Kinetic and Mechanistic Study of Oxidative Transformation of Benzaldehyde by Pyridinium-Chlorochromate in Acetic acid-Water Medium

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Abstract-

Kinetic reaction of oxidative conversion of benzaldehyde by pyridinium chlorochromate (PCC) have been accomplished in acetic acid and water (50 %) solvent medium in the presence of $HClO_4$ at 308K temperature. This reaction kinetics for oxidation shows first order dependence with respect to substrate and hydrogen ion $[H^+]$. As the dielectric constant of solvent increases the rate of oxidation shows a corresponding decrease. All experiments were carried out at 360nm optical density. Activation parameter have been estimated. A mechanism was proposed by observing experiments.

Key words- Benzaldehyde, PCC, oxidation etc.

1. Introduction: -

Aromatic and aliphatic aldehydes have many applications. Aromatic aldehydes act as a key chemical intermediate for the production of a variety of fine or special chemicals, such as

pharmaceuticals, drugs, dyestuffs, pesticides and perfume composition.

Oxidation of aldehydes into the corresponding carboxylic acids is one of the important methods in organic synthesis as the carboxylic acids are versatile intermediates in a variety of synthetic transformations[1]. A number of aromatic aldehydes have been oxidized by oxidants like imidazolinium dichromate[2], quinolinium dichromate[3] , quinolinium bromochromate[4-5] pyridinium bromochromate[6] , quinolinium fluorochromate[7] , 4(dimethylamino) pyridinium chlorochromate[8] in aqueous media.

The oxidation of benzaldehyde to benzoic acid is a very important oxidative transformation in organic chemistry. Oxidizing agents often used are PCC, PDC, and numerous other Cr(VI) complexes. PCC is well recognised as correy's[9] reagent is very useful oxidizing agent for oxidative conversion of benzaldehyde. PCC

is a convenient oxidizing agent which is used in oxidation of alcohols[10-12], amino acids[13-14], aldehydes[15-18], L-cysteine and aniline[19] etc.

The present work reports the kinetics of oxidation of substituted benzaldehydes by PCC and evaluates thereaction constants. Mechanistic aspects are also discussed.

2.Material and Method: -

All chemicals used were of A.R. grade (E. Merck), the liquid benzaldehydewere used after distillation.The oxidant pyridiniumchlorochromate (PCC),(Aldrich) was used. Acetic acid (A.R. grade) was distilled before use. Perchloric acid (E.Merck) was used after a check of its physical constants.As a source of [H^+], $HClO_4$ was used. PCC, benzaldehyde, acid solutions were prepared in acetic acid water mixture (50% v/v) ofdesired strength. Purity of benzaldehyde was checked by B.P.

PCC was prepared in the lab by the method described by Bhattacharjee et al. (1982). The orange solid, which separated and collected on sintered glass funnel dried for 1 Hour in vacuum. Its purity was checked by iodometric method, m.p. determination and IR spectral analysis. Standard PCC solution was prepared in used solvent mixture of acetic acid and water. All calibrate borosil glassware were used for experiments. For maintain required temperature electronic thermostat was used.

3.Kinetic measurements: -

The progress of the reaction was followed by measuring the absorbance of PCC at **lambda** max 360 nm in one cm thick cell placedin the thermos stated compartment of UV/VIS spectrophotometer VISI-SCAN-167(Systronics). No other reactant orproduct has any significant absorption at this wavelength.Pseudo-first order conditions were attained by keeping a largeexcess (·10 or greater) of the substrate over the oxidant. Thereactions were carried out at a constant temperature(± 0.1 K). The solvent was Acetic acid-water mixture (50% V/V) and the reactions were followedby monitoring the decrease in the concentration of PCC up to 80% completion of the reaction. The pseudofirst-order rate constant, (k_{obs}) was evaluated from the linear($R^2 >$ 0.994) plot of log[PCC] against time. Duplicate kinetic runs showed that the rate constants were reproducible to within $\pm 3\%$. The specific rate constant, k_s, was evaluated from the relation: $k_s = k_1 / [BA][H^+]$. The reactions were also carried out in acetic acid-water mixtures to study the effect of dielectric constant on the rate of the reactions. All reactions were performed under N_2 atmosphere.

4. Results and discussion

Benzaldehyde is oxidized by PCC in Acetic acid-water mixture (50% V/V) medium in the presence of $HClO_4$at 303 K maintaining pseudo-first-order conditions and the kinetic results along with conditions are given in Tables 1–3

The product analysis and stoichiometric determination suggested the following overall reaction:

$$Cr(VI) + Benzaldehyde \underset{}{\overset{H^+}{\rightleftharpoons}} Benzoic\ acid + Cr(III)$$
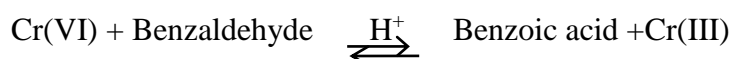
4.1. Stability of the oxidant (Pyridinium chlorochromate)

The solution of PCC in Acetic acid-water mixture solvent obeys Beer–Lambert's Law at k 360 nm. There was no change in optical density and spectra of PCC solution, without substrate in solvent mixture on long standing or heating up to 333–343 K.

4.2. Effect of varying oxidant concentration

The concentration of PCC was varied in the range 1×10^{-3} to 7×10^{-3} mol dm^{-3} at constant [BA], [HClO$_4$] at 308 Kand the rates were measured. (Table 1) The near constancyin the value of k_{obs} (pseudo-first-order rate constant) irrespectiveof the concentration confirms the first order dependenceon PCC.The reactions show first order kinetics with respect to PCC i.e. log absorbance versus time is straight line for more than 82% reaction.

4.3 Effect of substrate concentration: -

The concentration of the substrate BA was varied in therange 1.00×10^{-2} to 7.00×10^{-2} mol dm^{-3} at 308 K and keepingall other reactant concentrations as constant and the rates weremeasured (Table-1). The rate of oxidation increased progressivelyon increasing the concentration of BA. Plot of log k_{obs} versus log [substrate] is a straight line. The plot oflog k_1 versus log[BA] gave the slope of 1.112 (R^2 =0.99)indicating first order dependence on BA. Under pseudofirst-order conditions, the plot of $1/k_1$ versus 1/[S] (where S isthe substrate concentration) was linear with a negligible interceptindicating that the intermediate formed in a slow step gotconsumed in a subsequent fast step.

4.4 Effect of HClO$_4$ concentration:

Perchloric acid has been used as a source of H+ in reaction medium.The concentration of HClO$_4$ was varied in the range 0.50 to 2.0 mol dm-3 keeping all other reactant concentration as constant at 308 K and the rates were measured (Table-1). The acidcatalyzed nature of this oxidation is confirmed by an increasein the rate on the addition of HClO$_4$. The plot of k_1 versuslog[H$^+$] is a straight line (R2 =0.993) with a slope of 1.066.Therefore, order with respect to H$^+$is one. PCC may becomeprotonated in the presence of acid. The protonated PCC mayfunction as an effective oxidant[20] similar to that of chromium trioxide oxidation[21]. Protonated PCC is likely to be a better electrophileand a better oxidant compared to a neutral one. The effectsof the dielectric constant of the medium and the ionic strengthindicate the reaction to be of ion–dipole type. Thus in the reaction mechanism the protonated PCC species behaves as a dipole.

4.5 Effect of solvent composition:

The influence of solvent polarity has been studied in aceticacid–water mixture. The acetic acid (v/v) has been variedfrom 30% to 70% at fixed ionic strength, [BA], [PCC],[H+] and temperature (Table- 4). The rate of oxidation increaseswith decrease in polarity of solvent. In other words,a decrease in rate with increase in dielectric constant is observed,suggesting that a medium of low dielectric constant favorsthe oxidation process. This is due to polar character of thetransition state as compared to that of reactants. The plot oflog k1 versus 1/D (dielectric constant) is linear with positiveslope suggesting the presence of either dipole–dipole or ion–dipoletype of interaction between the oxidant and the substrate[22,23]. Amis[24] holds the view that in an ion–dipole reaction involving a positiveionic reactant, the rate would decrease with increasing dielectric constant of the medium and if the reactant were to be a negatively charged ion, the rate would increase with the increasing dielectric constant. In this case there is a possibilityof a positive ionic reactant, as the rate decreases with theincreasing dielectric constant of the medium. Due to the polar

nature of the solvent, transition state is stabilized, i.e., the polarsolvent molecules surround the transition state and result inless disproportion.

4.6 Effect of temperature: -

The reactions were studied in the temperature range from 303to 323 K to calculate the rate constants and various thermodynamicparameters (Tables 1 and 2). A plot of log k1 versus 1/T(inverse of absolute temperature) is a straight line with negativeslope. This shows that Arrhenius Equation is valid for thisoxidation. The large negative value of entropy of activation DS# suggests slow bimolecular reaction in the rate determiningstep and that the rate-determining transition state is less disorderlythan the reactants, i.e., a rigid transition state by an associativeprocess[25]. This transition statecomplex is unstable and the chromate ester bond breaks toform the product. According to Pearson[26] also the large negative entropy value obtained in thepresent study, suggests that the solvent molecules are stronglyoriented or 'frozen' around the ions thereby resulting in theloss of entropy and accounts for the lowering of rate coefficientvalues with increase in the polarity of the medium.

4.7. Effect of ionic strength:

The effect of ionic strength was studied to observe the effect of salt on the rate of oxidation in Debye–Huckel limit by varying concentration of $NaClO_4$ from 0.001 to 0.01 mol dm^{-3} providedother conditions being constant (Table-3). The rate of reaction remains almost unchanged while increasing the $NaClO_4$ concentration. It proves that interaction in rate determining step is not of ion–ion type[27].

4.8. Induced polymerization of acrylonitrile:

The reaction mixture in kinetic conditions to which a known amount of acrylonitrile (free from stabilizer) scavenger had been added initially, was kept for 24 h in an inert atmosphere

of N_2 fails to induce the polymerization of acrylonitrile. Then on dilution of the reaction mixture with methanol, no turbidity occurred, indicating the absence of free radical intervention.

5. Mechanism and rate law:

The order with respect to both [PCC] and [BA] is unity atfixed [H^+]. The oxidant undergoes protonation. The observedsalt and solvent effects showed that the reaction is between anion and a dipole in the slow rds and the cationic species is carbonium ion. The protonated PCC reacts with this oxo ion (carbonium ion) to form achromate ester which is an unstable species. This unstable complex breaks fast to form the product. Scheme-1 and rate law is proposed to explain the kinetic observations.

CHO   PCC Or PDC   COOH
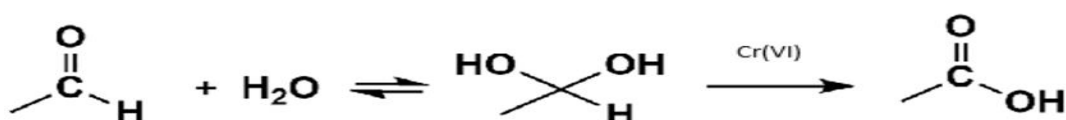
5. Conclusion

The oxidation of BA in partial non-aqueous medium by PCC proceedsvia the formation of an unstable chromate ester which isformed in the rate determining step. This unstable chromateester breaks to form the benzoic acid and Cr(III). PCC acts as two electron oxidant withoutinvolvement of free radicals in this oxidation.

Table- 1. Effect of [Subs] , [H$^+$], and Solvent Variations

[PCC] = 1x10 $^{-3}$ M,   T= 308K

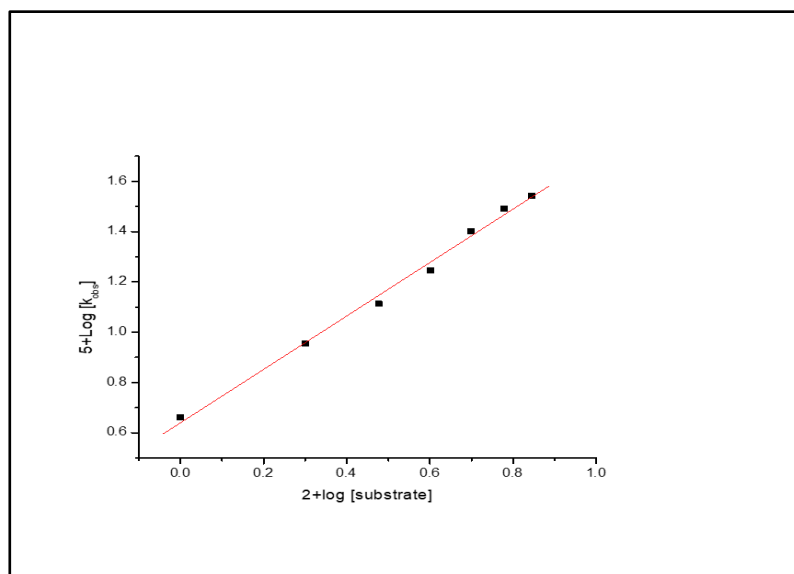| [Benzaldehyde] x 10 ^{2} M	[HClO$_4$]x 10 ^{3} M	% of Water in Water-acetic acid Mix	k x10^5 Sec^{-1}
1.0	0.5	50	4.58
2.0	0.5	50	9.02
3.0	0.5	50	12.98
4.0	0.5	50	17.03
5.0	0.5	50	22.02
6.0	0.5	50	25.96
7.0	0.5	50	30.01
1.0	0.5	50	4.58
1.0	0.75	50	6.68
1.0	1.0	50	8.9
1.0	1.25	50	11.29
1.0	1.5	50	12.98
1.0	2.0	50	17.56
1.0	0.5	30	3.37
1.0	0.5	40	3.93
1.0	0.5	50	4.58
1.0	0.5	60	5.30
1.0	0.5	70	8.07

Fig-VARIATION OF RATE WITH SUBSTRATE CONCENTRATION

log k_{obs} v/s log [substrate]

Table - 2 Effect of Temperature :
[Subs] = 1x 10^{-2}M , [HClO$_4$] = 0.5 M , [PCC] = 1x10^{-3}M

Temp. (in K)	k x10^5sec^{-1}
303	3.62
308	4.58
313	6.38
318	8.24
323	11.54

Table -3 Thermodynamic parameters for oxidation of benzaldehyde:

Log A	Energy of activation ΔEa $^{\#}$ KJmol^{-1}	Free Energy of activation ΔG $^{\#}$ KJmol^{-1}	Enthalpy of activation ΔH $^{\#}$ KJmol^{-1}	Entropy of activation ΔS $^{\#}$ Jmol^{-1}K^{-1}
6.04	47.25	85.66	44.7	-133.26

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