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Effect of Substituents on Kinetics of Phenols by Pyridinium Fluorochromate in Glacial Acetic Acid

S.G. PATIL* and S.B. JOSHI
Department of Chemistry, M.U. Mahavidyalaya, Udgir-413 517, India
E-mail: sg_patil123@rediff mail.com

The effect of substituents on the reaction rate for oxidation of phenol by pyridinium fluorochromate has been investigated in glacial acetic acid at 303 and 308 K by ploting log k_2 *vs.* 6_x. From the slope of the resulting straight line, the values of 'ρ' were calculated. The negative 'ρ' values in the reaction indicating the development of +ve charge at the reaction. The reaction is thus accelerated by electron donating substituents, which help to delocalize the +ve charge in the intermediate complex and correspondingly retarted by electron-withdrawing substituents. The Hammett treatment has been applied to these reactions and to different functional groups.

Key Words: Kinetics, Phenol, Pyridinium fluorochromate, Glacial acetic acid.

INTRODUCTION

Pyridinium fluorochromate (PFC) is reported to be neutral and mild oxident for selective oxidations. Kinetics of oxidation of some organic substrates by pyridinium fluorochromate have already been reported[1-4]. The kinetics of oxidation of some monohydric phenols by pyridinium fluorochromate[5,6]. However, the literature survey revealed that the effect of substituents on oxidation of phenols has not been reported.

EXPERIMENTAL

All chemicals were of analytical grade. Solvents were distilled before use. Pyridinium fluorochromate (PFC) was prepared from pyridine, aqueous 40 % hydrofluoric acid and Cr(VI) oxide used in a molar ratio 1:1.5:1. The bright orange crystalline[7] is isolated by filtration and drying over vacum (yield 93-94 %). Recrystallized the product from water (m.p. 106-108 ºC), collecting the recrystalline product used for oxidation reaction.

Kinetics measurements: The kinetic measurements have been carried out by (concentration of PFC reacted iodometrically as a function of time) Batch method recommended by Gnanapragasam and Yeddanapalli[8]. In this method, the PFC and phenol solutions in acetic acid (5 mL each) were taken in several iodine flasks and test tubes, respectively and were placed in thermostatic bath at a required temperature. The phenols solution was quickly added to PFC solution and the mixture was allowed to react for specific time, KI (10 %; 5 mL) solution was then added to stop the reaction and after 1 min, the liberated iodine was titrated against standard sodium thiosulfate solution.

The overall orders were evaluated by the fractional life method, graphical method and individual orders from the initial rates as well as by Ostwald's isolation method.

RESULTS AND DISCUSSION

The effect of substituents on the reaction rate for oxidation of phenol by pyridinium fluorochromate in acetic acid at 303 and 308 K is studied by ploting $\log k_2$ *vs.* σ_X. From the slope of the resulting straight line the values of 'ρ' is -2.20 and -1.92 at 303 and 308 K (Table-1).

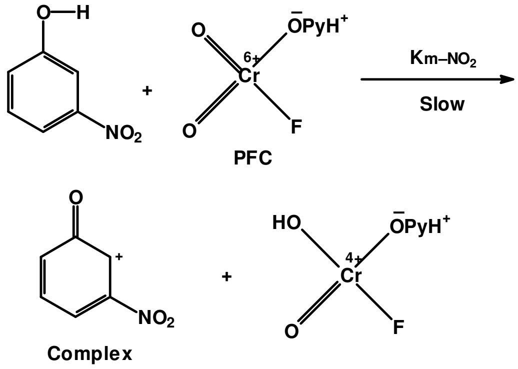
TABLE-1
EFFECT OF SUBSTITUENTS ON THE REACTION RATE FOR OXIDATION OF PHENOL BY PFC AT 303 K AND 308 K
[Phenol] = 0.05 M; Solvent: AcOH (100 %); [PFC] = 0.005 M

Substituents	σ_X	$K_2 \times 10^4$ (mol s^{-1})		$\log K_2$	
		303 K	308 K	303 K	308 K
-H	0	10.00	15.33	–3.00	–2.81
4-OH	–3.37	103.41	122.24	–1.98	–1.91
4-Me	–0.17	20.08	30.00	–2.69	–2.52
4-OMe	–0.27	17.00	26.66	–2.76	–2.57
3-OH	+0.12	13.66	20.01	–2.86	–2.69
3-Me	–0.07	15.33	22.00	–2.71	–2.65
4-Cl	+0.23	4.00	8.10	–3.39	–3.09
4-NO_2	+0.78	3.33	5.10	–3.48	–3.30
4-COOH	+0.41	0.80	1.50	–4.09	–3.82
3-NO_2	+0.71	0.45	0.83	–4.34	–4.07

The negative 'ρ' values in the reaction indicates the development of +ve charge at the reaction centre. The reaction is thus accelerated by electron-donating substituents, which help to delocalize the +ve charge in the intermediate complex and correspondingly retarded by electron-withdrawing substituents.

The introduction of electron-releasing group caused an increase in the rate of oxidation for phenol whereas electron-withdrawing groups caused a decrease in their rates. The rate decreases as the electron density at the reaction centre falls. Thus compounds withelectron-donating *p*-OH, *p*-CH_3 substituents show an enhanced rate of reaction and those with electron-withdrawing -NO_2, -Cl substituents are the least reactive.

The reaction is facilated by electron-releasing substituents. The order of rectivity is 4-OH > 2-OH > 4-CH_3 > 4-OCH_3 > 3-CH_3 > 3-OH > -H > 4-Cl > 3-NO_2 > 4-NO_2 > 4-COOH.

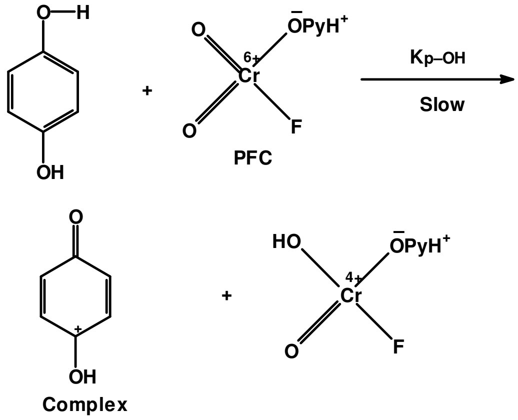


(1)

$$\sigma_{m\text{-}NO_2} = +0.71 \qquad \frac{K_{m-NO_2}}{K_H} = 0.045$$

The rate limiting step is slow with the formation of complex intermediate by eliminating H_2O molecule.

The *m*-nitro phenol (1) with $\sigma_{m\text{-}NO_2} = + 0.71$, is oxidized 0.045 times as fast as the unsubstituted phenol, the powerful electron-withdrawal strongly inhibiting the hydride ion transfer from *m*-nitro phenol to PFC.



(2)

$$\sigma_{p\text{-}OH} = -0.37 \qquad \frac{K_{p-OH}}{K_H} = 10.341$$

The *p*-hydroxy phenol (2) with $\sigma_{p\text{-}OH} = -0.37$, is oxidized 10.341 times as fast as the unsubstituted phenol, the powerful electron-releasing group assisting the hydride ion transfer more readily from *p*-hydroxy phenol to PFC and stabilising the intermediate complex leading to the positive charge.

Yukawa-Tsuno equation: The Yukawa-Tsuno equation (eqn. 3) is used for the introduction of a further parameter into the Hammett equation[9-11] *via* through-conjugation on the part of a *p*-substituent.

$$\log\frac{K_x}{K_H} = [\sigma_X + r(\sigma_X^+ - \sigma_X)] \qquad (3)$$

The 'r' is evaluated to establishing a set of new alternative σ_X values for the *p*-NO_2 and other comparable electron-withdrawing substituents. These revised values are generally referred to as $\sigma^-_{p\text{-}X}$ values and a number are compared with normal $\sigma_{p\text{-}X}$ values.

Exactly similar manner, a set of $\sigma^+_{p\text{-}X}$ values that make allowance for through conjugation by powerful electron-donating *p*-substitutents, a number of these revised figures are compared with the corresponding $\sigma_{p\text{-}X}$ values.

We can obtain ρ for the reaction by measuring K_X values for *m*-substituted compounds and then measure K_X for *p*-substituted compounds where the values of $\sigma_{p\text{-}X}$ and $\sigma^+_{p\text{-}X}$ or $\sigma^-_{p\text{-}X}$ are known.

Using Yukawa-Tsuno eqn. 3, 'r' is 1.00.

This will be so far advanced as the development of +ve charge in the intermediate if ρ is negtive (Table-2).

TABLE-2
REVISED SUBSTITUENT CONSTANTS FOR THE OXIDATION REACTION OF PHENOL BY PFC AT 308 K

Substituents	σ^+_{p-x}	σ_{p-x}
-OH	–0.50	–0.37
-Me	–0.16	–0.17
-OMe	–0.12	–0.27
	σ^-_{p-x}	σ_{p-x}
-Cl	+0.15	+0.23
-NO_2	+0.26	+0.78
-COOH	+0.56	+0.41

Exner's plot: To justify the application of the Hammett equaton, Exner's plot[12,13] of log k_2 at 298 K *vs.* log k_2 at 318 K drawn.

The Exner's plot for the oxidation of phenol by PFC is linear with slope is *ca.* 1 (Fig. 1).

Linear free-energy relationships can have mechanistic implication. If plot log k_2 *vs.* σ_X is linear, it implies that all reactions so correlated (throughout the series) follow a same mechanism.

The magnitude of s and its negative sign indicates a large electron demand at the reaction centre. The oxidation of phenols reaction proceeds through a carbocationic intermediate.

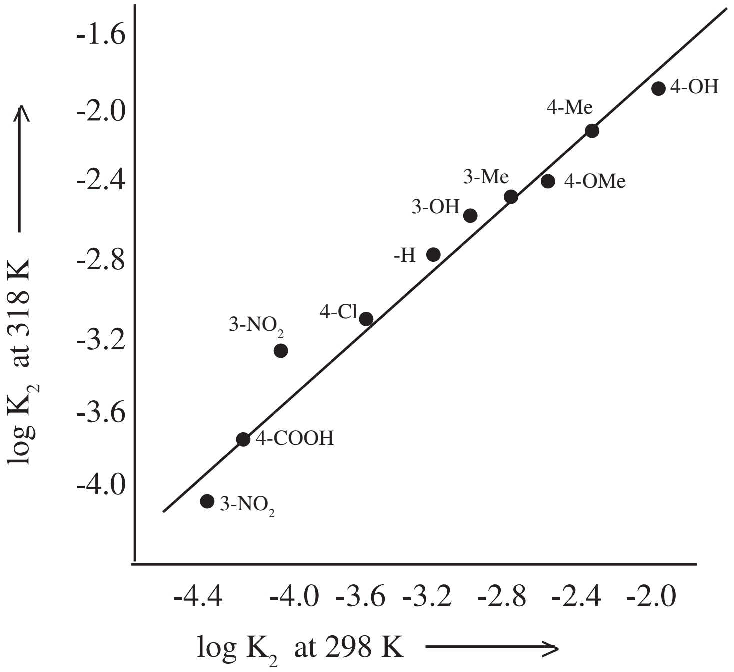


Fig. 1. Exner plot for the oxidation of phenol by PFC

$\Delta H^{\#}$ and $\Delta S^{\#}$ values agree with those of their oxidation reaction[1-5]. The relatively small positive values of $\Delta H^{\#}$ and large negative values of $\Delta S^{\#}$ show that the reactions pass through highly organised rate determining transition states in which bond formations as well advanced.

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