

# Kinetics of Os (VIII) Catalysed Oxidation of Benzaldehyde Anils by PDC

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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 OS(VIII) catalysed oxidation of benzaldehyde anils by PDC

**KEYWORDS** : PDC , parasubstituted , delocalized and components

## 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 , Chromylnitrate and Co – ordination complexes of Chromium trioxide .<sup>1-2</sup>

Chromium ( VI oxidations are usually performed under acidic condition . Co – solvents like ( Jones's 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.

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 Pycyclic organic substitutes . PFC was developed by Bhattacharjee and coworker . [2]<sup>4</sup>

In 1986 , Narayanan and Balasuramian<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.

They have also shown chromium peroxide complexes as versatile , mild and efficient oxidants in organic synthesis.[3] 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 ammonium chlorochromate , dimethylpyrazole chromate , tetrabutyl ammonium dichromate ,

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

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Quinolinium Chlorochromate was used by Bhavani et al to oxidize methyl phenyl sulphoxides. 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 pyrals . 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 .

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.[4]

## II.REACTIONS OF PYRIDINIUM DICHROMATE

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 , 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 Schmidt<sup>1</sup> prepared it in 1979.

Solutions of Pyridium dichromate in DMF rapidly oxidize allylic alcohols<sup>4</sup> to alpha , beta – unsaturated carbonyl compounds at 0 ° C. Kinetics and mechanism of oxidation of cyclic ketoximes by Pyridium dichromate and Quinolinium dichromate was investigated by Chidambaranathan et al<sup>2</sup>. Oxidation kinetics of Cyclanols by Pridiniumdichromate was studied by Padma et al <sup>3</sup>.

Kinetics and mechanism of oxidation of some *ortho*- substituted benzyl alcohol by PDC was studied by Kabilan and Thenmozhi.<sup>4</sup>

Kinetics and mechanism of oxidation of some substituted phenylmethyl sulphoxide using PDC was reported by Meenakshisundaram et al. <sup>5</sup> Oxidation of S – phenylmercaptoacetic acid and phenoxyacetic acid by PDC was studied by Kabilan and Krishnasamy.<sup>6</sup>

Gurumurthy et al <sup>7</sup> investigated a comparative study on the kinetics of oxidation of some secondary alcohols by 1 – chlorobenzotriazole and PDC .

## III.REACTIONS OF ANILS

Several oxidation of anils have been studied :

### 3.1.Effect of varying PCC concentration

The reaction was investigated by varying the concentration at constant substrate concentration .[5]The reaction was found to be first order with respect to PCC [ Table – 1.2 ]

Table -1.2

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

[ PCC ] x 10 <sup>3</sup>	Kobs. X 10 <sup>4</sup> s <sup>-1</sup>
1.2	1.932
1.5	1.921
2.00	1.811

### 3.2.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 . [6]The reaction was found to be first order with respect to anil . [ Table – 1.3 ]

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Table – 1.3

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

[ ANIL ] x 10 <sup>2</sup>	Kobs. X 10 <sup>4</sup> s <sup>-1</sup>
1.00	1.08
1.50	1.923
2.50	2.785
3.00	3.512

### 3.3.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 <sup>4</sup> s <sup>-1</sup>
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.

### 3.4.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 – 1.5

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

[H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ] x 10 <sup>4</sup>	Kobs. X 10 <sup>4</sup> s <sup>-1</sup>
5.0	1.932
7.5	2.872
10.0	3.871
12.	5.965

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### 3.5.Effect of varying Perchloric acid

The reaction was studied by varying the concentration of perchloric acid and by keeping other [reactants] constant. [7] The result indicate that as the concentration of Perchloric acid increased, the rate constant also increased. [ Table - 1.6 ]

Table -1.6

[ANIL] =  $1.5 \times 10^{-2}$  M      AcOH :H<sub>2</sub>O = 70:30 (V/V)  
[H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>] =  $5.0 \times 10^{-2}$  M      Temp. = 35 °c

[HClO <sub>4</sub> ] x 10 <sup>4</sup>	K <sub>obs</sub> . X 10 <sup>4</sup> s <sup>-1</sup>
3.90	1.932
5.80	2.785
7.70	2.952
9.70	4.609

### 3.6.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. [8] 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

[ANIL] =  $1.5 \times 10^{-2}$  M      AcOH :H<sub>2</sub>O = 70:30 (V/V)  
[H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>] =  $5.0 \times 10^{-2}$  M      [HClO<sub>4</sub>] =  $3.87 \times 10^{-3}$  M  
[ PCC ] =  $1.2 \times 10^{-3}$  M      Temp. = 35 °c

Table 2.5

[ NaClO <sub>4</sub> ] X 10 <sup>3</sup>	K <sub>obs</sub> x 10 <sup>4</sup> S <sup>-1</sup>
0.00	1.932
2.50	3.548
5.00	4.657
7.50	5.086
10.00	5.799

### 3.7.Effect of MnSO4

The reaction rate decreases tremendously with the increase in the concentration of MnSO<sub>4</sub> [ Table - 1.8 ] This may be due to the formation of Cr(VI) in the rate determining step.

Table - 1.8

[ANIL] =  $1.5 \times 10^{-2}$  M      AcOH : H<sub>2</sub>O = 70 : 30 (V/V)  
[H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>] =  $5.0 \times 10^{-2}$  M      [ PCC ] =  $1.2 \times 10^{-3}$  M  
[ HClO<sub>4</sub> ] =  $3.87 \times 10^{-3}$  M      Temp. = 35 °C

[ MnSO <sub>4</sub> ] X 10 <sup>4</sup>	K <sub>obs</sub> x 10 <sup>4</sup> S <sup>-1</sup>
0.00	1.932
1.00	1.053
2.00	0.723
3.00	0.575

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### 3.8 Effect of temperature

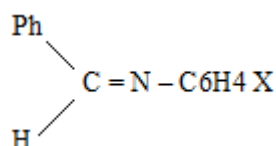
The rate of oxidation of some *meta* and *para* substituted anils had been studied at four different temperatures viz., 35<sup>0</sup> c , 40<sup>0</sup> c, 45<sup>0</sup> c and 50<sup>0</sup> c . [9]It was observed , as we expected ,that the rate increases very much with increase of temperature . [ Table – 1.9 ]

Table – 1.9  
 [Substrate] = 1.5 x 10<sup>-2</sup> M      ACOH :H2O = 70:30 (V/V)  
 [H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>] = 1.0 x 10<sup>-4</sup> M      [PCC ] = 1.2 x10<sup>-3</sup> M  
 [HClO<sub>4</sub>] = 4.0 x 10<sup>-3</sup> M      Temp. = 35<sup>0</sup> c

S.No.	Substituents	Kobs. X 10 <sup>4</sup> s <sup>-1</sup>			
		35 <sup>0</sup>	40 <sup>0</sup>	45 <sup>0</sup>	50 <sup>0</sup>
2	H	1.932	3.335	4.127	6.735
3	P -CH <sub>3</sub>	3.91	6.123	8.315	10.371
4	P – O CH3	6.22	9.132	12.612	16.431
5	p- Cl	1.023	2.425	3.671	4.923
6	m - Cl	0.705	1.412	2.213	3.824

## IV.EXPERIMENTAL

### 4.1. 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.[10] The purity of anils were checked by determining their melting points ( Table 2.1).

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Table – 2.1

S.No.			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

## 4.2.PREPARATION OF PDC

### 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.

### 4.3.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 . The remaining solution on evaporation yielded nitrozobenzene , which was identified by its characteristic UV spectrum .

### 4.4. Stoichiometry

The stoichiometry of the reaction was detrmind by carrying out several sets of experiments with varying amounts of [PDC] largely in excess over [anil].[11] The estimation of unreacted PCC showed that one mole of anil reacts with two mole of PDC [ ie ., 1 :1)

## V. DISCUSSION

Kinetics and mechanism of several organic substrates by PDC were documented ; but there are no systematic kinetics reports of the oxidation of Osmium (VIII) . Catalysed oxidation of benzaldehyde anils by Cr (VI) Complexes. This prompted us to undertake the title for investigation.

### 5.1.Effect of varying the 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>-3</sup> M respectively . Plot of log [ PDC ] versus time were linear , indicating a first order dependence on [ PDC]. The pseudo – first order rate constants k<sub>obs.</sub> calculated from the slopes of the above plots are found to be independent of the initial concentration of PDC . ( Table 3.1)

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Table 3.1  
[ANIL] =  $2.0 \times 10^{-2}$  M      AcOH : H<sub>2</sub>O = 70 : 30 (V/V)  
[HClO<sub>4</sub>] =  $7.0 \times 10^{-3}$  M      [ OsO<sub>4</sub> ] =  $1.0 \times 10^{-5}$  M  
Temp. = 40 °C

[ PDC] X 10 <sup>3</sup> M	K <sub>obs</sub> X 10 <sup>3</sup> S <sup>-1</sup>
1.0	9.87
2.0	10.02
3.0	9.95

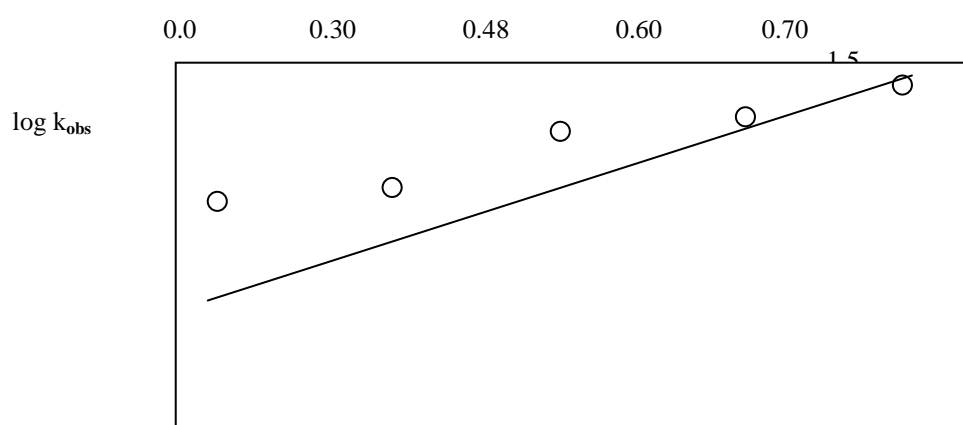
### 5.2.Effect of varying the of substrate

The concentration of Anil was varied  $1.0 - 5.0 / 10^{-2}$  M at fixed concentrations other reaction components. The rate of oxidation increases with increase of [ Anil] [Table 3.2 ]

Plots of log k<sub>obs</sub> versus log [ Anil ] gave straight line with slope equal to 1.09 [ Fig.1]. hence the order with respect to [substrate ] is unity. [12]

Table 3.2  
[PDC] =  $1.0 \times 10^{-3}$  M      AcOH : H<sub>2</sub>O = 70 : 30 (V/V)  
[HClO<sub>4</sub>] =  $7.0 \times 10^{-3}$  M      [ OsO<sub>4</sub> ] =  $1.0 \times 10^{-5}$  M  
Temp. = 40 °C

[ Anil] X 10 <sup>2</sup> M	k <sub>obs</sub> X 10 <sup>3</sup> S <sup>-1</sup>
1.0	4.45
2.0	9.87
3.0	15.70
4.0	21.76
5.0	28.14



### 5.3.Effects of varying concentration of Perchloric acid

The concentration of perchloric acid is varied from  $7.0$  to  $5.6 \times 10^{-3}$  M at a fixed concentration of other reaction ingredients. The rate of reaction increases with increase in [ HClO<sub>4</sub>] [ Table – 3.3 ]

The plots of log k<sub>obs</sub> versus log [ H<sup>+</sup> ] gave straight line with slope equal to 0.4 [ Fig.2]; hence the order with respect to [H<sup>+</sup>] is fractional .

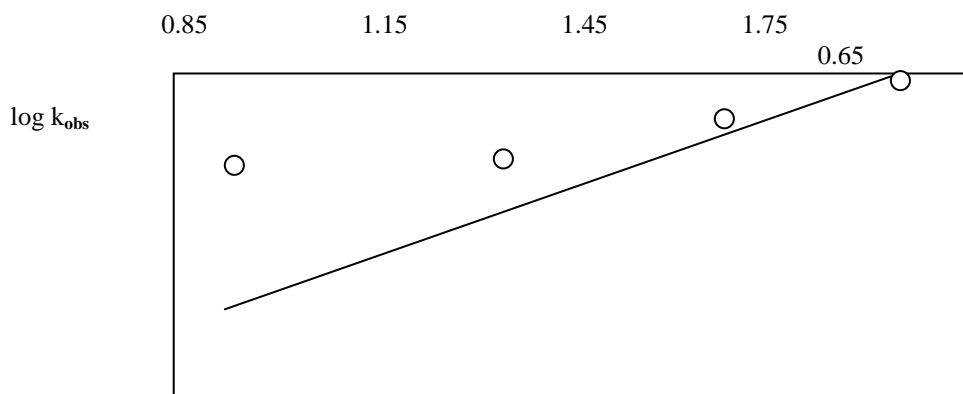
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Table 3.3  
 [Anil] =  $2.0 \times 10^{-2}$  M      AcOH : H<sub>2</sub>O = 70 : 30 (V/V)  
 [PDC] =  $1.0 \times 10^{-3}$  M      [OsO<sub>4</sub>] =  $1.0 \times 10^{-5}$  M  
 Temp. = 40 °C

[H <sup>+</sup> ] X 10 <sup>3</sup> M	k <sub>obs</sub> X 10 <sup>3</sup> S <sup>-1</sup>
7.0	4.45
14.0	5.72
28.0	7.52
56.0	8.81



### 5.4.Effects of varying [ OsO4]

The effect of [OsO<sub>4</sub>] has been studied by varying concentrations of OsO<sub>4</sub> at a given substrate concentration [ Table – 3.4] the rate was affected by increase of concentration in OsO<sub>4</sub>. The plot of log k<sub>obs</sub>. Versus log [OsO<sub>4</sub>] is linear ( r=0.999) with a slope of 0.46 [ Fig. 3]

Table 3.4  
 [Anil] =  $2.0 \times 10^{-2}$  M      AcOH : H<sub>2</sub>O = 70 : 30 (V/V)  
 [PDC] =  $1.0 \times 10^{-3}$  M      [OsO<sub>4</sub>] =  $1.0 \times 10^{-5}$  M  
 Temp. = 40 °C

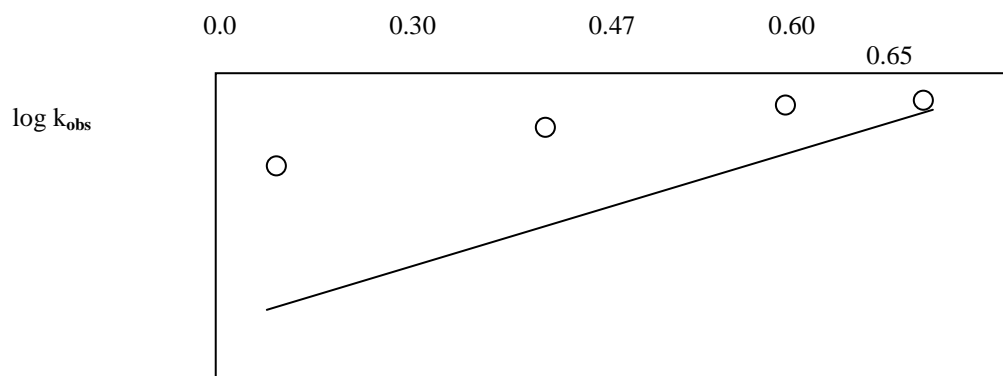
[OsO <sub>4</sub> ] X 10 <sup>5</sup> M	k <sub>obs</sub> X 10 <sup>3</sup> S <sup>-1</sup>
1	4.45
2	5.95
3	7.39
4	8.38



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### 5.5.Effects of Perchlorate

When the strength is increased by the of Sodium Perchlorate to the reaction mixture the  $k_{obs}$ . Is almost constant . It indicates the absence of ion – ion or ion – dipole interaction in the slow – step. [ Table 3.5]

Table 3.5

[Anil ] =  $2.0 \times 10^{-2}$  M      AcOH : H<sub>2</sub>O = 70 : 30 (V/V)  
[PDC] =  $1.0 \times 10^{-3}$  M      [ OsO<sub>4</sub> ] =  $1.0 \times 10^{-5}$  M  
Temp. = 40 °C

[OsO <sub>4</sub> ] X 10 <sup>5</sup> M	$k_{obs} \times 10^3 \text{ S}^{-1}$
1	4.45
2	5.95
3	7.39
4	8.38

### 5.6.Effect of solvent

The reaction is studied in acetic acid – water mixture of varying compositions. An increase in acetic acid , accelerate the reaction rate [ Table 3.6].

Table 3.6

[Anil ] =  $2.0 \times 10^{-2}$  M      AcOH : H<sub>2</sub>O = 70 : 30 (V/V)  
[PDC] =  $1.0 \times 10^{-3}$  M      [ OsO<sub>4</sub> ] =  $1.0 \times 10^{-5}$  M  
Temp. = 40 °C

% of Ac OH	$k_{obs} \times 10^3 \text{ S}^{-1}$
40 – 50	2.82
50 – 60	3.26
60 – 70	3.95
70 - 80	4.45

### 5.7. Test with Acrylonitrile

No polymerization was observed by the addition of Acrylonitrile to the reaction mixture showing the absence of free radicals.

### 5.8.Effect of temperature

The kinetic runs of some *meta* – and *para* – substituted anils have been studied at four different temperatures viz., 30 , 35 , 40 , 45<sup>0</sup> . the rate constant  $k_{obs}$ . Are given in the Table – 3.7. The thermodynamic parameters namely , enthalpy of activation and entropy of activation are calculated from the linear plots (  $k/ T$  ) against ( 1/T). (the logarithmic forms of Eyring's equation ) .

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Table 3.7  
 $[Anil] = 2.0 \times 10^{-2} M$        $AcOH : H_2O = 70 : 30 (V/V)$   
 $[PDC] = 1.0 \times 10^{-3} M$        $[OsO_4] = 1.0 \times 10^{-5} M$   
 $[HClO_4] = 7.0 \times 10^{-3} M$        $Temp. = 40^\circ C$

Temp. $^\circ C$	k <sub>obs</sub> $\times 10^3 S^{-1}$
30	2.21
35	3.55
40	4.45
45	7.20

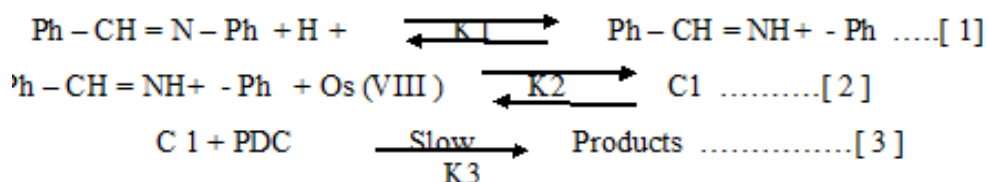
$$\Delta H^\ddagger = 57.86 \text{ KJ mole}^{-1}$$

$$\Delta S^\ddagger = 134.85 \text{ KJ mole}^{-1}$$

### VI.MECHANISM

The kinetics of oxidations of benzaldehyde anils by PDC in the presence of OsO<sub>4</sub> in acid medium is first order with respect to oxidant and fractional order with respect to OsO<sub>4</sub> and [H<sup>+</sup>]. The absence of Primary Salt effect shows that the slow – step in this reaction is only between neutral species. The possibility of radical formation is also ruled out by the presence of induced polymerization in the rate – determining step.

Based on these facts, the reaction mechanism Scheme – 3 has been proposed.



From the above mechanism the rate law is derived as follows :

$$\text{Rate} = k_3 [ C_1 ] [ PDC ] \dots\dots [ 4 ]$$

$$D[PDC] / dt = k_2 k_3 [ Anil ] [ H^+ ] [ OsO_4 ] [ PDC ] / ( 1 + k_2 [ Os(VIII) ] ) \dots\dots [ 5 ]$$

$$k_{obs} = k_1 k_2 k_3 [ Anil ] [ H^+ ] [ OsO_4 ] / ( 1 + k_2 [ Os(VIII) ] ) \dots\dots [ 6 ]$$

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