

SUBSTITUTED AROMATIC ANILS - A KINETIC STUDY USING PYRIDINIUM CHLOROCHROMATE (PCC)

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ABSTRACT : The kinetics of co - oxidation study of anils and oxalic acid by PCC in aqueous acetic acid had been studied under different experimental conditions. The order is one with respect to oxalic acid , anil , and PPC. The order is 1.5 with respect to $[H^+]$.

The oxidation was found to increase with increase of perchloric oxalic acids. The rate of the reaction was increased by the addition of $NaClO_4$.

The protonated species of the oxidant is involved in the rate - determining step. The effect of various meta and para - substituted anils on the reaction rate had been studied at four different temperatures viz., 35 , 40 , 45 and 50 °c and the thermodynamic parameters are also calculated. The analysis of rate constants of ortho substituents reveals that the localized and delocalized effects are major components while steric effect place only the minor role.

KEYWORDS : anils , PCC , rate , parameters , localized and delocalized

I. INTRODUCTION

The kinetics of oxidation reactions and the elucidation of the reaction mechanisms from the kinetic data have always been the most fascinating subjects in chemistry. In any kinetic investigation one may be interested to arrive at [i] the relationship between the rate and various factors like concentration of the reactants , temperature , reaction medium etc., and [ii] the interpretation of the empirical rate laws in the light of mechanism proposed.

II. GENERAL CHARACTERISTICS OF PYRIDINIUM CHLOROCHROMATE (PCC)

The kinetics and mechanism of oxidation reactions using Chromium (VI) oxidants are fairly wellstudied.¹⁻⁵ In recent ears a significant number of reactions has been reported with PCC .

PCC also known as Corey's reagent , was first prepared by Corey et al.^{6,7}

It is a complex of Chromium trioxide , Pyridine and hydrochloric acid.

The pure sample of PCC is quite stable for more than a month . Its solution in water and in acetic acid are also fairly stable. Its dilute solution either in water or in acetic acid shows maximum absorption in the UV region at $\lambda = 350$ nm . It liberates iodine quantitatively from acidified potassium iodine solution.

III.PREPARATION OF PYRIDINIUM CHLOROCHROMATE (PCC)

PCC was prepared by the method of Corey and Suggs.^{6,7}

To 184 ml of 6 ml of HCl (1: 1 mol.) was added 100 g of CrO_3 rapidly with stirring. After five minutes the homogeneous solution was cooled to 0 °c and 79.1 g (1ml) Pyridine was carefully added over 10 minutes. Recooling to 0 °c gave an yellow or orange solid (PCC)which was collected on a sintered glass funnel and dried for 1 h in vacuum (yield 180.8 g-84%).

IV.PURIFICATION OF ACETIC ACID

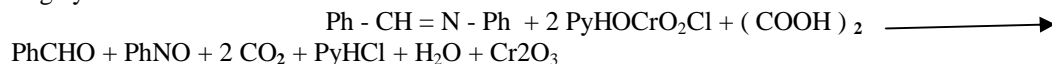
Acetic acid of AR grade was first refluxed with Chromium trioxide (20 g per litre) for 4 h . and then distilled. It was refluxed again with Chromium trioxide (2g per litre) for 2h. then it was fractionated through a Dufton column and the fraction at 117 - 118 ° was collected.

Purification of water

De -ionised water was distilled twice over Potassium permanganate in an all glass coming vessel. All the aqueous solutions were prepared using this double - distilled water.

V. STOICHIOMETRY

The stoichiometry of the reaction was determined by carrying out several sets of experiments with varying amounts of PCC largely in excess over anil. The estimation of unreacted PCC showed that one mole of anil reacts with two moles of PCC.



VI. PRODUCT ANALYSIS

Under kinetic condition the reaction was carried out and the products were separated and analysed. The products obtained were analysed by Co-TLC and IR spectrum as previously reported. It showed that benzaldehyde and nitrobenzene were products formed in the reaction. The liberation of CO₂ during the oxidation was detected as described earlier.

VII. KINETIC MEASUREMENTS

The reactions were carried out in 60% (v/v) acetic acid - water under pseudo - first order conditions taking always the substrate in excess. The solutions of the described concentrations were prepared.

1. PCC in water
2. Anil in acetic acid
3. Oxalic acid in water
4. Perchloric acid in water
5. Aluminium nitrate in water
6. Sodium perchlorate in water.

All the solutions were kept in a thermostat at constant temperature. The measurements were made between 30^o c to 45^o c . the required volumes of these solutions for each run were mixed and 2 ml aliquots of the reaction mixture were pipette out at convenient time intervals and quenched in 10 ml 3 % KI solution acidified with 3 M H₂SO₄ (10ml). the liberated iodine was titrated with standard sodium thiosulphate using starch. The pseudo - first order rate constants were evaluated from log titre values verses time plots.

VIII. RESULTS AND DISCUSSION

Experimental results indicate that the rate of oxidation of anils by Cr(VI) in the presence of oxalic acid is several times greater than the independent oxidation rates of anils and oxalic acid by Cr(VI)

In order to understand the nature of oxidized products of anils and to study the structure - reactivity relationships , we have undertaken the kinetic study of the PCC oxidation in acetic acid medium in the presence of oxalic acid.

8.1. Effect of varying PCC concentration

The reaction was investigated by varying the concentration at constant substrate concentration . The reaction was found to be first order with respect to PCC [Table - 1.2]

Table -1.2

$$\begin{aligned} [\text{Anil}] &= 1.5 \times 10^{-2} \text{ M} & \text{ACOH} : \text{H}_2\text{O} &= 70:30 \text{ (V/V)} \\ [\text{H}_2\text{C}_2\text{O}_4] &= 5.0 \times 10^{-2} \text{ M} & \text{Temp.} &= 35^{\circ} \text{ c} \\ [\text{HClO}_4] &= 3.87 \times 10^{-3} \text{ M} & & \end{aligned}$$

[PCC] x 10 ³	Kobs. X 10 ⁴ s ⁻¹
1.2	1.932
1.5	1.921
2.00	1.811

8.2. Effect of varying the concentration of Anil

The reaction was carried out under pseudo – first order conditions . In this study , the concentration of PCC , Oxalic acid , Perchloric acid and percentage of oxalic acid were kept constant and the concentration of the alone varied . The reaction was found to be first order with respect to anil . [Table - 1.3]

Table - 1.3

$$\begin{aligned}
 [\text{PCC}] &= 1.5 \times 10^{-3} \text{ M} & \text{ACOH :H}_2\text{O} &= 70:30 \text{ (V/V)} \\
 [\text{H}_2\text{C}_2\text{O}_4] &= 5.0 \times 10^{-2} \text{ M} & \text{Temp.} &= 35^\circ \text{ c} \\
 [\text{HClO}_4] &= 3.87 \times 10^{-3} \text{ M} & &
 \end{aligned}$$

[ANIL] x 10 ²	Kobs. X 10 ⁴ s ⁻¹
1.00	1.08
1.50	1.923
2.50	2.785
3.00	3.512

The reaction was found to be first order with respect to Anil.

8.3.Effect of varying solvent Composition

The reaction was studied by the different composition of acetic acid under constant [Reactants]. It was found that as the percentage of acetic acid increased, the rate decreased. [Table – 1.4]

Table – 1.4

$$\begin{aligned}
 [\text{ANIL}] &= 1.5 \times 10^{-3} \text{ M} & [\text{HClO}_4] &= 3.87 \times 10^{-3} \text{ M} \\
 [\text{H}_2\text{C}_2\text{O}_4] &= 5.0 \times 10^{-2} \text{ M} & \text{Temp.} &= 35^\circ \text{ c}
 \end{aligned}$$

% AcOH	Kobs. X 10 ⁴ s ⁻¹
40	3.921
50	3.207
60	3.256
70	1.932

It was found that the rate decreases with increase of percentage of acetic acid.

8.4.Effect of varying Oxalic acid

The reaction was carried out under by varying, the concentration of, Oxalic acid and by keeping other [reactans] constant. . The result indicate that as the concentration of oxalic acid increased, the rate constant also increased. [Table – 1.5]

Table -4

$$\begin{aligned}
 [\text{ANIL}] &= 1.5 \times 10^{-2} \text{ M} & \text{ACOH :H}_2\text{O} &= 70:30 \text{ (V/V)} \\
 [\text{HClO}_4] &= 3.87 \times 10^{-3} \text{ M} & \text{Temp.} &= 35^\circ \text{ c}
 \end{aligned}$$

[H ₂ C ₂ O ₄] x 10 ⁴	Kobs. X 10 ⁴ s ⁻¹
5.0	1.932
7.5	2.872
10.0	3.871
12.	5.965

It was found that the rate increases with increase of concentration of oxalic acid.

8.5.Effect of varying Perchloric acid

The reaction was studied by varying the concentration of perchloric acid and by keeping other [reactants] constant. The result indicate that as the concentration of Perchloric acid increased, the rate constant also increased.

[Table – 1.6]

Table -1.6

$$\begin{aligned}
 [\text{ANIL}] &= 1.5 \times 10^{-2} \text{ M} & \text{AcOH} : \text{H}_2\text{O} &= 70:30 \text{ (V/V)} \\
 [\text{H}_2\text{C}_2\text{O}_4] &= 5.0 \times 10^{-2} \text{ M} & \text{Temp.} &= 35^\circ \text{ c}
 \end{aligned}$$

$[\text{HClO}_4] \times 10^4$	$K_{\text{obs}} \times 10^4 \text{ s}^{-1}$
3.90	1.932
5.80	2.785
7.70	2.952
9.70	4.609

Effect of varying Sodium Perchlorate

To follow the Primary Salt effect, the reaction was studied with varying concentration of Sodium Perchlorate by keeping other [reactants] constant. It was found that as the concentration of Sodium Perchlorate increased, the rate constant also increased. This shows that the participation of ions which are similar in their sign or dipole-ion interaction in the rate determining step. [Table 1.7]

Table – 1.7

$$\begin{aligned}
 [\text{ANIL}] &= 1.5 \times 10^{-2} \text{ M} & \text{AcOH} : \text{H}_2\text{O} &= 70:30 \text{ (V/V)} \\
 [\text{H}_2\text{C}_2\text{O}_4] &= 5.0 \times 10^{-2} \text{ M} & [\text{HClO}_4] &= 3.87 \times 10^{-3} \text{ M} \\
 [\text{PCC}] &= 1.2 \times 10^{-3} \text{ M} & \text{Temp.} &= 35^\circ \text{ c}
 \end{aligned}$$

Table 2.5

$[\text{NaClO}_4] \times 10^3$	$K_{\text{obs}} \times 10^4 \text{ S}^{-1}$
0.00	1.932
2.50	3.548
5.00	4.657
7.50	5.086
10.00	5.799

Effect of MnSO4

The reaction rate decreases tremendously with the increase in the concentration of MnSO4 [Table - 1.8] This may be due to the formation of Cr(VI) in the rate determining step.

Table - 1.8

$$\begin{aligned}
 [\text{ANIL}] &= 1.5 \times 10^{-2} \text{ M} & \text{AcOH} : \text{H}_2\text{O} &= 70 : 30 \text{ (V/V)} \\
 [\text{H}_2\text{C}_2\text{O}_4] &= 5.0 \times 10^{-2} \text{ M} & [\text{PCC}] &= 1.2 \times 10^{-3} \text{ M} \\
 [\text{HClO}_4] &= 3.87 \times 10^{-3} \text{ M} & \text{Temp.} &= 35^\circ \text{ C}
 \end{aligned}$$

$[\text{MnSO}_4] \times 10^4$	$K_{\text{obs}} \times 10^4 \text{ S}^{-1}$
0.00	1.932
1.00	1.053
2.00	0.723
3.00	0.575

8.6.Effect of temperature

The rate of oxidation of some *meta* and *para* substituted anils had been studied at four different temperatures viz., 35^o c, 40^o c, 45^o c and 50^o c . It was observed , as we expected ,that the rate increases very much with increase of temperature . [Table – 1.9]

Table – 1.9

[Substrate] = 1.5 x 10⁻² M ACOH :H₂O = 70:30 (V/V)
 [H₂C₂O₄] = 1.0 x 10⁻⁴ M [PCC] = 1.2 x10⁻³ M
 [HClO₄] = 4.0 x 10⁻³ M

S.No.	Substituents	Kobs. X 10 ⁴ s ⁻¹			
		35 ^o	40 ^o	45 ^o	50 ^o
1	H	1.932	3.335	4.127	6.735
2	P -CH ₃	3.91	6.123	8.315	10.371
3	p-OCH ₃	6.220	9.132	12.612	16.431

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