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Oxidative Transformation Of Tartaric Acid By Pyridiniumdichromate In Non-Aqueous Medium Kinetic And Mechanistic Study

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Abstract

Oxidation of Tartaric acid by pyridiniumdichromate in DMSO (dimethylsuphoxide) as a solvent in presense of PTSA (p- toluenesulphonic acid). The reaction is first order with respect to oxidant and [H^+]. The reaction exhibit no primary kinetic isotop effect. The activation parameters have been evaluated. Michaelis – Menten type kinetics is observed. The rate of reaction decrease with an increase in the polarity of solvent indicating an ion-dipole interaction in the slow step.

Keywords: *Tartaric acid, PDC, DMSO, PTSA*

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I. Introduction:

Carboxylic and hydroxy acids are play significant role in many biological processes as well as in oraganic synthesis. Chromium compounds have been widely used in aqueous and non aqueous medium for the oxidation of a variety of organic compounds[1-3]. Oxidants such as Cr (VI) investigated by Hiran and Bikaneria[4], Hiran and Chaturvedi[5]. Hiran and Jain[6], Cr (VI) derivatives used in synthetic oraganic chemistry are drastic and non selective in nature. It has been noticed that these reagents are insoluble in most of the organic solvent. To overcome these restriction various derivatives of cr (VI) derivatives were introduced in synthetic organic chemistry as mild and selective oxidizing ragents in non-aqueous solvents. Pradeep K. Sharma et al[7] has been studies the kinetic of oxidation of thioglycolic acid, thiolactic acid and thiomalic acid by PDC in DMSO.

II. Materials And Method:

All the chemical and reagents were of analytical grad. Pyridiumdichromate was prepared by the method describe in the literature[8] and its purity was cheked by idometrically and IR spectrum. SPECTROSCOPIC DATA were obtained and compared with literature value. IR= λmax (KBr) = 3250, 1660 , 1500 , 1340 , 1100 , 950 , 870, 770cm.$^{-1}$

Stoichiometery and Product Analysis:

To determine the stoichiometry of a reaction a known slight excess of oxidant was added to a known amount of tartric acid, by keeping all other condition of reaction is constant and after some hours the residual of oxidant was determined spectrophotometrically at 355nm. The product of oxidation was Glyoxal and was identified by its 2, 4-dinitro phenyl hydrazine derivative. The stoichiometry of the reaction was found to correspond to the equation: [Oxidant] [Tartric acid] = [Glyoxal]

Prepartion of solution:

Pyridiniumdichromate solution was prepared by dissolving the known amount of PDC in DMSO with stirring and titrating it against previsely standirized sodium thiosulphate (Hypo) solution using starch as an indicator.

III. Result And Discussion

Effect of Substrate:

At constant [PDC], the rate constants for oxidation calculated at different intial concentration of substrates found to increase linearly with the increase in concentration of substrate ($2x10^{-2}$ M to $6x10^{-2}$ M). The result are summarized in table -1. A plot of log k v/s log [subs] gives a straight line with slope nearly one. Which tells that the oxidation is first order with respect to 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^+] = 0.02M to 1.6 M It was observed that the rate increases with increase in hydrogen concentration. log k v/s log [H^+] is a straight line and slope are near to one . The result are summarized in table-1.

Effect of Solvent composition:

Effect of solvent was studied by changing proportion of water and DMSO percentage. Composition was varied from 10 to 50% DMSO v/v increases in percentage of DMSO in solvent mixture rate of reaction increases, suggesting that a medium of dielectric constant favors the reaction. A plot of log k v/s 1/D (D=dielectric constant) is linear with a positive slope for the acids under study. This indicates that reaction an ion – dipole interaction in rate determining step [9-10]. Result are summarized in table 1.

Table 1. Effect of [subs], [H_+] and solvent composition.
[PTSA] = 3x10^{-3}M, [PDC] = 3x10 $^{-3}$ M, T= 303K

[Subs]x 10 ^{2} M	[PTSA]x 10 ^{3} M	H_2O –DMSO% v/v	K x10^{5} Sec^{-1}
2.0	3	0	33.73
3.0	3	0	49.84
4.0	3	0	60.24
5.0	3	0	75.39
6.0	3	0	92.15
2.0	3	0	33.73
2.0	3.5	0	61.45
2.0	4.0	0	88.78
2.0	4.5	0	205.61
2.0	5.0	0	233.67
2.0	5.5	0	514.07
2.0	6.0	0	560.80
2.0	3	10	26.91
2.0	3	20	17.51
2.0	3	30	14.08
2.0	3	40	12.26
2.0	3	50	11.34

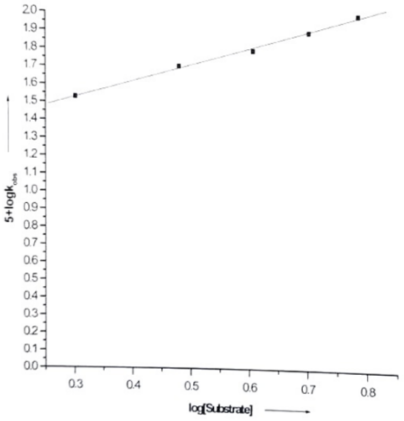
Effect of Temperature:

It was found that rate of oxidation of Tartaric acid increase with increase with respect to temperature. Plot of log k v/s 1/T (inverse of temperature) is straigh line. This shows that Arrhenius equation is valid for this oxidation.

[Subs] = 2x10^{-2} M , [PTSA] = 3x10^{-2} M ,[PDC] = 3x10^{-2}M

Temp. (in k)	Kx10 ^{5}sec^{-1}
303	33.73
308	48.03
313	74.58
318	109.66
323	167.02

The energy of activation is $\Delta Ea^{\#} = 65.43$ $KJmol^{-1}$ and entropy value is negative $\Delta S^{\#} = -18.76$ JK $^{-1}$ mol^{-1}. These data shows that the transition state is more rigid and extensively solvated than reactant.



IV. Conclusion:

Oxidative transformation of Tartaric acid is first order with respect to oxidant. Glasston [11] has pointed out that if enthalpy of activation ($\Delta H^{\#} = 62.91$ KJmol^{-1}) is large and positive the reaction will be normal and fast but if it is negative the reaction is slow. In this oxidation reaction negative value of entropy suggest either formation of cyclic structure or the activated state is more polar than the reaction. Negetive value of entropy also suggest that bimolecular reaction in the rate determining step in the presence of water as a solvent and involvement of a proton transfer during the rate determining step.

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