Journal of Molecular Liquids 155 (2010) 85–90

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Studies on the kinetics of tripropylammonium fluorochromate oxidation of some aromatic alcohols in non-aqueous media

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ARTICLE INFO

Article history:
Received 5 February 2010
Received in revised form 4 May 2010
Accepted 13 May 2010
Available online 21 May 2010

Keywords:
Tripropylammonium fluorochromate
Aromatic alcohols
Kinetics
Solvent effect

ABSTRACT

The oxidation of benzyl alcohol (BnOH) and a few *para*-substituted benzyl alcohols by tripropylammonium fluorochromate (TriPAFC) in dimethylsulphoxide (DMSO) leads to the formation of corresponding aldehydes. The reaction is first order each in TriPAFC and the alcohols. The reaction is catalysed by hydrogen ions. The hydrogen ion dependence has the form: $k_{obs} = a + b[\mathrm{H}^+]$. The oxidation of α α′-dideuterio benzyl alcohol exhibited a substantial primary kinetic isotope effect ($k_H/k_D = 5.45$ at 303 K). Oxidation of benzyl alcohol was studied in 19 different organic solvents. The solvent effect has been analysed using Kamlet's and Swain's multiparametric equation. A mechanism involving a hydride ion transfer *via* chromate ester is proposed.

1. 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 like pyridinium chlorochromate [1,2], tributylammonium chlorochromate [3], pyridinium fluorochromate [4], imidazolium fluorochromate [5], quinolinium chlorochromate [6], quinolinium flurochromate [7], tetraethylammonium chlorochromate [8], isoquinilinium bromochromate [9], benzimidazolum fluorochromate [10] and benzyltrimethylammonium fluorochromate [11] have been reported. Tripropylammonium fluorochromate (TriPAFC) is one such compound used for the oxidation of primary alcohols [12]. Kinetics of oxidation of alcohols by various oxidizing agents have been well studied [13–19].

Substituted benzyl alcohols are suitable for studying the structure–rate correlations, as a large number of monosubstituted benzyl alcohols are either commercially available or can be easily prepared. There seems to be no report on the oxidation of benzyl alcohols by TriPAFC. Therefore, we studied the kinetics of oxidation of benzyl alcohol and several *para*-substituted benzyl alcohols by TriPAFC in DMSO. The major objective of this investigation is to study the solvent effect for the substrates undergoing oxidation.

2. Experimental

2.1. Materials

Tripropylamie and chromium trioxide were obtained from Fluka (Buchs, Switzerland). The benzyl alcohols used were with substituents H, *p*-NMe$_2$, *p*-OMe, *p*-OEt, *p*-Me, *p*-F, *p*-Cl, *p*-Br, *p*-COOEt, *p*-CN and *p*-NO$_2$. The procedure used for the purification of alcohols has been described earlier [20]. Due to non-aqueous nature of the solvent, *p*-toluenesulfonic acid was used as a source of hydrogen ions. Solvents were purified by the usual methods [21].

2.2. Preparation of tripropylammonium fluorochromate

Tripropylammonium fluorochromate is easily prepared as follows: chromium (VI) oxide (15.0 g, 0.150 mol) was dissolved in water in a polyethylene beaker and 40% hydrofluoric acid (11.3 mL, 0.225 mol) was added with stirring at 0 °C. To the resultant orange solution, tripropylammine (28.3 mL, 0.150 mol) was added drop wise with stirring to this solution over a period of 0.5 h and stirring was continued for 0.5 h at 0 °C. The precipitated orange solid was isolated by filtration, washed with petroleum ether (3 × 60 mL) and dried in vacuum for 2 h at room temperature [12]. Yield 37.5 g (95%); mp 142 °C.

$$\underset{\text{Tripropyl amine}}{\mathrm{N(C_3H_7)_3}} \xrightarrow[0\,^{\circ}\mathrm{C}]{\mathrm{CrO_3\,/\,40\%\,HF}} \underset{\text{Tripropylammonium fluorochromate}}{\mathrm{(C_3H_7)_3NH^+[CrO_3F]^-}} \quad (1)$$

The bright orange crystalline reagent can be stored in polyethylene containers for long periods without decomposition. The chromium (VI) content may be easily determined iodometrically.

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doi:10.1016/j.molliq.2010.05.012

2.3. Product analysis

Product analysis was carried under kinetic conditions. In a typical experiment, benzyl alcohol (5.4 g, 0.05 mol) and tripropylammonium fluorochromate (2.63 g, 0.01 mol) were made up to 50 cm^3 in DMSO and kept in the dark for 24 h to ensure completion of the reaction. The solution was then treated with an excess (150 cm^3) of a saturated solution of 2, 4-dinitro phenyl hydrazine in 2 mol dm^{-3} HCl and kept overnight in a refrigerator. The precipitated 2, 4-dinitro phenyl hydrazone (DNP) was filtered off, dried, weighed, recrystallised from ethanol, and weighed again. The DNP was found identical (m.pt and mixed m.pt.) with DNP of benzaldehyde. (m.pt 234–236 °C, lit 237 °C). Similar experiments were performed with other alcohols also.

2.4. Kinetic measurements

The pseudo-first-order conditions were attained by maintaining a large excess (×15 or more) of alcohol over TriPAFC. The solvent was DMSO, unless specified otherwise. The reactions were followed, at constant temperatures (±0.01 K), by monitoring the decrease in [TriPAFC] spectrophotometrically at 368 nm. No other reactant or product has any significant absorption at this wavelength. The pseudo-first-order rate constant. k_{obs}, was evaluated from the linear ($r = 0.990$ to 0.999) plots of log [TriPAFC] against time for up to 80% reaction. Duplicate kinetic runs showed that the rate constants were reproducible to within ±3%. The second order rate constant k_2, was obtained from the relation $k_2 = k_{obs}/[\text{alcohol}]$. All experiments, other than those for studying the effect of hydrogen ions, were carried out in the absence of TsOH.

3. Results and discussion

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

3.1. Stoichiometric studies

The stoichiometry of the reaction was determined by carrying out several sets of experiments with varying amounts of TriPAFC largely in excess over benzyl alcohol. The estimation of unreacted TriPAFC showed that 1 mol of TriPAFC reacts with 1 mol of benzyl alcohol.

$$C_6H_5CH_2OH + CrO_2FOTriPNH \rightarrow C_6H_5CHO + CrOFOTriPNH + H_2O \qquad (2)$$

3.2. Rate law

The reactions were found to be first order with respect to TriPAFC. The individual kinetic runs were strictly first order to TriPAFC. Further, the pseudo-first-order rate constants do not depend on the initial concentration of TriPAFC. The reaction rate increases with an increase in the concentration of benzyl alcohols (Table 1).

3.3. Induced polymerization of acrylonitrile

The oxidation of benzyl alcohol by TriPAFC, in an atmosphere of nitrogen failed to induce the polymerization of acrylonitrile. Further, an addition of a radical scavenger, acrylonitrile, has no effect on the rate (Table 1).

3.4. Effect of acidity

The reaction is catalysed by hydrogen ions (Table 1). Hydrogen ion dependence has the following form $k_{obs} = a + b[H^+]$. The values of a and b, for benzyl alcohol at 303 K are $14.87 \pm 0.04 \times 10^{-5}$ s^{-1} and $20.74 \pm 0.09 \times 10^{-5}$ mol^{-1} dm^3 s^{-1} respectively ($r^2 = 0.996$).

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

10^3[TriPAFC] mol dm^{-3}	10^2 [BnOH] mol dm^{-3}	[TsOH] mol dm^{-3}	10^5 k_1 s^{-1}
0.5	2.0	0.0	15.08
1.0	2.0	0.0	15.26
1.5	2.0	0.0	15.12
2.0	2.0	0.0	15.04
2.5	2.0	0.0	15.06
1.0	4.0	0.0	30.10
1.0	6.0	0.0	45.40
1.0	8.0	0.0	60.74
1.0	10.0	0.0	76.10
1.0	2.0	0.1	16.50
1.0	2.0	0.2	19.80
1.0	2.0	0.4	23.10
1.0	2.0	0.6	27.10
1.0	2.0	0.8	31.60
1.0	2.0	0.0	14.98[a]

[a] Contained 0.001 mol dm^{-3} acrylonitrile.

3.5. Kinetic isotope effect

To ascertain the importance of the cleavage of the α-C–H bond in the rate-determining step, oxidation of α,α′-dideuterio benzyl alcohol was studied. Results showed the presence of a substantial primary kinetic isotope effect (Table 2).

3.6. Effect of solvent

The rate of oxidation of benzyl alcohols were determined in 19 different organic solvents. The choice of the solvents was limited by the solubility of TriPAFC and its reactivity with primary and secondary alcohols. There was no noticeable reaction with the solvents chosen. The kinetics were similar in all the solvents. The values of k_2 at 303 K are recorded in Table 3.

3.7. Effect of substituents

In order to study the effect of structure on reactivity, some *para*-substituted benzyl alcohols were subjected to oxidation kinetics by TriPAFC at four different temperatures *viz*., 298, 303, 308 and 313 K in DMSO. The activation parameters were calculated from k_2 at 298, 303, 308 and 313 K using the Eyring relationship by the method of least square and presented in Table 3. 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 [22]. The negative entropy of activation in conjunction with other experimental data supports the mechanism outlined in (Scheme 1).

Table 2
Kinetic isotope effect on the oxidation of benzyl alcohol by TriPAFC.

Substrate	$10^5 \times k_1$, s^{-1}			
	298 K	303 K	308 K	313 K
H	9.76	15.26	23.64	36.64
α,α′-BnOH	1.91	2.80	4.19	6.16
k_H/k_D	5.11	5.45	5.64	5.95

[BnOH] = 2.0×10^{-2} M, [TriPAFC] = 1.0×10^{-3} M.

Table 3
Activation parameters and second order rate constants for the oxidation of *para*-substituted benzyl alcohols by TriPAFC.

Substrate	103 × k_2, $dm^3mol^{-1}\,s^{-1}$				$\Delta H^{\#}$	$-\Delta S^{\#}$	$\Delta G^{\#}$ (303 K)
	298 K	303 K	308 K	313 K			
H	4.88	7.63	11.82	18.32	65.78 ± 0.5	68.50 ± 1.8	86.54 ± 1.0
p-OMe	18.86	30.42	46.84	73.00	67.13 ± 0.6	52.65 ± 1.8	83.08 ± 1.1
p-Me	9.20	14.62	22.22	34.42	60.17 ± 0.6	64.66 ± 2.1	79.76 ± 1.3
p-F	3.98	6.23	9.96	15.92	69.20 ± 1.1	58.80 ± 3.5	87.02 ± 2.1
p-Cl	2.96	4.56	7.30	11.54	68.07 ± 1.2	65.26 ± 3.9	87.84 ± 2.2
p-CN	0.51	0.77	1.22	1.96	67.16 ± 1.8	82.79 ± 5.8	92.24 ± 3.4
p-NO^2	0.28	0.42	0.68	1.10	74.55 ± 2.0	82.35 ± 7.0	99.50 ± 4.0
p-NMe^2	102.40	166.96	236.20	407.14	66.99 ± 3.5	56.63 ± 10.5	84.15 ± 6.6
p-OEt	17.92	26.85	43.92	68.40	67.37 ± 1.8	43.22 ± 5.6	80.46 ± 3.5
p-Br	2.42	3.66	5.96	9.34	68.77 ± 1.6	28.01 ± 5.0	77.25 ± 3.0
p-COOEt	0.88	1.54	2.44	3.66	70.95 ± 2.0	30.65 ± 6.8	80.23 ± 4.0

$\Delta H^{\#}$ in $kJ\,mol^{-1}$; $\Delta S^{\#}$ in $J\,K^{-1}\,mol^{-1}$; $\Delta G^{\#}$ in $kJ\,mol^{-1}$.
[BnOH] = 2.0×10^{-2} M, [TriPAFC] = 1.0×10^{-3} M.

3.8. Isokinetic relationship

The reaction is neither isoenthalpic nor isoentropic but complies with the compensation law also known as the isokinetic relationship.

$$\Delta H^{\#} = \Delta H^{o} + \beta \Delta S^{\#} \tag{3}$$

The isokinetic temperature β is the temperature at which all the compounds of the series react equally fast. Also, at the isokinetic temperature, the variation of substituent has no influence on the free energy of activation. In an isoentropic reaction, the isokinetic temperature lies at infinite and only enthalpy of activation determines the reactivity. The isokinetic temperature is zero for an isoenthalpic series, and the reactivity is determined by the entropy of activation [23]. The isokinetic relationship is tested by plotting the logarithms of rate constants at two different temperatures ($T_2 > T_1$) against each other according to Eq. (6).

$$\log k(\text{at } T_2) = a + b \log k(\text{at } T_1). \tag{4}$$

The linear relationship in Exner plots [24,25] at 4 + log k_2 (298 K) and 4 + log k_2 (303 K) observed in the present study implies the validity of the isokinetic relationship. Isokinetic temperature obtained is 484 K. The operation of isokinetic relationship reveals that all the substituted benzyl alcohols examined are oxidized through a common mechanism [26].

3.9. Hammett plot

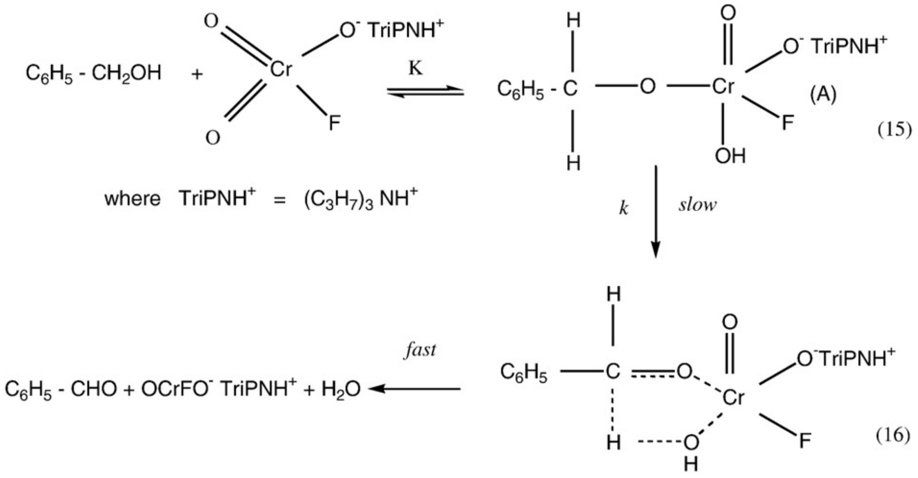
A Hammett's plot for the oxidation of benzyl alcohols by TriPAFC at various temperatures was found to be linear (Table 4). The value of the slope of the Hammett plot is known as reaction constant (ρ). Reaction constant values at different temperatures are given in Table 5. According to Hammett, the reaction with positive ρ values are accelerated by electron withdrawal from benzene ring, whereas those with negative ρ values are retarded by electron withdrawal from benzene ring [28]. In this oxidation reactions, the electron withdrawing groups decrease the rate and the electron donating groups increase the rate. These observations support the negative ρ values obtained from the Hammett plot.

3.10. The Kamlet–Taft Method for the examination of solvent effect

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 salvation energy relationship in Eq. (5) of Kamlet et al. [29]

$$\log k_2 = A_o + p\pi^* + b\beta + a\alpha \tag{5}$$

In this equation, π^* represents the solvent polarity, β the hydrogen bond acceptor basicities and α is the hydrogen bond donor acidity. A_o is the intercept term. It may be mentioned here that out of the 18 solvents, 12 have a value of zero for α.



Scheme 1. Acid-independent path.

Table 4
Second-order rate constants for the oxidation of benzyl alcohol by TriPAFC at 303 K in various solvents.

Solvents	$k_2 10^4$ $\mathrm{dm^{-3}\ mol^{-1}\ s^{-1}}$
Chloroform	22.3
1,2-Dichloroethane	18.1
Dichloromethane	25.4
DMSO	76.3
Acetone	22.6
DMF	37.0
Butanone	17.5
Nitrobenzene	32.5
Benzene	8.10
Cyclohexane	0.80
Toluene	6.90
Acetophenone	34.5
THF	11.0
tert-butyl alcohol	9.40
1,4-Dioxane	13.1
1,2-Dimethoxyethane	6.10
Carbon disulfide	3.20
Acetic acid	4.40
Ethyl acetate	8.60

Kamlet et al. [30] 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 benzyl 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 [29] and are given in Table 6. The linear dependence(LSER) on the solvent properties were used to correlate and predict a wide variety of solvent effect.

In order to explain the kinetic results through solvent polarity and basicity or acidity, the rate constants were correlated with the solvatochromic parameters π^*, α and β using total solvatochromic equation, Eq. (5). 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. (5), a biparametric equation involving π^* and β are given below in Eqs. (6)–(9).

$$\begin{gathered}\log k_2 = -3.95 + (1.65 \pm 0.20)\pi^* + (0.15 \pm 0.15)\beta - (0.11 \pm 0.14)\alpha \\ R^2 = 0.8670;\ \mathrm{SD} = 0.14;\ n = 18;\ \psi = 0.29\end{gathered} \tag{6}$$

Table 5
Reaction constant values for the oxidation of benzyl alcohol by TriPAFC at different temperatures[a].

Temperature (K)	Reaction constant (ρ)[b]	Correlation coefficient	Standard deviation
298	-1.68 ± 0.3	0.994	0.07
303	-1.66 ± 0.8	0.994	0.06
308	-1.61 ± 0.9	0.999	0.05
313	-1.57 ± 0.1	0.993	0.07

$[\mathrm{BnOH}] = 2.0 \times 10^{-2}$ M, $[\mathrm{TriPAFC}] = 1.0 \times 10^{-3}$ M.

[a] σ_p values were taken from reported works [27].

[b] The values were obtained by correlating log k_2 with σ_p for the reactions of oxidations.

Table 6
Solvent parameters [28].

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

$$\begin{gathered}\log k_2 = -4.00 + (1.70 \pm 0.16)\pi^* + (0.12 \pm 0.14)\beta \\ R^2 = 0.8624;\ \mathrm{SD} = 0.12;\ n = 18;\ \psi = 0.22\end{gathered} \tag{7}$$

$$\begin{gathered}\log k_2 = -4.02 + (1.72 \pm 0.17)\pi^* \\ r^2 = 0.8558;\ \mathrm{SD} = 0.16;\ n = 18;\ \psi = 0.29\end{gathered} \tag{8}$$

$$\begin{gathered}\log k_2 = -3.09 + (0.40 \pm 0.34)\beta \\ r^2 = 0.0780;\ \mathrm{SD} = 0.45;\ n = 18;\ \psi = 0.92\end{gathered} \tag{9}$$

Here n is the number of data points and ψ is the Exner's statistical parameter [31].

Kamlet's [29] triparametric equation explains ca. 86% of the effect of solvent on oxidation. However, by Exner's criterion [31] the correlation is not even satisfactory (cf. Eq. (9)). The major contribution is of solvent polarity. It alone accounted for ca. 80% of the data. Both α and β play relatively minor roles.

3.11. Swain's method

The data on solvent effect were analysed in terms of Swain's equation [32] of cation- and anion-solvating concept of the solvents also.

$$\log k_2 = aA + bB + C \tag{10}$$

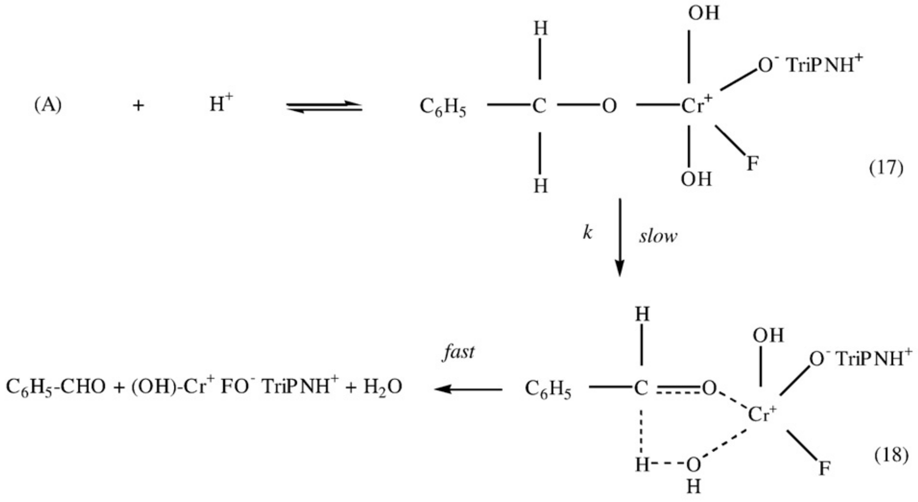
Here A represents the anion-solvating power of the solvent and B the cation-solvating power. C is the intercept term. $(A+B)$ is postulated to represent the solvent polarity. The rates in different solvents were analysed in terms of Eq. (10), separately with A and B and with $(A+B)$.

$$\begin{gathered}\log k_2 = (0.66 \pm 0.03)A + (1.72 \pm 0.02)B - 4.22 \\ R^2 = 0.9979;\ \mathrm{SD} = 0.02;\ n = 19;\ \psi = 0.03\end{gathered} \tag{11}$$

$$\begin{gathered}\log k_2 = 0.43(\pm 0.56)A - 3.02 \\ r^2 = 0.0312;\ \mathrm{SD} = 0.04;\ n = 19;\ \psi = 0.98\end{gathered} \tag{12}$$

$$\begin{gathered}\log k_2 = 1.73(\pm 0.12)B - 4.19 \\ r^2 = 0.9199;\ \mathrm{SD} = 0.12;\ n = 19;\ \psi = 0.18\end{gathered} \tag{13}$$

$$\begin{gathered}\log k_2 = 1.36 \pm 0.14(A + B) - 4.19 \\ r^2 = 0.8576;\ \mathrm{SD} = 0.18;\ n = 19;\ \psi = 0.25\end{gathered} \tag{14}$$



Scheme 2. Acid-dependent path.

The rates of oxidation of benzyl alcohol 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. 99% of the data. The correlation with anion-solvating power was very poor. The solvent polarity, represented by $(A+B)$, also accounted for ca. 86% of the data.

3.12. 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. Negative reaction constants are traditionally associated with an electron deficient centre in transition states: a convention originally developed from the analysis of substituent effects in nucleophilic displacement reactions. Negative reaction constants have been used by Banerji [33–35] as supporting evidence for oxidation mechanisms involving a hydride ion transfer in the rate-determining step.

Kwart and Nickel [36] have showed that a dependence of kinetic isotope effect on temperature can be gainfully employed to determine whether the loss of hydrogen proceeds through a concerted cyclic process or by an acylic one. The data for protio- and deuterio-benzyl alcohols, fitted to the expression: $k_H/k_D = A_H/A_D\ (-\Delta H^*/RT)$ [37,38] show a direct correspondence with the properties of a symmetrical transition state in which activation energy difference for protio and deuterio compounds is equal to the difference in the zero-point energy for the respective C–H and C–D bonds ($\approx$4.5 kJ mol^{-1}) and the entropies of activation of the respective reactions are almost equal.

It is well-established that intrinsically concerted sigmotropic reactions, characterized by transfer of hydrogen in a cyclic transition state, are the only truly symmetrical processes involving a linear hydrogen transfer [39]. Littler [40] has shown that a cyclic hydride transfer, in which the oxidation of alcohols by Cr(VI), involving six electrons and, being a Huckel-type system, is an allowed process. Thus, a transition state having a planar, cyclic and symmetrical structure can be envisaged for the decomposition of the ester intermediate. Hence, the overall mechanism is proposed to involve the formation of a chromate ester in a fast pre-equilibrium step and then a decomposition of the ester in a subsequent slow step *via* a cyclic concerted symmetrical transition state leading to the product.

The mechanism depicted in Scheme 1 leads to the following equation:

$$Rate = kK[\mathrm{BnOH}][\mathrm{TriPAFC}] \qquad (19)$$

It can be shown that

$$[\mathrm{TriPAFC}] = [\mathrm{TriPAFC}]_T / (1 + K[\mathrm{BnOH}]) \qquad (20)$$

Therefore,

$$-d[\mathrm{TriPAFC}]/dt = kK[\mathrm{BnOH}][\mathrm{TriPAFC}]_T / (1 + K[\mathrm{BnOH}]). \qquad (21)$$

Since the reaction is the first order with respect to each the alcohol and TriPAFC, one can assume that $1 >> K[\mathrm{BnOH}]$. The assumption is made because the concentration of alcohol is in the order of 0.001 to 0.002 mol dm^{-3} and which is very small compared with 1. The Eq. (22) can therefore, be written as

$$-d[\mathrm{TriPAFC}]/dt = kK[\mathrm{BnOH}][\mathrm{TriPAFC}]. \qquad (22)$$

This rate equation is in accord with the experimental results.

The observed dependence on the hydrogen ion concentration in the reaction shows that there is an additional acid-catalysed pathway. The acid-dependent pathway is given in Scheme 2.

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