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A COMPARATIVE STUDY OF OXIDATION OF TARTARIC ACID BY DIFFERENT CR (VI) OXIDANTS IN DMSO MEDIUM

Chemistry

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ABSTRACT

A comparative study of oxidation of Tartaric acid by different Cr (VI) oxidants [PCC, PDC,] has been studied in DMSO medium in the presence of PTSA by spectrophotometrically ($\lambda = 460$nm) at 303K. The reaction is first order with respect to PCC, PDC, $[H^+]$ and substrate. Michaelis-Menten type kinetics was observed. The reaction rate increases with increasing volume percentage of DMSO in reaction mixture, suggesting the involvement of an ion in the rate determining step. The reaction rates were studied at different temperature and the activation parameters has been computed. The reaction proceeds through formation of cyclic chromate-ester between protonated Oxidants and α-hydroxy acid.

KEYWORDS

Tartaric acid, PCC, PDC, Oxidation, DMSO.

INTRODUCTION: -

Oxidation of organic compounds under non-aqueous condition is a[1-5] important reaction in synthetic organic chemistry. Different[6-9] chromium(VI) derivatives have been reported as oxidant.α-Hydroxy acids are the class of organic compounds in which a hydroxyl group and a carboxylic group is present. These AHA (alpha hydroxy acids) and their derivatives have a wide application in various fields like biological, vital, cosmetic and organic synthesis. These are very important in the organic synthesis of aldehydes via oxidative cleavage of bonds. Hiran et al. [10] studied the oxidation of lactic and Mandelic acid by quinolinium dichromate in aqueous acetic acid medium.

Dangarh et al.[11] studied the kinetics of oxidation of lactic acid by PDC in per chloric acid medium. Active oxidizing species involved was protonated PDC.

MATERIAL AND METHOD: -

Oxidants Pyridiniumchlorochromate [12], Pyridiniumdichromate [13] were prepared by the method describe in the literature. The purity of the oxidants was checked by spectral analysis. Tartaric acid (A.R.grade) was used as supplied and purity was checked by its melting point. All other chemicals used in this investigation were of analytical reagent grade. Double distilled water was used throughout in the investigation.

All the solutions for the experiments were maintained at the specified temperature. The reaction progress was followed by monitoring the decreasing concentration of Oxidants spectrophotometrically at 460 nm for up to 80% of the reaction.

RESULT AND DISCUSSION: -

Stoichiometry and product analysis

The stoichiometry of the reaction was found to correspond to the equation.

$$\text{Tartaric acid} + \text{Oxidant} \rightarrow RCHO + Cr(III) + CO_2 + H_2O$$

Effect of oxidant: -

When Tartaric acid were in excess, the disappearance of Oxidants followed the first-order rate law. The first-order rate constants are independent of the initial concentration of the both of the oxidants. [Table 1]

Effect of Substrate: -

At constant [Oxidants], the rate constants for oxidation calculated at different initial concentration of substrates found to increase linearly ($2x10^{-2}$ M to $6x10^{-2}$ M). The results of the effect of substrate concentration on the rate constant are summarized in (Table - 1). A plot of log k against log [substrate] gives a straight line (fig-1). This 1revealed that the rate of oxidation is first order with respect to the acid.It has been found that plot of [1/k] versus (1/[substrate]) is straight line with an intercept on the rate ordinate, indicating the oxidation of Tartaric acid follows Michaelis–Menten type kinetics and proceeds through the formation of a complex between the oxidant and the substrate.

Effect of H^+ Ion Concentration: -

To the study effect of hydrogen ion p-toluenesulphonic acid [PTSA] was used. The rate of oxidation was studied from $[H^+] = 1x10$ to $5x10^3$ M. It was observed that rate increases with increase in hydrogen ion$^+$concentration. Log k v/s log [H] is a straight line in all the cases and the slopes are near 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 30 to 70% 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[14-16]. Wieberg and Evans[17] have made a similar approximation with regard to the same binary solvent system**.**

Effect of Temperature: -

Rate of oxidation increases with increase in temperature. Rate ofreactions were determined at different temperature (298 to 323 K). In all the cases, a plot of log k versus 1/T (inverse of absolute temperature) is a straight line. This shows that Arrhenius equation is valid for this oxidation. The entropy value is negative, 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 Tartaric acid is first order with respect to oxidant and $[H^+]$. Glasston[18] 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 our case, the negative value of entropy of activation suggests slow reaction and formation of cyclic structure from non-cyclic structure. 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.Among two Cr (VI) oxidants Tartaric acid oxidized faster with PDC. The reactivity of oxidation of Tartaric acid towards two oxidants was found to be PDC > PCC.

TABLE NO. 1

Effect of [Substrate], [H+] and Solvent

[SUBSTRATE]=2 X 10-2 M [PTSA] = 3 X 10-3 M T = 303 K

[Subs] $x10^{-2}$ M	[PTSA] X 10-3 M	Water in DMSO % v/v		
			PCC	PDC
2	1	0	13.51	43.59
3	1	0	16.81	46.68
4	1	0	19.76	48.89

5	1	0	22.69	50.93
6	1	0	25.18	52.71
2	1	0	13.51	43.59
2	1.5	0	15.56	50.21
2	2	0	17.24	57.25
2	2.5	0	20.12	64.25
2	3	0	22.35	71.21
2	3.5	0	24.59	77.21
2	4	0	26.65	85.32
2	1	0	13.51	43.59
2	1	10	31.25	36.85
2	1	20	29.85	35.27
2	1	30	28.74	34.31
2	1	40	27.36	33.03
2	1	50	26.21	31.82
2	1	60	25.17	30.42

TABLE NO. 2

[SUBSTRATE] = 2 X 10 M [PTSA] =1 X 10 M [OXIDANTS] = 2 X 10-^{3} M [DMSO]=100% v/v

Temperature (K)	Oxidants	
	PCC	PDC
298	10.41	40.67
303	13.51	43.59
308	17.51	47.18
313	22.71	50.58
318	29.44	53.61

TABLE NO. 3
THERMODYNAMIC PARAMETERS

[SUBSTRATE] = 2 X 10 M [PTSA] =1 X 10 M [OXIDANTS] = 2 X 10-^{3} M [DMSO]=100% v/v T= 303K

Tartaric acid	log A	$E_a^{\#}$ kJ mol^{-1}	$S^{\#}$ J $mol^{-1}K^{-1}$	$\Delta H^{\#}$ kJ mol^{-1}	$\Delta G^{\#}$ kJ mol^{-1}
PCC	7.40	40.93	-107.18	38.42	70.84
PDC	2.76	11.05	-196.06	8.53	67.91

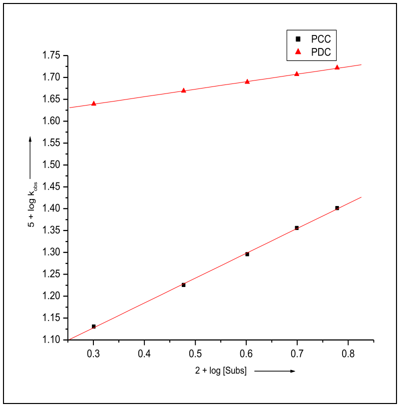

Fig- 1 Variation of rate with substrate concentration by different oxidants

log k_{obs} v/s log [substrate]

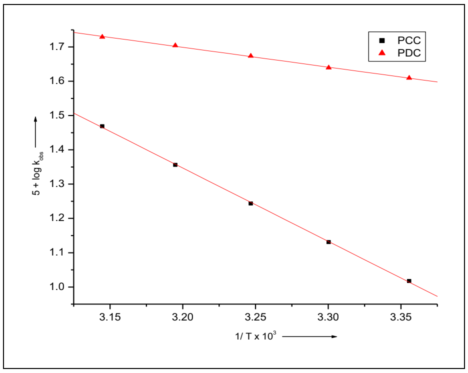

Fig-2 Variation of rate with Temperature by different oxidants

log k_{obs} v/s 1/T

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