Kinetics of Oxidation of Substituted Benzaldehydes by Quinolinium Chlorochromate

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Kinetics of oxidation of substituted benzaldehydes by quinolinium chlorochromate (QCC) have been studied in aquo-acetic acid in the presence of perchloric acid. The rates of oxidation show first order kinetics each in substrate [QCC] and [H⁺]. Electron-releasing substituents retard and the electron-withdrawing groups enhance the rate. Activation parameters have been computed and a suitable mechanism has been suggested. The validity of the Hammett equation has also been tested.

INTRODUCTION

The kinetics and mechanism of oxidation of aromatic aldehydes by various oxidants have been reported. However, there is no report on the oxidation of *meta* and *para*-substituted benzaldehydes with quinolinium chlorochromate (QCC). QCC is reported to be neutral and mild oxidant for selective oxidations. We report herein the kinetics of oxidation of some *meta* and *para*-substituted benzaldehydes by QCC in aquo-acetic acid (1 : 1 v/v) in the presence of perchloric acid.

EXPERIMENTAL

All the chemicals used were of analytical grade. The solid aldehydes were used as such and the liquid aldehydes were used after vacuum distillation. QCC was prepared by the method described in literature[1]. The purity of the oxidant was determined by iodometric assay. Acetic acid was purified by the standard method. Doubly distilled water was used for all purposes. Kinetic studies were carried out under pseudo-first order conditions by maintaining a large excess of the substrate over oxidant. The progress of the reactions was followed by estimating the unreacted oxidant iodometrically. The rate constants were determined by the least squares method, from the linear plots of log [QCC] versus time.

The product of oxidation of aldehyde by QCC was confirmed as the corresponding carboxylic acid by chemical methods and TLC technique. Stoichiometric studies showed that 3 mol of aldehyde consumed 2 mol of QCC in accordance with the following equation:

$$3ArCHO + 2QCC \xrightarrow{H^+} 3ArCOOH + 2Cr(III)$$
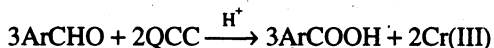
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RESULTS AND DISCUSSION

The reaction was found to be first order with respect to substrate as evidenced by the linear plot of log k_{obs} vs log [substrate] with a slope of unity. This was further demonstrated by constancy of k_2 ($k_2 = k_{obs}/$ [substrate]). The plots of log titre vs time were linear indicating a first order dependence of rate on [QCC]. The plot of [QCC] vs $1/k_{obs}$ is linear with unit slope. Such observations have been reported by several authors[2-4]. This may be due to the faster rate of formation of the intermediate compared to the rate of its decomposition.

It has been observed that increase in the percentage of acetic acid in the medium decreases the rate. The plot of log k_{obs} vs inverse of dielectric constant of the medium is linear with a positive slope. Change in ionic strength has no effect on the rate constant. The rate constants were found to increase with increase of [H$^+$] and shows a direct first order dependence on [H$^+$].

The activation parameters evaluated from the linear plots of log k_2 versus $1/T$ in the temperature range 303–333K are given in the table. The existence of a linear relationship (r = 0.988) between ΔH^* and ΔS^* indicates that similar mechanism is operating in the series. Further, a linear kinetic relationship is a necessary condition for the validity of linear free energy relationships[5,6]
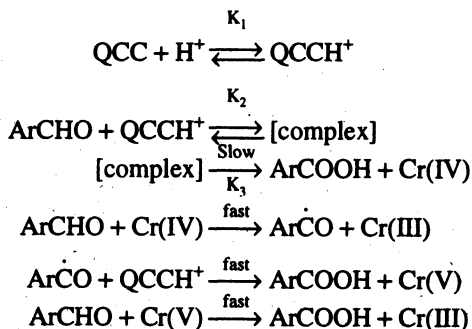
TABLE-1
ACTIVATION PARAMETERS FOR THE OXIDATION OF SUBSTITUTED
BENZALDEHYDES BY QCC

Substituents	Ea kJ mol^{-1}	ΔH^* kJ mol^{-1}	$-\Delta S^*$ JK^{-1} mol^{-1}	ΔG^* kJ mol^{-1}
H	47.1	44.4	139	87.3
p-OCH$_3$	63.2	60.6	102	91.9
p-CH$_3$	60.8	58.1	106	90.8
p-Cl	51.4	48.8	128	88.2
p-Br	50.8	48.2	129	87.9
p-I	44.7	42.2	147	87.7
p-CN	40.8	38.1	152	85.4
p-NO$_2$	47.6	44.9	128	84.6
m-OCH$_3$	42.4	39.8	159	88.8
m-CH$_3$	46.0	43.3	149	89.8
m-Cl	41.3	38.7	158	87.5
m-Br	46.6	43.9	140	87.0
m-NO$_2$	41.7	39.2	149	85.2

The oxidation rates of *meta-* and *para-*substituted benzaldehydes were subjected to Hammett equation. For the Hammett plot with ρ values, good correlation was obtained (ρ = + 1.18, r = 0.993). Similar phenomenon has been observed in the oxidation of substituted benzaldehydes by acid bromate[7] and pyridinium

chlorochromate[3]. The positive value indicates that electron-withdrawing sub-stituents increase the rate of oxidation and elecron-relasing substituents decrease the rate.

The experimental results can be accounted in terms of a mechanism involving an intitial two-electron transfer with the formation of Cr(IV) which subsequently 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. Aryl radical reduces QCC 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 as in the case of earlier observations[3, 8]. Since the aromatic aldehydes are not hydrated to any appreciable extent[9], the —CHO group is supposed to be the reactive species. The positive reaction constant accounts for the loss of aldehydic hydrogen atom as a proton[10]. The probable mechanism is

$$QCC + H^+ \overset{K_1}{\rightleftharpoons} QCCH^+$$

$$ArCHO + QCCH^+ \underset{Slow}{\overset{K_2}{\rightleftharpoons}} [complex]$$

$$[complex] \overset{K_3}{\longrightarrow} ArCOOH + Cr(IV)$$

$$ArCHO + Cr(IV) \overset{fast}{\longrightarrow} Ar\overset{.}{C}O + Cr(III)$$

$$Ar\overset{.}{C}O + QCCH^+ \overset{fast}{\longrightarrow} ArCOOH + Cr(V)$$

$$ArCHO + Cr(V) \overset{fast}{\longrightarrow} ArCOOH + Cr(III)$$

The above mechanism leads to the following rate equation,

$$Rate = K_3 [complex]$$

or $$Rate = K_1 K_2 K_3 [ArCHO][QCC][H^+]$$

The rate law in its final form accounts for the observed kinetics.

REFERENCES

1. J. Singh, P.S. Kalsi, G.S. Jawanda and B.R. Chhabra, *Chem. Ind.*, 751 (1986).
2. M. Krishna Pillay and A. Thirunavukkarasu, *Indian J. Chem.*, **20(B)**, 583 (1981).
3. M. Krishna Pillay and A. Abdul Jameel, *Indian J. Chem.*, **31A**, 46 (1992).
4. N. Venkasubramanian and V.S. Srinivasan, *Indian J. Chem.*, **8**, 57 (1970).
5. K. Karunakaran and K.P. Elango, *Oxid. Commun.* (in press).
6   J.E. Leffller, *J. Org. Chem.*, **31**, 533 (1966).
7. S. Anandan and R. Gopalan, *J. Indian Chem. Soc.*, **62**, 216 (1985).
8. K.B. Wiberg and T. Mill, *J. Am. Chem. Soc*, **80**, 3022 (1958).
9. J.M. Sayer, *J. Org. Chem.*, **40**, 2545 (1975).
10. G.E. Graham and F.H. Westheimer, *J. Am. Chem. Soc.*, **80**, 3030 (1959).