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Research Article

STRUCTURE REACTIVITY CORRELATION IN THE OXIDATION OF SUBSTITUTED BENZALDEHYDES BY MORPHOLINIUM FLUOROCHROMATES

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ABSTRACT

The first order kinetics was observed in the oxidation of 13 substituted Benzaldehydes by Morpholinium Fuorochromate (MFC) in dimethyl sulfoxide (DMSO). Corresponding benzoic acid was formed as product. Reaction follows first order kinetics with respect to both MFC and substituted Benzaldehydes. H^+ ion dependence has the form $k_{obs}= a + b [H^+]$ revealing promotion of reaction by H^+ions. The oxidation of deuteriated substituted Benzaldehyde (PhCDO) exhibited primary kinetic isotopic (multiparametric Equation. The two type of substituents viz p- and m-substituted Benzaldehydes showed excellent correlation in terms of Charton's triparametric L.D.R equation, whereas o-substituted Benzaldehydes were correlated well with tetraparametric L.D.R.S equation. The oxidation of p-substituents are more suceptible to the delocalisation effect whereas o- and m- substituents shows great affinity to the field effect. The positive values of H^+ shows electron deficient reaction centre in the rate determining step(RDS). The reaction was subjected to the steric effect by o- substituents. A suitable mechanism has been proposed.

Keyword: *Correlation Analysis, Halochromates, Kinetics, Mechanism, Oxidation*

INTRODUCTION

Chemical reactions are the deciding factors of the life cycle and chemical kinetics is mainly the study of redox-reactions by determining their mechanisms and analyzing reaction kinetics dealing with the study of change in concentration of their components in the reaction with respect to time. A wide application of Cr (VI) salts of have long been studied as oxidizing reagents in the synthetic organic chemistry due to their high reactivity, less sensitivity, non- selectivity and insolubility in most of the organic solvents. A large number of derivatives of Cr (VI) such as Pyridinium chlorochromate (Corey and Suggs, 1975), Quinolinium bromochromate (Yajurvedi *et al.*, 2009), Benzimidazolium chlorochromate (Das and Mohanty, 2014), Benzyltrimethylammonium fluorochromate (Mansoor Sheik and Safi Syed, 2009; Alhaji *et al.*, 2016), Imidazolium fluorochromate (Daiya *et al.*, 2012), Morpholinium fluorochromate (Sayyed Alangi *et al.*, 2011) etc. have been used for the study of various organic compounds. Morpholinium fluorochromate (MFC) is also one of such compounds used for oxidation of aryl alcohols on silica gel (Sayyed-Alangi *et al.*, 2011), oxidation of primary (Vyas *et al.*, 2015), secondary alcohols (Purohit and Mishra, 2016) and Thioacids (Rao *et al.*, 2016). So far no work has been reported for the kinetics of oxidation of substituted Benzaldehydes by MFC in non aquous medium. In continuation of our earlier work on MFC. In this paper we report kinetics and mechanism of oxidation of 13 substituted Benzaldehydes by MFC in DMSO as solvent. The mechanistic aspects are also discussed.

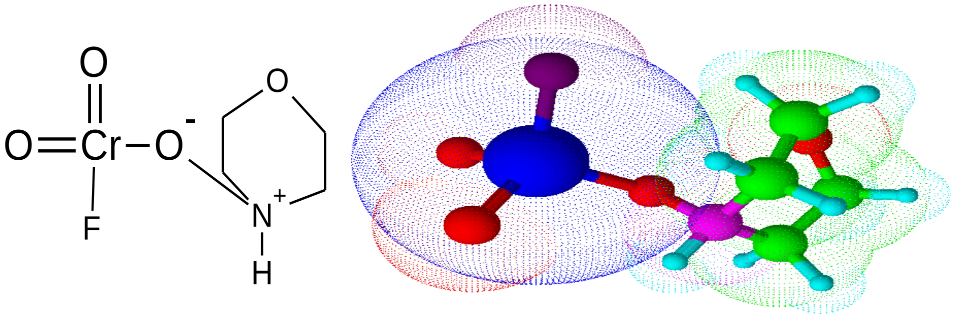
MATERIALS AND METHODS

Chemicals and Apparatus

All the substituted Benzaldehydes used were of A.R. Grade (E Merck Germany). MFC was prepared by reported methods (Sayyed-Alangi *et al.*, 2011) and its purity was checked by an iodometric method. The liquid and solid substituted Benzaldehydes were used after vacuum distillation under N_2 conditions and deuteriated Benzaldehydes (PhCDO) were prepared by the reported methods (Ishimoto *et al.*, 1995). Its NMR spectrum was 95±3% showing isotopic purity resembling with reported methods).

Kinetic Measurement

The pseudo-first order conditions were attained by maintaining a large excess (10 times or more) of the substituted Benzaldehyde over MFC. DMSO was used as non-aqueous solvent. The reactions were studied at constant temperatures (±0.1K), by monitoring the decrease in concentration of [MFC] using UV-spectrophotometer at 352 nm for 85% of the reaction. No other compound which is part of reaction has shown any significant absorption at this wavelength. A solution with known concentration of MFC, PTS and excess of substituted Benzaldehyde was used. Appearance of green color ensures the completion of reaction. The pseudo-first order rate constant, k_{obs}, was evaluated from the linear (r =0.930 - 0.999) plots of log [MFC] against time. Duplicate kinetic determination showed that the rate constants are generally less than ±4%. The second order rate constant, k_2, was obtained from the relation: $k_2 = k_{obs}$ / [substituted Benzaldehyde]. All experiments, other than those for studying the effect of hydrogen ions, were carried out in the absence of TsOH.



Morpholinium Fluorochromate

Product Analysis

In a typical kinetic experiment, substituted Benzaldehyde 5.25 g (0.05 mol) and MFC 1.58 g (0.01 mol) were made up to 50 cm^3 in DMSO and kept in the dark for ca. 12 hrs 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 recrystallization were 2.52 g (88%) and 2.38 g (83%) respectively. The DNP was found identical (m.p. and mixed m.p.) with the DNP of substituted Benzaldehyde. Similar experiments were performed with other substituted Benzaldehydes also. The oxidation state of chromium in completely reduced reaction mixtures, determined by an iodometric method was 3.12 ±12.

RESULTS AND DISCUSSION

Oxidation of Benzaldehydes by MFC tends to form the corresponding benzoic-acids. Analysis of products and the stoichiometric determination indicates the following overall reaction (1).

$$ArCHO + CrO_2FOMH \rightarrow Ar\text{-}COOH + (HO)\ Cr^{+}FOMH \qquad \textbf{(1)}$$

Thus, MFC undergoes a two electron change. This is in accordance with the earlier observations with PCC (Corey and Suggs, 1975) and other halo chromates.

Order of Reaction

The reaction follows first order kinetics with respect to MFC as evident by a linear plot log [MFC] versus time. The pseudo first order rate constant does not depend on initial concentration of MFC. A plot of log k_1 versus log [substituted Benzaldehydes] gave slope linearly passing through origin showed a first order dependence on the substituted Benzaldehyde. Figure (1) depicted a typical kinetic run. Table (1)

Effect of Catalyst

Para-toluene sulphonic acid (PTS) is selected as a source of hydrogen ions. The reaction is accelerated by hydrogen ions which is shown bya straight line for plot of log k_1 and log $[H^+]$. The hydrogen-ion dependence taking the form: k_{obs} = a +b [H+] Table(1). MFC may become protonated in the presence of acid and protonated MFC may function as an efficient and suitable oxidant. The values for a and b for substituted Benzaldehyde are $30.4\pm0.70\times10^{-4}$ s^{-1} and $51.8\pm1.16\times10^{-4}$ mol^{-1} dm^{-3} s^{-1} respectively (r^2 = 0.9972).

Induced Polymerization Test for Free Radicals

The oxidation of Benzaldehyde by MFC, 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^{-3} of 2, 6-di-t-butyl-4-methylphenol (Butylated HydroxyToluene or BHT). It was observed that BHT was recovered unchanged, almost quantitatively.

Effect of Temperature

Rate constant at different temperatures and the activation parameters were calculated for the oxidation of benzaldehydes by MFC Table (2). The log k_2 at different temperatures shows negative slope with respect to temperature in all the cases Figure (2). The Arrhenius equation is therefore, valid for this reaction. The correlation between activation enthalpies and entropies of the oxidation of the thirteen Benzaldehydes aren't very good, but are satisfactory (r^2 = 0.8756). Exner's plot Exner's (1964) between log k at 288 K and at 323 K was linear (r^2 =0.9991) Figure (3). The value of isokinetic temperature evaluated from the Exner's plot is 1206±192 K. The linear isokinetic correlation implies that all the Benzaldehydes are oxidized by the same mechanism and the changes in the rate are governed by changes in both the enthalpy and entropy of activation.

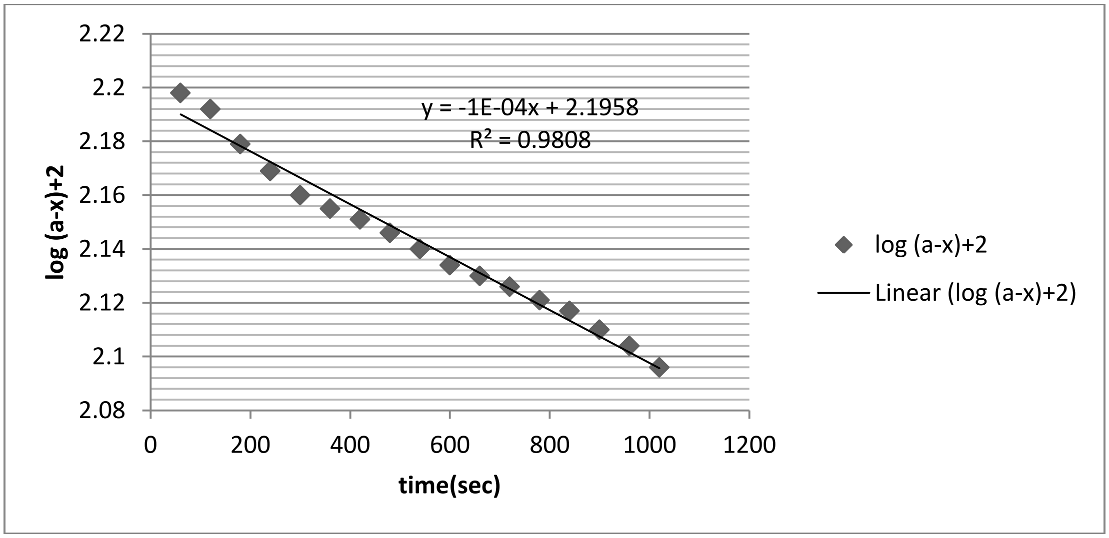


Figure 1: Oxidation of Benzaldehyde by MFC: A Kinetic Run

Table 1: Rate Constants for the Oxidation of Benzaldehyde by MFC at 303K Temperature

10^{-3} MFC (mol dm^{-3})	**Benzaldehyde (mol dm^{-3})**	**TsOH (mol dm^{-3})**	**10^{-4} k_{obs} (s^{-1})**
1.0	.10	.10	3.12
1.0	.20	.10	6.04
1.0	.40	.10	12.8
1.0	.60	.10	18.4
1.0	.80	.10	24.3
1.0	1.0	.10	29.6
1.0	2.0	.10	62.2
1.0	.40	.10	13.4

1.5	.40	.10	11.8
2.0	.40	.10	12.8
2.5	.40	.10	11.3
3.0	.40	.10	32.8
3.5	.40	.15	42.9
1.0	.10	.20	52.6
1.0	.10	.25	60.4
1.0	.10	.30	72.4
1.0	.10	.35	81.8
1.0	.40	.10	12.6

** contained 0.001 mol dm-3 acrylonitrile*

Table 2: Rate Constants and Activation Parameters of the Oxidation of Substituted Benzaldehydes by MFC

Substrate	**10^{-4} k$_2$ (dm^3 mol^{-1} s^{-1})**				**ΔH* (KJ mol^{-1})**	**ΔS* (J mol^{-1}K^{-1})**	**ΔG* (K J mol^{-1})**
	288 K	**298 K**	**308 K**	**318 K**			
H	11.7	29.2	72.9	171	65.5±O.4	-74±1	87.4±0.3
p-Me	24.6	60.3	145	325	63.4±0.2	-75±2	85.7±0.1
P-OMe	50.6	126	299	636	62.0±0.3	-74±2	83.9±0.3
p-F	11.2	29.7	74.4	171	66.8±0.2	70±1	87.4±0.2
p-Cl	7.03	18.8	47.9	112	67.4±0.3	-71±2	88.6±0.2
p-NO$_2$	0.55	1.54	4.23	11.3	74.1±0.4	-70±1	94.7±0.6
p-CF$_3$	1.61	4.42	11.9	27.3	69.2±0.3	-77±1	93.1±0.4
P-COOMe	2.18	5.87	15.8	36.7	69.5±0.2	-74±2	91.4±0.5
p-Br	6.94	18.9	46.4	108	67.2±0.1	-72±1	88.6±0.2
P-NHAr	24.4	62.4	144	324	63.3±0.2	-76±2	85.7±0.1
p-CN	0.97	2.70	7.23	18.9	71.2±0.1	-73±1	93.4±0.2
p-SMe	29.2	72.7	171	387	62.2±0.26	-76±1	85.3±0.1
P-NMe$_2$	216	516	1149	2345	59.1±0.3	-76±2	80.4±0.2

10^4[Benzaldehyde] = 2.0 mol dm^{-3}; 10^3[MFC] = 1.0 mol dm^{-3}; [H$^+$] = 0.10 mol dm^{-3}

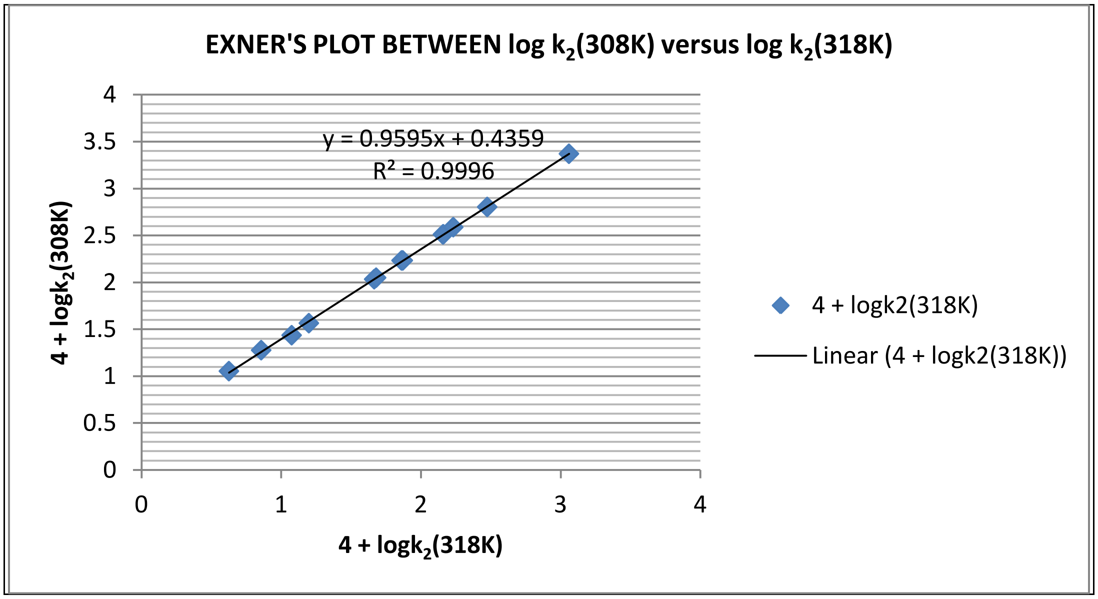


Figure 2: Exner's Plot between log k$_2$ (308K) Versus log k$_2$ (318K)

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 MFC as equation (2) 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 compounds (Soni *et al.,* 2008).

$MHOCrO_2FH + H^+ \rightarrow MHOCr^+(OH)OF$ **(2)**

Effect of Solvents

The rate constants k_2, in eighteen solvents (CS_2) was not considered as the complete range of solvent parameters were not available. They were correlated in terms of linear solvation energy relationship (3) of Kamlet *et al.*, (1983).

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

In this equation, π^* represents the solvent polarity, the hydrogen bond acceptor basicities and α is the hydrogen bond donor acidity. A_o is the intercept term. It may be mentioned here that out of the 18 solvents, 12 has a value of zero for α. The results of correlation analysis in terms of equation (3), a biparametric equation involving π^* and β, and separately with π^* and β are given

$sd = 0.16; n = 18; \psi = 0.3$

$\log k_2 = - 4.34 + 1.32 (\pm 0.18) \pi^* + 0.18 (\pm 0.12)\beta + 0.17 (\pm 0.12)\alpha$ **(4)**

$R^2 = 0.8740; sd = 0.12; n = 20; \Psi = 0.39$

Here, n is the number of data points and ψ is Exner's statistical parameter (Exner, 1964)

Kamlet's *et al.,* (1983) triparametric equation explain ca. 88 % of the effect of solvent on the oxidation. However, by Exner's (1964) criterion the correlation is not even satisfactory [(4)]. The major contribution is the solvent polarity. It alone accounted for ca. 85% of the data. Both β and α play relatively minor role. The data on the solvent effect were also analysed in terms of Swain's *et al.*, (1983) of cation- and anion-solvating concept of the solvents (5).

Table 3: Solvent Effect on the Oxidation of Benzaldehydes by MFC at 308K

Solvent	10^{-4} k_2 (dm^3 mol^{-1} s^{-1})	Solvent	10^{-4} k_2 (dm^3 mol^{-1} s^{-1})
Chloroform	22.4	Toluene	9.78
1,2-Dichloroethane	27.5	Acetophenone	33.9
Dichloromethane	30.8	Tetrahydrofuran	16.8
Dimethyl sulfoxide	72.9	t-Butyl alcohol	12.0
Acetone	25.2	1,4-Dioxane	14.6
DMF	46.8	1,2-dimethoxyethane	8.56
Butanone	19.8	Ethyl acetate	13.6
Nitrobenzene	35.6	Carbon disulfide	6.04
Benzene	10.8	Acetic acid	5.88
Cyclohexane	1.87		

$\log k_2 = a A + b B + C$ **(5)**

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).

$\log k_2 = 0.45 + (\pm 0.04) A + 1.42 (\pm 0.03) B – 4.17$ **(6)**

$R^2 = 0.9928; sd = 0.03; n = 19; \Psi = 0.09$

$\log k_2 = 0.26 (\pm 0.48) A – 3.86$ **(7)**

$r^2 = 0.0159; sd = 0.38; n = 20; \Psi = 1.03$

$\log k_2 = 1.37 (\pm 0.08) B – 4.32$ **(8)**

$r^2 = 0.9406; sd = 0.09; n = 20; \Psi = 0.25$

$\log k_2 = 1.10 \pm 0.13\,(A + B) - 4.19$ **(9)**
$r^2 = 0.8156$; sd = 0.17; n = 19; $\Psi = 0.44$

The rate of oxidation of Benzaldehydes in different solvents attributes an excellent correlation with Swain's *et al.*, (1983) equation.

Equation 6 with the cation-solvating power playing the major role. In fact, the cation -solvation alone account for ca. 94% of the data. The correlation with the anion-solvating power was very poor. The solvent polarity, represented by (A + B), also accounted for ca. 81% 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 ($r^2 = 0.5568$; sd = 0.26; $\Psi = 0.72$).

Correlation Analysis of Reactivity

The effect of structure on the reactivity has long been correlated in terms of the Hammett equation (Figure 4) or with dual substituent- parameter equations (Kamlet *et al.*, 1983; Swain *et al.*, 1983; Ehreson *et al.*, 1972). Charton's triparametric equation describes structure effect on chemical reactivity due to different mode of delocalization of electron by differ substituent.

Here, σ_l is 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 substituents to changes in the electronic demand by the active site. The latter two substituents parameters are related by equation (10).

$\sigma_D = \eta\,\sigma_e + \sigma_d$ (10)

In cases of oxidation of Para- and meta-substituted Benzaldehydes, multiple regression analysis indicated that both localization and delocalisation effects are significant (table 4). There is no collinearity between various substituents constants for the three series. The % contribution (Ehreson *et al.,* 1972) of the delocalized effect, P_D is given by following equation (12).

$P_D = (|D| \times 100) / (|L| + |D|)$ (11)

% contribution of the steric parameter to the total effect of the substituent, P, was determined by using equation (12).

$P_S = (|S| \times 100) / (L| + |D| + |S|)$ (12)

Table 4: Effect of Various Substituents on the Reactivity at Different Temperatures

T/K	L	D	R	S	η	R^2	sd	Ψ	P_D	P_S
Para- substituted										
288	-1.62	-1.89	-1.24	-	0.66	0.9987	0.004	0.02	53.8	-
298	-1.55	-1.85	-1.17	-	0.63	0.9878	0.003	0.01	54.4	-
308	-1.49	-1.72	-1.15	-	0.67	0.9956	0.052	0.08	53.6	-
318	-1.45	-1.73	-1.06	-	0.62	0.9987	0.02	0.02	54.6	-
Meta-substituted										
288	-1.97	-1.44	-1.20	-	0.85	0.9991	0.005	0.01	42.5	-
298	-1.89	-1.38	-1.13	-	0.82	0.9987	0.003	0.02	42.2	-
308	-1.82	-1.32	-1.00	-	0.76	0.9999	0.004	0.01	42.0	-
318	-1.76	-1.26	-1.06	-	0.71	0.9989	0.004	0.04	41.8	-
Ortho-substituted										
288	-1.82	-1.70	-1.42	1.26	0.82	0.9967	0.005	0.02	48.3	26.4
298	-1.75	-1.65	-1.25	1.18	0.75	0.9989	0.004	0.01	48.9	25.8
308	-1.67	-1.58	-1.26	1.07	0.80	0.9999	0.004	0.02	48.7	24.7
318	-1.60	-1.49	-1.10	1.03	0.74	0.9991	0.002	0.01	48.2	25.0

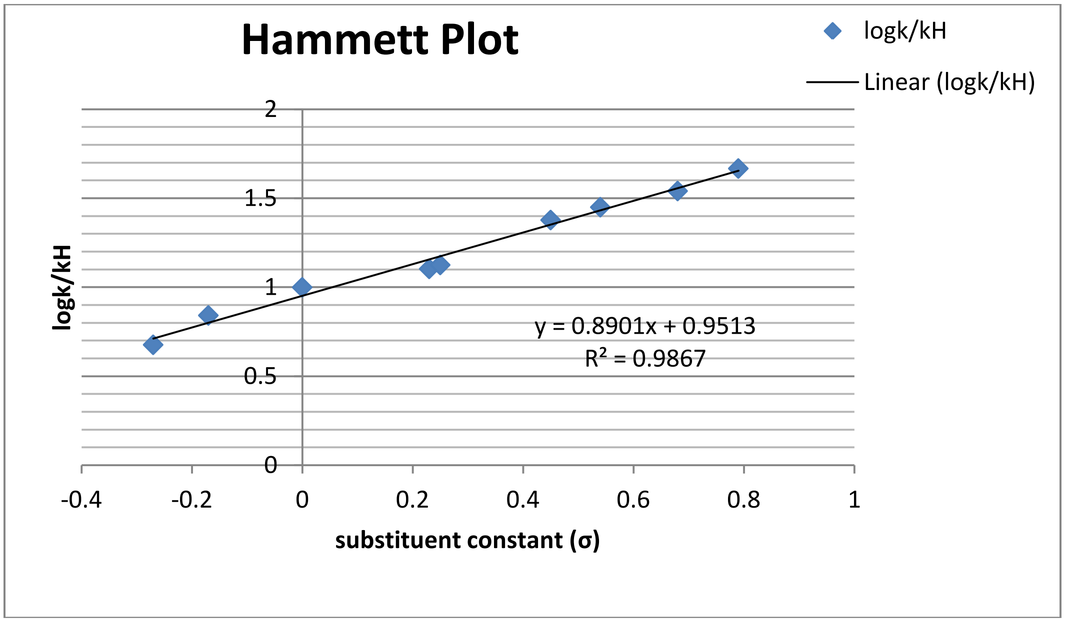


Figure 3: Hammett Plot (318K) for Oxidation of Substituted Benzaldehydes by MFC

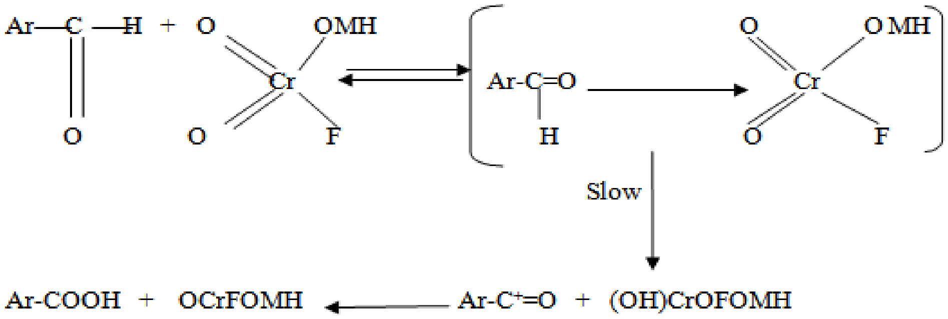
Mechanism

A hydrogen abstraction mechanism leading to the formation of a free radical 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 substantial isokinetic effect confirms the cleavage of an aldehydic C-H bond in the rate-determining step. The negative values of the localization, delocalization, and electrical effects i.e. of L, D and R representing an electron-deficient reaction centre in RDS. It is further supported by the positive value of η, which indicates that the substituent is better able to stabilize a cationic or electron-deficient reactive site. Therefore, a hydride ion transfer in mechanism is suggested by the major role of cation-solvating power of the solvents.

The hydride ion transfer may take place either by a cyclic process via an ester intermediate formation or by an acyclic one-step bimolecular process. It is well-established that intrinsically concerted sigmatropic reactions, characterized by transfer of hydrogen ion in a cyclic transition state, are the only truly symmetrical processes involving a linear hydrogen ion transfer (Woodward and Hoffmann, 1969)

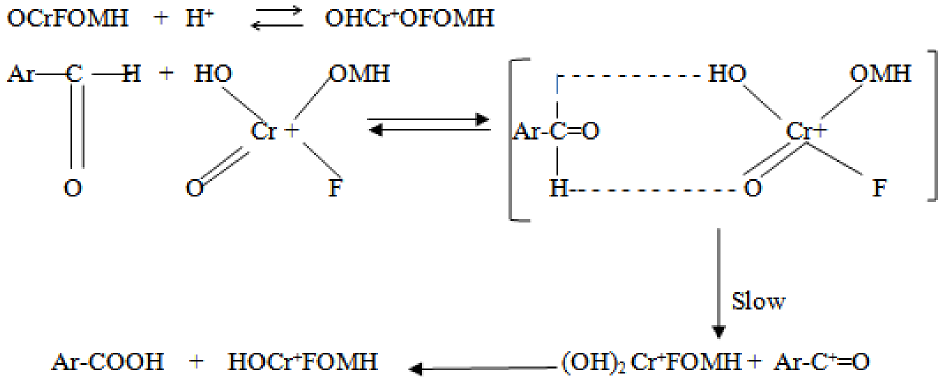
Litter (1971) has also shown that a cyclic hydride transfer, in the oxidation of alcohol by Cr (VI), involves six electrons and, being a Huckel-type system, is a planar, cyclic and symmetrical structure can be envisaged for the decomposition of the ester intermediate. Hence, the overall mechanism is proposed to involved the formation of a chromate ester in a fast pre-equilibrium step and then decomposition of the ester in a subsequent slow step via cyclic concerted symmetrical transition state leading to the product (Schemes 1 and 2).

Scheme1: Acid-Independent Path



Here MH^+ = Morpholinium Ion, Ar= substituted Benzaldehyde

Scheme 2: Acid Dependent Path



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