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Pyridinium Fluorochromate Oxidation of Salicylaldehyde in Acid Medium

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The kinetics of oxidation of salicylaldehyde by pyridinium fluorochromate has been studied in 90% acetic acid-water (v/v) medium. The reaction has unit dependence on each of the PFC, [H^+] and zero order with respect to substrate. Effect of neutral salt, *viz.*, NaCl shows the reaction to exhibit a negative salt effect. The rate of the reaction increases with increase in percentage of acetic acid. The reaction does not induce the polymerization of ethylacrylate. From the kinetic data obtained, the activation parameters have been calculated and a plausible mechanism has been proposed.

Key Words: Pyridinium fluorochromate, Oxidation, Salicylaldehyde.

INTRODUCTION

A good number of Cr(VI) complexes are being used in the oxidation of organic compounds especially in the construction of natural structures, synthesis of hormones, pheromones, prostaglandin and their synthones. Pyridinium fluorochromate (PFC) is reported to be neutral and mild oxidant for selective oxidations. Kinetics of oxidation of some organic substrates[1–7] by pyridinium fluorochromate has already been reported. However, the kinetics of oxidation of salicylaldehyde by PFC has not been reported so far and hence in the present work we report pyridinium fluorochromate oxidation of salicylaldehyde in acid medium.

EXPERIMENTAL

Materials and methods: PFC was prepared by dissolving chromium trioxide in water, hydrofluoric acid, adding pyridine and collecting the product[8]. Standard solution of PFC was prepared in aqueous acetic acid. Salicylaldehyde was distilled and the fraction collected at 197°C was used. Glacial acetic acid was purified by literature procedure[9]. All other chemicals used were of AnalaR grade. Triple distilled water was used throughout.

Kinetic measurements: The reaction was carried out under pseudo-first order conditions ([SAL] >> [PFC]) in glacial acetic acid containing sulphuric acid. The reaction was followed colorimetrically by observing the absorbance at 420 nm at different time intervals. The reactions were followed up to 70% completion. The pseudo-first order rate constants (K_{obs}) were evaluated from the linear plots of log [absorbance] *versus* time by the least squares method and were reproducible within ±3%.

Stoichiometry and product analysis: The stoichiometry of the reaction was determined for a number of reaction mixtures containing at least a threefold excess of oxidant over the substrate. The estimation indicated that one mole of the oxidant reacted with one mole of the substrate. The product salicylic acid was analyzed for m.p. and spectral data.

RESULTS AND DISCUSSION

The kinetics of oxidation of salicylaldehyde by pyridinium fluorochromate was investigated at several initial concentration of the reactants. When salicylaldehyde was in large excess, plots of log [absorbance] against time were found to be linear. From the slope of these plots, the pseudo-first order rate constant (K_{obs}) were obtained. The pseudo-first order rate constants in the oxidant calculated at different initial concentrations of the reactants were found to be independent of the substrate concentration. Such a behaviour is not uncommon with Cr(VI) oxidations and shows that monomeric Cr(VI) ion is the effective oxidant. As the concentration increases, a progressively smaller portion of the total amount is in the form of monomeric Cr(VI) ion and hence the rate constant decreases with increasing Cr(VI) concentration[10] (Table-1). Hence it is concluded that the reaction is first order with respect to the oxidant and zero order in salicylaldehyde.

TABLE-1
DEPENDENCE OF THE OXIDATION RATE ON PYRIDINIUM FLUOROCHROMATE (PFC) AND SALICYLALDEHYDE (SAL) AT 313 K

$[H^+] = 0.2$ mol dm^{-3}; Solvent = 90% AcOH, 10% H_2O (v/v)

[PFC] 10^3 (mol dm^{-3})	[SAL] 10^2 (mol dm^{-3})	k_1 10^4 (s^{-1})
3.25	8.00	3.43
7.70	8.00	2.30
9.75	8.00	1.65
13.00	8.00	1.01
16.25	8.00	0.82
7.70	8.00	2.30
7.70	12.00	2.26
7.70	14.00	2.32
7.70	24.00	2.29
7.70	28.00	2.31

The effect of acidity was studied by varying the concentration of sulphuric acid and the rate constants were found to increase with the increase in the concentration of sulphuric acid. A plot of log k against log $[H^+]$ gave a straight line with slope of unity, the correlation coefficient being 0.997 (Table-2). Added sodium chloride decreases the rate may be due to the interaction between chloride ion and protonated PFC and less reactive species[11] may be formed,

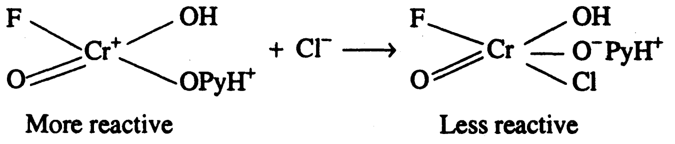

TABLE-2
DEPENDENCE OF RATE ON ACID AND SODIUM CHLORIDE AT 313 K

[PFC] = 7.70×10^{-3} mol dm^{-3}, [SAL] = 8.0×10^{-2} mol dm^{-3}
Solvent = 90% AcOH, 10% H_2O (v/v)

[H_2SO_4] (mol dm^{-3})	0.10	0.20	0.30	0.40	
$k_1 \times 10^4$ (s^{-1})	1.32	2.30	3.80	4.89	$r = 0.997$
[NaCl] (mol dm^{-3})	0.50	1.00	1.50	2.00	
$k_1 \times 10^5$ (s^{-1})	19.15	17.65	14.38	11.05	

The rate of the reaction increases with the increase in percentage of acetic acid. A straight line is obtained when the percentage of acetic acid is plotted against the rate constant (Table-3). In glacial acetic acid the reactive species may be acetochromate ion, powerful oxidizing species since the acetyl group increases the electron accepting power of chromium[12]. No turbidity has been noticed when a clear reaction mixture containing salicylaldehyde and PFC was allowed to stand with a drop of ethylacrylate ruling out a free radical mechanism.

TABLE-3
EFFECT OF CONCENTRATION OF SOLVENT ON REACTION RATE AT 313 K IN ACID MEDIA

[PFC] = 7.70×10^{-3} mol dm^{-3}, [SAL] = 8.0×10^{-2} mol dm^{-3}
[H^+] = 0.2 mol dm^{-3}

[AcOH—H_2O] (% v/v)	$k_1 \cdot 10^5$ (s^{-1})
60–40	10.11
70–30	14.43
80–20	18.66
90–10	23.05

The rate constants were measured at three different temperatures (Table-4) and the activation parameters have been calculated on the basis of the Arrhenius equation.

$\Delta H^{\#} = 52.19$ kJ mol^{-1}, $\Delta S^{\#} = -59.18$ cals deg^{-1}
$\Delta G^{\#} = 127.24$ kJ mol^{-1} at 303 K, $E_a = 54.70$ kJ mol^{-1}, $\log A = 7.61$

TABLE-4
DEPENDENCE OF THE OXIDATION RATE ON TEMPERATURE

[PFC] = 7.70×10^{-3} mol dm^{-3}, [SAL] = 8.0×10^{-2} mol dm^{-3}
[H^+] = 0.2 mol dm^{-3}, Solvent = 90% AcOH, 10%H_2O (v/v)

Temperature (K)	$k_1 \cdot 10^4$ (s^{-1})
303	1.22
313	2.30
323	4.61

Mechanism

In aqueous solutions of Cr(VI) at concentrations lower than 0.05 mol dm^{-3}, the monomeric form predominates. In this investigation the oxidant concentration is very low and under this condition the active oxidizing species is either $HCrO_4^-$ or acetochromate ion; a rate law has been derived to explain satisfactorily the observed facts.

$$HCrO_4^- + H^+ \xrightarrow{k_1} H_2CrO_4; \qquad \text{Slow}$$

$$H_2CrO_4^- + \text{Substrate} \xrightarrow{k_2} \underset{\substack{\downarrow \\ \text{Product}}}{\text{Intermediate}}; \qquad \text{Fast}$$

The rate equation becomes,

$$\text{Rate} = k_1[\text{PFC}][H^+]$$

The above rate law explains the first order dependence of the reaction rate on the oxidant and $[H^+]$.

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