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Correlation Analysis of Structure & Reactivity In The Oxidation of Aromatic Aldehydes By 2-Picolinium Chlorochromate

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Abstract: Oxidation of thirty-six monosubstituted benzaldehydes by 2-picoliniumchlorochromate (PICC) in dimethylsulphoxide (DMSO), leads to the formation of corresponding benzoic acids. 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 $k_{obs} = a + b\,[H^+]$. The oxidation of [^{2}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 tri-parametric LDR equation, whereas the oxidation of ortho-substituted benzaldehydes was correlated well with tetra-perametric 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 η suggests the presence of an electron-deficient reaction centre in the rate-determining step (r.d.s.). The reaction is subjected to steric acceleration by the ortho-substituents. A suitable mechanism has been proposed.

Keywords: Benzaldehydes, Correlation, Halochromate, Mechanism, Oxidation

1. Introduction

Halochromates have been used as slow and selective oxidizing reagents in synthetic organic chemistry **[1-5]**. 2-picolinium chlorochromate (PICC) is also one of such compounds used as mild and selective oxidizing agent in synthetic organic chemistry **[6]**. We have been interested in kinetics of oxidations by Cr (VI) species and have already published a few reports on oxidation by other pyridinium **[7,8]** and quinolinium halochromates **[9,10]**. In continuation of our earlier work, we report in the present article the kinetics of oxidation of some mono-substituted benzaldehydes by PICC in DMSO as solvent. The major objective of this investigation was to study the structure -reactivity correlation for the substrate undergoing oxidation.

2. Method

2.1. Materials and Methods

PICC was prepared by reported method **[6]** 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 **[11]**. The solid aldehydes were recrystallized from ethanol. Deuteriated benzaldehyde (PhCDO) was also prepared by the reported method **[12]**. Its 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.

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2.2. Analysis of product formed:

The product analysis was carried out under kinetic conditions. In a typical experiment, benzaldehyde 5.25 g, 0.05 mol) and PICC (1.58 g, 0.01 mol) were made up to 50 cm^3 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^3) of a saturated solution of 2,4-dinitrophenylhydrazine in 2 mol dm^{-3} 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 re-crystallization were 2.46 g (86%) and 2.38 g (81%) 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.

2.3. Kinetic Measurements:

The pseudo-first order conditions were attained by maintaining a large excess (× 15 or more) of the alcohol over PICC. The solvent was DMSO, unless specified otherwise. The reactions were followed, at constant temperatures (±0.1 K), by monitoring the decrease in [PICC] spectrophotometrically at 354 nm. No other reactant or product has any significant absorption at this wavelength. The pseudo-first order rate constant, k_{obs}, was evaluated from the linear (r = 0.990 - 0.999) plots of log [PICC] against time for up to 80% reaction. Duplicate kinetic runs showed that the rate constants were reproducible to within ±3%. All experiments, other than those for studying the effect of hydrogen ions, were carried out in the absence of TsOH.

3. 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.

3.1. Stoichiometry

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

$$\mathrm{ArCHO + CrO_2ClOPicH \longrightarrow ArCOOH + OCrClOPicH} \quad (1)$$

PICC undergoes two-electron change. This is in accordance with the earlier observations with structurally similar otherhalochromates also. It has already been shown that both pyridinium chlorochromate (PCC)**[13]** and pyridinium fluorochromate (PFC) **[14]** act as two electron oxidants and are reduced to chromium (IV) species determining the oxidation state of chromium by magnetic susceptibility, ESR and IR studies.

3.2. Rate laws

The reactions are of first order with respect to PiCC. Figure 1 depicts a typical kinetic run.Further, the pseudo-first order rate constant, k_{obs} is independent of the initial concentration of PiCC. The reaction rate increases with increase in the concentration of the aldehydes but not linearly (Table 1). A plot of $1/k_{obs}$ against 1/[Aldehydes] is linear (r > 0.995) with an intercept on the rate-ordinate (Figure 2). Thus, Michaelis-Menten type kinetics are observed with respect to the aldehydes. This leads to the postulation of following overall mechanism (2) and (3) and rate law (4).

$$\text{Aldehydes} + \text{PiCC} \overset{K}{\leftrightarrows} [\text{Complex}] \quad (2)$$

$$[\text{Complex}] \xrightarrow{k_2} \text{Products} \quad (3)$$

$$\text{Rate} = k_2\, K\, [\text{Aldehyde}]\, [\text{PiCC}]/(1+K\, [\text{Aldehyde}]) \quad (4)$$

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

10^3[PiCC] (moldm^{-3})	[Aldehyde] (moldm^{-3})	[TsOH] (moldm^{-3})	$10^4 k_{obs}$ (moldm^{-3})
1.0	0.10	0.0	4.46
1.0	0.20	0.0	6.59
1.0	0.40	0.0	8.66
1.0	0.60	0.0	9.67

1.0	0.80	0.0	10.3
1.0	1.00	0.0	10.7
1.0	1.50	0.0	11.2
1.0	3.00	0.0	11.9
2.0	0.40	0.0	8.82
4.0	0.40	0.0	8.37
6.0	0.40	0.0	8.55
8.0	0.40	0.0	8.46
1.0	0.20	0.0	6.75*
*Contains 0.001 mol dm^{-3} acrylonitrile			

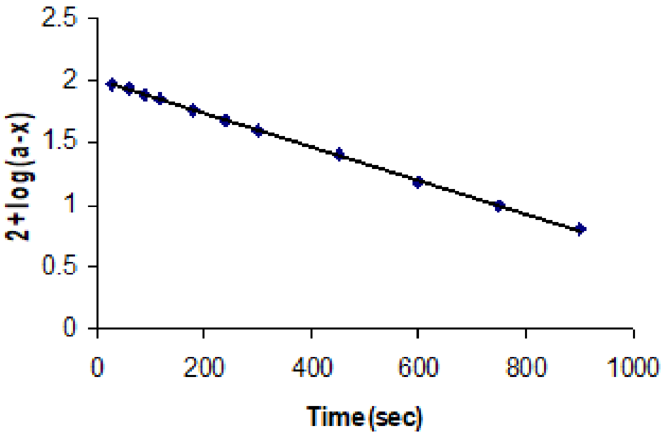


Figure 1. Oxidation of Benzaldehyde by PiCC: A Typical Kinetic Run.

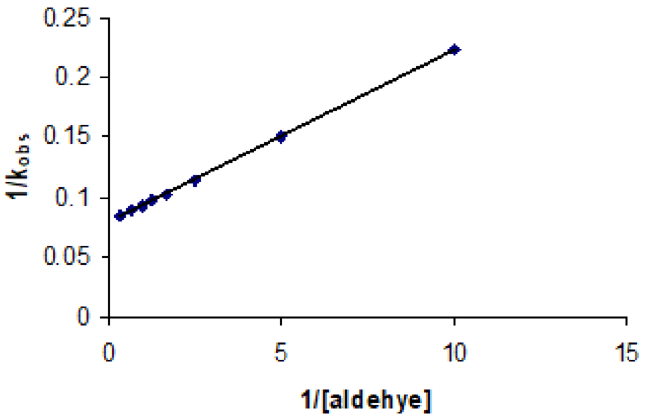


Figure 2. Oxidation of Benzaldehyde by PiCC: A Double Reciprocal Plot.

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

10^4k_2 / (dm^3 $mol^{-1}s^{-1}$)					ΔH^*	$-\Delta S^*$	ΔG^*
Diols	288 K	298 K	308 K	318 K	(kJ mol^{-1})	(J $mol^{-1}K^{-1}$)	(kJ mol^{-1})
H	4.86	12.6	31.5	79.2	68.2±0.7	72±2	89.5±0.6
p-Me	10.8	27.0	64.8	153	64.7±0.5	78±1	87.6±0.4
p-Ome	26.1	63.9	150	351	63.3±0.6	75±2	85.5±0.4
p-F	5.67	15.3	38.7	98.1	69.6±0.5	66±2	89.1±0.4
p-Cl	3.33	8.89	23.1	60.3	70.9±0.9	66±3	90.4±0.7

p-NO$_2$	0.21	0.64	1.89	5.35	79.6±0.6	58±2	96.9±0.5
p-CF$_3$	0.63	1.83	5.04	13.6	75.2±0.4	65±1	94.3±0.3
p-COOMe	0.84	2.34	6.48	17.0	74.0±0.6	66±2	93.7±0.5
p-Br	3.21	8.66	22.5	56.9	70.3±0.4	68±1	90.5±0.4
p-NHAc	11.7	29.7	71.1	171	65.4±0.5	75±0	87.4±0.4
p-CN	0.38	1.14	3.24	9.27	78.4±0.7	58±2	95.5±0.6
p-SMe	13.3	35.1	84.6	207	66.9±0.5	68±2	87.0±0.4
p-NMe$_2$	117	270	576	1250	57.3±0.4	83±1	82.0±0.4
m-Me	8.64	21.7	52.2	126	65.3±0.7	77±2	88.2±0.5
m-Ome	8.91	21.6	50.4	117	62.7±0.6	86±2	88.2±0.4
m-Cl	1.48	3.99	10.3	27.0	71.0±0.8	72±3	92.4±0.7
m-Br	1.46	3.92	10.2	26.1	70.6±0.6	74±2	92.4±0.5
m-F	1.86	4.95	12.6	32.4	69.8±0.7	74±2	91.8±0.6
m-NO$_2$	0.15	0.46	1.35	3.96	80.4±0.8	59±2	97.7±0.6
m-CO$_2$Me	0.78	2.20	6.03	16.2	74.4±0.6	59±2	93.8±0.5
m-CF$_3$	0.54	1.53	4.32	11.5	75.2±0.6	66±2	94.7±0.5
m-CN	0.27	0.81	2.34	6.66	78.7±0.7	59±2	96.3±0.6
m-SMe	5.75	14.4	34.2	82.0	64.7±0.6	83±2	89.2±0.5
m-NHAc	5.31	13.5	32.4	78.3	65.6±0.6	80±2	89.4±0.5
o-Me	37.8	85.5	186	405	57.5±0.5	92±2	84.8±0.4
o-OMe	54.9	122	270	585	57.5±0.7	89±2	83.9±0.5
o-NO$_2$	0.46	1.31	3.60	9.81	75.0±0.7	68±2	95.1±0.6
o-COOMe	2.88	7.29	18.0	44.1	66.7±0.7	82±2	90.9±0.6
o-NHAc	61.2	132	280	576	54.4±0.4	99±1	83.7±0.3
o-Cl	11.2	26.1	62.1	137	61.3±0.6	89±2	87.7±0.5
o-Br	14.0	32.4	74.7	165	60.9±0.8	88±3	87.2±0.6
o-I	20.7	47.6	104	225	57.9±0.4	96±1	86.3±0.3
o-CN	0.95	2.61	6.84	18.0	72.0±0.7	72±2	93.4±0.6
o-SMe	62.1	135	283	594	54.7±0.5	98±2	83.7±0.4
o-F	9.02	22.5	54.0	126	64.4±0.4	80±1	88.1±0.3
o-CF$_3$	5.58	13.5	31.5	72.0	62.3±0.4	91±1	89.4±0.3
PhCDO	0.80	2.18	5.73	15.0	71.8±0.7	75±2	93.9±0.5
k_H/k_D	6.08	5.78	5.50	5.28			

Table 3. Formation constants of PiCC-Aldehyde complexes and their thermodynamic parameters

K/ (dm^3 mol^{-1})					$-\Delta H^*$	$-\Delta S^*$	$-\Delta G^*$
Diols	288 K	298 K	308 K	318 K	(kJ mol^{-1})	(J mol^{-1}K^{-1})	(kJ mol^{-1})
H	6.21	5.49	4.50	3.69	15.9±0.8	31±3	6.63±0.7
p-Me	5.89	5.17	4.41	3.78	13.8±0.4	25±1	6.53±0.3
p-Ome	5.44	4.72	4.05	3.24	15.4±0.9	31±3	6.30±0.7
p-F	5.81	5.06	4.38	3.69	13.9±0.4	25±1	6.49±0.3
p-Cl	6.15	5.40	4.70	3.99	13.4±0.4	23±1	6.65±0.3
p-NO$_2$	5.90	5.13	4.47	3.78	13.7±0.4	25±1	6.53±0.3
p-CF$_3$	5.46	4.77	4.05	3.33	15.0±0.7	30v2	6.32±0.5
p-COOMe	5.32	4.62	3.87	3.15	15.8±0.7	33±2	6.32±0.6
p-Br	5.56	4.86	4.14	3.42	14.8±0.6	29±2	6.37±0.5
p-NHAc	6.13	5.40	4.68	3.96	13.5±0.5	24±1	6.64±0.4
p-CN	5.85	5.13	4.40	3.72	14.0±0.5	26±1	6.51±0.4
p-Sme	6.02	5.49	4.76	4.03	12.7±0.7	21±2	6.65±0.6
p-NMe$_2$	5.99	5.27	4.59	3.87	13.0±0.5	24±2	6.56±0.4
m-Me	5.45	4.77	4.05	3.33	14.9±0.7	29±2	6.32±0.5
m-Ome	5.73	5.03	4.29	3.57	14.5±0.6	27±2	6.45±0.5

m-Cl	6.20	5.48	4.76	4.05	13.3±0.5	23±1	6.68±0.4
m-Br	6.02	5.31	4.58	3.87	13.6±0.5	24±1	6.57±0.4
m-F	5.66	4.95	4.23	3.51	14.6±0.6	28±2	6.42±0.5
m-NO_2	5.27	4.55	3.83	3.15	15.5±0.6	32±2	6.21±0.5
m-CO_2Me	5.30	4.59	3.87	3.17	15.6±0.7	32±2	6.22±0.5
m-CF_3	5.56	4.86	4.14	3.42	14.8±0.6	29±2	6.37±0.5
m-CN	5.48	4.76	4.05	3.32	15.1±0.6	30±2	6.32±0.5
m-SMe	6.05	5.33	4.61	3.88	13.7±0.5	24±2	6.61±0.4
m-NHAc	5.96	5.24	4.53	3.83	13.7±0.5	24±1	6.57±0.4
o-Me	5.98	5.26	4.54	3.82	13.8±0.5	25±2	6.57±0.4
o-OMe	5.92	5.22	4.50	3.75	14.0±0.6	26±2	6.55±0.5
o-NO_2	6.11	5.39	4.67	3.96	13.5±0.5	23±1	6.64±0.4
o-COOMe	6.18	5.47	4.77	4.03	13.3±0.5	23±2	6.67±0.4
o-NHAc	5.43	4.71	3.95	3.27	14.8±0.7	29±2	6.23±0.6
o-Cl	5.79	5.04	4.32	3.63	14.3±0.4	27±1	6.47±0.4
o-Br	5.36	4.68	3.90	3.20	15.6±0.7	32±2	6.26±0.5
o-I	5.61	4.89	4.17	3.45	14.8±0.6	29±2	6.39±0.5
o-CN	6.15	5.43	4.73	3.96	15.4±0.6	31±2	6.29±0.4
o-SMe	5.82	5.13	4.38	3.96	12.5±0.3	21±1	6.52±0.3
o-F	5.00	4.28	3.55	2.85	16.7±0.7	36±2	6.04±0.6
o-CF_3	5.88	5.16	4.41	3.76	13.9±0.4	25±1	6.52±0.3
PhCDO	6.10	5.40	4.68	3.90	13.8±0.6	24±2	6.63±0.5

Table 4. Dependence of reaction rate on hydrogen ion concentration

[PiCC]=0.001moldm^{-3};		[Benzaldehyde]=1.00 moldm^{-3};			Temp.=298K	
[H$^+$]/moldm^3	0.10	0.20	0.40	0.60	0.80	1.00
$10^4 k_{obs}/s^{-1}$	5.22	6.12	7.79	8.64	10.8	12.6

The dependence of reaction rate on the reductant concentration was studied at different temperatures and the values of K and k2 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 k2 respectively at different temperatures (Tables 2 and 3).

3.3. Test for free radicals

The oxidation of benzaldehyde by PICC, in an atmosphere of nitrogen 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 mol dm^{-3} of 2,6-di-t-butyl-4-methylphenol (butylated hydroxytoluene or BHT). It was observed that BHT was recovered unchanged, almost quantitatively.

3.4. Effect of hydrogen ions:

The reaction is catalysed by hydrogen ions. The hydrogen-ion dependence taking the form: k_{obs}=a + b[H$^+$] (Table 4). The values for a and b for benzaldehyde are are $4.41\pm0.25\times10^{-4}$ s^{-1} and $7.97\pm0.41\times10^{-4}$ mol^{-1} dm^3 s^{-1} respectively (r^2=0.9897).

3.5. Kinetic isotope effect

To ascertain the importance of the cleavage of the aldehydic C–H bond in the rate–determining step, oxidation of α-deuterio-benzaldehyde (PhCDO) was studied. Results showed the presence of a substantial primary kinetic isotope effect (Table 2).

3.6. Effect of solvents

The oxidation of benzaldehyde was studied in 19 different organic solvents. The choice of solvents was limited by the solubility of PICC 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 formation constant K and decomposition constants k_2 are recorded in Table 5.

The correlation between activation enthalpies and entropies of the oxidation of the thirty- six banzaldehydes is linear (r = 0.9428), indicating the operation of a compensation effect **[15]**. The value of the isokinetic temperature is 583±35 K. However, according to Exner **[16]**, 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 was linear (r = 0.9986; Figure 3). The value of isokinetic temperature evaluated from the Exner's plot is 730±55 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.

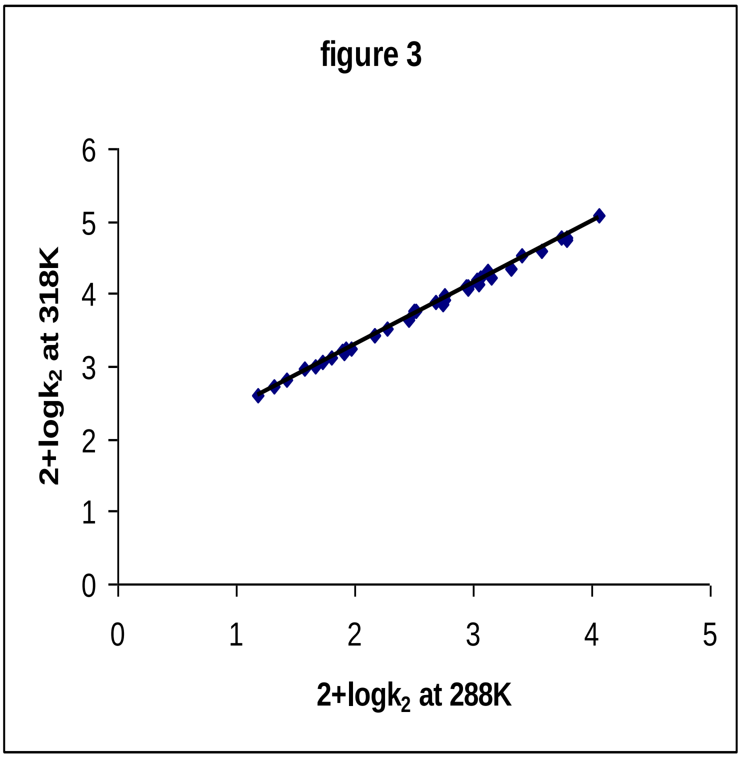


Figure 3. Exner’s Isokinetic Relationship in the oxidation of Substituted Benzaldehydes by PiCC

3.7. Reactive 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 PICC as equation (5) to yield a protonated Cr (VI) species which is a stronger oxidant and electrophile. Formation of a protonated Cr (VI) species has earlier been postulated in the reactions of structurally similar halochromate **[8]**.

$CrO_2ClOPicH + H^+ \leftrightarrows [HOCrOClOPicH]$ (5)

The rate constants k_2, in eighteen solvents (CS_2 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 **[17]**.

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

In this equation, π^* represents the solvent polarity, β the hydrogen bond acceptor basicities and α 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 α. The results of correlation analyses terms of equation (3), a biparametric equation involving π^* and β, and separately with π^* and β are given below (4) - (7).

$\log k_2 = -3.64 + 1.54(\pm 0.18)\ \pi^* + 0.14(\pm 0.15)\ \beta + 0.06(\pm 0.14)\alpha$ (7)

R^2=0.8656; sd=0.17; n=18; ψ=0.40

$\log k_2$=-3.66+1.56(±0.17) π^*+0.12 (±0.14) β (8)

R^2=0.8639; sd=0.16; n=18; ψ=0.39

$\log k_2 = -3.63 + 1.59\ (\pm 0.16)\ \pi^*$ (9)

r^2 = 0.8576; sd= 0.16; n= 18; ψ= 0.39

$\log k_2 = -2.74 + 0.39\ (\pm 0.34)\ \beta$ (10)

r^2 = 0.0784; sd= 0.41; n= 18; ψ = 0.99

Here n is the number of data points and ψ is Exner's statistical parameter **[18]**.

Kamlet's **[17]** tri parametric equation explains *ca*. 87% 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*. 85 % of the data. Both β and α play relatively minor roles.

The data on the solvent effect were also analysed in terms of Swain's equation **[19]** of cation- and anion-solvating concept of the solvents (11).

$\log k_2 = a A + b B + C$ (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).

$\log k_2$= 0.70+(±0.05) A + 1.60 (±0.04)B – 3.87 (12)

R^2= 0.9911; sd= 0.04; n= 19; ψ= 0.09

$\log k_2 = 0.48\ (\pm 0.53)\ A - 2.77$ (13)

r^2= 0.0456; sd= 0.43; n= 19; ψ= 1.00

$\log k_2 = 1.55(\pm 0.13)B - 3.64$ (14)

r^2= 0.8927; sd=0.14; n= 19; ψ= 0.36

$\log k_2 = 1.30 \pm 0.12\ (A+B) - 3.84$ (15)

r^2= 0.8765; sd= 0.16; n= 19; ψ = 0.34

The rates of oxidation of benzaldehyde in different solvents showed an excellent correlation in Swain's equation (cf. equation 9) with the cation-solvating power playing the major role. In fact, the cation-solvation alone account for *ca.* 99% of the data. The correlation with the anion-solvating power was very poor. The solvent polarity, represented by (A + B), also accounted for *ca.*88% of the data. In view of the fact that solvent polarity is able to account for *ca.*88% 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 = 0.5521; sd = 0.29; ψ = 0.69).

3.8. Correlation analysis of reactivity:

The effect of structure on reactivity has long been correlated in terms of the Hammett equation **[20]** or with dual substituent-parameter equations **[21,22]**. In the late 1980s, Charton **[23]** introduced a Tri parametric LDR equation (16) for the quantitative description of structural effects on chemical reactivities. This tri parametric equation results from the fact that substituent types differ in their mode of electron delocalization.

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

Here, σ_l is a localized (field and/or inductive) effect parameter, σ_d is the intrinsic delocalized electrical effect parameter when 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 (17).

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

Here η represents the electronic demand of the reaction site and is given by η= 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 **[21]**, therefore, modified the LDR equation to generate the LDRS equation (18).

$\log k_2 = L\ \sigma_l + D\ \sigma_d + R\ \sigma_e + S\ \upsilon + h$ (18)

Where υ is the well known Charton's steric parameter based on Van der Waals radii **[24]**.

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^2), and Exner's **[18]** parameter, 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 center in the activated complex for the r.d.s. The positive value of η adds a negative increment to σ_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) 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.

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

T/K	- L	- D	- R	S	H	R^2	sd	Ψ	P_D	P_S
Para-substituted										
288	1.62	2.07	1.19	-	0.57	0.9999	0.007	0.01	42.4	-
298	1.53	1.99	1.15	-	0.58	0.9998	0.001	0.02	42.6	-
308	1.44	1.89	1.07	-	0.57	0.9989	0.001	0.04	42.9	-
318	1.35	1.82	0.99	-	0.54	0.9999	0.008	0.01	43.6	-
Meta-substituted										
288	1.98	1.44	0.95	-	0.66	0.9998	0.004	0.01	33.0	-
298	1.89	1.36	0.89	-	0.65	0.9997	0.004	0.02	32.9	-
308	1.80	1.26	0.78	-	0.62	0.9989	0.003	0.04	32.8	-
318	1.71	1.17	0.69	-	0.59	0.9998	0.008	0.02	32.8	-
Ortho-substituted										
288	1.71	1.99	1.34	1.08	0.67	0.9999	0.003	0.01	39.5	19.4
298	1.62	1.89	1.26	0.99	0.67	0.9998	0.004	0.02	39.6	17.2
308	1.53	1.80	1.17	0.90	0.65	0.9999	0.002	0.01	40.0	16.7
318	1.46	1.70	1.08	0.81	0.69	0.9989	0.005	0.04	39.3	15.8

$$\log k_2=-1.42\ (\pm 0.36)\sigma_l-1.95(\pm 0.29)\sigma_d-3.17(\pm 1.64)\sigma_e-2.57 \quad (19)$$

$R^2=0.8866$; sd= 0.25; n= 12; ψ = 0.39

$$\log k_2=-2.04(\pm 0.42)\sigma_d-1.78(\pm 2.58)\sigma_e+0.72\ (\pm 0.48)\ \upsilon-3.40 \quad (20)$$

$R^2=0.7562$; sd= 0.37; n=12; ψ = 0.57

$$\log k_2=-1.91(\pm 0.80)\sigma_l-0.28(\pm 3.85)\sigma_e+1.15(\pm 0.72)\ \upsilon-2.22 \quad (21)$$

$R^2=0.4551$; sd= 0.58; n=12; ψ=0.85

Similarly, in the cases of the oxidation of para- and meta-subsituted 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 **[20]** of the delocalized effect, P_D, is given by following equation (22).

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

Similarly, the percent contribution of the steric parameter **[21]** to the total effect of the substituent, P_S, was determined by using equation (23).

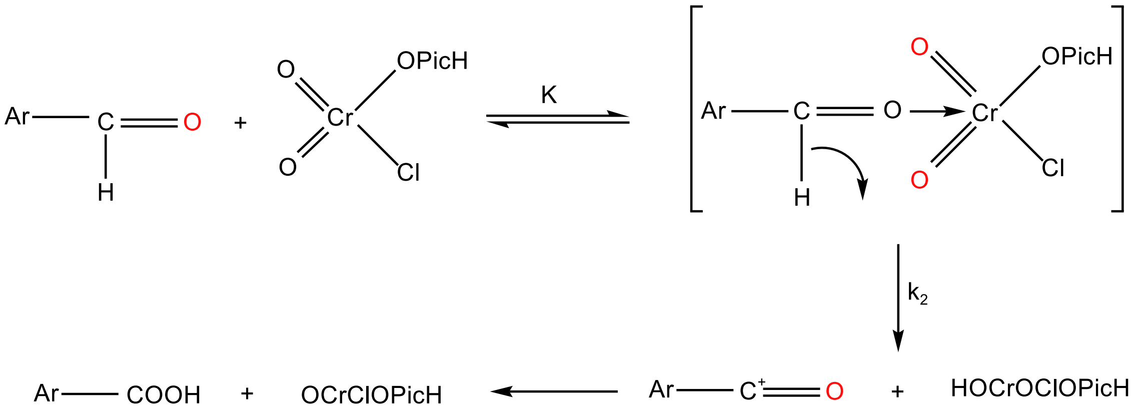
$$P_S=(|S|\times 100)/(|L|+|D|+|S|) \quad (23)$$

The values of P_D and P_S are also recorded in Table 6. The value of P_D for the oxidation of *para*-substituted benzaldehydes is *ca.*43% whereas the corresponding values for the *meta-* and *ortho*-substituted alcohols are *ca.* 33 and 39% 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_S value shows that the steric effect is significant in this reaction.

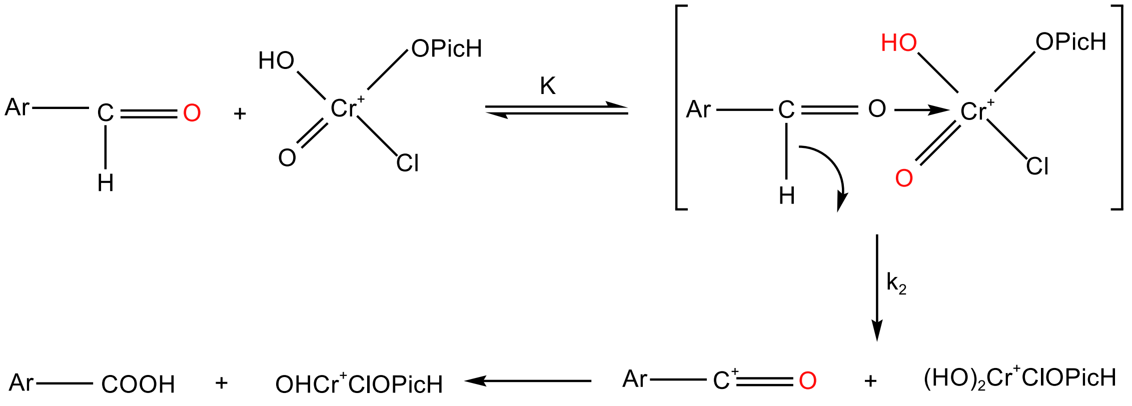
3.9. Mechanism

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 center in the rate-determining step. It is further supported by the positive value of η, 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. The hydride-ion transfer mechanism is also supported by the major role of cation-solvating power of the solvents. (Scheme 1 and 2).



Scheme - 1: Acid-Independent Path



Scheme - 2: 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 **[25]**.

4. Conclusions

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 α-C-H bond is cleaved in the rate-determining step. Both de-protonated and protonated forms of PiCC are the reactive oxidizing species.

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