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Oxidative Transformation of Malic Acid by Pyridiniumdichromate in Non-Aqueous Medium- Kinetic and Mechanistic Study

Chemistry

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ABSTRACT

The alpha-hydroxy acids (AHA) are naturally occurring organic acids.The oxidation of malic acid by pyridiniumdichromate has been studied spectrophotometrically in the presence of p-toluenesulphonic acid (PTSA) in dimethylsulphooxide(DMSO) as solvent. The reaction is first order with respect to oxidant and [H+]. Michaelis–Menten type kinetics is observed.The rate of reaction decreaseswith anincrease in the polarity of solvent indicating an ion–dipole interaction in the slow step. The reactions exhibit no primary kinetic isotope effect. The activation parameters have been evaluated.

Introduction-

Oxidation of organic compounds under non-aqueousconditions is an important reaction in syntheticorganic chemistry.[1-5]For this a number of different chromium(VI) derivatives have been reported.[6-9]

Many workers namely Karthikeyan[10], Das, Chaube and Mahanti[11], Karunakaran[12] and Kumbhatet al[13]. have been studied oxidation of hydroxy and carboxylic acids using Cr(VI) as chromic acid and its complexes. The oxidation of α-Hydroxy acids by Pyridinium Dichromate (PDC) has been studied by Ahmed S.Zaheer et.al[14].The reaction is pseudo first order, with respect to hydroxy acid, [H+] and [PDC].

Hiran et.al.[15] studied the oxidation of lactic and mandelic acid by quinolinium dichromate in aqueous acetic acid medium. The reaction is first order in each reactant. The kinetics of oxidation of lactic acid by pyridinium dichromate (PDC) in perchloric acid medium studied by Dangarh et al[16]

Materials and Method-

Pyridiniumdichromate was prepared by the method describe in the literature [13] and its purity was checked by iodometrically and by IR spectrum.

I R. = νmax (KBr) = 3250,1660,1500,1340,110,950,870,770 cm^{-1}

Malic acid (A.R.grade) was used as supplied. DMSO was purified by distillation. All other reagents used were of "AnalaR" grade.

The pseudo-first order conditions were attained by keeping a large excess of the hydroxy acid over PDC. The temperature was kept constant to ± 0.1 K.The solvent was DMSO. Thereactions progress was followed by monitoring the decrease in theconcentration of PDCspectrophotometrically at 385 nm forup to 80% of the reaction.

RESULTS AND DISCUSSION:

Effect of oxidant-

When Malic acid were in excess, the disappearance of PDC followed the first-order rate law. The first-order rate constants are independent of the initial concentration of the PDC when varied in the range (1–4) $\times 10^{-3}$mol/dm^{-3} at 303 K

Effect of Substrate-

At constant [PDC], the rate constants for oxidation calculated at different initial concentration of substrates found to increase linearly with the increase in concentration of substrates (2×10^{-2}M to 6×10^{-2}M). The results of the effect of substrate concentration on the rate constant are summarized in (Table - 1). A plot of log k_1 against log [substrate] gives a straight line in both cases(fig-1). This revealed that the rate of oxidation is first order with respect to the acid. It has been found that plot of [1/k_1] versus (1/[substrate]) is straight line with an intercept on the rate ordinate, indicating the oxidation of Malic acid follows Michaelis–Menten type kinetics and proceeds through the formation of a complex between the oxidant and the substrate.

Effect of H^+ Ion-

To study effect of hydrogen ion p-toluenesulphonic acid was used. The rate of oxidation was studied from [H^+] = 0.0 M to 1.6 M. It was observed that rate increases with increase in hydrogen ion concentration. log k_1v/s log [H^+] is a stright line in all the cases and the slopes arenear to one. The results are summarized in Table-1.

Effect of Solvent composition-

Effect of solvent was studied by changing proportion of DMSO and water; varied from 10 to 50 % water v/v. The reaction rate decreases with an increase in the percentage of water, suggesting that a low dielectric medium favors the oxidation (Table-1). A plot of log k_1 against 1/D (dielectric constant) is linear with a positive slope for the acids under study. This indicates an ion–dipole type of interaction in the rate-determining step[18-20]. Wieberg and Evans[21] have made a similar approximation with regard to the same binary solvent system.

For further confirmation we can apply the equation[22]

$$\ln k = \ln k_0 - \frac{N(D-1)}{RT(2D-1)}\left\{\frac{\mu_A^2}{r_A^3} + \frac{\mu_B^2}{r_B^3} - \frac{\mu_{\pm}^2}{r_{\pm}^3}\right\}$$

So if In k_1 v/s (D-1)/(2D+1) is stright line[23] with negative slope indicates that activated state is less polar, while positive slope indicates more polar activated state. In our study we get negative slope indicate that activated state is less polar, therefore, by increasing percentage of dioxane rate should increase; that is by decreasing dielectric constant rate of reaction will be favored, which we have observed in our study.

Effects of Mn (II) and Ce (III) Ion

It has been observed that addition of low concentration of Mn (II) and Ce (III) ions retard the rate of oxidation of acids. The retardation of the rate by addition of Mn(II) ion can be explained by te dispropotion of Cr(VI), Cr(V) and Cr(III). The general scheme of oxidation of acids with PDC may be represented as:

$Cr(VI) + R\text{-}CH(OH)COOH \longrightarrow R\text{-}CHO + Cr(IV)$

$Cr(VI) + Cr(IV) \longrightarrow 2Cr(V)$

$Cr(IV) + Mn(II) \longrightarrow Mn(III) + Cr(III)$

$Cr(IV) + Cr(V) \longrightarrow Cr(VI) + Cr(III)$

This may be taken as evidence for formation of Cr (IV) species and hence PDC is acting as two-electron transfer oxidant[16].

Effect of Temperature-

Rate of oxidation increases with increase in temperature. Rate of reactions were determined at different temperature (303 to 323 K). In all the cases, a plot of log k_{obs} versus 1/T (inverse of absolute temperature) is a straight line. This shows that Arrhenius equation is valid for this oxidation.

The energy of activation is 23.78 kJ mol^{-1}. The entropy values is negative and high suggesting that the transition state is more rigid and extensively solvated than the reactants. The negative entropy also suggests the formation of cyclic intermediate from acyclic species. (Table 2 &3)

Conclusion-

Oxidative transformation of Malic acid is first order with respect to oxidant in [H].Glasston[24] has pointed out that if entropy of activation is large and positive, the reaction will be normal and fast but if it is negative, the reaction is slow. In this case, the negative values of entropy of activation come under a category of slow reactions. In these oxidation reaction negative values of entropy suggest either formation of cyclic struture from non-cyclic structure or the activated state is more polar than the reactants. Negative value of entropy also suggest that bimolecular reaction in the rate-determining step. Bakore and Shyam Narain[25] suggest that oxidation of α -hydroxy by Cr(VI) is similar to that of isopropyl and benzaldehyde, which involve rupture of C-H bond on α -carbon. Kemp and Water[26] also suggest that C-H fission must occur with Cr(VI). It is well established that intrinsically concerted sigmatropic reactions, characterized by transfer of hydrogen in a cyclic transition state, are the only truly symmetrical processes involving a linear hydrogen transfer.[27] Littler[28] has also shown that a cyclic hydride transfer, in the oxidation of alcohols by Cr (VI), involves six electrons and, being a Huckel-type system, is an allowed process. Thus the overall mechanism is proposed to involve the formation of a chromate ester in a fast pre-equilibrium and then a decomposition of the ester in a subsequent slow step via a cyclic concerted symmetrical transition state leading to the product. The observed negative value of entropy of activation also supports a polar transition state.

TABLE NO. 1
Effect of [Substrate], [H^+] and Solvent
[PDC] = 2 x 10^{-3} M T = 308 K

[Substrate] x 10^2 M	[PTSA] x 10^3 M	Water in DMSO % v/v	k_1 x 10^5, sec^{-1}
2.0	3	0	17.84
3.0	3	0	23.07
4.0	3	0	29.09
5.0	3	0	34.78
6.0	3	0	40.68
2.0	3	0	17.84
2.0	3.5	0	20.07
2.0	4.0	0	22.3
2.0	4.5	0	25.57
2.0	5.0	0	28.85
2.0	5.5	0	31.74
2.0	6.0	0	34.63
2.0	3	10	16.08
2.0	3	20	11.77
2.0	3	30	9.78
2.0	3	40	8.67
2.0.	3	50	7.95

TABLE NO. 2
[Substrate] = 2 x 10^{-2} M [PTSA] =3 x 10^{-3} M
[PDC] = 2 x 10^{-3} M

Temp (K)	k_1 x 10^5, sec^{-1}
303	17.84
308	18.91
313	22.47
318	27.21
323	32.84

TABLE NO. 3
THERMODYNAMIC PARAMETERS

Substrate	log A	Energy of activation $\Delta E^{\#}$ kJ mol^{-1}	Entropy of activation $\Delta S^{\#}$ $Jmol^{-1}K^{-1}$	Free energy of activation $\Delta G^{\#}$ kJ mol^{-1}	Enthalpy of activation ΔH kJ mol^{-1}
Malic acid	4.57	23.78	-161.30	48.89	21.26

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