# Kinetics and Mechanism of Oxidation of Phenols by Pyridinium Fluorochromate in Glacial Acetic Acid

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Kinetics of oxidation of phenols such as *p*-hydroxy benzoic acid, *p*-chloro phenol, *m*-cresol, *p*-nitrophenol and *p*-cresol has been investigated, in glacial acetic acid as a solvent in the temperature range 25–45°C, using pyridinium fluorochromate (PFC) as a mild oxidation agent. The overall order of oxidation of the phenols is found to be two and the individual order as one in each reactant [the stoichiometry of the reaction is 1 : 1]. An increase in solvent polarity increases the reaction rate. The activation energy and other thermodynamic parameters are determined. A probable reaction mechanism is proposed.

Key words: Kinetics, mechanism, oxidation, phenols, pyridinium fluorochromate.

## INTRODUCTION

Pyridinium fluorochromate (PFC) is a very versatile oxidising agent for the oxidation of aromatic compounds. It is a neutral and mild ozidising agent and also a more convenient reagent for selective oxidation. Kinetics and oxidation of some organic substrates[1-5] by pyridinium dichromate have already been reported. The kinetics and mechanism of oxidation of phenols by pyridinium fluorochromate has been studied extensively in our laboratory in acetic acid medium.

## EXPERIMENTAL

Acetic acid (BDH) laboratory reagent (99.5% assay) was dried and distilled according to the method of Orton and Bradfield.

Pyridinium fluorochromate (PFC) was prepared from pyridine, aqueous 40% hydrofluoric acid, chromium(IV) oxide in the molar ratio (1 : 1.5 : 1 ). The bright orange crystalline reagent was isolated by filtration. It was then recrystallised from water (m.p. 106–109°C). The substrates were purified by recrystallisation. All other chemicals used were of A.R. grade.

**Kinetic Measurements:** The phenol and PFC solution in acetic acid ( 5 mL each) in test tubes and glass-stoppered bottles, respectively, were placed in a thermostat at required temperature. After the solutions reached the bath temperature, phenol solution was added quickly into PFC solution and the mixture was allowed to cool for a definite time, after which potassium iodide (10%, 5 mL) solution was added to stop the reaction. Immediately, after 1 min, the liberated iodine was titrated against standard sodium thiosulphate solution.

The kinetic studies were made by determining the concentration of PFC reacted iodometrically and expressing it as a function of time. 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 . The reaction follows 1 : 1 stoichiometry.
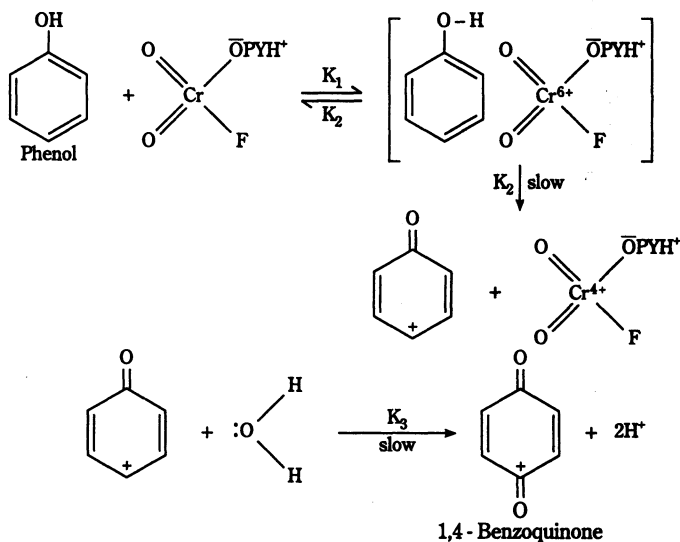
## RESULTS AND DISCUSSION

In the oxidation of phenols by PFC in glacial acetic acid solvent the overall order determined by fractional life method is found to be two (Table-1) at low and high concentrations. It is also proved by calculating second order rate constants ($K_2$) for the oxidation of phenols by PFC in acetic acid at 30°C by a graph of $1/(a-x)$ *vs.* time (t) to show overall order as two (Table-1).

The individual order for substrate and PFC determined by isolation method is found to be one (Table-2). It is also proved by calculating first order rate constants ($K_1$) for the oxidation of phenols by PFC in acetic acid at 30°C by a graph of log $(a-x)$ *vs.* time (t) to show overall order as one (Table-2)

The effect of solvent on the second order rate constant of substrate and PFC [0.05 m each] reaction is studied (Table-3). The results show that the dielectric constant and the rate of reaction are directly proportional to each other. The rate of reaction is faster in aqueous acetic acid than in 100% acetic acid.The effect of temperature on the reaction is studied by keeping the concentration of substrate = PFC = 0.05 M in 100% acetic acid. The second order rate constants are determined in the temperature range 25–45°C (Table-4). The energy of activation values are calculated from the graph relating to the rate constants at different temperatures, against 1/T. The other thermodynamic parameters are also calculated. The comparatively small value of energy of activation may be attributed to the rapid oxidation and the high value of energy of activation may be due to slow rate of reaction in the acetic acid medium.

On the basis of the observed results, the following mechanism can be proposed[6]:

**Mechanism**



1,4 - Benzoquinone

TABLE-1

DETERMINATION OF OVERALL ORDER OF OXIDATION OF PHENOLS BY PFC BY FRACTIONAL LIFE METHOD AT 30°C  [Phenol] = [PFC]

| Substrate | PFC reacted (%) | $C_1$ (mol $L^{-1}$) | $C_2$ (mol $L^{-1}$) | $t_1$ (sec) | $t_2$ (sec) | Order | $K_2 \times 10^5$ |
|---|---|---|---|---|---|---|---|
| *p*-hydroxy benzoic acid | 20 | 0.050 | 0.0250 | 160 | 300 | 1.90 | 0.84 |
| | | | | | | | 0.92 |
| | 20 | 0.025 | 0.0125 | 300 | 550 | 1.86 | 0.91 |
| *p*-chloro phenol | 20 | 0.050 | 0.0250 | 90 | 186 | 2.03 | 7.56 |
| | | | | | | | 7.64 |
| | 20 | 0.025 | 0.0125 | 186 | 340 | 1.86 | 7.41 |
| *m*-cresol | 20 | 0.050 | 0.0250 | 30 | 62 | 2.04 | 10.10 |
| | | | | | | | 10.18 |
| | 20 | 0.025 | 0.0125 | 62 | 108 | 1.92 | 10.08 |
| *p*-nitro phenol | 20 | 0.050 | 0.0250 | 54 | 110 | 2.00 | 2.86 |
| | | | | | | | 2.92 |
| | 20 | 0.025 | 0.0125 | 110 | 218 | 1.98 | 2.94 |
| *p*-cresol | 20 | 0.050 | 0.0250 | 27 | 56 | 2.03 | 12.48 |
| | | | | | | | 12.59 |
| | 20 | 0.025 | 0.0125 | 56 | 110 | 1.96 | 12.41 |

$C_1$ and $C_2$ = Initial concentrations; $t_1$ and $t_2$ = Time required for constant percentage of reaction

TABLE-2

DETERMINATION OF INDIVIDUAL ORDER OF OXIDATION OF PHENOLS BY PFC IN ACETIC ACID AT 30°C

| Substrate | PFC reacted (%) | $C_1$ (mol $L^{-1}$) | $C_2$ (mol $L^{-1}$) | $t_1$ (sec) | $t_2$ (sec) | Order | $K_1 \times 10^5$ |
|---|---|---|---|---|---|---|---|
| **p-Hydroxy benzoic acid** | | | | | | | |
| (a) order in *p*-hydroxy benzoic acid | 20 | 0.010 | 0.0050 | 62 | 74 | 1.16 | 2.26 |
| [PFC] = 0.05 M | 20 | 0.005 | 0.0025 | 74 | 78 | 1.12 | 2.50 |
| | | | | | | | 2.23 |
| (b) order in PFC [*p*-hydroxy benzoic | 20 | 0.010 | 0.0050 | 44 | 56 | 1.20 | 1.03 |
| acid] = 0.05 M | 20 | 0.005 | 0.0025 | 56 | 68 | 1.20 | 1.09 |
| | | | | | | | 1.11 |
| **p-Chloro phenol** | | | | | | | |
| (a) order in *p*-chloro phenol [PFC] | 20 | 0.010 | 0.0050 | 40 | 48 | 1.23 | 2.71 |
| = 0.05 M | 20 | 0.005 | 0.0025 | 48 | 56 | 1.23 | 2.68 |
| | | | | | | | 2.64 |
| (b) order in PFC [*p*-chloro phenol] | 20 | 0.010 | 0.0050 | 106 | 120 | 1.17 | 1.55 |
| = 0.05 M | 20 | 0.005 | 0.0025 | 120 | 136 | 1.17 | 1.54 |
| | | | | | | | 1.41 |
| **m-Cresol** | | | | | | | |
| (a) order in *m*-cresol [PFC] | 20 | 0.010 | 0.0050 | 310 | 365 | 1.17 | 4.10 |
| = 0.05 M | 20 | 0.005 | 0.0025 | 365 | 400 | 1.11 | 4.12 |
| | | | | | | | 4.09 |
| (b) order in PFC [*m*-cresol] | 20 | 0.010 | 0.0050 | 190 | 220 | 1.16 | 5.70 |
| = 0.05 M | 20 | 0.005 | 0.0025 | 220 | 250 | 1.11 | 5.71 |
| | | | | | | | 5.70 |

| Substrate | PFC reacted (%) | $C_1$ (mol $L^{-1}$) | $C_2$ (mol $L^{-1}$) | $t_1$ (sec) | $t_2$ (sec) | Order | $K_1 \times 10^5$ |
|---|---|---|---|---|---|---|---|
| **$p$-Nitro phenol** | | | | | | | |
| (a) order in $p$-nitro phenol [PFC] | 20 | 0.010 | 0.0050 | 40 | 48 | 1.20 | 2.81 |
| = 0.05 M | 20 | 0.005 | 0.0025 | 48 | 54 | 1.22 | 2.80 |
| | | | | | | | 2.81 |
| (b) order in PFC [$p$-nitro phenol] | 20 | 0.010 | 0.0050 | 30 | 36 | 1.23 | 4.16 |
| = 0.05 M | 20 | 0.005 | 0.0025 | 36 | 42 | 1.20 | 4.18 |
| | | | | | | | 4.12 |
| **$p$.Cresol** | | | | | | | |
| (a) order in $p$-cresol [PFC] | 20 | 0.010 | 0.0050 | 62 | 68 | 1.28 | 3.10 |
| = 0.05 M | 20 | 0.005 | 0.0025 | 68 | 76 | 1.11 | 3.12 |
| | | | | | | | 3.09 |
| (b) order in PFC [$p$-cresol] | 20 | 0.010 | 0.0050 | 42 | 50 | 1.22 | 5.16 |
| = 0.05 M | 20 | 0.005 | 0.0025 | 50 | 62 | 1.21 | 5.16 |
| | | | | | | | 5.18 |

TABLE -3

SOLVENT EFFECT

Temperature = 30°C, [PFC] = [Phenol] = 0.05 M

| Solvent % AcOH | Dielectrical constant (D) | $K_2 \times 10^5$ (mol $L^{-1}$ sec$^{-1}$) | | | | |
|---|---|---|---|---|---|---|
| | | Substrate | | | | |
| | | $p$-hydroxy benzoic acid | $p$-chloro phenol | $m$-cresol | $p$-nitro phenol | $p$-cresol |
| 100 : 0 | 6.15 | 0.86 | 7.48 | 10.12 | 2.90 | 12.50 |
| 95 : 5 | 8.75 | 1.66 | 8.20 | 10.96 | 3.10 | 12.74 |
| 90 : 10 | 10.77 | 2.22 | 8.64 | 11.86 | 3.48 | 12.98 |
| 85 : 15 | 12.66 | 2.98 | 8.98 | 12.60 | 3.90 | 13.10 |
| 80 : 20 | 15.22 | 3.33 | 9.40 | 13.52 | 4.10 | 13.40 |

TABLE-4

SECOND ORDER RATE CONSTANTS OF OXIDATION OF PHENOLS BY PFC IN
ACETIC ACID AT DIFFERENT TEMPERATURES

[Phenol] = [PFC] = 0.05M

| Substrate | $K_2 \times 10^5$ (mol $L^{-1}$ sec$^{-1}$) | | | | | $\Delta E^{\#}$ (kJ mol$^{-1}$) | $\Delta H^{\#}$ (kJ mol$^{-1}$) | $-\Delta S^{\#}$ | $\Delta G^{\#}$ (kJ mol$^{-1}$) | log A |
|---|---|---|---|---|---|---|---|---|---|---|
| | Temperature (K) | | | | | | | | | |
| | 298 | 303 | 308 | 313 | 318 | | | | | |
| $p$-Hydroxy benzoic acid | 0.40 | 0.80 | 1.58 | 2.96 | 4.10 | 96.40 | 93.85 | 32.44 | 83.92 | 11.52 |
| $p$-Chloro phenol | 6.82 | 7.44 | 8.12 | 8.92 | 9.46 | 77.06 | 74.76 | 78.33 | 50.98 | 9.15 |
| $m$-Cresol | 6.25 | 10.00 | 18.07 | 25.00 | 29.60 | 64.25 | 61.90 | 118.21 | 25.70 | 7.07 |
| $p$-Nitro phenol | 2.10 | 2.94 | 3.30 | 4.20 | 4.92 | 48.18 | 45.78 | 181.56 | 10.08 | 3.77 |
| $p$-Cresol | 12.08 | 12.56 | 12.77 | 13.12 | 13.33 | 31.98 | 29.52 | 223.18 | 38.72 | 1.60 |

$\Delta H^{\#}$, $\Delta S^{\#}$, $\Delta G^{\#}$ and log A are calculated at 308 K.

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