Michaelis-Menten Behaviour in the Oxidation of Benzaldehydes by Pyridinium Chlorochromate (Corey's Reagent)

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The oxidation of benzaldehyde, 3,4-dimethoxy benzaldehyde, *p*-methoxy benzaldehyde, *m*-NO₂-benzaldehyde, and *m*-chlorobenzaldehyde by pyridinium chlorochromate (Corey's reagent) are reported. Michaelis-Menten behaviour is observed. The rate determining step appears to be the decomposition of a complex of benzaldehyde with PCC either through a loss of H^+ or H^- ions.

Introduction

Pyridinium chlorochromate[1] (Corey's reagent) in non-aqueous medium has been observed to bring about efficient oxidation of a large number of functional groups and mechanism of the oxidation of benzyl alcohol, mandelic acid, benzhydrol, alkylsulphides, primary aromatic amines, cyclic alcohols have been reported.[2-8] What was important in the studies is that in several cases conclusive evidence regarding nature of interaction between the substrate and pyridinium chlorochromate (PCC) has not been furnished, except in case of alkylsulphides where it could be established that alkylsulphide moiety forms a complex with the PCC moiety which may be similar to an ester intermediate envisaged in the chromic acid oxidations. The complex then breaks down to the products in the rate limiting step. In order to understand the role of PCC species in the oxidation processes, we have undertaken the kinetic studies of the oxidation process of aromatic aldehydes which forms the subject matter of this communication.

Oxidation of aromatic aldehydes in chlorobenzene-nitrobenzene medium by PCC proceeds at a measurable rate at temperatures exceeding 50°C. The stoichiometry of the reaction was determined by equilibrating excess of PCC with benzaldehyde. Analysis of the mixture for PCC and aldehyde indicated a stoichiometry of 1 : 1. The product of oxidation was observed to be benzoic acid.

Experimental

Aldehydes and substituted aldehydes were used after purification and checking of the physical constants. Pyridinium chlorochromate was prepared by the method of Corey and Suggs[1] (1975) and was estimated iodometrically. All the solvents were distilled in an all glass apparatus and the middle fractions were collected and used in running the experiment.

Appropriate quantities of the substrate (aldehydes) were taken in a 50 m*l* flask in the desired solvent mixture so that pseudo first order condition was maintained. The oxidant was also prepared in the similar way in another 50 m*l* flask. The flasks along with a reaction vessel were kept in a thermostat maintained at a desired temperature within ± 0.1°C for about 40 minutes. The reaction was initiated by withdrawing 25 m*l* each of the reactants into the reaction vessel. At different time intervals 5 m*l* aliquots of the reac-

tion mixture was withdrawn into a conical flask containing 10% KI solution, 6 N HCl and 2 to 4 m*l* of NaHCO₃. The liberated I₂ was titrated against a standard thio solution using starch as indicator. In the solvent composition used, the reaction mixture was homogeneous and the PCC remained stable over the period of the kinetics. Experiments in the presence of acrylamide was performed by adding appropriate amount of acrylamide to the substrate flask.

Kinetics of oxidation of benzaldehyde and substituted benzaldehydes by PCC was carried at 50°C in chlorobenzene-nitrobenzene (95 : 5 V/V) mixtures, under pseudo first order conditions with respect to the oxidant. Disappearance of PCC was found to be first order in PCC as seen from the linearity of the log $[PCC]_T$ *vs.* time plots and constancy of individual rate constants in a single run. In order to evaluate the order with respect to benzaldehyde, kinetics was studied at constant concentration of PCC and varying concentrations of benzaldehydes. The kinetic data are collected in the Table 1 and 1A.

Increase of benzaldehyde concentration led to slow increase of first order rate constants. Plot of k_{obs} (min⁻¹) versus benzaldehyde concentration was observed to be a curve reaching a limiting value for all substituents except *p*-OCH₃-derivative. A plot of this type is a pointer to operation of a Michaelis-Menten type of kinetics in these oxidation processes. In such a situation, plot of k_{obs}^{-1} *vs.* $[Benzaldehyde]^{-1}$ is expected to be linear and perfect linearity was actually observed (Figure 1). Similar observations were also obtained with substituted benzaldehydes, such as *m*-chloro, *m*-nitro, 3,4-dimethoxy benzaldehyde. Although Michaelis-Menten kinetics is strictly applicable when one of the reactants is a catalyst whose concentration is constant during the reaction. In the present case though none of the two reactants is a catalyst, concentration of the substrate is in large excess compared to that of the oxidant. Therefore concentration of the substrate can be considered as constant during the oxidation. In the circumstances it is not very much wrong to explain the saturation of rate by Michaelis-Menten kinetics. In case of *p*-methoxy benzaldehyde a negative intercept was observed, which implied that Michaelis-Menten behaviour is not exhibited.

The observation in case of *p*-methoxybenzaldehyde indicates either greater instability of the complex or a complex with very small equilibrium constant is formed.
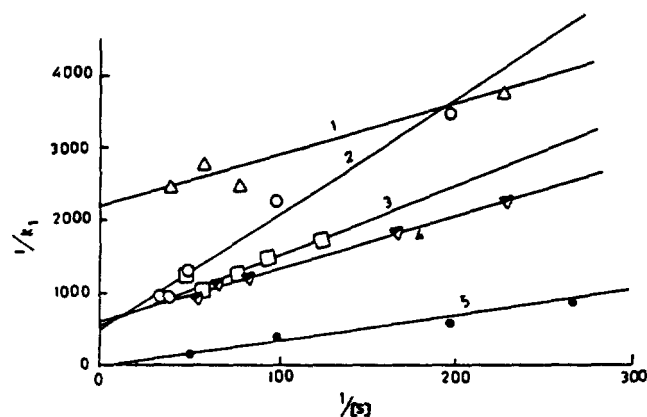
Activation parameters. For evaluating activation para-

Table 1. Rate Constants for the Oxidation of Benzaldehydes by PCC at Different Temperatures

$10^4[PCC] = (3.5 \pm 0.5)$ M, Solvent $= C_6H_5Cl : C_6H_5NO_2$ (95 : 05 V/V)

Substrate	$10^3[S]$ M.	Temp. ℃	$10^4 k_1$ min^{-1}	$10^2 k_2$ M^{-1}·min^{-1}
1	2	3	4	5
Benzaldehyde	5	50	2.88	5.76
	10		4.46	4.46
	20		7.93	3.96
	25		10.06	4.02
3,4-Dimethoxy-	4.36		4.36	10.00
Benzaldehyde	6.02		5.56	9.2
	12.04		8.38	6.95
	15.05		9.13	6.06
	18.06		10.7	5.92
m-Chloro-	4.37		2.7	6.17
Benzaldehyde	12.75		4.10	3.22
	17.00		3.61	2.12
	26.2		4.2	1.59
m-Nitro-	8.02		5.91	7.37
Benzaldehyde	10.6		6.85	6.42
	13.10		8.17	6.22
	17.04		10.22	5.73
	21.6		8.36	3.86
Benzaldehyde	2.37	60	9.34	38.1
	3.7		12.05	32.5
	5.01		13.62	27.18
	17.78		18.11	10.18
	23.7		18.4	7.75
3,4-Dimethoxy-	4.5		10.5	23.34
Benzaldehyde	9.6		17.23	17.8
	14.1		17.6	12.4
	19.3		20.8	10.8
m-Chloro-	3.16		2.48	7.85
Benzaldehye	7.94		3.84	4.84
	11.58		4.08	3.53
	14.75		4.45	3.01
m-Nitro-	6.93		4.7	6.78
Benzaldehyde	10.58		5.61	5.3
	21.46		7.02	3.27
	29.16		6.27	2.15
Benzaldehyde	2.28	70	11.73	51.33
	4.58		18.57	40.47
	7.64		21.06	27.5
	10.66		33.6	31.5
	15.23		37.6	24.7
3,4-Dimethoxy-	4.34		14.98	34.5
Benzaldehyde	8.68		25.85	29.78
	10.13		22.28	21.98
	14.46		30.68	21.2
	21.7		37.74	17.48
m-Nitro-	5.34		12.75	23.84
Benzaldehyde	16.35		18.14	11.09
	22.02		18.95	8.6
	27.95		27.10	9.6

Table 1A. Rate Constants for the Oxidation of p-Methoxy Benzaldehyde at Different Temperatures

$10^4[PCC] = (3.5 \pm 0.5)$ M, Solvent $= C_6H_5Cl : C_6H_5NO_2$ (95 : 05 V/V)

10^3 [s] M	Temp. ℃	$10^3 k_1$·min^{-1}	$10 k_2$·M^{-1}·min^{-1}
5.08	35	1.61	3.17
10.57		3.16	2.99
17.18		5.25	3.06
3.00	45	1.20	4.01
4.97		2.51	5.05
7.51		3.65	4.86
15.80		7.18	4.55
2.20	70	2.46	11.16
6.61		7.13	10.79
11.01		15.02	13.63
16.52		20.81	12.59

Figure 1. Plot of $1/k_1$ vs. $1/[S]$. Solvent $= C_6H_5Cl : C_6H_5NO_2$ (95 : 05 V/V) at 50℃. 1. m-Chlorobenzaldehyde. 2. Benzaldehyde. 3. m-Nitrobenzaldehyde. 4. 3,4-Dimethoxy benzaldehyde. 5. p-Methoxy benzaldehyde.

meters, pseudo first order rate constants obtained at three temperatures were used for obtaining the Arrhenius plot. Energy of activation and entropy of activation were computed from the slope of the Arrhenius plot. The data are given in Table 2. The enthalpy values vary between 22.8 to 39.8 K·J·mol^{-1}, whereas entropy of activation ranges between -182 to -233 J·K^{-1}·mol^{-1}.

The oxidation rate was not observed to change in presence of acrylamide and no polymerisation of acrylamide was also observed when it was introduced into the reaction vessel.

Solvent effect. The oxidation process was found to be retarded by using higher proportion of nitrobenzene in the solvent mixture. The correlation of log k_1 versus D^{-1} is a straight line with a positive intercept indicating the reaction being an iondipole type. As is well known ion-dipole reactions are accelerated in presence of low dielectric solvent.[9]

Structure-reactivity relationship. Of the substituted benzaldehydes subjected to oxidation by PCC, no doubt the p-methoxy derivative with highest electron releasing ability reacts fastest and m-nitro derivative reacted with slowest rate. p-Nitrobenzaldehyde could not be oxidised at 50℃. Si-

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Table 2. Activation Parameters of Benzaldehydes by PCC in Chlorobenzene : Nitrobenzene (95 : 05 V/V)

Temp. 50℃.

Substrate	ΔE mol^{-1}	ΔH^* k·J·mol^{-1}	$-\Delta S^*$ J·mol^{-1}·K^{-1}
Benzaldehyde	25.6	22.8	233
3,4-Dimethoxy benzaldehyde	42.7	39.8	183.9
m-Nitro benzaldehyde	37	34.3	196.5
p-Methoxy benzaldehyde	37.3	34.6	182.1

Table 3. Equilibrium Constants (K) and Michaelis-Menten Rate Constants k_d in the Oxidation of Benzaldehydes
Solvent = Chlorobenzene : Nitrobenzene (95 : 05 V/V)

Temp. 50℃

Substrate	k_d·M^{-1}·min^{-1}	K·M^{-1}
Benzaldehyde	2.1×10^{-3}	30.6
3,4-Dimethoxy benzaldehyde	1.66×10^{-3}	84.5
m-Nitro benzaldehyde	1.81×10^{-3}	55.0
m-Chlorobenzaldehyde	4.65×10^{-4}	232.2

nce the oxidation of aldehyde did not follow a simple rate law, it is unjustified to examine the structure reactivity pattern using gross rate constants. On the other hand the following steps can be envisaged to explain the observed kinetics

$$\phi CHO + PCC \underset{}{\overset{k}{\rightleftharpoons}} \text{Complex (C)}$$

$$C \xrightarrow{k_d} product$$
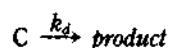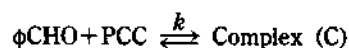
From these steps rate of disappearance of [PCC] is given by

$$\frac{-d[PCC]}{dt} = \frac{k_d K[PCC][\phi CHO]}{1 + K[\phi CHO]}$$

or $$\frac{d[PCC]}{dt} / [PCC] = k_{obs} = \frac{k_d K[\phi CHO]}{1 + K[\phi CHO]}$$

Rearranging the rate equation we get

$$1/k_{obs} = 1/k_d + \frac{1}{k_d K[\phi CHO]}$$

As already mentioned K and k_d values obtained from the linear plots of $1/k_{obs}$ vs. $1/[\phi CHO]$ have been recorded in Table 3.

For the purpose of structure-reactivity corelation, Michaelis-Menten constants 'K' and decomposition rate contant k_d referred above were used. As no σ value for 3,4-dimethoxy benzaldehyde was available sum of σ_p and σ_m values for *p*-methoxy and *m*-methoxy substituents respectively was used as the σ value for the 3,4-dimethoxy derivative. A near linear plot in the correlation of $\log K$ against σ values (Figure 2) having a positive slope suggests that formation of the PCC-benzaldehyde complex is assisted by withodrawing groups and the releasing groups do not favour formation of the complex.
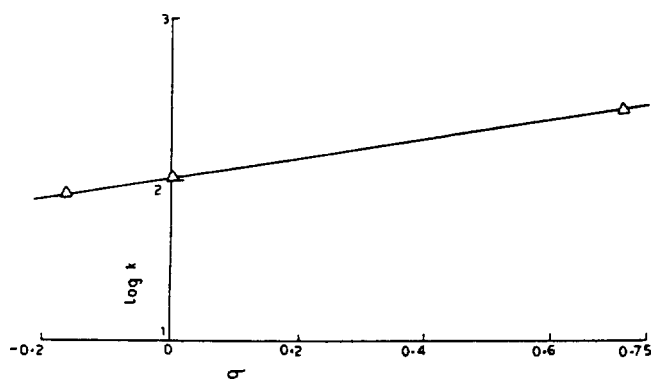
Figure 2. Plot of $\log K$ vs. substituent constants (σ). Solvent = $C_6H_5Cl : C_6H_5NO_2$ (95 : 05 V/V) at 70℃.
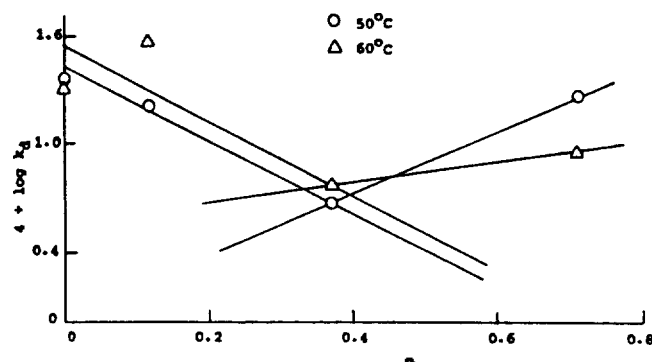
Figure 3. Plot of $\log k_d$ vs. substitutent constants (σ). Solvent = $C_6H_5Cl : C_6H_5NO_2$ (95 : 05 V/V) at Temp. 50℃ and Temp. 60℃.

Since 3,4-dimethoxy derivative reacted slower than *p*-OCH₃ derivative, σ value for *m*-methoxy if used fits the plot of $\log K$ vs. σ.

Attempts to correlate $\log k_d$ (i.e., decomposition rate) with σ presented a completely different picture. For this plot σ for *m*-OCH₃ was also used as that for 3,4-dimethoxy derivative. It appears there is change in the sign of the slope of the plot (Figure 3) suggesting a change in mechanism during the decomposition process. When the releasing groups are present, probably loss of hydride ion from the benzaldehyde occurs in the slow step which in turn transfers its electron pair to the chromium centre in a fast step forming the products. When withdrawing groups are present, loss of H⁺ appears to be responsible for rate limiting decomposition of the complex. Recently Pati *et al.*[10] have demonstrated such a dual mechanism in the oxidation of benzaldehydes by trichloroisocyanuric acid.

Oxidation of benzaldehyde and substituted benzaldehydes by Chromic Acid in aqueous acetic acid medium has been reported by Wiberg and Coworkers.[11] These workers have established that the reaction proceeds through an ester intermediate that is formed between benzaldehyde hydrate and Cr(VI) either by reversible esterification of the hydrate or the reversible addition of chromic acid across the carbonyl group. This ester then decomposes to give the products in the rate limiting step. Similar conclusions have been drawn by Grahm and Westheimer[12] too in denzaldehyded oxidations.

However, chromic acid oxidations in aqueous medium are

vitiated by incursion of intermediate valence states of chromium such as Cr(V) and Cr(IV); whose contribution to the overall oxidation have been quantified. But no such incursion of intermediate valence states of chromium occurs in case of modified chromium(VI) and the kinetic data in the present study can be interpreted for the elucidation of oxidation by Cr(VI) species alone. Further use of hydrocarbon solvents and absence of any acid catalysis in these reactions preclude involvement of aldehyde hydrates.

Hence it can be concluded that the aromatic aldehydes form a complex with pyridinium chlorochromate similar to an ester proposed in Cr(VI) oxidations which then decomposes to products in the slow step. Break down of the complex is probably initiated by cleavage of the C-H bond which may involve either a H^- or H^+ transfer as already proposed. However no H-atom transfer is envisaged since no radical has been detected during the oxidation process. Cleavage of C-H bond based on kinetic isotope effect in the Cr(VI) oxidations has been postulated by Wiberg & Mill.[15]

The magnitude of ρ values obtained in the plot of $\log K$ versus σ and $\log k_d$ versus σ in the present study point to, as already mentioned, facility of the ester or the complex formation in aldehydes with withdrawing groups but a change in the sign of the ρ-σ plot in the decomposition step as one goes from releasing groups to withdrawing groups ultimately suggests that either a H^+ or H^- ion is involved. Probably loss of H^- characterises decomposition of the ester complex of aldehydes with electron releasing groups and H^+ loss is involved in the decomposition of complex with electron withdrawing groups.

The reduction product of pyridinium chlorochromate is a Cr(IV) species but not Cr(III). This has been established to be the case by Brown *et al.*[13] from stoichiometric studies. Subsequently Patro *et al.*[14] have confirmed the findings of Brown & Coworkers from magnetic susceptibility measurements. Keeping these facts in mind the plausible mechanism of oxidation of benzaldehyde by pyridinium chlorochromate can be picturised as follows:

Acknowledgement.

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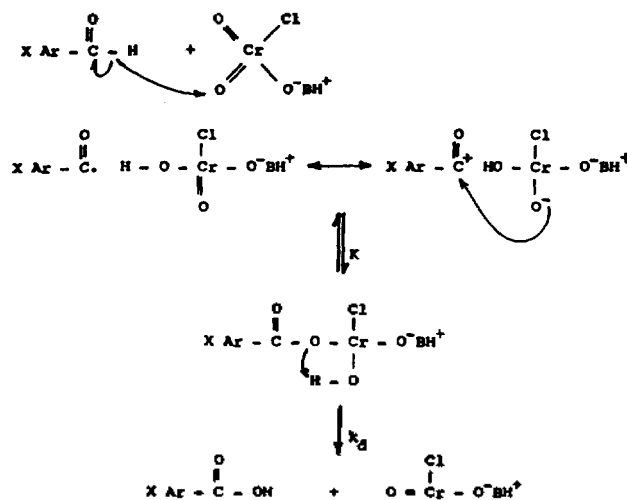
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