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Oxidation of þara-methoxy mandelic acid by Quinolinium Fluorochrome - A Kinetic Study

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Abstract : ***This paper reports the results of Quinolinium fluorochrome (QFC) mediated oxidation of þara-methoxy mandelic acid in aqueous acetic acid medium under first-order conditions. The substrate order is complex. The reaction is catalysed by acid, being nearly first-order in acidity. The stoichiometry corresponds to the reaction of one mole of QFC for one mole of þ-methoxy hydroxy acid. The reaction does not induce polymerization of acrylonitrile, C-C bond fission in the rate-determining step was suggested. A mechanism in which rate-controlling breakdown of the complex is suggested to yield the resulting product through deprotonation with a cyclic transition state.***

Key words **: þ-methoxy hydroxy acid, Quinolinium fluorochromate, kinetics, oxidation, stoichiometry.**

1. INTRODUCTION

Quinolinium compounds of fluorochromate (QFC) have long been known [1] but the literature contains a few examples of the use of QFC was made by Banerji *et al.* [2] for the oxidation of aliphatic aldehydes and subsequently, several papers have appeared on the oxidations of organic compounds inclusive of benzaldehyde [3] with allied oxidants too. Nevertheless, a systematic kinetics investigation of the organic substrates by QFC has not been caried out. It is with this prime aim that we undertook, the task of study in context of the oxidation of þara-methoxy hydroxy acid. A systematic study of hydroxy acid and substituted hydroxy acids with other oxidants have already been reported with IQCC [4], NDC [5], halo-oxidants [6-9], $KMnO_4$ [10], Cr(VI) [11], vanadium(V) [12] , but the work lacks to be incomplete in many aspects. The aim of this work was to obtain kinetic evidence in dealing the mechanism.

2. EXPERIMENTAL

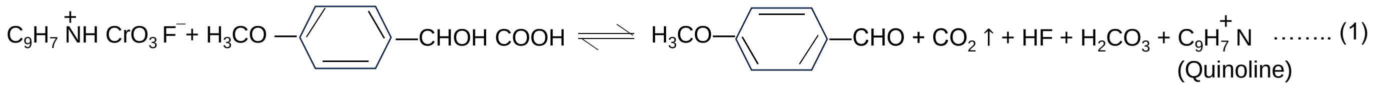
Materials : þ-methoxy mandelic acid (Aldrich) was used in required volume of acetic acid (B.D.H.) and distilled water mixture. All other chemicals and reagents employed were of A.R. analytical grade. The solution of synthesized sample of QFC was prepared as per reported method[1] and tested the stability under the same operating conditions.

Kinetics : The oxidation of substrate was studied under the first-order kinetic conditions i.e. [QFC] << [p-methoy mandelic acid]. The solution of substrate and oxidant (QFC) in suitable amounts were allowed to equilibrate in a previously adjusted thermostat (precision + / -0.1^0C). The solutions were mixed to start the reaction after temperature equilibrium was attained.

Aliquots (2 cm^3) of the reaction mixture were withdrawn at regular time intervals and unreacted QFC was estimated iodometrically. The rate constants (k_{obs}) were determined from the liner plots of log unreacted [QFC] versus time.

3. RESULTS AND DISCUSSION

The stoichiometry of the reaction was determined under defined pre-set conditions of the reaction. Thus, certain reaction was allowed to take place in a special vessel at 5^0 C for 5 h. The excess of QFC was determined iodometrically after completion of the reaction. The results indicate that one mole of the QFC needs a mole of substrate corresponding to stoichiometry depicted by equation (1)



The oxidation product i.e. p-methoxy benzaldehyde (bþ. 143^0 C) identified by 2,4-dinitrophenyl hydrazone test and further confirmed by TLC.

The ionic strength was varied (five-fold concentration) with sodium perchlorate on oxidation rate, but the influence was found to be negligible, pointing thereby the ion-dipole nature of the reaction. Furthermore, the addition of monomer polyacrylonitrile to reaction mixture does not produce polymerization. The above version for the free radical's presence was also ignored by the test carried out with butylated hydroxy toluene (B.H.T.).

QFC dependence : The concentration of quinolinium fluorochromate was varied (0.333×10^{-3} to 1.25×10^{-3} mol dm^{-3}) at fixed conditions of other reagents (Table: 1). A plot of initial rates versus [QFC] yielded a straight line passing through origin, conforming a first-order dependence on [QFC]. Moreover, the evaluated approximately unit slope of the plots of lg $\frac{[QFC]_o}{[QFC]_t}$ against time (Figure 1) also supported the above order of kinetics.

Table 1: Initial rates of the reaction of QFC with þ-methoxy mandelic acid : Variation of [QFC]

[p-methoxy mandelic acid] = 0.666×10^{-3} (mol dm^{-3}) ; $[H^+] = 5.0 \times 10^{-3}$ (mol dm^{-3}) ;
$CH_3COOH : H_2O = 30 : 70$ %, (v/v) ; Temp. ≃ 278 K

$[QFC] \times 10^{-3}$ (mol dm^{-3})	0.333	0.666	1.25
$k \times 10^4$ (s^{-1})	9.38	9.22	9.41

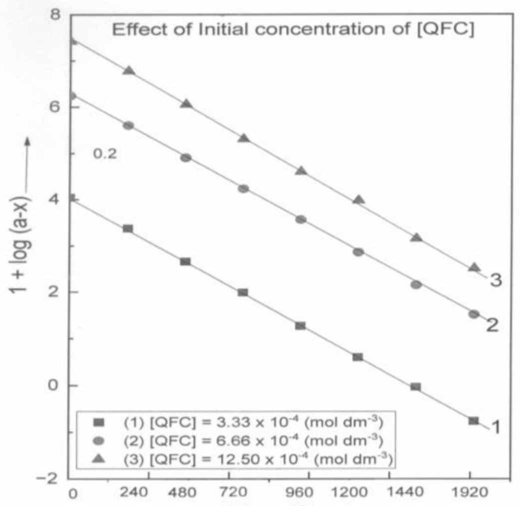


Fig. 1 Plot of log (a-x) vs. time

$[p\text{-}CH_3OC_6H_4(CHOH)\cdot COOH] = 6.66 \times 10^{-2}$ (mol dm^{-3}) ;
$[H^+] = 0.50 \times 10^{-2}$ (mol dm^{-3}) ;
$CH_3COOH\text{-}H_2O = 30\%$ (vv) ;
Temp. = 278 K

þ-methoxy mandelic acid dependence : The concentration of para-methoxy mandelic acid was varied at fixed concentrations of the other ingredients and QFC. The initial rates (k mol dm^{-3} s^{-1}) for the substrate studied were computed employing integration and graphical methods, are reported in (Table: 2). The rate increases and tends to a limiting value with increasing [þ-methoxy mandelic acid] such a trend follows Michaelis-Menten type kinetics (Figure: 2) (double reciprocal plot of $\frac{\mathbf{1}}{\boldsymbol{k_{obs}}}$ vs. 1/[þ-methoxy mandelic acid], with positive intercept on ordinate axis. The reaction under investigation thus show fractional-order kinetics with respect to þ-methoxy mandelic acid. The values of second-order $\boldsymbol{k_2} = \frac{\boldsymbol{k}}{[\boldsymbol{subst}.]}$ does not show constancy, this indicates that an adduct is formed between reacting species of oxidant and bifunctional group of substrate at transition state.

Table 2 : Variation of [þ-methoxy mandelic acid] at ≃ 278 K

$[QFC] = 0.666 \times 10^{-3}$ (mol dm^{-3}) ; $[H^+] = 5.0 \times 10^{-3}$ (mol dm^{-3}) ;
$CH_3COOH : H_2O = 30 : 70$ %, (v/v)

[þ-methoxy mandelic acid] × 10^2 (mol dm-^{3})	0.15	0.20	0.25	0.	0.40	0.50	0.666
10^4 k_{obs} (s^{-1})	5.22	6.25	7.36	8.5	9.05	9.61	9.22

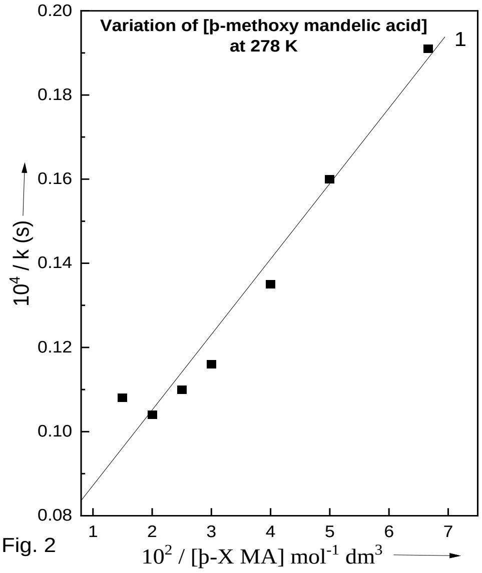


Fig. 2

Michaelis-Menten plot 1/ k_{obs} vs. 1/[þ-X MA]
[QFC] = 0.666 $\times 10^{-3}$ (mol dm^{-3}) ;
$[H^+]$ = 5.0 $\times$ 10^{-3} (mol dm^{-3}) ;
CH_3COOH : H_2O = 30 : 70 %, (v/v)

Table 3 : Thermodynamic and activation parameters for the reaction between þ-$CH_3OC_6H_4$ (CHOH)·COOH and QFC

Substrate	Ea kJ mol^{-1}	$\Delta H^\#$ kJ mol^{-1}	$\Delta G^\#$ kJ mol^{-1}	$-\Delta S^\#$ JK^{-1} mol^{-1}
þ-methoxy mandelic acid	36.22	33.39	71.03	132.98

Hydrogen-ion Dependence: The hydrogen-ion concentration was varied (0.333 $\times 10^{-2}$ to 0.80 $\times 10^{-2}$ mol dm^{-3}) at experimental conditions. It was found that the reaction under investigation is almost acid catalyzed. The rate of oxidation increases proportionality to some extent showing first-order kinetics but values of k_2 second-order are not fairly constant a it obeys the kinetics of the form k_{obs} a + b $[H^+]$ [13].

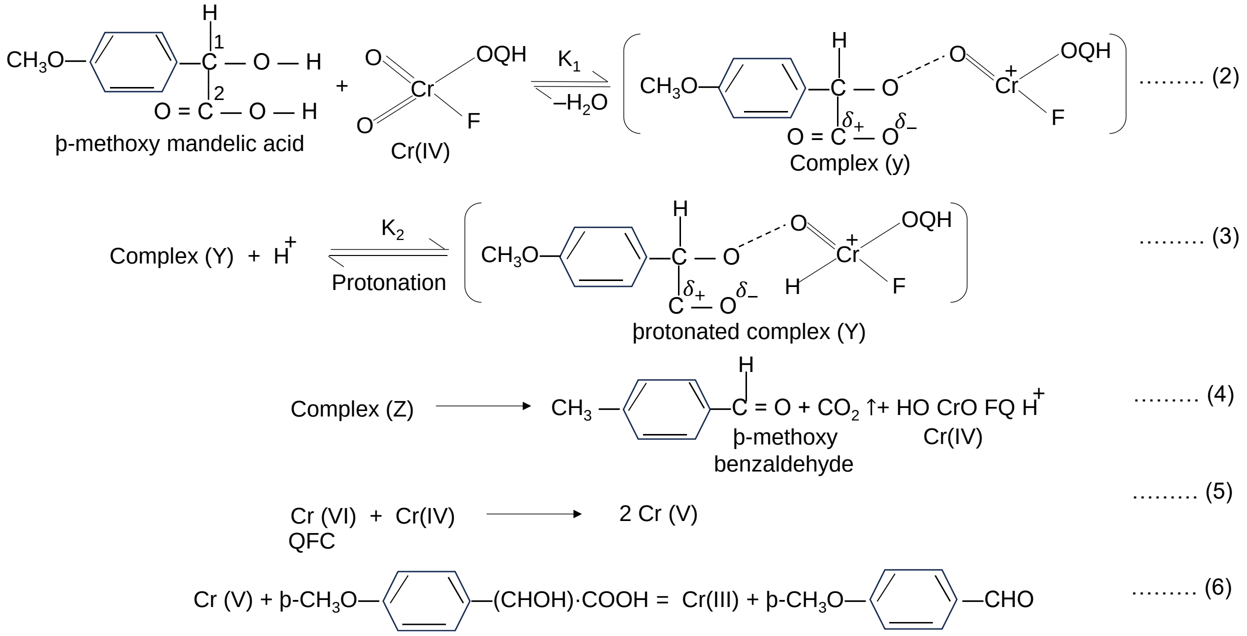
Effect of rate on Solvent polarity: The kinetics of the reaction has been investigated by changing the composition of CH_3COH (20% to 50%, v/v) in the reaction mixture while keeping other ingredients and temperature unaltered. The rate of oxidation retarded by decreasing dielectric constant of the medium suggested that reaction may occur between ions of opposite charges. The Amis plot of lg k vs. $\frac{D-1}{2D+1}$ yielded negative slope conforming a rate-limiting step with charge dispersal and Swain's hypothesis [14].

Reaction mechanism : The acid catalysis may well be attributed to a protonation of QFC to yield a protonated Cr(VI) species which is stronger oxidant and electrophile.

$$Q\ HO\ CrO_2\ F + \overset{+}{H} \rightleftharpoons Q\ \overset{+}{H}OCr\ (OH)\ OF \qquad \ldots\ldots\ldots\ (1)$$

This has earlier been postulated in the reaction of structurally, similar to PCC [15], and PFC [16].

The following proposed mechanism is based on the experimental findings and information about the intermediate complex,



In suggested mechanism, the cleavage of C-C bond is followed by its decomposition in rds to give product of the reaction. The rate law could be discussed below Cr(VI) can be determined on applying the equilibrium condition.

$$\underset{(S)}{\text{Substrate}} + \text{QFC} \underset{}{\overset{K_1}{\rightleftharpoons}} \text{Complex (Y)} \quad \text{.........} (1)$$

$$\text{Complex Y} + H^+ \overset{K_2}{\rightleftharpoons} \text{Complex (Z)} \quad \text{.........} (2)$$

$$\text{Complex (Z)} \xrightarrow[\text{rds slow}]{k} \text{Product} + \text{Cr(IV)} \quad \text{.........} (3)$$

$$\therefore \frac{-d}{dt}[Cr(VI)] = k[Z] = k\,K_1K_2[H^+][S] \times [Cr(VI)] \;\ldots\ldots(4)$$

The loss of QFC leads to the rate law equation (5)

$$\frac{-d}{dt}[Cr(VI) = \frac{k\,K_1K_2[H^+][S][Cr(VI)]_t}{1 + K_1K_2[H^+][S]} \qquad \ldots\ldots(5)$$

or $k_{obs} = \frac{kK_1K_2[H^+][S]}{1+K_1K_2[H^+][S]}$ ……..(6)

Here, $[Cr(VI)_t = [Cr)VI) + [Z]$ ……… (7)

Since, K_1 is low and yielded (Y) which get react with substrate (S).

or $\frac{1}{k_{obs}} = \frac{1}{kK_1K_2[H^+][S]} + \frac{1}{k}$ …….(8)

The reaction is well characterized by equation (6) or equation (7).

The plot of $[\text{rate}]^{-1}$ versus $[\text{þ-MeOMA}]^{-1}$ yielded straight line with non-zero intercept verifies this complex mechanism. Similar kinetic features has also been reported by eminent kineticsts [17,18].

The structure the substrate supports rate-determining oxidative de-carboxylation due to heterolytic fission of C_1 - C_2 bond in transition state of cyclic chromate ester that simultaneous development of partial charges on C_1 and C_2 carbon is decarboxylated that later on oxidized to -CHO group. The positive character of C_1 is thus stabilized by electron donating methoxy (CH_3O) group. The M^+ effect of this group also helps in decarboxylation of C_1 positive charge. The thermodynamic and activation parameters were also determined for the kinetics of reaction.

Conclusion

The reaction of þara-methoxy mandelic acid and Quinolinium fluorochromate in aqueous acetic acid medium yields þ-methoxy benzaldehyde as a product based on stoichiometry (1:1). The reaction exhibited first-order with respect to QFC (oxidant) and complex nature to substrate. The rate of kinetics was observed as k_{obs} a + b $[H^+]$ for acid. The proposed mechanism indicated the fission of C-C bond and accounts for the experimental observation and the deduced rate law.

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Conflict of Interest

-- none --

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