

# Structure-reactivity correlation in the oxidation of ortho-substituted benzaldehydes by Tetrakis (pyridine) Silver Dichromate

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**ABSTRACT:** Oxidation of twelve monosubstituted benzaldehydes by tetrakis (pyridine) silver dichromate in dimethyl sulphoxide, leads to the formation of corresponding benzoic acids. The reaction is of first order with respect to tetrakis (pyridine) silver dichromate and aldehydes. The reaction is promoted by hydrogen ions; the hydrogen-ion dependence has the form  $k_{obs} = a + b [H^+]$ . The oxidation of deuterated benzaldehyde exhibits substantial primary kinetic isotope effect. The reaction was studied in nineteen different organic solvents and the effect of solvent was analysed using Taft's and Swain's multi-parametric equations. The rates of the oxidation of ortho-substituted benzaldehydes were correlated well with tetraparametric LDRS equation. Ortho-substituted compounds displays 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.

**KEYWORDS:** Benzaldehydes, Correlation analysis, Kinetics, Mechanism, Dichromate.

## I. INTRODUCTION

Various inorganic salts of Cr (VI) are well known oxidizing reagents used in synthetic organic chemistry for the oxidation of organic compounds. However, these salts are rather drastic and nonselective oxidants. Further, they are insoluble in most of the organic solvents. Therefore, miscibility is a one of the problem. To overcome these limitations, a large number of organic derivatives of Cr (VI) have been prepared and used in organic synthesis as mild and selective oxidizing reagents in non-aqueous solvents<sup>1</sup>; tetrakis (pyridine) silver dichromate (TPSD) is also one of such compounds reported by Firouzabadi et al.<sup>2</sup> used as mild and selective oxidizing agent in synthetic organic chemistry. Only a few reports on the oxidation aspects of TPSD are available in the literature<sup>3-6</sup>. We have been interested in the kinetic and mechanistic aspects of the oxidations by complex salts of Cr (VI) and have already published a few reports on oxidation by halochromates<sup>9-11</sup>. In continuation of our earlier work, we report in the present article the kinetics of oxidation of some monosubstituted benzaldehydes by TPSD in DMSO as solvent. The major objective of this investigation was to study the structure-reactivity correlation for the substrate undergoing oxidation.

## II. MATERIALS AND METHODS

### Materials:

TPSD was prepared by reported method<sup>2</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<sup>12</sup>. The solid aldehydes were recrystallized from ethanol. Deuterated benzaldehyde (PhCDO) was also prepared by the literature method<sup>13</sup>. Its isotopic purity, as ascertained by its NMR spectrum, was 97±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.

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## Product analysis:

The product analysis was carried out under kinetic conditions. In a typical experiment, benzaldehyde (5.25 g, 0.05 mol) and TPSD (7.48 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 2.46 g (86%) and 2.28 g (80%) 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  $3.92 \pm 0.10$ .

## Kinetic Measurements:

The pseudo-first order conditions were attained by maintaining a large excess ( $\times 15$  or more) of the aldehyde over TPSD. The solvent was DMSO, unless specified otherwise. The reactions were followed, at constant temperatures ( $\pm 0.1$  K), by monitoring the decrease in [TPSD] spectrophotometrically at 370 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  $\log [\text{TPSD}]$  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.

## III. 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 TPSD results in the formation of corresponding benzoic acids. Analysis of products and the stoichiometric determinations indicate the following overall reaction as equation (1).



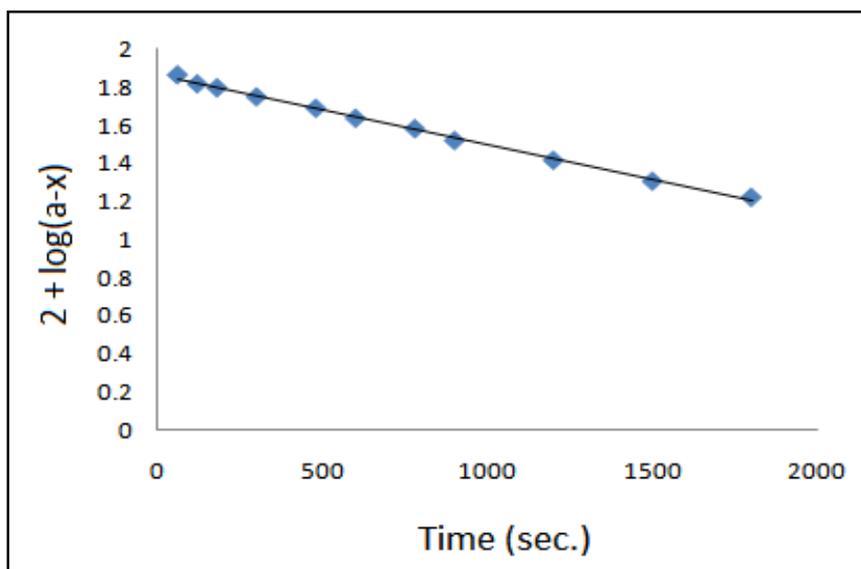
Thus, TPSD undergoes a three-electron change. This is in accord with the earlier observations with TPSD<sup>7</sup>. The other halochromates<sup>8-11</sup> as well as both pyridiniumfluorochromate (PFC)<sup>14</sup> and pyridiniumchlorochromate (PCC)<sup>15</sup> act as two electron oxidants and are reduced to chromium (IV) species.

## Test for free radicals:

The oxidation of benzaldehyde by TPSD, in an atmosphere of nitrogen failed to induce the polymerisation 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 mol dm<sup>-3</sup> of 2,6-di-*t*-butyl-4-methylphenol (butylated hydroxytoluene or BHT). It was observed that BHT was recovered unchanged, almost quantitatively.

## Rate laws:

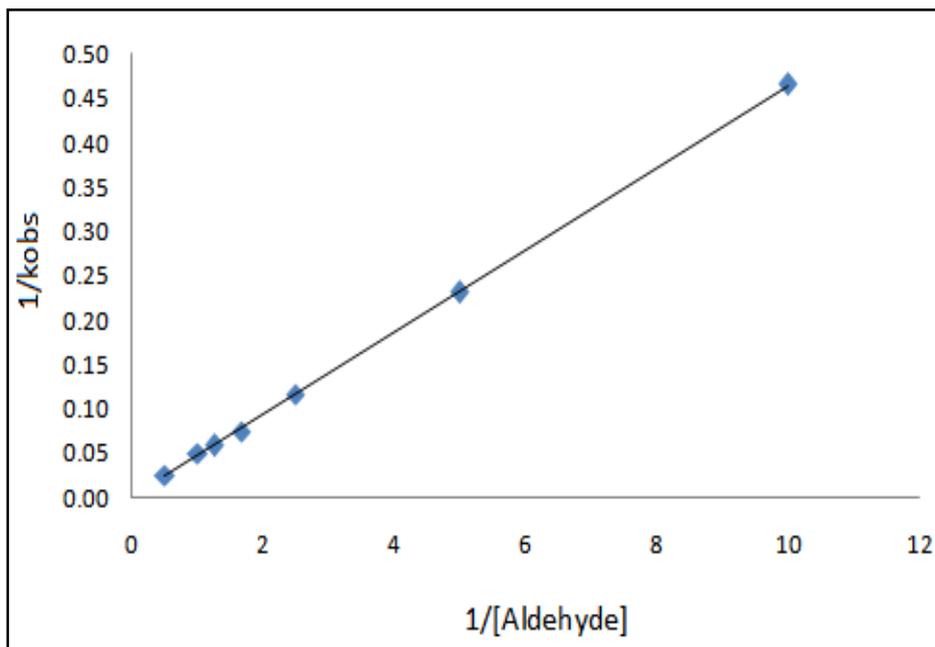
The reactions were found to be first order with respect to TPSD. Figure-1 depicts a typical kinetic run. Further, the pseudo first order rate constant,  $k_{\text{obs}}$ , was independent of initial concentration of TPSD. The reaction rate increases linearly with increase in the concentration of the aldehydes (Table 1).



**Figure 1.** Oxidation of benzaldehyde by TPSD: A typical kinetic run

A double reciprocal plot of  $1/k_{obs}$  against  $1/[\text{Aldehyde}]$  is linear ( $r^2 > 0.995$ ) as shown in Figure 2.

The dependence of reaction rate on the reductant concentration was studied at different temperatures and the values of  $K$  and  $k_2$  were evaluated from the double reciprocal plots. The activation parameters of the decomposition of the complexes were calculated from the values of  $k_2$  at different temperatures (Tables 2).



**Figure 2.** Oxidation of benzaldehyde by TPSD: A double reciprocal plot.

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**Effect of acidity:**

The reaction is catalysed by hydrogen ions (Table 3). The hydrogen-ion dependence taking the form as equation-2.

$$k_{obs} = a + b [H^+] \quad (2)$$

The values for *a* and *b* for benzaldehyde are  $19.98 \pm 0.22 \times 10^{-4} \text{ s}^{-1}$  and  $34.2 \pm 0.36 \times 10^{-4} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  respectively ( $r^2 = 0.999$ ). This suggests that, TPSD is protonated is a fast pre-equilibrium and both the protonated and unprotonated forms are reactive oxidizing species.

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

$10^3[\text{TPSD}]$ (mol dm <sup>-3</sup> )	[Aldehyde] (mol dm <sup>-3</sup> )	[TsOH] (mol dm <sup>-3</sup> )	$10^4 k_{obs}$ (s <sup>-1</sup> )
1.00	0.10	0.00	2.15
1.00	0.20	0.00	4.32
1.00	0.40	0.00	8.55
1.00	0.60	0.00	13.5
1.00	0.80	0.00	17.1
1.00	1.00	0.00	19.8
1.00	2.00	0.00	40.5
2.00	0.40	0.00	9.63
4.00	0.40	0.00	8.10
6.00	0.40	0.00	9.27
8.00	0.40	0.00	8.82
1.00	0.40	0.00	9.00*

\* contained 0.001 mol dm<sup>-3</sup> acrylonitrile.

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### Kinetic isotope effect:

To ascertain the importance of the cleavage of the aldehydic C–H bond in the rate-determining step, the oxidation of [<sup>2</sup>H] benzaldehyde (PhCDO) was studied. The results ( $k_H/k_D = 5.76$  at 298 K) showed the presence of a substantial primary kinetic isotope effect (Table 2).

**Table 2.** Rate constants and activation parameters for the decomposition of TPSD-Aldehyde complexes.

Substituents	$10^4 k_2, \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$				$\Delta H^*$	$\Delta S^*$	$\Delta G^*$
	288 K	298 K	308 K	318 K	$\text{kJ mol}^{-1}$	$\text{J mol}^{-1} \text{K}^{-1}$	$\text{kJ mol}^{-1}$
H	7.83	19.8	48.6	117	66.1±0.6	-75 ± 2	88.4±0.5
o-Me	70.2	153	324	675	54.8±0.5	-96 ± 1	83.3±0.4
o-Ome	68.4	144	315	666	55.4±0.9	-95 ± 3	83.4±0.7
o-NO <sub>2</sub>	0.84	2.34	6.21	16.2	72.5±0.5	-72 ± 2	93.7±0.4
o-COOMe	5.85	14.4	35.1	81.0	64.3±0.5	-84 ± 2	89.2±0.4
o-NHAc	90.0	212	432	864	54.6±0.7	-95 ± 2	82.7±0.5
o-Cl	17.7	40.5	91.8	198	59.7±0.1	-91 ± 1	86.7±0.1
o-Br	22.5	51.3	117	243	58.1±0.3	-94 ± 1	86.0±0.3
o-I	37.8	83.7	180	378	55.9±0.4	-98 ± 1	84.8±0.3
o-CN	1.74	4.63	11.7	29.7	69.3±0.7	-95 ± 2	82.7±0.5
o-Sme	88.2	207	423	855	54.8±0.6	-94 ± 2	82.7±0.5
o-F	10.8	26.1	61.2	135	61.7±0.2	-88 ± 1	87.7±0.2
o-CF <sub>3</sub>	13.5	30.6	69.3	153	59.1±0.7	-95 ± 2	82.7±0.5
PhCDO	1.28	3.44	8.71	22.0	69.5±0.5	-79 ± 2	92.8±0.2
$k_H/k_D$	6.12	5.76	5.58	5.32			

**Table 3.** Dependence of the reaction rate on hydrogen ion concentration.

[Benzaldehyde] = 0.10 mol dm <sup>-3</sup> ; [TPSD] = 0.001 mol dm <sup>-3</sup> ; Temp. 298 K.						
[TsOH], mol dm <sup>-3</sup>	0.10	0.20	0.40	0.60	0.80	1.00
$10^4 k_{\text{obs}}/\text{s}^{-1}$	23.4	27.0	33.3	40.5	47.7	54.0

### Effect of solvents:

The oxidation of benzaldehyde was studied in 19 different organic solvents. The choice of solvents was limited by the solubility of TPSD 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  $k_2$  are recorded in Table 4.

The correlation between activation enthalpies and entropies of the oxidation of the twelve benzaldehydes is not satisfactory ( $r^2 = 0.5701$ ), indicating there is no operation of a compensation effect<sup>16</sup>. The value of the isokinetic temperature is  $620 \pm 5$  K. However, according to Exner<sup>17</sup>, an isokinetic relationship between the calculated values of activation enthalpies and entropies is often vitiated by random experimental errors. Exner suggested an alternative method for establishing the isokinetic relationship. Exner's plot between  $\log k_2$  at 288 K and at 318 K (Figure 3) was linear ( $r^2 = 0.999$ ). The value of isokinetic temperature evaluated from the Exner's plot is 766 K. The linear isokinetic

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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.

**Table 4.** Solvent effect on the oxidation of benzaldehyde by TPSD at 298 K

Solvents	$10^4 k_2 (s^{-1})$
Chloroform	38.0
1,2-Dichloroethane	45.7
Dichloromethane	39.8
DMSO	117
Acetone	41.7
DMF	57.5
Butanone	30.2
Nitrobenzene	43.7
Benzene	15.8
Cyclohexane	1.51
Toluene	12.0
Acetophenone	51.3
THF	22.4
t-Butylalcohol	14.5
1,4-Dioxane	21.4
1,2-Dimethoxyethane	10.5
Carbon disulfide	17.0
Acetic acid	5.62
Ethyl acetate	7.94

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 (Equation 3) of Kamlet and Taft<sup>18</sup>.

$$\log k_2 = A_0 + \rho\pi^* + b\beta + a\alpha \quad (3)$$

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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. It may be mentioned here that out of the 18 solvents, 13 has a value of zero for  $\alpha$ . The results of correlation analyses terms of biparametric equation involving  $\pi^*$  and  $\beta$ , and separately with  $\pi^*$  and  $\beta$  are given below by Equations (4) - (7).

$$\log k_2 = -3.72 + 1.56 (\pm 0.20) \pi^* + 0.26 (\pm 0.15) \beta + 0.12 (\pm 0.15) \alpha \quad (4)$$

$R^2 = 0.8421$ ;  $sd = 0.19$ ;  $n = 18$ ;  $\psi = 0.40$

$$\log k_2 = -3.75 + 1.58 (\pm 0.19) \pi^* + 0.27 (\pm 0.15) \beta \quad (5)$$

$R^2 = 0.8351$ ;  $sd = 0.19$ ;  $n = 18$ ;  $\psi = 0.41$

$$\log k_2 = -3.71 + 1.65 (\pm 0.20) \pi^* \quad (6)$$

$r^2 = 0.8010$ ;  $sd = 0.20$ ;  $n = 18$ ;  $\psi = 0.45$

$$\log k_2 = -2.81 + 0.55 (\pm 0.33) \beta \quad (7)$$

$r^2 = 0.1430$ ;  $sd = 0.42$ ;  $n = 18$ ;  $\psi = 0.96$

Here  $n$  is the number of data points and  $\psi$  is Exner's statistical parameter<sup>19</sup>.

Kamlet's<sup>18</sup> triparametric equation explain *ca.* 84 % of the effect of solvent on the oxidation. However, by Exner's criterion the correlation is not even satisfactory [cf. (4)]. The major contribution is of solvent polarity. It alone accounted for *ca.* 80 % 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>20</sup> equation of cation and anion-solvating concept of the solvents (Eq. 8).

$$\log k_2 = aA + bB + C \quad (8)$$

Here  $A$  represents the anion-solvating power of the solvent and  $B$  is 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 (Eq. 8), separately with  $A$  and  $B$  and with  $(A + B)$ .

$$\log k_2 = 0.64 (\pm 0.07) A + 1.74 (\pm 0.05) B - 3.95 \quad (9)$$

$R^2 = 0.9860$ ;  $sd = 0.05$ ;  $n = 19$ ;  $\psi = 0.11$

$$\log k_2 = 0.40 (\pm 0.56) A - 2.77 \quad (10)$$

$r^2 = 0.0290$ ;  $sd = 0.45$ ;  $n = 19$ ;  $\psi = 1.01$

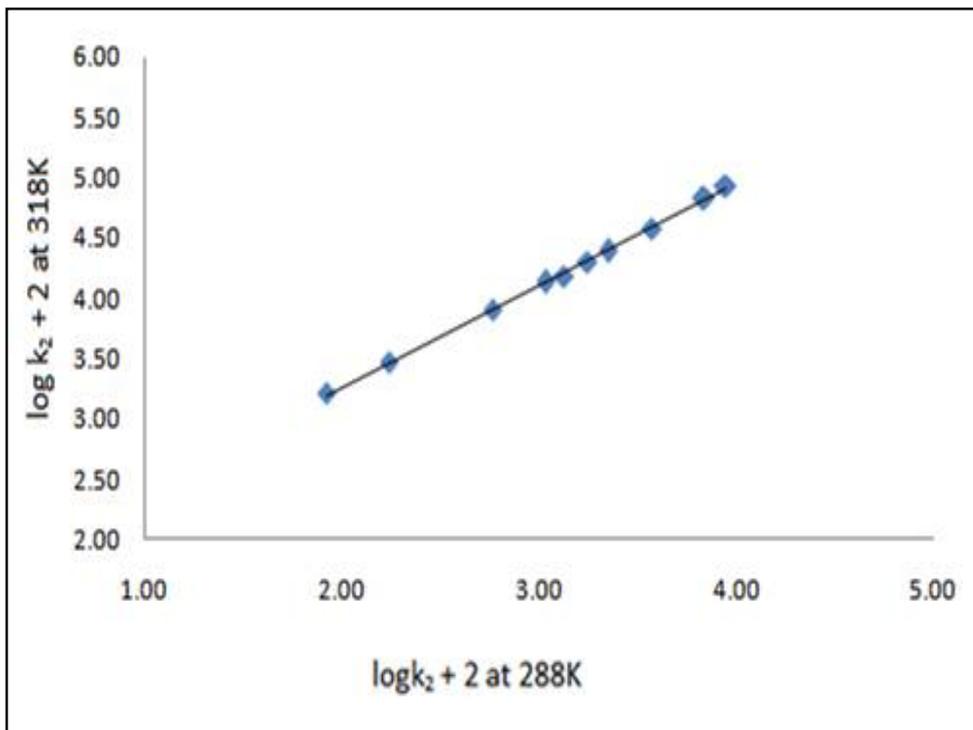
$$\log k_2 = 1.69 (\pm 0.12) B - 3.74 \quad (11)$$

$r^2 = 0.9140$ ;  $sd = 0.13$ ;  $n = 19$ ;  $\psi = 0.29$

$$\log k_2 = 1.37 \pm 0.15 (A + B) - 3.92 \quad (12)$$

$r^2 = 0.8423$ ;  $sd = 0.18$ ;  $n = 19$ ;  $\psi = 0.40$

The rates of oxidation of benzaldehyde in different solvents showed an excellent correlation in Swain's equation (Eq. 9) with the cation-solvating power playing the major role. In fact, the cation-solvation alone account for *ca.* 91% of the data. The correlation with the anion-solvating power was very poor. The solvent polarity, represented by  $(A + B)$ , also accounted for *ca.* 84% of the data. In view of the fact that solvent polarity is able to account for *ca.* 84% 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 ( $r^2 = 0.503$ ;  $sd = 0.33$ ;  $\psi = 0.76$ ).



**Figure 3.** Exner's Isokinetic Relationship in the oxidation of benzaldehydes by TPSD.

**Correlation analysis of reactivity:**

The effect of structure on reactivity has long been correlated in terms of the Hammett equation<sup>21</sup> or with dual substituent-parameter equations<sup>22,23</sup>. In the late 1980s, Charton<sup>24</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.

$$\log k_2 = L \sigma_1 + D \sigma_d + R \sigma_e + h \tag{13}$$

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 Eq. (14).

$$\sigma_D = \eta \sigma_e + \sigma_d \tag{14}$$

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>24</sup>, therefore, modified the LDR equation to generate the LDRS Eq. (15).

$$\log k_2 = L \sigma_1 + D \sigma_d + R \sigma_e + S \upsilon + h \tag{15}$$

Where  $\upsilon$  is the well known Charton's steric parameter based on Vander Waals radii<sup>25</sup>.

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The rates of oxidation of *ortho*-substituted benzaldehydes show an excellent correlation in terms of the LDRS equation (Table 5). We have used the standard deviation (sd), the coefficient of multiple determination ( $R^2$ ), and Exner's<sup>19</sup> parameter,  $\psi$ , as the measures of goodness of fit.

The oxidation of *ortho*-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.

**Table 5.** Temperature dependence for the reaction constants for the oxidation of *ortho*-substituted benzaldehydes by TPSD.

T/K	-L	-D	-R	S	$\eta$	$R^2$	Sd	$\psi$	$P_D$	$P_S$
288	-1.79	-1.69	-1.38	1.26	0.89	0.9997	0.013	0.02	51.4	26.6
298	-1.70	-1.61	-1.25	1.26	0.82	0.9999	0.007	0.01	48.6	26.1
308	-1.62	-1.53	-1.15	1.09	0.75	0.9989	0.004	0.04	48.6	25.7
318	-1.55	-1.43	-1.09	0.99	0.76	0.9999	0.005	0.01	48.0	24.9

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  $\sigma_d$ , reflecting 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  $\upsilon$  and (iii)  $\sigma_1$ ,  $\sigma_e$  and  $\upsilon$ . The absence of significant correlations showed that all the four substituent constants are significant.

$$\log k_2 = -1.49 (\pm 0.40) \sigma_1 - 1.96 (\pm 0.31) \sigma_d - 3.42 (\pm 1.80) \sigma_e - 2.42 \quad (16)$$

$$R^2 = 0.8715; \quad \text{sd} = 0.27; \quad n = 12; \quad \psi = 0.41$$

$$\log k_2 = -2.05 (\pm 0.44) \sigma_d - 1.88 (\pm 2.73) \sigma_e + 0.80 (\pm 0.50) \upsilon - 3.32 \quad (17)$$

$$R^2 = 0.7421; \quad \text{sd} = 0.39; \quad n = 12; \quad \psi = 0.59$$

$$\log k_2 = -1.99 (\pm 0.80) \sigma_1 - 0.34 (\pm 3.85) \sigma_e + 1.24 (\pm 0.72) \upsilon - 2.42 \quad (18)$$

$$R^2 = 0.4842; \quad \text{sd} = 0.55; \quad n = 12; \quad \psi = 0.83$$

There is no significant colinearity between the various substituents constants for the series. The percent contribution<sup>25</sup> of the delocalized effect,  $P_D$ , is given by following equation (19).

$$P_D = (|D| \times 100) / (|L| + |D|) \quad (19)$$

Similarly, the percent contribution of the steric parameter to the total effect of the substituent,  $P_S$ , was determined by using equation (20).

$$P_S = (|S| \times 100) / (|L| + |D| + |S|) \quad (20)$$

The values of  $P_D$  and  $P_S$  are also recorded in Table 5. The value of  $P_D$  for the oxidation of *ortho*-substituted aldehydes is ca. 49%. 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

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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 positive value of  $S$  showed a steric acceleration of the reaction. This may be explained on the basis high ground state energy of the sterically crowded aldehydes. Since the crowding is relieved in the in the product benzoic acids as well as the transition state leading to it, the transition state energy of the crowded and un-crowded aldehydes do not differ much and steric acceleration, therefore results.

The benzoyl cation is reported have a considerable ketene character<sup>26</sup> and is thus linear. The linear structure of acylium cation has been confirmed by X-ray crystallography also<sup>27</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.

## IV. 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 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 (Scheme 1 and 2). The hydride-ion transfer mechanism is also supported by the major role of cation-solvating power of the solvents.

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>28</sup>.

Initially Cr(VI) is reduced to Cr(IV). It is likely to react with another Cr(VI) to generate Cr(V) which is then reduced in a fast step to the ultimate product Cr(III). Such a sequence of reactions in Cr(VI) oxidations is well known<sup>29</sup>.

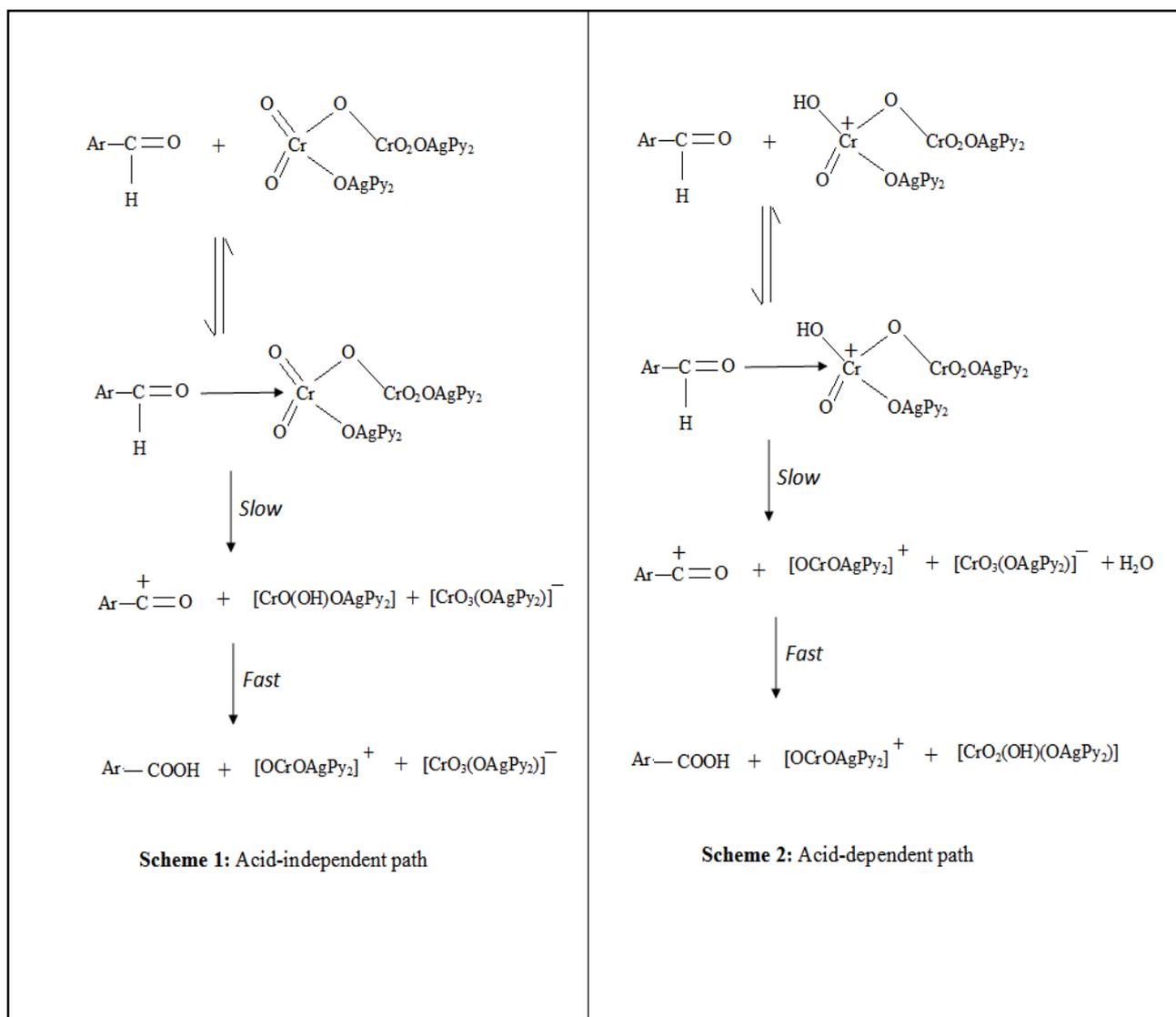
## V. CONCLUSION

The reaction is proposed to proceed through a hydride-ion transfer from aldehyde to the oxidant in the rate-determining step. Both de-protonated and protonated forms of TPSD are the reactive oxidising species. An aldehydic C-H bond is cleaved in the rate-determining step.

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