Kinetics and Mechanism of Oxidation of Malic Acid by Morpholinium Fluorochromate in Aqueous Acetonitrile Medium

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Abstract: Kinetics of oxidation of malic acid by morpholinium fluorochromate (MFC) in 50% (v/v) acetonitrile-water solvent mixture at 298 K in the presence of perchloric acid has been studied spectrophotometrically. The reaction is first order each with respect to malic acid, MFC and H^+ ion. Variation of ionic strength of the reaction medium or addition of acrylonitrile does not influence the reaction. However, the rate of reaction decreases significantly on addition of manganese sulphate. The reaction is favoured by lowering of solvent polarity. Activation parameters, E_a, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$ have been evaluated from the rate constant values measured at four different temperatures using Arrhenius and Eyring equations. Based on these findings, a suitable mechanism has been proposed.

Keywords: Oxidation, Kinetics, Mechanism, Malic acid, Morpholinium fluorochromate

Introduction

Chromium compounds have been used in aqueous and non-aqueous medium for the oxidation of a variety of organic compounds. A number of new chromium(VI) compounds containing heterocyclic bases such as pyridinium chlorochromate[1], pyridinium bromochromate[2], quinolium chlorochromate[3], bipyridinium chlorochromate[4], quinolium bromochromate[5], imidazolium fluorochromate[6], pyridinium fluorochromate[7], tributylammonium chlorochromate[8], tripropylammonium fluorochromate[9], quinolinium fluorochromate[10], imidazolium dichromate[11], morpholinium chlorochromate[12] *etc.,* have been developed to improve the selectivity of oxidation of organic compounds. Morpholinium fluorochromate (MFC) is also an effective oxidant which has not been used so far in the oxidation of hydroxy acids. Further, this reagent does not react with acetonitrile, which is a suitable medium for studying kinetics and mechanism. Many well known hydroxy acids are useful building blocks in organic synthesis, the most common and simple are malic acid, glycolic acid, lactic acid, mandelic acid *etc*., Malic acid is a dicarboxylic acid which contributes to the pleasantly sour taste of fruits and

is used as food additive. Malic acid is widely used in medications and food industries. Hereunder we report the results obtained in the kinetic study of oxidation of malic acid in acetonitrile-water mixture with MFC to elucidate a probable mechanism of oxidation.

Experimental

All the chemicals used were of AR Grade. MFC was prepared by a modified literature method[13] and its purity was checked by determining Cr(VI) concentration iodometrically. Analar grade malic acid (Aldrich) was used as such. All the solutions used in the study were made in distilled acetonitrile or doubly distilled water.

Kinetic measurements

The reactions were carried out under pseudo first order conditions by keeping an excess of substrate over MFC. The kinetic runs were carried out in 50% acetonitrile-50% water (v/v) solvent mixture. The reactions were followed spectrophotometrically by monitoring the decrease in absorption of MFC at 368 nm for up to 3 half-lives. No attempts were made to keep the ionic strength of the reaction medium constant as the reactions were not influenced by changes in ionic strength. The pseudo-first order rate constants, k_{obs}, were determined by least square method from the linear plots of log[MFC] *versus* time. Replicate runs showed that the rate constants were reproducible to within ±3%. The second order rate constants, k_2, were calculated as k_{obs}/[substrate]. All kinetic runs, other than those for studying the effect of hydrogen ions, were carried out in absence of perchloric acid.

Product analysis

In a typical experiment, solutions of malic acid and MFC in 2:1 molar ratio were mixed and kept aside in dark for about 24 h to ensure completion of reaction. It was then treated with 50 mL of a saturated solution of 2,4-dinitrophenyl hydrazine and kept overnight in a refrigerator. The precipitated 2,4-dinitrophenyl hydrazone (DNP) was filtered off, dried and recrystallised from ethanol. The product was identical to an authentic sample of DNP (melting point and mixed melting point) of the corresponding keto acid. The oxidation state of chromium in completely reduced reaction mixtures, as determined iodometrically, was 3.91±0.31.

Stoichiometry

In a typical experiment, a reaction mixture containing 10 times excess of MFC over malic acid was prepared and allowed to react overnight. Then the unreacted MFC was estimated iodometrically, which established a 1:1 stoichiometry between MFC and malic acid, as represented in the following scheme.

$$(COOH)CH_2CH(OH)COOH + O_2CrFOMH + H^+ \rightarrow$$
$$OCrFOMH + (COOH)CH_2COCOOH + H_2O$$
Scheme 1

Results and Discussion

Oxidation of malic acid by MFC was carried out in 50% acetonitrile and 50% water medium at 298 K, under pseudo first-order conditions. As it was found that ionic strength of the reaction medium had no significant effect on reaction rate, constancy of ionic strength was not maintained throughout the present study.

The values of k_{obs} were calculated for different concentrations of MFC by maintaining other parameters at constant values. The data in Table 1 show that the pseudo first order rate constant (k_{obs}) remains almost constant on varying the concentration of MFC. This result, coupled with the excellent linearity observed in log [MFC] *versus* time plots, ensures that the order of the

reaction with respect to [MFC] is one. The k_{obs} values calculated for different concentrations of malic acid at a constant [MFC] are also included in Table 1. The data show that the rate increases with increase in [malic acid] in a first-order fashion. The k_2 values remain constant when [malic acid] is varied. The plot of k_{obs} *versus* [malic acid] is excellently linear passing through origin (Figure 1; r = 0.999). The double logarithmic plot between k_{obs} and [malic acid] (r = 0.999; slope = 1.01 ± 0.01) is excellently linear with a slope value equal to nearly one. These observations confirm the first-order nature of the reaction with respect to [malic acid].

Table 1. Pseudo first-order and second-order rate constants for the oxidation of malic acid by MFC in 50:50 acetonitrile-water (v/v) mixture at 298 K

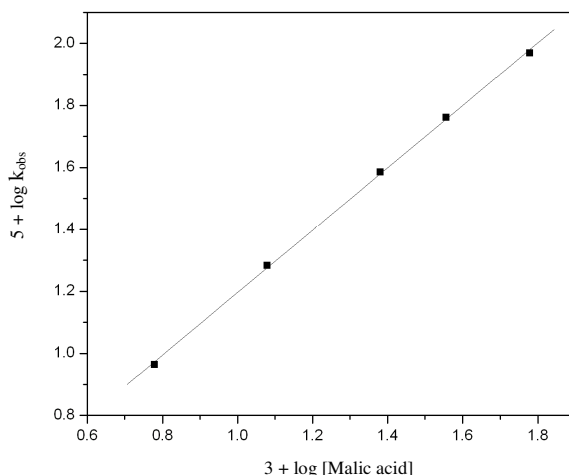| 10^3, MFC, M	10^2, Malic acid, M	10^2, H$^+$, M	$10^4 k_{obs}$, s^{-1}	$10^2 k_2{}^c$, M^{-1}s^{-1}
0.5	0.6	2.0	0.92±0.07	1.53±0.12
0.5	1.2	2.0	1.93±0.14	1.61±0.12
0.5	2.4	2.0	3.85±0.32	1.60±0.13
0.5	3.6	2.0	5.78±0.50	1.61±0.14
0.5	6.0	2.0	9.31±0.84	1.55±0.14
1.0	6.0	2.0	9.24±0.88	1.54±0.15
2.0	6.0	2.0	9.26±0.86	1.54±0.14
3.0	6.0	2.0	9.30±0.81	1.55±0.13
5.0	6.0	2.0	9.39±0.85	1.56±0.14
0.5	1.2	0.5	0.44±0.03	0.37±0.03
0.5	1.2	1.0	0.99±0.07	0.83±0.06
0.5	1.2	3.5	3.15±0.22	2.63±0.18
0.5	1.2	5.0	4.55±0.30	3.79±0.25

Figure 1. Double logarithmic plot between k_{obs} and [Malic acid] for the oxidation of malic acid with MFC

The values of k_{obs} were calculated at different concentrations of H$^+$, keeping the [MFC] and [Malic acid] at constant values. The k_{obs} value increases linearly with increase in [H$^+$] (Table 1), establishing the catalytic behavior of perchloric acid. The plot of k_{obs} *versus* [H$^+$] is excellently linear passing through origin (Figure 2; r = 0.999). The double logarithmic plot between k_{obs} and [H$^+$] (r = 0.999; slope = 0.996±0.021) is excellently linear with a slope value equal to nearly one. These observations establish that the reaction follows first-order kinetics with respect to [H$^+$].

Similar results with respect to [oxidant], [substrate] and [H⁺] have been reported in the oxidation of olymeri acids by tripropylammonium fluorochromate,[9] imidazolium dichromate[11], pyridinium chlorochromate[14], KMnO₄ and of aldehydes[15] by benzimidazolium fluorochromate[16] and benzyltrimethylammonium fluorochromate[17].
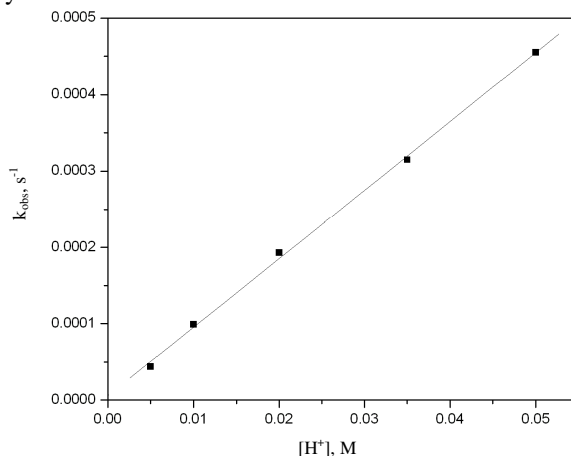

Figure 2. Plot of k_{obs} *versus* [H⁺] for the oxidation of malic acid with MFC

The effect of ionic strength on the reaction rate was studied by varying the ionic strength of the medium by adding different quantities of NaClO₄, maintaining other parameters constant (Table 2). The data reveal that variation of ionic strength of the medium has no significant effect on reaction rate. This result shows the participation of a neutral species as a reactant in the rate-determining step. The kinetic runs carried out in the presence of acrylonitrile (Table 2) establish that the reaction fails to initiate the olymerization of added acrylonitrile. Absence of any effect of added acrylonitrile on the reaction discounts[18] the possibility of formation of free radicals during the course of the reaction as a result of a one-electron oxidation.

Table 2. Influence of ionic strength (**I**) and acrylonitrile (AN) on reaction rate for the oxidation of malic acid by MFC in 1:1 acetonitrile-water (v/v) mixture at 298 K[a]

[I], M	$10^4 k_{obs}, s^{-1}$	10^3. AN, M	$10^4 k_{obs}, s^{-1}$
0.01	1.93 ± 0.14	0	1.93 ± 0.14
0.03	1.95 ± 0.13	1.0	1.92 ± 0.11
0.06	1.90 ± 0.15	3.0	1.88 ± 0.13
0.10	1.86 ± 0.11	6.0	1.85 ± 0.13

[a]*General conditions: [MFC] = 0.0005 M; [Malic acid] = 0.012 M.*

The oxidation of malic acid with MFC was conducted in presence of differing amounts of MnSO₄ and the rate constant values measured are included in Table 3. The data show that the rate of reaction decreases significantly with increasing concentration of added MnSO₄. This result reveals[19,20] a direct two electron reduction of Cr(VI) to Cr(IV). The effect of the solvent composition on the reaction rate was studied by varying the acetonitrile content in the solvent mixture from 40% to 80% and the measured k_{obs} values (Table 3) show that the rate of reaction increases remarkably with increase in the percentage proportion of acetonitrile in the solvent medium, establishing that the reaction between malic acid and MFC is favoured by a solvent of low dielectric constant. The plot

of log k_{obs} *versus* 1/D (Amis plot) is linear (r = 0.998; slope = 119.03), with positive slope, indicating[21] that the rate-determining step involves an interaction between a cation and a dipole.

Table 3. Influence of added manganous sulphate and solvent polarity on reaction rate for the oxidation of malic acid by MFC at 298 K[a]

10^3, Mn^{2+}, M	$10^4 k_{obs}$, s^{-1}	%CH$_3$CN, v/v[b]	$10^4 k_{obs}$, s^{-1}
0	1.93±0.14	40	1.40±0.11
0.50	1.68±0.12	60	2.57±0.21
0.80	1.45±0.11	70	3.51±0.28
1.20	1.31±0.10	80	5.42±0.48

[a]*General conditions: [MFC] = 0.0005 M; [Malic acid] = 0.012 M; Solvent = 1:1 acetonitrile-water (v/v) mixture unless otherwise stated.* [b]*Rest was water*

The reaction was carried out at three other temperatures (303, 313 and 323 K) keeping other experimental conditions constant. The values of k_2 (M^{-1}s^{-1}) are 0.0161, 0.0262, 0.0572 and 0.121 at 298, 303, 313 and 323 K, respectively. From the Arrhenius and Eyring plots, the thermo-dynamic parameters for the oxidation of malic acid were found to be E_a = 64.0±1.3 kJ/mol, $\Delta H^{\ddagger}$ = 61.4 ± 1.3 kJ/mol, $\Delta G^{\ddagger}$ (298 K) = 83.2 ± 1.9 kJ/mol and $\Delta S^{\ddagger}$ = −73.0 ± 1.8 JK^{-1}mol^{-1}.

Mechanism

Absence of any effect of added acrylonitrile indicates the non-involvement of free-radical species and thus discounts the possibility of one-electron transfer in the rate-determining step. The solvent effect points to an interaction between a cation and a dipole in the rate-determining step and supports a transition state, which is more polar than the reactant state. Retardation of the rate of oxidation by the added Mn^{2+} ion implies a two-electron transfer in the rate-determining step. The observed acid-catalysis may well be attributed to protonation of MFC to yield protonated Cr(VI) species which is a stronger oxidant and electrophile. Formation of a protonated Cr(VI) species has earlier been postulated in the reactions of quinolinium fluorochromate[22] and pyridinium chlorochromate[23]. Based on the above kinetic observations, a mechanism (Scheme 2) involving a hydride-ion transfer from O – H group to MFC has been suggested for the oxidation of malic acid with MFC.

R=CH$_2$COOH, MH=Morpholinium
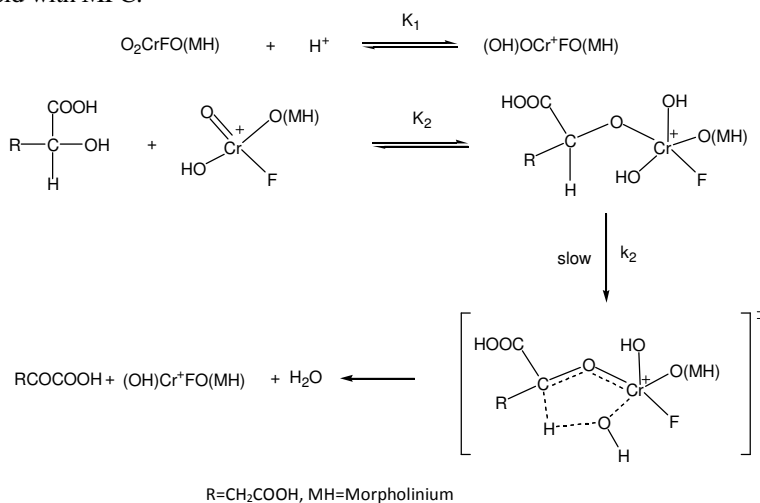
Scheme 2

The rate law can be given as

$$\text{Rate} = K_1 K_2 k_2 [\text{BTMAFC}][\text{Malic acid}][\text{H}^+]$$

This rate law explains the first-order dependence of the reaction on [MFC], [Malic acid] and [H$^+$]. The observed negative value of entropy of activation suggests a slow bimolecular reaction forming a rigid-transition state by an associative process in the rate-determining step. The chromate ester bond in this unstable transition state breaks to form the products. As the charge separation takes place in the transition state, the charged ends become highly solvated. This results in an immobilization of a large number of solvent molecules, resulting in loss of entropy[22].

Conclusion

The oxidation of malic acid with morpholinium fluorochromate involves a direct hydride ion transfer from the substrate to oxidant, resulting in the formation of oxo acid and Cr(IV) as products. This mechanism is supported by the experimental data such as the reaction stoichiometry, the effect of solvent polarity, the effect of added Mn^{2+} and the activation parameters.

Acknowledgement

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