



# CORRELATION ANALYSIS OF REACTIVITY IN THE OXIDATION OF SUBSTITUTED BENZALDEHYDES BY BIS[DIPYRIDINESILVER(I)] DICHROMATE

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Oxidation of thirty six monosubstituted benzaldehydes by bis[dipyridinesilver(I)] dichromate (BDS) in dimethylsulphoxide (DMSO), leads to the formation of corresponding benzoic acids. The reaction is of first order with respect to BDS. A Michaelis-Menten type kinetics was observed with respect to the reactants. The reaction is promoted by hydrogen ions; the hydrogen-ion dependence has the form  $k_{\text{obs}} = a + b [\text{H}^+]$ . The oxidation of [<sup>2</sup>H]benzaldehyde (PhCDO) exhibited a 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 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.

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isotopic purity, as ascertained by its NMR spectrum, was 96±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 methods.

## Product analysis

The product analysis was carried out under kinetic conditions. In a typical experiment, benzaldehyde (5.25 g, 0.05 mol) and BDS (7.48 g, 0.01 mol) were made up to 50 mL 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 mL) 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 2.55 g (89 %) and 2.38 g (83 %) respectively. The DNP was found identical (m.p. and mixed m.p.) with the DNP of benzaldehyde. Similar experiments were performed with other alcohols also. The oxidation state of chromium in completely reduced reaction mixtures, determined by an iodometric method was 3.90±0.10.

## Introduction

Halochromates and dichromates have been used as mild and selective oxidizing reagents in synthetic organic chemistry.<sup>1</sup> Bis[dipyridinesilver (I)] dichromate (BDS) is also one of such compounds used as mild and selective oxidizing agent in synthetic organic chemistry.<sup>2</sup> We have been interested in kinetics of oxidations by dichromates and have already published a few reports on oxidation by BDS.<sup>3-6</sup> In continuation of our earlier work, we report in the present article the kinetics of oxidation of some monosubstituted benzaldehydes by BDS in DMSO as solvent. The major objective of this investigation was to study the structure-reactivity correlation for the substrate undergoing oxidation.

## Experimental

### Materials

BDS was prepared by reported method<sup>2</sup> and its purity was checked by an 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>7</sup> The solid aldehydes were recrystallized from ethanol. Deuteriated benzaldehyde (PhCDO) was also prepared by the reported method.<sup>8</sup> Its

### Kinetic Measurements

The pseudo-first order conditions were attained by maintaining a large excess ( $\times 15$  or more) of the alcohol over BDS. The solvent was DMSO, unless specified otherwise. The reactions were followed, at constant temperatures ( $\pm 0.1\text{K}$ ), by monitoring the decrease in [BDS] spectrophotometrically at 354 nm. No other reactant or product has any significant absorption at this wavelength. The pseudo-first order rate constant,  $k_{\text{obs}}$ , was evaluated from the linear ( $r = 0.990-0.999$ ) plots of

log [BDS] 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 alcohols. Since the results are similar, only representative data are reproduced here.

### Stoichiometry

Oxidation of benzaldehydes by BDS results in the oxidation of corresponding benzaldehydes. Analysis of products and the stoichiometric determinations indicate the following overall reaction (1).

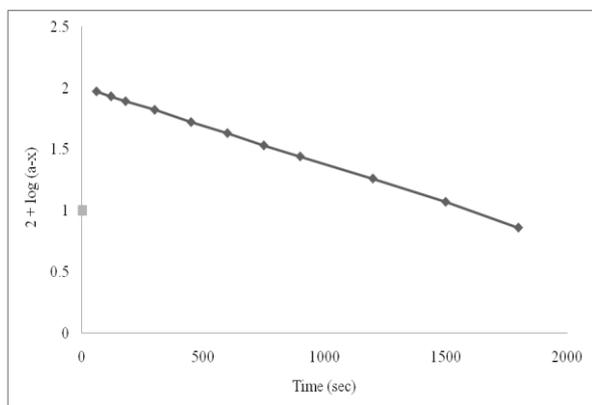


### Test for free radicals

The oxidation of benzaldehyde by BDS, 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 hydroxy-toluene or BHT). It was observed that BHT was recovered unchanged, almost quantitatively.

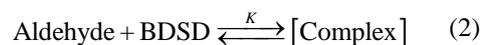
### Rate laws

The reactions are of first order with respect to BDS. Figure 1 depicts a typical kinetic run. Further, the pseudo-first order rate constant,  $k_{\text{obs}}$  is independent of the initial concentration of BDS. The reaction rate increases with increase in the concentration of the aldehydes but not linearly (Table 1).

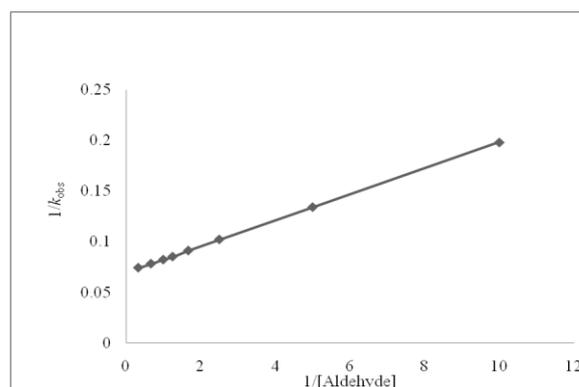


**Figure 1.** Oxidation of Benzaldehydes by BDS: A typical kinetic run.

A plot of  $1/k_{\text{obs}}$  against  $1/[\text{Aldehydes}]$  is linear ( $r > 0.995$ ) with an intercept on the rate-ordinate (Figure 2). Thus, Michaelis-Menten type kinetics is observed with respect to the aldehydes. This leads to the postulation of following overall mechanism (2) and (3) and rate law (4).



$$\text{Rate} = \frac{k_2 K [\text{Aldehyde}] [\text{BDS}]}{1 + K [\text{Aldehyde}]} \quad (4)$$



**Figure 2.** Oxidation of Benzaldehydes by BDS: A double reciprocal plot.

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

$10^3[\text{BDS}],$ mol dm <sup>-3</sup>	$[\text{Aldehyde}],$ mol dm <sup>-3</sup>	$[\text{TsOH}],$ mol dm <sup>-3</sup>	$10^4 k_{\text{obs}},$ s <sup>-1</sup>
1.0	0.10	0.00	5.06
1.0	0.20	0.00	7.49
1.0	0.40	0.00	9.85
1.0	0.60	0.00	11.0
1.0	0.80	0.00	11.7
1.0	1.00	0.00	12.2
1.0	1.50	0.00	12.8
1.0	3.00	0.00	13.6
2.0	0.40	0.00	9.72
4.0	0.40	0.00	9.20
6.0	0.40	0.00	9.45
8.0	0.40	0.00	9.63
1.0	0.20	0.00	7.74*

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

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 thermodynamic parameters of the complex formation and activation parameters of the decomposition of the complexes were calculated from the values of  $K$  and  $k_2$  respectively at different temperatures (Tables 2 and 3).

**Table 2.** Formation constants for the decomposition of BDS–Aldehyde complexes and thermodynamic parameters.

Substituent	<i>K</i> dm <sup>3</sup> mol <sup>-1</sup>				<i>-ΔH</i>	<i>-ΔS</i>	<i>-ΔG</i>
	288 K	298 K	308 K	318 K	kJ mol <sup>-1</sup>	J mol <sup>-1</sup> K <sup>-1</sup>	kJ mol <sup>-1</sup>
H	6.23	5.42	4.57	3.72	15.5±0.7	30±2	6.63±0.6
p-Me	5.90	5.07	4.30	3.45	16.0±0.8	32±2	6.48±0.6
p-OMe	5.45	4.62	3.85	3.06	17.0±0.7	37±2	6.24±0.6
p-F	5.85	5.02	4.25	3.40	16.1±0.8	33±3	6.45±0.6
p-Cl	6.18	5.38	4.54	3.73	15.3±0.6	30±2	6.61±0.5
p-NO <sub>2</sub>	5.92	5.10	4.32	3.51	15.7±0.7	31±2	6.49±0.5
p-CF <sub>3</sub>	5.56	4.73	3.92	3.11	17.1±0.8	37±3	6.29±0.6
p-COOMe	5.35	4.55	3.75	2.96	17.4±0.8	38±3	6.19±0.6
p-Br	5.65	4.85	4.05	3.25	16.5±0.7	34±2	6.36±0.6
p-NHAc	6.15	5.31	4.55	3.70	15.2±0.7	29±2	6.60±0.5
p-CN	5.89	5.07	4.30	3.48	15.7±0.7	32±2	6.48±0.5
p-SMe	6.05	5.22	4.41	3.60	15.6±0.6	31±2	6.55±0.5
p-NMe <sub>2</sub>	5.98	5.17	4.38	3.52	15.8±0.8	32±2	6.52±0.6
m-Me	6.12	5.33	4.52	3.65	15.5±0.8	30±3	6.59±0.6
m-OMe	5.58	4.70	3.95	3.10	17.2±0.8	37±3	6.30±0.6
m-Cl	5.67	4.83	4.08	3.20	16.8±0.9	36±3	6.63±0.7
m-Br	5.99	5.20	4.40	3.51	15.9±0.9	32±3	6.53±0.7
m-F	5.94	5.10	4.35	3.48	15.9±0.8	32±2	6.49±0.6
m-NO <sub>2</sub>	6.18	5.35	4.55	3.78	14.9±0.5	28±2	6.62±0.4
m-CO <sub>2</sub> Me	5.55	4.75	3.90	3.12	17.1±0.7	37±2	6.29±0.6
m-CF <sub>3</sub>	5.90	5.10	4.30	3.45	16.0±0.8	32±3	6.48±0.6
m-CN	6.21	5.42	4.55	3.80	15.0±0.5	29±2	6.63±0.4
m-SMe	6.03	5.25	4.45	3.63	15.3±0.7	30±2	6.56±0.6
m-NHAc	5.50	4.71	3.85	3.06	17.4±0.8	38±3	6.27±0.6
o-Me	5.85	5.03	4.20	3.45	15.9±0.6	32±2	6.45±0.4
o-OMe	5.40	4.55	3.80	3.00	17.2±0.7	38±2	6.21±0.6
o-NO <sub>2</sub>	5.80	4.95	4.20	3.34	16.3±0.8	34±3	6.42±0.3
o-COOMe	6.20	5.36	4.55	3.75	15.2±0.6	29±2	6.62±0.4
o-NHAc	5.90	5.10	4.26	3.45	16.1±0.7	33±2	6.48±0.6
o-Cl	6.30	5.45	4.68	3.85	14.9±0.6	28±2	6.67±0.5
o-Br	5.36	4.52	3.70	2.95	17.6±0.7	39±2	6.18±0.5
o-I	5.89	5.05	4.30	3.45	15.9±0.7	32±2	6.47±0.6
o-CN	5.68	4.90	4.05	3.28	16.4±0.7	34±2	6.37±0.6
o-SMe	6.08	5.25	4.45	3.60	15.7±0.7	31±2	6.56±0.6
o-F	5.76	4.93	4.15	3.36	16.1±0.6	33±2	6.41±0.5
o-CF <sub>3</sub>	5.15	4.36	3.55	2.75	18.3±0.9	42±3	6.07±0.7
PhCDO	5.82	5.01	4.21	3.42	15.9±0.7	32±2	6.44±0.5

**Effect of acidity**

The reaction is catalysed by hydrogen ions. The hydrogen-ion dependence taking the form:  $k_{\text{obs}} = a + b [\text{H}^+]$  (Table 4). The values for *a* and *b* for benzaldehyde are  $4.94 \pm 0.31 \times 10^{-4} \text{ s}^{-1}$  and  $9.30 \pm 0.51 \times 10^{-4} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  respectively ( $r^2 = 0.9883$ ). This suggests that BDS is protonated is a fast pre-equilibrium and both the protonated and unprotonated forms are reactive oxidizing species.

**Kinetic isotope effect**

To ascertain the importance of the cleavage of the aldehydic C–H bond in the rate-determining step, oxidation of  $\alpha, \alpha$ -dideuterio-benzaldehyde (PhCDO) 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 was limited by the solubility of BDS 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 5.

The correlation between activation enthalpies and entropies of the oxidation of the thirty- six benzaldehydes is linear ( $r^2 = 0.9150$ ), indicating the operation of a compensation effect.<sup>9</sup> The value of the isokinetic temperature is  $641 \pm 33 \text{ K}$ . However, according to Exner,<sup>10</sup> an isokinetic relationship between the calculated values of activation enthalpies and entropies is often vitiated by random experimental errors.

**Table 3.** Rate constants and activation parameters for the decomposition of BSD-Aldehyde complexes.

Substituents	10 <sup>4</sup> k <sub>2</sub> , dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>				ΔH*	-ΔS*	ΔG*
	288 K	298 K	308 K	318 K	kJ mol <sup>-1</sup>	J mol <sup>-1</sup> K <sup>-1</sup>	kJ mol <sup>-1</sup>
H	5.58	14.4	36.0	86.4	67.0±0.3	75±1	89.2±0.3
p-Me	12.6	30.6	74.7	171	63.8±0.5	79±2	87.3±0.4
p-OMe	28.8	69.3	162	360	61.6±0.3	80±1	85.3±0.2
p-F	5.76	15.3	38.7	95.4	68.6±0.4	69±1	89.1±0.3
p-Cl	3.42	9.27	23.9	59.4	69.9±0.8	69±1	90.3±0.2
p-NO <sub>2</sub>	0.22	0.65	1.89	5.31	78.3±0.7	63±2	96.8±0.6
p-CF <sub>3</sub>	0.67	1.98	5.31	14.4	75.0±0.6	65±2	94.2±0.4
p-COOMe	0.92	2.52	7.02	18.0	73.2±0.6	69±2	93.5±0.5
p-Br	3.36	9.00	23.4	58.4	70.0±0.5	69±2	90.4±0.4
p-NHAc	12.9	32.4	78.3	180	64.4±0.2	77±1	87.2±0.2
p-CN	0.39	1.17	3.33	9.00	77.1±0.3	62±1	95.4±0.2
p-SMe	15.3	38.7	92.7	207	63.6±0.1	78±1	86.8±0.1
p-NMe <sub>2</sub>	144	306	666	1350	54.5±0.5	91±2	81.6±0.4
m-Me	10.8	26.1	63.9	144	63.4±0.5	82±2	87.7±0.4
m-OMe	12.6	29.7	70.2	153	61.0±0.4	89±1	87.4±0.3
m-Cl	1.71	4.68	12.6	29.7	70.2±0.5	73±2	91.9±0.4
m-Br	1.70	4.59	11.7	28.8	69.8±0.6	75±2	92.0±0.4
m-F	2.25	6.03	15.3	37.8	69.0±0.3	76±1	91.4±0.3
m-NO <sub>2</sub>	0.14	0.45	1.26	3.60	79.5±0.5	62±2	97.8±0.4
m-CO <sub>2</sub> Me	0.81	2.25	6.21	16.2	73.6±0.6	68±2	93.8±0.5
m-CF <sub>3</sub>	0.54	1.53	4.32	11.7	75.6±0.7	65±2	94.7±0.6
m-CN	0.27	0.81	2.25	6.30	77.2±0.6	65±2	96.3±0.5
m-SMe	7.83	18.9	46.8	99.9	62.6±0.6	88±2	88.5±0.5
m-NHAc	6.84	17.1	41.4	96.3	64.6±0.4	82±1	88.8±0.3
o-Me	57.6	126	279	567	55.7±0.4	95±1	83.8±0.3
o-OMe	73.8	162	360	747	56.4±0.5	90±2	83.2±0.4
o-NO <sub>2</sub>	0.45	1.35	3.51	9.36	74.1±0.5	71±2	95.1±0.5
o-COOMe	3.51	8.91	21.6	51.3	65.5±0.4	84±1	91.4±0.3
o-NHAc	93.6	198	422	846	53.5±0.4	98±1	82.7±0.3
o-Cl	14.4	33.3	77.4	171	60.4±0.5	90±2	87.1±0.4
o-Br	18.0	43.2	97.2	207	59.5±0.1	91±1	86.5±0.3
o-I	29.7	67.5	144	306	56.5±0.4	97±1	85.4±0.3
o-CN	1.02	2.79	7.29	18.0	70.4±0.2	77±1	93.3±0.2
o-SMe	92.7	202	425	855	53.9±0.1	97±1	82.7±0.1
o-F	9.90	24.3	59.4	135	64.0±0.4	81±1	87.9±0.3
o-CF <sub>3</sub>	7.83	18.9	43.2	95.4	60.9±0.2	93±1	88.6±0.2
PhCDO	0.92	2.52	6.70	16.8	71.3±0.4	75±1	93.5±0.3
k <sub>H</sub> /k <sub>D</sub>	6.07	5.71	5.37	5.14			

Exner suggested an alternative method for establishing the isokinetic relationship. Exner's plot between log k<sub>2</sub> at 288 K and at 318 K was linear (*r* = 0.9992). The value of isokinetic temperature evaluated from the Exner's plot is 731±41 K. The linear isokinetic correlation implies that all the alcohols are oxidized by the same mechanism and the changes in the rate are governed by changes in both the enthalpy and entropy of activation.

**Table 4.** Dependence of the reaction rate on hydrogen-ion concentration.

[TsOH], mol dm <sup>-3</sup>	0.10	0.20	0.40	0.60	0.80	1.00
10 <sup>4</sup> k <sub>obs</sub> /s <sup>-1</sup>	5.29	6.93	8.82	9.81	12.6	14.4

[Benzaldehyde] 0.10 mol dm<sup>-3</sup>; [BSD] 0.001 mol dm<sup>-3</sup>; Temp. 298 K.

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 (6) of Kamlet et al.<sup>11</sup>

$$\log k_2 = A_0 + p\pi^* + b\beta + \alpha \quad (6)$$

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 equation (6), a biparametric equation involving  $\pi^*$  and  $\beta$ , and separately with  $\pi^*$  and  $\beta$  are given below (7) - (10).

$$\log k_2 = -3.69 + 1.60 (\pm 0.20)\pi^* + 0.20 (\pm 0.17)\beta + 0.14 (\pm 0.15)\alpha \quad (7)$$

$$R^2 = 0.8610; sd = 0.19; n = 18; \psi = 0.42$$

$$\log k_2 = -3.72 + 1.65 (\pm 0.19)\pi^* + 0.16 (\pm 0.15)\beta \quad (8)$$

$$R^2 = 0.8434; sd = 0.19; n = 18; \psi = 0.42$$

$$\log k_2 = -3.69 + 1.69 (\pm 0.19)\pi^* \quad (9)$$

$$r^2 = 0.8334; sd = 0.19; n = 18; \psi = 0.42$$

$$\log k_2 = -2.76 + 0.45 (\pm 0.36)\beta \quad (10)$$

$$r^2 = 0.0880; sd = 0.44; n = 18; \psi = 0.98$$

Kamlet's<sup>11</sup> triparametric equation explain *ca.* 86% of the effect of solvent on the oxidation. However, by Exner's criterion the correlation is not even satisfactory [cf.(7)]. The major contribution is of solvent polarity. It alone accounted for *ca.* 83 % 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 equation<sup>13</sup> of cation- and anion-solvating concept of the solvents (11).

$$\log k_2 = aA + bB + C \quad (11)$$

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 equation (8), separately with  $A$  and  $B$  and with ( $A + B$ ).

$$\log k_2 = 0.64 + (\pm 0.05)A + 1.73 (\pm 0.03)B - 3.92 \quad (12)$$

$$R^2 = 0.9938; sd = 0.04; n = 19; \psi = 0.08$$

$$\log k_2 = 0.40 (\pm 0.57)A - 2.73 \quad (13)$$

$$r^2 = 0.0274; sd = 0.46; n = 19; \psi = 1.01$$

$$\log k_2 = 1.68 (\pm 0.12)B - 3.71 \quad (14)$$

$$r^2 = 0.9225; sd = 0.13; n = 19; \psi = 0.29$$

$$\log k_2 = 1.37 \pm 0.14(A+B) - 3.88 \quad (15)$$

$$r^2 = 0.8456; sd = 0.18; n = 19; \psi = 0.40$$

The rates of oxidation of benzaldehyde in different solvents showed an excellent correlation in Swain's equation (cf. equation 12) with the cation-solvating power playing the major role. In fact, the cation-solvation alone account for *ca.* 92 % of the data. The correlation with the anion-solvating power was very poor. The solvent polarity, represented by ( $A + B$ ), also accounted for *ca.* 85 % of the data. In view of the fact that solvent polarity is able to account for *ca.* 89 % 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 ( $r^2 = 0.5453$ ;  $sd = 0.32$ ;  $\psi = 0.69$ ).

### Correlation analysis of reactivity

The effect of structure on reactivity has long been correlated in terms of the Hammett equation<sup>14</sup> or with dual substituent-parameter equations.<sup>15,16</sup> In the late 1980s, Charton<sup>17</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.

$$\log k_2 = L\sigma_1 + D\sigma_d + R\sigma_e + h \quad (16)$$

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 equation (17).

$$\sigma_D = \eta\sigma_e + \sigma_d \quad (17)$$

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.

**Table 5.** Solvent effect on the oxidation of benzaldehyde by BDSO at 298 K.

Solvents	K	$k_{obs}, s^{-1}$
Chloroform	5.45	44.3
ClCH <sub>2</sub> CH <sub>2</sub> Cl	6.35	53.7
CH <sub>2</sub> Cl <sub>2</sub>	5.58	41.7
DMSO	5.42	144
Acetone	5.54	43.7
DMF	5.63	83.2
Butanone	4.92	29.5
Nitrobenzene	4.23	60.3
Benzene	5.56	14.8
Cyclohexane	5.50	1.78
Toluene	5.33	11.5
Acetophenone	5.12	66.1
THF	5.33	20.4
t-Butylalcohol	5.90	18.6
1,4-Dioxane	5.15	21.9
1,2-Dimethoxyethane	4.83	13.5
CS <sub>2</sub>	5.16	5.89
Acetic acid	5.05	7.59
Ethyl acetate	5.11	17.0

**Table 6.** Temperature dependence for the reaction constants for the oxidation of substituted benzaldehydes by BDSO.

T/K	-L	-D	-R	S	η	R <sup>2</sup>	sd	ψ	P <sub>D</sub>	P <sub>S</sub>
para substituted										
288	1.71	2.07	1.38	-	0.67	0.9999	0.007	0.01	54.8	-
298	1.61	1.98	1.23	-	0.62	0.9998	0.005	0.02	55.2	-
308	1.53	1.89	1.17	-	55.3	0.9989	0.002	0.04	55.3	-
318	1.44	4.80	1.02	-	0.57	0.9999	0.004	0.09	55.6	-
meta substituted										
288	2.09	1.63	1.20	-	0.74	0.9997	0.004	0.02	43.8	-
298	1.96	1.53	1.06	-	0.69	0.9998	0.006	0.02	43.8	-
308	1.90	1.45	0.99	-	0.68	0.9998	0.008	0.02	44.3	-
318	1.79	1.33	0.80	-	0.60	0.9998	0.007	0.02	42.6	-
ortho substituted										
288	1.90	2.07	1.48	1.27	0.71	0.9999	0.006	0.01	52.1	24.2
298	1.79	1.96	1.45	1.17	0.74	0.9998	0.004	0.02	52.3	23.8
308	1.72	1.89	1.34	1.08	0.73	0.9989	0.005	0.04	52.4	23.0
318	1.63	1.79	1.31	0.99	0.73	0.9999	0.004	0.01	52.3	22.4

For *ortho*-substituted compounds, it is necessary to account for the possibility of steric effects and Charton,<sup>17</sup> therefore, modified the LDR equation to generate the LDRS equation (17).

$$\log k_2 = L\sigma_1 + D\sigma_d + R\sigma_e + S\nu + h \quad (18)$$

where  $\nu$  is the well known Charton's steric parameter based on Van der Waals radii.<sup>18</sup>

The rates of oxidation of *ortho*-, *meta*-, and *para*-substituted benzaldehydes show an excellent correlation in terms of the LDR/LDRS equations (Table 6). We have used the standard deviation (*sd*), the coefficient of multiple determination (*R*<sup>2</sup>), and Exner's<sup>15</sup> 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 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  $\sigma_d$ , 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  $\nu$  and (iii)  $\sigma_1$ ,  $\sigma_e$  and  $\nu$ . The absence of significant correlations showed that all the four substituent constants are significant.

$$\log k_2 = -1.55 (\pm 0.43) \sigma_1 - 2.03 (\pm 0.29) \sigma_d - 3.72 (1.94) \sigma_e - 2.45 \quad (19)$$

$$R^2 = 0.7437; sd = 0.40; n = 12; \psi = 0.58$$

$$\log k_2 = -2.13 (\pm 0.46) \sigma_d - 20.3 (\pm 2.84) \sigma_e + 0.88 (\pm 0.52) \nu - 3.39 \quad (20)$$

$$R^2 = 0.8630; sd = 0.30; n = 12; \psi = 0.42$$

$$\log k_2 = -2.08 (\pm 0.83) \sigma_1 - 0.43 (\pm 3.99) \sigma_e + 1.33 (\pm 0.75) \nu - 2.43 \quad (21)$$

$$R^2 = 0.4924; sd = 0.57; n = 12; \psi = 0.81$$

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.

The percent contribution<sup>18</sup> of the delocalized effect, *P<sub>D</sub>*, is given by following equation (22).

$$P_D = (|D| \times 100) / (|L| + |D|) \quad (22)$$

Similarly, the percent contribution of the steric parameter<sup>25</sup> to the total effect of the substituent, *P<sub>S</sub>*, was determined by using equation (23).

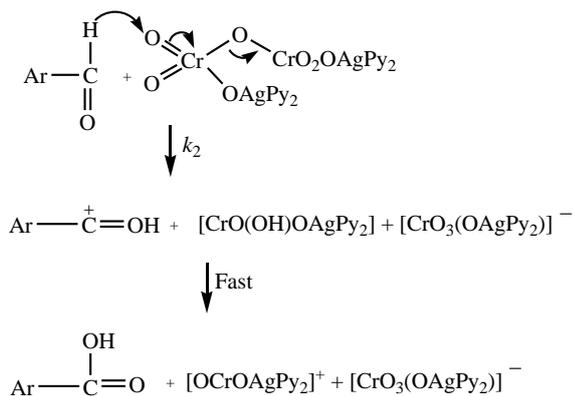
$$P_S = (|S| \times 100) / (|L| + |D| + |S|) \quad (23)$$

The values of *P<sub>D</sub>* and *P<sub>S</sub>* are also recorded in Table 6. The value of *P<sub>D</sub>* for the oxidation of *para*-substituted benzaldehydes is *ca.* 55 % whereas the corresponding values for the *meta*- and *ortho*-substituted aldehydes are *ca.* 43 and 52 %, 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 alcoholic group from the plane of the benzene ring. The magnitude of the *P<sub>S</sub>* value shows that the steric effect is significant in this reaction.

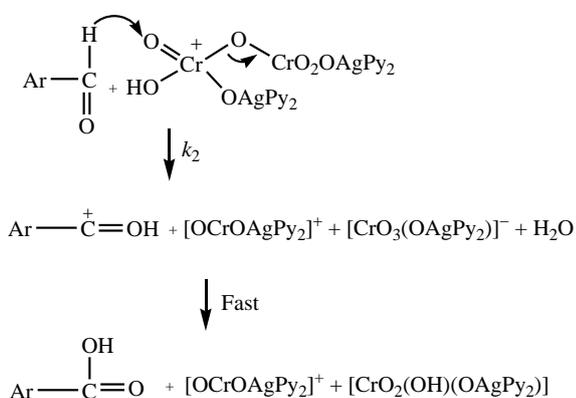
The positive value of *S* showed a steric acceleration of the reaction. This may be explained on the basis high ground state energy of the sterically crowded alcohols. Since the crowding is relieved in the in the product aldehyde as well as the transition state leading to it, the transition state energy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

## 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 stabilize a cationic or electron-deficient reactive site. Therefore, a hydride-ion transfer in the rate-determining step is suggested. The hydride-ion transfer mechanism is also supported by the major role of cation-solvating power of the solvents. (Schemes 1 and 2).



**Scheme 1.** Acid-independent pathway.



**Scheme 2.** Acid-dependent pathway.

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>19</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>20</sup>

## Conclusion

The reaction is proposed to proceed through a hydride-ion transfer from aldehyde to the oxidant in the rate-determining step. It has also been observed that an  $\alpha$ -C–H bond is cleaved in the rate-determining step. Both unprotonated and protonated forms of BDSO are the reactive oxidising species.

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