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Oxidation of aliphatic alcohols by triethylammonium chlorochromate in non-aqueous medium – A kinetic and mechanistic study

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Abstract The oxidation of some aliphatic alcohols by triethylammonium chlorochromate (Tri-EACC) in dimethyl sulfoxide leads to the formation of the corresponding carbonyl compounds. The reaction is first order with respect to TriEACC. The reaction exhibited Michaelis–Menten type kinetics with respect to alcohol. The reaction is catalyzed 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$_2$OH) exhibits a substantial primary kinetic isotope effect. Oxidation of aliphatic alcohol was studied in 19 different organic solvents. The solvent effect has been analysed using Kamlet's and Swain's multi-parametric equation. A suitable mechanism has been proposed.

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1. Introduction

Chromium(VI) is established as a versatile oxidant for many types of substrates varying from metal ions to naturally occurring organic compounds, and has a wide range of applications spanning the synthesis of sulfur nanoparticles (Lan et al., 2005) and the determination of biological oxygen demand in organic polluted water. Cr(VI) as chromate or dichromate is highly soluble in water, and is reported to be highly toxic (Losi et al., 1994; Viamajala et al., 2004), there is continued interest in the development of new chromium(VI) reagents for the effective and selective oxidation of organic substrates, in particular alcohols, under mild conditions. Therefore, the search for new oxidizing agents is of interest to synthetic organic chemists.

Many such reagents have been developed in recent years with some success, some of the important entries in the list of reagents are tetramethylammonium fluorochromate (Ghammami and Sadeghy, 2005), caffeinilium chlorochromate (Shirini et al., 2003), quinolinium chlorochromate (Elango et al., 2002), benzimidazolium fluorochromate (Mansoor, 2010), tributylammonium chlorochromate (TriBACC) (Mansoor and Shafi, 2010a,b), prolinium chlorochromate (Mamaghani et al., 2002) and tripropylammonium fluorochromate (Mansoor and Shafi, 2010a,b).

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Triethylammonium chlorochromate (Ghammamy and Dastpeyman, 2008) is also one such oxidant that developed recently. It is more efficient and a stronger oxidizing agent. This new compound is more efficient for quantitative oxidation of several organic substrates and has certain advantages over similar oxidizing agents in terms of the amount of oxidant and solvent required, short reaction times and high yields. In this paper, we describe the kinetics and mechanism of the oxidation of eight primary and three secondary aliphatic alcohols by TriEACC in dimethyl sulfoxide (DMSO) as the solvent.

Kinetics of oxidation of aliphatic alcohols by various oxidizing agents has been well studied (Sharma and Baghmar, 2001; Banerji et al.,1999, 2005, 2008; Jamel,1999). Large number of aliphatic alcohols are either commercially available or can be easily prepared. There seems to be no report on the oxidation of aliphatic alcohols by TriEACC. Therefore, we studied the kinetics of oxidation of aliphatic alcohols by TriEACC in DMSO. In aqueous solutions primary alcohols are usually oxidized to carboxylic acids (Lee and Spitzer, 1970; Robertson, 1941), while in the absence of water the oxidation will stop at the aldehyde. The major objective of this investigation is to study the solvent effect for the substrates undergoing oxidation and to propose a suitable mechanism for the oxidation.

2. Materials and methods

2.1. Reagents

Triethylamine and chromium trioxide were obtained from Fluka (Buchs, Switzerland). The aliphatic alcohols used were methanol, ethanol, propanol-1, butanol-1, pentanol-1, hexanol-1, heptanol-1, octanol-1, propanol-2, butanol-2 and pentanol-2. The procedure used for the purification of alcohols has been described earlier (Banerji et al., 1993). $[1,1-^2H_2]$ ethanol ($MeCD_2OH$) was prepared by Kalpan's method (Kalpan, 1958). Its isotopic purity, as ascertained by its NMR spectra, was $91 \pm 4\%$. 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 (Perrin et al., 1966).

2.2. Preparation of triethylammonium chlorochromate $(C_2H_5)_3NH^+[CrO_3Cl^-]$

Chromium(VI) oxide (1.0 g, 0.01 mol) was dissolved in water and 6 M hydrochloric acid (0.25 ml, 0.015 mol) was added with stirring at 0 °C. To the resulting orange solution, triethylamine (0.101 ml, 0.01 mol) was added drop-wise with stirring over a period of 30 min and the stirring was continued for 30 min at −4 °C. The precipitated orange solid was isolated by filtration, washed with petroleum ether (3 × 60 ml) and dried under vacuum for 2 h at room temperature (Ghammamy and Dastpeyman, 2008). Yield: (54%); m.p. 120 °C;

$$N(C_2H_5)_3 \underset{0\,°C}{\overset{CrO_3/6\,M\,HCl}{\rightarrow}} (C_2H_5)_3NH^+[CrO_3Cl]^- \qquad (1)$$

Triethyl amine   Triethylammonium chlorochromate
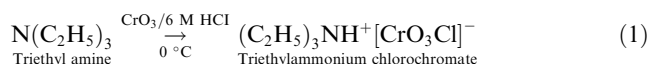
2.3. Product analysis

The product analysis was carried out under kinetic conditions. In a typical experiment, ethanol (2.30 g, 0.05 mol) and Tri-EACC (2.37 g, 0.01 mol) were made up to 50 cm^3 in DMSO and kept in the dark for about 15 h 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 2.0 g (90%) and 1.8 g (80%), 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 71% to 83%, 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 3.94 ± 0.16.

3. Experimental procedures

3.1. Kinetic measurements

The reactions were followed under pseudo-first-order conditions by keeping a large excess (×15 or greater) of the alcohol over TriEACC. 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 TriEACC spectrophotometrically at 364 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[TriEACC] against time. Duplicate kinetic runs showed that the rate constants were reproducible to within ±3%. Multivariate and simple linear regression analyses were carried out by the least-squares method.

4. Results and discussion

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

4.1. Stoichiometric studies

The oxidation of alcohols results in the formation of the corresponding carbonyl compounds. The overall reaction may be represented as Eq. (1):

$$RCH_2OH + CrO_2ClO^-NH^+Et_3$$
$$\rightarrow RCHO + H_2O + CrOClO^-NH^+Et_3 \qquad (1)$$

Thus TriEACC undergoes a two-electron change. This accords with the earlier observations with PFC (Banerji, 1988a,b) and QFC (Murugesan and Pandurangan, 1995).

4.2. Rate law

The reaction is first order with respect to TriEACC. Michaelis–Menten type kinetics was observed with respect to alcohols (Table 1). A plot of log k_{obs} vs log[EtOH] is linear with slope va-

Table 1 Effect of varying the concentration of [EtOH], [TriEACC] and [H$^+$] on the rate of reaction at 303 K.

$10^3 \times$ [TriEACC] (mol dm^{-3})	$10^2 \times$ [EtOH] (mol dm^{-3})	[TsOH] (mol dm^{-3})	$10^4 \times k_{obs}$ (s^{-1})
1.0	4.0	0.0	19.36 ± 0.08
2.0	4.0	0.0	19.24 ± 0.06
3.0	4.0	0.0	19.86 ± 0.10
4.0	4.0	0.0	19.04 ± 0.04
5.0	4.0	0.0	19.44 ± 0.11
1.0	2.0	0.0	9.96 ± 0.05
1.0	6.0	0.0	26.50 ± 0.20
1.0	8.0	0.0	34.30 ± 0.26
1.0	10.0	0.0	44.20 ± 0.18
1.0	4.0	0.2	38.43 ± 0.24
1.0	4.0	0.4	45.60 ± 0.16
1.0	4.0	0.6	57.34 ± 0.12
1.0	4.0	0.8	71.80 ± 0.26
1.0	4.0	1.0	86.20 ± 0.28
1.0	4.0	0.0	19.98[a] ± 0.08

[a] Contained 0.001 mol dm^{-3} acrylonitrile.
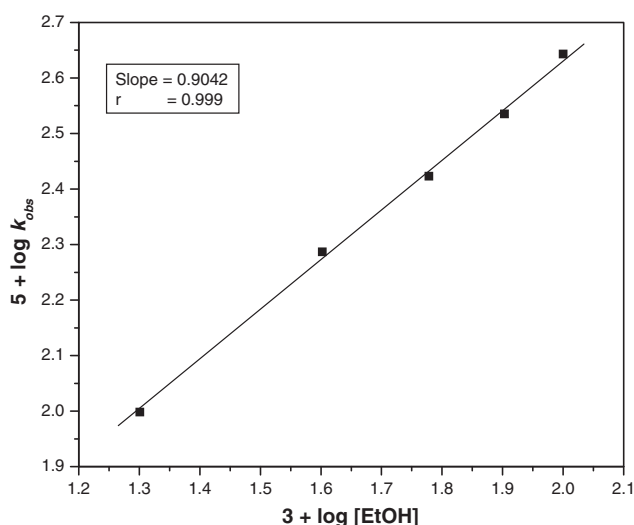
Figure 1 Order plot for the oxidation of aliphatic alcohol by triethylammonium chlorochromate at 303 K.

lue of 0.9042 (Fig. 1). This indicates the following Eqs. (2) and (3) to represent the mechanism. Eq. (4) represents the rate law:

$$\text{Alcohol} + \text{TriEACC} \overset{K}{\rightleftharpoons} [\text{Complex}] \quad (2)$$

$$\text{Complex} \overset{k_2}{\rightarrow} \text{Product} \quad (3)$$

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

4.3. 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).

4.4. Thermodynamic parameters

The variation in alcohol concentration was studied at four temperatures and the values of k_2 and K were evaluated from the double reciprocal plots. The thermodynamic parameters for the complex formation is calculated and presented in Table 2. The activation parameters for the disproportionation have been evaluated from the slope and intercept of Eyring's plot of log(k_2/T) against $1/T$, from k_2 at 298, 303, 308 and 313 K by the method of least squares and presented in Table 3. A representative Eyring's plot for the disproportionation of ethyl alcohol by TriEACC is given in Fig. 2. The least square method gives the values and standard errors of enthalpy and entropy of activation, respectively. Statistical analysis of the Eyring equation clearly confirms that the standard errors of $\Delta H^{\#}$ and $\Delta S^{\#}$ correlate.

$(\Delta S^{\#}) = 1/T_{av}(\Delta H^{\#})$, where T_{av} is the centre of the temperature range was used. It follows that in most solution phase studies $(\Delta S^{\#}) \approx (\Delta H^{\#}) \times 0.003$ K^{-1} (Lente et al., 2005). The negative entropy of activation suggests a definite orientation in the transition state and this may be in part due to the solvation of the activated complex.

4.5. Kinetic isotope effect

To ascertain the importance of cleavage of the C–H bond in the rate-determining step, oxidation of [1,1-^{2}H$_2$] ethanol was

Table 2 Formation constants of the TriEACC–RCH$_2$OH complexes and thermodynamic parameters.

Substrate	K (dm^3 mol^{-1})				$-\Delta H^{\#}$	$-\Delta S^{\#}$	$-\Delta G^{\#}$ (303 K)
	298 K	303 K	308 K	313 K			
Methanol	3.40	3.06	2.75	2.45	19.42 ± 0.4	42.70 ± 1.1	6.70 ± 0.5
Ethanol	4.39	3.90	3.50	3.16	19.51 ± 0.2	41.80 ± 0.6	6.84 ± 0.3
Propanol-1	5.26	4.72	4.16	3.58	22.40 ± 1.2	46.50 ± 3.0	8.30 ± 1.0
Butanol-1	4.10	3.50	2.90	2.50	28.52 ± 0.6	57.60 ± 1.5	11.10 ± 1.0
Pentanol-1	4.60	3.80	3.20	2.60	31.66 ± 1.0	66.35 ± 3.0	11.63 ± 1.1
Hexanol-1	4.30	3.60	3.10	2.50	30.06 ± 1.2	63.95 ± 3.4	10.69 ± 1.1
Heptanol-1	5.10	4.50	3.90	3.50	22.46 ± 1.0	50.15 ± 3.0	7.26 ± 0.8
Octanol-1	4.70	3.94	3.32	2.78	29.61 ± 0.5	62.95 ± 1.0	10.55 ± 0.7
Propanol-2	5.22	4.40	3.60	2.90	32.95 ± 1.3	69.80 ± 4.0	11.8 ± 0.8
Butanol-2	3.80	3.40	3.05	2.70	20.12 ± 0.4	47.70 ± 1.0	5.69 ± 0.5
Pentanol-2	4.20	3.50	3.20	2.80	22.81 ± 1.4	50.90 ± 4.0	7.38 ± 0.9

$\Delta H^{\#}$ in kJ mol^{-1}; $\Delta S^{\#}$ in J K^{-1} mol^{-1}; $\Delta G^{\#}$ in kJ mol^{-1}.
[Substrate] = 4.0×10^{-2} M; [TriEACC] = 1.0×10^{-3} M.

Table 3 Rate constants for the decomposition of TriEACC–RCH$_2$OH complexes and activation parameters in DMSO.

Substrate	$10^4 \times k_2$ (s^{-1})				$\Delta H^{\#}$	$-\Delta S^{\#}$	$\Delta G^{\#}$ (303 K)
	298 K	303 K	308 K	313 K			
Methanol	1.74	2.80	4.48	7.20	70.80 ± 1.0	79.40 ± 3.0	94.85 ± 2.0
Ethanol	48	75	120	180	66.23 ± 0.8	67.02 ± 2.3	86.55 ± 1.5
Propanol-1	151	244	390	624	70.64 ± 0.6	42.49 ± 1.8	83.51 ± 1.2
Butanol-1	254	410	615	935	64.14 ± 1.0	59.66 ± 3.0	82.71 ± 2.1
Pentanol-1	334	530	791	1203	63.66 ± 1.0	60.85 ± 3.0	82.09 ± 2.0
Hexanol-1	5700	8100	11,800	17,000	54.70 ± 1.2	66.15 ± 3.6	74.74 ± 2.4
Heptanol-1	8400	13,200	18,500	28,000	58.58 ± 2.0	49.35 ± 6.0	73.50 ± 4.0
Octanol-1	15,000	21,000	31,000	45,000	53.61 ± 1.5	58.95 ± 4.5	71.43 ± 3.0
Propanol-2	20,000	27,000	37,000	57,000	45.76 ± 1.0	85.37 ± 3.0	71.62 ± 2.0
Butanol-2	23,600	32,500	45,000	62,500	47.86 ± 0.6	77.33 ± 2.0	71.79 ± 1.0
Pentanol-2	29,000	38,000	49,000	65,000	38.86 ± 0.8	105.65 ± 2.4	70.87 ± 1.5

$\Delta H^{\#}$ in kJ mol^{-1}; $\Delta S^{\#}$ in J K^{-1} mol^{-1}; $\Delta G^{\#}$ in kJ mol^{-1}.
[Substrate] = 4.0×10^{-2} M; [TriEACC] = 1.0×10^{-3} M.
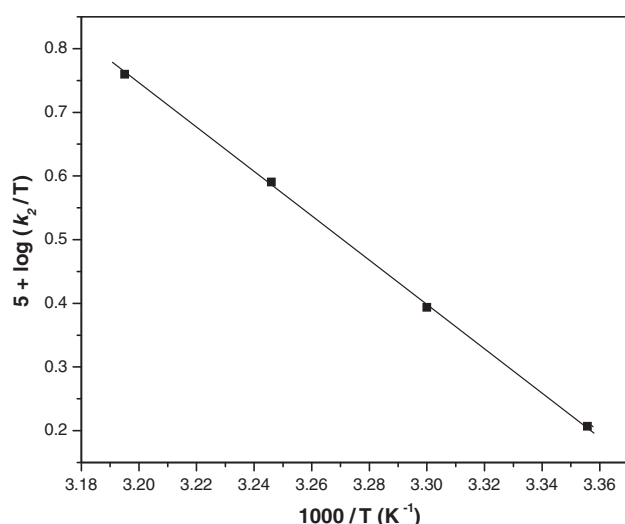
Figure 2 Eyring's plot for the oxidation of aliphatic alcohol by triethylammonium chlorochromate.

studied. The results showed the presence of a substantial primary kinetic isotope effect (Table 4).

4.6. Effect of acidity

The reaction is catalyzed by hydrogen ions. The hydrogen-ion dependence has the following form Eq. (5). The results are recorded in Table 1:

$$K_{obs} = a + b[H^+] \tag{5}$$

To determine whether the acidity is affecting the formation constant, K, and/or the rate constant, k_2, of the disproportionation, the effect of variation in the alcohol concentration was studied at different acidities. Results showed that K is not appreciably affected by changes in the acidity, whereas the value of k_2 vary. The values of a and b, for ethanol, are $23.35 \pm 0.3 \times 10^{-4}$ s^{-1} and $60.87 \pm 0.4 \times 10^{-4}$ mol^{-1} dm^3 s^{-1}, respectively ($r^2 = 0.9926$).

4.7. Isokinetic relationship

There is no significant isokinetic relationship between the activation enthalpies and entropies of the oxidation of eleven alcohols ($r^2 = 0.6788$). A correlation between the calculated values of enthalpies and entropies of activation is often vitiated by the experimental errors associated with them. Exner (1964) has suggested an alternative method of testing the validity of isokinetic relationship. An Exner's plot between log k_2 at 298 K and at 303 K was linear ($r^2 = 0.9960$) (Fig. 3). The value of isokinetic temperature evaluated from the Exner's plot is 644 ± 22 K. The linear isokinetic correlation implies that all the alcohols are oxidized by the same mechanism and are governed by the changes in both the enthalpy and entropy of the activation.

4.8. Solvent effect

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

Table 4 Rate constants for the decomposition of TriEACC–EtOH complex and kinetic isotope effect.

Substrate	$10^4 \times k_2$ (s^{-1})			
	298 K	303 K	308 K	313 K
Ethanol	48 ± 0.66	75 ± 0.80	120 ± 1.20	180 ± 0.76
MeCD$_2$OH	9.39 ± 0.14	13.76 ± 0.20	21.27 ± 0.24	30.25 ± 0.13
k_H/k_D	5.11	5.45	5.64	5.95

[EtOH] = 4.0×10^{-2} M; [TriEACC] = 1.0×10^{-3} M.
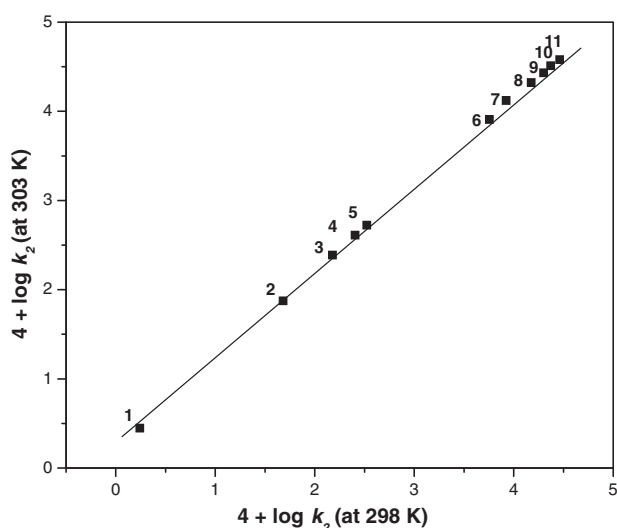
Figure 3 Exner's plot for the oxidation of aliphatic alcohol by triethylammonium chlorochromate between $4 + \log k_2$ (at 303 K) and $4 + \log k_2$ (at 298 K). (1) Methanol; (2) ethanol; (3) propanol-1; (4) butanol-1; (5) pentanol-1; (6) hexanol-1; (7) heptanol-1; (8) octanol-1; (9) propanol-2; (10) butanol-2; (11) pentanol-2.

4.9. Solvent–reactivity correlation

4.9.1. The Kamlet–Taft method for the examination of solvent effect

In order to obtain a deeper insight into the various solvent–solvent–solute interactions, which influence reactivity, the solvatochromic comparison method developed by Kamlet et al. (1983) has been used. This method may be used to unravel, quantify, correlate and rationalize multiple interacting solvent effects on the reactivity. The kinetic data were correlated with the solvatochromic parameters α, β and π^* characteristic of different solvents in the form of following LSER:

$$\log k_2 = A_o + p\pi^* + b\beta + a\alpha \tag{6}$$

where π^* is an index of solvent dipolarity/polarizability, which measures the ability of the solvent to stabilize a charge or a dipole by virtue of its dielectric effect, α is the solvent HBD (hydrogen bond donor) acidity, β is the solvent HBA (hydrogen bond acceptor) basicity of the solvent in a solute to solvent hydrogen bond and A_o is the intercept term.

The rate constants of oxidation, k_2, in 18 solvents (CS$_2$ was not considered, as the complete range of solvent parameters was not available) were correlated in terms of the linear solva-

Table 6 Solvent parameters (Kamlet et al., 1983).

Solvent	π^*	α	β
Chloroform	0.58	0.44	0.00
1,2-Dichloroethane	0.81	0.00	0.00
Dichloromethane	0.82	0.30	0.00
DMSO	1.00	0.00	0.76
Acetone	0.71	0.08	0.48
DMF	0.88	0.00	0.69
Butanone	0.67	0.06	0.48
Nitrobenzene	1.01	0.00	0.39
Benzene	0.59	0.00	0.10
Cyclohexane	0.00	0.00	0.00
Toluene	0.54	0.00	0.11
Acetophenone	0.90	–	0.49
THF	0.58	0.00	0.55
tert-Butyl alcohol	0.41	0.68	1.01
1,4-Dioxane	0.55	0.00	0.37
1,2-Dimethoxyethane	0.53	0.00	0.41
Carbon disulfide	–	–	–
Acetic acid	0.64	1.12	–
Ethyl acetate	0.55	0.00	0.45

tion energy relationship equation (6) of Kamlet et al. (1983). It may be mentioned here that out of the 18 solvents, 12 have a value of zero for α.

Kamlet et al. (1981) established that the effect of a solvent on the reaction rate should be given in terms of the following properties: (i) the behaviour of the solvent as a dielectric, facilitating the separation of opposite charges in the transition state, (ii) the ability of the solvent to donate a proton in a solvent-to-solute hydrogen bond and thus stabilize the anion in transition state and (iii) the ability of the solvent to donate an electron pair and, therefore, stabilize the initial aliphatic alcohol, by way of a hydrogen bond between the alcoholic proton and the solvent electron pair. The parameter π^* is an appropriate measure of the first property, while the second and third properties are governed by the parameters α and β, respectively. The solvent parameters (π^*, α and β) are taken from the literature (Kamlet et al., 1983) and are given in Table 6.

In order to explain the kinetic results through the solvent polarity and basicity or acidity, the rate constants were correlated with the solvatochromic parameters π^*, α and β using total solvatochromic equation, Eq. (6). The correlation of kinetic data was realized by means of multiple linear regression analysis. It was found that the rate constants in 19 solvents showed satisfactory correlation with the π^*, α and β solvent parameters. The results of correlation analysis in terms of Eq (6), a

Table 5 Rate constants for the decomposition of TriEACC–RCH$_2$OH complexes at 303 K in various solvents.

Solvents	$10^4 \times k_2$ (s^{-1})	Solvents	$10^4 \times k_2$ (s^{-1})
Chloroform	20.3 ± 0.40	Toluene	6.70 ± 0.04
1,2-Dichloroethane	19.1 ± 0.18	Acetophenone	33.6 ± 0.20
Dichloromethane	24.5 ± 0.16	THF	10.4 ± 0.16
DMSO	75.0 ± 0.80	*tert*-Butyl alcohol	9.10 ± 0.11
Acetone	22.3 ± 0.20	1,4-Dioxane	12.6 ± 0.10
DMF	37.0 ± 0.12	1,2-Dimethoxyethane	5.60 ± 0.14
Butanone	17.5 ± 0.08	Carbon disulfide	2.90 ± 0.08
Nitrobenzene	30.4 ± 0.18	Acetic acid	4.10 ± 0.06
Benzene	7.10 ± 0.06	Ethyl acetate	8.10 ± 0.04
Cyclohexane	0.72 ± 0.02		

biparametric equation involving π^* and β are given below in Eqs. (7)–(10):

$$\log k_2 = -4.08 + (1.66 \pm 0.20)\pi^* + (0.24 \pm 0.12)\beta \\ + (0.18 \pm 0.06)\alpha \tag{7}$$

$R^2 = 0.8456; \quad SD = 0.11; \quad n = 18; \quad \psi = 0.35$

$$\log k_2 = -4.11 + (1.75 \pm 0.15)\pi^* + (0.16 \pm 0.08)\beta \tag{8}$$

$R^2 = 0.8524; \quad SD = 0.10; \quad n = 18; \quad \psi = 0.28$

$$\log k_2 = -4.09 + (1.79 \pm 0.19)\pi^* \tag{9}$$

$r^2 = 0.8628; \quad SD = 0.11; \quad n = 18; \quad \psi = 0.24$

$$\log k_2 = -3.11 + (0.43 \pm 0.38)\beta \tag{10}$$

$r^2 = 0.7922; \quad SD = 0.35; \quad n = 18; \quad \psi = 0.88$

Here n is the number of data points and ψ is the Exner's statistical parameter (Mansoor, 2010).

Kamlet's triparametric equation (Kamlet et al., 1983) explains $ca.$ 85% of the effect of solvation on the oxidation. However, by Exner's criterion (Exner, 1966) the correlation is not even satisfactory (cf. Eq. (10)). The major contribution is of solvent polarity. It alone accounted for $ca.$ 79% of the data. Both α and β play relatively minor roles.

4.9.2. The Swain's method for the examination of solvent effect

The data on solvent effect were analyzed in terms of Swain's equation (Swain et al., 1983) of cation- and anion-solvating concept of the solvents also:

$$\log k_2 = aA + bB + C \tag{11}$$

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. (11), separately with A and B and with $(A + B)$:

$$\log k_2 = (0.64 \pm 0.03)A + (1.80 \pm 0.02)B - 4.30 \tag{12}$$

$R^2 = 0.9919; \quad SD = 0.04; \quad n = 19; \quad \psi = 0.12$

$$\log k_2 = 0.48(\pm 0.27)A - 3.08 \tag{13}$$
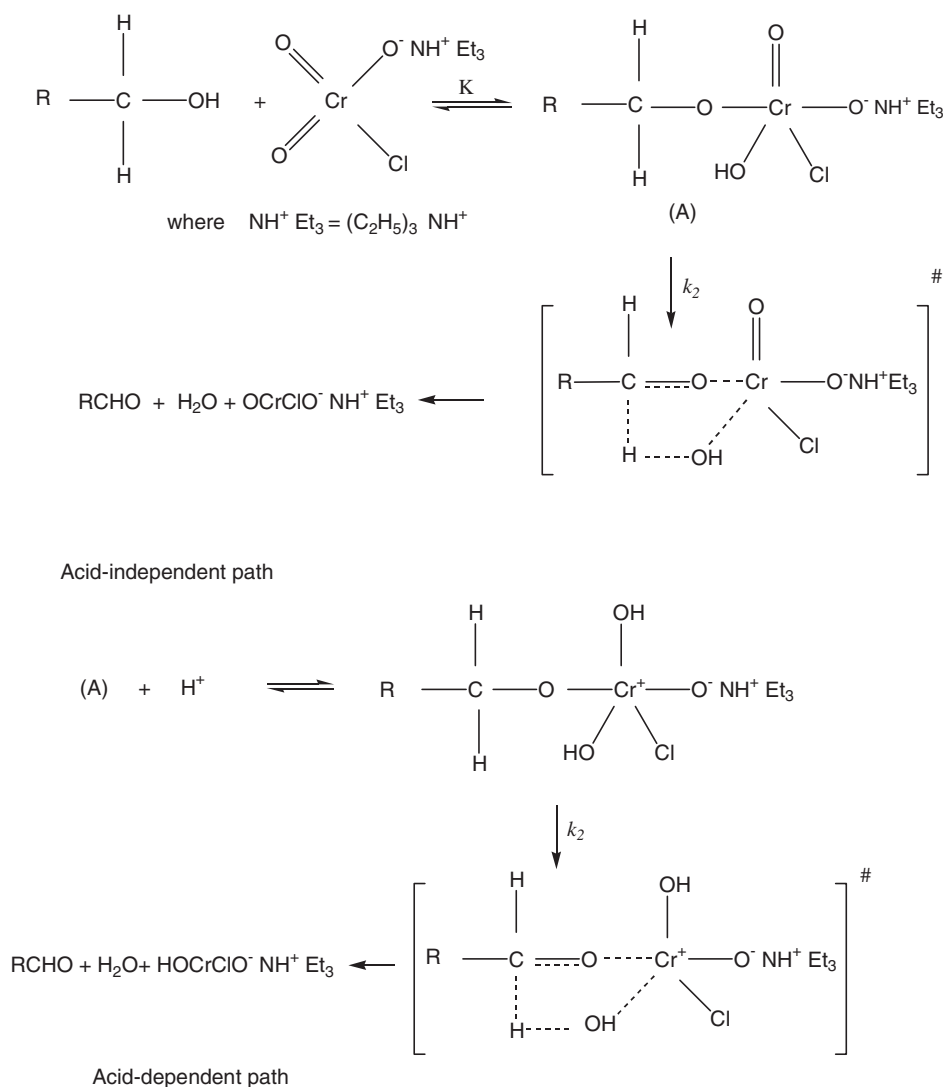
$r^2 = 0.0305; \quad SD = 0.08; \quad n = 19; \quad \psi = 0.88$

$$\log k_2 = 1.75(\pm 0.14)B - 4.18 \tag{14}$$

$r^2 = 0.9419; \quad SD = 0.19; \quad n = 19; \quad \psi = 0.35$

$$\log k_2 = 1.43 \pm 0.16(A + B) - 4.29 \tag{15}$$

$r^2 = 0.8876; \quad SD = 0.23; \quad n = 19; \quad \psi = 0.55$

Scheme 1 Mechanism of oxidation of aliphatic alcohols by TriEACC.

The rates of decomposition of TriEACC–RCH$_2$OH complexes in different solvents showed an excellent correlation in Swain's equation with the cation-solvating power playing the major role. In fact, the cation solvation alone accounts for *ca.* 94% of the data. The correlation with anion-solvating power was very poor. The solvent polarity, represented by $(A + B)$, also accounted for *ca.* 88% of the data.

4.10. Mechanism of oxidation

A hydrogen abstraction mechanism leading to the formation of the free radicals is unlikely in view of the failure to induce polymerization of acrylonitrile and no effect of the radical scavenger on the reaction rate. Therefore, a hydride-ion transfer in the rate-determining step is suggested (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. The hydride-transfer mechanism is also supported by the major role of cation-solvating power of the solvents. Therefore, it is likely that the oxidation involves a hydride-ion transfer via a chromate ester. This postulation is supported by an analysis of the temperature dependence of kinetic isotope effect. Kwart and Nickel (1973) 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 $k_H/k_D = A_H/A_D \exp(E_a/RT)$ (Kwart and Latimer, 1971; Kwart and Slutsky, 1972) shows 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^{-1}) and the frequency factors and the entropies of activation of the respective reactions are nearly equal. Similar phenomena were observed earlier in the oxidation of diols by BPCC (Banerji et al., 1997) and that of alcohols by PFC (Banerji, 1988a,b). Bordwell (1974) has documented 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 (Woodward and Hoffman, 1969). Littler (1971) 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).

5. Conclusion

The oxidation of eight primary and three secondary aliphatic alcohols by triethylammonium chlorochromate (TriEACC) in dimethyl sulfoxide were studied. The oxidation leads to the formation of the corresponding carbonyl compounds. The reaction is first order with respect to TriEACC. The reaction exhibited Michaelis–Menten type kinetics with respect to the alcohol. The reaction is catalyzed by hydrogen ions. The hydrogen-ion dependence has the form: $k_{obs} = a + b$ [H$^+$]. Oxidation of aliphatic alcohol was studied in 19 different organic solvents. The solvent effect has been analyzed using Kamlet's and Swain's multi-parametric equation. A hydrogen abstraction mechanism has been proposed.

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