



Comparative Study of Oxidative Transformation of Aromatic Aldehydes by Pyridiniumdichromate in Partial Aqueous Medium

Prerana Bairagi¹, B. K. Dangarh² and Monika Jangid^{1*}

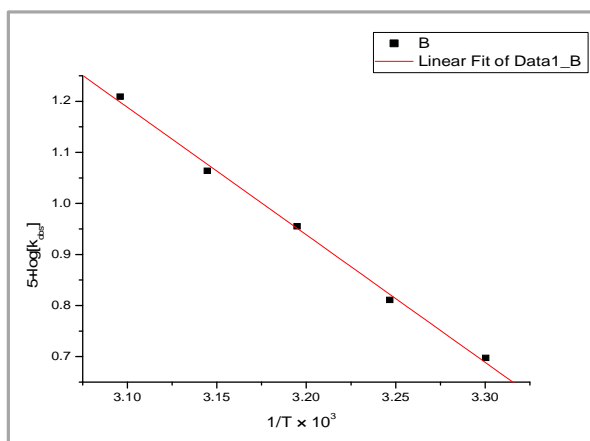
1. Pacific University of Higher Education and Research, Udaipur, Rajasthan, **INDIA**
 2. Department of Chemistry, Govt.P.G. College, Neemuch, Madhya Pradesh, **INDIA**
- Email: monikajangid24@gmail.com, bairagiprerandhar@gmail.com

Accepted on 22nd October, 2023

ABSTRACT

The oxidation of five mono substituted benzaldehydes the present work deals with kinetic study of the oxidation of *p*-Methoxy benzaldehydes and *p*-Chloro benzaldehyde by pyridinium chlorochromate (PDC) in aqueous acetic acid solution the oxidation has been carried out in HClO_4 as solvent. The reaction is first order with respect to PDC in both aromatic alcohol i.e. *p*-Methoxy benzaldehyde and *p*-Chloro benzaldehyde Michaelis-Menten-type kinetics were observed with respect to aldehyde .indicating the oxidation of both the alcohols Michaelis-Menton type kinetics is observed. The effect of solvent composition indicated that the reaction rate increases with an increase in the polarity of the solvent. The rate decreases with the increase in the water content of the medium. The reaction rate has been determined at different temperature and activation parameters calculated for oxidation reaction. A suitable mechanism has been proposed.

Graphical Abstract:



Variation of Rate with Temperature

Keywords: *p*-Methoxybenzaldehyde, *p*-chlorobenzaldehyde, PDC, Oxidation, Kinetic Mechanism.

INTRODUCTION

Selective oxidation of p-Methoxybenzaldehyde and p-Chlorobenzaldehyde can be easily accomplished by using Pyridiniumdichromate (PDC) reagents. Kinetics of oxidation of substituted benzaldehydes by various oxidizing agents has been well studied [1, 2]. It is used as an oxidant for oxidation of alcohols [3], amino acids [4] and aldehydes etc. In this paper we describe kinetics of oxidation of p-Methoxybenzaldehyde and p-Chlorobenzaldehyde by PDC in perchloric acid. Electron withdrawing substituents are found to increase the reaction and electron releasing substituents are found to retard the rate of the reaction and the rate data obey the Hammett relationship. The products of the oxidation are the corresponding acids. The rate decreases with the increase in the water content of the medium. A suitable mechanism is proposed. The effect of varying the composition of the mixture from the bulk solvent to the solvation sphere is called preferential solvation. Specific and selective oxidation of organic compounds under non aqueous conditions is an important reaction in PDC was prepared in the lab by the method described by Corey *et al.*, 1979. Synthetic organic chemistry Cr based oxidizing reagents have proved as remarkable for oxidizing alcohols as PCC, PDC, QDC, QxDC, MDC and many more.

Cr(VI) as chromate or dichromate is highly soluble in water, and is reported to be highly toxic [5] there are continued interest in the development of new Cr(VI) reagents for the effective and selective oxidation of organic substrates, under mild conditions. Therefore, the search for new oxidizing agents is of interests to synthetic organic chemists. Many such reagents have been studied in recent years with some success, some of the important entries in the list of reagents Aretripropylammoniumfluorochromate [6] Morpholiniumchlorochromate [7] Tetramethylammoniumfluorochromate [8] Benzimidazoliumfluorochromate [9], Tributylammoniumchlorochromate [10]. Oxidative transformation of benzaldehyde to benzoic acid is a very selective oxidation in organic chemistry. PDC is well recognized as Corey reagent is very useful oxidizing agent for oxidative conversion of benzaldehyde. PDC is a convenient oxidizing agent which is used in oxidation of alcohols [11, 12], amino acids [13] and aldehydes [14].

MATERIALS AND METHODS

All reagents were A.R. grade which we use for analysis. PDC used in acidic medium. All experiments were carried out at 308 K temperature. All solutions which are used in investigations were made by using distilled water and acetic acid. PDC synthesized by stabilized method and purity was examined by iodometry. HClO_4 was used as source of hydrogen ion PDC was synthesized by method given by Corey and Suggs. Orange substance (PDC) was collected over sintered glass funnel dried for 1 h in vacuum. Purity was checked by m.p.. All glass wares were of borosil. The optical density of the reaction mixture was measured by Spectrophotometer at 360 nm by using Systronics VISISCAN 167.

Kinetic Measurements: Beer Lambert's law was followed by reaction mixture of oxidant. The optical density of the reaction mixture was fixed by Spectrophotometer at 360 nm by using Systronics VISISCAN 167. The reactions were carried out at a constant temperature. The solvent was Acetic acid-water mixture (50% V/V) and the reaction was followed by monitoring the decrease in the concentration of PDC up to 80% completion of the reaction. The pseudo-first-order rate constant, was evaluated from the linear ($R^2 > 0.994$) plot of $\log [\text{PDC}]$ against time. The reaction was also carried out in acetic acid-water mixtures to study the effect of dielectric constant on the rate of the reactions.

Effect of Oxidant Concentration: The reactions are of First-order with respect to PDC i.e. \log absorbance versus time is straight line for more than 80% reaction. Further the value of k_{obs} is independent of the initial concentrations of PDC.

Effect of Substrate Concentration: The rate of oxidation increased on increasing the concentration of alcohols. Plot of $\log k_{\text{obs}}$ versus $\log [\text{substrate}]$ is a straight line.

Effect of $[\text{H}^+]$ Concentration: The effect of hydrogen ion concentration on the rate of the oxidation was studied by varying $[\text{H}^+]$ while keeping the concentration of other reactants constant. Since there is no effect of ionic strength on reaction rate therefore ionic strength was not kept constant. A steady increase in oxidation rate with increase in the acidity of the medium suggests the formation of protonated PDC in the rate determining step. The plot of $\log k_{\text{obs}}$ against $\log [\text{H}^+]$ is linear therefore the order of reaction with $[\text{H}^+]$.

Effect of Solvent Composition: At constant $[\text{H}^+]$ the rate of oxidation increases with increase in percentage of acetic acid-water mixture. In other words a decrease in rate with increase in dielectric constant of solvent is observed. This is due to polar character of the transition state as compared to the reactants. the logarithm of the rate constant of a reaction between ions should vary linearly with the reciprocal of the dielectric constant if reaction involves ion-dipole type of interaction. As we increases the ratio of benzene, dielectric constant decrease that's why rate of reaction increases. The influence of solvent polarity has been studied in acetic acid-water mixture. The acetic acid (v/v) has been varied from 30% to 70% at fixed ionic strength, $[\text{BA}]$, $[\text{PCC}]$, $[\text{H}^+]$ and temperature. The rate of oxidation increases with 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 favors the oxidation process. This is due to polar character of the transition state as compared to that of reactants. The plot of $\log k$ versus $1/D$ (dielectric constant) is linear with positive slope.

Effect of Temperature: The rates of oxidation of p-Methoxy Benzaldehyde and p-Chloro Benzaldehyde were observed at various temperature and the reactions obey Arrhenius equation. Energy of activation was calculated by slopes of straight line obtained plotting $\log k$ versus $1/T$ table 2. The activation parameters for both the Benzaldehyde are calculated. The rate constant were measures with the range of 303-323 K.

RESULTS AND DISCUSSION

Benzaldehyde is oxidized by PDC in acetic acid-water mixture (50% v/v) medium in the presence of perchloric acid at 303 K maintaining pseudo-first-order kinetics. The product analysis and stoichiometric determination stability of the oxidant (pyridinium dichromate) the solution of PDC in acetic acid-water mixture solvent obeys beer-lamberts law at λ 360 nm.

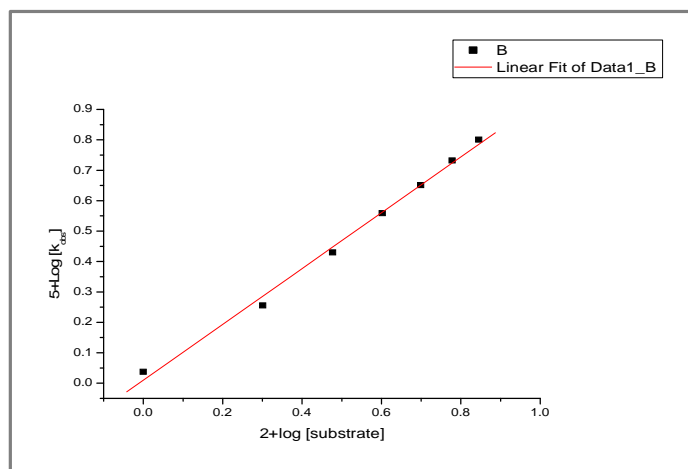


Figure 1. Variation of Rate with Substrate Concentration $\log k_{\text{obs}}$ v/s $\log [\text{substrate}]$ (p-Methoxybenzaldehyde) Ref. Table 1.

There was no change in optical density and spectra of PDC solution, without substrate in solvent mixture on long standing or heating up to 303-323 K. the rate of reaction decreases with increasing dielectric constant of solvent by varying the solvent by mixing. Energy of activation suggests C-H bond breaking in rate determining step and negative entropy of activation indicates formation of cyclic from non-cyclic or more polar than reactants structure formation. a study increase in the oxidation rate with an increase in the acidity of the medium suggests the formation of protonated PDC in the rate- determining step. The plot of $\log k_{\text{obs}}$ against $\log [H^+]$ is linear with a slope of nearly one suggesting that one protons may involve in the rate-determining step.

Table 1. Effect of [Substrate], $[H^+]$ and Solvent [PCC]= 1×10^{-3} M T=308 K

[Substrate] 10^2 M	[HClO ₄] M	% of H ₂ O in Acetic acid	$k_{\text{obs}} \times 10^5 \text{ sec}^{-1}$	
			p-Methoxy benzaldehyde	p-Chloro benzaldehyde
1.0	0.5	50	1.09	6.47
2.0	0.5	50	1.8	12.80
3.0	0.5	50	2.69	18.95
4.0	0.5	50	3.62	25.05
5.0	0.5	50	4.48	31.12
6.0	0.5	50	5.4	38.28
7.0	0.5	50	6.32	44.86
1.0	0.5	50	1.09	6.47
1.0	0.75	50	1.45	9.45
1.0	1.0	50	1.79	12.68
1.0	1.25	50	2.24	15.88
1.0	1.5	50	2.68	18.96
1.0	2.0	50	3.32	23.4
1.0	0.5	30	0.95	4.75
1.0	0.5	40	1.03	5.52
1.0	0.5	50	1.09	6.47
1.0	0.5	60	1.33	7.45
1.0	0.5	70	1.42	11.41

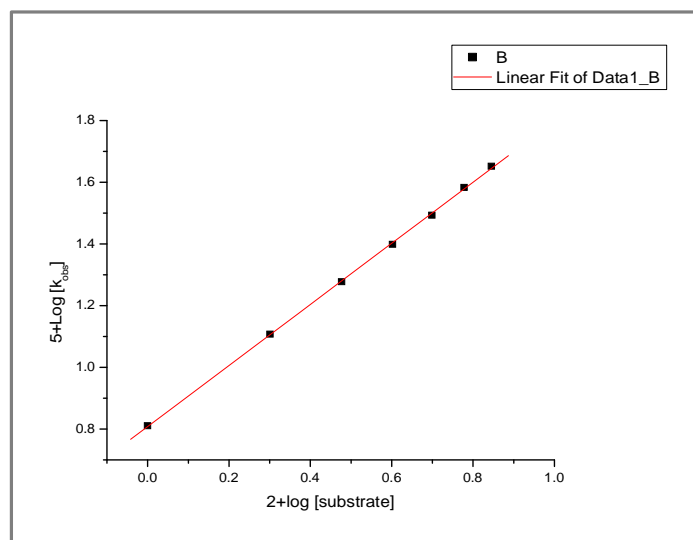
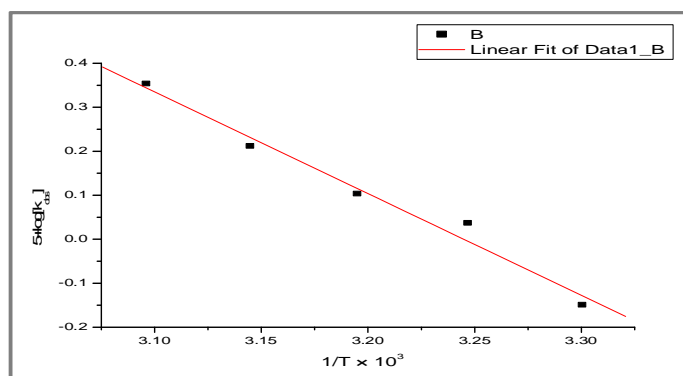
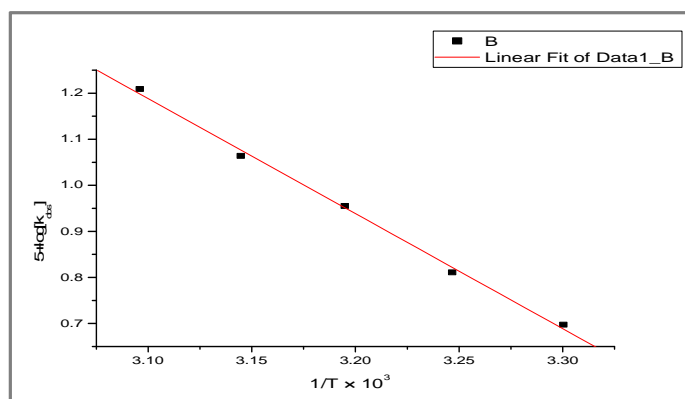


Figure 2. Variation of Rate with Substrate Concentration
 $\log k_{\text{obs}}$ v/s $\log [\text{substrate}]$ (p-cl Benzaldehyde) Ref-Table 1.

Table 2. Variation of Rate with Temperature

Temperature °K	$k_1 \times 10^5 \text{ sec}^{-1}$	
	p-Methoxybenzaldehyde	p-Chlorobenzaldehyde
303	0.71	4.98
308	1.09	6.47
313	1.27	9.02
318	1.63	11.58
323	2.26	16.18

**Figure 3.** Variation of Rate with Temperature
 $\log k_{\text{obs}}$ v/s $1/T$ (p-methoxy benzaldehyde) Ref-Table 2.**Figure 4.** Variation of Rate with Temperature
 $\log k_{\text{obs}}$ v/s $1/T$ (p-chloro benzaldehyde) Ref-Table 2.**Table 3.** Thermodynamic Parameters

Substrate	E_a KJ mol ⁻¹	log A	ΔS J mol ⁻¹ K ⁻¹	ΔH KJ mol ⁻¹	ΔG KJ mol ⁻¹
p-Methoxy benzal dehyde	44.24	4.85	-156.04	41.68	89.74
p-Chlorobenzal dehyde	47.79	6.23	-129.55	45.23	85.13

APPLICATION

Aromatic Aldehyde, Benzaldehyde is commonly many application in cosmetics, food additives and fragrances. General ,it is considered safe to be used in the food industry. Their study will help to understand many use and significance of our daily life and many fields. It has an application on synthetic ,industrial chemistry, research and development, quality control and sometime in analysis also.

CONCLUSION

In the Comparative study of oxidative transformation of benzaldehyde, p-methoxy benzaldehyde, p-chloro benzaldehyde, Rate constant is independent of initial concentration of oxidants, On increasing the temperature, rate of reaction are also increases for all the substrate, Thermodynamic parameters are calculated for all the benzaldehyde and Substitute benzaldehyde .Oxidation of benzaldehyde and Substitute benzaldehyde is first order with respect to the oxidants.

REFERENCES

- [1]. S. S. Mansoor, Kinetic and mechanism of oxidation of benzaldehyde by benzimidazolium fluorochromate in aqueous acetic acid medium, *Asian J.Chem.*, **2010**, 22(10), 7591-7600.
- [2]. K. Krishnasamy, D. Devanathan, J. Dhaemaraja, Kinetics and mechanism of oxidation of substituted benzaldehyde by 4-(dimethylamino) pyridinium chlorochromate, *Trans. metal Chem.*, **2007**, 32(1), 922-926.
- [3]. E. J. Corey, J. W. Suggs, Classic oxidation of alcohols using pyridinium chlorochromate, *Tetrahedran Lett.*, **1975**, 16(1), 2647-2650.
- [4]. M. E. Losi, C. Amrhein, W. T. Frankenberger. Environmental Biochemistry of Chromium, *Rev. Environ, Contam. Toxicol.*, **1994**, 136 (1), 91-121.
- [5]. S. Viamajala, B. M. Peyton, R. Sani, W. A. Apel, J .N. Petersen, Toxic Effects of Chromium (VI) on Anaerobic and Aerobic Growth of *Shewanella oneidensis* MR-1, *Biotech. Prog.*, **2004**, 20(1), 87-95.
- [6]. S. S. Mansoor, S. S. Shafi, Studies on the kinetics of Tripropylammonium Fluorochromate oxidation of some aromatic alcohols in non-aqueous media, *J. Mol. Liq.*, **2010**, 155 (2), 85-90.
- [7]. N. Malani, M. Baghmar, P.K. Sharma, Kinetics and mechanism of the oxidation of some organic sulphides by morpholinium chlorochromate, *Int. J. Chem. Kinet.*, **2009**, 41(1), 65-72.
- [8]. B. Sadeghy, Sh. Ghammami, Oxidation of alcohols with tetramethylammonium fluorochromate in acetic acid, *Russ, J. Gen. Chem.*, **2005**, 75(1), 1886-1888.
- [9]. S. S. Mansoor, S. S. Shafi, Oxidation of aniline and some para-substituted anilines by benzimidazolium fluorochromate in aqueous acetic acid medium-A kinetic and mechanistic study, *Arab. J. Chem.*, **2014**, 7(2), 171-176.
- [10]. S. S. Mansoor, S. S. Shafi, Oxidation of Benzhydrol by Tributylammonium chlorochromate: a kinetic and mechanistic study, *React. Kinet. Mech. Catal.*, **2010**, 100(1), 21-31.
- [11]. H. Kwart, J. H. Nickle, Transition states in chromium (VI) oxidation of alcohols, *J. Am. Chem. Soc.*, **1973**, 95 (10), 3394-3396.
- [12]. K. K. Banerji. Kinetics and mechanism of the oxidation of alcohols by pyridinium chlorochromate, *Bull. Chem.Soc. Jpn.*, **1978**, 51(9), 2732-2734.
- [13]. E. Karim, M. E. Mahanti, Kinetics of oxidation of serine and threonine by Quinolinium dichromate, *Comm. Un .*, **1998**, 21(4) , 559-564.
- [14]. M. K. Pillay, A. A. Jameel. Kinetics of oxidation of para- and meta-substituted benzaldehydes by pyridinium chlorochromate, *Indian J. Chem .*, **1992**, 31(1), 46-48.