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OXIDATION OF ALIPHATIC PRIMARY ALCOHOLS BY TETRAETHYLAMMONIUM CHLOROCHROMATE: A KINETIC AND MECHANISTIC APPROACH

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ABSTRACT

The oxidation of nine aliphatic primary alcohols by tetraethylammonium chlorochromate (TEACC) in dimethylsulphoxide leads to the formation of corresponding aldehydes. The reaction is first order with respect to both; TEACC and the alcohol. The reaction is catalysed by hydrogen ions. The hydrogen-ion dependence has the form: $k_{obs} = a + b [H^+]$. The oxidation of [1,1-$^2H_2$]ethanol ($MeCD_2OH$) exhibits a substantial primary kinetic isotope effect. 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.

Key words: Correlation analysis, Halochromates, Kinetics, Mechanism, Oxidation

INTRODUCTION

Halochromates have been used as mild and selective oxidizing reagents in synthetic organic chemistry[1-5]. Tetraethylammoniumchlorochromate (TEACC) is also one of such compounds used for the oxidation of benzylic alcohols[6]. We have been interested in the kinetic and mechanistic aspects of the oxidation by complexed Cr (VI) species and several reports (including TEACC) have already reported from our laboratory[7-9]. In continuation of our earlier work with Cr (VI), we report here the kinetics and mechanism of oxidation of nine aliphatic primary alcohols by TEACC in dimethylsulphoxide (DMSO) as solvent. The mechanistic aspects are discussed. A suitable mechanism has also been proposed.

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EXPERIMENTAL

Materials

TEACC was prepared by the reported method[6] and its purity was checked by iodometric method. The procedures used for the purification of alcohols have been described earlier[10]. [1,1- $^2H_2$]Ethanol ($MeCD_2OH$) was prepared by Kalpan's method[11]. 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[12].

Product analysis

The product analysis was carried out under kinetic conditions. In a typical experiment, ethanol (2.30 g, 0.05 mol) and TEACC (2.22 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-dinitrophenylhydrazone (DNP) was filtered off, dried, weighed, recrystallized from ethanol and weighed again. The yield of DNP before and after recrystallization was 1.98 g (89%) and 1.74 g (77%), 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 73 to 85%, 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 ± 0.15.

Kinetic measurements

The reactions were followed under pseudo-first-order conditions by keeping a large excess (× 15 or greater) of the alcohol 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 370 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 [TEACC] 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 $k_2 = k_{obs}/[\text{Alcohol}]$. 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).

$$RCH_2OH + O_2CrClO^-N^+Et_4 \longrightarrow RCHO + OCrClO^-N^+Et_4 + H_2O \quad \ldots(1)$$

TEACC undergoes two-electron change. This is in accordance with the earlier observations with PFC[13], PCC[14] and TEACC[9] also. It has already been shown that both PFC[13] and PCC[14] act as two electron oxidants and are reduced to chromium (IV) species by determining the oxidation state of chromium by magnetic susceptibility, ESR and IR studies.

Rate laws

The reaction is first order with respect to TEACC. Further the pseudo-first order rate constant, k_{obs}, is independent of the initial concentration of TEACC. The reaction is first order with respect to the alcohol also (Table 1).

Table 1: Rate constants for the oxidation of ethanol by TEACC at 298 K

10^3 [TEACC] mol dm^{-3}	[Alcohol] mol dm^{-3}	[TsOH] mol dm^{-3}	10^4 k_{obs} s^{-1}
1.00	0.10	0.00	13.2
1.00	0.20	0.00	23.5
1.00	0.40	0.00	47.0
1.00	0.60	0.00	71.1
1.00	0.80	0.00	92.7
1.00	1.00	0.00	126
2.00	0.20	0.00	24.3
4.00	0.20	0.00	22.5
6.00	0.20	0.00	25.2
8.00	0.20	0.00	23.4
1.00	0.40	0.00	49.5*

* contained 0.001 mol dm^{-3} acrylonitrile

Induced polymerization of acrylonitrile

The oxidation of alcohols, in an atmosphere of nitrogen, failed to induce polymerisation 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).

Effect of temperature

The rates of oxidation of ten secondary alcohols were determined at different temperatures and the activation parameters were calculated (Table 1).

Effect of acidity

The reaction is catalyzed by hydrogen ions (Table 2). The hydrogen-ion dependence has the following form of equation (2). The values of a and b, for ethanol, are 13.6 ± 0.36 × 10^{-4} s^{-1} and 22.1 ± 0.59 ×10^{-4} mol^{-1} dm^3 s^{-1} respectively (r^2 = 0.9971).

$$k_{obs} = a + b\,[H^+] \qquad \ldots(2)$$

Table 2: Effect of hydrogen ion concentration on the oxidation of ethanol by TEACC

[TEACC] = 0.001 mol dm^{-3}			[Alcohol] = 0.10 mol dm^{-3}		Temp. = 298 K	
$[H^+]$	0.10	0.20	0.40	0.60	0.80	1.00
$10^4\ k_{obs}/s^{-1}$	16.2	18.0	22.5	26.1	31.5	36.0

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).

Table 3: Rate constants and activation parameters for oxidation of alcohols, RCH_2OH, by TEACC

Alcohol (R)	$10^4\ k_2$ / dm^3 mol^{-1} s^{-1} at				Δ $H^\#$	Δ $S^\#$	Δ $G^\#$
	288K	298K	308K	318K	(kJ mol^{-1})	(J mol^{-1} K^{-1})	(kJmol^{-1})
H	1.15	3.71	11.4	34.2	83.5 ± 0.6	– 31 ± 2	92.5 ± 0.5

Cont…

Alcohol (R)	**10^4 k_2 / dm^3 mol^{-1} s^{-1} at**				**Δ $H^\#$**	**Δ $S^\#$**	**Δ $G^\#$**
	288K	**298K**	**308K**	**318K**	**(kJ mol^{-1})**	**(J mol^{-1} K^{-1})**	**(kJmol^{-1})**
Me	55.8	126	270	576	56.6 ± 0.4	– 92 ± 1	83.8 ± 0.3
Et	90.0	198	405	837	53.9 ± 0.4	– 97 ± 1	82.7 ± 0.
n-Pr	153	315	612	1170	49.0 ± 0.2	– 110 ± 1	81.6 ± 0.1
n-Bu	170	351	675	1260	48.2 ± 0.2	– 112 ± 1	81.3 ± 0.1
i-Pr	243	486	900	1660	46.1 ± 0.3	– 116 ± 1	80.5 ± 0.2
$ClCH_2$	1.62	4.41	11.7	27.9	69.9 ± 0.3	– 75 ± 1	92.1 ± 0.3
$MeOCH_2$	10.8	26.1	60.3	135	61.5 ± 0.3	– 88 ± 1	87.7 ± 0.2
t-Bu	2160	3360	4910	7200	27.9 ± 0.2	– 161 ± 1	75.8 ± 0.2
$MeCD_2OH$	9.27	21.6	48.0	106	59.2 ± 0.4	– 98 ± 1	88.2 ± 0.3
k_H/k_D	6.02	5.83	5.63	5.43			

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 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.

Table 4: Effect of solvents on the oxidation of ethanol by TEACC at 298 K

Solvents	**10^5 k_2 / s^{-1}**	**Solvents**	**10^5 k_2 /s^{-1}**
Chloroform	33.9	Acetic acid	8.32
1,2-Dichloroethane	41.7	Cyclohexane	1.29
Dichloromethane	45.7	Toluene	11.7
DMSO	126	Acetophenone	47.9
Acetone	38.9	THF	20.9
N,N-Dimethylformamide	63.1	t-Butyl alcohol	17.0
Butanone	17.8	1,4-Dioxane	18.6
Nitrobenzene	51.3	1,2-Dimethoxyethane	10.2
Benzene	14.8	Carbon disulphide	5.25
Ethyl acetate	14.1		

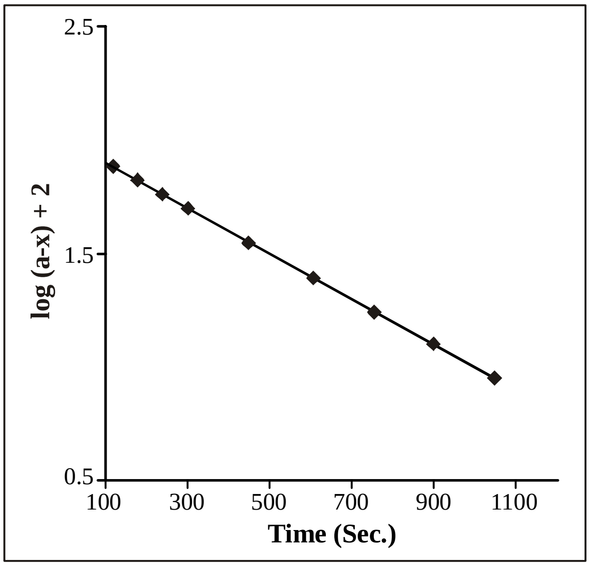


Fig. 1: Oxidation of ethyl alcohol by TEACC: A typical kinetic run

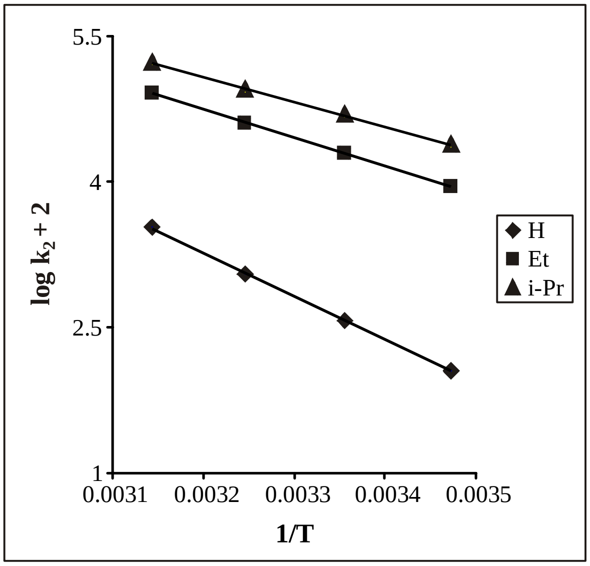


Fig. 2: Oxidation of alcohols by TEACC: Effect of temperatures

The activation enthapies and entropies of the oxidation of the nine aliphatic alcohols are linearly related (r = 0.9963). The value of isokinetic temperature evaluated[15-17] from this plot is 481 ± 31 K. The correlation was tested and found genuine by applying Exner's criterion[18]. An Exner's plot between log k_2 at 288 K and at 318 K was linear (r = 0.9879).

The value of isokinetic temperature evaluated from the Exner’s plot is 445 ± 25 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.

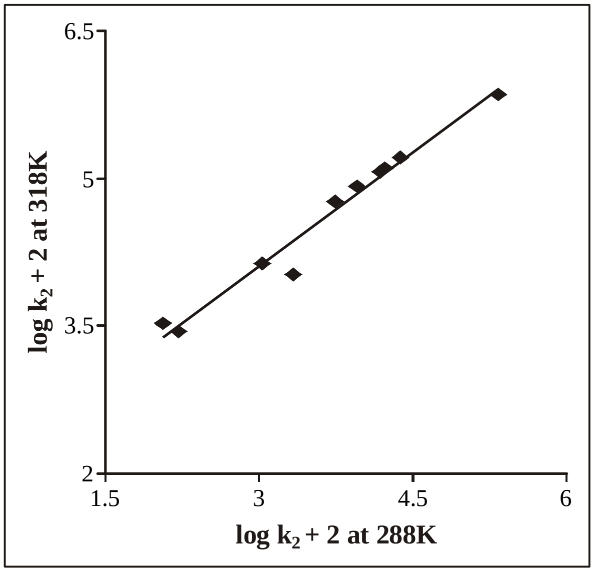


Fig. 3: Exner’s isokinetic relationship in the oxidation of alcohols by TEACC

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 protonation of TEACC to yield a protonated Cr (VI) species, which is a stronger oxidant and electrophile (Eq. 3).

$$[O_2CrCl\ O^-N^+Et_4] + H^+ \rightleftharpoons [H\overset{+}{Cr}OCl\ O^-\ N^+\ Et_4] \qquad ...(3)$$

Formation of a protonated Cr (VI) species has earlier been postulated in the reactions of structurally similar PCC[19] and QFC[20].

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[21] (Eq. 4).

$$\log k_2 = A_0 + p\pi^* + b\beta + a\alpha \quad \ldots(4)$$

$$\log k_2 = -4.22 + 1.64 (\pm 0.19)\, \pi^* + 0.16 (\pm 0.16)\, \beta + 0.15 (\pm 0.15)\, \alpha \quad \ldots(5)$$

$R^2 = 0.8654$; $sd = 0.18$; $n = 18$; $\psi = 0.40$

$$\log k_2 = -4.21 + 1.66 (\pm 0.18)\, \pi^* + 0.15 (\pm 0.15)\, \beta \quad \ldots(6)$$

$R^2 = 0.8643$; $sd = 0.17$; $n = 18$; $\psi = 0.39$

$$\log k_2 = -4.24 + 1.70 (\pm 0.17)\, \pi^* \quad \ldots(7)$$

$r^2 = 0.8555$; $sd = 0.17$; $n = 18$; $\psi = 0.39$

$$\log k_2 = -2.82 + 0.44 (\pm 0.36)\, \beta \quad \ldots(8)$$

$r^2 = 0.0864$; $sd = 0.43$; $n = 18$; $\psi = 0.98$

Here n is the number of data points and ψ is the Exner's statistical parameter[22].

Kamlet's[21] triparametric equation explains *ca.* 87% of the effect of solvent on the oxidation. However, by Exner's criterion[22] the correlation is not even satisfactory (cf. 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[23] equation (9) of cation- and anion-solvating concept of the solvents also.

$$\log k_2 = aA + bB + C \quad \ldots(9)$$

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. (9), separately with A and B and with (A + B).

$$\log k_2 = 0.75 (\pm 0.07)\, A + 1.69 (\pm 0.05)\, B - 3.99 \quad \ldots(10)$$

$R^2 = 0.9867$; $sd = 0.06$; $n = 19$; $\psi = 0.12$

$$\log k_2 = 0.57 (\pm 0.56)\, A - 2.83 \quad \ldots(11)$$

$r^2 = 0.0463;\ sd = 0.45;\ n = 19;\ \psi = 1.00$

$$\log k_2 = 1.63\ (\pm 0.14)\ B - 3.75 \qquad (12)$$

$r^2 = 0.8875;\ sd = 0.16;\ n = 19;\ \psi = 0.34$

$$\log k_2 = 1.38 \pm 0.13\ (A + B) - 3.96 \qquad \ldots(13)$$

$r^2 = 0.8739;\ sd = 0.16;\ n = 19;\ \psi = 0.36$

Here n is the number of data points and ψ is the Exner's statistical parameter[22].

The rates of oxidation of ethanol in different solvents showed an excellent correlation in Swain's equation (cf. equation 10) 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.* 87% of the data. In view of the fact that solvent polarity is able to account for *ca.* 82% 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 ($r^2 = 0.5077$; sd = 0.33; $\psi = 0.72$).

Correlation analysis of reactivity

The rates of oxidation of the alcohols failed to yield any significant correlation separately with Taft's[24] σ^* and E_s values [eqs. (14) and (15)].

$$\log k_2 = -1.99\ (\pm 0.33)\ \Sigma\sigma^* - 1.70 \qquad \ldots(14)$$

$r^2 = 0.8355;\ sd = 0.42;\ \psi = 0.43;\ n = 9$

$$\log k_2 = -1.07\ (\pm 0.32)\ \Sigma E_s - 2.19 \qquad \ldots(15)$$

$r^2 = 0.6117;\ sd = 0.65;\ \psi = 0.66;\ n = 9$

The rates were, therefore, correlated in terms of Pavelich-Taft's[25] dual substituent-parameter (DSP) equation (Eq. 16).

$$\log k_2 = \rho^* \sigma^* + \delta E_s + \log k_0 \qquad \ldots(16)$$

The values of substituent constants were obtained from the compilation by Wiberg[24]. The correlations are excellent; the reaction constants being negative (Table 4). There is no significant collinearity ($r^2 = 0.2322$) between σ^* and E_s values of the nine substituents.

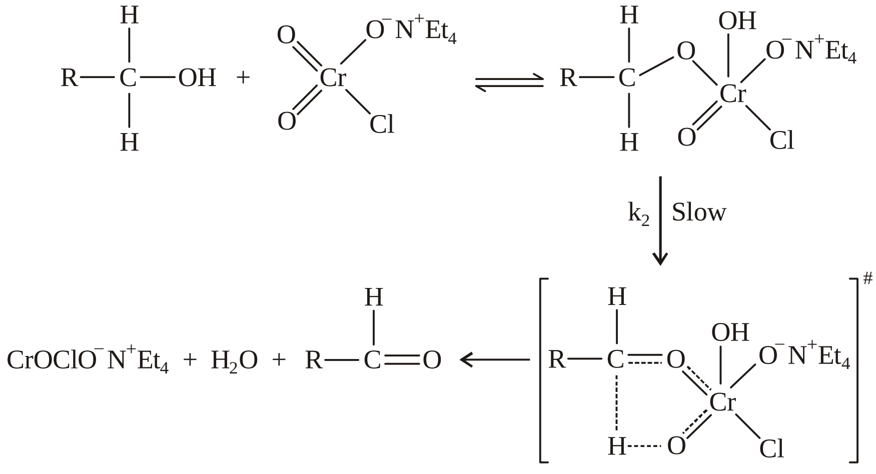
Table 5: Temperature dependence of the reaction constant

Temp./ K	ρ^*	δ	r^2	sd	ψ
288	–1.62 ± 0.01	–0.71 ± 0.01	0.9999	0.003	0.01
298	–1.53 ± 0.02	–0.63 ± 0.01	0.9998	0.003	0.02
308	–1.42 ± 0.01	–0.54 ± 0.02	0.9989	0.005	0.02
318	–1.35 ± 0.02	–0.45 ± 0.02	0.9999	0.005	0.01

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 uncrowded alcohols do not differ much and steric acceleration, therefore, results.

Mechanism

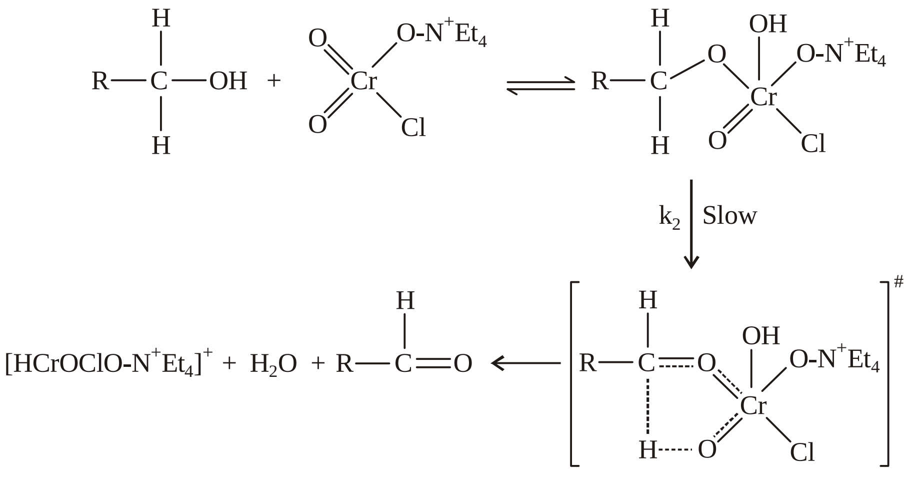
The presence of a substantial primary kinetic isotope effect confirms the cleavage of an α-C-H bond in the rate-determining step. The large negative value of the polar reaction constant together with substantial deuterium isotope effect indicate that the transition state approaches a carbocation in character. 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**).



Scheme 1

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[26] 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 $k_H/k_D = A_H/A_D \exp(E_a/RT)$[27-28] 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 ($\approx$ 4.5 kJ/mol) and the frequency factors and the entropies of activation of the respective reactions are nearly equal. Bordwell[29] 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[30]. Littler[31] 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**).

$$\mathrm{OCrOClO^-N^+Et_4} + \mathrm{H^+} \rightleftharpoons [\mathrm{HOCrOClO{-}N^+Et_4}]^+$$



Scheme 2

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