Oxidative Decarboxylation of Dicarboxylic Acid by Pyridiniumdichromate- Kinetic and Mechanistic Study

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Abstract: Oxidation of dicarboxylic acid *viz*-oxalic acid by pyridiniumdichromate (PDC) in perchloric acid medium has been studied. Active oxidizing species involved is protonated PDC. First order plot is observed for log(a-x) *versus* time. Effect of concentration of PDC, $HClO_4$, Mn(II), Ce(III) and ionic strength has been investigated. Thermodynamic parameters have been evaluated. Energy of activation is 51.22 kJ mol^{-1}. Entropy of activation is low and negative. The activation energy does not correspond to C-C bond breaking, but the reaction products indicate C-C bond breaking. A cyclic complex formation, which undergoes C-C fission, has been suggested.

Keywords: Oxalic acid, Pyridiniumdichromate, Oxidation, Kinetics

Introduction

Studies of oxidation processes have many fold advantages not only in living system but also in analytical, commercial, synthetic and industrial fields. PDC is a mild and selective oxidizing agent and soluble in water and many organic solvents. Kumbhat[1] *et al*. oxidizes formic and oxalic acid by QBC in DMSO and reported that the main product was carbon dioxide. The reaction was first order with respect with respect to QBC. Mohanty *et al.*[2] studied the oxidation of oxalate and glyoxylate by iodine in the temperature range of 70^0 – 80 ^{0}C and reported that change in ionic strength have no effect on reaction rate; while decrease in rate is observed with decrease in pH. The author confirmed that protonated form of oxalate and glyoxylate have lower reactivities. In this paper we propose to investigate the mechanism of oxidation by pyridiniumdichromate (PDC) and to check the reactivity towards PDC, we have selected oxalic acid as the substrate.

Experimental

All solutions were prepared in double distilled water. Pre-determined volume of known concentration of oxalic acid, perchloric acid and water were mixed in a glass stoppered flask kept in a thermostat at constant temperature (308 ±0.1K). Reaction was initiated by adding

pyridiniumdichromate solution. Aliquots (2.0 mL) were withdrawn at known intervals of time and concentration of the oxidant was determined iodometrically. All chemicals used were AR grade or were purified before use. Purity was checked by m.p. and b. p.

Results and Discussion

Effect of oxidant concentration

The PDC concentration was varied in the range 1×10^{-3} to 3×10^{-3} mol dm^{-3} and the linearity of plots of log [PDC] *vs.* time indicated a reaction order in [PDC] as unity. This was also confirmed by varying the [PDC], which did not show any change in pseudo-first order rate constants k_{obs} (Table 1). The first order plot is straight line.

Table 1. Effect of [Oxalic acid] and [PDC] on the oxidation of Oxalic acid by PDC [HClO$_4$]=5.0×10^{-1} mol dm^{-3} Temp= 308 K

10^2[Oxalic acid] mol dm^{-3}	10^3 [PDC] mol dm^{-3}	10^5 k_{obs} s^{-1}
2.0	2.0	13.76
2.5	2.0	19.73
3.0	2.0	26.97
3.5	2.0	38.64
4.0	2.0	46.37
4.5	2.0	56.92
5.0	2.0	69.31
2.0	1.0	13.68
2.0	1.25	13.87
2.0	1.5	13.50
2.0	1.75	14.10
2.0	2.0	13.76
2.0	2.5	14.18
2.0	3.0	13.92

Effect of substrate concentration

The substrate, [oxalic acid] was varied in the range 2.0×10^{-2} to 5.0×10^{-2} mol dm^{-3} at 308 K keeping all other reactant concentration and conditions constant. Rate of oxidation of oxalic acid increases with increasing substrate concentration. (Table 1). Log k *versus* log [substrate] is a straight line with slope 1.8. This observation is similar to oxidation of oxalic acid by chromic acid[3].

Effect of initially added products

The effect of initially added products such as pyridine in the concentration range 2.0×10^{-2} to 2.0×10^{-1} mol dm^{-3} keeping all other conditions constant did not show any significant effect on the rate of reaction. It shows that there is no hydrolysis of PDC in kinetic condition and hence oxidant is quite stable in kinetic condition.

Effect of varying acidity

The effect of acid on the reaction was studied by using perchloric acid at constant concentration of oxalic acid and PDC. 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 (Table 2). Log k *versus* log [H$^+$] is a straight line and order with respect to hydrogen ion is 0.3, which is an exception. This is contrary to observation of Kumbhat[1] and Banerji[4], where the order is one with respect to hydrogen ion concentration. The plot of k *vs.* [H$^+$] are linear

and intercept at y-axis is nearly zero. It confirms that the reaction is acid catalyzed. Since protonation of the acid is not possible, therefore, it can be concluded that protonated oxidant is active species in this oxidation.

Table 2. Effect of [H$^+$] ion[a]

10x[HClO$_4$] mol dm^{-3}	10^5 k$_{obs}$ s^{-1}
1.0	9.03
2.0	10.93
3.0	12.15
4.0	13.39
5.0	13.76
6.0	14.71
7.0	15.41
8.0	16.31
9.0	17.28
10.0	18.06
11.0	19.10
12.0	20.18

[a]*General Condition : [Oxalic acid] = 2x10-2 mol dm^{-3} [PDC] = 2.0x10-3 mol dm^{-3} Temp = 308 K*

Effect of solvent polarity

Effect of solvent polarity was studied (Table 3) by changing proportion of water and 1,4 dioxane; percentage composition was varied from 0 to 10% dioxane v/v. Since there is no literature value of water-dioxane solution of different composition, therefore we have calculated dielectric constant using law of mixture and data for pure dioxane and water[6,7] assuming a linear relationship in the limited range 0 to 30% of solvent compositions used in our studies. Wieberg and Evans[8] have made a similar approximation with regard to the same binary solvent system. Looking to the nature of reaction, it can be either ion-dipole or dipole-dipole[9]. Many workers like Jain[10], and Hiran *et al.*[11] suggested ion-dipole type of interaction in the oxidation of organic substrates by Cr(VI)-complexes. Although the dielectric constants of the medium by itself is inadequate to account for the solvent influence[12], the relative solvation and greater electrostatic attraction of solute for the more polar compounds of mixed solvent may produce a field of dielectric constant near the solute particle, which is entirely different from the average dielectric constants. Solvent-solute interaction therefore may be more important factor in affecting the reaction rate compared to the dielectric constants[13].

It was observed that log k *versus* 1/dielectric constant is straight line with the positive slope. This indicates that reaction is ion-dipolar and further by positive slope, we can say it is cation-dipole interaction in rate determining step[14].

Effect of temperature

Rate of reactions were determined at different temperature (298 to 323 K). A plot of log k$_{obs}$ *versus* 1/T (inverse of absolute temperature) is a straight line (Table 4). Energy of activation is 51.22 kJ mol^{-1}. Entropy of activation is low and negative.

Energy of activation does not correspond to carbon–carbon bond fission in the decomposition of organic substrate by Cr(VI) in rate determining step[15]. But the reaction product indicate C-C bond breaking. This may be due to lowering of activation energy ($\Delta E^{\#}$ = 51.22 kJ mol^{-1}) due to involvement of many equilibria. Decrease in entropy suggests formation of cyclic complex (may be unstable). Calculation of activation parameters showed that this reaction is not enthalpy controlled.

Table 3. Effect of solvent[a]

Dioxane % v/v	$10^5 \, k_{obs} \, s^{-1}$
0.0	13.76
5.0	19.03
10.0	25.07
15.0	29.18
50.0	32.34
25.0	37.12
30.0	41.96

Table 4. Effect of temperature[a]

Temp K	$10^5 \, k_{obs} \, s^{-1}$
298	6.51
303	9.82
308	13.76
313	18.26
318	25.64
323	35.82
328	46.12
333	57.62

[a]*General Condition : [Oxalic acid]= 2.0×10^2 mol dm-3 [PDC]=2.0×10^{-3} mol dm^{-3} [HClO$_4$]= 5×10^{-1} mol dm^{-3}*

Variation of rate with Mn(II) ion

It was observed that an addition of Mn(II) ion retard the rate of oxidation with increase in concentration of Mn(II) ion.(Table 5). Such observations were also reported by Hiran *et.al*[16], The retardation of the reaction rate can be explained by disproportionation of Cr(VI) to Cr(V) and Cr(III), catalyzed by Mn(II). Thangarajan and Gopalan[14] also observed similar effect of Mn(II) and Ce(III) ions in oxidation of 2-propanol by chromic acid in dioxane-water system. Nalwaya[11] also observed similar results in oxidation of aromatic aldehydes and alcohol by QBC in dioxane-water medium. This confirms that PDC act as two-electron oxidant in the oxidation of oxalic acid[17].
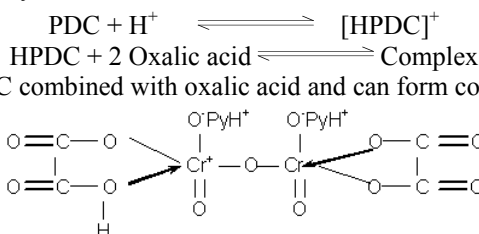
Table 5. Effect of Mn(II) [a]

10^3 [Mn(II)] mol dm^{-3}	$10^5 \, k_{obs} \, s^{-1}$
0.0	13.76
2.0	10.84
4.0	7.92
6.0	5.39
8.0	3.86
10.0	2.92

[a]*General Condition : [Oxalic acid]= 2.0×10^2 mol dm-3 [PDC]=2.0×10^{-3} mol dm^{-3} [HClO$_4$]= 5×10^{-1} mol dm^{-3}*

Conclusion

Rate of oxidation of oxalic acid increases with increase in substrate concentration. Log k_1 *versus* log [substrate] is a straight line with slope =1.8. This observation is similar to oxidation of oxalic acid by chromic acid[18].

$$PDC + H^+ \rightleftharpoons [HPDC]^+$$
$$HPDC + 2 \, Oxalic \, acid \rightleftharpoons Complex$$

Both Cr(VI) of PDC combined with oxalic acid and can form compound like (Figure 1).

Figure 1. A ternary complex with oxalic acid

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