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Correlation analysis of reactivity in the oxidation of some *para*- substituted benzhydrols by triethylammonium chlorochromate in non-aqueous media

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Abstract Triethylammonium chlorochromate (TriEACC) oxidation of some *para*-substituted ben-zhydrols (BH) in dimethylsulfoxide (DMSO) leads to the formation of corresponding benzophe-nones. The reaction was run under pseudo-first-order conditions. The reaction is catalyzed by hydrogen ions. The hydrogen ion dependence has the form: $k_{obs} = a + b[H^+]$. Various thermody-namic parameters for the oxidation have been reported and discussed along with the validity of isokinetic relationship. Oxidation of benzhydrol was studied in 18 different organic solvents. The rate data showing satisfactory correlation with Kamlet–Taft solvatochromic parameters (α, β and π^*) suggests that the specific solute–solvent interactions play a major role in governing the reac-tivity, and the observed solvent effects have been explained on the basis of solute–solvent complex-ation. A suitable mechanism of oxidation has been proposed.

1. Introduction

Specific and selective oxidation of organic compounds under non-aqueous conditions is an important reaction in synthetic organic chemistry. Chromium(VI) reagents are widely used in organic chemistry for oxidation of primary and secondary alcohols to carbonyl compounds. In recent years, some new chromium(VI) based reagents like tripropyl ammonium flu-orochromate (Mansoor and Shafi, 2016), tetraethylammonium bromochromate (Mansoor and Shafi, 2011), tetrabutylammo-nium bromochromate (Ghammamy et al., 2007), tetrahepty-lammonium bromochromate (Ghammamy et al., 2009), tetrahexylammonium fluorochromate (Koohestani et al., 2008), tetramethylammonium fluorochromate (Sadeghy and Ghammami, 2005), benzimidazolium fluorochromate (Mans-oor and Shafi, 2014), isoquinolinium bromochromate (Patwari et al., 2009) and tetraethylammonium chlorochromate (Mans-oor and Shafi, 2015) were proposed.

Triethylammonium chlorochromate (Ghammamy et al., 2007) is also one such oxidant developed recently. It is a more

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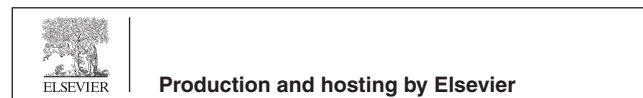
efficient and stronger oxidizing agent. This new compound is more efficient for quantitative oxidation of several organic substrates and has certain advantages over similar oxidizing agents in terms of the amount of oxidant and solvent required, short reaction times and high yields.

The kinetics of oxidation of benzhydrols have been studied by many reagents such as 2,2′-bipyridyl-Cu(II) permanganate (Grover et al., 1996), pyridinium chlorochromate (Venkataraman et al., 1978), tributylammonium chlorochromate (Mansoor and Shafi, 2010), chloramine-T (Rangappa et al., 1997), *N*-bromosuccinimide (Venkatasubramanian and Thiagarajan, 1969; Hiran et al., 2005), Tl(III) (Hiran et al., 2004), and *N*-bromopthalimide (Jagdeesh et al., 2009). We have been interested in the kinetic and mechanistic studies of Cr(VI) species. Literature survey reveals that no report is available on the kinetics of oxidation of benzhydrols by TriEACC. It was considered important to investigate oxidation by TriEACC. Hence, we report herein the kinetics of oxidation of some *p*-substituted benzhydrols by TriEACC in 18 different organic solvents.

2. Experimental

2.1. Materials

Triethylamine and chromium trioxide were obtained from Fluka (Buchs, Switzerland). The benzhydrols used were with substituents H, *p*-OCH$_3$, *p*-CH$_3$, *p*-F, *p*-Cl, and *p*-NO$_2$. The solvents acetonitrile (MeCN), chloroform (CF), 1,2-dichloroethane (DCE), dichloromethane (DCM), dimethyl sulfoxide (DMSO), acetone (Me$_2$CO), dimethylformamide (DMF), butanone (Bu), nitrobenzene (NB), benzene (Bz), cyclohexane (CH), toluene (TE), acetophenone (Ph$_2$CO), tetrahydrofuran (THF), *tert*-butanol (*t*-BuOH), 1,4-dioxane (DO), 1,2-dimethoxyethane (DME) and ethyl acetate (EA), are of analytical grade and purified by conventional methods (Perrin et al., 1966). Due to non-aqueous nature of the solvent, *p*-toluene sulfonic acid (TsOH) was used as a source of hydrogen ions.

Analar grade (Qualigens Fine Chemicals, Mumbai) benzhydrol (BH), *p*-chloro benzhydrol (*p*-Cl), *p*-methyl benzhydrol (*p*-Me), *p*-methoxy benzhydrol (*p*-OMe) and *p*-nitro benzhydrol (*p*-NO$_2$) (Lancaster, UK) were used for the kinetic study. The purity of benzhydrols was checked by m.p and IR spectrum.

Deuterated (α-C-D) benzhydrols were prepared by the method of Shanker and Suresh (Shanker and Suresh, 1970). α-D-benzhydrols were prepared by refluxing corresponding benzhydrols (α-C-H) in D$_2$O for 2–3 h, removing the solvent under pump, and repeating the process three times to ensure complete exchange of protons. PMR analysis was conducted to confirm the deuterated (α-C-D) benzhydrols.

2.2. Preparation of triethylammonium chlorochromate $(C_2H_5)_3$ NH^+ $[CrO_3Cl^-]$

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%); mp 120 °C;

$$N(C_2H_5)_3 \underset{\text{Triethyl amine}}{} \xrightarrow[0\,°C]{CrO_3/6\,M\ HCl} \underset{\text{Triethylammonium chlorochromate}}{(C_2H_5)_3NH^+[CrO_3Cl^-]} \tag{1}$$
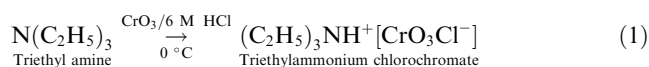
2.3. Product analysis

Product analysis was carried under kinetic conditions. In a typical experiment, benzhydrol (1.8 g, 0.01 mol) and TriEACC (5.56, 0.02 mol) were made up to 100 ml in DMSO and kept in the dark for 24 h to ensure 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 over night in a refrigerator. The solvent was removed and the precipitated 2,4-dinitrophenylhydrazone (DNP) was filtered off, dried, weighed, recrystallized from ethanol, and weighed again. The DNP was found identical (m.pt and mixed m.pt.) with DNP of benzophenone (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 TriEACC. The solvent was DMSO, unless specified otherwise. The reactions were followed, at constant temperatures (± 0.01 K), by monitoring the decrease in [TriEACC] spectrophotometrically at 359 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 ($r = 0.990$–0.999) plots of log [TriEACC] 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.

2.5. Data analysis

Correlation analysis was carried out using Microcal origin (version 6) computer software. The goodness of the fit was discussed using the correlation coefficient (r in the case of simple linear regression and R in the case of multiple linear regression) and standard deviation (SD).

3. Results and discussion

The rate data were determined for *p*-H, *p*-OCH$_3$, *p*-CH$_3$, *p*-Cl and *p*-NO$_2$ substituted benzhydrols and the results are reported in Table 1.

3.1. Stoichiometric studies

The stoichiometry of the reaction was determined by carrying out several sets of experiments with varying amounts of TriEACC largely in excess over benzhydrol. The estimation of unreacted TriEACC showed the following reaction

Table 1 Pseudo-first-order rate constants for the oxidation of *para*-substituted benzhydrols by TriEACC at 303 K in DMSO.

10^3[TriEACC] (mol dm^{-3})	10^2[BH] (mol dm^{-3})	[H$^+$] (mol dm^{-3})	$10^5\ k_I$ (s^{-1})				
			H	*p*-OCH$_3$	*p*-CH$_3$	*p*-Cl	*p*-NO$_2$
0.5	2.0	0.0	13.16	52.10	25.10	8.00	0.75
1.0	2.0	0.0	13.22	52.04	25.12	8.02	0.76
1.5	2.0	0.0	13.12	52.00	25.02	8.06	0.74
2.0	2.0	0.0	13.20	52.08	25.00	8.04	0.76
2.5	2.0	0.0	13.14	50.06	25.16	8.02	0.74
1.0	1.0	0.0	6.59	26.04	12.50	4.06	0.38
1.0	1.5	0.0	9.80	38.92	18.68	5.96	0.56
1.0	2.5	0.0	16.36	64.92	31.30	10.00	0.96
1.0	3.0	0.0	19.70	77.92	37.40	11.90	1.12
1.0	2.0	0.1	14.35	55.60	27.00	6.28	0.82
1.0	2.0	0.2	17.20	67.65	32.02	8.40	0.98
1.0	2.0	0.4	20.02	78.50	37.00	12.56	1.16
1.0	2.0	0.6	23.42	92.12	43.80	14.66	1.32
1.0	2.0	0.8	27.30	107.20	51.00	17.48	1.54
1.0	2.0	0.0	13.02	51.88	25.00	8.06	0.69[a]

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

$$(C_6H_5)_2CHOH + CrO_2ClO^-NH^+Et_3$$
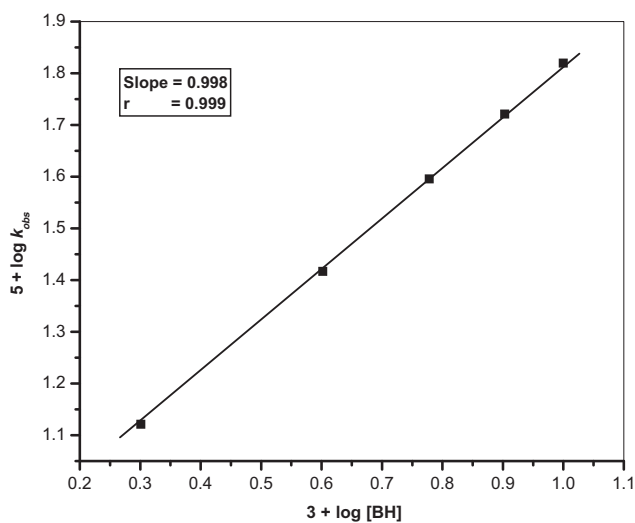$$\rightarrow (C_6H_5)_2CO + CrOClO^-NH^+Et_3 + H_2O \qquad (2)$$
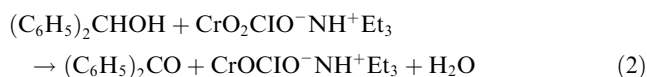
3.2. Order of reaction

The oxidation of benzhydrols with TriEACC in DMSO yields benzophenone. The rate of oxidation was found to be first order in [BH]. Linear plots of log k_{obs} versus log [BH] with unit slope demonstrate the first-order dependence of the rate on [BH] (Fig. 1). Similar results were obtained for the substituted benzhydrols also. The near constancy in the values of k_{obs} irrespective of the concentration of the TriEACC confirms the first order dependence on TriEACC (Table 1).

3.3. Effect of acidity

The reaction is catalyzed by hydrogen ions (Table 1). The hydrogen ion dependence has the following form $k_{obs} = a + b$

[H$^+$]. The values of a an b, for benzhydrol at 303 K are $13.01 \pm 0.4 \times 10^{-5}\,s^{-1}$ and $17.73 \pm 0.8 \times 10^{-5}\,mol^{-1}dm^3s^{-1}$ respectively ($r^2 = 0.996$).

3.4. Induced polymerization of acrylonitrile

The oxidation of benzhydrol by TriEACC, 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).

3.5. Kinetic isotope effect

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

3.6. Structure–reactivity correlation

The kinetics of oxidation of *para*-substituted benzhydrols were studied at four different temperatures *viz.*, 298, 303, 308 and 313 K (Table 2) in DMSO. The second order rate constants were calculated. An examination of these data indicates that the oxidation is accelerated by electron releasing substituents and retarded by electron withdrawing substituents in the phenyl ring. The order of the reactivity is as follows: *p*-OCH$_3$ > *p*-CH$_3$ > *p*-H > > *p*-Cl > *p*-NO$_2$.

Figure 1 Plot of log k_{obs} versus log [BH] for the oxidation of benzhydrol by TriEACC at 303 K in DMSO.

Table 2 Kinetic isotope effect on the oxidation of benzhydrol by TriEACC.

Substrate	$10^5 \times k_I$, (s^{-1})			
	298 K	303 K	308 K	313 K
H	8.70	13.22	19.16	28.40
α-C-D	1.67	2.39	3.51	4.85
k_H/k_D	5.20	5.53	5.45	5.86

[BH] = 2.0×10^{-2} mol dm^{-3}; [TriEACC] = 1.0×10^{-3} mol dm^{-3}.
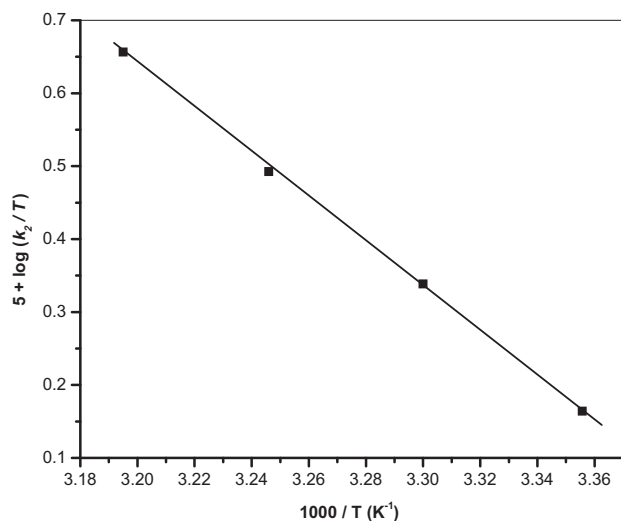
Figure 2 Eyring's plot of log (k_2/T) versus $1000/T$ for the oxidation of benzhydrol by TriEACC in DMSO at four different temperatures.

Figure 3 Exner's plot of log k_2 (298 K) versus log k_2 (308 K) for the oxidation of substituted benzhydrol by TriEACC in DMSO.
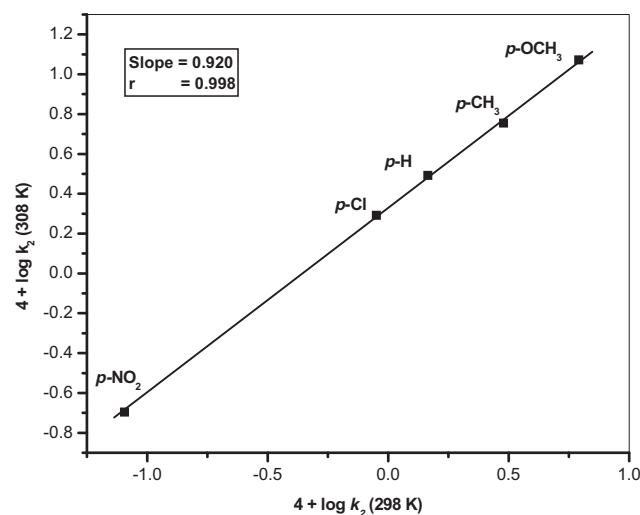
The enthalpy of activation, entropy of activation and free energy of activation were calculated from k_2 at 298, 303, 308 and 313 K using the Eyring relationship (Fig. 2) by the method of least square and presented in Table 3. The least square method gives the values and standard errors of enthalpy and entropy of activation respectively. Statistical analysis of the Eyring equation clearly confirms that the standard errors of $\Delta H^{\#}$ and $\Delta S^{\#}$ correlate (Lente et al., 2005). The entropy of activation is negative for all the benzhydrols.

3.7. Isokinetic relationship

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

$$\Delta H^{\#} = \Delta H^{\circ} + \beta \Delta S^{\#} \qquad (3)$$

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 (Bhuvaseshwari and Elango,

2007). 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. (4).

$$\log k\,(\mathrm{at}\,T_2) = a + b \log k\,(\mathrm{at}\,T_1) \qquad (4)$$

The linear relationship in Exner plots (Exner, 1964; Exner et al., 1973) at $3 + \log k_2$ (298 K) and $3 + \log k_2$ (308 K) observed in the present study implys the validity of the isokinetic relationship. Exner's plot is shown in Fig. 3 (slope = 0.920, $r = 0.999$, isokinetic temperature = 501 K). The operation of isokinetic relationship reveals that all the substituted benzhydrols are oxidized through a common mechanism (Leffler and Grunwald, 1963).

3.8. Hammett plot

A linear plot is obtained when σ for different substituents were plotted against log k_2. The value of slope of Hammett plot is known as reaction constant (ρ). Reaction constant values at different temperatures are given in Table 4. The Hammett plot is shown in Fig. 4 ($r = 0.995$, sd = 0.08) with $\rho = -1.66$ at 303 K. According to Hammett, the reaction with positive ρ values is accelerated by electron withdrawal from the benzene ring, whereas those with negative ρ values are retarded by electron withdrawal from the benzene ring (Hammett, 1940). In these oxidation reactions, the electron withdrawing groups

Table 3 Activation parameters and second order rate constants for the oxidation of *para*- substituted benzhydrols by TriEACC in DMSO.

Substrate	$10^3 k_2$ (dm^3 mol^{-1}s^{-1})				$\Delta H^{\#}$ kJ mol^{-1}	$-\Delta S^{\#}$ JK^{-1}mol	$\Delta G^{\#}$ kJ mol^{-1} (at 303 K)
	298 K	303 K	308 K	313 K			
H	4.35	6.61	9.58	14.20	58.26 ± 1.0	94.64 ± 3.0	86.93 ± 2.0
p-OCH$_3$	18.40	26.02	36.40	54.06	52.75 ± 2.0	101.26 ± 6.0	83.43 ± 3.8
p-CH$_3$	8.97	12.56	17.50	25.60	51.34 ± 2.0	111.90 ± 6.0	85.24 ± 3.8
p-Cl	2.66	4.01	6.04	9.08	60.90 ± 1.0	89.89 ± 3.0	88.13 ± 1.8
p-NO$_2$	0.24	0.38	0.62	0.98	70.46 ± 1.0	77.79 ± 3.0	94.03 ± 1.9

10^2 [Substrate] = 2.0 mol dm^{-3}; 10^3 [TriEACC] = 1.0 mol dm^{-3}.

Table 4   Reaction constant values for the oxidation of benzhydrol by TriEACC at different temperatures [a].

Temperature (K)	Reaction constant (ρ) [b]	Correlation coefficient	Standard deviation
298	-1.71 ± 0.7	0.996	0.07
303	-1.66 ± 0.3	0.994	0.04
308	-1.59 ± 0.5	0.993	0.06
313	-1.56 ± 0.9	0.996	0.07

$[BH] = 2.0 \times 10^{-2}$ mol dm^{-3}; $[TriEACC] = 1.0 \times 10^{-3}$ mol dm^{-3}
[a] σ_p Values were taken from reported works (Hammett, 1940).
[b] The values were obtained by correlating log k_2 with σ_p for the reactions of oxidations.
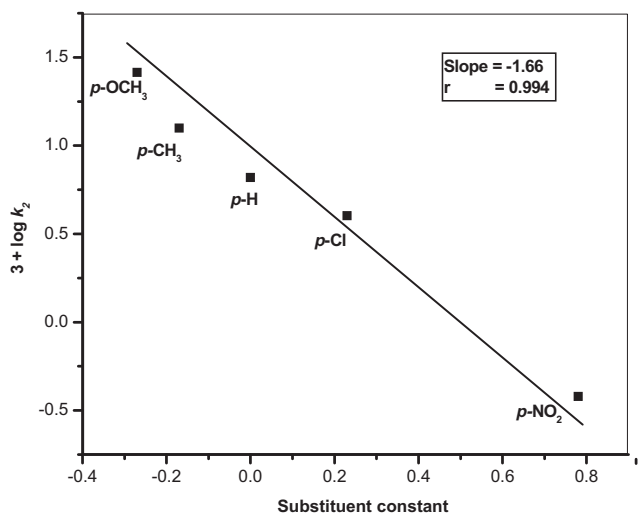
Figure 4   Hammett plot of log k_2 versus Substituent constant σ_p for the oxidation of substituted benzhydrol by TriEACC in DMSO at 303 K.

decrease the rate and the electron donating groups increase the rate. These observations supporting the negative ρ values are obtained from the Hammett Plot.

### 3.9. Solvent–reactivity correlation

The rate of oxidation of benzhydrol is determined in 18 different organic solvents *viz.*, MeCN, CF, DCE, DCM, DMSO, Me$_2$CO, DMF, Bu, NB, Bz, CH, TE, Ph$_2$CO, THF, *t*-BuOH, DO, DME and EA. The choice of the solvents was limited by the solubility of TriEACC 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 four different temperatures were determined. The thermodynamic parameters were also calculated for the oxidation of benzhydrol in 18 different organic solvents and the values are recorded in Table 5. Negative entropy of activation indicates a greater degree of ordering in the transition state than in the initial state, due to an increase in solvation during the activation process. The isokinetic relationship of benzhydrol in 18 different organic solvent is shown in Fig. 5. The existence of a linear relationship (slope = 0.914, $r = 0.995$, isokinetic temperature = 478 K) between $4 + \log k_2$ (298 K) and $4 + \log k_2$ (308 K) indicates that a common mechanism is operating in all studied solvent systems.

The influence of solvent on the rate of any reaction can be described in terms of solvation which is a stabilization process. Two viewpoints have been established on the solvation

Table 5   Activation parameters and second order rate constants for the oxidation of benzhydrol by TriEACC in 18 different organic solvents.

Substrate	$10^3 k_2$ (dm^3 mol^{-1} s^{-1})				$\Delta H^{\#}$ kJ mol^{-1}	$-\Delta S^{\#}$ JK^{-1} mol	$\Delta G^{\#}$ kJ mol^{-1} (at 303 K)
	298 K	303 K	308 K	313 K			
MeCN	5.40	7.70	10.40	14.46	47.96 ± 1.0	127.42 ± 3.0	86.56 ± 1.8
CF	1.35	1.90	2.52	3.70	48.68 ± 2.0	136.55 ± 6.0	90.05 ± 3.5
DCE	1.02	1.62	2.44	3.54	61.75 ± 1.3	94.87 ± 3.8	90.49 ± 2.5
DCM	1.52	2.20	3.30	4.74	56.67 ± 1.0	108.85 ± 3.0	89.65 ± 2.0
DMSO	4.50	6.60	9.40	13.50	54.07 ± 0.6	108.44 ± 1.8	86.92 ± 1.2
Me$_2$CO	1.12	1.85	3.08	5.08	75.62 ± 1.0	47.52 ± 3.0	89.86 ± 1.8
DMF	2.37	3.32	4.64	6.50	49.56 ± 0.7	128.90 ± 2.0	88.62 ± 1.5
Bu	1.10	1.50	2.13	2.88	47.67 ± 1.0	141.66 ± 3.0	90.59 ± 2.1
NB	1.90	2.75	3.96	5.86	55.49 ± 1.2	110.95 ± 3.0	89.10 ± 1.8
Bz	0.46	0.72	1.16	1.80	68.35 ± 1.0	79.65 ± 3.0	92.48 ± 2.0
CH	0.04	0.07	0.11	0.18	74.48 ± 1.4	479.16 ± 4.0	96.61 ± 2.6
TE	0.42	0.62	0.96	1.40	60.31 ± 1.0	107.38 ± 3.0	92.84 ± 1.9
Ph$_2$CO	2.30	3.06	4.16	5.68	44.22 ± 1.2	147.02 ± 3.5	88.76 ± 2.2
THF	0.58	0.95	1.58	2.62	75.47 ± 1.2	53.76 ± 3.4	91.75 ± 2.0
t-BuOH	0.52	0.83	1.36	2.20	72.18 ± 1.2	64.84 ± 3.3	92.12 ± 2.0
DO	0.76	1.13	1.70	2.54	59.92 ± 1.0	103.40 ± 3.0	91.15 ± 1.7
DME	0.31	0.50	0.80	1.28	70.65 ± 0.8	74.84 ± 2.2	93.32 ± 1.4
EA	0.44	0.75	1.26	2.10	78.11 ± 0.5	46.69 ± 1.5	92.25 ± 1.0

10^2 [Substrate] = 2.0 mol dm^{-3}; 10^3 [TriACC] = 1.0 mol dm^{-3}.
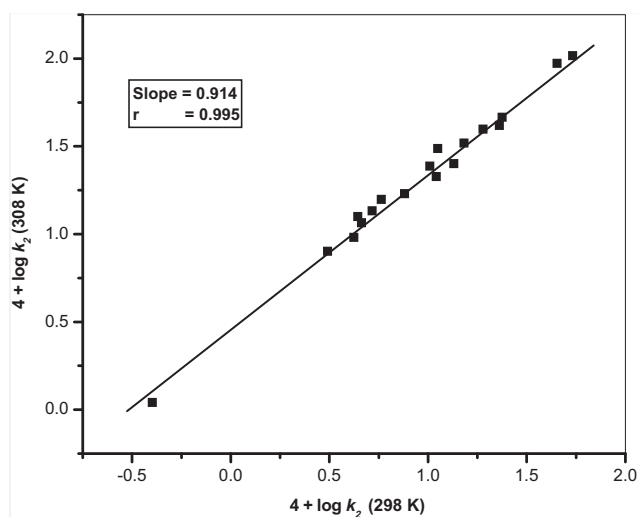
Figure 5 Exner's plot of $\log k_2$ (298 K) versus $\log k_2$ (308 K) for the oxidation of benzhydrol by TriEACC in 18 different organic solvents.

phenomenon. According to the first, a solvent is considered as a homogeneous continuum which surrounds the solute molecules and exerts long range interactions. The strength of these interactions with the solute molecules is described in terms of macroscopic physical properties of the solvent like dielectric constant (ε) and refractive index (η). According to the second view point, a solvent is considered to be anisotropic and inhomogeneous which exerts short range forces on the solute molecules. These forces are chemical in nature, and result in the formation of solvation complexes through donor–acceptor bonds which are localized and directed in space. The strength of these interactions is described in terms of solvation parameters namely hydrogen bond donor acidity (α), hydrogen bond acceptor basicity (β), etc., Thus the solvent can solvate the solute by exhibiting any of these interactions with the specific sites in the solute. Hence, the effect of solvent on the rate of the reaction can be described in terms of multi parameteric equation which involves different solvation parameters given by Kamlet–Taft (Kamlet et al., 1983).

3.10. The Kamlet–Taft method for the examination of Solvent effect

In order to get a deeper understanding about the various solvent–solvent–solute interactions which influence reactivity, we applied the following Kamlet–Taft equation.

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

In this equation, π^* represents an index of solvent dipolarity/oplarizability, which measures the ability of the solvent to stabilize a charge or a dipole by virtue of its dielectric effect, α is the solvent hydrogen bond donor (HBD) acidity, β is the solvent hydrogen bond acceptor (HBA) basicity of the solvent in a solute to solvent hydrogen bond. A_o is the intercept term, it is the regression value of the solute property in the reference solvent cyclohexane.

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 behavior of the solvent as a dielectric,

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

Solvent	π^*	α	β
Acetonitrile	0.75	0.19	0.31
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-Butylalcohol	0.41	0.68	1.01
1,4-Dioxane	0.55	0.00	0.37
1,2-Dimethoxyethane	0.53	0.00	0.41
Ethyl acetate	0.55	0.00	0.45

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 stabilizing the anion in transition state and (iii) the ability of the solvent to donate an electron pair and therefore stabilizing the initial 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. The linear dependence (LSER) on the solvent properties was used to correlate and predict a wide variety of solvent effect.

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. (5). The correlation of kinetic data was realized by means of multiple linear regression analysis. The regression coefficients s, a, and b measure the relative susceptibilities of the solvent – dependent solute property $\log k$ to the indicated solvent parameter. The rates of oxidation for all the compounds studied showed good correlations with solvent via the above LSER. The correlation results obtained are as follows:

it was found that the rate constants in nine 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).

$$\log k_2 = -3.95 + (1.65 \pm 0.20)\pi^*$$
$$+ (0.15 \pm 0.07)\beta - (0.14 \pm 0.06) \tag{6}$$
$$R^2 = 0.8670; \quad SD = 0.14; \quad n = 18; \quad \psi = 0.29$$

$$\log k_2 = -4.00 + (1.70 \pm 0.16)\pi^* + (0.14 \pm 0.06)\beta$$
$$R^2 = 0.8624; \quad SD = 0.12; \quad n = 18; \quad \psi = 0.22 \tag{7}$$

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

$$\log k_2 = -3.09 + (0.40 \pm 0.34)\beta \qquad (9)$$
$$r^2 = 0.0780; \quad SD = 0.45; \quad n = 18; \quad \psi = 0.92$$

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

Kamlet's (Kamlet et al., 1983) triparametric equation explains ca. 86% of the effect of solvent on the oxidation. However, by Exner's criterion (Exner, 1966) 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. The Swain's method

Swain et al. (1983) believed that the specific solvation is determined principally by the acidity and the basicity of the solvent. The data are analyzed using a two-parameter equation involving anion-solvating tendency (A) and cation-solvating tendency (B).

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

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 analyzed in terms of Eq. (10), separately with A and B and with $(A + B)$.

$$\log k_2 = (0.69 \pm 0.03)A + (1.79 \pm 0.02)B - 4.25 \qquad (11)$$
$$R^2 = 0.9983; \quad SD = 0.02; \quad n = 18; \quad \psi = 0.03$$
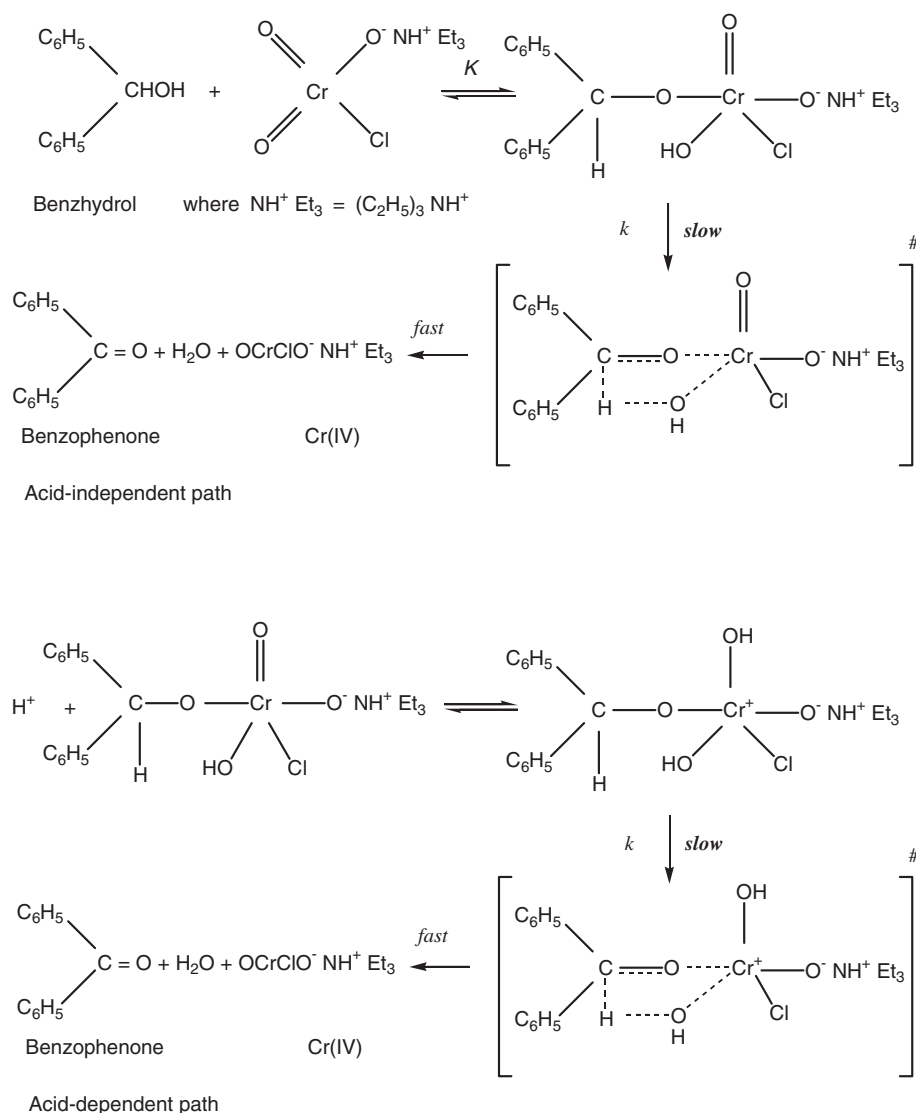
$$\log k_2 = 0.55(\pm 0.36)A - 3.02 \qquad (12)$$
$$r^2 = 0.0312; \quad SD = 0.04; \quad n = 18; \quad \psi = 0.98$$

$$\log k_2 = 1.79(\pm 0.10)B - 4.19 \qquad (13)$$
$$r^2 = 0.9199; \quad SD = 0.12; \quad n = 18; \quad \psi = 0.18$$

$$\log k_2 = 1.41 \pm 0.14(A + B) - 4.19 \qquad (14)$$
$$r^2 = 0.8576; \quad SD = 0.18; \quad n = 18; \quad \psi = 0.25$$

Scheme 1 Mechanism of oxidation of Benzhydrol by TriEACC.

The rates of oxidation of benzhydrol 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 (1978a,b, 1988) as supporting evidence for oxidation mechanisms involving a hydride-ion transfer in the rate determining step. The negative entropy of activation also supports the mechanism outlined in Scheme 1.

Kwart and Nickel (1973) 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-benzhydrols, fitted to the expression: $kH/kD = AH /AD (-\Delta H^*/RT)$ (Kwart and Latimer, 1971; Kwart and Slutsky, 1972) 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 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 Hoffmann, 1969). Littler (1971) 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:

$$\text{Rate} = kK[\text{BH}][\text{TriEACC}] \qquad (15)$$

It can be shown that [TriEACC]

$$= [\text{TriEACC}]_{\text{T}}/(1 + K[\text{BH}]) \qquad (16)$$

Therefore,

$$-\text{d}[\text{TriEACC}]/\text{dt} = kK[\text{BH}][\text{TriEACC}]_{\text{T}}/(1 + K[\text{BH}]) \qquad (17)$$

Since the reaction is the first order with respect to each of the benzhydrol and TriEACC, one can assume that $1 >> K[\text{BH}]$. The assumption is made because the concentration of benzhydrol is in the order of 0.001–0.002 mol dm^{-3} and which is very small compared with 1. The Eq. (18) can therefore, be written as

$$-\text{d}[\text{TriEACC}]/\text{dt} = kK[\text{BH}][\text{TriEACC}] \qquad (18)$$

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-catalyzed pathway. The acid-dependent pathway is given in Scheme 1.

4. Conclusions

The oxidation of benzhydrol by Triethylammonium chlorochromate (TriEACC) is the first order with respect to [BH] and [TriEACC]. The reaction is catalyzed by hydrogen ions. The hydrogen ion dependence has the form: $k_{\text{obs}} = a + b[\text{H}^+]$. Various thermodynamic parameters for the oxidation have been reported and discussed along with the validity of isokinetic relationship. The entropy of activation is negative, suggesting the formation of a complex in a rate-determining step. Oxidation of benzhydrol was studied in 18 different organic solvents. The solvent effect has been analyzed using the Kamlet multi parametric equation. A suitable mechanism of oxidation involving a hydride-ion transfer in the rate determining step is suggested.

References

Banerji, K.K., 1978a. J. Chem. Soc.. Perkin Trans. 2, 639–641.
Banerji, K.K., 1978b. Bull. Chem. Soc. Jpn. 51, 2732–2734.
Banerji, K.K., 1988. J. Org. Chem. 53, 2154–2159.
Bhuvaseshwari, D.S., Elango, K.P., 2007. Int. J. Chem. Kinet. 39, 657–663.
Exner, O., 1964. Nature, p. 488.
Exner, O., Streitwiser, J.R., Talt, R.W., 1973. Progress in Physical Organic Chemistry. John Wiley, New York, p. 41.
Exner, O., 1966. Collect. Czech. Chem. Commun. 31, 3222–3251.
Ghammamy, S., Mehrani, K., Afrand, H., Hajighahrammani, M., 2007. Afr. J. Pure Appl. Chem. 1 (1), 008–010.
Ghammamy, S., Dastpeyman, S., 2008. J. Chin. Chem. Soc. 55, 229–232.
Ghammamy, S., Mehrani, K., Afrand, H., Javanshir, Z., Rezaeibehbahani, G., Moghimi, A., Aghbolagh, Z.S., 2009. J. Chil. Chem. Soc. 54, 491–493.
Grover, A., Varshney, S., Banerji, K.K., 1996. Indian J. Chem. 35B, 171–178.

Hammett, L.P., 1940. Physical Organic Chemistry, 1st ed. McGraw-Hill, New York.

Hiran, B.L., Malkani, R.K., Rathore, N., 2005. Kinet. Catal. 46, 360–365.

Hiran, B.L., Malkani, R.K., Nalwaya, N., Chand, K., Rathore, N., 2004. Oxid. Commun. 27, 98–102.

Jagdeesh, B., Archana, C., Balaji, M., Fulchand, C., Mazahar, F., Milind, U., 2009. J. Indian Chem. Soc. 86, 481–484.

Kamlet, M.J., Abboud, J.L.M., Abraham, M.H., Taft, R.W., 1983. J. Org. Chem. 48, 2877–2887.

Kamlet, M.J., Abboud, J.L.M., Taft, R.W., 1981. Prog. Phys. Org. Chem. 13, 485–633.

Koohestani, B., Javanshir, Z., Ghammamy, S., Mehrani, K., Afrand, H., Saghatforoush, L., 2008. J. Mex. Chem. Soc. 52, 116–119.

Kwart, H., Nickel, J.H., 1973. J. Am. Chem. Soc. 95, 3394–3396.

Kwart, H., Latimer, M.C., 1971. J. Am. Chem. Soc. 93, 3770.

Kwart, H., Slutsky, J., 1972. J. Chem. Soc. Chem. Commu., 1182–1183.

Leffler, J.F., Grunwald, E., 1963. Rates and Equilibrium of Organic Reactions. Wiley, New York.

Lente, G., Fabian, I., Poe, A.J., 2005. New J. Chem. 29, 759–760.

Littler, J.S., 1971. Tetrahedron 27, 81–91.

Mansoor, S.S., Shafi, S.S., 2016. Correlation analysis of reactivity in the oxidation of some organic diols by tripropylammonium fluorochromate in non-aqueous media. Arab. J. Chem. 9, S602–S609.

Mansoor, S.S., Shafi, S.S., 2011. Z Phys. Chem. 225, 249–263.

Mansoor, S.S., Shafi, S.S., 2014. Oxidation of aniline and some para-substituted anilines by benzimidazolium fluorochromate in aqueous acetic acid medium – a kinetic and mechanistic study. Arab. J. Chem. 7, 171–176.

Mansoor, S.S., Shafi, S.S., 2010. Reac. Kinet. Mech. Cat. 100, 21–31.

Mansoor, S.S., Shafi, S.S., 2015. Oxidation of methionine by tetraethylammonium chlorochromate in non-aqueous media – a kinetic and mechanistic study. Arab. J. Chem. 8, 480–486.

Patwari, S.B., Khansole, S.V., Vibhute, Y.B., 2009. J. Iran Chem. Soc. 6, 399–404.

Perrin, D.D., Armarego, W.L., Perrin, D.R., 1966. Purification of Organic Compounds. Pergamon Press.

Rangappa, K.S., Ramachandran, H., Mahadevappa, D.S., 1997. J. Phys. Org. Chem. 10, 159–166.

Sadeghy, B., Ghammami, S., 2005. Russ. J. Gen. Chem. 75, 1886–1888.

Shanker, R., Suresh, K.S., 1970. Curr. Sci. 39, 65.

Swain, C.G., Swain, M.S., Powel, A.L., Alunni, S., 1983. J. Am. Chem. Soc. 105, 502–513.

Venkataraman, K.S., Sundaram, S., Venkatasubramanian, N., 1978. Indian J. Chem. 16B, 84–88.

Venkatasubramanian, N., Thiagarajan, V., 1969. Can. J. Chem. 47, 694–697.

Woodward, R.W., Hoffmann, R., 1969. Angew. Chem. Int. Ed. Eng. 8, 781–853.