.3
Butane-2,3	35.1	73.8	153	306	52.5±0.4	110±1	85.1±0.3
Butane-1,2	9.99	23.4	53.1	108	58.1±0.4	101±1	88.0±0.3
Propan-1,3	15.3	34.2	76.5	162	57.5±0.4	100±1	87.0±0.3
Butane-1,3	19.8	42.3	91.8	180	53.8±0.5	110±2	86.5±0.4
Butane-1,4	22.5	46.8	96.3	189	51.6±0.3	117±1	86.3±0.3
Pentane-1,5	32.4	67.5	135	279	51.9±0.7	113±2	85.4±0.6
DED	0.27	0.75	1.93	5.00	71.3±0.5	85±2	96.5±0.4
k_H/k_D	6.00	5.76	5.49	5.22			

Table 3. Formation constants for the decomposition of PICC–Diols complexes and thermodynamic parameters

K ($dm^3\ mol^{-1}$)					$-\Delta H^*$	$-\Delta S^*$	$-\Delta G^*$
Diols	288 K	298 K	308 K	318 K	(kJ mol^{-1})	(J $mol^{-1}K^{-1}$)	(kJ mol^{-1})
Ethane-1,2	5.67	5.02	4.41	3.80	12.6±0.4	21±1	6.47±0.3
Propan-1,2	6.03	5.42	4.78	4.14	12.0±0.4	19±1	6.65±0.3
Butane-2,3	5.94	5.31	4.70	4.06	12.1±0.4	19±1	6.61±0.3
Butane-1,2	6.30	5.68	5.06	4.42	11.5±0.4	16±1	6.77±0.3
Propan-1,3	6.57	5.96	5.31	4.66	11.2±0.4	15±1	6.89±0.3
Butane-1,3	5.85	5.25	4.59	3.95	12.5±0.5	20±2	6.56±0.4
Butane-1,4	5.58	4.93	4.32	3.71	12.8±0.4	22±1	7.42±0.3
Pentane-1,5	6.48	5.88	5.22	4.61	11.2±0.3	15±1	6.85±0.3
DED	5.76	5.15	4.50	3.88	12.5±0.4	21±1	6.52±0.3

Test for free radicals: The oxidation of diols, by PICC, in an atmosphere of nitrogen failed to induce the polymerisation of acrylonitrile. Further, addition of acrylonitrile had no effect on the rate (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.

Effect of hydrogen ions: The reaction is catalyzed by hydrogen ions (Table 4). The hydrogen-ion dependence has the form: $k_{obs} = a + b [H^+]$. The values of a and b for ethanediol are $7.17 \pm 0.29 \times 10^{-4}$ s^{-1} and $13.9 \pm 0.48 \times 10^{-4}$ mol^{-1} dm^3 s^{-1} respectively ($r^2 = 0.9952$).

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

[PICC] = 0.001 mol dm^{-3}; [Ethane Diol] = 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}	7.47	8.82	10.8	13.5	16.2	18.0

Kinetic isotope effect: To ascertain the importance of the cleavage of the α-C-H bond in the rate-determining step, the oxidation of DED was studied. Results (Tables 2 and 3) showed the formation constants, K, of the intermediate complex of the deuteriated and protiated diols do not differ much, however, the rate of disproportionation of the intermediate exhibited the presence of a substantial primary kinetic isotope (k_H/k_D = 5.76 at 298 K).

Reactive oxidizing species: The observed hydrogen-ion dependence suggests that the reaction follows two mechanistic pathways, one is acid-independent and the other is acid-dependent. The acid-catalysis may well be attributed to a protonation of PICC to yield a protonated Cr(VI) species which is a stronger oxidant and electrophile (5).

$$[O_2CrClO\text{-}PicH^+] + H^+ \leftrightarrows [HOCrOClO\text{-}PicH^+] \quad (5)$$

Formation of a protonated Cr(VI) species has earlier been postulated in the reactions of structurally similar halochromates.

Effect of organic solvents: The oxidation of ethanediol was studied in 19 different organic solvents. The choice of solvents was limited due to the solubility of PICC and its reaction with primary and secondary alcohols. There was no reaction with the solvents chosen. The values of formation constants K and decomposition constants of the complex, k_2 are recorded in Table 5.

Table 5. Effect of solvents on the oxidation of Propan-1,2-diol by PICC at 308 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	5.88	63.1	Toluene	4.54	24.0
1,2-Dichloroethane	5.76	77.6	Acetophenone	5.31	75.8
Dichloromethane	6.12	60.3	THF	4.59	39.8
DMSO	5.42	180	t-Butylalcohol	5.85	25.1
Acetone	6.03	70.8	1,4-Dioxane	5.74	33.9
DMF	5.95	95.5	1,2-Dimethoxyethane	5.90	22.4
Butanone	5.86	51.3	CS_2	5.99	11.2
Nitrobenzene	5.66	79.4	Acetic Acid	5.57	10.7
Benzene	5.77	27.5	Ethyl Acetate	5.39	31.6
Cyclohexane	6.31	3.47			

A satisfactory linear correlation (r^2 = 0.9390) between the values of activation enthalpies and entropies of oxidation of diols 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]. The value of the isokinetic temperature is 564±54 K. An Exner's plot between log k_2 at 288K and at 318K was linear (r^2 = 0.9976) (Figure 3). The value of isokinetic temperature is 643±70 K. The linear isokinetic correlation implies that all the diols 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.

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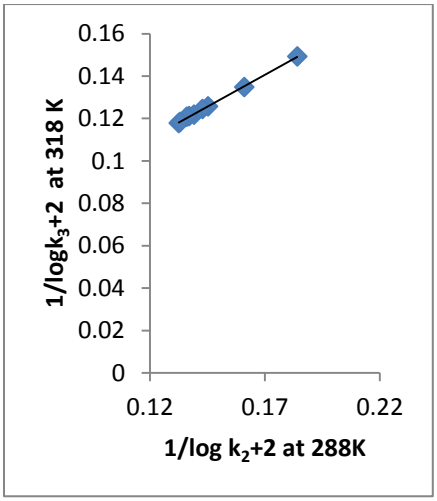

Fig. 3. Exner's Isokinetic Relationship in the oxidation of Diols by PICC

Solvent effect: The rate constants, k_2, for the oxidation of ethanediol in 18 organic solvents (CS_2 was not considered, as the complete range of solvent parameters was not available) did not exhibit any significant correlation in terms of the linear solvation energy relationship (5) of Kamlet et al[16].

$$\log k_2 = A_0 + pc^* + b\beta + a\alpha \quad (5)$$

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, 13 have a value of zero for α. The results of correlation analyses in terms of equation (5), a biparametric equation involving π^* and β, and separately with π^* and β are given below equations (6) - (9).

$$\log k_2 = -4.68 + (1.37 \pm 0.19)\,\pi^* + (0.22 \pm 0.15)\,\beta - (0.15 \pm 0.16)\,\alpha \quad (6)$$
$R^2 = 0.8381;\ sd = 0.17;\ n = 18;\ \Psi = 0.44$

$$\log k_2 = -4.62 + (1.45 \pm 0.19)\,\pi^* + (0.08 \pm 0.15)\,\beta \quad (7)$$
$R^2 = 0.8122;\ sd = 0.18;\ n = 18;\ \Psi = 0.46$

$$\log k_2 = -4.36 + (1.47 \pm 0.18)\,\pi^* \quad (8)$$
$r^2 = 0.8088;\ sd = 0.18;\ n = 18;\ \Psi = 0.45$

$$\log k_2 = -2.53 + (0.34 \pm 0.32)\,\beta \quad (9)$$
$r^2 = 0.0642;\ sd = 0.39;\ n = 18;\ \Psi = 0.99$

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

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Kamlet's[16] triparametric equation explains *ca.* 84% of the effect of solvent on the oxidation. However, by Exner's criterion[17] the correlation is not even satisfactory (*cf.* equation 6). The major contribution is of solvent polarity. It alone accounted for *ca.* 81% 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 (10) of cation- and anion-solvating concept of the solvents also.

$$\log k_2 = aA + bB + C \quad (10)$$

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 equation (11), separately with A and B and with (A + B).

$$\log k_2 = (0.40 \pm 0.05)\,A + (1.54 \pm 0.03)\,B - 3.54 \quad (11)$$
$$R^2 = 0.9922;\ sd = 0.04;\ n = 19;\ \Psi = 0.09$$

$$\log k_2 = 0.18(\pm 0.51)\,A - 2.48 \quad (12)$$
$$r^2 = 0.0074;\ sd = 0.41;\ n = 19;\ \Psi = 1.02$$

$$\log k_2 = 1.51(\pm 0.08)\,B - 3.41 \quad (13)$$
$$r^2 = 0.9566;\ sd = 0.09;\ n = 19;\ \Psi = 0.21$$

$$\log k_2 = 1.16 \pm 0.15(A + B) - 3.50 \quad (14)$$
$$r^2 = 0.7830;\ sd = 0.19;\ n = 19;\ \Psi = 0.48$$

The rates of oxidation of ethanediol in different solvents showed an excellent correlation in Swain's equation (cf. equation 11) with the cation-solvating power playing the major role. In fact, the cation-solvation alone account for *ca.* 96% of the data. The correlation with the anion-solvating power was very poor. The solvent polarity, represented by (A + B), also accounted for *ca.* 77% of the data. In view of the fact that solvent polarity is able to account for *ca.* 78% 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 ($r^2 = 0.4976$; sd = 0.29; $\psi = 0.73$).

Correlation analysis of reactivity: The rates of oxidation of the four vicinal diols in DMSO showed the excellent correlation with Taft's σ^* values[19] with negative reaction constants (Table 6), this indicates the presence of an electron-deficient rate-determining step. Here $\Sigma\ \sigma^*$ represents the sum of the substituent constants for the substituents present on the two alcoholic

carbons of the vicinal diols. The fact that σ^* values alone able to account for 99% of the data showed that steric factors do not play any significant role in the reaction. The magnitude of the reaction constants decreases with an increase in the temperature, indicating that selectivity decreases with an increase in the reactivity.

Table 6. Reaction constants of the oxidation of vicinal diols by PICC

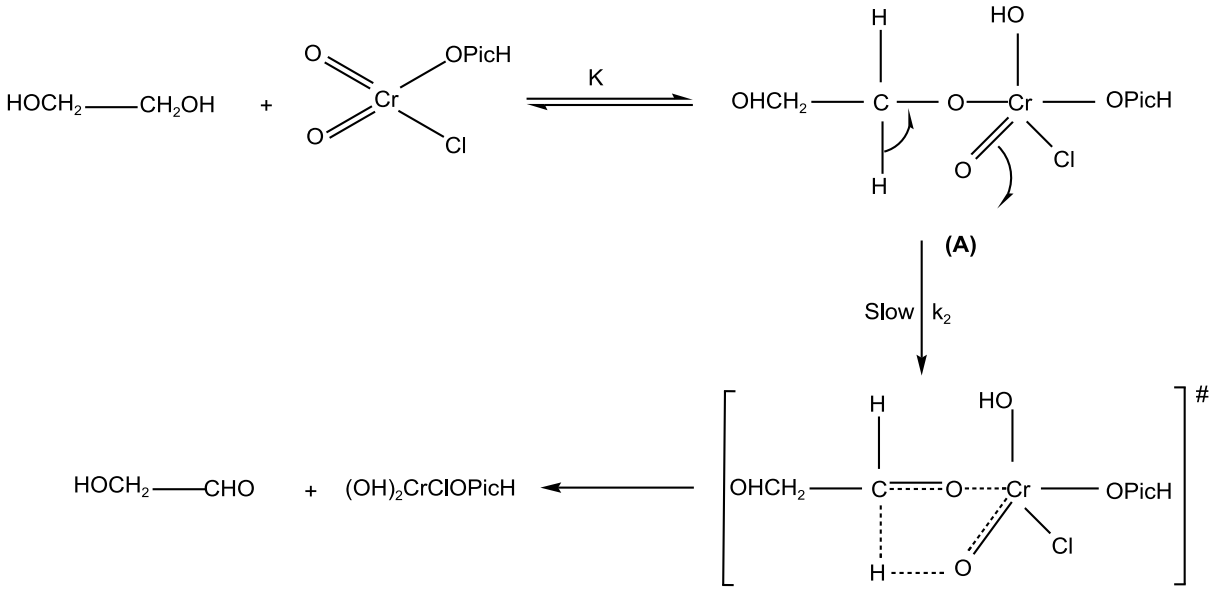
Temp./ K	$-\rho^*$	r^2	Sd	ψ
288	1.36±0.09	0.9906	0.07	0.11
298	1.26±0.09	0.9895	0.06	0.12
308	1.18±0.09	0.9878	0.06	0.13
318	1.09±0.06	0.9936	0.04	0.09

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 negative values of the polar reaction constant together with substantial deuterium isotope effect indicate that the transition state has an electron-deficient carbon centre. Hence the transfer of a hydride-ion from diol to the oxidant is suggested. The hydride-transfer mechanism is also supported by the major role of cation-solvating power of solvents.

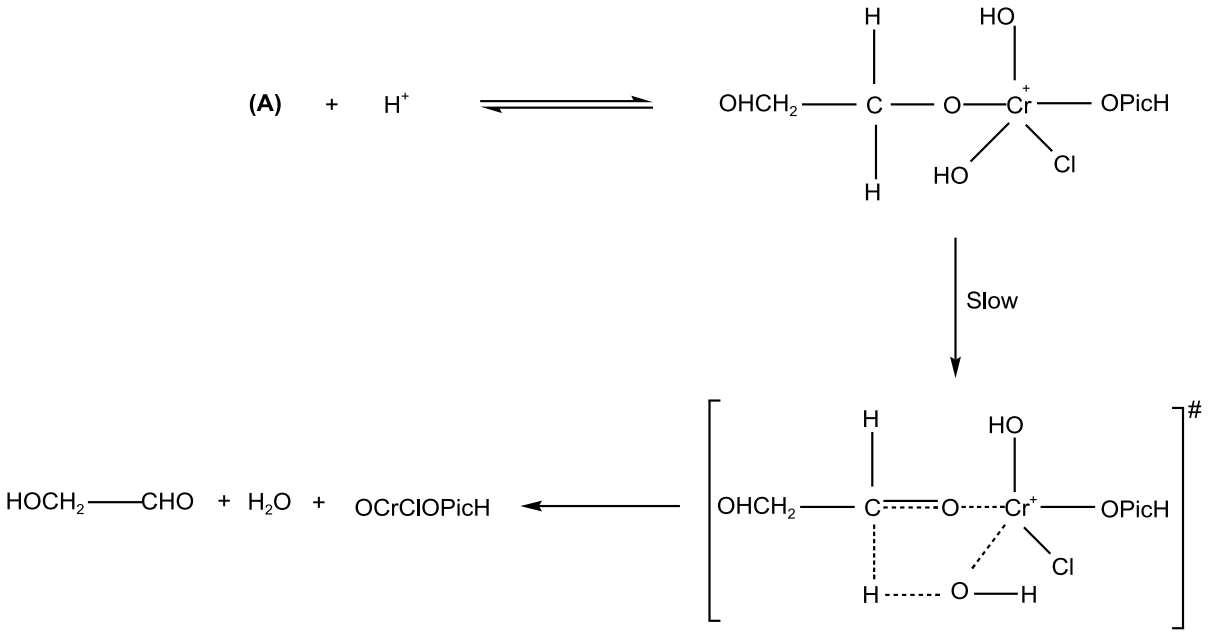
The hydride ion transfer may take place either by a cyclic process via an ester intermediate or by an acyclic one-step bimolecular process. Kwart and Nickle[20] have shown that a study of the dependence of the kinetic isotope effect on temperature can be gainfully employed to resolve this problem. The data for protio- and deuterio-ethandiols, fitted to the familiar expression $k_H/k_D = A_H/A_D \exp(E_a/RT)$[21,22] 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. Bordwell[23] has documented a very cogent evidence against the occurrence of concerted one-step bimolecular processes by hydrogen transfer and it is evident that in the present studies also the hydrogen transfer does not occur by an acyclic bimolecular 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[24]. Littler[25] 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).



Scheme - 1 - Acid Independent Path

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).



Scheme - 2 - Acid Dependent Path

It is of interest to recall that pinacol is oxidized by chromic acid but not by PICC. Chatterjee and Mukherji[26] reported an abrupt change from butane-2,3-diol to pinacol, the latter reacting very fast. As pointed out by Littler[25], a cyclic ester mechanism is forbidden in the diol-Cr(VI) reaction. Chromic acid oxidation of pinacol may therefore involve two one- electron steps. Chromic acid oxidations are known to induce polymerization of acrylamide under certain conditions[27]. No such observation has yet been recorded with PICC. Thus the capability of chromic acid and the inability of PICC to act as a one-electron oxidant may explain the different behaviour of pinacol towards these two oxidants.

CONCLUSIONS

Oxidation of these diols indicated the involvement of the formation of a chromate esterin fast pre-equilibrium and then a disproportionation of the ester in a subsequent slow step via a cyclic concerted symmetrical transition state leading to the product, carbonyl compound.

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