

## Structure-Reactivity Correlation in the Oxidation of Substituted Benzaldehydes by Tetraethylammonium Chlorochromate

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Oxidation of 36 monosubstituted benzaldehydes by tetraethylammonium chlorochromate in dimethyl sulphoxide, leads to the formation of corresponding benzoic acids. The reaction is of first order with respect to chlorochromate and aldehydes. The reaction is promoted by H<sup>+</sup>; the H<sup>+</sup> dependence has the form  $k_{\text{obs}} = a + b[\text{H}^+]$ . The oxidation of deuterated benzaldehyde exhibits substantial primary kinetic isotope effect. The reaction was studied in 19 different organic solvents and the effect of solvent was analyzed using Taft's and Swain's multiparametric equations. The rates of the oxidation of *para*- and *meta*-substituted benzaldehydes showed excellent correlation in terms of Charton's triparametric LDR equation, whereas the oxidation of *ortho*-substituted benzaldehydes were correlated well with tetraparametric LDRS equation. The oxidation of *para*-substituted benzaldehydes is more susceptible to the delocalized effect than is the oxidation of *ortho*- and *meta*-substituted compounds, which display a greater dependence on the field effect. The positive value of  $\eta$  suggests the presence of an electron-deficient reaction centre in the rate-determining step. The reaction is subjected to steric acceleration by the *ortho*-substituents. A suitable mechanism has been proposed.

**Key Words:** Benzaldehydes, Correlation analysis, Kinetics, Mechanism, Halochromate.

### INTRODUCTION

Pyridinium and quinolinium halochromates have been used as mild and selective oxidizing reagents in synthetic organic chemistry<sup>1,2</sup>. Tetraethylammonium chlorochromate (TEACC) is also one of such compounds used as mild and selective oxidizing agent in synthetic organic chemistry<sup>3</sup>. A few reports on the oxidation by TEACC are available in the literature *e.g.*, oxidation of hydroxy acids<sup>4</sup>, phosphorus oxyacids<sup>5</sup> and thioacids<sup>6</sup>. We have been interested in kinetics of oxidations by Cr(VI) species and have already published a few reports on oxidation by these halochromates<sup>7-10</sup>. In continuation of our earlier work, we report in the present article the kinetics of oxidation of some monosubstituted benzaldehydes by TEACC in DMSO as solvent. The major objective of this investigation is to study the structure-reactivity correlation for the substrate undergoing oxidation.

### EXPERIMENTAL

Tetraethylammonium chlorochromate (TEACC) was prepared by reported method<sup>3</sup> 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. The solid aldehydes were recrystallized from ethanol. Deuterated benzaldehyde was also prepared by the literature method. Its isotopic purity, as ascertained by its NMR spectrum, was  $97 \pm 5\%$ . Due to non-aqueous nature of the solvent, toluene-*p*-sulphonic acid (TsOH) was used as a source of hydrogen ions. Solvents were purified by the usual literature methods.

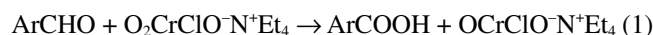
**Product analysis:** The product analysis was carried out under kinetic conditions. In a typical experiment, benzaldehyde (5.25 g, 0.05 mol) and TEACC (2.66 g, 0.01 mol) were made up to 50 cm<sup>3</sup> in DMSO and kept in the dark for *ca.* 15 h to ensure completion of the reaction. The solution was then treated with an excess (200 cm<sup>3</sup>) of a saturated solution of 2,4-dinitrophenylhydrazine in 2 mol dm<sup>-3</sup> 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 2.61 g (88%) and 2.47 g (84%), respectively. The DNP was found identical (m.p. and mixed m.p.) with the DNP of benzaldehyde. Similar experiments were performed with other aldehydes also. The oxidation state of chromium in completely reduced reaction mixtures, determined by an iodometric method was  $3.95 \pm 0.15$ .

**Kinetic measurements:** The pseudo-first order conditions were attained by maintaining a large excess ( $\times 15$  or more) of the aldehyde over TEACC. The solvent was DMSO, unless specified otherwise. The reactions were followed, at constant temperatures ( $\pm 0.1$  K), by monitoring the decrease in [TEACC] spectrophotometrically at 365 nm. No other reactant or product has any significant absorption at this wavelength. The pseudo-first order rate constants,  $k_{\text{obs}}$ , were evaluated from the linear ( $r = 0.990 - 0.999$ ) plots of  $\log [\text{TEACC}]$  against time for up to 80 % reaction. Duplicate kinetic runs showed that the rate constants were reproducible to within  $\pm 3$  %. The second order rate constant,  $k_2$ , was obtained from the relation:  $k_2 = k_{\text{obs}}/[\text{aldehyde}]$ . All experiments, other than those for studying the effect of hydrogen ions, were carried out in the absence of TsOH.

## RESULTS AND DISCUSSION

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

**Stoichiometry:** Oxidation of benzaldehydes by tetraethylammonium chlorochromate results in the formation of corresponding benzoic acids. Analysis of products indicated the following overall reaction as eqn. 1.



Thus TEACC undergoes a two-electron change. This is in accord with the earlier observations with TEACC<sup>4</sup> and other halochromates<sup>7-10</sup>. It has already been shown that both pyridinium fluorochromate (PFC)<sup>11</sup> and pyridinium chlorochromate (PCC)<sup>12</sup> act as two electron oxidants and are reduced to chromium(IV) species.

**Rate laws:** The reactions were found to be first order with respect to TEACC. The individual kinetic runs were strictly first order to TEACC. Further, the pseudo-first order rate constant,  $k_{\text{obs}}$ , was independent of initial concentration of TEACC. The reaction showed a first order dependence on the aldehyde concentration also (Table-1). The first order kinetics was maintained up to the 80 % of the reaction.

TABLE-1  
RATE CONSTANTS FOR THE OXIDATION OF  
BENZALDEHYDES BY TEACC AT 308 K

$10^3 [\text{TEACC}]$ ( $\text{mol dm}^{-3}$ )	[Aldehyde] ( $\text{mol dm}^{-3}$ )	[TsOH] ( $\text{mol dm}^{-3}$ )	$10^4 k_{\text{obs}}$ ( $\text{s}^{-1}$ )
1.0	0.10	0.0	5.94
1.0	0.20	0.0	12.1
1.0	0.40	0.0	23.4
1.0	0.60	0.0	36.0
1.0	0.80	0.0	48.6
1.0	1.00	0.0	58.5
2.0	0.40	0.0	24.3
4.0	0.40	0.0	22.5
6.0	0.40	0.0	25.2
8.0	0.40	0.0	23.1
1.0	0.20	0.0	12.6*

\*Contained  $0.001 \text{ mol dm}^{-3}$  acrylonitrile.

**Test for free radicals:** The oxidation of benzaldehyde by TEACC, in nitrogen atmosphere failed to induce the polymerization of acrylonitrile. Further, an addition of a radical

scavenger, acrylonitrile, had no effect on the rate (Table-1). To further confirm the absence of free radicals in the reaction pathway, the reaction was carried out in the presence of  $0.05 \text{ mol dm}^{-3}$  of 2,6-di-*t*-butyl-4-methylphenol (butylated hydroxy-toluene or BHT). It was observed that BHT was recovered unchanged, almost quantitatively.

**Effect of acidity:** The reaction is catalyzed by hydrogen ions. The  $\text{H}^+$  dependence taking the form:  $k_{\text{obs}} = a + b[\text{H}^+]$  (Table-2). The values for  $a$  and  $b$  for benzaldehyde are  $6.36 \pm 0.26 \times 10^{-4} \text{ s}^{-1}$  and  $10.1 \pm 0.43 \times 10^{-4} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ , respectively ( $r^2 = 0.9963$ ).

TABLE-2  
DEPENDENCE OF THE REACTION RATE  
ON HYDROGEN-ION CONCENTRATION  
[benzaldehyde]  $0.10 \text{ mol dm}^{-3}$ ; [TEACC]  
 $0.001 \text{ mol dm}^{-3}$ ; temperature 298 K

[TsOH] ( $\text{mol dm}^{-3}$ )	0.10	0.20	0.40	0.60	0.80	1.00
$10^4 k_{\text{obs}}$ ( $\text{s}^{-1}$ )	6.93	8.46	10.80	12.60	14.40	16.20

**Effect of temperature:** The rates of the oxidation of benzaldehydes by TEACC were determined at different temperatures and the activation parameters were calculated (Table-3). The  $\log k_2$  at different temperatures is linearly related to the inverse of the temperature in all the cases (Fig. 1). The Arrhenius equation is therefore, valid for this reaction.

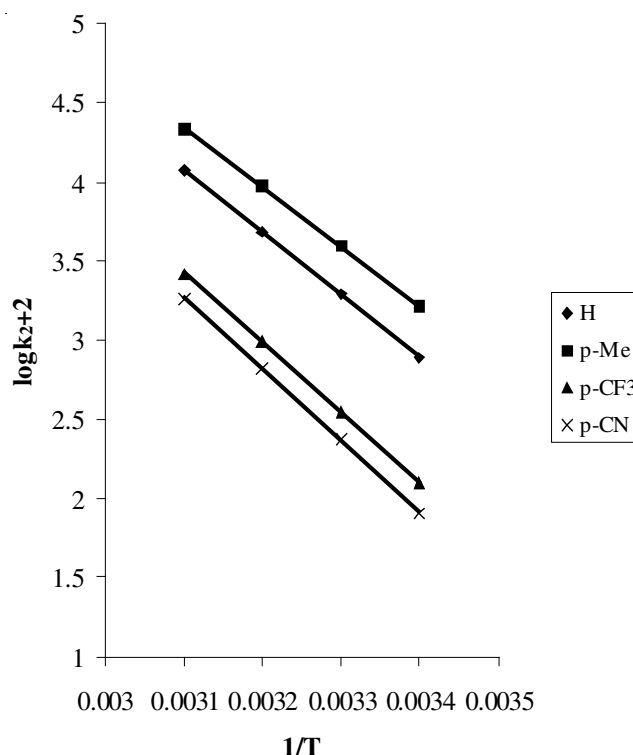


Fig. 1. Oxidation of benzaldehydes by TEACC: effect of temperature

**Kinetic isotope effect:** To ascertain the importance of the cleavage of the aldehydic C-H bond in the rate-determining step, oxidation of deuterio-benzaldehyde was studied. Results showed the presence of a substantial primary kinetic isotope effect (Table-3).

**Effect of solvents:** The oxidation of benzaldehyde was studied in 19 different organic solvents. The choice of solvents

TABLE-3  
RATE CONSTANTS AND ACTIVATION PARAMETERS OF THE OXIDATION OF SUBSTITUTED BENZALDEHYDES BY TEACC

Subst.	$10^4 k_2$ (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )				$\Delta H^*$ kJ mol <sup>-1</sup>	$\Delta S^*$ J mol <sup>-1</sup> K <sup>-1</sup>	$\Delta G^*$ kJ mol <sup>-1</sup>
	288 K	298 K	308 K	318 K			
H	9.45	23.40	58.50	135.00	65.2 ± 0.5	-77 ± 2	88.0 ± 0.4
<i>p</i> -Me	20.70	48.60	108.00	252.00	60.6 ± 0.9	-86 ± 3	86.2 ± 0.7
<i>p</i> -Ome	47.70	108.00	261.00	558.00	60.4 ± 0.8	-80 ± 3	84.1 ± 0.6
<i>p</i> -F	108.00	27.90	71.10	162.00	66.5 ± 0.3	-71 ± 1	87.6 ± 0.6
<i>p</i> -Cl	6.75	17.10	44.10	108.00	68.0 ± 0.7	-70 ± 2	88.7 ± 0.
<i>p</i> -NO <sub>2</sub>	050.00	1.44	4.23	10.80	75.9 ± 0.6	-64 ± 2	94.9 ± 0.5
<i>p</i> -CF <sub>3</sub>	1.35	3.78	10.80	27.00	73.9 ± 0.6	-63 ± 2	92.5 ± 0.5
<i>p</i> -COOMe	1.80	4.95	13.50	33.30	71.7 ± 0.4	-68 ± 1	91.8 ± 0.3
<i>p</i> -Br	6.48	16.30	43.20	99.90	67.4 ± 0.7	-73 ± 2	88.8 ± 0.6
<i>p</i> -NHAc	22.50	54.90	126.00	288.00	62.0 ± 0.4	-81 ± 1	85.9 ± 0.3
<i>p</i> -CN	0.87	2.43	7.02	18.00	74.7 ± 0.8	-64 ± 2	93.5 ± 0.5
<i>p</i> -Sme	27.00	65.70	153.00	342.00	61.9 ± 0.3	-80 ± 1	85.5 ± 0.2
<i>p</i> -NMe <sub>2</sub>	216.00	468.00	990.00	1980.00	53.8 ± 0.2	-90 ± 1	80.6 ± 0.2
<i>m</i> -Me	17.10	40.50	96.30	207.00	61.0 ± 0.4	-86 ± 1	86.6 ± 0.3
<i>m</i> -Ome	17.70	41.40	98.10	216.00	61.2 ± 0.5	-86 ± 2	86.6 ± 0.4
<i>m</i> -Cl	2.88	7.47	19.80	45.90	68.1 ± 0.6	-77 ± 2	90.8 ± 0.3
<i>m</i> -Br	2.90	7.29	18.90	45.00	67.5 ± 0.6	-79 ± 2	90.8 ± 0.5
<i>m</i> -F	3.51	8.91	22.58	53.10	66.6 ± 0.4	-80 ± 1	90.4 ± 0.3
<i>m</i> -NO <sub>2</sub>	0.30	0.88	2.52	6.93	77.2 ± 0.6	-64 ± 2	96.1 ± 0.5
<i>m</i> -CO <sub>2</sub> Me	1.53	4.23	10.80	28.80	71.6 ± 0.8	-70 ± 3	92.3 ± 0.7
<i>m</i> -CF <sub>3</sub>	1.08	2.90	8.10	20.70	72.7 ± 0.8	-69 ± 3	93.1 ± 0.6
<i>m</i> -CN	0.54	1.53	4.41	11.70	75.8 ± 0.6	-64 ± 2	94.7 ± 0.5
<i>m</i> -SMe	11.70	28.80	68.40	153.00	62.8 ± 0.2	-83 ± 1	87.5 ± 0.1
<i>m</i> -NHAc	10.80	25.20	61.20	135.00	61.9 ± 0.7	-87 ± 2	87.8 ± 0.5
<i>o</i> -Me	98.10	207.00	450.00	891.00	53.7 ± 0.5	-97 ± 2	82.6 ± 0.4
<i>o</i> -Ome	94.50	199.00	441.00	873.00	54.3 ± 0.7	-95 ± 2	82.6 ± 0.6
<i>o</i> -NO <sub>2</sub>	0.90	2.52	6.84	17.10	72.3 ± 0.3	-72 ± 1	93.5 ± 0.2
<i>o</i> -COOMe	7.20	17.10	43.20	97.20	64.0 ± 0.8	-83 ± 3	88.7 ± 0.6
<i>o</i> -NHAc	144.00	297.00	621.00	1190.00	51.3 ± 0.4	-99 ± 1	81.7 ± 0.3
<i>o</i> -Cl	22.50	51.30	117.00	252.00	58.9 ± 0.4	-91 ± 1	86.0 ± 0.3
<i>o</i> -Br	29.70	67.50	153.00	315.00	57.7 ± 0.4	-93 ± 1	85.4 ± 0.3
<i>o</i> -I	51.30	108.00	243.00	495.00	55.0 ± 0.8	-97 ± 3	84.1 ± 0.7
<i>o</i> -CN	2.00	5.22	13.50	32.40	68.3 ± 0.3	-79 ± 1	91.7 ± 0.3
<i>o</i> -SMe	135.00	288.00	603.00	1170.00	52.4 ± 0.2	-99 ± 1	81.8 ± 0.2
<i>o</i> -F	13.50	31.50	76.50	171.00	62.2 ± 0.7	-84 ± 2	87.2 ± 0.6
<i>o</i> -CF <sub>3</sub>	17.10	39.60	90.90	189.00	58.7 ± 0.4	-94 ± 1	86.7 ± 0.3
PhCDO	1.55	4.02	10.80	25.20	68.3 ± 0.6	-81 ± 2	92.3 ± 0.5
$k_H/k_D$	5.96	5.71	5.52	5.29	-	-	-

was limited by the solubility of TEACC and its reaction with primary and secondary alcohols. There was no reaction with the solvents chosen. Kinetics is similar in all the solvents. The values of  $k_2$  are recorded in Table-4.

TABLE-4  
SOLVENT EFFECT ON THE OXIDATION OF  
BENZALDEHYDE BY TEACC AT 298 K

Solvent	$10^4 k_2$ (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )	Solvent	$10^4 k_2$ (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )
Chloroform	63.1	Toluene	18.2
1,2-Dichloroethane	83.2	Acetophenone	87.1
Dichloromethane	66.1	Tetrahydrofuran	33.9
Dimethyl sulfoxide	234	<i>t</i> -Butyl alcohol	27.5
Acetone	58.9	1,4-Dioxane	30.2
DMF	123	1,2-Dimethoxyethane	17.4
Butanone	51.3	Ethyl acetate	22.4
Nitrobenzene	95.5	Carbon disulfide	14.8
Benzene	19.9	Acetic acid	7.76
Cyclohexane	1.86		

A satisfactory correlation ( $r^2 = 0.8432$ ; slope =  $585 \pm 42$  K) between activation enthalpies and entropies of the oxidation of the 36 benzaldehydes indicated the operation of compensation effect in this reaction<sup>13</sup>. The reaction also exhibited an excellent isokinetic effect, as determined by Exner's criterion<sup>14</sup>. An Exner's plot between  $\log k_2$  at 288 K and at 318 K was linear (Fig. 2) ( $r = 0.9991$ ;  $sd = 0.09$ ;  $\psi = 0.05$ ; slope =  $0.8405 \pm 0.0061$ ). The value of isokinetic temperature is  $707 \pm 39$  K. The linear isokinetic correlation implies that all the aldehydes are oxidized by the same mechanism and the changes in the rate are governed by changes in both the enthalpy and entropy of activation.

**Reactivity oxidizing species:** The observed hydrogen-ion dependence suggests that the reaction follows two mechanistic pathways, one acid-independent and another acid-dependent. The acid-catalysis may well be attributed to a protonation of TEACC as eqn. 2 to yield a protonated Cr(VI) species which is a stronger oxidant and electrophile. Formation of a protonated

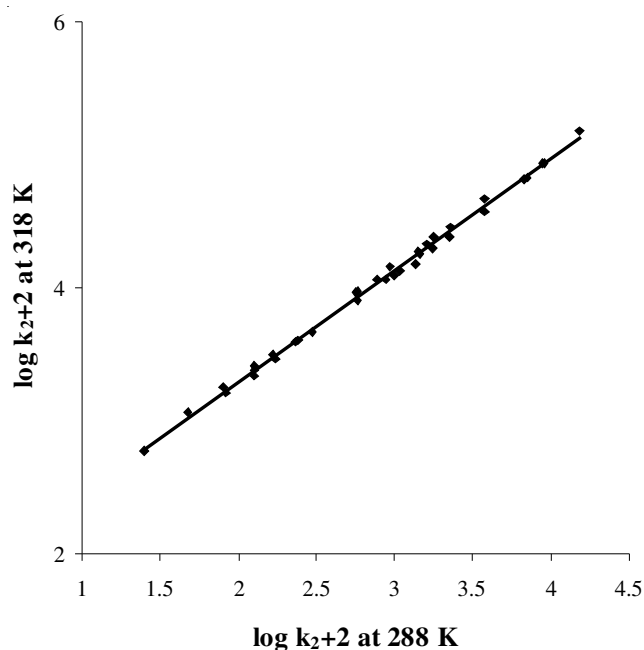
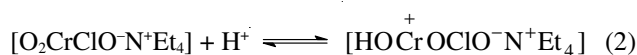


Fig. 2. Exner's isokinetic relationship in the oxidation of benzaldehydes by TEACC

Cr(VI) species has earlier been postulated in the reactions of structurally similar PCC<sup>15</sup>.



The rate constants  $k_2$ , in eighteen solvents (CS<sub>2</sub> was not considered as the complete range of solvent parameters was not available) were correlated in terms of linear solvation energy relationship (LSER) of Kamlet and Taft<sup>16</sup>  $\log k_2 = A_0 + p\pi^* + b\beta + a\alpha$ .

In this equation,  $\pi^*$  represents the solvent polarity,  $\beta$  the hydrogen bond acceptor basicities and  $\alpha$  is the hydrogen bond donor acidity.  $A_0$  is the intercept term. The results of correlation analyses terms of biparametric equation involving  $\pi^*$  and  $\beta$  and separately with  $\pi^*$  and  $\beta$  are given below eqns. 3-6.

$$\log k_2 = -3.63 + 1.56(\pm 0.19)\pi^* + 0.20(\pm 0.16)\beta + 0.13(\pm 0.15)\alpha \quad (3)$$

$$R^2 = 0.8772; \text{ sd} = 0.18; n = 18; \psi = 0.72$$

$$\log k_2 = -3.64 + 1.77(\pm 0.18)\pi^* + 0.19(\pm 0.15)\beta \quad (4)$$

$$R^2 = 0.8769; \text{ sd} = 0.17; n = 18; \psi = 0.70$$

$$\log k_2 = -3.60 + 1.82(\pm 0.18)\pi^* \quad (5)$$

$$r^2 = 0.8637; \text{ sd} = 0.18; n = 18; \psi = 0.68$$

$$\log k_2 = -2.61 + 0.51(\pm 0.38)\beta \quad (6)$$

$$r^2 = 0.0992; \text{ sd} = 0.46; n = 18; \psi = 1.00$$

here  $n$  is the number of data points and  $\psi$  is Exner's<sup>17</sup> statistical parameter.

Kamlet's<sup>16</sup> triparametric equation explain *ca.* 88 % of the effect of solvent on the oxidation. However, by Exner's criterion the correlation is not even satisfactory [eqn. 3]. The major contribution is of solvent polarity. It alone accounted for *ca.* 86 % of the data. Both  $\beta$  and  $\alpha$  play relatively minor roles.

The data on the solvent effect were also analysed in terms of Swain's<sup>18</sup> equation of cation- and anion-solvating concept of the solvents;

$$\log k_2 = aA + bB + C.$$

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

$$\log k_2 = 0.8 + (\pm 0.04)A + 1.80(\pm 0.03)B - 3.86 \quad (7)$$

$$R^2 = 0.9959; \text{ sd} = 0.03; n = 19; \psi = 0.07$$

$$\log k_2 = 0.60(\pm 0.59)A - 2.62 \quad (8)$$

$$r^2 = 0.0565; \text{ sd} = 0.48; n = 19; \psi = 1.01$$

$$\log k_2 = 1.74(\pm 0.15)B - 3.58 \quad (9)$$

$$r^2 = 0.8822; \text{ sd} = 0.17; n = 19; \psi = 0.25$$

$$\log k_2 = 1.49 \pm 0.12(A + B) - 3.83 \quad (10)$$

$$r^2 = 0.8957; \text{ sd} = 0.16; n = 19; \psi = 0.43$$

The rates of oxidation of benzaldehyde in different solvents showed an excellent correlation in Swain's equation (eqn. 7) with the cation-solvating power playing the major role. In fact, the cation-solvation alone account for *ca.* 88 % of the data. The correlation with the anion-solvating power was very poor. The solvent polarity, represented by ( $A + B$ ), also accounted for *ca.* 89 % of the data. In view of the fact that solvent polarity is able to account for *ca.* 82 % of the data, an attempt was made to correlate the rate with the relative permittivity of the solvent. However, a plot of  $\log k_2$  against the inverse of the relative permittivity is not linear ( $r^2 = 0.5399$ ;  $\text{sd} = 0.34$ ;  $\psi = 0.75$ ).

**Correlation analysis of reactivity:** The effect of structure on reactivity has long been correlated in terms of the Hammett equation<sup>19</sup> or with dual substituent-parameter equations<sup>20,21</sup>. In the late 1980s, Charton<sup>22</sup> introduced a triparametric LDR equation for the quantitative description of structural effects on chemical reactivities. This triparametric equation results from the fact that substituent types differ in their mode of electron delocalization.

Here,  $\sigma_1$  is a localized (field and/or inductive) effect parameter,  $\sigma_d$  is the intrinsic delocalized electrical effect parameter when active site electronic demand is minimal and  $\sigma_e$  represents the sensitivity of the substituent to changes in electronic demand by the active site. The latter two substituent parameters are related by eqn. 11.

$$\sigma_D = \eta\sigma_e + \sigma_d \quad (11)$$

Here  $\eta$  represents the electronic demand of the reaction site and is given by  $\eta = R/D$  and  $\sigma_D$  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<sup>22</sup>, therefore, modified the LDR equation to generate the LDRS eqn. 12.

$$\log k_2 = L\sigma_1 + D\sigma_d + R\sigma_e + Sv + h \quad (12)$$

where  $v$  is the well known Charton's steric parameter based on van der Waals radii<sup>23</sup>.

The rates of oxidation of *ortho*-, *meta*- and *para*-substituted benzaldehydes show an excellent correlation in terms of the LDR/LDRS equations (Table-5). We have used the standard deviation (sd), the coefficient of multiple determination ( $R^2$ ) and Exner's parameter,  $\psi$ , 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  $\eta$  adds a negative increment to  $\sigma_d$ , 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)  $\sigma_1$ ,  $\sigma_d$  and  $\sigma_e$  (ii)  $\sigma_d$ ,  $\sigma_e$  and  $\nu$  and (iii)  $\sigma_1$ ,  $\sigma_e$  and  $\nu$ . The absence of significant correlations showed that all the four substituent constants are significant.

$$\log k_2 = -1.65(\pm 0.46)\sigma_1 - 1.78(\pm 0.36)\sigma_d - 3.76(\pm 2.09)\sigma_e - 2.21 \quad (13)$$

$$R^2 = 0.8209; \text{ sd} = 0.32; n = 12; \psi = 0.47$$

$$\log k_2 = -1.87(\pm 0.46)\sigma_d - 1.91(\pm 2.85)\sigma_e + 0.96(\pm 0.53)\nu - 3.19 \quad (14)$$

$$R^2 = 0.7080; \text{ sd} = 0.41; n = 12; \psi = -0.63$$

$$\log k_2 = -2.05(\pm 0.72)\sigma_1 - 0.44(\pm 3.47)\sigma_e + 1.39(\pm 0.65)\nu - 2.30 \quad (15)$$

$$R^2 = 0.5658; \text{ sd} = 0.49; n = 12; \psi = 0.47$$

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 substituent constants for the three series.

The per cent contribution<sup>23</sup> of the delocalized effect,  $P_D$ , is given by following eqn. 16.

$$P_D = \frac{(D \times 100)}{(L + D)} \quad (16)$$

Similarly, the per cent contribution of the steric parameter to the total effect of the substituent,  $P_S$ , was determined by using eqn. 17.

$$P_S = \frac{(S \times 100)}{(L + D + S)} \quad (17)$$

The values of  $P_D$  and  $P_S$  are also recorded in Table-5. The value of  $P_D$  for the oxidation of *para*-substituted benzaldehydes is ca. 57 % whereas the corresponding values for the *meta*- and *ortho*-substituted 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. The magnitude of the  $P_S$  value shows that the steric effect is significant in this reaction.

The benzoyl cation is reported to have a considerable ketene character<sup>24</sup> and is thus linear. The linear structure of acylium cation has been confirmed by X-ray crystallography also<sup>25</sup>. The change from  $sp^2$  to  $sp$  results in steric relief. This relief will be greater in crowded reductants and is reflected in observed steric acceleration.

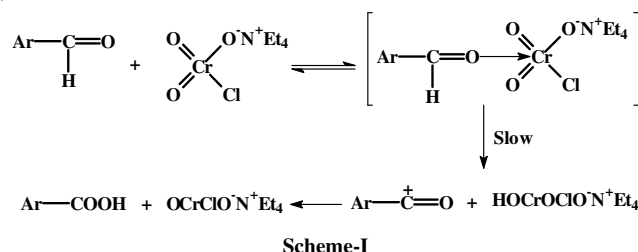
**Mechanism:** A hydrogen abstraction mechanism leading to the formation of the free radicals is unlikely in view of the failure to induce polymerization of acrylonitrile and no effect of the radical scavenger on the reaction rate. The presence of a substantial kinetic isotope effect confirms the cleavage of an aldehydic-C-H bond in the rate-determining step. The negative values of the localization and delocalization electrical effects *i.e.*, of L, D and R points to an electron-deficient reaction centre

TABLE-5  
TEMPERATURE DEPENDENCE FOR THE REACTION CONSTANTS FOR THE  
OXIDATION OF SUBSTITUTED BENZALDEHYDES BY TEACC

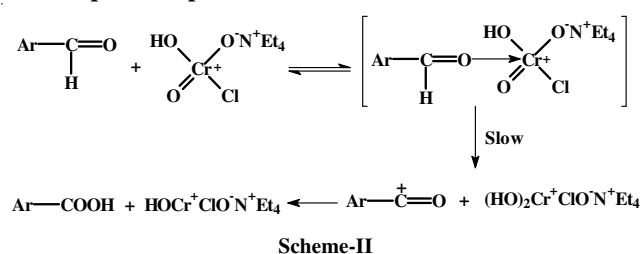
T (K)	L	D	R	S	$\eta$	$R^2$	sd	$\psi$	$P_D$	$P_S$
<i>para</i> -substituted										
288	-1.54	-1.97	-1.32	-	0.67	0.9999	0.007	0.02	56.1	-
298	-1.45	-1.88	-1.27	-	0.65	0.9998	0.007	0.01	56.5	-
308	-1.33	-1.79	-1.16	-	0.65	0.9998	0.009	0.02	57.4	-
318	-1.28	-1.71	-1.07	-	0.63	0.9989	0.009	0.04	57.2	-
<i>meta</i> -substituted										
288	-1.98	-1.44	-1.12	-	0.78	0.9998	0.007	0.04	42.1	-
298	-1.89	-1.35	-1.10	-	0.81	0.9999	0.004	0.01	41.7	-
308	-1.80	-1.28	-0.97	-	0.76	0.9997	0.009	0.02	41.6	-
318	-1.70	-1.18	-0.95	-	0.81	0.9997	0.009	0.01	40.9	-
<i>ortho</i> -substituted										
288	-1.89	-1.80	-1.35	1.35	0.75	0.9999	0.004	0.02	48.8	26.8
298	-1.79	-1.70	-1.33	1.26	0.78	0.9998	0.007	0.04	48.7	26.5
308	-1.71	-1.62	-1.26	1.17	0.78	0.9999	0.003	0.01	48.6	26.0
318	-1.62	-1.53	-1.17	1.07	0.76	0.9998	0.004	0.02	48.6	23.4

in the rate-determining step. It is further supported by the positive value of  $\eta$ , which indicates that the substituent is better able to stabilise a cationic or electron-deficient reactive site. Therefore, a hydride-ion transfer in the rate-determining step is suggested (Schemes I and II). The hydride-ion transfer mechanism is also supported by the major role of cation-solvating power of the solvents.

#### Acid-independent path



#### Acid-dependent path



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<sup>26</sup>.

It is interesting to compare here the present results with those of oxidation of hydroxy acids with TEACC<sup>4</sup>. Both hydroxy acids and benzaldehydes show similar effect of solvents. Swain's cation solvation<sup>18</sup> explained > 90 % of data in both the reactions. Anion-solvation and relative permittivity played insignificant role. Both the reactions showed the presence of substantial primary kinetic isotope effect, confirming the cleavage of the C-H bonds in the rate-determining step. However, there is a major difference in the mechanism. The oxidation of hydroxy acids is proposed to proceed through a symmetrical cyclic transition state *via* a chromate ester, while an acyclic hydride-ion transfer has been proposed for the oxidation of

the benzaldehydes. The natures of the correlation analyses of reactivities in the two cases are, of course, different, dictated by different nature of the compounds.

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