Arabian Journal of Chemistry (2014) 7, 171–176

King Saud University

Arabian Journal of Chemistry

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ORIGINAL ARTICLE

Oxidation of aniline and some *para*-substituted anilines by benzimidazolium fluorochromate in aqueous acetic acid medium – A kinetic and mechanistic study

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Received 5 September 2010; accepted 22 October 2010
Available online 30 October 2010

KEYWORDS

Aniline;
Benzimidazolium fluorochromate;
Kinetics;
Oxidation

Abstract The oxidation kinetics of some *para*-substituted anilines by benzimidazolium fluorochromate (BIFC) have been studied in aqueous acetic acid media in the presence of perchloric acid. The reaction is first order with respect to both aniline and BIFC and is catalysed by a hydrogen ion. The rate data obey Hammett relationship. The products of oxidation are the corresponding azo benzenes. Based on the kinetic results and product analysis, a suitable mechanism has been proposed for the reaction of BIFC with anilines.

1. Introduction

Chromium compounds have been used in aqueous and non-aqueous medium for the oxidation of a variety of organic compounds. Chromium compounds especially Cr(VI) reagents have been versatile reagents and are capable of oxidizing almost all the oxidisible organic functional groups (Wiberg, 1965). The development of newer chromium(VI) reagents for the oxidation of organic substrates continues to be of interest.

A number of new chromium(VI) containing compounds like pyrazinium chlorochromate (Sekar and Prabaharan, 2008), benzyltrimethyl ammonium chlorochromate (Mansoor and Shafi, 2009), triethylammonium chlorochromate (Sharma et al., 2010), morpholinium chlorochromate (Sharma et al., 2009a,b), 4-(dimethylamino) pyridinium chlorochromate (Rajarajan et al., 2008), quinolinium fluorochromate (Banerji et al., 2002), quinolinium bromochromate (Hiran et al., 2002), quinolinium dichromate (Medien, 2003), tributyl ammonium chlorochromate (Mansoor and Shafi, 2010a), tripropyl ammonium fluorochromate (Mansoor and Shafi, 2010b) and isoquinolinium bromochromate (Vibhute et al., 2009) have been used to study the kinetics and mechanism of various organic compounds.

The oxidation of aromatic amines by different oxidants have been the subject of study by various workers due to the complex behavior of their mode of oxidation due to the formation of polymeric products, many of which find application in

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Peer review under responsibility of King Saud University.

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http://dx.doi.org/10.1016/j.arabjc.2010.10.020

drug and dyestuff industries. Kinetics and mechanism of oxidation of *p*-substituted anilines by peroxy sulphate ion in acetic acid–water medium have been reported (Gupta, 1985).

The present study focuses on the study of kinetics and mechanism of oxidation of *para* substituted anilines by BIFC in aqueous acetic acid media. Anilines (aromatic amines) are the most widespread and principal contaminants of industrial waste waters. These comprise of an important class of environmental contaminants and they are the building blocks for many textile dyes, agrochemicals and other class of synthetic chemicals. The reaction pathways of aromatic amines in natural systems are dominated by redox reactions with soil and sediment constituents. Better understanding of the mechanism of oxidation of such compounds/contaminants to harmless products is the important goal for basic research and industrial applications, hence, the present study.

One of the important tools in deciding the mechanism of reaction is the study of substituent effects and thermodynamic parameters. The isokinetic relationship is also an important tool for deciding the nature of a mechanism. Keeping this in view, a systematic study has been made to establish the reactivity and to decide the nature of the mechanism followed in the oxidation of several *para*-substituted anilines by BIFC.

Kinetics of oxidation of anilines by various oxidizing reagents have been well studied (Elango and Bhuvaseshwari, 2006a,b,c,d, 2007a,b; Patwari et al., 2009). However the kinetics of oxidation of substituted anilines by BIFC, a Cr(VI) reagent has not yet been studied. Hence, we have considered it worthwhile to study the kinetics and mechanism of oxidation of anilines by BIFC.

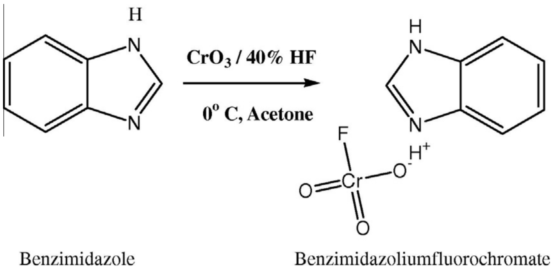
2. Experimental

2.1. Materials and reagents

All the chemicals and solvents used were of analytical grade. The anilines used were with substituents H, *p*-OCH_3, *p*-CH_3, *p*-Cl and *p*-NO_2. The solid anilines were used as such and the liquid anilines were used after vacuum distillation. Acetic acid was purified by the standard method and the fraction distilling at 118 °C was collected. Double distilled water was used for all purposes.

2.2. 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 (Murugesan et al., 2005). The purity of BIFC was checked by the iodometric method.



(1)

2.3. Kinetic measurements

The reactions were carried out under pseudo-first-order conditions by keeping an excess of substrate over BIFC. The temperature was kept constant to ±0.1 K. The progress of the reaction was followed by estimating the unreacted oxidant iodometrically at 298, 303, 308 and 313 K for up to 80% of the reaction. 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%.

2.4. Data analysis

Correlation analysis was carried out using Microcal Origin (Version 6.1) computer software. The goodness of the fit is discussed using the correlation coefficients and standard deviations.

2.5. Stoichiometry and product analysis

The stoichiometry of the reaction was determined by carrying out several sets of experiments with varying amounts of BIFC largely in excess over aniline. The estimation of unreacted BIFC showed that 1 mol of BIFC reacts with 1 mol of aniline. The oxidative products were analysed using preparative TLC on silica gel, which yields azobenzene m.p 66 °C (Lit 68 °C) and UV Abs. (EtOH) at λ_{max} 320 nm.

3. Results and discussion

The kinetics of oxidation of aniline by BIFC 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.

3.1. Order of reaction

The rate of oxidation was found to be first order each in [BIFC] and [Substrate]. Linear plots of log k_1 versus log [Substrate] (Fig. 1) with unit slope (H: slope = 1.03 ± 0.04, r = 0.997; *p*-OCH_3: slope = 1.02 ± 0.03, r = 0.998; *p*-CH_3: slope = 1.01 ± 0.03, r = 0.999; *p*-Cl: slope = 1.04 ± 0.04, r = 0.997; and *p*-NO_2: slope = 1.01 ± 0.03, r = 0.998) demonstrate the first-order dependence of the rate on [Substrate]. The k_1 values at different [Substrate] are given in Table 1. The k_1 values obtained at different concentration of BIFC reveal that the rates are almost independent of the initial concentration of BIFC. This ensures that the order of the reaction with respect to BIFC is one.

The dependence of the reaction rate on the hydrogen ion concentration has been investigated at different initial concentrations and keeping the concentrations of the other reactants constant (Table 1). It may be seen that the rate of reaction increases linearly with an increase in the hydrogen ion concentration. This establishes that the reaction rate is first order with respect to the hydrogen ion concentration. A plot of log k_1 versus log $[H^+]$ is linear (Fig. 2), showing that the reaction proceeds completely through an acid catalysed pathway (Banerji et al., 1986a,b).

Table 1 Effect of variation of [Aniline], [BIFC] and [H^+] on the rate of reaction at 303 K.

10^3 [BIFC] (mol dm^{-3})	10^2 [Aniline] (mol dm^{-3})	[H^+] (mol dm^{-3})	10^4 k_1 (s^{-1})				
			H	*p*-OCH_3	*p*-CH_3	*p*-Cl	*p*-NO_2
0.5	2.0	0.25	18.46	26.20	22.70	10.42	3.62
1.0	2.0	0.25	18.56	26.40	22.40	10.56	3.60
1.5	2.0	0.25	18.44	26.34	22.20	10.30	3.48
2.0	2.0	0.25	18.42	26.56	22.10	10.12	3.56
2.5	2.0	0.25	18.32	26.12	22.96	10.52	3.70
1.0	1.0	0.25	8.96	12.80	10.88	5.12	1.76
1.0	1.5	0.25	13.36	19.20	16.48	7.68	2.72
1.0	2.5	0.25	23.52	32.96	27.20	12.64	4.48
1.0	3.0	0.25	27.28	39.84	33.60	15.20	5.28
1.0	2.0	0.15	11.12	15.44	13.22	6.28	2.08
1.0	2.0	0.20	14.64	21.02	17.66	8.40	2.78
1.0	2.0	0.30	22.16	31.28	26.42	12.56	4.28
1.0	2.0	0.35	25.68	36.70	30.66	14.66	4.92
1.0	2.0	0.25	18.48	26.32	22.46	10.48	3.65[a]
1.0	2.0	0.25	15.22	21.12	18.36	8.76	2.94[b]

Solvent composition = 50% AcOH – 50% H_2O (v/v).

[a] Contained 0.001 mol dm^{-3} acrylonitrile.

[b] In the presence of 0.003 mol dm^{-3} Mn(II).

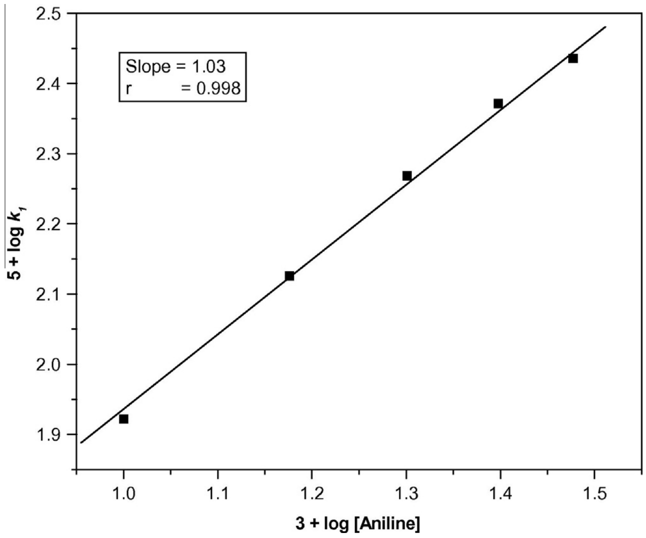


Figure 1 Plot of log k_1 versus log [Aniline] for the oxidation of aniline by BIFC.

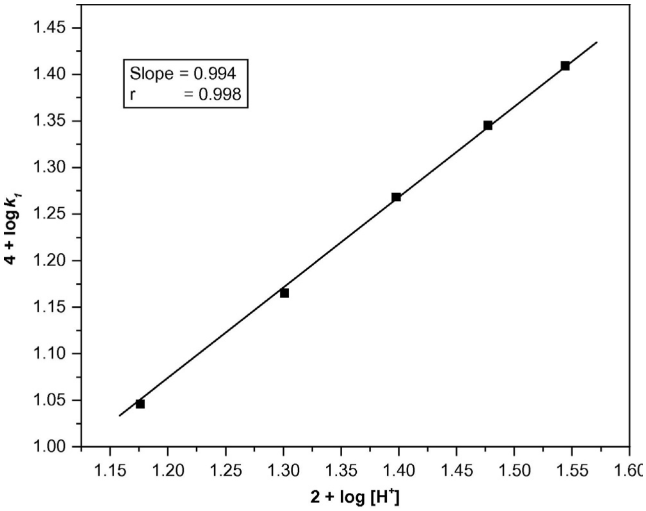


Figure 2 Plot of log k_1 versus log [H^+] for the oxidation of aniline by BIFC.

3.2. 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% to 70%. The pseudo-first-order rate constants were estimated for the oxidation reactions of all of the substituted anilines, with BIFC in the presence of perchloric acid at a constant ionic strength. The reaction rate increases markedly with the increase in the proportion of acetic acid in the medium (Table 2). When the acid content increases in the medium, the acidity of the medium is increased whereas the dielectric constant of the medium is decreased. These two effects cause the rate of the oxidation to increase markedly. The enhancement of the reaction rate with an increase in the amount of acetic acid generally may be attributed to two factors, *viz*, (i) the increase in acidity occurring at constant [H^+] and (ii) the decrease in the dielectric constant with an increase in the acetic acid content. The plots of log k_1 against the inverse of the dielectric constant are linear with positive slopes, indicating an interaction between a positive ion and a dipolar molecule (Banerji et al., 1986a,b).

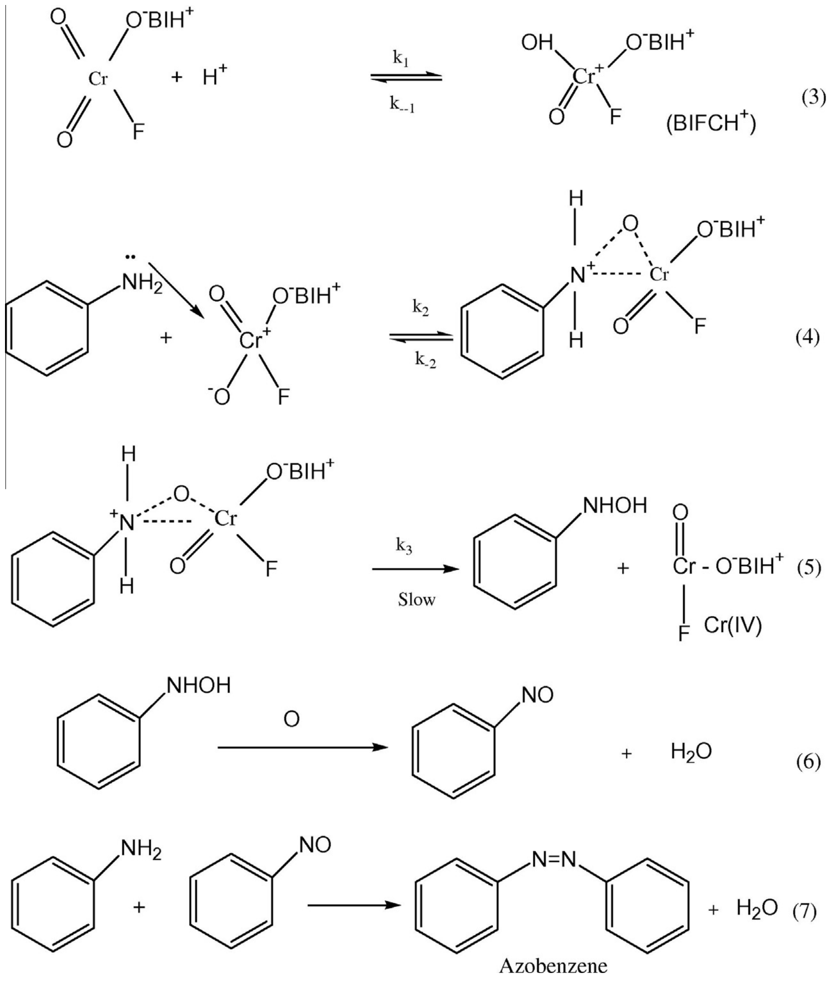
3.3. Mechanism of oxidation

The sequence of reactions for the oxidation of anilines by BIFC in perchloric acid is shown in Scheme 1. The oxidation of anilines by BIFC in acetic acid water medium is remarkably

Table 2 Effect of varying solvent polarity on the rate of reaction at 303 K.

%Acetic acid–water (v/v)	Dielectric constant	10^4 k_1 (s^{-1})				
		H	p-OCH_3	p-CH_3	p-Cl	p-NO_2
30–70	72.0	13.46	20.90	18.02	6.66	2.34
40–60	63.3	15.30	23.76	21.16	8.56	3.02
50–50	56.0	18.56	26.40	22.40	10.56	3.60
60–40	45.5	20.96	29.58	25.26	12.96	4.32
70–30	38.5	23.47	33.12	28.41	14.51	4.85

10^2 [Substrate] = 2.0 mol dm^{-3}; 10^3 [BIFC] = 1.0 mol dm^{-3}; [H^+] = 2.5×10^{-1} mol dm^{-3}.



Scheme 1

slow, but is catalysed in the presence of perchloric acid, and the reaction proceeds at a comfortable rate. C

Catalysis by perchloric acid suggests protonation of BIFC species rather than the aniline molecule, which would have resulted in retardation. The protonated BIFC is difficult to visualize but participation of protonated chromium(VI) oxidation is well known (Wiberg, 1985). The reaction did not promote polymerization of acrylonitrile indicating the absence of free radicals. However, the addition of Mn(II) (0.003 mol dm^{-3}), in the form of $MnSO_4$ retards the rate of oxidation. This indicates the involvement of Cr(IV) intermediate in the oxidation of anilines by Cr(VI) reagent. Mn(II) ion reduces Cr(IV) formed to Cr(III). In the absence of Mn(II) ion, formed Cr(IV) reduces Cr(VI) to Cr(V) and the oxidation of anilines by Cr(V) is fast (Karunakaran and Suesh, 2004). The decrease in the rate of Cr(VI) reduction on the addition of Mn(II) has been attributed to the removal of Cr(IV) by reaction (Khan et al., 2004) with Mn(II).

$$\mathrm{Cr(IV)} + \mathrm{Mn(II)} \rightarrow \mathrm{Cr(III)} + \mathrm{Mn(II)} \qquad (2)$$

The reaction proceeds with the formation of a complex followed by the loss of hydride ion. The complex is formed likely by concerted transfer of oxygen from the oxidant to *N*-atom and electron pair from *N*-atom to Cr(VI). The negative ρ value is indicative of the presence of a positive nitrogen center, which would mean depletion of lone-pair electron density, and this can be facilitated only when the oxidant forms a complex with the substrate in which the nitrogen lone-pair can be used up in coordinating with an electron-deficient center, preferably a metal ion. A similar mechanism has been postulated for the oxidation of anilines by pyridinium chlorochromate in chlorobenzene–nitrobenzene mixture (Panigrai and Mahapatro, 1982) and by nicotinium dichromate in benzene-*tert*-butanol mixture (Elango and Bhuvaseshwari, 2006a,b,c,d). Further, such a complex formation is supported by the negative entropy of activation observed. The above mechanism leads to the following rate law

$$-d[\mathrm{BIFC}]/dt = k_1k_2k_3[\mathrm{Aniline}][\mathrm{BIFC}][\mathrm{H}^+] \quad (8)$$

3.4. Structure reactivity correlation

In order to study the effect of structure on reactivity, some *para*-substituted anilines 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 the presence of perchloric acid. Substrate effect reveals that *para*-substituted anilines are also first order dependent. The second order rate constants at four different temperatures and the activation parameters are given in Table 3. It is interesting to note that the reactivity decreases in the order p-OCH_3 > p-CH_3 > p-H > p-Cl > p-NO_2 for the substituents.

3.5. Activation parameters

The activation parameters were calculated from k_2 at 298, 303, 308 and 313 K using the Eyring relationship by the method of least square and is presented in Table 3. The reaction is neither isoenthalpic nor isoentropic but complies with the compensation law also known as the isokinetic relationship

$$\Delta H^{\#} = \Delta H^{0} + \beta\Delta S^{\#} \quad (9)$$

The isokinetic temperature β is the temperature at which all the compounds of the series react equally fast. Also, at the isokinetic temperature, the variation of the substituent has no influence on the free energy of activation. In an isoentropic reaction, the isokinetic temperature lies at infinity 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 (Elango and Bhuvaseshwari, 2007a,b). 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. (10).

$$\log k(\mathrm{at}\ T_2) = a + b\log k(\mathrm{at}\ T_1) \quad (10)$$

The linear relationship in Exner plots (Exner, 1964; Exner et al., 1973) at 4 + log k_2 (303 K) and 4 + log k_2 (308 K) observed in the present study imply the validity of the isokinetic relationship (Fig. 3). Isokinetic temperature is calculated as 456 K. The operation of the isokinetic relationship reveals that all the substituted anilines examined are oxidized through a common mechanism (Leffler and Grunwald, 1963).

3.6. Hammett plot

A linear free energy relationship is attempted by casting the data in Hammett equation. The value of the slope of Hammett plot is known as reaction constant (ρ). Reaction constant values at different temperatures are given in Table 4. The Ham-

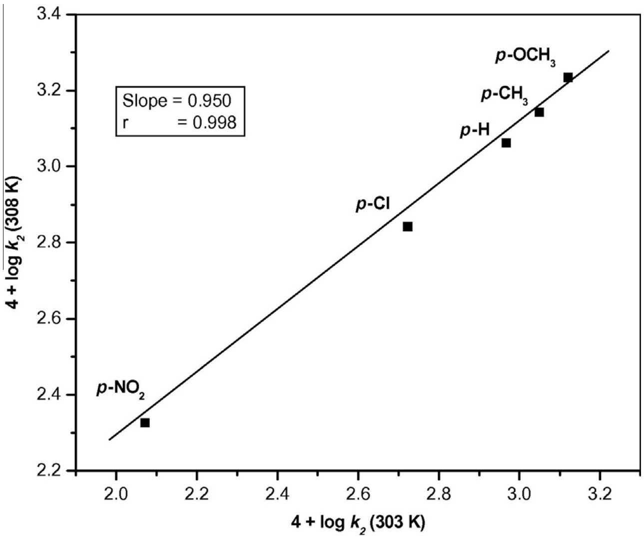


Figure 3 Exner's plot of 4 + log k_2 (308 K) versus 4 + log k_2 (303 K) for the oxidation of aniline by BIFC.

Table 3 Activation parameters and second order rate constants for the oxidation of *para*-substituted anilines by BIFC in aqueous acetic acid medium.

Substrate	$10^2\ k_2$ (dm^3 mol^{-1} s^{-1})				E_a (kJ mol^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$-\Delta S^{\#}$ (JK^{-1} mol)	$\Delta G^{\#}$ (kJ mol^{-1}) (at 303 K)
	298 K	303 K	308 K	313 K				
H	7.15	9.28	11.54	14.05	34.83	32.30	158.36	80.28
p-OCH_3	10.16	13.20	17.16	21.45	38.85	36.31	143.95	79.92
p-CH_3	8.65	11.20	13.90	19.96	48.48	39.63	132.47	79.76
p-Cl	4.60	5.28	6.65	8.32	31.09	28.54	175.02	81.57
p-NO_2	1.39	1.80	2.12	2.88	26.47	33.84	166.96	84.42

10^2 [Substrate] = 2.0 mol dm^{-3}; 10^3 [BIFC] = 1.0 mol dm^{-3}; 10 [H$^+$] = 2.5 mol dm^{-3}.
Solvent composition = 50% AcOH – 50% H_2O (v/v).

Table 4 Reaction constant values at different temperatures.

Temperature (K)	Reaction constant, ρ	Correlation coefficient	Standard deviation
298	−0.8979	0.994	0.05
303	−0.8633	0.995	0.03
308	−0.8466	0.997	0.02
313	−0.8043	0.996	0.06

10^2 [Substrate] = 2.0 mol dm^{-3}; 10^3 [BIFC] = 1.0 mol dm^{-3}; 10 [H$^+$] = 2.5 mol dm^{-3}.
Solvent composition = 50% AcOH – 50% H_2O (v/v).

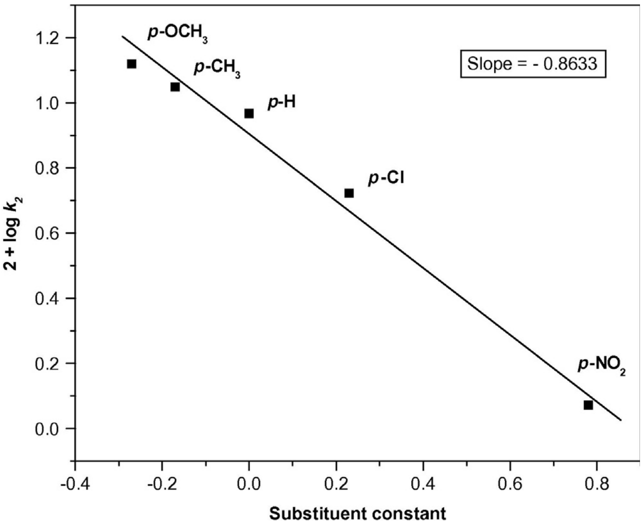


Figure 4 Hammett plot of 2 + log k_2 versus substituent constant, σ at 303 K for the oxidation of aniline by BIFC.

mett plot is also linear (Fig. 4). According to Hammett, the reaction with positive ρ values are accelerated by electron withdrawal from the benzene ring, whereas those with negative ρ values are retarded by electron withdrawal from the benzene ring (Hammett, 1940). In these oxidation reactions, the electron withdrawing groups decrease the rate and the electron donating groups increase the rate. These observations supporting the negative ρ values are obtained from the Hammett Plot.

4. Conclusions

In this paper we have reported the detailed mechanism of oxidation of aniline and some *para*-substituted anilines by BIFC. The reaction is first order each in [Aniline], [BIFC] and [H$^+$]. The oxidation of *para*-substituted anilines yield the corresponding azo benzenes. Since aniline is very harmful to the environment, its removal from the environment is the ultimate goal of basic research. For this purpose, deep understanding of the mechanism of the process of aniline is needed. The negative ρ values obtained from the Hammett plot reveals that a positively charged reactive intermediate is formed during the oxidation process. Similarly the negative value of $\Delta S^{\#}$ provided support for the formation of the activated complex in the slow step.

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