Asian Journal of Chemistry Vol. 19, No. 4 (2007), 2721-2728

Kinetic and Mechanistic Studies on the Oxidation of Benzaldehyde with Piperazinium Dichromate in Aqueous Acetic Acid Solution

V. KANNAPPAN* and K. PARAMESHWARI
Post Graduate and Research Department of Chemistry,
Presidency College, Chennai-600 005, India

This paper contains the results obtained in the detailed kinetic investigations on the oxidation of benzaldehyde by piperazinium dichromate (PZD) in 50 % aqueous acetic acid (v/v) solution. The order in substrate, order in oxidant are established by integral and differential methods. The influence of [$HClO_4$], temperature and addition of neutral salt on the kinetics of this reaction are studied. The activation parameters ($\Delta H^{\#}$, $\Delta S^{\#}$ and $\Delta G^{\#}$) are determined accurately for this reaction from the effect of temperature on the rate constant. On the basis of kinetic evidence and product analysis, a suitable mechanism has been proposed.

Key Words: Kinetics, Oxidation, Piperazinium dichromate, Benzaldehyde.

INTRODUCTION

Extensive kinetics studies have been made on the oxidation of several organic substrates by pyridinium cholorochromate, imidazolinium dichromate and quinolinium fluorochromate containing Cr(VI) by earlier workers. However, there are no reports so far on the kinetics of oxidation of these substrates with piperazinium dichromate. There are some reports on the oxidation of substituted benzaldehydes by quinolinium fluoro chromate[1] and pyridinium chlorochromate[2] in aqueous acetic acid solution. The oxidation of benzaldehydes by pyridinium fluorochromate[3] and aliphatic aldehydes by pyridinium fluorochromate[4], pyridinium bromochromate[5], quinolinium fluorochromate[6] and bipyridyl chlorochromate[7] in DMSO has also been reported. But, no detailed kinetic investigation has been done so far on the oxidation of benzaldehyde with piperazinium dichromate (PZD), which is mild, efficient and practical reagent for oxidation reactions. Hence, kinetic studies were made under different conditions of concentration, temperature and solvent polarity. In the present work, the kinetic and mechanistic aspects of benzaldehyde (BA) with piperazinium dichromate (PZD) is reported.

EXPERIMENTAL

All the chemicals used were of Analar grade. Fischer AR grade glacial acetic acid was further purified by the method of Orton and Bradfield[8]. Aqueous acetic acid, *i.e.*, 65, 60, 55 and 50% were prepared by mixing appropriate volumes of double distilled water and dry acetic acid. Double distilled water was prepared by distilling distilled water over alkaline potassium permaganate in an all glass distillation set. Merck sample of perchloric acid (60 % purity) was obtained and used as such for kinetic studies and potassium perchlorate AR made in Germany was used.

Piperazinium dichromate was prepared by Movassagh *et al.*[9] procedure and characterized it quantitatively by IR spectral data. The PZD prepared by this method was only 75 % pure and thus we modified the method. We prepared PZD by the following method.

Chromium(VI) oxide (0.046 mol) was mixed with 5 mL water, 6 mL 60% perchloric acid. This solution was added in portions to piperazine (0.0233 mol) in 10 mL water at room temperature and the mixture was stirred for 5 min. The bright orange solid formed was recrystallized from hot water, filtered under suction and washed with acetone and then with water. The solid was air-dried. It is estimated to be 99% pure by iodometric method.

Kinetic measurements: The kinetic runs were carried out at constant temperature in an electrically operated thermostat. The accuracy was ± 0.1ºC. It was provided with a Sunvic relay and the temperature was measured by using Jackson thermometer. The kinetics of reaction had been followed by estimating the unreacted oxidants in each case iodometrically towards a starch-iodide end point against standard sodium thiosulphate. The stoichiometry of the reaction between piperazinium dichromate and benzaldehyde was determined under kinetic concentrations and was found to be 2 : 3.

Product analysis: In the present work, the product formed in the reaction PZD (0.2 M) with benzaldehyde (0.1 M) was carefully analyzed and identified as benzoic acid using bicarbonate test which gave brisk effervescence with the product, establishing the presence of carboxylic group and the product was further identified by infrared studies.

RESULTS AND DISCUSSION

In the present study, the order in substrate, order in oxidant are determined for the oxidation of benzaldehyde with PZD in 50% aqueous acetic acid (v/v) at 303 K before determining activation parameters. The rate measurements were made under pseudo order condition and in the presence of 0.08 M perchloric acid to ensure chromium in +6 oxidation state in the solvent studied.

In order to determine the order with respect to (PZD), the rates were measured by taking (BA) in excess and keeping it constant and changing the (PZD). The plot of log (rate) against log (PZD) was linear (Fig. 1) with a slope of 0.5. Thus the order in (PZD) is 0.5. The values of log (rate) used in this plot are in Table-1.

TABLE-1

PZD-BA REACTION VARIATION OF [PZD]

Solvent = 50 % aqueous acetic acid (v/v) $[BA] = 0.2$ M

Temperature = 303 K $[HClO_4] = 0.08$ M

[PZD]/M	Rate/10^{-6}M,S^{-1}	3+log [PZD]	6+log (RATE)
0.015	9.714	1.1761	0.9874
0.010	7.333	1.0000	0.8653
0.008	5.666	0.9031	0.7533
0.006	4.222	0.7781	0.6255

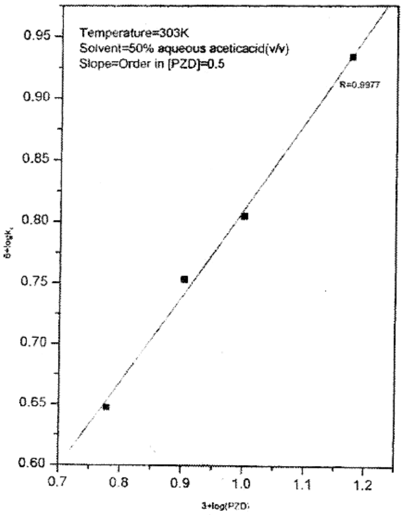


Fig. 1. Plot of 6+log k_1 against 3+log (PZD)

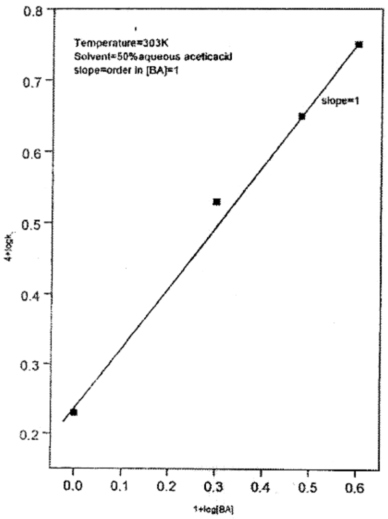


Fig. 2. Plot of 4+log k_1 *vs.* 1+log (BA)

To establish the order with respect to [BA], isolation technique was used. Runs were made by taking [BA] in large excess and varied. But, [PZD] was low and kept constant. The pseudo first order rate constant at various [BA] are given in Table-2.

The plot of $\log_1$ *vs.* log [BA] is linear (Fig. 2) with a slope of unity. Thus, the reaction is first order with respect to [BA].

It has been found that the oxidation of benzaldehyde in aqueous acetic acid by PZD was catalyzed by perchloric acid. In order to propose a

TABLE-2
PZD-BA REACTION VARIATION OF [BA]

Solvent = 50 % aqueous acetic acid (v/v) [PZD] = 0.01 M
Temperature = 303 K $[HClO_4]$ = 0.08 M

[BA],M	1+log [BA]	$K_1/10^{-4}$, S^{-1}	4+log k_1
0.1	0.00	1.706	0.23
0.2	0.30	3.378	0.53
0.3	0.48	4.478	0.65
0.4	0.60	5.629	0.75

suitable mechanism for the acid catalyzed oxidation of benzaldehyde, the effect of $[HClO_4]$ on the rate of the reaction was studied. It was found that the increase in $[HClO_4]$ increased the rate of the reaction. Rate constants were determined under identical conditions of [PZD], [BA] and temperature at various $[HClO_4]$. These values are presented in Table-3. Plot of k_1 *vs.* log $[HClO_4]$ is in Fig. 3. The plot is linear and from the slope, the order with respect to $[HClO_4]$ was calculated. The reaction is first order with respect to $[HClO_4]$.

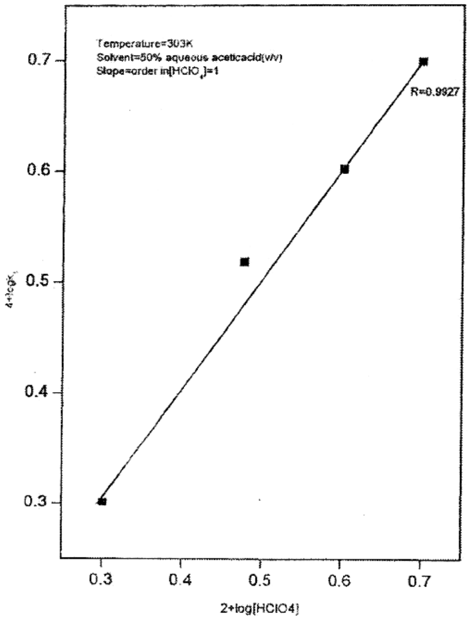


Fig. 3. Plot of 4+log k_1 against 2+log $[HClO_4]$

The influence of ionic strength was studied in the presence of $KClO_4$ of different concentration keeping other factors constants and there was virtually no effect of ionic strength on the rate constant. Thus, the reaction is of ion-dipole type.

TABLE-3
PZD-BA REACTION VARIATION OF [$HClO_4$]

Solvent = 50 % aqueous acetic acid (v/v) [PZD] = 0.01 M
Temperature = 303 K [BA] = 0.01 M

[$HClO_4$],M	$K_1/10^{-4}$, S^{-1}	2+log [$HClO_4$]	4+log k_1
0.02	2.000	0.3010	0.3010
0.03	3.333	0.4771	0.5185
0.04	4.000	0.6020	0.6020
0.05	5.000	0.6990	0.6990

The influence of solvent on the rate of the reaction was also investigated by varying the percentage of acetic acid and water. Fig. 4 is Amis plot while Fig. 5 is Laidler-Eyring plot. These plots indicate that the rate of the reaction decreases with increase in the dielectric constant of the medium. These observations indicate that the transition state may be less polar than the reactants.

TABLE-4
PZD-BA REACTION EFFECT OF TEMPERATURE

Solvent = 50% aqueous acetic acid (v/v) [PZD] = 0.01 M
[$HClO_4$] = 0.08 M [BA] = 0.1 M

Temperature	$1/T/10^{-3}$,K^{-1}	$k_1/10^{-4}$,S^{-1}	10+lnk_1	15+ln (k_1/T)
288	3.470	1.667	1.301	0.6377
293	3.410	2.000	1.483	0.8026
298	3.350	3.333	1.993	1.2960
303	3.300	4.000	2.176	1.4620

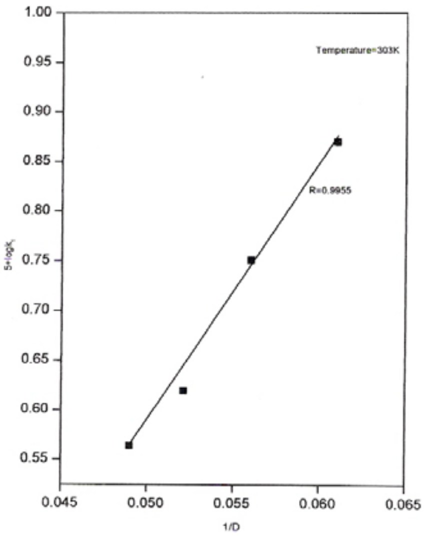


Fig. 4. Plot of 5+logk_1 *vs.* 1/D

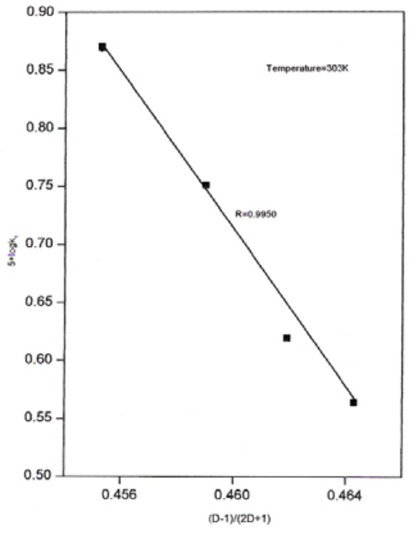


Fig. 5. Plot of 5+log k_1 *vs.* (D-1)/2D+1)

The reaction was studied at various temperatures to evaluate activation parameters. The pseudo first order rate constant at different temperatures are given in Fig. 6 and 7 and the values are given in Table-4.

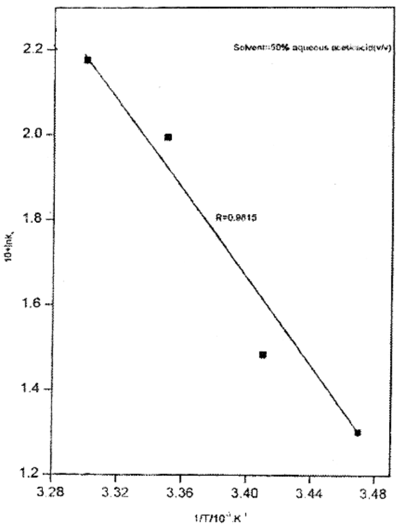


Fig. 6 Arrhenius plot

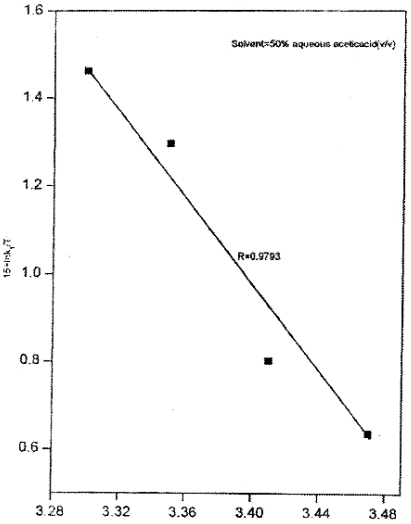


Fig. 7 Plot of 15+ln (k_1/T) *vs.* 1/T

TABLE-5
STOICHIOMETRY OF PZD-BA REACTION
Solvent = 50% aqueous acetic acid (v/v)
Temperature = 303 K

[BA]/M	[PZD]/M		[PZD]/M	Stoichiometry
	Initial	Unreacted	Consumed	[BA: [PZD]
0.02	0.08	0.0684	0.0116	1:0.58
0.03	0.03	0.0077	0.0273	1:0.78
0.04	0.04	0.0100	0.0300	1:0.75
0.04	0.04	0.0126	0.0324	1:0.72

TABLE-6
BENZALDEHYDE-PIPERAZINIUM DISCHROMATE REACTION
ARRHENIUS AND ACTIVATION PARAMETERS
[BA] = 0.1 M, [PZD] = 0.01 M, [$HClO_4$] = 0.08 M
Solvents = 50% aqueous acetic acid (v/v), Temperature = 298 K

$E_a/_{kJmol}{}^{-1}$	$\Delta H^{\#}$/kJmol^{-1}	$\Delta S^{\#}$/Jk^{-1}mol^{-1}	$\Delta G^{\#}$/kJmol^{-1}	A/s^{-1}
44.06	41.57	183	96.10	1.755 x 10^4

Mechanism

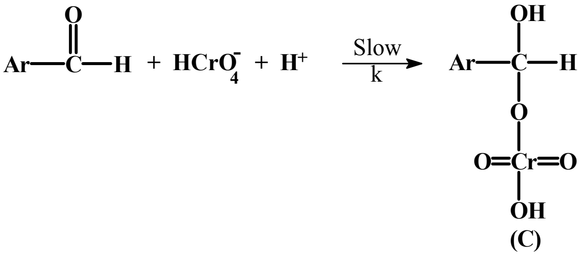
The following mechanism is proposed for the oxidation of benzaldehyde by piperazinium dichromate. In aqueous solution of PZD the following equilibrium exists.

Step I : $Pz^{2+}Cr_2O_7^{2-} + H_2O \underset{}{\overset{K}{\rightleftharpoons}} 2HCrO_4^- + Pz^{2+}$

(Pz^{2+} is spectator ion in the reaction)

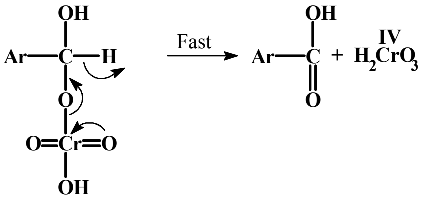
Where K is the equilibrium constant. The slow step is the attach of $HCrO_4^-$ at the carbonyl carbon of the aldehyde in the presence of H^+ ion to form the complex (C).

Step II:



(C)

Step III :



(C)

The complex after a series of electron shifts decomposes into benzoic acid and H_2CrO_3 in which chromium is in + 4 state

$Cr(IV) + Cr(V) \xrightarrow{\text{Fast}} 2\ Cr\ (V)$

$Cr(V) + ArCHO + H_2O \xrightarrow{\text{Fast}} ArCOOH + Cr\ (III) + 2H^+$

The over all stoichiometric equation can be written as

$2HCrO_4^- + 3\ ArCHO + 8H^+ \longrightarrow 3\ ArCOOH + 2Cr^{3+} + 5H_2O$

The observed stoichiometry confirms this.

The rate law can be deduced for this reaction from the proposed mechanism. According to the mechanism,

$$\text{Rate} = k[ArCHO]\ [HCrO_4^-]\ [H^+] \quad (1)$$

From the equilibrium,

$$K = [HCrO_4^-]^2 / [PZD] \quad (2)$$

or

$$[HCrO_4^-] = K^{1/2}\ [PZD]^{1/2} \quad (3)$$

Substituting this value in equation 1, we get

Rate = k $K^{½}$ [ArCHO] $[PZD]^{0.5}$ $[H^+]$ (4)

Rate = $k_{observed}$ [ArCHO] $[PZD]^{0.5}$ $[H^+]$ (5)

Where $k_{observed}$ = k $K^{½}$ (6)

This mechanism proposed explains all the kinetic and non-kinetic observations.

ACKNOWLEDGEMENT

One of the authors, Mrs. K. Parameswari is thankful to the University Grants Commission, New Delhi, for the award of teacher fellowship.

REFERENCES

1. K.P. Ilango and K. Karunakaran, *Oxid. Commu.*, **19**, 50 (1996).
2. M.K. Pillay and A.A. Jameel, *Indian J. Chem.*, **31A**, 46 (1992).
3. S. Agarwal, K. Chowdhary and K.K. Banerji, *J. Org. Chem.*, **56**, 5111 (1991).
4. A. Agarwal, K. Chowdhary and K.K. Banerji, *J. Chem. Res.*, 86 (1990).
5. R. Khanchandan, P.K. Sharma and K.K. Banarji, *Indian J. Chem.*, **35A**, 576 (1996).
6. M. Khurana, P.K. Sharma and K.K. Banerji, *React. Kinet. Catal.*, **67**, 341 (1999).
7. V. Kumbhat, P.K. Sharma and K.K. Banerji, *Indian J. Chem.*, **39A**, 1169 (2000).
8. K.J.P. Orton and A.E. Bradfield, *J. Chem. Soc.*, 983 (1927).
9. B. Movassagh, M.M. Lakouraj and K. Ghodrati, *Indian J. Chem.*, **41B**, 1293 (2002).

(*Received*: 22 February 2006; *Accepted*: 27 December 2006) AJC-5312