



# CORRELATION ANALYSIS OF REACTIVITY IN THE OXIDATION OF SOME *PARA*-SUBSTITUTED BENZALDEHYDES BY IMIDAZOLIUM FLUOROCHROMATE IN NON-AQUEOUS MEDIA

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The kinetics of oxidation of several *para*-substituted benzaldehydes by imidazolium fluorochromate (IFC) has been studied in the presence of *p*-toluenesulphonic acid (TsOH) in different (hydrogen bond donor and hydrogen bond acceptor) organic solvents. The reaction was run under pseudo-first-order conditions. Various thermodynamic parameters for the oxidation have been reported and discussed along with the validity of isokinetic relationship. The rate data showing satisfactory correlation with Kamlet-Taft solvatochromic parameters ( $\alpha$ ,  $\beta$  and  $\pi^*$ ) which suggests that the specific solute-solvent interactions play a major role in governing the reactivity, and the observed solvent effects have been explained on the basis of solute-solvent complexation.

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organic reactions but also to organometallic and inorganic reactions.

Two groups of workers set out general equations for the correlations of solvent effects through multiple regression analysis. Koppel and Palm<sup>8</sup> used the four-parameter Eq.(1)

$$\log k = \log k_o + gf(\epsilon) + pf(n) + eE + bB \quad (1)$$

in which

$f(\epsilon)$  is a dielectric constant function, usually

$$Q = (\epsilon - 1)/(2\epsilon + 1),$$

$f(n)$  is a refractive index function,  $(n^2 - 1)/(n^2 + 2)$ ,

$E$  and  $B$  are measures of the electrophilic and nucleophilic solvation ability of the solvent, respectively.

Koppel and Palm<sup>8</sup> and later Shorter *et al*<sup>7</sup> quite successfully applied Eq.(1) to a variety of reaction types.

The Kamlet-Taft group of workers<sup>11</sup> used the alternative equation for the study of solvent effects using multiple regression analysis. However, there are considerable advantages to be gained by the use of Kamlet-Taft equation.<sup>12</sup>

Extensive studies on the mechanism of oxidation of benzaldehyde (Bez) by several Cr(VI) oxidants have been reported.<sup>13-19</sup> In recent years, some new chromium(VI) based reagents like imidazolium fluorochromate,<sup>20</sup> morpholinium chlorochromate,<sup>21</sup> tetraethylammonium bromochromate,<sup>22</sup> quinolinium bromochromate,<sup>23</sup> tripropylammonium fluorochromate,<sup>24</sup> tributylammonium chlorochromate,<sup>25</sup> tetrakis(pyridine)silver dichromate,<sup>26</sup> tetraethylammonium chlorochromate<sup>27</sup> and bis(bispyridine)silver(I) dichromate<sup>28</sup> were proposed for the kinetic study.

## Introduction

The effect of different solvent on the rates of chemical changes was one of the earliest kinetic problems to be studied.<sup>1-3</sup> The development of correlation analysis in the area of solvent effects has proved to be a slow and difficult process and only within the last twenty years has there been any considerable progress. Application of the techniques of multiple regression has proved to be strikingly successful and has greatly increased understanding of the role of the solvent.

Over the years, two main methods for the examination of the solvent effects on the reaction rates have been developed. First, the rate constants, either as  $\log k$  or as  $\Delta G^\ddagger$  may be correlated with a physical parameter characteristic of the solvent, for example dielectric constant, solubility parameter, viscosity, *etc.*, or with an empirical solvent parameter, such as  $Y$ ,  $Z$ .<sup>4-6</sup> This type of analysis has been extended to multiple linear correlation with a number of solvent parameters, notably by Shorter *et al.*<sup>7</sup> on the reaction of diazodiphenylmethane (DDM) and benzoic acid and more generally by Koppel and Palm<sup>8</sup> and by Kamlet and Taft and their co-workers.<sup>9-11</sup> In the second method the solvent effect on  $\log k$  or  $\Delta G^\ddagger$  is dissected into contributions of the reactants (initial state) and the transition state, followed, where possible, by a comparison of solvent effect on the transition state with solvent effect on solutes that might function as suitable models for the transition state. This method has been applied not only to a number of standard

Imidazolium fluorochromate (IFC) was reported to be mild, stable and selective oxidant.<sup>29</sup> Literature review showed that there seems to be only very few reports using IFC.<sup>30-31</sup> Recently, oxidation of thirty six monosubstituted benzaldehydes by imidazolium fluorochromate (IFC) in dimethylsulphoxide (DMSO) has been reported.<sup>32</sup> The study shows that 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. Hence, in the present study, an attempt has been made to study the kinetics of the oxidation of some *para*-substituted benzaldehydes by IFC in seven organic solvents *viz.*, dimethyl formamide, dimethyl sulphoxide, *tert*-butanol, acetic acid, acetone, 1,4-dioxane and 1,2-dichloroethane, with the aim of obtaining a better insight into the mechanism and solvation models of the reaction. The solvent effects on the reaction rates were analysed using Kamlet-Taft equation.

## Experimental Procedure

### Materials

All the chemicals and solvents used were of analytical grade. The solvents dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), *tert*-butanol (*t*-BuOH), acetic acid (AcOH), acetone (Me<sub>2</sub>CO), 1,4-Dioxane (DO), 1,2-dichloroethane (DE) are of analytical grade and was purified by conventional methods. Benzaldehydes (Aldrich or Merck, India) were used with substituents H, *p*-Me, *p*-OMe, *p*-Cl, *p*-NMe<sub>2</sub> and *p*-NO<sub>2</sub>. Solid benzaldehydes were used as such, and liquid benzaldehydes were used after vacuum distillation.

### Preparation of Imidazolium fluorochromate

40 % Hydrofluoric acid (11.3 mL, 0.23 mole) was added dropwise to imidazole (13.62 g, 0.2 mol) cooled in ice in a polythene beaker with constant stirring. A clear solution was obtained within 5 min. Dry and well powdered chromium trioxide (20 g, 0.2 mol) was added to this solution slowly with stirring. The resulting mixture was then heated on water-bath for 30 min and left overnight in a refrigerator. Bright red orange crystals of IFC formed were separated by filtration and dried *in vacuo* for 2 – 3 h. The reagent IFC, can be stored in a polythene container without appreciable loss in its activity.<sup>24</sup> Yield (85 %); m.p. 126 – 128 °C. Its purity was checked by the iodometric method.

### Kinetic Measurements

The reactions were carried out under pseudo-first order conditions by keeping an excess of substrate over IFC. The progress of the reactions was followed by estimating the unreacted oxidant iodometrically at 298, 303, 308 and 313 K. The rate constants were determined by the least-square method from the linear plots ( $r > 0.96$ ) of  $\log [\text{IFC}]$  versus time. Replicate runs showed that the rate constants were reproducible to within  $\pm 3\%$ .

### Data analysis

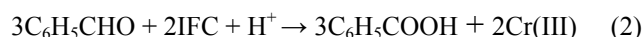
Correlation analysis were carried out using Microcal Origin (version 6) computer software. The goodness of the fit was discussed using the correlation coefficient ( $r$  in the case of simple linear regression and  $R$  in the case of multiple regression) and standard deviation ( $SD$ ). The percentage contribution ( $P_x$ ) of a parameter to the total effect on the reactivity was computed using the regression coefficient of each parameter as reported earlier.<sup>33</sup>

### Product analysis

Product analysis was made under mineral acid catalyzed conditions in benzaldehydes. Keeping concentration of IFC in excess over benzaldehydes, the two solutions were mixed and *p*-toluenesulphonic acid was also added in DMF. The reaction mixture was set aside for about 24 h to ensure completion of the reaction. The reaction mixture was then evaporated with ether. The ether layer was washed with water many times. The ether layer was kept on a water bath for the evaporation of ether and cooled in ice bath to obtain the product (mp. 121 °C). The product was dissolved in benzene and a careful TLC analysis was done with benzoic acid and benzaldehyde as references. Only one spot corresponding to benzoic acid was obtained. Formation of benzoic acid was further confirmed by mixing the product with pure benzoic acid and noting that there was no change in the melting point. Benzoic acid as product is also confirmed by IR spectroscopy (C=O str, 1686 cm<sup>-1</sup>; O-H str, 3006 cm<sup>-1</sup>; C-H str, 2834 cm<sup>-1</sup>).

### Stoichiometric studies

Stoichiometric analysis showed that 3 mol of substrate consumed 2 mol of IFC in accordance with Eqn. (2) to give the corresponding carboxylic acids.



## Results and discussion

The kinetic studies were carried out under pseudo-first-order conditions with the  $[\text{substrate}] > [\text{IFC}]$ . The first order dependence of the reaction on IFC is obvious from the linearity of the plots of  $\log [\text{IFC}]$  versus time. Further more, the pseudo-first-order rate constants,  $k_{\text{obs}}$ , do not depend on the initial concentration of IFC (Table 1).

The rate of oxidation increased progressively on increasing the concentration of benzaldehyde, indicating first order dependence with substrate. The plot of  $\log k_{\text{obs}}$  versus  $\log [\text{Bez}]$  gave a straight line with unit slope. The second order rate constant  $k_2$  is invariant supporting the first order dependence on  $[\text{Bez}]$ . The oxidation of benzaldehyde by IFC is catalyzed by *p*-toluenesulphonic acid. Catalysis by TsOH suggests protonation of the IFC species. The participation of protonated species in Cr(VI) oxidation is well known.<sup>34</sup> The reaction did not promote polymerization of acrylonitrile indicating the absence of free radicals (Table 1).

**Table 1.** Effect of varying the concentration of [Bez], [IFC] and [H<sup>+</sup>] on the rate of reaction at 303 K

10 <sup>3</sup> [IFC] mol dm <sup>-3</sup>	10 <sup>2</sup> [Bez] mol dm <sup>-3</sup>	[TsOH] mol dm <sup>-3</sup>	10 <sup>5</sup> <i>k</i> <sub>obs</sub> s <sup>-1</sup>
0.5	2.0	0.4	14.08
1.0	2.0	0.4	14.20
1.5	2.0	0.4	14.12
2.0	2.0	0.4	14.24
2.5	2.0	0.4	14.16
1.0	4.0	0.4	27.96
1.0	6.0	0.4	41.80
1.0	8.0	0.4	65.84
1.0	10.0	0.4	69.78
1.0	2.0	0.2	6.98
1.0	2.0	0.3	10.22
1.0	2.0	0.5	17.10
1.0	2.0	0.6	20.48
1.0	2.0	0.8	27.94
1.0	2.0	0.4	14.02 <sup>a</sup>

<sup>a</sup> Contained 0.001 mol dm<sup>-3</sup> acrylonitrile.

### Thermodynamic parameters and the Isokinetic relationship

The activation parameters for some *para*-substituted benzaldehydes in DMF were calculated from *k*<sub>2</sub> at 298, 303, 308 and 313 K using the van't Hoff plot by the method of least squares and are presented in Table 2. The data presented in Table 2 indicates that the oxidation is neither isoenthalpic nor isentropic but complies with the compensation law also known as the isokinetic relationship.

$$\Delta H^\ddagger = \Delta H^\circ + \beta \Delta S^\ddagger \quad (3)$$

The isokinetic temperature  $\beta$ , is the temperature at which all the compounds of the series react equally fast. Also, at the isokinetic temperature, the variation of substituent has no influence on the free energy of activation. In an isoentropic reaction, the isokinetic temperature lies at infinite and only enthalpy of activation determines the reactivity. The isokinetic temperature is zero for an isoenthalpic series, and the reactivity is determined by the entropy of activation.<sup>35</sup> The operation of the isokinetic relationship is tested by plotting the logarithms of rate constants at two different temperatures ( $T_2 > T_1$ ) against each other according to Eq (4).

$$\log k \text{ (at } T_2) = a + b \log k \text{ (at } T_1) \quad (4)$$

In the present study, linear plots imply the validity of the isokinetic relationship. A representative plot between  $\log k_2$  at 308 K and  $\log k_2$  at 303 K is shown in Fig.1 ( $r = 0.984$ ,  $SD = 0.08$ , isokinetic temperature =  $397 \pm 12$  K). The operation of isokinetic relationship reveals that all the substituted benzaldehydes examined follow a common mechanism.

The oxidation of *para*-substituted benzaldehydes were studied in seven different organic solvents. The pseudo-first-order rate constants were determined and presented in Table 3. The values of  $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$  and  $\Delta G^\ddagger$  were also calculated for reaction at different solvents and presented in Table 4. Negative entropy of activation indicates a greater degree of

ordering in the transition state (TS) than in the initial state, due to an increase in solvation during the activation process. The existence of a linear relationship ( $r = 0.971$ ,  $SD = 0.06$ , isokinetic temperature =  $481 \pm 11$  K) between  $\log k_2$  at 308 and  $\log k_2$  at 303K indicates that a single mechanism is operating in all studied solvent systems (Fig. 2).

### Solvent –Reactivity Correlation

Solvent effects on the rates of reactions are as important as structural effects. The solute-solvent interactions are of two types, namely, specific and nonspecific interactions. The specific solute-solvent interactions are short-range interactions and are chemical in nature. The intensity of nonspecific interactions are measured in terms of bulk solvent parameters like relative permittivity ( $\epsilon_r$ ), dipolarisability ( $\pi^*$ ), etc., Here we discussed about both types of solute-solvent interactions.

### Laidler-Eyring Equation

The reaction was studied in different pure organic solvents with a range of 44 units of relative permittivity. The influence of relative permittivity on the rate can be described by the equation of Laidler and Eyring.<sup>36</sup>

$$d \ln k / d (1/\epsilon_r) = e^2 Z^2 (1/r - 1/r^*) / 2kT \quad (5)$$

where

*k* is the rate constant,

*Z* the net charge,

*r* the effective radius, and

*r*<sup>\*</sup> the radius of the activated species.

Correlations of *k*<sub>obs</sub> with the inverse of solvent relative permittivity was poor indicating that the reaction rate depended on more than one solvent property.

Using idealized theories, the solvent relative permittivity is often predicted to serve as a quantitative measure of solvent polarity. However, this approach is often inadequate since these theories regard solvents as a non-structured continuum, not composed of individual solvent molecules with their own solvent interactions and they do not take into account specific solute-solvent interactions such as hydrogen bonding and electron pair donor / electron pair acceptor interactions, which often play a dominating role in solute-solvent interactions.

No single microscopic physical parameter could possibly account for the multitude of solute-solvent interactions on the molecular microscopic level. Thus, bulk solvent properties like the relative permittivity and ionizing power will poorly describe the microenvironment around the reacting species, which governs the stability of transition state and hence the rate of the reaction. Hence, there have been a variety of attempts to quantify different aspects of solvent polarity and then use the resultant parameters to interpret solvent effects on reactivity through multiple regression. Various attempts for the above solvent-solute interactions based on linear solvation energy relationship (LSER) have been developed.

**Table 2.** Effect of temperature on the rate of oxidation of some *para*- substituted benzaldehydes by IFC in DMF and activation parameter for the oxidation

Substrates	$10^3 \times k_2, \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$				$\Delta H^\ddagger, \text{kJ mol}^{-1}$	$-\Delta S^\ddagger, \text{J mol}^{-1} \text{K}^{-1}$	$\Delta G^\ddagger, \text{kJ mol}^{-1}$
	298 K	303 K	308 K	313 K			
H	4.60	7.10	11.20	17.60	66.92±1.3	65.23±4.3	86.62±2.0
<i>p</i> -OMe	3.96	6.00	9.30	14.30	63.98±1.2	76.26±4.0	87.08±2.4
<i>p</i> -Me	6.20	9.90	13.40	20.00	57.84±2.5	92.85±8.0	85.97±4.0
<i>p</i> -Cl	13.00	21.60	32.60	53.40	70.51±0.7	44.40±2.0	83.96±1.0
<i>p</i> -NMe <sub>2</sub>	7.80	12.20	17.54	28.40	64.06±0.5	70.32±2.0	85.36±1.0
<i>p</i> -NO <sub>2</sub>	6.32	9.80	15.60	24.30	67.31±1	61.27±3.5	85.87±1.8

[Bez]= $2.0 \times 10^{-2}$  M; [IFC]= $1.0 \times 10^{-3}$  M; [H<sup>+</sup>]=0.4 M;  $\Delta G^\ddagger$  at 303 K

**Table 3.** Pseudo-first order rate constants ( $10^5 k_{obs}, \text{s}^{-1}$ ) for the oxidation of some *para*-substituted benzaldehydes by IFC in different organic solvents at 303 K

Solvents	Substituents in benzaldehydes					
	None	<i>p</i> -OMe	<i>p</i> -Me	<i>p</i> -NMe <sub>2</sub>	<i>p</i> -Cl	<i>p</i> -NO <sub>2</sub>
AcOH	0.30	0.42	0.53	1.33	0.71	0.85
Me <sub>2</sub> CO	9.20	12.00	12.90	22.80	15.10	19.80
<i>t</i> -BuOH	0.60	0.73	1.14	2.64	1.65	2.48
DE	59.80	72.00	94.30	261.00	184.00	402.00
DMF	14.20	12.00	19.80	24.40	29.30	27.30
DMSO	8.60	17.30	18.00	43.20	24.50	34.80
DO	11.11	14.12	11.03	19.62	30.71	42.85

[Bez]= $2.0 \times 10^{-2}$  M; [IFC]= $1.0 \times 10^{-3}$  M; [H<sup>+</sup>]=0.4 M.

### The Kamlet-Taft Method for the Examination of Solvent Effect

In order to obtain a deeper insight into the various solvent–solvent–solute interactions, which influence reactivity, the solvatochromic comparison method developed by Kamlet<sup>10</sup> has been used. This method may be used to unravel, quantify, correlate and rationalize multiple interacting solvent effects on reactivity. The kinetic data were correlated with the solvatochromic parameters  $\alpha$ ,  $\beta$  and  $\pi^*$  characteristic of different solvents in the form of following LSER:

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

where

$\pi^*$  is an index of solvent dipolarity/polarizability, which is a measure of the ability of a solvent to stabilize a charge or a dipole by virtue of its dielectric effect.

$\alpha$  represents the scale of the solvent HBD (hydrogen bond donor) acidity. It describes the ability of a solvent to donate a proton, or accept an electron pair in a solvent-to-solute hydrogen bond.

$\beta$  represents the scale of solvent HBA (hydrogen bond acceptor) basicity, in other words the ability of a solvent to donate an electron pair, or accept a proton in a solvent-to-solute hydrogen bond.

$A_0$  is the intercept term.

Kamlet *et al*<sup>11</sup> established that the effect of a solvent on the reaction rate should be given in terms of the following properties:

- The behaviour of the solvent as a dielectric, facilitating the separation of opposite charges in the transition state.
- The ability of the solvent to donate a proton in a solvent-to-solute hydrogen bond and thus stabilize the anion in transition state and
- The ability of the solvent to donate an electron pair and therefore stabilize the initial methionine, by way of a hydrogen bond.

The parameter  $\pi^*$  is an appropriate measure of the first property, while the second and third properties are governed by the parameters  $\alpha$  and  $\beta$  respectively. The linear dependence (LSER) on the solvent properties were used to correlate and predict a wide variety of solvent effect.

The rates of the reactions for all the compounds studied show a good correlation with the solvent with an explained variance of *ca.* 95%. Such a good correlation indicates that the existence of both specific and non-specific solute-solvent interactions in the present study. From the values of the regression coefficients, the contribution of each parameter, on a percentage basis to reactivity were calculated<sup>25</sup> and listed in Table 5. The observation of this multiple regression analysis<sup>37</sup> leads to the following conclusions:

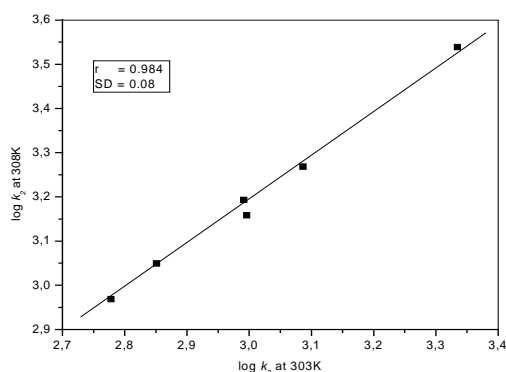
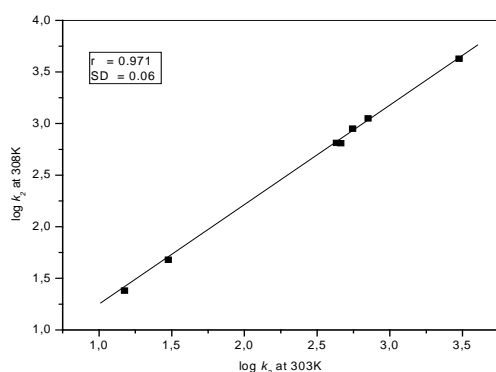
**Table 4.** Effect of temperature on the rate of oxidation of benzaldehyde by IFC in different solvents and activation parameter for the oxidation

Substrates	$10^3 \times k_2, \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$				$\Delta H^\ddagger, \text{kJ mol}^{-1}$	$-\Delta S^\ddagger, \text{J mol}^{-1} \text{K}^{-1}$	$\Delta G^\ddagger, \text{kJ mol}^{-1}$
	298 K	303 K	308 K	313 K			
AcOH	0.10	0.15	0.24	0.36	64.80±1.3	104.24±4.2	96.38±2.0
Me <sub>2</sub> CO	3.36	4.60	6.44	9.28	50.77±1.5	122.17±4.5	87.78±2.0
<i>t</i> -BuOH	0.18	0.30	0.48	0.74	70.55±1	79.63±3.0	94.67±1.5
DE	18.70	29.90	38.50	60.12	57.32±2.5	85.44±8.0	83.20±4.0
DMF	4.60	7.10	9.90	17.60	66.92±1.2	65.27±4.5	86.70±2.2
DMSO	2.80	4.30	5.90	10.40	64.87±2	76.22±6	87.96±3.0
DO	3.58	5.55	8.90	13.50	66.55±1	68.54±3	87.32±1.5

[Bez]= $2.0 \times 10^{-2}$  M; [IFC]= $1.0 \times 10^{-3}$  M; [H<sup>+</sup>]=0.4 M;  $\Delta G^\ddagger$  at 303 K

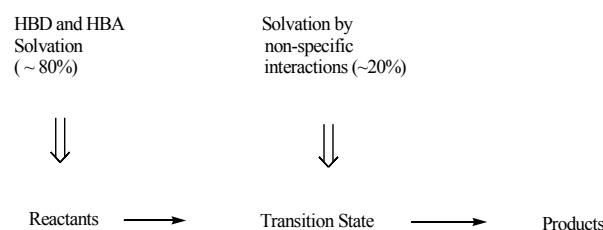
**Table 5.** Statistical results and weighted percentage contributions for the correlation of rate of oxidation ( $k_{obs}$ ) of some *para*-substituted benzaldehydes by IFC with Kamlet-Taft Solvatochromic parameters  $\alpha$ ,  $\beta$  and  $\pi^*$ 

Substituent	$R^2$	SD	$a$	$b$	$s$	$P_\alpha$	$P_\beta$	$P_{\pi^*}$
H	0.978	0.10	-1.40	-1.21	0.58	44	38	18
<i>p</i> -OMe	0.992	0.15	-1.40	-1.30	0.85	39	37	24
<i>p</i> -Me	0.964	0.40	-1.32	-1.06	1.11	38	30	32
<i>p</i> -Cl	0.933	0.16	-1.27	-1.08	1.18	35	31	34
<i>p</i> -NMe <sub>2</sub>	0.992	0.11	-1.59	-1.26	0.80	44	34	22
<i>p</i> -NO <sub>2</sub>	0.970	0.31	-1.61	-1.38	0.77	43	37	20

**Figure 1.** The isokinetic plot for some *para*-substituted benzaldehydes by IFC in DMF in the presence of *p*-TsOH at two different temperatures ( $\log k_2$  at 308 K versus  $\log k_2$  at 303 K)**Figure 2.** The isokinetic plot for the unsubstituted benzaldehydes in all solvents in the presence of *p*-TsOH at two different temperatures ( $\log k_2$  at 308 K versus  $\log k_2$  at 303 K)

- (i) The rate of the reaction is strongly influenced by specific solute-solvent interactions as indicated by the percentage contributions of  $\alpha$  and  $\beta$  parameters.
- (ii) The negative sign of the coefficients of  $\alpha$  and  $\beta$  terms suggests that the specific interaction between the reactants and the solvent, through HBD and HBA properties, is more than that between the transition state and the solvent.
- (iii) The rate of the reaction is also influenced by  $\pi^*$ , which is a measure of the solvent to stabilize a charge or a dipole by virtue of its dielectric effect. The positive sign of the coefficient of this term in the above equation suggests that the transition state is extensively solvated by such solvents than by the reactants.

Considering these points the solvation models of the reactants and the transition state can be represented as:



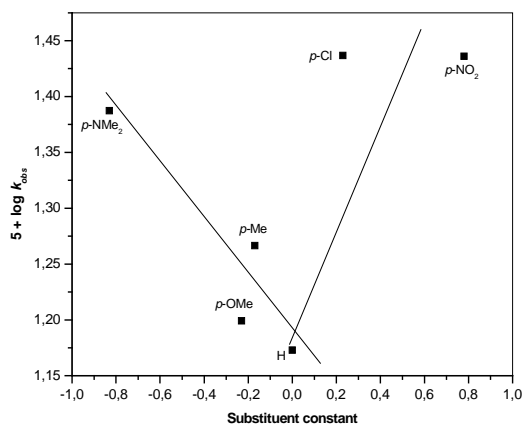
Thus it can be concluded that in the present system the reactants are extensively solvated by specific solute-solvent interactions than by the transition state. The transition state is solvated through non-specific solute-solvent interactions.

Increase in dipolarity / polarisability or decrease in HBD and HBA property of the medium accelerates the rate of the reactions.

### Structure - reactivity correlation

The effect of substituents on the rate was studied with some *para*- substituted benzaldehydes. The results in Table 3 revealed that both electron-releasing and electron-withdrawing substituents in the ring accelerate the rate of oxidation. According to Hammett<sup>38</sup> reaction with positive  $\rho$  values are accelerated by electron withdrawal from benzene ring, whereas those with negative  $\rho$  values are retarded by electron withdrawal from benzene ring.

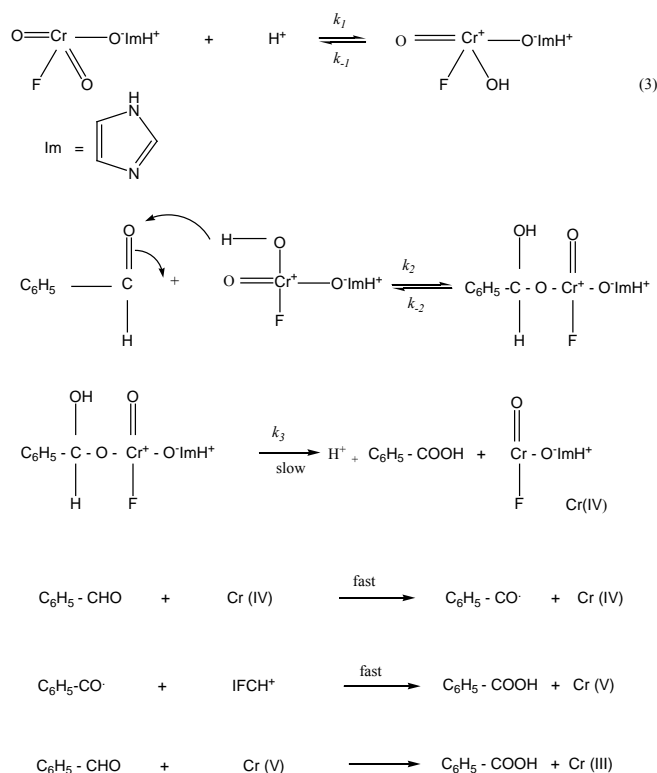
The plot of  $\log k_{obs}$  versus the Hammett's substituent constant  $\sigma$  shows two different lines, for groups comprising of electron-releasing (*p*-OMe, *p*-Me and *p*-NMe<sub>2</sub>) and electron-withdrawing (*p*-Cl and *p*-NO<sub>2</sub>) substituents, converging at a point. It is represented in Fig. 3. Further, the concave curve indicates that the rate of complex formation, a process which is facilitated by the presence of electron-releasing groups, is competing with the rate of its decomposition products, a reaction which is accelerated by the presence of electron-withdrawing groups. Due to this competition, the Hammett plot shows a break. Such anomalous curves have been reported in the oxidation of benzaldehydes by trichlorocyanuric acid<sup>39</sup> and quinolinium chlorochromate.<sup>37,40</sup> This may be due to the fact that the  $\rho$  values for the given reactants, are influenced by both non-specific and specific solvent effects.<sup>41</sup> This is an indication of the existence of specific and non-specific solvent-solute interactions.



**Figure 3.** Hammett's plot for the oxidation of some *para*-substituted benzaldehydes by IFC in DMF in the presence of *p*-TsOH at 303 K

### Mechanism

The kinetic results showed that the rate of oxidation of benzaldehydes was dependent on the first powers of the concentrations of each substrate, oxidant and acid. The acid catalysis of the reaction leads to the conversion of protonated IFC. A probable mechanism consistent with the kinetic and non-kinetic observation is given in Scheme 1.



**Scheme 1.** Mechanism of oxidation of benzaldehyde by IFC in DMF in the presence of *p*-TsOH

The mechanism shown in Scheme 1 leads to the following rate law:

$$-d[\text{IFC}]/dt = k_1 k_2 k_3 [\text{Bez}][\text{IFC}][\text{H}^+] \quad (7)$$

### Conclusion

The correlation of the reaction rates with solvent parameters using the Kamlet – Taft equation indicates the existence of both specific and non specific solute – solvent interactions. The linear and multiple regression analysis may be used to separate and quantify the specific and non specific solvational effects on the title reaction. From the regression coefficients, information on the solvent – reactant and solvent – transition state interactions is obtained and the solvation models are proposed. Structure-reactivity correlation studies indicate the applicability of dual mechanism in the reaction.

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