JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2001; **14:** 650–656
DOI:10.1002/poc.413

Correlation analysis of reactivity in the oxidation of substituted benzaldehydes by pyridinium hydrobromide perbromide

Meenakshi Aneja, Seema Kothari and Kalyan K. Banerji*

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

Received 3 August 2000; revised 2 March 2001; accepted 5 April 2001

ABSTRACT: The oxidation of benzaldehyde and 35 monosubstituted benzaldehydes by pyridinium hydrobromide perbromide (PHPB) in aqueous acetic acid leads to the formation of the corresponding benzoic acids. The reaction is first order with respect to each of the benzaldehydes and PHPB. Addition of pyridinium bromide has no effect on the rate of oxidation. The oxidation of [^{2}H]benzaldehyde (PhCDO) indicated the presence of a substantial kinetic isotope effect. The effect of solvent composition indicated that the reaction rate increases with increase in the polarity of the solvent. The rates of oxidation of *meta*- and *para*-substituted benzaldehydes were correlated in terms of Charton's triparametric LDR equation whereas those of *ortho*-substituted benzaldehydes were correlated with a tetraparametric LDRS equation. The oxidations of *para*- and *ortho*-substituted benzaldehydes are more susceptible to the delocalization effect while the oxidation of *meta*-substituted compounds displays 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 subjected to steric hindrance by the *ortho* substituents. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: Kinetics; mechanism; oxidation; correlation analysis; polyhalide; aromatic aldehydes

INTRODUCTION

Pyridinium hydrobromide perbromide (PHPB) is one of the quaternary polyhalides, which have been used as effective halogenating and oxidizing agents in synthetic organic chemistry.[1–3] 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 the kinetic and mechanistic aspects of oxidation by polyhalide compounds and many reports have emanated from our laboratory,[4–8] including that on the oxidation of aliphatic aldehydes by PHPB.[9] In continuation of our earlier studies, we report here the kinetics of oxidation of benzaldehyde and 35 monosubstituted benzaldehydes by PHPB in aqueous acetic acid as solvent. The major objective of this investigation was to study the structure–reactivity correlation for the substrate undergoing oxidation.

RESULTS

Oxidation of the aromatic aldehydes by PHPB results in the formation of the corresponding benzoic acids. Analyses of products and stoichiometric determinations indicate the following overall reaction:

$$\mathrm{ArCHO} + \mathrm{PyH^+Br_3^-} + \mathrm{H_2O} \rightarrow \mathrm{ArCOOH} + \mathrm{PyH^+Br^-} + 2\mathrm{HBr} \qquad (1)$$

Rate laws

The reactions were found to be first order with respect to PHPB. The individual kinetic runs were strictly first order in PHPB. Further, the pseudo-first-order rate constants, k_{obs}, do not depend on the initial concentration of PHPB. The reaction rate increases linearly with increase in the concentration of aldehydes (Table 1).

Induced polymerization of acrylonitrile

The oxidation of benzaldehyde, in an atmosphere of nitrogen, failed to induce polymerization of acrylonitrile. Further, the addition of acrylonitrile had no effect on the reaction rate (Table 1).

Effect of substituent

The rates of the oxidation of benzaldehyde and 35

**Correspondence to:* K. K. Banerji, Department of Chemistry, J. N. V. University, Jodhpur 342 005, India.

Contract/grant sponsor: Council of Scientific and Industrial Research (India).

Table 1. Rate constants for the oxidation of benzaldehyde by PHPB at 318 K

10^3 [PHPB] (mol dm^{-3})	[PhCHO] (mol dm^{-3})	10^4 k_{obs}(s^{-1})
1.0	0.05	3.65
1.0	0.10	7.19
1.0	0.20	15.0
1.0	0.30	22.5
1.0	0.50	35.8
1.0	1.00	72.1
2.0	0.20	14.5
4.0	0.20	15.3
6.0	0.20	15.5
8.0	0.20	14.8
1.0	0.30[a]	22.0

[a] Contained 0.005 mol dm^{-3} acrylonitrile.

monosubstituted benzaldehydes 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 aldehydic C—H bond in the rate-determining step, the oxidation of [^{2}H]benzaldehyde (PhCDO) was studied. The results (Table 2) showed the presence of a substantial kinetic isotope effect (k_H/k_D = 5.75 at 298 K).

Effect of solvent composition

The rate of oxidation was determined in solvents containing different amounts of acetic acid and water.

Table 2. Rate constants and activation parameters of the oxidation of substituted benzaldehydes by PHPB

	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	3.81	10.2	27.0	72.1	72.0 ± 1.0	−61 ± 3	90.0 ± 0.8
p-Me	10.5	25.0	64.1	160	66.8 ± 1.4	−71 ± 5	87.7 ± 1.1
p-OMe	52.1	110	260	650	61.5 ± 2.3	−76 ± 7	84.0 ± 1.8
p-F	6.51	15.3	41.0	105	68.4 ± 1.8	−69 ± 6	88.9 ± 1.4
p-Cl	4.12	10.5	27.8	76.2	71.4 ± 1.6	−62 ± 5	89.9 ± 1.3
p-Br	4.14	10.5	28.0	76.0	71.3 ± 1.6	−63 ± 5	89.9 ± 1.2
p-CF_3	0.58	1.75	5.27	15.4	80.7 ± 0.9	−46 ± 3	94.4 ± 0.7
p-CO_2Me	0.91	2.65	7.85	22.0	78.5 ± 0.9	−50 ± 3	93.3 ± 0.7
p-NO_2	0.26	0.81	2.67	7.70	83.9 ± 0.9	−42 ± 3	96.2 ± 0.7
p-NHAc	20.5	47.5	110	311	65.8 ± 2.6	−69 ± 5	86.2 ± 2.1
p-CN	0.43	1.30	4.09	11.4	81.0 ± 0.8	−48 ± 3	95.1 ± 0.6
p-SMe	30.6	65.6	160	420	63.9 ± 2.6	−72 ± 6	85.3 ± 2.0
p-NMe_2	595	1000	2240	5300	53.4 ± 3.6	−84 ± 8	78.4 ± 2.9
m-Me	6.38	16.4	42.0	115	70.6 ± 1.5	−62 ± 5	88.8 ± 1.2
m-OMe	5.10	13.1	33.3	88.0	69.6 ± 1.2	−67 ± 4	89.4 ± 1.0
m-Cl	1.03	3.00	8.55	23.7	77.0 ± 0.7	−54 ± 2	93.1 ± 0.6
m-Br	1.04	3.10	8.67	24.2	77.2 ± 0.6	−54 ± 2	93.0 ± 0.5
m-F	1.06	3.14	8.70	24.5	76.9 ± 0.8	−54 ± 3	93.0 ± 0.6
m-NO_2	0.17	0.57	1.89	5.58	86.3 ± 0.4	−37 ± 2	97.2 ± 0.4
m-CO_2Me	0.81	2.40	7.05	20.0	78.9 ± 0.8	−50 ± 3	93.6 ± 0.6
m-CF_3	0.53	1.64	4.95	13.8	80.3 ± 0.4	−48 ± 1	94.6 ± 0.3
m-CN	0.29	0.90	2.93	8.47	83.5 ± 0.9	−42 ± 3	96.0 ± 0.7
m-SMe	4.30	11.8	30.7	80.3	71.6 ± 0.7	−61 ± 2	89.7 ± 0.5
m-NHAc	3.57	9.38	24.4	65.3	71.1 ± 1.2	−65 ± 4	90.2 ± 0.9
o-Me	1.92	5.46	15.1	41.5	75.4 ± 0.8	−55 ± 3	91.6 ± 0.7
o-OMe	7.60	19.7	49.2	125	68.4 ± 0.8	−68 ± 3	88.4 ± 0.7
o-NO_2	0.081	0.31	1.04	3.06	89.7 ± 0.8	−31 ± 3	98.8 ± 0.6
o-COOMe	0.20	0.70	2.04	6.55	85.9 ± 1.1	−37 ± 4	96.8 ± 0.9
o-NHAc	1.40	4.17	11.4	32.5	76.9 ± 0.9	−52 ± 3	92.3 ± 0.7
o-Cl	0.50	1.55	4.73	13.8	81.7 ± 0.7	−44 ± 2	94.7 ± 0.6
o-Br	0.36	1.27	3.50	10.9	83.1 ± 1.3	−42 ± 4	95.4 ± 4.0
o-I	0.30	1.00	3.10	9.00	83.8 ± 0.2	−41 ± 1	95.8 ± 0.2
o-CN	0.12	0.43	1.28	4.25	87.2 ± 1.2	−37 ± 4	98.0 ± 1.0
o-SMe	2.37	6.70	18.4	48.5	74.1 ± 0.5	−58 ± 2	91.1 ± 0.4
o-F	1.60	4.62	12.6	34.5	75.2 ± 0.7	−57 ± 2	92.0 ± 0.5
o-CF_3	0.038	0.16	0.48	1.68	92.4 ± 1.8	−28 ± 6	101 ± 1.4
PhCDO	0.65	1.77	4.77	13.5	74.2 ± 1.4	−68 ± 5	94.3 ± 1.1
k_H/k_D	5.91	5.75	5.66	5.60			

Table 3. Effect of solvent composition on the oxidation of benzaldehyde by PHPB with [PHPB] = 0.001 mol dm^{-3}, [benzaldehyde] = 1.0 mol dm^{-3} and temperature = 318 K

AcOH (%)	20	30	50	60	70	80
$10^4\ k_{obs}$ (s^{-1})	410	205	72.1	27.7	19.8	10.0

It was observed that the rate increased with increase in the amount of water in the solvent mixture (Table 3).

Effect of pyridinium bromide

The rates of oxidation were not affected by an addition of pyridinium bromide (Table 4).

DISCUSSION

A plot of logk_2 at 288 K is linearly related to logk_2 at 318 K (r^2 = 0.9994, slope = 0.830 ± 0.003). The value of the isokinetic temperature is 646 ± 15 K. A linear isokinetic relationship is a necessary condition for the validity of linear free energy relationships.[10] It also implies that all the aldehydes for which the rates of oxidation are so correlated are oxidized by the same mechanism.[10]

In solutions, PHPB may undergo the following reactions.

$$\mathrm{PyH^+Br_3^-} \rightleftharpoons \mathrm{Br_2} + \mathrm{PyH^+Br^-} \qquad (2)$$

$$\mathrm{PyH^+Br_3^-} \rightleftharpoons \mathrm{Br_3^-} + \mathrm{PyH^+} \qquad (3)$$

The probable oxidizing species in a solution of PHPB are, therefore, PHPB itself, tribromide ion and molecular bromine. However, a strict first-order dependence on PHPB and the absence of any effect of pyridinium bromide rule out both bromine and tribromide ion as the reactive oxidizing species. Hence PHPB itself is the reactive oxidizing species in this reaction. Similar results were obtained in the oxidation of aliphatic aldehydes.[9]

Solvent composition effect

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:[11]

$$\log k_2 = \log k_0 + mY \qquad (4)$$

The plot of log k_2 versus Y is linear (r^2 = 0.9980) with $m = 0.81 \pm 0.02$. The value of m suggests that there is a considerable charge separation in the transition state of the reaction.

Table 4. Effect of pyridinium bromide on the rate of oxidation of benzaldehyde by PHPB with [PHPB] = 0.001 mol dm^{-3}, [benzaldehyde] = 1.0 mol dm^{-3} and temperature = 318 K

[PyHBr] (mol dm^{-3})	0.0	0.01	0.02	0.04	0.08	0.12
$10^4\ k_{obs}$ (s^{-1})	72.1	73.5	71.5	72.0	71.2	74.0

Correlation analysis of reactivity

The reaction rates of the *meta*- and *para*-substituted compounds were correlated in terms of the Hammett equation[12] but the correlation was not satisfactory [Eqn. (5)]. We used the standard deviation (sd), the coefficient of determination (r^2/R^2) and Exner's[13] parameter, ψ, as the measures of goodness of fit:

$$\log k_2 = -2.22 \pm 0.13\sigma - 2.61 \qquad (5)$$

$$r^2 = 0.9245, \mathrm{sd} = 0.22, n = 24, \psi = 0.20$$

The data showed wide scatter. The rate constants of many para-substituted compounds, capable of electron donation by resonance, are higher than those expected from their Hammett σ values. This indicates that in the transition state of the reaction, there is an electron-deficient centre, which is stabilized by cross-conjugation with the electron-donating substituent at the *para* position. Hence the rate constants of *para*-substituted compounds were correlated with Brown's σ^+ values,[14] but the correlation was not good:

$$\log k_2 = -1.23 \pm 0.07\sigma^+ - 2.94 \qquad (6)$$

$$r^2 = 0.9624, \mathrm{sd} = 0.18, n = 13, \psi = 0.14$$

In view of the failure of the correlation analyses in terms of Hammett and Brown's equations, the rates were correlated in terms of the Yukawa–Tsuno[15] equation. Although the results are better, the correlation is still not very good:

$$\log k_2 = -1.38 \pm 0.24[\sigma^0 + 0.80(\sigma^+ - \sigma^0)] - 2.87 \qquad (7)$$

$$r^2 = 0.9646, \mathrm{sd} = 0.19, n = 12, \psi = 0.15$$

The data for the p-NHAc compound were not included in this correlation as the σ^0 value is not available.[15]

Since the correlations with single substituent parameter equations and the Yukawa–Tsuno equation are not very good, the rates were correlated in terms of Charton's[16] LDR equation:

$$\log k_2 = L\sigma_l + D\sigma_d + R\sigma_e + h \qquad (8)$$

Table 5. Temperature dependence of the reaction constants for the oxidation of substituted benzaldehydes by PHPB

Substitution	Temperature (K)	L	D	R	S	η	R^2	sd	ψ	P_D	P_S
Para	288	−1.46 ± 0.02	−2.45 ± 0.01	−3.42 ± 0.06	—	1.40	0.9998	0.013	0.11	62.7	—
	298	−1.38 ± 0.02	−2.24 ± 0.02	−3.13 ± 0.07	—	1.40	0.9997	0.016	0.014	61.9	—
	308	−1.27 ± 0.03	−2.10 ± 0.02	−3.08 ± 0.08	—	1.47	0.9995	0.019	0.018	62.3	—
	318	−1.23 ± 0.03	−2.04 ± 0.02	−3.06 ± 0.08	—	1.50	0.9996	0.019	0.016	62.4	—
Meta	288	−1.89 ± 0.01	−1.09 ± 0.01	−1.49 ± 0.05	—	1.37	0.9998	0.010	0.012	36.6	—
	298	−1.76 ± 0.02	−1.02 ± 0.02	−1.39 ± 0.09	—	1.36	0.9994	0.014	0.020	36.7	—
	308	−1.63 ± 0.02	−0.92 ± 0.02	−1.34 ± 0.09	—	1.46	0.9990	0.013	0.022	36.1	—
	318	−1.58 ± 0.02	−0.88 ± 0.02	−1.25 ± 0.09	—	1.42	0.9992	0.015	0.023	35.8	—
Ortho	288	−1.60 ± 0.01	−1.97 ± 0.01	−2.74 ± 0.06	−1.31 ± 0.01	1.39	0.9999	0.010	0.009	55.2	26.8
	298	−1.46 ± 0.01	−1.79 ± 0.01	−2.51 ± 0.06	−1.17 ± 0.01	1.40	0.9998	0.010	0.015	55.1	26.5
	308	−1.37 ± 0.02	−1.71 ± 0.02	−2.51 ± 0.11	−1.14 ± 0.02	1.47	0.9995	0.020	0.012	55.5	27.0
	318	−1.32 ± 0.01	−1.60 ± 0.01	−2.23 ± 0.07	−1.05 ± 0.01	1.39	0.9998	0.010	0.015	54.8	26.4

where h is the intercept term, σ_l is a localized (field and/or inductive) effect parameter, σ_d is the intrinsic delocalized (resonance) electrical effect parameter when the 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

$$\sigma_D = \eta\sigma_e + \sigma_d \tag{9}$$

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, therefore, modified the LDR equation to generate the LDRS equation:[16]

$$\log k_2 = L\sigma_l + D\sigma_d + R\sigma_e + S\nu + h \tag{10}$$

where ν is the well-known Charton's steric parameter based on Van der Waals radii.[17]

The rates of oxidation of *ortho*-, *meta*- and *para*-substituted benzaldehydes show excellent correlations in terms of the LDR/LDRS equations (Table 5). All three series of substituted benzaldehydes meet the requirement of a minimum number of substituents for analysis by the LDR and LDRS equations.[16] The comparison of the L and D values for the substituted benzaldehydes showed that the oxidation of *para*- and *ortho*-substituted benzaldehydes is more susceptible to the delocalization effect than to the localized effect. However, the oxidation of *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 an 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 stabilize a cationic species. The negative value of S indicates that the reaction is subject to steric hindrance by an *ortho* substituent.

To test the significance of localized, delocalized and steric effects in the *ortho*-substituted benzaldehydes, multiple linear regression analyses were carried out with (i) σ_l, σ_d and σ_e, (ii) σ_l, σ_e and ν, (iii) σ_d, σ_e and ν and (iv) σ_l, σ_d and ν. However, the correlations were not significant, showing that all the four substituent constants are significant:

$$\log k_2 = -1.70 \pm 0.43\sigma_l - 1.72 \pm 0.34\sigma_d - 0.24 \pm 1.95\sigma_e - 3.39 \tag{11}$$

$$R^2 = 0.8359, \mathrm{sd} = 0.30, n = 13, \psi = 0.33, \text{ temperature } 298\text{ K}$$

$$\log k_2 = -1.73 \pm 0.76\sigma_l - 1.58 \pm 3.65\sigma_e - 1.04 \pm 0.68\nu - 2.64 \tag{12}$$

$$R^2 = 0.4970, \mathrm{sd} = 0.52, n = 13, \psi = 0.61, \text{ temperature } 298\text{ K}$$

$$\log k_2 = -1.92 \pm 0.38\sigma_d - 2.98 \pm 2.32\sigma_e - 1.41 \pm 0.43\nu - 3.44 \tag{13}$$

$$R^2 = 0.7980, \mathrm{sd} = 0.33, n = 13, \psi = 0.37, \text{ temperature } 298\text{ K}$$

$$\log k_2 = -1.49 \pm 0.17\sigma_l - 1.76 \pm 0.14\sigma_d - 1.01 \pm 1.15\nu - 2.95 \tag{14}$$

$$R^2 = 0.9737, \mathrm{sd} = 0.12, n = 13, \psi = 0.13, \text{ temperature } 298\text{ K}$$

Similarly, in the oxidation of *para*- and *meta*-substituted benzaldehydes, multiple regression analyses indicated that both localization and delocalization effects are significant. There is no significant collinearity between the various substituent constants for the three series.

The percentage contribution[16] of the delocalized effect, P_D, is given by the equation

$$P_D = \frac{(|D| \times 100)}{(|L| + |D|)} \tag{15}$$

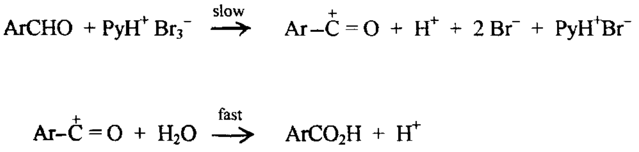
Similarly, the percentage contribution of the steric parameter[16] to the total effect of the substituent, P_S, was determined by using the equation

$$P_S = \frac{(|S| \times 100)}{(|L| + |D| + |S|)} \tag{16}$$

The values of P_D and P_S are given in Table 5. The value of P_D for the oxidation of *para*-substituted benzaldehydes is ca 62% whereas the corresponding values for the *meta*- and *ortho*-substituted aldehydes are ca 36 and 55%, respectively. This shows that the balance of localization and delocalization effects is different for differently substituted benzaldehydes. The less pronounced resonance effect from the *ortho* position than from the *para* position may be due to the twisting away of the aldehydic 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

The cleavage of the aldehydic C—H bond in the rate-determining step is confirmed by the presence of a substantial kinetic isotope effect. A one-electron oxidation, giving rise to free radicals, is unlikely in view of the failure to induce polymerization of acrylonitrile and the zero effect of the radical scavenger on the reaction rate. The 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 transition state of 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 large negative values of *L, D* and *R* indicate that the electron demand of the reaction on the substituents is very high. This, coupled with large deuterium isotope effect, points to a considerable carbocationic character in the transition state. Hence the rate-determining step can be visualized as a hydride-ion transfer involving a late product-like transition state. The structure of the transition state should therefore be close to a linear acylium cation, $Ar-\overset{+}{C}{=}O$. The energy profile of this reaction should resemble that of solvolytic formation of a vinyl cation.



$$ArCHO + PyH^+Br_3^- \xrightarrow{slow} Ar-\overset{+}{C}{=}O + H^+ + 2Br^- + PyH^+Br^-$$

$$Ar-\overset{+}{C}{=}O + H_2O \xrightarrow{fast} ArCO_2H + H^+$$

Scheme 1

The correlation of vinyl cation formation, in terms of the Yukawa–Tsuno equation,[15] is reported to yield $\rho \approx -4$ and $r \approx 1.1$. In the present reaction the value of ρ is -1.38 and that of r is 0.80 [cf. Eqn. (7)]. The significantly low ρ value and resonance demand may be attributed to a stronger electron donation from the carbonyl oxygen than from $=CH_2$. It is of interest to compare here the results obtained in earlier studies using Charton's LDR/LDRS equations. Charton[16] reported that in the solvolysis of 4-substituted cumyl chlorides, the magnitudes of *L, D* and *R* are much larger (−5.02, −7.37 and −9.73, respectively, at 298 K) than those obtained in the present study. This may well be due to the dispersal of the positive charge, on the carbon, by the adjacent carbonyl oxygen, in addition to that by the phenyl group. However, the value of η, the electronic demand of the reaction site, is comparable in the two reactions (1.3 and 1.4). We have applied these equations to many oxidation reactions.[18–22]

The values of the reaction constants are given in Table 6. These reactions involve the formation of a cationic species in the rate-determining step either by a hydride-ion transfer from the reductant to the oxidant or by an addition of halogen to the sulfide. The magnitudes of *R* and η in the oxidation of aromatic aldehydes by benzyltrimethylammonium chlorobromate (BTMACB) are lower than those observed in the present reaction. This shows that in the oxidation by BTMACB,[18] the transition state is more reactant-like rather than product-like. In the rest of the reactions, the polar reaction constants have comparable values. The positive steric constant in the oxidation of alcohols[22] implies a steric acceleration, whereas in other reactions a steric hindrance by the *ortho* substituents is indicated. The above comparison supports the proposed mechanism.

The abstraction of a hydride ion from an aldehydic C—H bond has been proposed for several oxidizing species. Formation of an acylium cation has been suggested in the oxidation of benzaldehyde[23] and acetaldehyde.[24] Similarly oxidation of aromatic aldehydes by BTMACB[18] is also proposed to involve a hydride-ion transfer in the rate-determining step.

A mechanism involving the transfer of a hydride ion is supported by the observed effect of solvent composition. The observed negative value of the entropy of activation also supports the proposed mechanism. As PHPB and the aldehyde come together in the transition state to form a single activated complex, their freedom to move separately is curtailed. This is reflected in a loss of entropy.

Table 6. Reaction constants of the oxidation reactions in terms of Charton's LDR/LDRS equations at 298 K

Substitution	Oxidant/reductant[a]	L	D	R	η	S	Ref.
Para	BTMACB/ArCHO	−1.59	−1.75	−1.31	0.75	—	18
	PHPB/ArSMe	−1.43	−2.11	−2.89	1.37	—	19
	BTMAB/ArSMe	−1.40	−2.09	−2.85	1.36	—	20
	HABR/ArSMe	−1.41	−2.09	−3.01	1.44	—	21
	BTMACI/ArCH$_2$OH	−1.59	−2.15	−3.10	1.44	—	22
	PHPB/ArCHO	−1.38	−2.24	−3.13	1.40	—	This work
Meta	BTMACB/ArCHO	−1.64	−1.08	−0.72	0.67	—	18
	PHPB/ArSMe	−1.72	−0.99	−0.95	0.96	—	19
	BTMAB/ArSMe	−1.68	−1.01	−1.03	1.02	—	20
	HABR/ArSMe	−1.72	−1.05	−1.29	1.23	—	21
	BTMACI/ArCH$_2$OH	−1.89	−1.04	−1.46	1.40	—	22
	PHPB/ArCHO	−1.76	−1.04	−1.39	1.36	—	This work
Ortho	BTMACB/ArCHO	−1.61	−1.53	−1.10	0.79	−1.03	18
	PHPB/ArSMe	−1.46	−1.66	−2.25	1.36	−1.13	19
	BTMAB/ArSMe	−1.42	−1.72	−2.10	1.22	−1.15	20
	HABR/ArSMe	−1.47	−1.71	−2.67	1.56	−1.14	21
	BTMACI/ArCH$_2$OH	−1.87	−1.69	−2.53	1.50	1.23	22
	PHPB/ArCHO	−1.46	−1.79	−2.51	1.40	−1.17	This work

[a] BTMACB = benzyltrimethylammonium chlorobromate; BTMAB = benzyltrimethylammonium tribromide; HABR = hexamethylenetetramine-bromine; BTMACI = benzyltrimethylammonium dichloroiodate.

Although the contribution of the steric term is significant, its interpretation is not straightforward. The structure of the transition state where the aryl ring is perpendicular to the elongated C—H bond should lead to a lesser degree of steric interaction between the *ortho* substituent and the reaction centre. Perhaps the observed steric hindrance by the *ortho* substituent is due to the hindrance to the approach of the oxidizing species by the *ortho* substituent.

It is of interest to compare here the results of the oxidation of aliphatic aldehydes[9] by PHPB with those of the aromatic aldehydes. Aliphatic aldehydes exhibited Michaelis–Menten kinetics with respect to the reductant whereas the aromatic aldehydes exhibited a first-order dependence on the reductant. This difference may well be due to the fact that the aliphatic aldehydes are extensively hydrated in aqueous or mixed aqueous solvents[25] to yield a *gem*-diol. Aromatic aldehydes are not known to undergo hydration to any significant extent.[25] The *gem*-diols are likely to behave more like alcohols and the oxidation of alcohols by PHPB is known to exhibit Michaelis–Menten kinetics.[26] The magnitude[9] of the kinetic isotope effect is much less in the oxidation of acetaldehyde ($k_H/k_D = 3.23$ at 298 K) than that obtained in the present reaction. This is consistent with a non-linear transition state implied in the rate-determining disproportionation of an intermediate complex. The higher magnitude of the kinetic isotope effect in the oxidation of benzaldehyde indicates a bimolecular reaction via a linear transition state. Both the reactions showed a linear relationship in terms of the Grunwald–Winstein equation. However, the value of m is relatively small (0.47) in the oxidation of acetaldehyde compared with that in benzaldehyde (0.81). This indicates that the degree of charge separation is much greater in the oxidation of the aromatic aldehydes than it is in the oxidation of aliphatic aldehydes. This is also consistent with the proposal that the oxidation of aromatic aldehydes involves a direct hydride-ion transfer whereas that of aliphatic aldehydes proceeds via an intermediate complex.[9]

EXPERIMENTAL

Materials. The aldehydes were commercial products. The liquid aldehydes were purified through their hydrogensulfite addition compounds and distilling them, under nitrogen, just before use.[27] The solid aldehydes were recrystallized from ethanol. PHPB was prepared by the reported method.[1] Its purity was checked by an iodometric method. [^{2}H]Benzaldehyde (PhCDO) was prepared by a reported method.[28] Acetic acid was refluxed with chromic oxide and acetic anhydride for 6 h and fractionated.

Product analysis. The product analysis was carried out under kinetic conditions. In a typical experiment, freshly distilled benzaldehyde (5.30 g, 0.05 mol) and PHPB (3.20 g, 0.01 mol) were diluted to 100 ml in 1:1 (v/v) acetic acid–water. The reaction mixture was allowed to stand for ca 10 h to ensure completion of the reaction. It was rendered alkaline with NaOH, filtered and the filtrate evaporated to dryness under reduced pressure. The residue was dissolved in the minimum quantity of concentrated HCl and cooled in crushed ice to yield crude acid (1.13 g), which was recrystallized from hot water to produce pure benzoic acid (1.08 g, 87%, m.p. 120 °C).

Stoichiometry. To determine the stoichiometry, PHPB (1.60 g, 0.005 mol) and benzaldehyde (0.106 g, 0.001 mol) were diluted to 100 ml in 1:1 (v/v) acetic acid–water. The reaction mixture was allowed to stand for ca 10 h to ensure the completion of the reaction. The residual PHPB was determined spectrophotometrically at 358 nm. Several determinations, with differently substituted benzaldehydes, showed that the stoichiometry is 1:1.

Kinetic measurements. The reactions were carried out under pseudo-first-order conditions by maintaining a large excess of the aldehyde (×15 or more) over PHPB. The solvent was 1:1 (v/v) acetic acid–water, unless mentioned otherwise. The reactions were carried out at a constant temperature (±0.1 K) and were followed up to 80% reaction by monitoring the decrease in [PHPB] at 358 nm. The pseudo-first-order rate constants, k_{obs}, were computed from the linear ($r^2 > 0.995$) least-squares plots of log[PHPB] versus time. Duplicate kinetic runs showed that the rate constants were reproducible to within ±4%.

Acknowledgements

Thanks are due to the Council of Scientific and Industrial Research (India) for financial support.

REFERENCES

1. Fieser L, Fieser M. *Reagents for Organic Synthesis*, vol. 1. New York: Wiley, 1967; 967.
2. Djerassi C, Schloz CR. *J. Am. Chem. Soc.* 1948; **70**: 417; Fieser LF. *J. Chem. Educ.* 1954; **31**: 291.
3. Perelman M, Farkas E, Fornefeld EJ, Kraay RJ, Rapala EJ. *J. Am. Chem. Soc.* 1960; **82**: 2402.
4. Goel S, Kothari S, Banerji KK. *J. Chem. Res. (S)* 1996; **230**: (*M*) 1318; *J. Chem. Res. (S)* **510**: (*M*) 2901.
5. Suri D, Kothari S, Banerji KK. *J. Chem. Res. (S)* 1996; **228**: (*M*) 1301; *J. Chem. Res. (S)* 1995; **274**: (*M*) 1734.
6. Anjana, Kothari S, Banerji KK. *J. Chem. Res. (S)* 1999; **476**: (*M*) 2118.
7. Rao PSC, Goel S, Kothari S, Banerji KK. *Indian J. Chem.* 1998; **37B**: 1129.
8. Goswami G, Kothari S, Banerji KK. *J. Chem. Res. (S)* 1999; **176**: (*M*) 813.
9. Devi J, Kothari S, Banerji KK. *J. Chem. Res. (S)* 1993; **400**: (*M*) 2680.
10. Exner O. *Collect. Czech. Chem. Commun.* 1964; **29**: 1094.
11. Fainberg AH, Winstein S. *J. Am. Chem. Soc.* 1956; **78**: 2770.
12. Johnson CD. *The Hammett equation*. Cambridge: Cambridge University Press, 1973; 78.
13. Exner O. *Collect. Czech. Chem. Commun.* 1966; **31**: 3222.
14. Brown HC, Okamoto Y. *J. Am. Chem. Soc.* 1958; **80**: 4979.
15. Tsuno Y, Fujio M. *Adv. Phys. Org. Chem.* 1999; **32**: 267.
16. Charton M. *Prog. Phys. Org. Chem.* 1986; **18**: 287.
17. Charton M. *J. Org. Chem.* 1975; **40**: 407.
18. Raju VS, Sharma PK, Banerji KK. *J. Org. Chem.* 2000; **65**: 3322.
19. Vyas VK, Jalani N, Kothari S, Banerji KK. *J. Chem. Res. (S)* 1996; **370**: (*M*) 2201.
20. Goel S, Varshney S, Kothari S, Banerji KK. *J. Chem. Res. (S)* 1996; **510**: (*M*) 2901.
21. Choudhary K, Suri D, Kothari S, Banerji KK. *J. Phys. Org. Chem.* 2000; **13**: 283.
22. Rao PSC, Suri D, Kothari S, Banerji KK. *J. Chem. Res. (S)* 1998; **510**: (*M*) 2251.
23. Pearlmutter-Hayman P, Weissmann Y. *J. Am. Chem. Soc.* 1962; **84**: 2323.
24. Kaplan L. *J. Am. Chem. Soc.* 1958; **80**: 2639.
25. Bell RP. *Prog. Phys. Org. Chem.* 1964; **1**: 10.
26. Mathur D, Sharma PK. Banerji KK. *J. Chem. Soc., Perkin Trans. 2* 1993; 205.
27. Wiberg KB, Stewart R. *J. Am. Chem. Soc.* 1955; **77**: 1786.
28. Wiberg KB. *J. Am. Chem. Soc.* 1954; **76**: 5371.