JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2002; **15:** 721–727
DOI: 10.1002/poc.541

Correlation analysis of reactivity in oxidation of substituted benzyl alcohols by tetrabutylammonium tribromide

Ashok Kumar, Pradeep K. Sharma and Kalyan K. Banerji*

Department of Chemistry, J.N.V. University, Jodhpur 342 005, India

Received 18 February 2002; revised 3 April 2002; accepted 21 May 2002

ABSTRACT: Oxidation of benzyl alcohol and some *ortho-*, *meta-* and *para*-monosubstituted benzyl alcohols by tetrabutylammonium tribromide (TBATB) in aqueous acetic acid leads to the formation of corresponding benzaldehydes. The reaction is first order each in TBATB and the alcohol. The oxidation of [1,1-$^2H_2$]benzyl alcohol ($PhCD_2OH$) exhibited a substantial kinetic isotope effect. Addition of tetrabutylammonium chloride or potassium bromide did not affect the rate. Tribromide ion has been postulated as the reactive oxidizing species. The reaction rate increases with increase in the polarity of the solvent. The rates of oxidation of *meta-* and *para*-substituted benzyl alcohols showed excellent correlation in terms of Charton's triparametric LDR, equation whereas the oxidation of *ortho*-substituted benzyl alcohols correlated best with the LDRS equation. The oxidation of *para*-substituted benzyl alcohols is more susceptible to the delocalization effect than is the oxidation of *ortho-* and *meta*-substituted compounds, which display a greater dependence on the field effect. The positive value of η suggests the presence of an electron-deficient reaction centre in the rate-determining step. The reaction is subject to steric acceleration by the *ortho*-substituents. A suitable mechanism is proposed. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: alcohols; correlation analysis; mechanism; oxidation; tribromide

INTRODUCTION

Tetraalkylammonium polyhalides are widely used as halogenating reagents in synthetic organic chemistry.[1–3] Recently, tetrabutylammonium tribromide (TBATB) has been used for the bromination and oxidation of some selected organic substrates.[4–7] The polyhalides are more suitable than molecular halogens because of their solid nature, ease of handling, stability, selectivity and excellent product yield. We have been interested in kinetic and mechanistic studies of the reactions of polyhalides and several reports have already emanated from our laboratory.[8–10] 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 TBATB. Therefore, we studied the kinetics of oxidation of benzyl alcohol and several monosubstituted benzyl alcohols by TBATB in aqueous acetic acid as solvent. The major objective of this investigation was to study the structure–reactivity correlation for the substrates undergoing oxidation.

RESULTS

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

Oxidation of benzyl alcohols by TBATB results in the formation of the corresponding benzaldehydes. Analyses of products and stoichiometric determinations indicate the following overall reaction:

$$ArCH_2OH + (C_4H_9)_4N^+Br_3^- \longrightarrow ArCHO + (C_4H_9)_4N^+ + 2\ H^+ + 3\ Br^- \quad (1)$$

Rate laws

With [alcohol] $\gg$[TBATB], the reactions were found to be first order with respect to TBATB (Fig. 1). Further, the pseudo-first-order rate constants, k_{obs}, do not depend on the initial concentration of TBATB. The reaction rate increases linearly with increase in the concentration of benzyl alcohols (Table 1).

Induced polymerization of acrylonitrile

The oxidation of benzyl alcohol, in an atmosphere of nitrogen, failed to induce the polymerization of acryloni-

---

*Correspondence to: K. K. Banerji, Department of Chemistry, J.N.V. University, Jodhpur 342 005, India.
E-mail: banerjikk@rediffmail.com
Contract/grant sponsor: University Grants Commission (India).

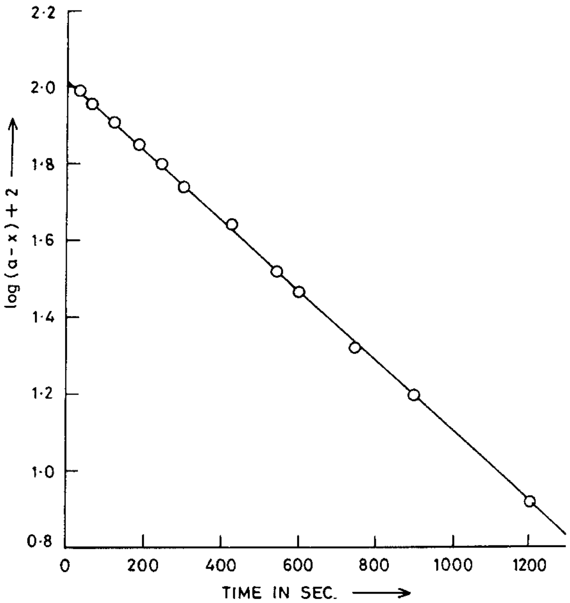


Figure 1. Semi-logarithmic plots for a typical kinetic run. [Benzyl alcohol] = 1.00 mol dm^{-3}, [TBATB] = 0.001 mol dm^{-3}, temperature = 308 K

trile. Further, the addition of acrylonitrile had no effect on the rate of oxidation (Table 1).

Effect of substituents

The rates of oxidation of monosubstituted benzyl alcohols were determined at different temperatures and the activation parameters were calculated (Table 2).

Kinetic isotope effect

To ascertain the importance of the cleavage of the α-C—H bond in the rate-determining step, the oxidation of [1,1-$^2H_2$]benzyl alcohol was studied. The results showed the presence of a substantial kinetic isotope effect ($k_H/k_D \approx 3.7$), which is almost independent of temperature (Table 3).

Effect of tetrabutylammonium chloride

The rates of oxidation were not affected by the addition of tetrabutylammonium chloride (TBACl) (Table 4).

Effect of solvent composition

The rate of oxidation was determined in solvents containing different amounts of acetic acid and water. It was observed that the rate increased with increase in the amount of water in the solvent mixture (Table 5).

Table 1. Rate constants for the oxidation of benzyl alcohol by TBATB at 308 K

10^3[TBATB] (mol dm^{-3})	[Alcohol] (mol dm^{-3})	10^4 k_{obs} (s^{-1})
1.0	0.10	2.16
1.0	0.20	4.23
1.0	0.40	8.48
1.0	0.40[a]	8.56[a]
1.0	0.60	12.8
1.0	0.80	17.0
1.0	1.00	21.1
1.0	2.00	42.7
2.0	0.20	4.11
4.0	0.20	3.76
6.0	0.20	4.00
8.0	0.20	4.54

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

Effect of potassium bromide

The rate of oxidation of benzyl alcohol decreases with increase in the concentration of potassium bromide but reaches a limiting value at [KBr] ≈ 0.16 mol dm^{-3} (Table 6).

DISCUSSION

An isokinetic plot between activation enthalpies and entropies of oxidation of the 36 alcohols is not very good ($r^2 = 0.9354$). The value of isokinetic temperature is 568 ± 26 K. However, according to Exner,[11] an isokinetic relationship between the calculated values of enthalpies and entropies of activation is often vitiated by the random experimental errors associated with them. Exner[11] suggested an alternative method of testing the validity of isokinetic relationship. An Exner plot (Fig. 2) between log k_2 at 288 K and log k_2 at 318 K is linear ($r^2 = 0.9986$). The isokinetic temperature is 680 ± 22 K. The linear isokinetic correlation implies that all the alcohols are oxidized by the same mechanism and the changes in the rate are governed by the changes in both the enthalpy and entropy of activation.

We earlier carried out some conductivity measurements to determine the nature of TBATB in aqueous acetic acid solution.[10] It was observed that acetic acid has very low conductivity. Addition of TBATB increases the conductivity of the solution. We measured the conductivity of TBATB in solvents containing different proportions of acetic acid (100–30%) and also water. We found that the conductivity increases sharply as the water content is increased and reaches a limiting value in about 60% acetic acid–water mixture. TBATB can be considered as an ionic compound, which exists under our reaction conditions as tetrabutylammonium and tribro-

Table 2. Rate constants and activation parameters of the oxidation of substituted benzyl alcohols by TBATB

	$10^4\ k_2$ ($dm^3\ mol^{-1}\ s^{-1}$)						
Substituent	288 K	298 K	308 K	318 K	ΔH^* ($kJ\ mol^{-1}$)	ΔS^* ($J\ mol^{-1}\ K^{-1}$)	ΔG^* ($kJ\ mol^{-1}$)
H	3.31	8.41	21.1	52.7	67.7 ± 0.8	-77 ± 3	90.5 ± 0.7
p-Me	6.90	16.3	40.4	97.0	64.7 ± 1.1	-81 ± 4	88.8 ± 0.9
p-OMe	16.2	37.8	88.8	202	61.5 ± 0.7	-85 ± 2	86.8 ± 0.6
p-F	3.37	8.41	22.0	56.0	68.9 ± 1.0	-73 ± 4	90.4 ± 0.9
p-Cl	2.26	5.73	15.2	38.5	69.6 ± 1.0	-74 ± 3	91.4 ± 0.8
p-NO_2	0.16	0.49	1.45	4.22	80.4 ± 0.7	-58 ± 2	97.6 ± 0.6
p-CF_3	0.47	1.28	3.60	9.85	74.8 ± 1.1	-69 ± 4	95.1 ± 0.9
p-COOMe	0.63	1.80	4.82	13.0	74.1 ± 0.6	-69 ± 2	94.4 ± 0.5
p-Br	2.00	5.14	15.8	34.7	70.1 ± 0.9	-73 ± 3	91.7 ± 0.7
p-NHAc	7.38	18.0	43.0	106	64.9 ± 1.0	-80 ± 3	88.6 ± 0.8
p-CN	0.30	0.83	2.45	6.85	76.9 ± 1.0	-65 ± 3	96.1 ± 0.8
p-SMe	9.13	22.0	52.4	126	63.9 ± 0.9	-81 ± 3	88.1 ± 0.7
p-NMe_2	77.3	170	360	790	56.2 ± 0.8	-91 ± 3	83.1 ± 0.7
m-Me	5.69	14.1	34.5	83.3	65.6 ± 0.7	-80 ± 2	89.2 ± 0.6
m-OMe	5.41	13.5	33.3	80.8	66.1 ± 0.7	-79 ± 2	89.3 ± 0.5
m-Cl	0.99	2.68	7.12	19.2	72.6 ± 1.0	-70 ± 3	93.3 ± 0.8
m-Br	0.96	2.61	7.00	18.1	72.0 ± 0.6	-72 ± 2	93.4 ± 0.5
m-F	1.11	3.16	8.35	22.3	73.4 ± 0.6	-66 ± 2	93.0 ± 0.5
m-NO_2	0.11	0.35	1.04	3.18	82.6 ± 0.6	-54 ± 3	98.4 ± 0.4
m-CO_2Me	0.59	1.61	4.38	11.8	73.5 ± 0.9	-71 ± 3	94.6 ± 0.7
m-CF_3	0.39	1.14	3.14	8.90	76.6 ± 0.9	-64 ± 3	95.5 ± 0.7
m-CN	0.19	0.61	1.74	5.11	80.6 ± 0.7	-56 ± 2	97.1 ± 0.5
m-SMe	3.82	9.68	24.1	59.6	67.1 ± 0.8	-78 ± 3	90.2 ± 0.6
m-NHAc	3.43	8.75	21.9	54.6	67.6 ± 0.8	-77 ± 3	90.4 ± 0.6
o-Me	25.4	58.0	123	266	56.8 ± 0.5	-92 ± 2	85.8 ± 0.4
o-OMe	22.3	52.2	111	242	57.7 ± 0.5	-96 ± 1	86.1 ± 0.4
o-NO_2	0.31	0.92	2.40	6.46	74.1 ± 0.6	-74 ± 2	96.1 ± 0.5
o-COOMe	2.18	5.72	13.5	33.0	66.1 ± 0.6	-86 ± 2	91.5 ± 0.5
o-NHAc	29.2	72.2	146	298	56.0 ± 1.0	-99 ± 3	85.4 ± 0.8
o-Cl	5.66	14.4	32.1	73.4	62.1 ± 0.6	-92 ± 2	89.3 ± 0.4
o-Br	7.28	18.2	39.7	89.0	60.6 ± 0.6	-95 ± 2	88.7 ± 0.4
o-I	12.0	29.1	61.0	132	58.5 ± 0.7	-98 ± 2	87.6 ± 0.6
o-CN	0.64	1.81	4.56	11.8	71.1 ± 0.6	-79 ± 2	94.4 ± 0.4
o-SMe	28.4	69.5	141	295	56.4 ± 0.9	-98 ± 3	85.4 ± 0.7
o-F	3.58	9.42	22.2	52.8	65.5 ± 0.4	-84 ± 1	90.3 ± 0.3
o-CF_3	4.44	11.3	24.6	56.1	61.3 ± 0.7	-96 ± 2	89.9 ± 0.5
α,α-BA	0.89	2.27	6.01	14.1	68.0 ± 0.8	-87 ± 2	93.7 ± 0.6

Table 3. Kinetic isotope effect in the oxidation of benzyl alcohol by TBATB

	$10^4\ k_2$ ($dm^3\ mol^{-1}\ s^{-1}$)		
Temperature (K)	Benzyl alcohol (BA)	Deuteriated BA	k_H/k_D
288	3.31	0.89	3.72
298	8.41	2.27	3.70
308	21.1	6.01	3.68
318	52.7	14.1	3.74

mide ions as shown in the equation

$$(C_4H_9)_4NBr_3 \rightleftharpoons (C_4H_9)_4N^+ + Br_3^- \tag{2}$$

No effect of added tetrabutylammonium ion also indicates that the equilibrium (2) lies far towards the right. Similar results were obtained in the oxidation of aliphatic aldehydes by TBATB.[10] Thus, in the present reaction also the reactive oxidizing species is the tribromide ion.

Tribromide ion is known to dissociate to bromine and

Table 4. Effect of tetrabutylammonium chloride on the rate of oxidation of benzyl alcohol by TBATB ([TBATB] = 0.001 mol dm^{-3}, [benzyl alcohol] = 1.0 mol dm^{-3}, temperature = 308 K)

10^3[TBACl] (mol dm^{-3})	0.00	0.5	1.0	2.0	3.0	4.0
$10^4\ k_{obs}$ (s^{-1})	21.1	22.4	20.3	21.7	20.0	22.8

Table 5. Effect of solvent composition on the rate of the oxidation of benzyl alcohol by TBATB ([TBATB] = 0.001 mol dm^{-3}, [benzyl alcohol] = 1.0 mol dm^{-3}, temperature = 308 K)

AcOH (%)	25	40	50	60	72
10^4 k_{obs} (s^{-1})	105	37.5	21.1	13.1	7.48

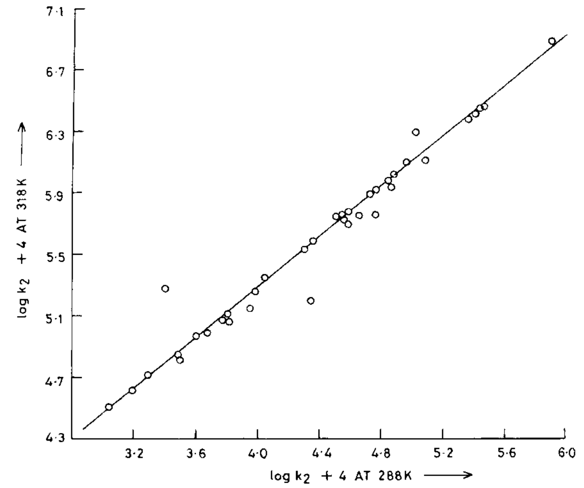


Figure 2. Exner isokinetic plot between log k_2 at 288 and 318 K

bromide ion:

$$\mathrm{Br_3^-} \rightleftharpoons \mathrm{Br_2} + \mathrm{Br^-} \tag{3}$$

and the value of the dissociation constant has been reported.[12] The oxidation of benzyl alcohol by bromine is reported to be much faster[13] as compared with this reaction. The effect of addition of bromide ion (cf. Table 6) indicated that as [Br$^-$] increases, the concentration of bromine and its contribution to the oxidation of benzyl alcohol decrease and become almost negligible at [KBr] ≈ 0.16 mol dm^{-3}. As a large excess (0.2 mol dm^{-3}) of bromide ion was added in the present reaction, the oxidation due to bromine will be suppressed. Thus in the present reaction the reactive oxidizing species is the tribromide ion.

The increase in the rate of oxidation with increase in the polarity of the medium suggests that the transition state is more polar than the reactants. The solvent effect was analysed using the Grunwald–Winstein equation:[14]

$$\log k_2 = \log k_0 + mY \tag{4}$$

The plot of log k_2 versus Y is linear ($r^2 = 0.9996$) with $m = 0.78 \pm 0.01$. The value of m suggests that there is a considerable charge separation in the transition state of the reaction.

The effect of structure on reactivity has long been correlated in terms of the Hammett equation[15] or with dual substituent-parameter equations.[16,17] In the late 1980s, Charton and Charton[18] introduced a triparametric LDR equation for the quantitative description of structural effects on chemical reactivities. In this work we have applied the LDR equation to the rate constants, k_2:

$$\log k_2 = L\sigma_l + D\sigma_d + R\sigma_e + h \tag{5}$$

where σ_l is a localized (field and/or inductive) effect parameter, σ_d is the intrinsic delocalized electrical effect parameter when active site electronic demand is minimal and σ_e represents the sensitivity of the substituent to changes in electronic demand by the active site. The last two substituent parameters are related by the equation

$$\sigma_D = \eta\sigma_e + \sigma_d \tag{6}$$

where η represents the electronic demand of the reaction site and is given by $\eta = R/D$, and σ_D represents the delocalized electrical parameter of the diparametric LD equation.

For *ortho*-substituted compounds, it is necessary to account for the possibility of steric effects and Charton and Charton[18] therefore modified the LDR equation to generate the LDRS equation:

$$\log k_2 = L\sigma_l + D\sigma_d + R\sigma_e + S\nu + h \tag{7}$$

where ν is the well known Charton's steric parameter based on van der Waals radii.[19]

The rates of oxidation of *ortho-*, *meta-* and *para*-substituted benzyl alcohols show an excellent correlation in terms of the LDR/LDRS equations (Table 7). All three series of substituted benzyl alcohols meet the requirement of a minimum number of substituents for analysis by LDR and LDRS equations.[18] We have used the standard deviation (SD), the coefficient of multiple determination (R^2) and Exner's[20] parameter, ψ, as the measures of goodness of fit.

The comparison of the L and D values for the substituted benzyl alcohols showed that the oxidation of *para*-substituted benzyl alcohols is more susceptible to the delocalization effect than to the localized effect.

Table 6. Effect of potassium bromide on the rate of oxidation of benzyl alcohol by TBATB ([TBATB] = 0.001 mol dm^{-3}, [benzyl alcohol] = 1.0 mol dm^{-3}, temperature = 308 K)

[KBr] (mol dm^{-3})	0.00	0.04	0.08	0.12	0.16	0.20	0.24
10^4 k_{obs} (s^{-1})	26.4	25.0	23.7	22.4	21.3	21.1	21.2

Table 7. Temperature dependence of the reaction constants for the oxidation of substituted benzyl alcohols by TBATB

T (K)	L	D	R	S	η	R^2	SD	ψ	P_D	P_S
para-Substituted—										
288	−1.58	−1.94	−1.47	—	0.76	0.9998	0.015	0.01	55.2	—
298	−1.49	−1.83	−1.38	—	0.75	0.9997	0.014	0.01	55.1	—
308	−1.40	−1.75	−1.32	—	0.75	0.9998	0.013	0.01	55.6	—
318	−1.32	−1.66	−1.27	—	0.77	0.9997	0.012	0.01	55.7	—
meta-Substituted—										
288	−1.95	−1.32	−1.09	—	0.73	0.9996	0.012	0.02	40.4	—
298	−1.82	−1.24	−0.94	—	0.76	0.9994	0.016	0.02	40.5	—
308	−1.72	−1.18	−0.90	—	0.76	0.9994	0.014	0.02	40.7	—
318	−1.61	−1.11	−0.83	—	0.75	0.9992	0.016	0.03	40.8	—
ortho-Substituted—										
288	−1.84	−1.59	−1.29	1.16	0.81	0.9998	0.009	0.01	46.4	25.3
298	−1.73	−1.53	−1.16	1.10	0.76	0.9999	0.001	0.01	46.9	24.1
308	−1.66	−1.45	−1.06	0.99	0.73	0.9999	0.001	0.01	46.6	24.1
318	−1.58	−1.36	−0.98	0.90	0.72	0.9999	0.002	0.01	46.3	24.4

However, the oxidation of *ortho*- and *meta*-substituted compounds exhibited a greater dependence on the field effect. In all cases, the magnitude of the reaction constants decreases with increase in temperature, pointing to a decrease in selectivity with increase in temperature.

All three-regression coefficients, *L, D* and *R*, are negative, indicating an electron-deficient carbon centre in the activated complex for the rate-determining step. The positive value of η adds a negative increment to σ_d, increasing the electron-donating power of the substituent and its capacity to stabilise a cationic species. The positive value of *S* indicates that the reaction is subject to steric acceleration by an *ortho*-substituent.

To test the significance of localized, delocalized and steric effects in the *ortho*-substituted benzyl alcohols, multiple regression analyses were carried out with (i) σ_l, σ_d and σ_e [Eqn. (8)], (ii) σ_d, σ_e and ν [Eqn. (9)] and (iii) σ_l, σ_e and ν [Eqn. (10)]. The absence of significant correlations showed that all the four substituent constants are significant.

$$\log k_2 = -1.46\ (\pm 0.37)\ \sigma_l - 1.51\ (\pm 0.29)\ \sigma_d - 2.98\ (\pm 1.65)\ \sigma_e - 2.34 \tag{8}$$

$$R^2 = 0.8479; \quad \mathrm{SD} = 0.25; \quad n = 12; \quad \psi = 0.32$$

$$\log k_2 = -1.60\ (\pm 0.43)\ \sigma_d - 1.59\ (\pm 2.64)\ \sigma_e + 0.72\ (\pm 0.49)\ \nu - 3.19 \tag{9}$$

$$R^2 = 0.6633; \quad \mathrm{SD} = 0.38; \quad n = 12; \quad \psi = 0.49$$

$$\log k_2 = -1.87\ (\pm 0.62)\ \sigma_l - 0.31\ (\pm 2.95)\ \sigma_e + 1.11\ (\pm 0.55)\ \nu - 2.40 \tag{10}$$

$$R^2 = 0.5779; \quad \mathrm{SD} = 0.42; \quad n = 12; \quad \psi = 0.56$$

Similarly, in the cases of the oxidation of *para*- and *meta*-substituted benzyl alcohols, multiple regression analyses with (i) σ_l and σ_d, (ii) σ_d and σ_e and (iii) σ_l and σ_e, indicated that all three substituent constants are needed to explain the effect of structure on the rate constants. There is no significant collinearity between the various substituents constants for the three series.

The percent contribution[19] of the delocalized effect, P_D, is given by the following equation:

$$P_D = (|D| \times 100)\ /\ (|L| + |D|) \tag{11}$$

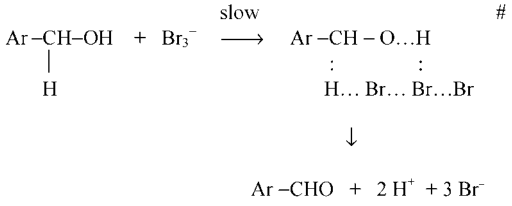
Similarly, the percentage contribution of the steric parameter[19] to the total effect of the substituent, P_S, was determined by using the equation

$$P_S = (|S| \times 100)\ /\ (|L| + |D| + |S|) \tag{12}$$

The values of P_D and P_S are given in Table 7. The value of P_D for the oxidation of *para*-substituted benzyl alcohols is ca 55% whereas the corresponding values for the *meta*- and *ortho*-sobstituted alcohols are ca 40 and 46%, respectively. This shows that the balance of localization and delocalization effects is different for differently substituted benzyl alcohols. The less pronounced resonance effect from the *ortho*-position than from the *para*-position may be due to the twisting away of the alcohol group from the plane of the benzene ring. The magnitude of the P_S value shows that the steric effect is significant in this reaction.

Mechanism

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 acrylonitrile on the reaction rate. The presence of a substantial kinetic isotope effect confirms the cleavage of an α-C—H bond in the rate-determining step. The



Scheme 1

negative values of the localization and delocalization electrical effects, i.e. of *L, D* and *R*, point to an electron-deficient reaction centre in the rate-determining step. This is further supported by the positive value of η, which indicates that the substituent is better able to stabilize a cationic or electron-deficient reactive site. Therefore, a hydride-ion transfer in the rate-determining step is suggested (Scheme 1). The observed effect of solvent composition on the reaction rate also supports a mechanism involving the transfer of a hydride ion.

The positive value of *S* showed 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 and also in the transition state leading to the transition state energy of the crowded and uncrowded alcohols do not differ much, steric acceleration therefore results.

The temperature invariance of the primary kinetic isotope effect (cf. Table 3) can be interpreted in terms of a mechanism in which two bonds are cleaved more or less synchronously. Therefore, a rate-determining step involving cleavage of both the C—H and O—H bonds can be envisaged. The low magnitude (-0.8 to -2.0) of the polar reaction constants also supports the occurrence of a synchronous mechanism. However, the correlation analysis of the substituent effect indicated the presence of an electron-deficient carbon centre in the transition state. It seems, therefore, that in the transition state the cleavage of the C—H bond, yielding an electron-deficient carbon centre, is ahead of the cleavage of the O—H bond. The transition state remains polar in this mechanism and is consistent with the observed solvent effect. The solvent effect is similar to that found for synchronous homopolar reactions. A non-linear transition state, implied in the synchronous mechanism, is supported by the relatively low magnitude of the kinetic isotope effect ($k_H/k_D \approx 3.7$). The oxidation of ethanol by pyridinium hydrobromide perbromide[21] also was reported to involve a non-linear transition state and the kinetic isotope effect was found to be ca 3.5. The mechanism depicted in Scheme 1 accounts for all the observed results.

The observed negative value of the entropy of activation also supports the proposed mechanism. As the charge separation takes place, the charged ends become highly solvated. This results in an immobilization of a large number of solvent molecules, reflected in the loss of entropy.[22]

EXPERIMENTAL

Materials. The preparation, purification and specification of the substituted benzyl alcohols have been described earlier.[23] TBATB was prepared by the reported method[1] and its purity checked by an iodimetric method. [1,1-$^2H_2$]Benzyl alcohol ($PhCD_2OH$) was prepared by the reduction of ethyl benzoate by lithium aluminium deuteride.[24] Its isotopic purity, as ascertained by its ^{1}HNMR spectrum, was $94 \pm 2\%$. Acetic acid was refluxed with chromic oxide and acetic anhydride for 6 h and then fractionated.[25]

Product analysis. The product analysis was carried out under kinetic conditions. In a typical experiment, benzyl alcohol (10.8 g, 0.1 mol), KBr (0.2 mol) and TBATB (3.45 g, 0.01 mol) were made up to 50 ml in 1:1 (v/v) acetic acid–water and kept in the dark for ca 12 h to ensure completion of the reaction. The solution was then treated with an excess (200 ml) 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 yields of DNP before and after recrystallization were 2.15 g (94%) and 1.72 g (75%), respectively. The DNP was found to be identical (m.p. and mixed m.p.) with the DNP of benzaldehyde. In similar experiments, with the other substituted benzyl alcohols the yields of DNP, after recrystallization, were in the range 74–85%.

Kinetic measurements. The reactions were studied under pseudo-first-order conditions by keeping an excess ($\times 15$ or greater) of the substrate over TBATB. The solvent was 1:1 (v/v) acetic acid–water, unless mentioned otherwise. Tribromide ion is known to dissociate to a large extent to bromine and bromide ion. The value[12] of the dissociation constant in 1:1 (v/v) acetic acid–water is ca 0.02 mol dm^{-3}. To suppress the dissociation, all kinetic runs were carried out in the presence of an excess (0.2 mol dm^{-3}) of potassium bromide. The reactions were studied at constant temperature (± 0.1 K) and were followed by monitoring the decrease in the concentration of TBATB at 394 nm for up to 80% reaction. Pseudo-first-order rate constants, k_{obs}, were evaluated from linear plots ($r > 0.995$) of log[TBATB] against time. Duplicate kinetic runs showed that the rate constants are reproducible to within $\pm 3\%$. Simple and multivariate regression analyses were carried out by the least-squares method. The second-order rate constant, k_2, was determined from the relation $k_2 = k_{obs}$/[alcohol].

Acknowledgement

Thanks are due to the University Grants Commission (India) for financial assistance.

REFERENCES

1. Kajigaeshi S, Kakinami T, Okamoto T, Fujisaki S. *Bull. Chem. Soc. Jpn.* 1987; **60**: 1159–1165.
2. Kajigaeshi S, Kakinami T, Yamasaki H, Fujisaki S, Okamoto T. *Bull. Chem. Soc. Jpn.* 1988; **61**: 2681–2687.
3. Kajigaeshi S, Kakinami T, Okamoto T, Nakahari H, Fujikawa M. *Bull. Chem. Soc. Jpn.* 1987; **60**: 4187–4192.
4. Choudhary MK, Khan AT, Patel BK. *Tetrahedron Lett.* 1998; **39**: 8163–8166.
5. Berthalot J, Guette C, Ouchefoune M, Desbens PL, Basselier JJ. *J. Chem. Res. (S)* 1986; 381–382; *Synth. Communn.* 1986; **16**: 1641–1642.
6. Kajigaeshi S, Kawamuki H, Fujisaki S. *Bull. Chem. Soc. Jpn.* 1989; **62**: 2585–2590.
7. Kajigaeshi S, Morikawa Y, Fujisaki S, Kakinami T, Nishihira K. *Bull. Chem. Soc. Jpn.* 1989; **64**: 336–342.
8. Bohra A, Sharma PK, Banerji KK. *J. Chem. Res. (S)* 1999; 308–309: (*M*) 1343–1362.
9. Raju VSR, Sharma PK, Banerji KK. *J. Org. Chem.* 2000; **65**: 3322–3325.
10. Baghmar M, Sharma PK. *Int. J. Chem. Kinet.* 2001; **33**: 390–397.
11. Exner O. *Prog. Phys. Org. Chem.* 1973; **10**: 411–433.
12. Bradfield AE, Jones B, Orton KJP. *J. Chem. Soc.* 1929; 2810–2814.
13. Aukett P, Barker IRL. *J. Chem. Soc., Perkin Trans. 2* 1972: 568–574.
14. Fainberg AH, Winstein S. *J. Am. Chem. Soc.* 1956; **78**: 2770–2773.
15. Johnson CD. *The Hammett Equation*. Cambridge University Press: Cambridge, 1973; 78–82.
16. Ehrenson S, Brownlee RTC, Taft RW. *J. Am. Chem. Soc.* 1974; **94**: 9113–9120.
17. Swain CG, Unger SH, Rosenquest NR, Swain MS. *J. Am. Chem. Soc.* 1983; **105**: 492–501.
18. Charton M, Charton B. *Bull. Soc. Chim. Fr.* 1988; 199–207, and references cited therein.
19. Charton M. *J. Org. Chem.* 1975; **40**: 407–415.
20. Exner O. *Collect. Czech. Chem. Commun.* 1966; **31**: 3222–3228.
21. Mathur D, Sharma PK, Sharma, Banerji KK, *J. Chem. Soc., Perkin Trans. 2* 1993: 203–205.
22. Gould ES. *Mechanism and Structure in Organic Chemistry*. Holt, Rinehart and Winston: New York, 1964.
23. Banerji KK. *J. Org. Chem.* 1988; **54**: 2154–2157.
24. Bunnett JF, Gavies GV, Tanida H. *J. Am. Chem. Soc.* 1962; **84**: 1606–1610.
25. Perrin DD, Armarego WL, Perrin DR. *Purification of Organic Compounds*. Pergamon Press: Oxford, 1966.