

# Kinetics of Oxidation of Aromatic Anil by Pyridinium Dichromate

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**ABSTRACT** : 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. In this paper we have studied the kinetics of oxidation of aromatic anil by Pyridinium dichromate

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

## I.INTRODUCTION

Among oxo derivatives of variable valence metals , Chromium compound play the most important role , in oxidative reaction . A number of Chromium reagents are readily available . Almost every oxidisable functional group may undergo Chromium oxidation .Chromium ( VI ) containing reagents include Chromium acid , dichromate ion , Chromyl chloride , chromyl acetate , t – butyl Chromate , Chromyl nitrate and Co – ordination complexes of Chromium trioxide .<sup>1-2</sup>

Chromium ( VI ) oxidations are usually performed under acidic condition . Co – solvents like ( Jones' reagent ) benzene , methylenechloride ( Two Phase system ) are often added in order to deal with water insoluble organic complexes . The oxidation rate is generally high under acid catalysed conditions , however the low pH of the reaction medium and the presence of water favouring hydrolytic condition exclude the use of this class of reagents for the oxidation of molecules containing acid sensitive groups.[1]

Polymer supported Chromium ( VI ) reagents have also been developed. These reagents offer the advantage of reducing the work of procedure to more filtration . Recently some neutral or almost neutral Chromium (VI) reagents have been developed to effect oxidation under mild conditions.[2]

Pyridinium Chlorochromate (PCC) introduced by Corey et al<sup>3</sup> is widely used in the oxidation of alcohols. Pyridinium flourochromate has a less pronounced acidity and is an effective agent for the oxidation of Plicyclic organic substitutes . PFC was developed by Bhattacharjee and coworker .[3]<sup>4</sup>

In 1986 , Narayanan and Balasuramaniam<sup>5</sup> introduced Pyridinium bromochromate . This is an efficient oxidant for alcohols and a brominating agent as well .

Firouzahadi and Coworkers used Zinc chromates. This is a very useful reagent for the oxidation of variety of organic compounds , including alcohols , oximes , olefins and aromatic hydrocarbons.[4][5]

They have also shown chromium peroxide complexes as versatile , mild and efficient oxidants in organic synthesis.

Chlorotrimethyl Silone , Imidazolium dichromate , 2,2' – Bipyridyl chlorochromate (BPCC) and the corresponding chromate (BPC) have been proposed as oxidants for the oxidation of the hydroxyl group to thr carbonyl group.

4 – ( dimethyl amino ) – pyridinium chlorochromate and chromyl nitrate have been shown to be efficient and mild oxidant in aprotic media.

Naphthyridium chlorochromate , Pyrazinium chlorochromate, tetrabutyl ammoniumchlorochromate, dimethylpyrazole chromate , tetrabutyl ammonium dichromate ,

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Pyridine complex of oxodiperoxochromium and the dipyridine complex of chromium trioxide are some of the Chromium (VI) oxidants introduced in the last twenty years.

Quinolinium Chlorochromate was used by Bhavani et al to oxidize methyl phenyl sulphoxides.[6]

Quinolinium dichromate was introduced by Balasubramanian and Prathiba<sup>6</sup> as an effective oxidant under non – aqueous conditions.

Pyridium Chlorochromate (PCC) is irreplaceable in the generation of functional groups in highly unsaturated carbinols and pyrrols . yet mildly acidic character of Pyridinium chlorochromate precludes its use with acid sensitive substrates or products. Pyridium Chlorochromate oxidation has been investigated under various condition on different substrates .[7]

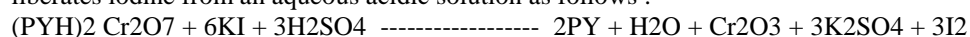
Despite the introduction of numerous oxidants based on chromium (VI) not much work has been done to investigate the mechanism of oxidation in these cases.

## II.PYRIDIDIUM DICHROMATE AS AN OXIDANT

Pyridium dichromate in acetic anhydride was shown to be an efficient oxidant for alcohols by Anderson and coworkers .

Pyridium dichromate (PDC) ( C<sub>3</sub>H<sub>5</sub>NH)<sup>+</sup> 2 Cr<sub>2</sub>O<sub>7</sub> a stable bright orange solid ( mp. 144 – 146<sup>0</sup> c) is simply prepared in quantity by dissolving CrO<sub>3</sub> in a minimum of water, adding Pyridine and collecting the precipitated product. The composition and structure of the product was confirmed by elemental analysis and infrared spectrum ( nujoil null ) which showed bands at 930,875,765 and 730 cm<sup>-1</sup>(characteristic of dichromate ion 27 ).

PDC is very soluble in water , dimethylformamide , dimethyl sulphoxide or dimethyl acetamide and the solutions are relatively stable.[8] It is sparingly soluble in methylchloride , ethanol – free chloroform of acetone , and not noticeably soluble in hexane , toluene ether or ethylacetate . Although PDC dissolves in acetonitrile , the solution is not stable .Most of the experiments have been carried out with solution of PDC in DMF or in methylene chloride suspensions. It liberates iodine from an aqueous acidic solution as follows :



## IV.REACTIONS OF PDC

Pyridium dichromate (PDC) in N,N – dimethyl formamide or dichloromethane is nearly neutral non – aqueous chromium (VI) oxidant. This species probably present in the Sarret and Conferth oxidizing mixtures. Although specific reference has been made to oxidation of alcohols by Pyridium dichromate itself in a short note 28 , there is no indication of any unusual effectiveness , utility , or advantage to be gained by the preformed pyridium dichromate as a discrete oxidizing species before Corey and Schnuidt prepared it in 1979.

Solutions of Pyridium dichromate in DMF rapidly oxidize allylic alcohols<sup>44</sup> to alpha , beta – unsaturated carbonyl compounds at 0<sup>0</sup> C. Kinetics and mechanism of oxidation of cyclic ketoximes by Pyridium dichromate and Quinolinium dichromate was investigated by Chidambaranathan et al. <sup>7</sup>

Oxidation kinetics of Cyclanols by Pridiniumdichromate was studied by Padma et al

Kinetics and mechanism of oxidation of some *ortho*- substituted benzyl alcohol by PDC was studied by Kabilan and Thenmozhi.

Kinetics and mechanism of oxidation of some substituted phenylmethyl sulphoxide using PDC was reported by Meenakshisundaram et al. <sup>8</sup>

Oxidation of S – phenylmercaptoacetic acid and phenoxyacetic acid by PDC was studied by Kabilan and Krishnasamy.<sup>9</sup>

Gurumurthy et al <sup>10</sup> investigated a comparative study on the kinetics of oxidation of some secondary alcohols by 1 – chlorobenzotriazole and PDC .

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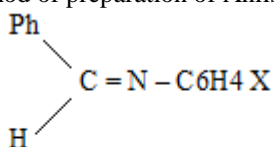
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## V.EXPERIMENTAL

### 5.1.PREPARATION OF ANILS

General method of preparation of Anils :



Where X = H , p - CH<sub>3</sub> , p - OCH<sub>3</sub> , p - Cl , p - Br , P - COOH ,  
p - NO<sub>2</sub> , m - CH<sub>3</sub> , m - Cl , m - NO<sub>2</sub>

The anils were prepared 87a by refluxing equimolar quantities of benzaldehyde and aniline or substituted anilines in alcohol for about 2 to 3 hrs. The resulting solution was cooled and poured into the cold water . The precipitated anil was filtered , washed , dried and recrystallised from alcohol. The purity of anils were checked by determining their melting points ( Table 1.1).

Table – 1.1

S.No.	R'		m.pt. 0 C	
	R'	R'	Observed	Literature
1	H	H	54.5	54
2	p - CH <sub>3</sub>	H	36.0	35
3	p -OCH <sub>3</sub>	H	61.0	60
4	p - Cl	H	62.5	62
5	p -Br	H	57.0	56 – 57
6	PCOOH	H	134.0	135
7	p - NO <sub>2</sub>	H	121.0	120
8	m - Cl	H	58.5	58
9	m - CH <sub>3</sub>	H	114.0	115
10	m - NO <sub>2</sub>	H	65.0	66

### 5.2.Preparation Of Pyridinium Chlorochromate (PDC)

Pyridine ( 80.6 ml ) was gradually added to a cooled solution of 100 gm ( 1 mol ) of Cr<sub>2</sub>O<sub>3</sub> in 100 ml water at 30 C . The solution was distilled with 400 ml of acetic acetone and cooled to 20 c . After 3 hrs. the orange crystals were collected , washed with acetone and dried in vacuuo.

### 5.3.Purification of Acetic acid

Acetic acid of AR grade was first refluxed with chromium trioxide ( 20g per litre ) for 4hrs. and then distilled . It was refluxed again with Chromium trioxide again with chromium trioxide ( 2g per litre ) for 2 hrs. Then it was fractionated through a Dufton column and the fraction at 117 – 118<sup>0</sup> was collected.

### 5.4.Purification of water

De – ionized water was distilled over Potassium Permanganate in an all glass corning vassel . All the aqueous solutions were prepared using this double – distilled water .

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## VI.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.[7]

1. Anil in acetic acid
2. PCC in water
3. Sodium perchlorate in water
4. Perchloric acid in water

All the solutions were thermostated atleast one hour before use .

The progress of the reaction was monitored by withdrawing aliquots from the reaction mixture at regular intervals of time and estimating the unreacted PDC by iodometric method.

## VII.PRODUCT ANALYSIS

The reactants in the ratio anil : PDC ( 1 : 10 ) in the 70 % acetic acid were mixed under kinetic conditions . The products of oxidation were identified as the corresponding benzaldehyde and nitrosobenzene . benzaldehyde was characterized as the 2, 4 – dinitrophenyl hydrozone derivative .[8] The remaining solution on evaporation yielded nitrosobenzene , which was identified by its characteristic UV spectrum .

## VIII.STOICHIOMETRY

The stoichiometry of the reaction was determined by carrying out several sets of experiments with varying amounts of [PDC] largely in excess over [anil]. The estimation of unreacted PCC showed that one mole of anil reacts with two mole of PDC [ ie ., 1 :1)

## IX.RESULTS AND DISCUSSIONS

Kinetics and mechanism of several organic substrates by PDC 1- 12 were documented. But there are no systematic kinetic reports of the oxidation of Osmium ( VIII ) . Catalysed oxidation of benzaldehyde anils by Os ( VIII ) complexes . This prompted us to undertake the title for investigation .

Effect of Varying concentration of PDC

The kinetics of the above reaction was investigated with [ PDC ] = 1.0 – 3.0 / 10<sup>-3</sup> M and [ Anil] = 2.0 / 10<sup>-2</sup> M respectively.

### 9.1.Effect of varying the concentration Oxidant

The oxidation of aromatic anil by PDC was investigated at several initial concentrations of the oxidant in 70 % acetic acid media. The plot of log [PDC] Vs time ie., the plot log titre Vs time was linear indicating a first order dependence of rate on PDC ; values of the pseudo first order rate constants  $k_{obs}$  were calculated from the plots , according to the first order equation by the method of least squares .[9]. reaction was found to be First order in PCC as shown by the linear plot of log titre value vs time (Table – 2.1 ).

Table – 2.1

$$[ANIL] = 9.995 \times 10^{-3} \text{ M} \quad \text{AcOH : H}_2\text{O} = 70 : 30 \text{ (V/V)}$$

$$[ \text{HClO}_4 ] = 7 \times 10^{-3} \text{ M} \quad \text{Temp.} = 35^\circ \text{C}$$

[ PCC ] X 10 <sup>4</sup>	$K_{obs} \times 10^4 \text{ S}^{-1}$
5.35	5.02
10.6	5.89
16.0	5.92
21.3	5.95

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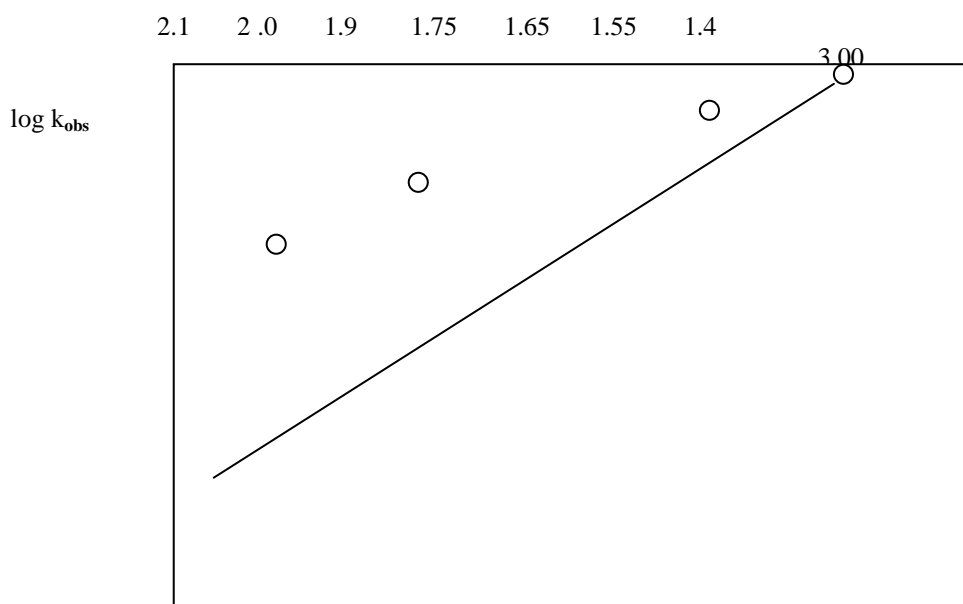
### 9.2.Effect of varying the concentrations of Substrate

The reaction was carried out under with varying concentration s of Anil , always kept in excess , with constant concentrations of PDC.[10][11] The rate constant in k increased linearly with substrate concentration ( Fig. 1 ) with a slope of 0.62 indicating fractional order dependence on the substrate concentration ( Table – 2 .2)

Table – 2.2

[PDC] =  $1.06 \times 10^{-5}$  M      AcOH : H<sub>2</sub>O = 70 : 30 (V/V)  
[ HClO<sub>4</sub> ] =  $7 \times 10^{-3}$  M      Temp. = 35 °C

[ ANIL ] X 10 <sup>-3</sup>	K <sub>obs</sub> x 10 <sup>4</sup> S <sup>-1</sup>
9.99	5.890
14.99	7.210
19.99	8.830
24.97	10.450



### 9.3.Effect of varying Solvent Composition

The reaction was studied under the three different acetic acid composition under constant [reactants]. It was found that as the percentage of acetic acid increased , the rate constant increased. The enhanced rate may be attributed to the formation of acetochromate ion . The acetyl group enhances the electron accepting power of chromium , there by fecilitating the reaction [ Table 2.3]

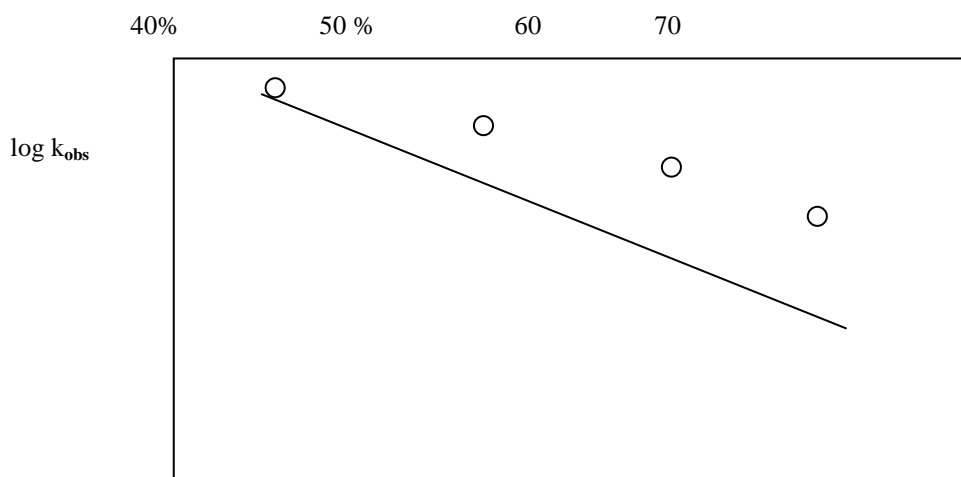
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Table – 2.3  
 [ANIL] =  $9.995 \times 10^{-3}$  M      AcOH : H<sub>2</sub>O = 70 : 30 (V/V)  
 [ HClO<sub>4</sub> ] =  $7 \times 10^{-3}$  M      Temp. = 35 °C

% AcOH	K <sub>obs</sub> × 10 <sup>4</sup> S <sup>-1</sup>
60	3.21
70	5.89
80	12.27
70	1.932



### 9.4.Effect of varying Perchloric Acid

The reaction was studied with varying concentration of Perchloric acid and by keeping other [reactants] constant.[12] It was found that as the concentration of Perchloric acid increased, the rate constant also increased [ Table 1.6]. The plot of log [ HClO<sub>4</sub> ] against logK<sub>obs</sub>. gave slope of 0.47 ( Table 2.4 ; Fig. 2 )

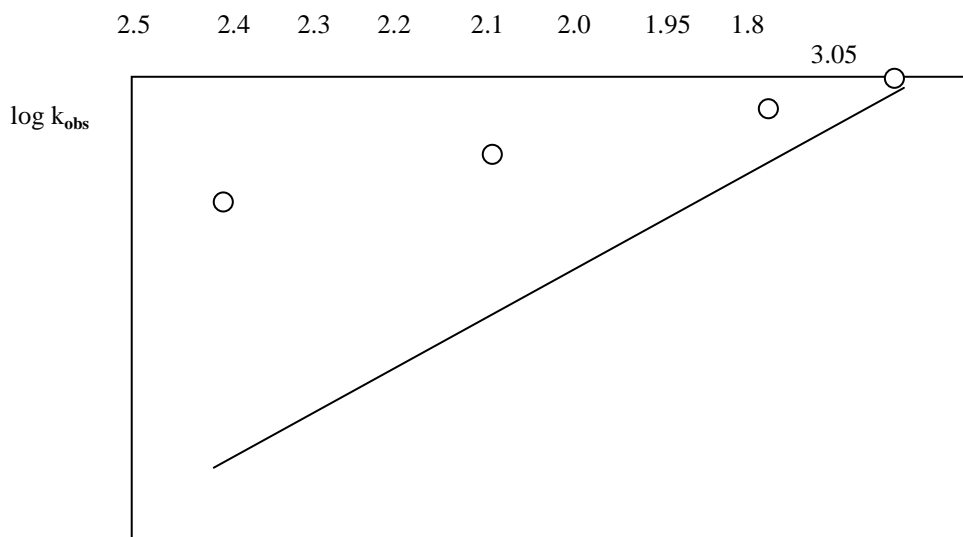
Table – 2.4  
 [ANIL] =  $9.995 \times 10^{-3}$  M      AcOH : H<sub>2</sub>O = 70 : 30 (V/V)  
 [ HClO<sub>4</sub> ] =  $7 \times 10^{-3}$  M      Temp. = 35 °C

[ HClO <sub>4</sub> ] × 10 <sup>3</sup>	K <sub>obs</sub> × 10 <sup>4</sup> S <sup>-1</sup>
3.5	4.63
7.0	5.89
10.5	7.07
14.0	9.21

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### 9.5.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. [13]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 2.5].]

Table 2.5

[ANIL] = 9.995 X 10<sup>-3</sup> M      AcOH : H<sub>2</sub>O = 70 : 30 (V/V)  
[ HClO<sub>4</sub> ] = 7 X 10<sup>-3</sup> M      Temp. = 35 °C

[ Na <sub>2</sub> ClO <sub>4</sub> ] X 10 <sup>3</sup>	K <sub>obs</sub> x 10 <sup>4</sup> S <sup>-1</sup>
10.00	5.89
14.98	6.02
19.98	6.65

### 9.6.Effect of MnSO<sub>4</sub>

The reaction rate decreases tremendously with the increase in the concentration of MnSO<sub>4</sub> [ Table - 2.6 ] This may be due to the formation of Cr(VI) in the rate determining step.

Table - 2.6

[ANIL] = 9.995 X 10<sup>-3</sup> M      AcOH : H<sub>2</sub>O = 70 : 30 (V/V)  
[ HClO<sub>4</sub> ] = 7 X 10<sup>-3</sup> M      Temp. = 35 °C

[ MnSO <sub>4</sub> ] X 10 <sup>3</sup>	K <sub>obs</sub> x 10 <sup>4</sup> S <sup>-1</sup>
0.00	5.89
1.00	4.05
2.00	3.81
3.00	3.51

### 9.7.Effect of Temperature

The rate of oxidation of some meta , and para – substituted benzaldehyde anils has been studied at four different temperatures viz., 30<sup>0</sup> , 35<sup>0</sup> , 40<sup>0</sup> , 45<sup>0</sup> c . The rate of the reaction increases with temperature as expected.[14] The K<sub>obs</sub> values were calculated ( Table 2.7 )

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Table – 2.7

[Substrate ] =  $9.99 \times 10^{-3} \text{M}$   
[ PDC ] =  $1.06 \times 10^{-5} \text{M}$

AcOH : H<sub>2</sub>O = 70 : 30 (V/V)  
[ HClO<sub>4</sub> ] =  $7 \times 10^{-3} \text{M}$

S.No.	Substituent	$K_{\text{obs}} \times 10^4 \text{ S}^{-1}$			
		30 <sup>0</sup>	35 <sup>0</sup>	40 <sup>0</sup>	45 <sup>0</sup>
1.	H	4.59	5.89	7.38	9.64
2.	P – CH <sub>3</sub>	5.35	7.25	9.01	11.20
3.	P – OCH <sub>3</sub>	6.45	8.45	9.53	13.98
4.	p - Cl	3.52	4.48	5.72	7.85
5.	p – NO <sub>2</sub>	1.80	2.24	3.09	4.03
6.	m – Cl	2.92	3.80	4.56	6.02
7.	m – NO <sub>2</sub>	1.85	2.35	3.38	4.32

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