Hammett Plot Behaviour for the Oxidation of Para- Substituted Phenols by Chromium (Vi) Compound

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Abstract

Imidazolium fluorochromate (IFC) is one of the chromium (VI) mild oxidant. This oxidant can be used to oxidize some para substituted phenols such as *p*-methyl, *p*-carboxy, *p*-nitro, *p*-chloro, *p*-methoxy, *p*-bromo, it shows that the reaction was first order concerning [IFC], phenols and fractional order concerning [H⁺]. There is a negligible change of reaction rate was observed during the addition of sodium perchlorate. Decrease the rate of reaction for increase the dielectric constant and manganous sulphate concentration. Absence of free radical mechanism while the addition of a drop of acrylonitrile. Thermodynamic and activation parameters were calculated from Eyring's equation using thermostat in the temperature range 298 K to 313K. The substrate concentration and temperature variation can be studied for the para substituted phenols. From the attained kinetic investigations, a suitable mechanism and rate law was derived. The structure-reactivity relationship can be calculated using the drawn of Hammett plot. An excellent correlation is obtained from Exner's plot of log $k_{1 (303 K, 308 K, 313 K)}$ *versus* log $k_{1 (298K)}$. It indicates that mentioned *para*- substituted phenols follow a uniform mechanism.

Key words: Imidazolium fluorochromate, Phenols, Hammett plot, Kinetic studies, Eyring plot

Chemical kinetics is a vital part of physical chemistry which deals with the reaction rate under the given condition of pressure, concentration and temperature. Understanding the reaction rate under varying conditions of pressure, concentration, and temperature is crucial for predicting how a reaction proceeds and for optimizing conditions for industrial processes. In general, the change of concentration of the reactant and product against time is considered for the determination reaction rate. Since temperature affects the rate of reaction, the isothermal condition of the reacting mixture is maintained throughout the reaction [1-3]. Chemical reactions always take place in several consecutive steps which are not indicated by the stoichiometric equation, in such cases it is studied by the kinetics method and provide information regarding the equilibrium state of the reaction with complexity. Half-life period time or completion period time methods are used for kinetic investigation [4-8]. The intense, fast reactions are examined using stopped-flow, molecular beam flow techniques. But the other reactions can be monitored by conductometry, pH-metry, colorimetry, titrations, etc.

The selectivity and pacifying nature of the novel chromium (VI) oxidants have been synthesized [9-11]. The naturally occurring Chromium (VI) and Chromium (III) species differ in their biological and physio chemical activities. Oxidation of some phenols by different chromium compounds have been reported earlier [12-18]. Some organic oxidation reactions were reported by imidazolium fluorochromate [19-22].

MATERIALS AND METHODS

Imidazolium fluorochromate

Imidazolium fluorochromate [23] can be easily prepared by the addition of hydrofluoric acid and imidazole with chromic acid in water. It is a red-orange crystals, the reactivity cannot be changed for few months. Molecular formula and structure of imidazolium fluorochromate was confirmed by elemental analysis and spectral studies.

Pheonls

Phenol and *para*- substituted phenols were purchased from Sigma Aldrich and the purification was done by the distillation process. Initially, the phenols were dissolved in NaOH solution in a round bottomed flask and ether was added and shaken well to remove the impurities and phenol were liberated on acidification. It was condensed with diethyl ether and dehydrated over dried Na_2SO_4. The solvent acetic acid (E Merck) was distilled by Orton and Bradfield [24] method. Perchloric acid, sodium perchlorate, acrylonitrile and manganous sulphate (E Merck) were purchased as AnalaR grade and used as such.

Method

The oxidation reactions were preceded by the phenol concentration always higher over that of imidazolium fluorochromate. Notable volumes of phenol and its solvent acetic acid, catalyst and its solvent double distilled water were

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assorted to take the ratio of acetic acid in demand value and placed in thermostat at common temperature 303K. The oxidation reaction was initiated by adding the mentioned volume of chromium (VI) compound (IFC) to the concoction. Instantly, the minimum volume of reaction mixture was transferred into the quartz cuvette and again place it same reaction flask. It is repeated at decisive time breaks and the change in the strength of IFC by using digital spectrometer (ELICO CL 23 MINI SPEC) λ_{max} = 470 nm. The rate constant (psuedo-first-order) for every run was determined from the slope values obtained from the plot of log OD (absorbance) against time.
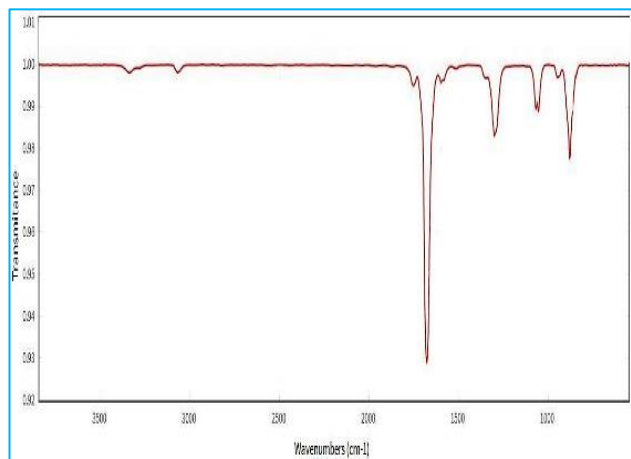
Product analysis

Equal molar concentrations of imidazolium fluorochromate (1 M) and phenol (1 M) were mixed with a small addition of perchloric acid. The mixture was slightly heated and placed at room temperature for a day. The resultant solution was extracted with diethyl ether and the product was dehydrated with dried sodium sulphate. It was washed thoroughly with water and evaporated the solvent in a hot water bath. The product quinone was obtained after cooling and it was further confirmed by the spectral studies (Fig 1). Further, the product was screened for Mass spectra (Fig 2), and the results proved to be the same.
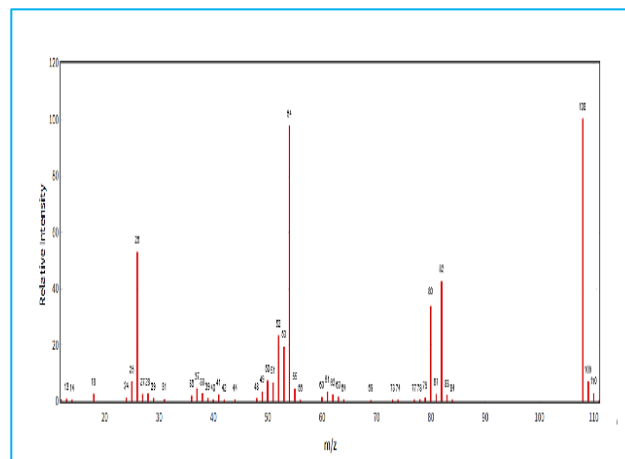

Fig 1 IR spectrum of quinone

Fig 2 Mass spectrum of quinone

RESULTS AND DISCUSSION

Pseudo-first order condition was continued throughout oxidation of phenol (C_6H_5OH) using imidazolium fluorochromate (IFC) in aqueous acetic acid solvent. This oxidation kinetic measurements were monitored using digital spectrometer and the rate constant was determined from the plot of log OD (absorbance) against time in seconds. It was decreasing the reaction rate with increase of imidazolium fluorochromate concentration. It is ascribed to the reduce in current concentration of chromium (VI) species in the reaction medium [25]. Further, it was evidenced by the plot of $1/k_1$ against 1/[IFC] ought to be linear (Fig 3).

The rate of reaction was raised linearly on changing the concentration of the phenol as shown in (Table 1). The plot of log k_1 against log [Phenol] with a good correlation and unit slope (1.055), it shows that first order with respect to phenol. The fractional slope (0.69) was obtained from the plot of log k_1 against log [H^+], it implies that perchloric acid acts as catalyst. There is a negligible change of reaction rate was observed during the addition of sodium perchlorate. It indicates that, the participation of charged species in the slow step. The reaction rate was raised with the rise in the percentage of medium (acetic acid). The positive slope (+28.58) with good correlation of plot was obtained from log k_1 against 1/D (Fig 4). It indicates that, ion-dipole interaction [26-27] in the slow step.
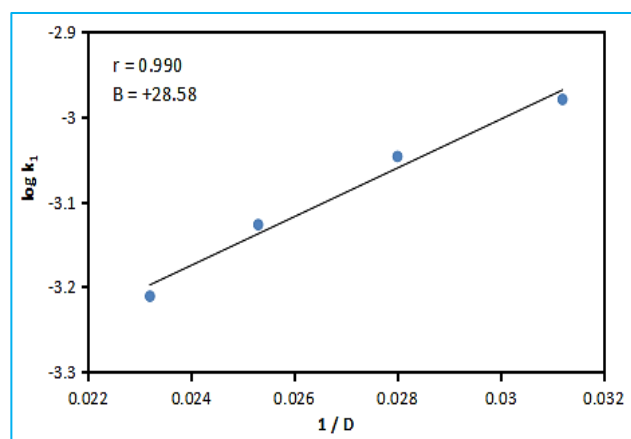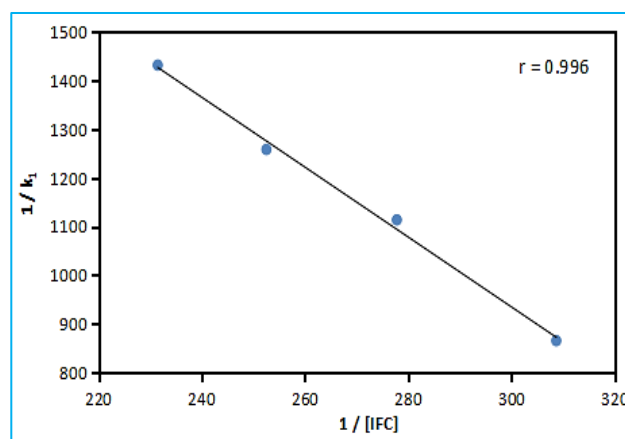

Fig 3 Plot of 1 / k_1 against 1 / [IFC]

Fig 4 Plot of log k_1 against 1/D

The addition of acrylonitrile, which is a very good trapper of free radicals, did not have any retarding effect on the reaction. It indicates that no free radical's participation in the reaction. But it is possible that, this oxidation reaction involves a two-electron transfer process in the mechanism for observing the noticeable decrease of reaction rate by adding various concentration of manganous sulphate.
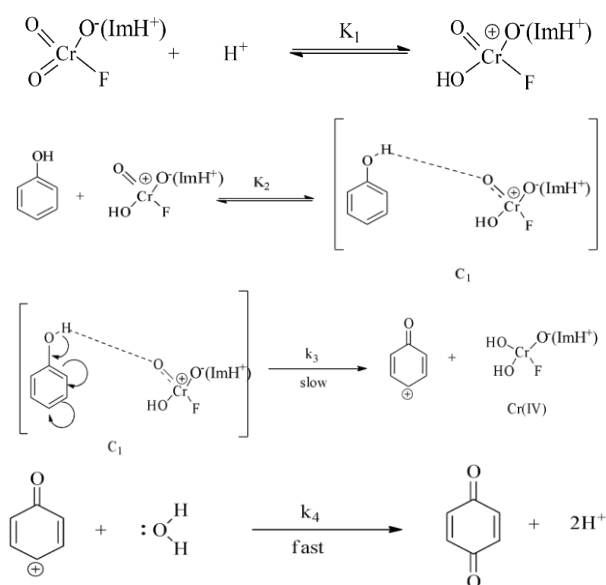
Table 1 Rate data for the oxidation of phenol by IFC at 303 K

$[IFC]10^3$ $(mol\ dm^{-3})$	$[Phenol]\ 10^2$ $(mol\ dm^{-3})$	$[HClO_4]$ $(mol\ dm^{-3})$	% AcOH:H$_2$O (v/v)	$[NaClO_4]\ 10^3$ $(mol\ dm^{-3})$	$[MnSO_4]\ 10^3$ $(mol\ dm^{-3})$	$k_1\ 10^4$ (s^{-1})
3.24	5.0	0.75	60:40	-	-	11.54
3.60	5.0	0.75	60:40	-	-	8.98
3.96	5.0	0.75	60:40	-	-	7.95
4.32	5.0	0.75	60:40	-	-	6.99
3.60	4.0	0.75	60:40	-	-	6.99
3.60	5.0	0.75	60:40	-	-	8.98
3.60	6.0	0.75	60:40	-	-	10.96
3.60	7.0	0.75	60:40	-	-	12.56
3.60	5.0	0.50	60:40	-	-	5.69
3.60	5.0	0.75	60:40	-	-	8.98
3.60	5.0	1.00	60:40	-	-	12.08
3.60	5.0	1.25	60:40	-	-	15.07
3.60	5.0	0.75	60:40	0.00	-	8.98
3.60	5.0	0.75	60:40	0.30	-	8.92
3.60	5.0	0.75	60:40	0.60	-	8.95
3.60	5.0	0.75	60:40	0.90	-	9.04
3.60	5.0	0.75	50:50	-	-	6.15
3.60	5.0	0.75	55:45	-	-	7.47
3.60	5.0	0.75	60:40	-	-	8.98
3.60	5.0	0.75	65:35	-	-	10.46
3.60	5.0	0.75	60:40	-	0.00	8.98
3.60	5.0	0.75	60:40	-	0.60	5.74
3.60	5.0	0.75	60:40	-	1.20	5.42
3.60	5.0	0.75	60:40	-	1.80	5.04

Mechanism and rate law

The phenol was oxidized by imidazolium fluorochromate; it was catalyzed by perchloric acid. The reaction was first order concerning [IFC], phenols and fractional order concerning [H$^+$]. There is a negligible change of reaction rate was observed during the addition of sodium perchlorate. Absence of free radical mechanism while the addition of a drop of acrylonitrile. But, the study on the effect of manganous sulphate concentration suggested that, the rate controlling process was produced tetravalent chromium, involving a two-electron change.

The active oxidizing species CrO$_3$F$^-$ [28] was involved in the protonated form which the concentration of chromium (VI) as very much lower. Product analysis was clearly indicating that the quinone. From these comments, the subsequent mechanism (Scheme 1) and rate law were proposed.

Scheme 1 Mechanism of oxidation of phenol by imidazolium fluorochromate

Rate law

Rate $= k_3C_1$
$= k_3K_2\ [HCrO_3F^-]\ [Phenol]$
$= k_3K_2K_1\ [IFC]\ [H^+]\ [Phenol]\ /\ 1 + K_1[H^+]$

Table 2 Effect of substrate concentration on oxidation of phenols by IFC

Substituents	$[Phenols]\ 10^2$ $(mol\ dm^{-3})$	$k_1\ 10^4$ (s^{-1})	Order with respect to [S]
-H	4.0	6.99	1.055
	5.0	8.98	
	6.0	10.96	
	7.0	12.56	
p-CH$_3$	4.0	11.99	0.999
	5.0	14.89	
	6.0	18.19	
	7.0	20.84	
p-COOH	4.0	1.76	1.061
	5.0	2.26	
	6.0	2.79	
	7.0	3.15	
p-NO$_2$	4.0	1.01	0.968
	5.0	1.29	
	6.0	1.53	
	7.0	1.72	
p-Cl	4.0	3.88	0.998
	5.0	4.73	
	6.0	5.74	
	7.0	6.78	
p-OCH$_3$	4.0	13.99	0.945
	5.0	18.45	
	6.0	20.94	
	7.0	23.99	
p-Br	4.0	3.97	1.021
	5.0	4.89	
	6.0	5.99	
	7.0	7.00	

Imidazolium fluorochromate oxidation with para substituted phenols

Para substituted phenols viz., *p*-methyl, *p*-carboxy, *p*-nitro, *p*-chloro, *p*-methoxy, *p*-bromo phenols were oxidized with same imidazolium fluorochromate in protic solvent system. The oxidation process was conducted at 303 K in 60% of aqueous acetic acid medium. The rate of reactions was raised linearly on changing the concentration of the *para-* substituted phenols as shown in (Table 2). The plot of log k_1 against log [Phenols] with a good correlation and unit slopes (0.945 - 1.061), it shows that first order with respect to para substituted phenols. The target *para-* substituted phenols of reaction rate were increased with the raise of temperature range from 298 K to 313 K. The thermodynamic and activation parameters have been calculated [29] from the Eyring's plot. The calculated entropy of activation values is negative, it implies that the transition state contains widespread solvation over the reactants. It also indicates the reactants are less disorderly oriented in the slow step of mechanism.

An approximately same values of free energy change ($\Delta G^{\#}$) in the oxidation of *para-* substituted phenols by imidazolium fluorochromate follows the parent mechanism. The isokinetic temperature β was obtained from the slope 2.57 K from the isokinetic plot ($\Delta H^{\#}$ against $\Delta S^{\#}$) (Fig 5). This value is lesser than the reaction temperature, it implies that the oxidation reaction was entropy controlled [30]. An excellent correlation (r = 0.997 - 0.999) is obtained from Exner's plot of log $k_{1\,(303\,K,\,308\,K,\,313\,K)}$ *versus* log $k_{1\,(298K)}$. It indicates that mentioned *para-* substituted phenols follow a uniform mechanism.

Table 3 Thermodynamic and activation parameters

S. No.	p-Substituted phenols	Order w.r.to substrate	$k_1 \times 10^4$ (s⁻¹)				$\Delta H^{\#}$ (kJmol⁻¹)	$-\Delta S^{\#}$ (JK⁻¹mol⁻¹)	$\Delta G^{\#}$ (kJmol⁻¹) at 303 K	E_a (kJmol⁻¹) at 303 K	r
			303 K	313 K	323 K	333 K					
1.	4-H	1.05	7.85	8.98	10.44	12.03	8.52	204.52	70.49	11.03	0.999
2.	4-CH₃	0.99	13.01	14.89	16.91	19.44	7.86	204.91	69.95	10.38	0.998
3.	4-COOH	1.06	1.97	2.26	2.75	3.15	9.72	205.51	71.99	12.24	0.996
4.	4-NO₂	0.96	0.98	1.29	1.69	2.27	17.70	181.24	72.61	20.22	0.999
5.	4-Cl	0.99	4.02	4.73	5.69	6.99	11.31	205.63	73.61	13.83	0.997
6.	4-OCH₃	0.94	16.25	18.45	21.65	25.97	9.41	198.95	69.69	11.93	0.994
7.	4-Br	1.02	4.01	4.89	6.21	7.99	14.42	187.23	71.15	16.94	0.997

From this oxidation reaction, the structure-reactivity can be determined by the Hammett plot [31] (Fig 6). The negative 'ρ' value (-1.149) indicates that electron-withdrawing substituents decrease the rate of oxidation and electron-releasing substituents enhance the rate of the reaction. Correlation of rate data with σ is also satisfactory with r = 0.995, suggesting a reaction centre has higher electron density in the transition state than in the starting material.
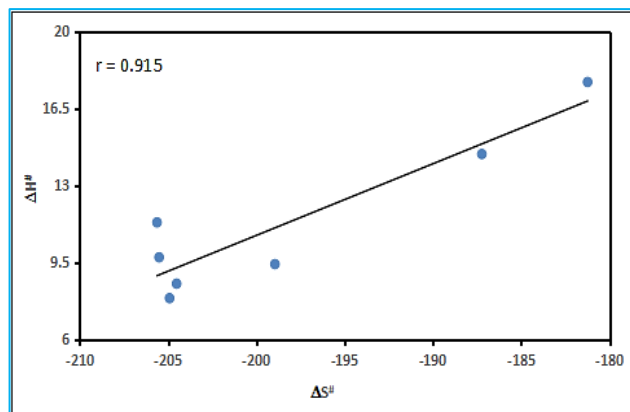

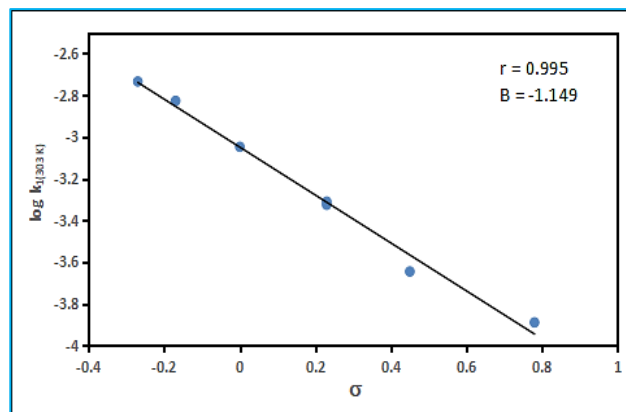Fig 5 Isokinetic plot of $\Delta H^{\#}$ *versus* $\Delta S^{\#}$

Fig 6 Hammett plot of log $k_{1(303\,K)}$ *versus* σ

CONCLUSION

The kinetics and oxidation of phenol and target of six *para-* substituted phenols by imidazolium fluorochromate under pseudo-first-order conditions have been studied in an aqueous acetic acid medium at 303 K. From the Hammett plot behavior, the nature of electron donating and electron with drawing substituents imparts the development of carbocation centre and its transition state.

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