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Kinetics and Mechanism of Oxidation of Benzaldehyde by Benzimidazolium Fluorochromate in Aqueous Acetic Acid Medium

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The kinetics of oxidation of benzaldehyde (BA) by benzimidazolium fluorochromate (BIFC) in aqueous acetic medium has been studied at 303 K. The reaction is first order with respect [BIFC], [BA] and [H^+]. The reaction has been found to be catalyzed by H^+ ions. To study the effect of structure reactivity relationships, some *para*-substituted benzaldehydes were subjected to oxidation by benzimidazolium fluorochromate at four different temperatures and thermodynamic parameters were calculated. The Exner plot showed that all the *para*-substituted benzaldehydes are oxidized by the same mechanism. The Hammett plot is linear with positive ρ values. The products of the oxidation are the corresponding acids. From the observed kinetic results a suitable mechanism has been proposed.

Key Words: Benzimidazolium fluorochromate, Oxidation, Kinetics, Benzaldehyde.

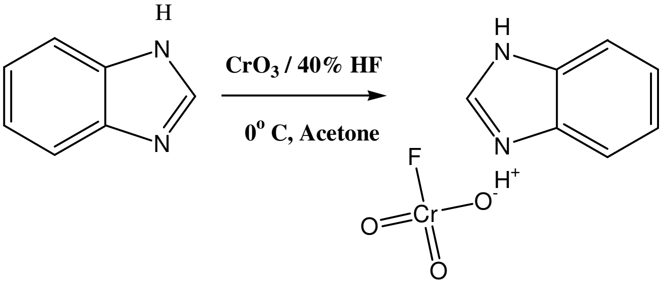
INTRODUCTION

A number of new chromium(VI) containing compounds like pyridinium bromochromate[1], quinolinium chlorochromate[2], 2,2'-bipyridinium chlorochromate[3], pyridinium chlorochromate[4], quinolinium fluorochromate[5], quinolinium bromo chromate[6], benzyltrimethyl ammonium fluorochromate[7], pyridinium fluorochromate[8], imidazolium fluorochromate[9] and isoquinolinium bromochromate[10] have been used to study the kinetics and mechanism of various organic compounds. Kinetics of oxidation of substituted benzaldehydes by various oxidizing agents have been well studied[11-17]. A search of literature showed that there seems to be no report on the kinetics of oxidation of benzaldehydes by BIFC. Hence, we report herein the kinetics of oxidation of some *para*-substituted benzaldehydes by benzimidazolium fluorochromate in aqueous acetic acid medium in the presence of perchloric acid.

EXPERIMENTAL

All benzaldehydes used were of AnalaR Grade (E Merck, Germany). The solid benzaldehydes were used as such and the liquid benzaldehydes were used after vacuum distillation. Acetic acid was purified by standard method and the fraction distilling at 118 ºC was collected.

Preparation of benzimidazolium fluorochromate: Benzimidazolium fluorochromate has been prepared from benzimidazole, 40 % hydrofluoric acid and chromium trioxide in the molar ratio 1:1.3:1 at 0 °C. BIFC is obtained as yellow orange crystals. It is non-hygroscopic, light insensitive on storage[18]. The purity of BIFC was checked by the iodometric method.



(1)

Benzimidazole Benzimidazolium fluorochromate

Kinetic measurements: The reactions were followed under pseudo-first-order conditions by maintaining a large excess (× 15 or more) of the benzaldehyde over BIFC. The temperature was kept constant to ± 0.1 K. The reactions were followed by monitoring the decrease in the concentration of BIFC spectrophotometrically at 368 nm by using Simadzu UV/visible spectrophotometer with recording facilities for up to 80 % of the reaction. No other reactant or product has any significant absorption at this wavelength. The pseudo-first-order rate constants, k_{obs}, were evaluated from the linear plots of log [BIFC] against time. Duplicate kinetic runs showed that the rate constants were reproducible to within ± 4 %. Correlation analysis were carried out using Microcal Origin (Version 6.1) computer software.

Product analysis: Product study was made under mineral acid catalyzed conditions in benzaldehyde. Keeping concentration of BIFC in excess over benzaldehydes, the two solutions were mixed and perchloric acid was also added in 50 % acetic acid -50 % water mixture. The reaction mixture was set aside for about 24 h to ensure completion of the reaction. The reaction mixture was then evaporated and extracted with ether. The ether layer was washed with water many times. The ether layer was then kept on a water bath for the evaporation of ether and cooled in an ice bath to obtain the product (m.p. 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.

Stoichiometric studies: Stoichiometric analysis showed that 3 mol of aldehyde consumed 2 mol of BIFC in accordance with eqn. 2 to give the corresponding carboxylic acid.

$$3ArCHO + 2BIFC + H^+ \rightarrow 3ArCOOH + 2Cr(III) \qquad (2)$$

RESULTS AND DISCUSSION

The title reaction was studied in 50 % acetic acid -50 % water medium at 303 K, under the pseudo-first-order conditions. The observed pseudo-first-order rate constants (k_{obs}) are given in Table-1.

TABLE-1
EFFECT OF VARYING THE CONCENTRATION OF [BA], [BIFC] AND [H^+] ON THE RATE OF THE REACTION AT 303 K
SOLVENT-COMPOSITION = 50 % AcOH-50 % H_2O (v/v)

10^3 [BIFC] (mol dm^{-3})	10^2 [BA] (mol dm^{-3})	[H^+] (mol dm^{-3})	$10^4 k_1$ (s^{-1})
0.5	2.0	0.32	2.16
1.0	2.0	0.32	2.18
1.5	2.0	0.32	2.18
2.0	2.0	0.32	2.14
2.5	2.0	0.32	2.20
1.0	1.0	0.32	1.00
1.0	1.5	0.32	1.62
1.0	2.5	0.32	2.60
1.0	3.0	0.32	3.16
1.0	2.0	0.16	1.04
1.0	2.0	0.48	3.20
1.0	2.0	0.64	4.26
1.0	2.0	0.80	5.40

Effect of varying substrate concentration: The concentration of BIFC was varied in the range 5.0×10^{-4}-2.5×10^{-3} mol dm^{-3} and keeping all other reactant concentrations as constant and the rates were measured (Table-1). The near constancy in the value of k_1 irrespective of the concentration of the BIFC confirms the first order dependence on BIFC.

The substrate benzaldehyde was varied in the range of 1.0×10^{-2}-2.5×10^{-2} mol dm^{-3} at 303 K and keeping all other reactant concentrations as constant and the rates were measured (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_{obs} *versus* log [BA] gave the slope of 1.033 (r = 0.997) (Fig. 1) shows that this oxidation reaction was first order with respect to [BA]. The second order rate constant k_2 is invariant supporting the first order dependence on [BA].

Effect of varying perchloric acid concentration: The perchloric acid concentration was varied in the range of 0.16-0.80 mol dm^{-3} and keeping the concentrations of all other reactant concentrations as constant and the rates were measured (Table-1). The increase in [$HClO_4$] in the oxidation reaction increases the rate of the reaction and shows a direct first order dependence on [$HClO_4$]. A plot (Fig. 2) of log k_1 against log [H^+] is linear. Change in ionic strength by the addition of $NaClO_4$ has no effect on the rate constant.

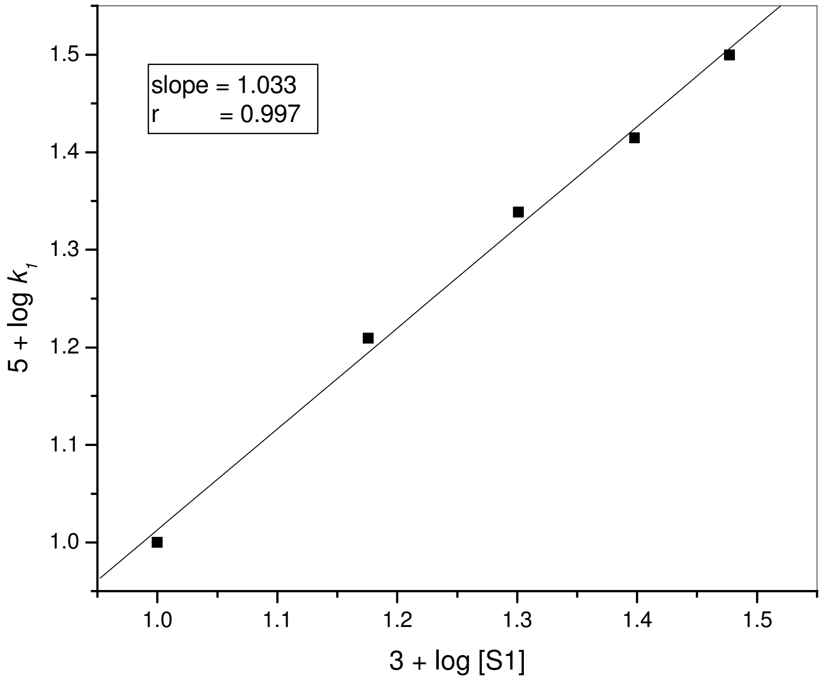


Fig. 1. Order plot for the substrate for the oxidation of benzaldehyde by benzimidazolium fluorochromate at 303 K

Effect of varying solvent composition: The effect from solvent composition on the reaction rate was studied by varying the concentration of acetic acid from 30-70 %. The pseudo-first-order rate constants were estimated for the oxidation reactions of all of the substituted benzaldehydes, with BIFC in the presence of perchloric acid at a constant ionic strength. The reaction rate is increases markedly with the decrease in the proportion of acetic acid in the medium (Table-2). The decrease in the dielectric constant of the medium with increase in the rate of the reaction suggests that the involvement of an ion and a neutral molecule in the rate-determining step.

TABLE-2
EFFECT OF VARYING SOLVENT POLARITY ON THE RATE OF REACTION AT 303 K
[BA] = 2.0×10^{-2} mol dm^{-3}; [BIFC] = 1.0×10^{-3} mol dm^{-3}; [H$^+$] = 0.32 mol dm^{-3}

Acetic acid (%)-water (v/v)	Dielectric constant	$10^4 \times k_1$ (s^{-1})				
		H	*p*-OCH$_3$	*p*-CH$_3$	*p*-Cl	*p*-NO$_2$
30-70	72.0	2.63	1.02	1.60	4.42	17.37
40-60	63.3	2.40	0.92	1.44	3.94	15.54
50-50	56.0	2.18	0.82	1.28	3.58	13.96
60-40	45.5	1.85	0.72	1.10	3.04	10.90
70-30	38.5	1.63	0.64	0.91	2.62	9.22

Mechanism and rate law: Based on the present experimental observations and from the reports of previous work[19], an initial two electron transfer with the formation of chromium(IV) has been formulated. Chromium(IV) reacts with an aldehyde molecule to form an aryl radical and Cr(III). The radical formation has been tested with the monomer acrylonitrile when a polymer precipitated in methanol under nitrogen atmosphere. Aryl radical reduces BIFC to Cr(V) which further reacts with another aldehyde molecule by a two electron transfer to form Cr(III). The involvement of intermediate valance states of chromium in the reaction has been tested with the induced oxidation by Mn(II). The reaction proceeds with the formation of a monochromate ester as the intermediate (**Scheme-I**). Since the rate of the reaction is the decomposition of the monochromate ester, the rate law given as:

$$\text{Rate} = k_1k_2k_3[\text{BA}][\text{BIFC}][\text{H}^+]$$

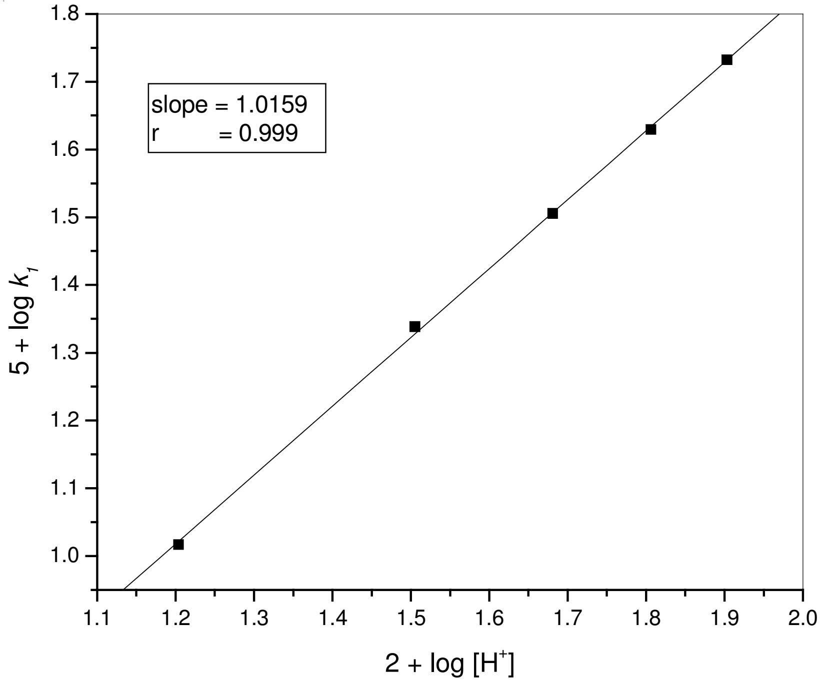
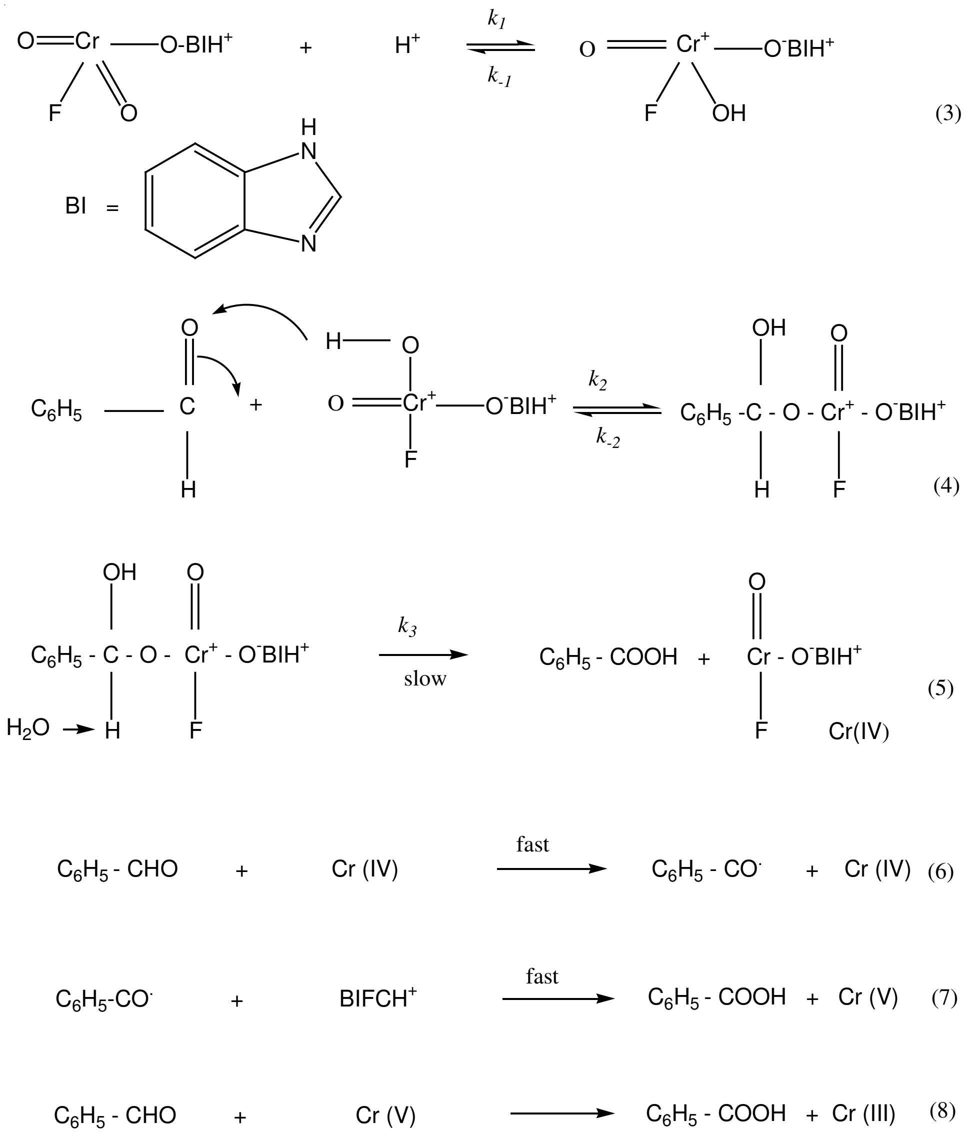


Fig. 2. Order plot for [H$^+$] for the oxidation of benzaldehyde by benzimidazolium fluorochromate at 303 K

Structure reactivity correlation: In order to study the effect of structure on reactivity, some *para*-substituted benzaldehydes were subjected to oxidation kinetics by BIFC at four different temperatures *viz*., 298, 303, 308 and 313 K in 50-50 % (v/v) acetic acid-water medium in presence of perchloric acid. The Arrhenius plot is given in Fig. 3. Substrate effect reveals that *para*-substituted benzaldehydes also first order dependence. The second order rate constants at four different temperatures are given in the Table-3.



Scheme-I

It is interesting to note that the reactivity decreases in the order p-NO_2 > p-CN > p-Cl > p-H > p-CH_3 > p-OCH_3 for the substituents.

The activation parameters were calculated from k_2 at 298, 303, 308 and 313 K using the van't Hoff plot by the method of least squares and are presented in Table-3. The reaction is neither isoenthalpic nor isoentropic but complies with the compensation law also known as the isokinetic relationship. The isokinetic temperature 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

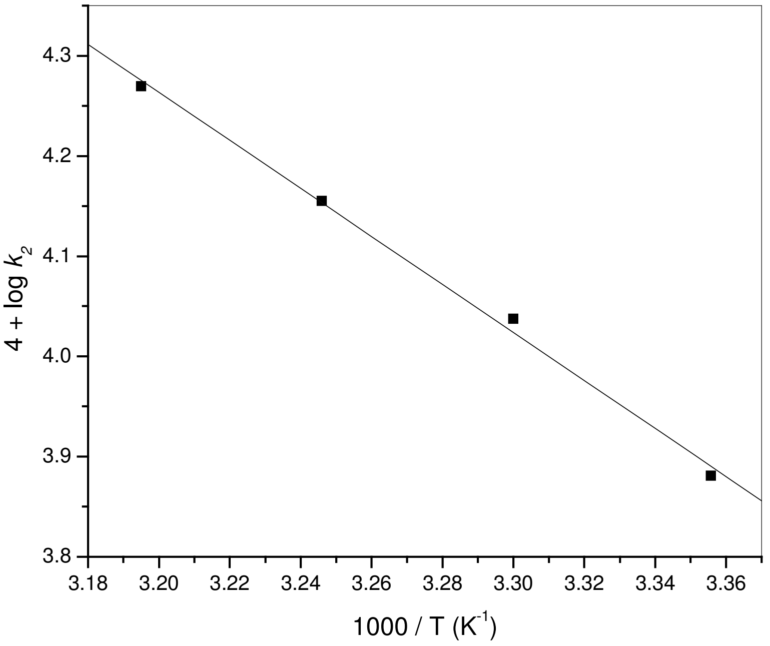


Fig. 3. Arrhenius plot of log k_2 *versus* 1000/T for the oxidation of benzaldehyde by benzimidazolium fluorochromate

TABLE-3
ACTIVATION PARAMETERS AND SECOND ORDER RATE CONSTANTS FOR THE OXIDATION OF *para*-SUBSTITUTED BENZALDEHYDES BY BENZIMIDAZOLIUM FLUOROCHROMATE
[BA] = 2.0×10^{-2} M; [BIFC] = 1.0×10^{-3} M; [H^+] = 0.32 M
Solvent composition = 50 % AcOH-50 % H_2O (v/v)

Substrate	$10^2 \times k_2$ (dm^3 mol^{-1} s^{-1})				E_a (kJ mol^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$-\Delta S^{\#}$ (kJ mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})
	298 K	303 K	308 K	313 K				
H	0.76	1.09	1.43	1.86	45.90	43.37	139.76	85.71
p-OCH_3	0.28	0.41	0.58	0.85	57.02	54.48	111.02	88.11
p-CH_3	0.43	0.64	0.79	1.09	46.57	44.07	142.26	87.01
p-Cl	1.43	1.79	2.32	2.73	34.00	31.43	174.72	84.37
p-NO_2	5.54	6.98	8.28	10.30	31.50	28.62	172.86	80.99

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[20]. 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 eqn. 9.

$$\log k \text{ (at } T_2) = a + b \log k \text{ (at } T_1) \quad (9)$$

Isokinetic temperature: In the present study, linear plots imply the validity of the isokinetic relationship. A representative plot is shown in Fig. 4 (slope = 0.9372, r = 0.999, isokinetic temperature = 415 K). The operation of isokinetic relationship reveals that all the substituted benzaldehydes examined follow a common mechanism.

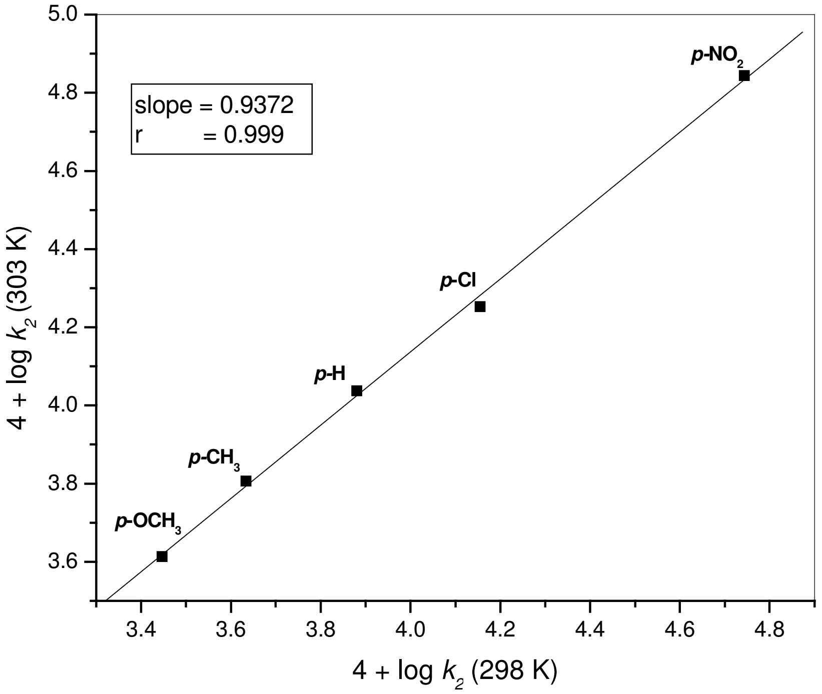


Fig. 4. Exner's plot for the oxidation of benzaldehyde by benzimidazolium fluorochromate between 4 + log k_2 (298 K) and 4 + log k_2 (303 K)

TABLE-4
REACTION CONSTANT VALUES AT DIFFERENT TEMPERATURES*
[BA] = 2.0×10^{-2} M; [BIFC] = 1.0×10^{-3} M; [H^+] = 0.32 M;
Solvent composition = 50 % AcOH-50 % H_2O (v/v)

Temperature (K)	Reaction constant (ρ)**	Correlation coefficient	Standard deviation
298	1.23	0.992	0.08
303	1.15	0.991	0.07
308	1.10	0.993	0.06
313	1.04	0.996	0.04

*σ_p Values were taken from reported works[21]. **The values were obtained by correlating log k_2 with σ_p for the reactions of oxidations.

Hammett plot: The Hammett plot is also linear (r = 0.991, SD = 0.06) (Table-4) with ρ = + 1.1527 at 303 K (Fig. 5). According to Hammett reaction with positive ρ values are accelerated by electron withdrawal from benzene ring, whereas those with negative ρ values are retarded by electron withdrawal from benzene ring[21]. In this oxidation reactions, the electron withdrawing group increases the rate and the electron donating group decreases the rate. These observations supporting the positive ρ value obtained from the Hammett plot.

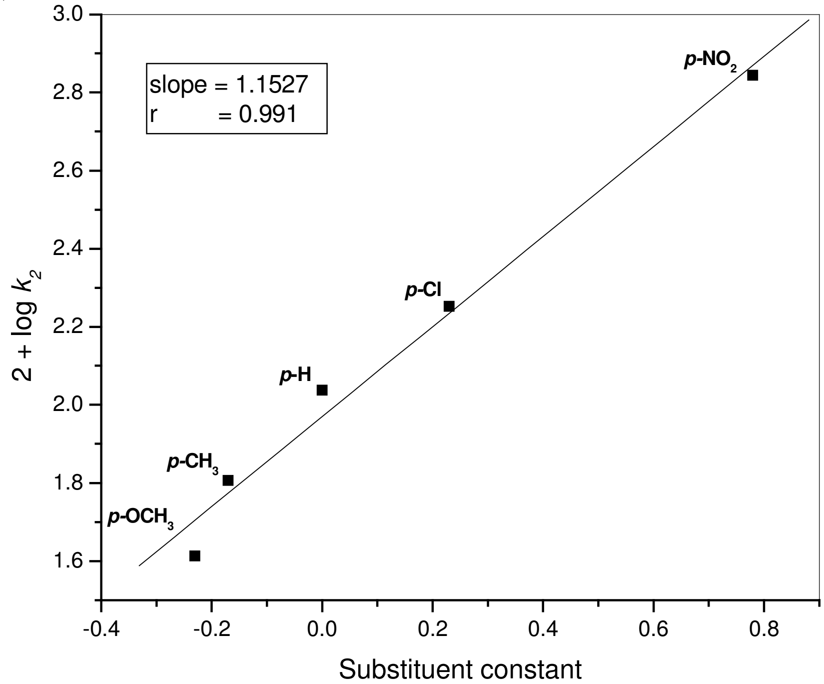


Fig. 5. Hammett plot for the oxidation od benzaldehyde by benzimidazolium fluorochromate at 303 K

Conclusion

The oxidation of benzaldehyde by BIFC is an acid catalyzed reaction and yields the corresponding benzoic acid as the product. The reaction is first order each in [substrate], [oxidant] and $[H^+]$. The stoichiometry was found to be 3 mol of aldehydes consuming 2 mol of BIFC. The negative values of $\Delta S^\#$ provided support for the formation of a rigid activated complex.

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