KINETICS AND MECHANISM OF THE OXIDATION OF SUBSTITUTED BENZALDEHYDES WITH BIS(PYRIDINE) SILVER PERMANGANATE

Jayshree Banerji,[a] László Kótai,[b] Pradeep K. Sharma,[c] and K.K. Banerji[d]*

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The oxidation of thirty-six *ortho-, meta-* and *para*-substituted benzaldehydes by bis(pyridine)silver permanganate (BPSP) resulted in the formation of the corresponding benzoic acids. The reaction is first order with respect to both BPSP and aldehydes. The reaction is catalyzed by hydrogen ions. The rate of reaction increases with an increase in the amount of acetic acid in the solvent. The correlation analyses of the rate of oxidation of thirty-six aldehydes were performed in terms of Charton's LDR and LDRS equations. The rate of oxidation of *meta*- and *para*-substituted benzaldehydes showed excellent correlation with Charton's LDR equation. The rates of *ortho*-compounds showed excellent correlation with LDRS equation. The oxidation of *para*-compounds is more susceptible to the delocalization effect. The oxidation of *ortho*- and *meta*-compounds exhibited a greater dependence on the field effect. The polar reaction constants are negative indicating an electron-deficient centre in the rate-determining step. A mechanism involving a rate-determining hydride transfer from the aldehyde to the protonated BPSP has been proposed.

* Corresponding Authors
Fax: +91 291 2557540
E-Mail: banerjikk@gmail.com
[a] Department of Chemistry, RGP Mahavidyalaya, Kolar Road, Bhopal 462042, India ű
[b] Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, H-1025, Pusztaszeri u. 59-67, Budapest, Hungary
[c] Department of Chemistry, J N V University, Jodhpur 342011, India
[d] Faculty of Science, National Law University, Mandore, Jodhpur 342304, India

1. Introduction

Bis(pyridine)silver permanganate (BPSP) is a mild and selective oxidizing agent. It is found to be better reagent than potassium permanganate in many reactions, e.g. oxidative alkylamination of electron-deficient (hetero) aromatic compounds.[1] We have reported its thermally induced intra-molecular redox reaction,[2] the oxidation of oxalic and formic acid[3] and of organic sulfides[4] with BPSP. The oxidation of aldehydes with BPSP has not been reported, therefore, we have undertaken this work.

2. Experimental Section

2.1 Materials

BPSP was prepared by reported method[5] and its purity was checked by iodometric method. The aldehydes were commercial products. The liquid aldehydes were purified through their bisulfite addition compounds and distilling them, under nitrogen, just before use.[6] The solid aldehydes were recrystallized from ethanol.

Deuteriated benzaldehyde (PhCDO) was also prepared by the literature method.[7] Its isotopic purity, as ascertained by its NMR spectrum, was 97±3%. Perchloric acid was used as a source of hydrogen ions. Acetic acid was refluxed with acetic anhydride and chromic oxide for 3 h and then distilled.

2.2 Product Analysis

The product analysis was carried out under kinetic conditions. In a typical experiment, freshly distilled benzaldehyde(0.05 mol) and BPSP (0.01 mol) were made up to 50 cm^3 in 1:1 acetic acid-water (v/v) and kept in the dark for *ca*. 10 h to ensure completion of the reaction. It was rendered alkaline with NaOH, filtered and filtrate evaporated to under reduced pressure. The residue was dissolved in minimum amount of concd. HCl and cooled in ice to yield crude acid (2 g), which was recrystallized from hot water to produce pure benzoic acid (1.9 g, 90%, m.p. 121^o C).

2.3 Kinetic Measurements

The reactions were studied under pseudo-first-order conditions by keeping a large excess of the aldehyde (× 15 or larger) over BPSP. The solvent was 1:1 (v/v) acetic acid-water, unless stated otherwise. The reactions were studied at constant temperature (±0.1 K) and followed up to 80% completion by monitoring the decrease in absorption due to BPSP at 529 nm. The pseudo-first-order constants, k_{obs}, were computed from the linear ($r > 0.990$) least-squares plots of log[BPSP] versus time plots. Duplicate kinetic runs showed that rate constants are reproducible within ±4%. Preliminary experiments showed that the oxidation is not sensitive to changes in ionic strength, therefore, no attempt was keep it constant.

3. Results and Discussion

The rate laws and other data were obtained for all compounds investigated. Since the results are similar only representative data are reproduced here.

3.1 Stoichiometry

The oxidation of aromatic aldehydes resulted in the formation of corresponding benzoic acid (1)

$$ArCHO + 2Mn^{VII} + 3H_2O \rightarrow ArCO_2H + 2Mn^{IV} + 6H^+ \quad (1)$$

Thus BPSP is reduced to Mn(IV). To confirm that Mn(IV) is indeed formed as a result of reduction of BPSP by aldehydes, the rate were determined by monitoring the increase in [Mn(IV)] at 418 nm also.[8,9] The rates of decay at 529 nm and increase at 418 nm agreed within ±7%. BPSP has virtually no absorption at 418 nm. This agrees with the observations of earlier workers.[8,9]

3.2 Rate Laws

The reactions are first order with respect to BPSP. Further, the values of k_{obs}, are independent of initial concentration of BPSP. The reaction rate increases linearly with an increase in the concentration of aldehydes showing that the reaction is first order with respect to aldehydes also. The rate of oxidation increases linearly with an increase in the acidity of the solution (Table 1).

Table 1. Rate constants for the oxidation of benzaldehyde by BPSP at 298 K

10^3[BPSP] mol dm^{-3}	[Aldehyde] mol dm^{-3}	[H$^+$] mol dm^{-3}	10^4 k_{obs} s^{-1}
1.0	0.10	1.0	2.33
1.0	0.20	1.0	4.62
1.0	0.40	1.0	9.36
1.0	0.60	1.0	14.0
1.0	0.80	1.0	18.2
1.0	1.00	1.0	23.3
1.0	2.00	1.0	46.7
2.0	0.40	1.0	9.36
4.0	0.40	1.0	9.56
6.0	0.40	1.0	9.12
8.0	0.40	1.0	9.61
1.0	1.00	0.2	4.70
1.0	1.00	0.4	9.32
1.0	1.00	0.6	14.1
1.0	1.00	0.8	18.7
1.0	0.40	1.0	9.54*

*contained 0.001 mol dm^{-3} acrylonitrile

3.3 Test for free radicals

The oxidation of benzaldehyde, in an atmosphere of nitrogen, failed to induce polymerization of acrylonitrile. In blank experiments, with the aldehyde absent, no noticeable consumption of BPSP was observed. The addition of acrylonitrile had no effect on the reaction rate (Table 1). To further confirm the absence of free radicals in the reaction pathway, the reaction was carried out in the presence of 0.05 mol dm^{-3} of 2,6-di-*t*-butyl-4-methylphenol (butylated hydroxytoluene or BHT). It was found that BHT was recovered unchanged almost quantitatively.

3.4 Effect of Substituents

The rates of oxidation of a number of *ortho*-, *meta*- and *para*-substituted benzaldehydes were determined at different temperatures and the activation parameters were calculated (Table 2).

3.5 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 (k_H/k_D = 5.66 at 298 K) showed the presence of a substantial primary kinetic effect (Table 2).

3.6 Effect of Solvent Composition

The rate of oxidation of was determined in solutions containing different amounts of acetic acid and water. It was observed that the rate of oxidation increased with an increase in the amount of acetic acid in the solvent (Table 3). The rate of oxidation increases with an increase in the amount of acetic acid in the solvent. This may be attributed to the change in the acidity of the medium with a change in the amount of acetic acid. Hammett's acidity function, H_0, for low concentration of perchloric acid in a series of acetic acid-water mixtures has been determined.[10] It is observed that the acidity increases as the concentration of acetic acid increases. The present reaction is an acid-catalyzed one and with an increase in the acidity of the solution, the rate is expected to increase.

3.7 Correlation Analysis of Reactivity

The correlation between the activation enthalpies and entropies of the oxidation of the thirty-six aldehydes is just satisfactory (r^2 = 0.9132), indicating the presence of a weak compensation effect.[11] However, a correlation between the calculated values of enthalpies and entropies is often vitiated by the experimental errors associated with them. The reaction exhibited an excellent isokinetic relationship, as determined by Exner's method.[12] An Exner's plot between log k_2 at 288 K and at 318 K was linear (r^2 = 0.9970, slope = 0.8350 ± 0.0078). The value of isokinetic temperature evaluated from the Exner's plot is 469±27 K. The linear isokinetic correlation implies that all the aldehydes are oxidized by the same mechanism and the change in the rate of oxidation is governed by changes in both the enthalpy and entropy of the activation.

The rate constants for the oxidation of *meta*- and *para*-substituted benzaldehydes were correlated in terms of Hammett equation[13] but no significant correlation was obtained (Eqn. 2).

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

Substrate	10^4 k_2 (dm^3 mol^{-1} s^{-1})				ΔH^*	ΔS^*	ΔG^*
	288K	298K	308K	318K	kJ mol^{-1}	J mol^{-1} K^{-1}	kJ mol^{-1}
H	8.80	23.3	57.6	139	67.3±0.3	−70 ± 1	88.0±0.2
p-Me	18.5	47.0	113	252	63.8±0.1	−76 ± 1	86.3±0.1
p-OMe	43.0	105	234	556	62.0±0.9	−75 ± 3	84.3±0.7
p-F	10.6	28.8	72.0	176	68.6±0.3	−63 ± 1	87.5±0.2
p-Cl	6.51	18.0	46.1	114	70.0±0.1	−63 ± 1	88.7±012
p-NO_2	0.52	1.71	4.90	14.0	80.7±0.5	−47 ± 2	94.5±0.4
p-CF_3	1.36	4.02	12.1	31.1	77.4±0.6	−51 ± 2	92.3±0.5
p-CO_2Me	2.00	5.35	14.6	37.3	71.9±0.8	−67 ± 3	91.6±0.6
p-Br	6.32	17.5	44.6	112	70.3±0.3	−63 ± 1	88.8±0.3
p-NHAc	22.0	52.5	127	290	63.0±0.5	−77 ± 2	85.9±0.5
p-CN	0.90	2.81	8.00	21.4	77.8±0.1	−52 ± 1	93.3±0.1
p-SMe	25.0	62.7	149	340	63.7±0.2	−74 ± 1	85.5±0.2
p-NMe_2	178	412	843	1770	55.4±0.5	−86 ± 2	80.9±0.4
m-Me	17.7	40.0	97.0	220	61.7±0.5	−84 ± 3	86.5±0.6
m-OMe	16.5	41.5	98.3	224	63.6±0.2	−78 ± 1	86.6±0.2
m-Cl	2.70	7.41	19.9	46.3	69.9±0.5	−71 ± 2	90.8±0.4
m-Br	2.68	7.28	18.5	46.6	69.8±0.4	−71 ± 1	90.9±0.3
m-F	3.35	0.07	23.4	54.1	68.3±0.4	−75 ± 1	90.4±0.3
m-NO_2	0.30	0.91	2.53	7.05	77.4±0.5	−63 ± 2	96.1±0.4
m-CO_2Me	1.45	4.25	11.3	28.9	72.3±0.2	−64 ± 1	92.3±0.2
m-CF_3	1.02	2.90	8.66	21.7	75.6±0.8	−59 ± 3	93.1±0.6
m-CN	0.52	1.53	4.30	11.9	76.8±0.6	−61 ± 2	94.7±0.4
m-SMe	11.4	29.0	66.6	145	61.9±0.4	−86 ± 1	87.5±0.3
m-NHAc	9.92	25.0	63.1	142	65.3±0.4	−76 ± 2	87.8±0.3
o-Me	80.0	182	400	812	56.4±0.2	−89 ± 1	82.9±0.2
o-OMe	75.7	176	380	798	57.1±0.1	−87 ± 1	83.0±0.1
o-NO_2	1.00	2.74	7.41	19.8	73.2±0.7	−68 ± 3	93.3±0.7
o-CO_2Me	6.60	17.2	41.0	98.7	65.9±0.5	−77 ± 2	88.8±0.4
o-NHAc	112	252	520	1060	54.3±0.2	−94 ± 1	82.1±0.2
o-Cl	19.2	46.7	107	233	60.8±0.1	−86 ± 1	86.2±0.1
o-Br	25.4	61.6	137	308	60.6±0.4	−85 ± 1	85.6±0.3
o-I	43.0	98.6	214	445	56.8±0.1	−93 ± 1	84.5±0.1
o-CN	1.96	5.44	14.0	35.9	71.1±0.5	−69 ± 1	91.6±0.4
o-SMe	108	240	490	1000	53.8±0.3	−96 ± 1	82.3±0.2
o-F	13.0	30.8	72.5	170	62.7±0.8	−83 ± 3	87.3±0.6
o-CF_3	15.0	36.1	82.6	184	61.0±0.2	−87 ± 1	86.9±0.2
PhCDO	1.51	4.12	10.6	26.3	69.9±0.2	−76 ± 1	92.3±0.2
k_H/k_D	5.83	5.66	5.43	5.29			

Table 3. Effect of Solvent Composition on the Reaction Rate
[BPSP] 0.001 mol dm^{-3} [PhCHO] 0.60 mol dm^{-3} [H^+] 1.0 mol dm^{-3} T = 298 K

% Acetic acid (v/v)	20	30	50	60	70
10^4 k_{obs} (s^{-1})	5.76	10.5	14.0	24.6	38.0

$$\log k_2 = -1.77\pm0.14\sigma - 2.51 \quad (2)$$

$r^2 = 0.8778$, sd = 0.24, $n = 24$, $T = 298$ K

It has been stated[14] that in the absence of proximity effects, the polar effects of *ortho*-substituents parallel those of *para*-substituents. In this case, however, the rate constants of *ortho*- and *para*-substituted benzaldehydes are not linearly related (Eqn. 3). This indicates that the polar effects are not solely responsible for the observed effect of *ortho*-substituents on this reaction.

$$\log k_{ortho} = 0.91\pm0.16 \log_{para} - 3.42 \quad (3)$$

$r^2 = 0.7733$, sd = 0.33, $n = 11$, $T = 298$ K

There have been many attempts to describe a single substituent-parameter equation for *ortho*-substituents. Charton[14] has compiled a list 32 sets of such constant. We analyzed the rate constants of the *ortho*-compounds in terms of *ortho*-substituent constant, σ_o, of Tribble and Traynham[15] which has the biggest set of data, but the correlation is unsatisfactory (Eqn. 4).

$$\log k_2 = -0.78\pm0.22\ \sigma_o - 2.99 \quad (4)$$

$r^2 = 0.5723$, sd = 0.52, $n = 11$, $T = 298$ K

The data for *o*-NO_2 and *o*-SMe were not included in this correlation as the σ_o values are not available.

Since the rate constants failed to yield satisfactory correlation with any single substituent-parameter equation, the rates were analyzed in terms of Taft's[16] and Swain-Lupton's [17] dual substituent-parameter equations. However, no satisfactory correlation was obtained in of these equations also. In the late 1980s, 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 (5) to the rate constants, k_2.

$$\log k_2 = L\,\sigma_l + D\,\sigma_d + R\,\sigma_e + h \quad (5)$$

Here, σ_l is a localized (field and/or inductive) effect parameter, σ_d is the intrinsic delocalized 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 latter two substituent parameters are related by equation (6)

$$\sigma_D = \eta\sigma_e + \sigma_d \quad (6)$$

Here 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,[18] therefore, modified the LDR equation to generate the LDRS equation (7).

$$\log k_2 = L\,\sigma_l + D\,\sigma_d + R\,\sigma_e + S\,\nu + h \quad (7)$$

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 benzaldehydes show an excellent correlation in terms of the LDR/LDRS equations (Table 4). We have used the standard deviation (sd), the coefficient of multiple determination (R^2), and Exner's parameter,[20] ψ, as the measures of goodness of fit.

The comparison of the *L* and *D* values for the substituted benzaldehydes showed that the oxidation of *para*-substituted benzaldehydes is more susceptible to the delocalization effect than to the localized effect. 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 an increase in the 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 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 benzaldehydes, multiple regression analyses were carried out with (i) σ_l, σ_d and σ_e (ii) σ_d, σ_e and υ and (iii) σ_l, σ_e and υ. The absence of significant correlations showed that all the four substituent constants are significant.

$$\log k_2 = -1.47\ (\pm0.43)\sigma_l - 1.69\ (\pm0.34)\sigma_d - 3.51\ (\pm1.95)\sigma_e - 2.24 \quad (8)$$

$R^2 = 0.8268$; sd= 0.30; $n = 13$; $\psi = 0.47$

$$\log k_2 = -1.78\ (\pm0.44)\sigma_d - 1.80\ (\pm2.72)\sigma_e + 0.89\ (\pm0.50)\upsilon - 3.16 \quad (9)$$

$R^2 = 0.7042$; sd = 0.39; $n = 13$; $\psi = 0.62$

$$\log k_2 = -1.95\ (\pm0.69)\sigma_l - 0.41(\pm3.30)\ \sigma_e + 1.31\ (\pm0.62)\upsilon - 2.32 \quad (10)$$

$R^2 = 0.5635$; sd = 0.47; $n = 13$; $\psi = 0.75$

Similarly in the cases of 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 substituents constants for the three series.

Table 4. Temperature dependence for the reaction constants for the oxidation of substituted benzaldehydes by BPSP

T/K	L	D	R	S	η	R^2	sd	ψ	P_D	P_S
Para-substituted										
288	–1.47	–1.90	–1.25	-	0.66	0.9996	0.016	0.02	56.4	-
298	–1.35	–1.82	–1.16	-	0.64	0.9998	0.009	0.01	57.4	-
308	–1.26	–1.70	–1.06	-	0.68	0.9998	0.008	0.01	57.4	-
318	–1.16	–1.62	–0.98	-	0.60	0.9999	0.004	0.01	58.3	-
Meta-substituted										
288	–1.99	–1.42	–1.16	-	0.82	0.9995	0.015	0.03	41.6	-
298	–1.87	–1.35	–1.11	-	0.82	0.9999	0.007	0.01	41.9	-
308	–1.79	–1.27	–0.90	-	0.71	0.9995	0.014	0.03	41.5	-
318	–1.71	–1.16	–0.84	-	0.72	0.9995	0.013	0.03	40.6	-
Ortho-substituted										
288	–1.77	–1.71	–1.24	1.25	0.73	0.9998	0.011	0.02	49.1	26.4
298	–1.71	–1.62	–1.25	1.17	0.77	0.9999	0.003	0.01	48.6	26.0
308	–1.63	–1.53	–1.13	1.09	0.74	0.9999	0.006	0.01	48.4	25.7
318	–1.53	–1.43	–1.09	0.99	0.76	0.9998	0.008	0.02	48.3	25.1

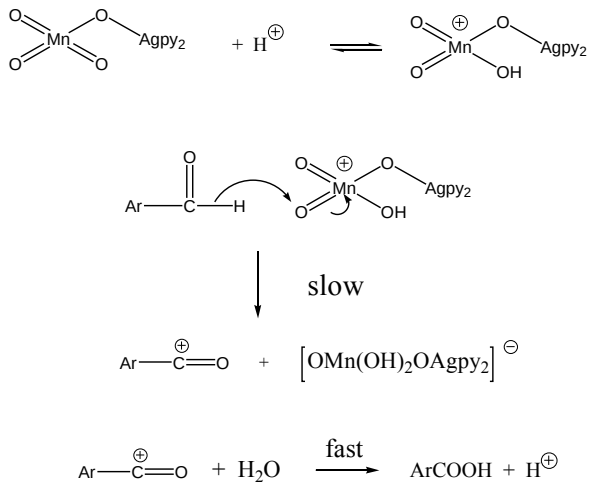
The percent contribution[18] of the delocalized effect, P_D, is given by following equation (11).

$$P_D = (|D| \times 100) / (|L| + |D|) \quad (11)$$

Similarly, the percent contribution[18] of the steric parameter to the total effect of the substituent, P_S, was determined by using equation(12).

$$P_S = (|S| \times 100) / (|L| + |D| + |S|) \quad (12)$$

The values of P_D and P_S are also recorded in Table 4. The value of P_D for the oxidation of *para*-substituted benzaldehydes is *ca.* 57% whereas the corresponding values for the *meta*- and *ortho*-sobstituted aldehydes are *ca.* 42 and 48% 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.



Scheme 1

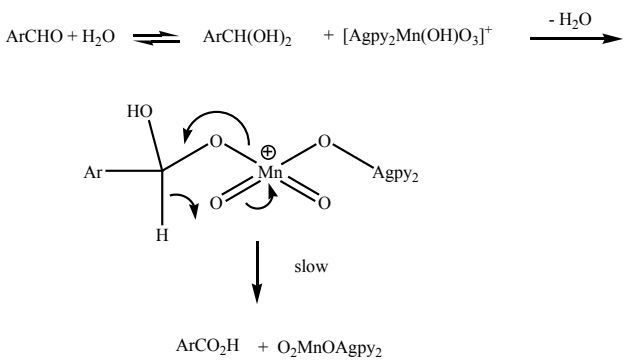
The magnitude of the P_S value shows that the steric effect is significant in this reaction.

3.8 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 the radical scavenger on the reaction rate. The presence of a substantial kinetic isotope effect confirms the cleavage of the aldehydic C-H bond in the rate determining step. The linear increase in the rate with acidity indicates (a) presence of a protonation pre-equilibrium, (b) that the protonation constant is small and (c) the protonation is not complete within the acid range studied and (d) only the protonation species is reactive. This suggests the presence of a pre-equilibrium protonation of BPSP to yield a better oxidant and electrophile.

$$[Agpy_2]MnO_4 + H^+ \leftrightarrows [Agpy_2Mn(OH)O_3]^+$$

The negative values of the localization and delocalization electrical effects i.e. of L, D and R points to an electron-deficient reaction centre in the rate-determining step. It 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. The benzoyl cation is reported to have a considerable keten character.[21] The linear structure of the acylium cation has also been confirmed by X-ray crystallography.[22] The change from sp^2 to *sp* hybridization results in steric relief. This relief is greater in crowded reductants and is reflected in the observed steric acceleration. The observed negative value of entropy of activation also supports the proposed mechanism. As the charge separation takes place in the transition state, the charged ends become highly solvated. This results in an immobilization of a large number of solvent molecules, reflected in the loss of entropy.[23]



Scheme 2

An alternative mechanism involving a rapid ester formation between the aldehyde hydrate and protonated BPSP (Scheme 2) is also possible. The reaction involving *gem*-diol form, as shown, is likely to be a low-energy pathway as compared to that in Scheme 1. However, the value of hydration constant of benzaldehyde[24] at 298 K is 1.1 x 10^{-2}. Benzaldehyde, therefore, hydrated to an extent of *ca.*1% in solution. In view of this, the involvement of the hydrated form is less likely. Further, a non-linear transition state, implied in the ester mechanism is likely to result in a lower kinetic isotope effect than observed.

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