



CORRELATION ANALYSIS OF REACTIVITY IN THE OXIDATION OF SOME VICINAL AND NON-VICINAL DIOLS BY TETRAETHYLAMMONIUM CHLOROCHROMATE

**S. POHANI, P. PANCHARIA, P. PUROHIT, S. VYAS and
PRADEEP K. SHARMA***

Department of Chemistry, J. N. V. University, JODHPUR - 342 005 (Raj.) INDIA

ABSTRACT

The kinetics of oxidation of four vicinal, four non-vicinal diols and two of their monoethers by tetraethylammonium chlorochromate (TEACC) have been studied in dimethylsulphoxide (DMSO). The main product of oxidation is the corresponding hydroxycarbonyl compound. The reaction is first order in TEACC and the diols. The reaction is catalysed by hydrogen ions. The hydrogen ion dependence is taking the form : $k_{\text{obs}} = a + b[\text{H}^+]$. The oxidation of [1,1,2,2- $^2\text{H}_4$] ethanediol exhibits a substantial primary kinetic isotope effect ($k_{\text{H}}/k_{\text{D}} = 5.70$ 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.

Key words: Correlation analysis, Diols, Oxidation, Tetraethylammonium chlorochromate.

INTRODUCTION

Specific 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 reported¹⁻⁵. Tetraethylammonium chlorochromate (TEACC) is also one such compound used for the oxidation of benzyl alcohols⁶. There seems to be no report on the oxidation aspects using tetraethylammonium chlorochromate (TEACC). We have been interested in the kinetic and mechanistic aspects of the oxidation by complexed Cr (VI) species and several studies by halochromates have already been reported⁷⁻¹⁰. In the present paper, we report the kinetics of the oxidation of diols.

* Author for correspondence; E-mail: drpkvs27@yahoo.com

EXPERIMENTAL

Materials

The diols and the monoethers (BDH or Fluka) were distilled under reduced pressure before use. TEACC was prepared by the reported method⁶. [1,1,2,2-²H₄]Ethanediol (DED) was prepared by reducing diethyl oxalate with lithium aluminium deuteride¹¹. Its isotopic purity, determined by its NMR spectrum, was $90 \pm 3\%$. 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. Solvents were purified by the usual methods¹².

Product analysis

Product analysis was carried out under kinetic conditions. In a typical experiment, ethanediol (0.1 mol) and TEACC (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 was 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-dinitrophenylhydrazone (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 mixtures, determined by an iodometric method, was 3.95 ± 0.10 .

Kinetic measurements

The reactions were followed under pseudo-first order conditions keeping a large excess (x 15 or greater) of the diols over TEACC. 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 TEACC spectrophotometrically at 365 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 evaluated from the linear ($r = 0.995 - 0.999$) plots of $\log [\text{TEACC}]$ against time. Duplicate kinetic runs showed that the rate constants were reproducible to within $\pm 4\%$. All experiments, other than those for studying the effect of hydrogen ions, were carried out in the absence of TsOH.

RESULTS AND DISCUSSION

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 TEACC. The overall reaction may, therefore, be written as equation (1).



TEACC undergoes a two-electron change. This is in accord with the earlier observations with both; PFC⁷ and MCC¹⁰. It has already been proved earlier that both pyridinium fluorochromate (PFC)¹³ and pyridinium chlorochromate (PCC)¹⁴ act as two electron oxidants and are reduced to chromium (IV) species.

The rate laws and other experimental data were obtained for all the diols investigated. As the results were similar, only representative data are reproduced here. There is no noticeable oxidation of pinacol by TEACC under our reaction conditions.

Rate laws

The reaction is found to be first order with respect to TEACC. The individual kinetic runs were strictly first order to TEACC. Further the pseudo-first order rate constants do not depend on the initial concentration of TEACC. The rate increases linearly with an increase in the concentration of diol (Table 1). Thus, the reaction is first order with respect to diol also. Figure 1 depicts a typical kinetic run.

Table 1: Rate constants for the oxidation of ethanediol by TEACC at 308 K

10^3 [TEACC] mol dm ⁻³	[diol] mol dm ⁻³	10^5 k _{obs} s ⁻¹
1.0	0.10	9.54
1.0	0.20	19.7
1.0	0.40	39.6
1.0	0.60	59.4
1.0	0.80	78.3
1.0	1.00	96.3
2.0	0.40	38.5
4.0	0.40	40.7
6.0	0.40	39.0
8.0	0.40	41.4
1.0	0.20	20.7 ^a

^a Contained 0.001 mol dm⁻³ acrylonitrile

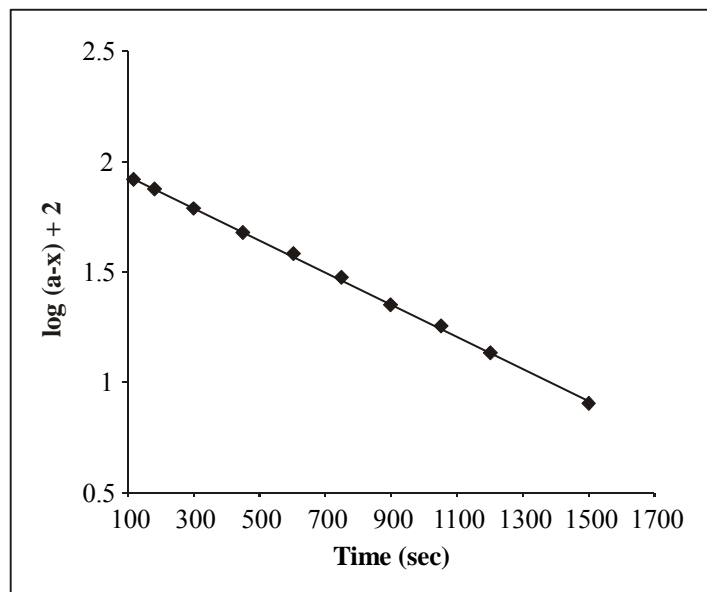


Fig. 1: Oxidation of Ethane-diol by TEACC: A typical kinetic run

Induced polymerisation of acrylonitrile/Test for free radicals

The oxidation of diols, by TEACC, 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.

Table 2: Dependence of the reaction rate on hydrogen-ion concentration

[Ethanediol] 0.10 mol dm^{-3}	[TEACC] $0.001 \text{ mol dm}^{-3}$			Temp. 308 K		
[TsOH]/ mol dm^{-3}	0.10	0.20	0.40	0.60	0.80	1.00
$10^5 k_{\text{obs}}/\text{s}^{-1}$	11.0	13.2	16.2	19.5	23.4	27.0

Effect of temperature

The rates of oxidation of all the diols were determined at four different temperatures and the activation parameters were calculated (Table 3). The $\log k_2$ at different temperatures

is linearly related to the inverse of the absolute temperature in all cases (Fig. 2). The Arrhenius equation is, therefore, valid for these oxidations.

Table 3: Rate constants and the activation parameters for the oxidation of diols by TEACC

Diols	$10^4 k_2 / s^{-1}$				ΔH^*	ΔS^*	ΔG^*
	288	298	308	318 K	$kJ mol^{-1}$	$J mol^{-1} K^{-1}$	$kJ mol^{-1}$
Ethane-1,2-diol	1.71	4.05	9.63	21.6	62.0 ± 0.5	-102 ± 2	92.3 ± 0.4
Propane-1,2-diol	7.27	16.5	36.1	80.7	58.4 ± 0.7	-103 ± 2	88.9 ± 0.6
Butane-2,3-diol	31.5	66.6	135	279	52.2 ± 0.6	-110 ± 2	85.4 ± 0.5
Butane-1,2-diol	9.81	21.9	47.2	104	57.3 ± 0.7	-104 ± 2	88.2 ± 0.6
Propane-1,3-diol	12.6	28.8	62.1	135	57.5 ± 0.5	-101 ± 1	87.5 ± 0.4
Butane-1,3-diol	15.8	33.3	72.0	144	53.8 ± 0.5	-112 ± 2	87.1 ± 0.4
Butane-1,4-diol	18.9	41.4	92.7	189	56.2 ± 0.5	-102 ± 2	86.6 ± 0.4
Pentane-1,5-diol	27.0	57.6	117	225	51.4 ± 0.2	-116 ± 1	85.8 ± 0.1
3-Methoxybutan-1-ol	32.4	68.4	144	297	53.7 ± 0.6	-107 ± 2	85.3 ± 0.5
2-Methoxyethanol	10.8	26.1	60.3	135	61.5 ± 0.3	-88 ± 3	87.7 ± 0.2
DED*	0.29	0.71	1.75	4.07	64.7 ± 0.6	-108 ± 2	96.6 ± 0.4
k_H/k_D	5.90	5.70	5.50	5.31			

*[1,1,2,2-²H₄]ethane-1,2-diol

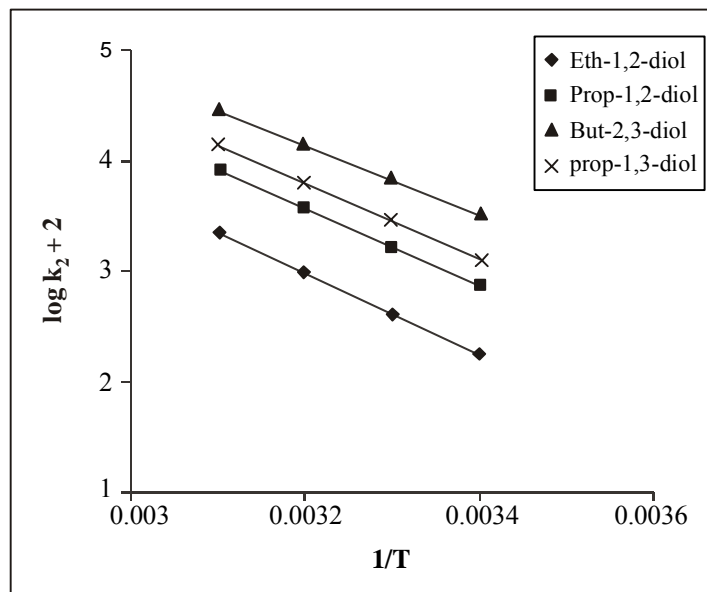


Fig. 2: Oxidation of ethanediol by TEACC: Effect of temperature

Effect of acidity

The reaction is catalyzed by hydrogen ions (Table 2). The hydrogen-ion dependence has the following form: $k_{\text{obs}} = a + b [\text{H}^+]$. The values of a and b for ethanediol are $9.34 \pm 0.21 \times 10^{-4} \text{ s}^{-1}$ and $17.5 \pm 0.35 \times 10^{-4} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, respectively ($r^2 = 0.9984$).

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. The results recorded in Tables 4, showed that the reaction exhibited a substantial primary kinetic isotope effect ($k_{\text{H}}/k_{\text{D}} = 5.70$ at 298 K).

Table 4: Effect of solvents on the oxidation of propan-1,2-diol by TEACC at 298 K

Solvents	$10^5 k_2 /$ ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)	Solvents	$10^5 k_2 /$ ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)
Chloroform	41.7	Acetic acid	6.46
1,2-Dichloroethane	51.3	Cyclohexane	1.86

Cont...

Solvents	$10^5 k_2/$ ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)	Solvents	$10^5 k_2/$ ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)
Dichloromethane	56.2	Toluene	14.8
DMSO	165	Acetophenone	75.9
Acetone	46.8	THF	27.5
N,N-Dimethylformamide	79.4	<i>t</i> -Butyl alcohol	18.6
Butanone	38.9	1,4-Dioxane	24.5
Nitrobenzene	63.1	1,2-Dimethoxyethane	14.5
Benzene	18.2	Carbon disulphide	7.94
Ethyl acetate	20.9		

Effect of solvents

The oxidation of ethanediol was studied in 19 different organic solvents. The choice of solvents was limited due to the solubility of TEACC and its reaction with primary and secondary alcohols. There was no reaction with the solvents chosen. The kinetics were similar in all the solvents. The values of k_2 are recorded in Table 4.

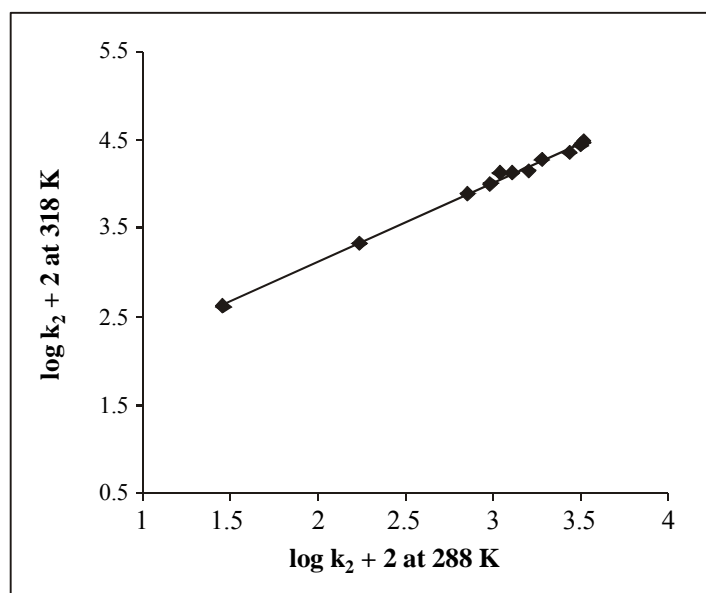


Fig. 3: Exner's isokinetic relationship in the oxidation of diols by TEACC

The values of $\log k_2$ at 288 K and $\log k_2$ at 318 K for the oxidation of ten compounds are linearly related ($r^2 = 0.9914$) (Fig. 3). The value of isokinetic temperature evaluated^{15,16} from this plot is 1029 ± 51 K. The correlation was tested and found genuine by using Exner's criterion¹⁷. A linear isokinetic correlation implies that all the compounds are oxidized by the same mechanism. The linear correlation here involves two typical monohydric alcohols viz. 2-methoxyethanol and 3-methoxybutan-1-ol. Thus, it seems likely that the diols also behave like monohydric alcohols towards TEACC. This is further supported by the isolation of hydroxyaldehyde as the product and the resistance of pinacol towards the oxidation by TEACC.

Reactivity of 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 TEACC to yield a protonated Cr (VI) species, which is a stronger oxidant and electrophile (2).



Formation of a protonated Cr (VI) species has earlier been postulated in the reactions of structurally similar QFC¹⁸ and MCC¹⁹.

Solvent effect

The rate constants, k_2 , for the oxidation of ethane diol 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 (3) of Kamlet *et al.*²⁰

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

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 (3), a biparametric equation involving π^* and β , and separately with π^* and β are given below in equations (4) - (7).

$$\log k_2 = -4.39 + (1.57 \pm 0.20) \pi^* + (0.22 \pm 0.16) \beta - (0.26 \pm 0.16) \alpha \quad \dots(4)$$

$$R^2 = 0.8623; \text{sd} = 0.18; n = 18; \Psi = 0.41$$

$$\log k_2 = -4.32 + (1.67 \pm 0.20) \pi^* + (0.13 \pm 0.17) \beta \quad \dots(5)$$

$$R^2 = 0.8345; \text{sd} = 0.19; n = 18; \Psi = 0.43$$

$$\log k_2 = -4.35 + (1.70 \pm 0.19) \pi^* \quad \dots(6)$$

$$r^2 = 0.8275; \text{sd} = 0.19; n = 18; \Psi = 0.43$$

$$\log k_2 = -2.70 + (0.43 \pm 0.37) \beta \quad \dots(7)$$

$$r^2 = 0.0786; \text{sd} = 0.44; n = 18; \Psi = 0.99$$

Here n is the number of data points and Ψ is the Exner's statistical parameter²¹.

Kamlet's²⁰ triparametric equation explains ca. 86% of the effect of solvent on the oxidation. However, by Exner's criterion²¹, the correlation is not even satisfactory (cf. equation 4). 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 equation²² (8) of cation- and anion-solvating concept of the solvents also.

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

Here A represents the anion-solvating power of the solvent and B is 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 (8), separately with A and B and with $(A + B)$.

$$\log k_2 = (0.45 \pm 0.04) A + (1.74 \pm 0.03) B - 4.17 \quad \dots(9)$$

$$R^2 = 0.9946; \text{sd} = 0.04; n = 19; \Psi = 0.08$$

$$\log k_2 = 0.21 (\pm 0.57) A - 2.64 \quad \dots(10)$$

$$r^2 = 0.0075; \text{sd} = 0.46; n = 19; \Psi = 1.02$$

$$\log k_2 = 1.70 (\pm 0.09) B - 4.32 \quad \dots(11)$$

$$r^2 = 0.9587; \text{sd} = 0.09; n = 19; \Psi = 0.21$$

$$\log k_2 = 1.31 \pm 0.17 (A + B) - 4.21 \quad \dots(12)$$

$$r^2 = 0.7853; \text{sd} = 0.22; n = 19; \Psi = 0.48$$

The rates of oxidation of ethanol in different solvents showed an excellent correlation in Swain's equation (cf. equation 9) with the cation-solvating power playing the major role. In fact, the cation-solvation alone account 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. 79% of the data. In view of the fact that solvent polarity is able to account for ca. 79% 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 ($r^2 = 0.5103$; $sd = 0.33$; $\psi = 0.72$).

Correlation analysis of reactivity

The rates of oxidation of the four vicinal diols in DMSO showed the excellent correlation with Taft's σ^* values²³ with negative reaction constants (Table 5). This indicates the presence of an electron-deficient rate-determining step. The fact that σ^* values alone is 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. This shows that selectivity decreases with an increase in the reactivity. Here $\Sigma \sigma^*$ represents the sum of the substituent constants for the substituents present on the two alcoholic carbons of the vicinal diols.

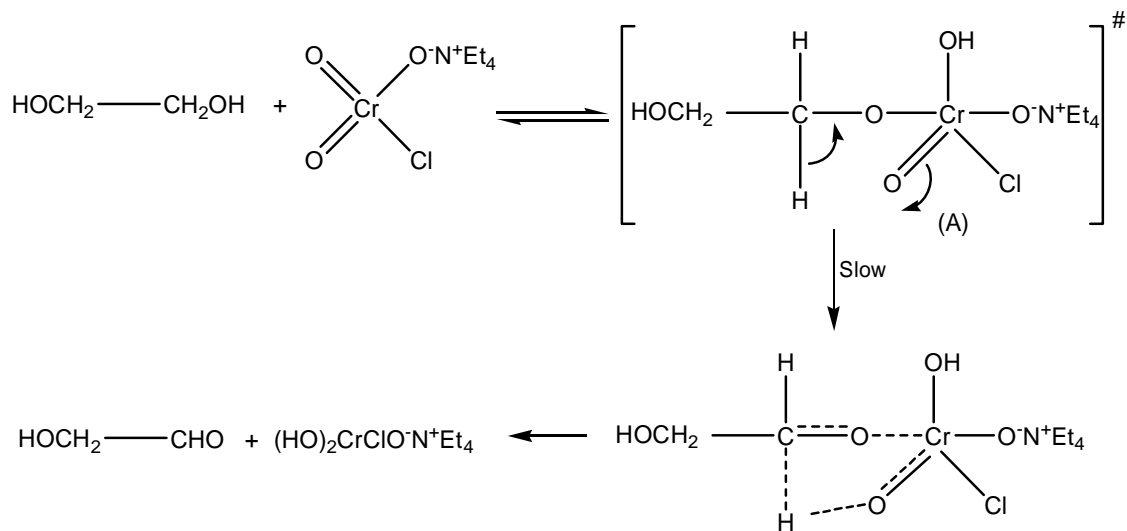
Table 5: Reaction constants of the oxidation of vicinal diols by TEACC

T/K	ρ^*	R^2	sd	ψ
288	-1.29 ± 0.10	0.9879	0.07	0.12
298	-1.24 ± 0.09	0.9875	0.06	0.13
308	-1.17 ± 0.09	0.9876	0.06	0.12
318	-1.13 ± 0.10	0.9853	0.07	0.14

MECHANISM

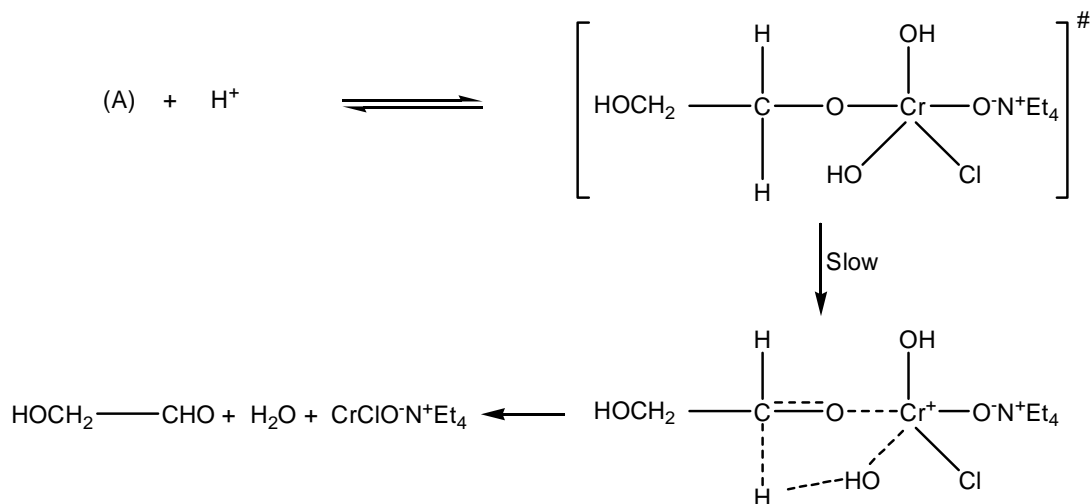
The presence of a substantial primary kinetic isotope effect confirms the cleavage of an α -C-H bond in the rate-determining step. The negative value of the polar reaction constant together with substantial deuterium isotope effect indicate that the transition state approaches a carbocation in character. Hence, the transfer of 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 the 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. This postulation is supported by an analysis of the temperature dependence of kinetic isotope effect. Kwart and Nickle²⁴ 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 $k_H/k_D = A_H/A_D \exp(E_a/RT)$ ^{25,26} 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 oxidation of hydroxyl acids¹⁷ by QFC and benzyl alcohols¹⁸ by MCC. Bordwell²⁷ 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 transfer²⁸. Littler²⁹ 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

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

It is of interest to recall that pinacol is oxidized by chromic acid but not by TEACC. Chatterjee and Mukherji³⁰ reported an abrupt change from butane-2,3-diol to pinacol, the latter reacting very fast. As pointed out by Littler²⁹, 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 conditions³⁰. No such observation has yet been recorded with TEACC. Thus, the capability of chromic acid and the inability of TEACC to act as a one-electron oxidant may explain the different behaviour of pinacol towards these two oxidants.

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