Research Articles

STUDY ON DECARBOXYLATION OF MANDELIC ACID AND Þ-CHLORO MANDELIC ACID THROUGH OXIDATION BY ISOQUINOLINIUM CHLOROCHROMATE

Tajun Ansari[1*], Manisha Pradhan[1]

1. *Department of Chemistry, Govt. Girls P.G. College, Rewa (M.P.) India.*

Abstract: Isoquinolinium chlorochromate (IQCC) has been employed to de-caboxylate mandelic acid and Þ-chloro mandelic acid in aqueous acetic acid medium in presence of H^+ ion at 30 and 35 ^{0}C. The reactions exhibit first-order kinetics both with respect to concentration of oxidant (IQCC) and H^+ ions. The fractional-order rate coefficient was observed for substrates. The de-carboxylation rate decreases with increasing percentage composition of solvent. The reactions fail to induced the polymerisation with acrylonitrile (monomer). The complex formed between substrate and reacting species H_2CrO_4 was ascertained in transition state in the rate determining slow step. The appropriate mechanism was suggested, and rate law was derived accordingly in conformity with the kinetic findings.

INTRODUCTION

In past decade IQCC has been surged in designing as an oxidant to explore its utility in the synthetic chemistry.[1] IQCC is a stable, non-hygroscopic oxidising agent has been extensively employed in the oxidation of alcohols,[2] aniline,[3] phenols,[4] etc. in acidic medium. Owing to presence of bi-functional groups, mandelic acid and Þ-chloro mandelic acid exhibit different modes of oxidation in mechanistic steps, in which the rupture of C–H or C-C bond occur under different reaction conditions.[5] The literature survey envisage that no information on the oxidation of mandelic acid and Þ-chloro mandelic acid with IQCC is available till date. So we thought it worthwhile, in the present probe to communicate the results of decarboxylation of mandelic acid and Þ-chloro mandelic acid by IQCC.

EXPERIMENTAL

Isoquinolinium chlorochromate was prepared as per norms laid down in literature method.[6] The mandelic acid and Þ-chloro mandelic acid were used of analytical grade being sparingly soluble in water, therefore, their solution was prepared in acetic acid (B.DH.). Fractionated acetic acid was used as a solvent. All other chemicals were of A.R. grade. The other reagent's solutions were prepared in double distilled water and standardized where ever necessary.

KINETIC METHOD

The kinetic reactions were analytically examined under pseudo first-order condition [IQCC] << [substrate] in 30% aqueous acetic acid medium in presence of H_2SO_4. The kinetic investigations were made by withdrawing the 2 ml aliquots of reaction mixtures for the disappearance of oxidant (IQCC) iodometrically using starch as an indicator at regular intervals of time. Prior to this, the solution were contained in separate flasks and placed in well equipped thermostat fitted with stirrer and high sensitive thermometer maintained with an accuracy of $\pm$ 01 ^{0}C to equilibrate the temperature of both the solutions.

The observed rate constant was determined employing integrated and graphical methods.

RESULTS AND DISCUSSION

The influences of variables on the rate of oxidation have been ascribed.

(a) The order of the reaction was kinetically measured by varying five times concentration of oxidant (IQCC) and was found to be unity as derived by the linearity of log (a-x) vs. time plots, over 80% of the reaction.

(b) The reactions were observed to be fractional-order kinetics in substrates at their higher concentrations. The study indicates that the second order constant k_2 value does not show constancy. The capability of forming complex between reacting species H_2CrO_4 and substrates was confirmed by the double reciprocal plots of 1/ [k] vs. 1/ [substrate], which intercepted on rate ordinate (Y-axis) with positive intercept.

(c) The rate of reaction increased with increase in five times more concentrations of the H^+ ions (Table 1). The plot of log k vs. log $[H^+]$ gave approximately unit slope (Fig. 1) indicating simply that the reaction is an acid catalysed[7] one.

Table 1 : Effect of concentration of acid on reaction rate
$10^2 \times$ [Substrate] (mol dm^{-3}) = 2.0 (1), 2.50 (2) ; $10^3 \times$ [IQCC] (mol dm^{-3}) = 2.0 (1, 2) ;
CH$_3$COOH-H$_2$O %, (v/v) = 30 (1, 2) ;
Temp. K = 303 (1), 308 (2).

$10^2 \times$ [substrate] (mol dm^{-3})	$10^4 \times k$ (s^{-1})	
	Mandelic acid (1)	**Þ-chloromandelic acid (2)**
0.25	1.14	-
0.50	1.89	1.26
1.00	3.49	2.34
1.25	4.35	3.11
1.50	4.92	3.87
2.00	-	4.78
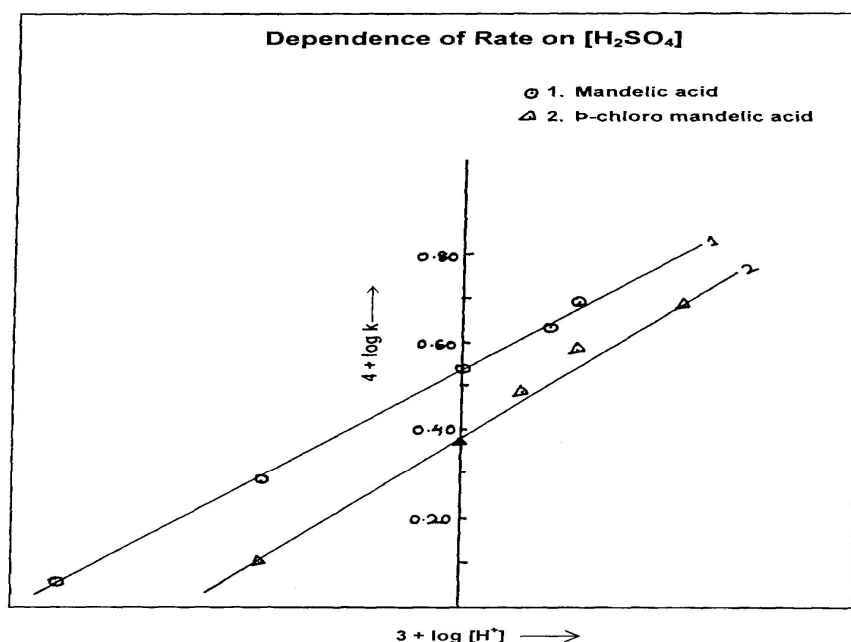
Fig. 1 $10^2 \times$[Substrate] (mol dm^{-3}) = 2.0 (1), 2.50 (2) ;$10^3 \times$[IQCC](mol dm^{-3}) = 2.0 (1, 2);
CH$_3$COOH-H$_2$O %, (v/v) = 30 (1, 2) ; Temp. K = 303 (1), 308 (2)

(d)   The polarity of the medium was varied by using different percentage composition of acetic acid (20 to 50%, v/v) (Table 2). The rate of decarboxylation through oxidation decreased with increasing percentage of acetic acid (decrease of polarity) in the reaction mixture. A plot of log k vs. inverse of dielectric constant (D) of the medium was linear with a negative slope (Fig. 2) suggesting as anion dipole interaction in accordance with the Amis equation.[8]

Table 2 : Effect of Solvent polarity on reaction rate

$10^2 \times$ [Substrate] (mol dm^{-3}) = 2.0 (1), 2.50 (2) ; $10^3 \times$ [IQCC] (mol dm^{-3}) = 2.0 (1, 2) ;
$10^3 \times$ [H$^+$] (mol dm^{-3}) = 1.0 (1), 1.25 (2) ; Temp.   K = 303 (1), 308 (2).

HOAc-H$_2$O % (v/v)	10^3 / D	$\longleftarrow \quad 10^4$ k (s^{-1}) $\longrightarrow$	
		Mandelic acid (1)	Þ-chloro mandelic acid (2)
20	17.17	4.12	3.72
30	19.15	3.49	3.11
40	21.98	2.62	2.33
50	25.64	2.05	1.60

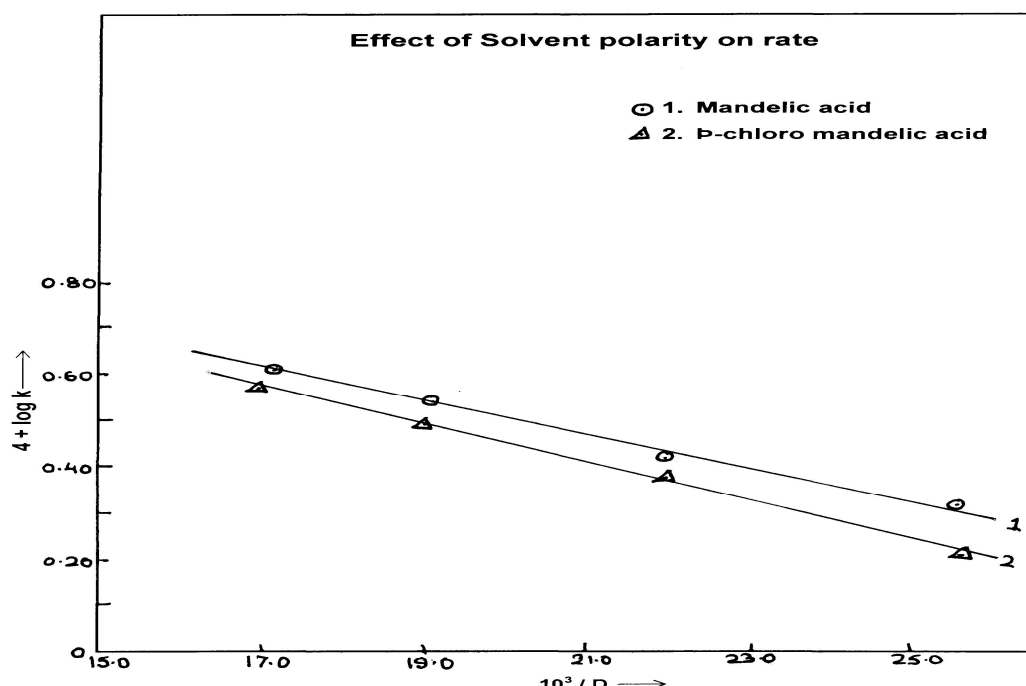**Effect of Solvent polarity on rate**

⊙ 1. Mandelic acid
△ 2. Þ-chloro mandelic acid

Fig. 2 $10^2 \times$[Substrate] (mol dm^{-3}) = 2.0 (1), 2.50 (2) ;
$10^3 \times$[IQCC](mol dm^{-3}) = 2.0 (1, 2);
$10^3 \times$[H$^+$](mol dm^{-3}) = 1.0 (1), 1.25 (2) ;
Temp. K = 303 (1), 308 (2)

(e)   The primary salt effect shows neutrality towards the rate of oxidation with NaCl and ionic strength of medium has no impact on rate of oxidation. When reaction mixture allowed to treat with acrylonitrile monomer, no sign of induced polymerization was observed suggesting that free radical based mechanism was ruled out in the reaction.

The stoichiometry of the oxidation reactions between mandelic acid, Þ-chloro mandelic acid ad IQCC was experimentally determined and indicated 1:1 mole ratio which may be represented by equation as under :


(I.Q.C.C.)
(Isoquinolinium chlorochromate)
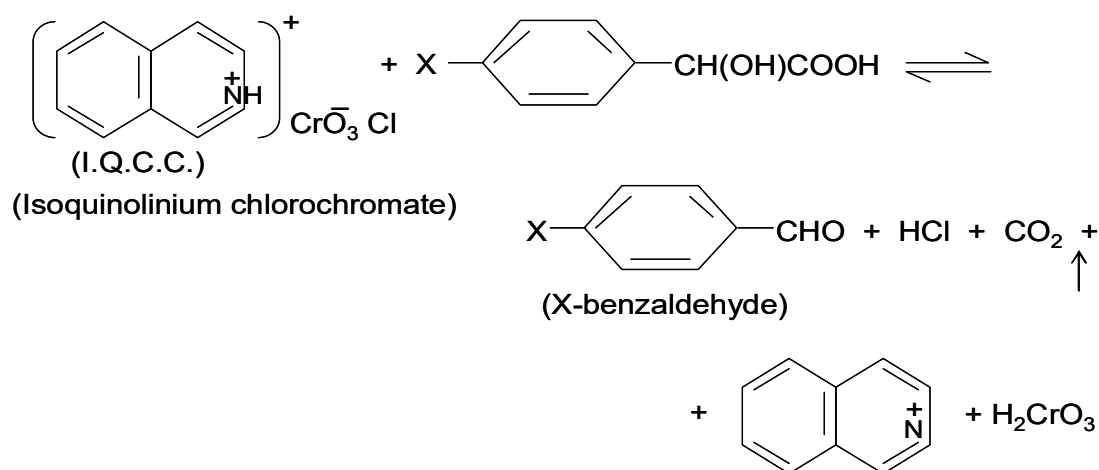
(X-benzaldehyde)

where, X = -H, and -Cl for the corresponding mandelic acid, and Þ-chloro mandelic acid respectively.

The products benzaldehyde and Þ-chloro benzaldehyde were identified by physical and chemical methods and also by forming their 2 : 4-DNP, derivatives.

Mechanism

On the basis experimental data, a tentative mechanism for the reactions have been formulated as :

.... (1)

.... (2)

.... (3)

$$H_2CrO_3 \xrightarrow{\text{fast}} H_2O + \tfrac{1}{2} Cr + \tfrac{1}{2} CrO_4$$

.... (4)
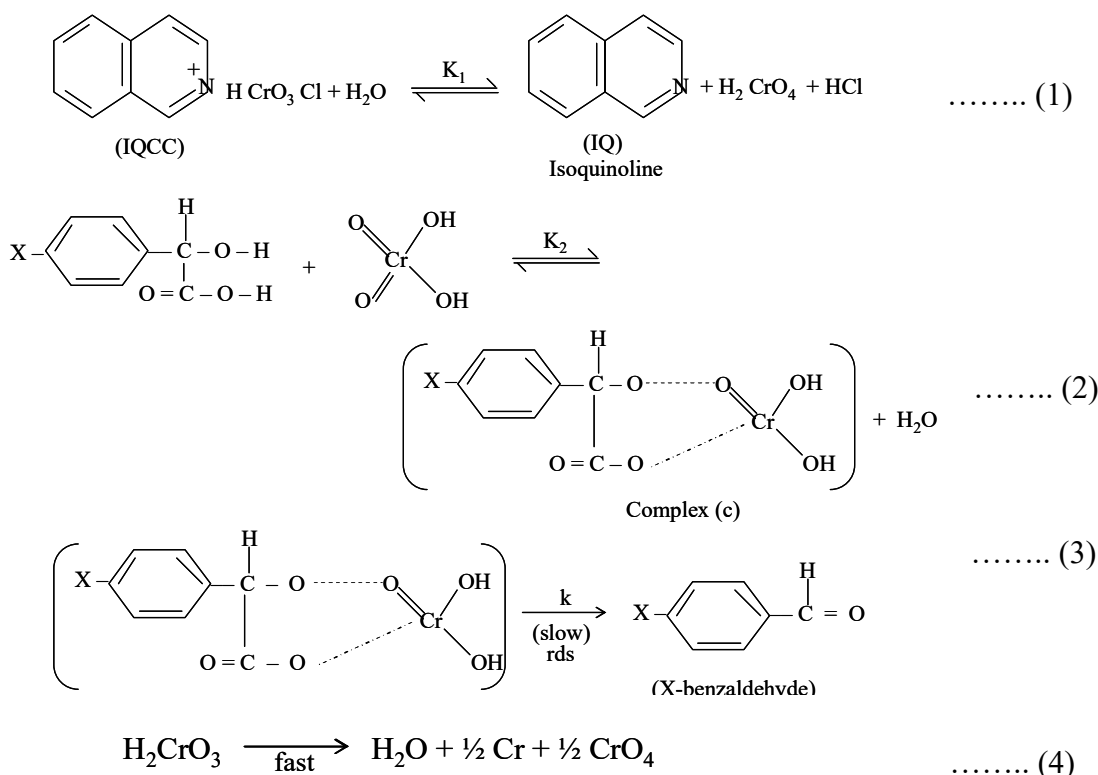
Considering the various steps involved in the postulated mechanism after applying steady state approximation, the final rate law equation may be written as :

.... (5)

$$k_{obs} = \frac{k\,K_1\,K_2\,[S]\,[H^+]}{[IQ]\,K_1 + [\,K_1\,[H^+] + K_1\,K_2\,[S]\,[H^+]}$$

In the proposed mechanism it may be assumed that $K_1 \ll K_2$. Hence, equation (6) becomes

.... (6)

$$k_{obs} = k$$

The derived equation (5) accounts all the observed experimental findings. The transforming the equation (5) and plotting k^{-1}_{obs} Vs. $1/$ [substrate], yield with positive intercept on Y-axis favours the existence of complex in the reaction mechanism at transition state.

In the present endeavour is proportional outlook of the reactivity and structures of substrates which was observed in the following order :

Mandelic acid $>$ Þ-chloro mandelic acid
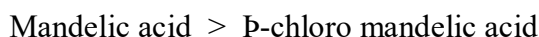
Hydroxy acids being weak acids, containing hydroxyl (-OH) and –COOH groups showing a variety of reactions. The substrates is expected to remain completely in an ionized from. Hence, attack of reacting species H_2CrO_4 occurs at secondary alcoholic (-CHOH) group of the neutral molecule forming complex, which causes decarboxylation at heterolytic C-C bond fission in the rate determining slow step to form the products. Here C_1 facilitate the oxidation and C_2 leads the site of decarboxylation due to electron deficient transition state.
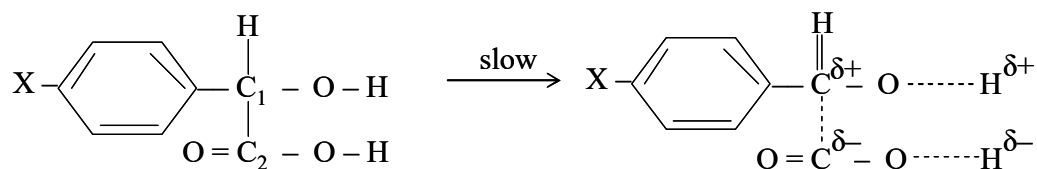
In addition to this –Cl exhibits negative inductive effect, electron attracting groups causes destabilization of transition state, consequently, decreases the rate of reaction of Þ-chloro mandelic acid. Similar trend of mechanism have already being reported for mandelic acid and Þ-chloro mandelic acid by a couple of authors with different oxidants such as NDC,[9] KMnO$_4$,[10] and halo oxidant[11] etc. Generally energy of activation is measure of reactivity which was observed lowest value (58.84 kJ mol^{-1}) for mandelic acid and highest value (61.73 kJ mol^{-1}) for Þ-chloro mandelic acid (Table 3). The high negative value of entropy of activation ($\Delta S^{\#}$) shows the ability of H_2CrO_4 to react with substrate, which measures the disorder of the reaction. The almost similar values of Gibbs free energy ($\Delta G^{\#}$) indicate that identical mechanism prevails in the reactions. Overall the study suggested that reactions are found enthalpy controlled.

Table 3 : Activation parameters for the de-carboxylatin of mandelic acid and Þ-chloro mandelic acid by IQCC

Substrate	E_a kJ (mol^{-1})	A (s^{-1})	$\Delta H^{\#}$ kJ (mol^{-1})	$\Delta G^{\#}$ kJ (mol^{-1})	$-\Delta S^{\#}$ JK^{-1} (mol^{-1})
Mandelic acid	58.84	4.03×10^6	54.66	84.71	98.46
Þ-chloro mandelic acid	61.73	7.05×10^6	59.64	87.00	88.11

Conclusion

The reacting species of isoquinolinium chlorochromate (IQCC) is H_2CrO_4, that attacks to hydroxyl secondary alcoholic (-CHOH) group of substrates causes C-C fission, in the slow process, which decomposed to benzaldehyde and Þ-chloro benzaldehyde. The stoichiometric ratio (1:1) was determined. The order of reactivity based on thermodynamic parameters and negative inductive effect was discussed.

References:

[1]   Patwari, S.B., Khansole, S.V., and Vibhute Y.B. : Bulletin of the Catalysis Society of India, 2009, 8, 114-120.

[2]   Patwari, S.B., Khansole, S.V., and Vibhute Y.B. : J. Iran. Chem. Soc., 2009, 6(2), 399-404.

[3]   Patwari, S.B., Khansole, S.V., and Vibhute Y.B. : Chinese Chemical Letters, 2009, 20(3), 256-260

[4]   Patwari, S.B., Khansole, S.V., and Vibhute Y.B. : J. Indian Chem. Soc., 2009, 86(12), 1343-1346.

[5]   Lopez, C., Gonzalez, C., Cossio, F.P. and Palmo, C. : Synth. commun. 1965, <u>15</u>, 1197.

[6]   Vogel, A.I. : A Text Book of Quantitatives Inorganic Analysis", E.L.B.S., 2010, IInd Ed., 318.

[7]   Palaniappan, A.N., Sekar, K.G., Ravishankar, M. : Oxidn. Commun., 1995, 18, 52.

[8]   Amis, E.S. : Solvlent Effects on Reaction Rates and Mechanism, Academic Press, New York, 1996.

[9]   Mishra, Sakuntala, Swami, M.N., Manikpuri, Nagmani, and Dwivedi, Arvind Prasad : Int. J. Adv. Res. Chem. Sc., 2018, 5(2), 9-13.

[10]   Amorim, J.A., and R.R. : J. Thermochim acta, 2012, <u>8</u>, 408.

[11]   Malarvili, D., Pandeeswaran, M., Bhuvaneshwari, D.S., and Elango, K.P. : J. Indian Chem. Soc., 2005, 83, 893-898.