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Kinetics and Mechanism of Oxidation of Disubstituted Benzaldehydes by Pyridinium Chlorochromate

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The kinetics of oxidation of benzaldehyde and several disubstituted benzaldehydes by pyridinium chlorochromate (PCC) have been studied in binary solvent mixture of 50% (v/v) aqueous acetic acid. The reaction is first order each in [aldehyde], [PCC] and [H^+]. Addition of monomer to the reaction mixture gives a polymer. Activation parameters have been computed and a suitable mechanism has been postulated.

INTRODUCTION

The Corey's reagent, pyridinium chlorochromate (PCC), is reported to be a more versatile oxidant.[1] This converts alcohols into carbonyl products smoothly at room temperature. It is also found to oxidise the carbonyl compounds into the corresponding acids. In continuation of our earlier reports about the mechanism of oxidation of aldehydes by PCC[2], the kinetics of the oxidation of disubstituted benzaldehydes are reported.

EXPERIMENTAL

All the chemicals used were of analytical grade (E. Merck, Germany) and used as such. PCC was prepared by the reported method[1] and the purity was checked by estimating Cr(VI) iodometrically. The aldehydes taken for investigation are benzaldehyde (BA), 2,3-dimethoxybenzaldehyde (2,3-DMBA), 2,4-dimethoxybenzaldehyde (2,4-DMBA), 3,4-dimethoxybenzaldehyde (3,4-DMBA), 3,4-methylenedioxybenzaldehyde (3,4-MDBA) and 2,4-dichlorobenzaldehyde (2,4-DCBA).

Kinetic measurements were initiated by mixing appropriate volumes of thermally pre-equilibrated reactant solutions under pseudo-first order conditions. [Aldehyde] $\gg$ [PCC]. The progress of the reaction was followed by iodometric determination of unreacted PCC. The pseudo-first order rate constants (k_1) were determined by the least squares method.

Stoichiometric studies showed that 3 mol of aldehyde consumed 2 mol of PCC in accordance with equation (1) to give the corresponding carboxylic acids which were characterised by chemical methods and TLC technique.

$$3ArCHO + 2PCC \rightarrow 3ArCOOH + 2Cr(III) \quad (1)$$

RESULTS AND DISCUSSION

Under pseudo-first order conditions, the individual kinetic runs are first order with respect to [PCC] as shown by the linear plots of log [PCC] versus time (Table-1). Further, the reaction rate decreases as the concentration of PCC increases. The plot of [PCC] versus $1/k_1$ is linear with unit slope (r 0.999). Such observations have been reported by several authors.[3, 4] This may be due to the faster rate of formation of the PCC-ester as the intermediate compared to the rate of ester decomposition.[5]

TABLE-1
EFFECT OF VARYING [PCC] ON REACTION RATE

10^3 [Aldehyde] = 4.00 mol dm^{-3}, [H$^+$] = 1.00 mol dm^{-3}, Acetic acid = 50% (v/v), μ = 1.2 mol dm^{-3}, T = 303 K

10^3 [PCC] mol dm^{-3}	10^5 k_1, s^{-1}					
	BA	2,3-DMBA	2,4-DMBA	3,4-DMBA	3,4-MDBA	2,4-DCBA*
1.00	12.70	13.70	7.34	8.67	45.4	18.80
2.00	10.40	12.30	6.74	5.21	41.1	15.50
3.00	8.65	11.10	6.18	3.78	37.2	12.70
4.00	7.52	10.10	5.85	2.93	33.9	11.00
5.00	6.49	9.32	5.44	2.36	30.4	9.78

*Acetic acid = 70% (v/v).

A plot of log k_1 against log [Aldehyde] is linear with unit slope (1.02 ± 0.006, r 0.999) and a plot of k_1 against [Aldehyde] also gives a good straight line (r 0.999) passing through the origin (Table-2). These observations lead to the conclusion that the order in [Aldehyde] is unity. The second order rate constant, k_2 (= k_1/Aldehyde), is invariant supporting the first order dependence on [Aldehyde].

TABLE-2
EFFECT OF VARYING [ALDEHYDE] ON REACTION RATE

10^3 [PCC] = 1.00 mol dm^{-3}, [H$^+$] = 1.00 mol dm^{-3}, Acetic acid = 50% (v/v), μ = 1.2 mol dm^{-3}, T = 303 K

10^2 [Aldehyde] mol dm^{-3}	10^5 k_1, s^{-1}					
	BA	2,3-DMBA	2,4-DMBA	3,4-DMBA	3,4-MDBA	2,4-DCBA*
1.00	3.01	3.42	1.80	2.12	10.50	4.84
2.00	6.32	6.75	3.55	4.23	20.90	9.31
3.00	9.38	9.95	5.52	5.81	33.60	13.90
4.00	12.7	13.70	7.34	8.67	45.40	18.80
5.00	15.8	16.40	9.46	10.50	—	23.10

*Acetic acid = 70% (v/v)

The increase in $[H^+]$ (0.2–1.0 mol dm^{-3} $HClO_4$) increases the reaction rate and shows a direct first order dependence on $[H^+]$. Increase in the percentage of acetic acid in the solvent mixture (30–80% (v/v)) decreases the rate and a positive slope is obtained for the plot of log k_1 versus 1/D. Change in ionic strength has no effect on k_1 ($NaClO_4$ as the neutral salt).

The activation energies were computed from a plot of log k_2 versus 1/T for the temperature range 303–313 K (Table-3). The activation enthalpies and entropies are linearly related (r 0.984). The existence of a linear relationship between $\Delta H^\ddagger$ and $\Delta S^\ddagger$ indicates that similar mechanism is operating in the series.[6]

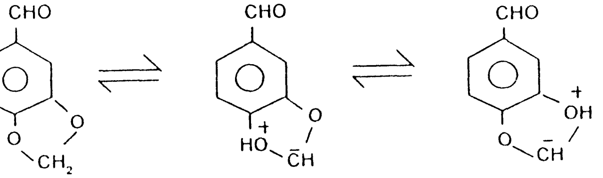
TABLE-3

SECOND ORDER RATE CONSTANTS AND ACTIVATION PARAMETERS FOR PCC OXIDATION OF DISUBSTITUTED BENZALDEHYDES

Aldehyde	$10^3 k_2$, $dm^3 mol^{-1} s^{-1}$				$\Delta H^\ddagger$ (± 0.2) kJ mol^{-1}	$-\Delta S^\ddagger$ (± 0.5) kJ mol^{-1} K^{-1}	$\Delta G^\ddagger$ (± 2.5) kJ mol^{-1}
	303 K	313 K	323 K	333 K			
BA	3.13	5.39	9.13	14.80	40.2	154	89.5
2 3-DMBA	3.35	5.67	9.69	15.50	40.4	159	91.0
2,4-DMBA	1.83	3.13	4.68	7.33	35.7	180	92.8
3,4-DMBA	2.08	4.33	8.34	15.30	53.1	121	91.6
3,4-MDBA	10.90	21.30	44.90	87.00	55.9	98.5	87.2
2,4-DCBA	4.68	8.56	14.70	26.10	45.1	141	89.9

The pseudo-first order rate constants for the disubstituted benzaldehydes are found to be low compared to the monosubstituted aldehydes[2] and also lower than the calculated values obtained based on additivity principle.[7] The methoxy and chlorosubstituents are found to decrease the rate in the oxidation of benzaldehydes by PCC.[8] Presence of such groups adjacent to the aldehyde group may enhance the steric effect. Combination of both the steric and electrical effects leads to the deceleration of the reaction rate as was observed by Charton.[9]

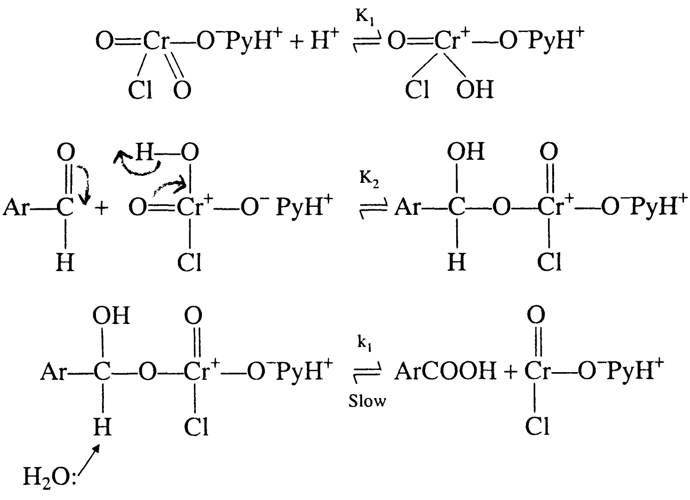
For the 3,4-methylenedioxybenzaldehyde, the rate constant is found to be very high. The methylene group is flanked with two electronegative oxygen atoms. Oxygen may abstract a proton from the methylene group to form —OH$^+$— -with different canonical forms. Since —OH$^+$— is capable of attracting electron density from the benzene ring, there may be decrease in electron density at the reaction centre of carbonyl carbon leading to the enhanced rate.



Based on the present experimental observations and from the reports of previous works with PCC[10–12] and chromic acid[13–15] oxidations, an initial two-electron transfer with reformation of Cr(IV) has been formulated. Cr(IV) reacts with an aldehyde molecule to form an aryl radical and Cr(III). The radical formation has been tested with the monomer acrylonitrile when a polymer precipitated in methanol under nitrogen atmosphere. This has been confirmed by a single derivative curve obtianed in EPR spectrum. Aryl radical reduces PCC to Cr(V) which further reacts with another aldehyde molecule by a two-electron transfer to form Cr(III). The involvement of the intermediate valence states of chromium in the reaction has been tested with the induced oxidation by Mn(II). The reaction rate is found to decrease to one-third as in the case of chromic acid oxidation aldehydes.

Since the aromatic aldehydes are not hydrated to any appreciable extent[16, 17] and no reaction is known in which the nucleophilic attack on tetrahedral carbon of aldehyde hydrate is faster than that of free aldehyde[18], the —CHO group is supposed to be the reactive species. The reaction proceeds with the formation of a PCC-ester as the intermediate (Scheme 1).

SCHEME-1



$$\underset{\substack{/\ \ \backslash\backslash \\ \mathrm{Cl}\ \ \mathrm{O}}}{\mathrm{O{=}Cr}}{-}\mathrm{O^-PyH^+} + \mathrm{H^+} \overset{K_1}{\rightleftharpoons} \underset{\substack{/\ \ \backslash \\ \mathrm{Cl}\ \ \mathrm{OH}}}{\mathrm{O{=}Cr^+}}{-}\mathrm{O^-PyH^+} \quad (2)$$

$$\mathrm{Ar}{-}\underset{\mathrm{H}}{\overset{\mathrm{O}}{\overset{\|}{\underset{|}{\mathrm{C}}}}} + \mathrm{O{=}}\underset{\mathrm{Cl}}{\overset{\mathrm{H{-}O}}{\overset{|}{\underset{|}{\mathrm{Cr^+}}}}}{-}\mathrm{O^-\,PyH^+} \overset{K_2}{\rightleftharpoons} \mathrm{Ar}{-}\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\overset{|}{\underset{|}{\mathrm{C}}}}}{-}\mathrm{O}{-}\underset{\mathrm{Cl}}{\overset{\mathrm{O}}{\overset{\|}{\underset{|}{\mathrm{Cr^+}}}}}{-}\mathrm{O^-PyH^+} \quad (3)$$

$$\mathrm{Ar}{-}\underset{\substack{\mathrm{H}\\ \nearrow \\ \mathrm{H_2O:}}}{\overset{\mathrm{OH}}{\overset{|}{\underset{|}{\mathrm{C}}}}}{-}\mathrm{O}{-}\underset{\mathrm{Cl}}{\overset{\mathrm{O}}{\overset{\|}{\underset{|}{\mathrm{Cr^+}}}}}{-}\mathrm{O^-PyH^+} \underset{\text{Slow}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ArCOOH} + \underset{\mathrm{Cl}}{\overset{\mathrm{O}}{\overset{\|}{\underset{|}{\mathrm{Cr}}}}}{-}\mathrm{O^-PyH^+} \quad (4)$$

$$\mathrm{ArCHO} + \mathrm{Cr(IV)} \xrightarrow{\text{Fast}} \mathrm{Ar\dot{C}O} + \mathrm{Cr(III)} \quad (5)$$

$$\mathrm{Ar\dot{C}O} + \mathrm{PCCH^+} \xrightarrow{\text{Fast}} \mathrm{ArCOOH} + \mathrm{Cr(IV)} \quad (6)$$

$$\mathrm{ArCHO} + \mathrm{Cr(V)} \xrightarrow{\text{Slow}} \mathrm{ArCOOH} + \mathrm{Cr(III)} \quad (7)$$

Involvement of water molecule in the rate-limiting step should give a better correlation between the logarithm of rate constant and the pH[19] which has been observed.

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