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Oxidative Transformation of Mandelic acid by Pyridiniumdichromate in non-aqueous medium kinetic and mechanistic study

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Abstract

The alpha-hydroxy acids (AHA) are naturally occurring organic acid. The oxidation of mandelic acid by pyridiniumdichromate has been studied spectrophotometrically in presence of p-toluenesulphonic acid (PTSA) in dimethylsulphoxide (DMSO) as a solvent. The rate of reaction decrease & with an increase in polarity of solvent indicating an ion-dipole interaction in the slow step. The reaction exhibit no primary kinetic isotope effect. The activation parameters have been evaluated.

Key words: Kinetics, Mandelic acid, Oxidation, PDC, DMSO, PTSA.

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 solvent. The oxidation of α -Hydroxy acids by pyridiniumdichromate (PDC) has been studied by Ahmed S-zaheer *et al.*¹. The reaction is pseudo first Order with respect to hydroxyl acid $[H^+]$ and $[PDC]$. Hiran *et al.*² studied the oxidation of lactic and mandelic acid by quionlinium dichromate in aqueous acetic acid medium. The kinetics of oxidation of oxalic acid by pyridinium dichromate in perchloric acid medium studied by Dangarh *et al.*³. Bakore and Shyamnarayan studied⁴. Oxidation of lactic, malic and madelic acids by cromic acid.

Materials and Method

Pyridiniumdichromate was prepared by the method describe in the literature⁵ and its purity was checked by iodometrically and by IR spectrum. SPECTROSCOPY DATA were obtained and compared with literature value.

IR = λ_{\max} . (KBr) = 3250, 1660, 1500, 1340, 110, 950, 870, 770 cm^{-1}

Preparation of Solutions:

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

Result and Discussion

Effect of Substrate:

At constant [PDC], the rate constants for oxidation were calculated at different initial concentration of acids and found to increase linearly with increase in concentration of acid (2×10^{-2} M). The results at the effect of substrate concentration on the rate constant are summarized in (Table 1). A plot at $\log k$ v/s $\log [\text{subs.}]$ gives a straight line with slope nearly one. This revealed that the rate of oxidation is first order with respect to the substrate.

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 low dielectric constant favors the reaction. A plot of $\log k$ vs $1/D$ (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 step⁶⁻⁸. Result are summarized in (Table 1).

Effect of Oxidant:

When Mandelic acid in excess compared to that of PDC, it is observed that logarithm of concentration of PDC decreases linearly with time. It is showing that the rate law of the reaction is first order with respect to oxidant pyridiniumdichromate (PDC) varied in the range (1×10^{-3} to 4×10^{-3} mol/dm^{-3} at 303k).

Effect of $[H^+]$ Ion:

To study effect of hydrogen ion p-toluenesulphonic acid was used. The rate of oxidation was studied from $[H^+] = 0.02$ M to 1.6 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 Temperature:

It was found that rate of oxidation increases with temperature. Plot of $\log k$ against $1/T$ (inverse of absolute temperature) is linear line. This shows that Arrhenius equation is valid for this oxidation. The energy of activation is $69.16 \text{ KJ mol}^{-1}$ and the entropy value is negative ($-20.99 \text{ Jmol}^{-1} \text{ K}$). This shows that the transition state is more rigid and extensively solvated than the reactants. The negative entropy also suggest the formation of cyclic intermediate from acyclic species.(Table 2 & 3).

Table 1. Effect of [Substrate], $[H^+]$ and Solvent :
 $[PTSA] = 3 \times 10^{-3} M$ $[PDC] = 3 \times 10^{-3} M$ $T = 303 K$

$[sub] \times 10^2 M$	$[PTSA] \times 10^3 M$	Water-DMSO% in v/v	$k \times 10^5 sec^{-1}$
2.0	3	0	5.73
3.0	3	0	8.58
4.0	3	0	12.86
5.0	3	0	16.39s
6.0	3	0	21.27
2.0	3	0	5.73
2.0	3.5	0	7.45
2.0	4.0	0	10.22
2.0	4.5	0	12.66
2.0	5.0	0	15.83
2.0	5.5	0	19.58
2.0	6.0	0	23.03
2.0	3	10	16.08
2.0	3	20	11.7
2.0	3	30	79.78
2.0	3	40	8.67
2.0	3	50	7.95

VARIATION OF RATE WITH PERATOLOUNE SULPHONIC ACID

Log k vs $\log [H^+]$

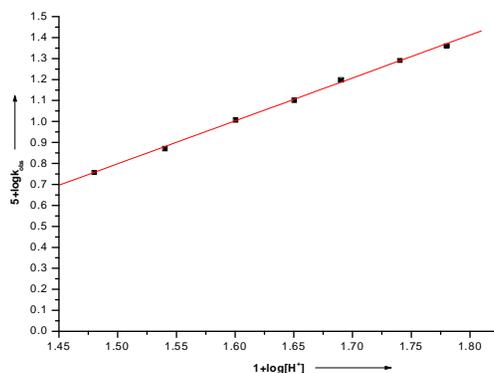


Table 2

$[Substrate] = 2 \times 10^{-2} M$ $[PTSA] = 3 \times 10^{-2} M$ $[PDC] = 3 \times 10^{-2} M$

Temp. (in k)	$k \times 10^5 sec^{-1}$
303	5.73
308	9.72
313	13.37
318	22.84
323	31.41

Table 3. Thermodynamic parameter

Substrate	log A	Energy of activation $\Delta E_a^\# \text{ kJmol}^{-1}$	Entropy of activation $\Delta S^\#$ $\text{Jmol}^{-1} \text{ K}^{-1}$	Free Energy activation $\Delta G^\# \text{ kJmol}^{-1}$	Enthalpy of activation $\Delta H^\# \text{ kJmol}^{-1}$
Mandelic acid	11.90	69.16	-20.99	6.42	66.64

Conclusion

Oxidative transformation of Mandelic acid is first order with respect to oxidant. Glasston⁹ 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 these oxidation reaction negative value of entropy suggest either formation of cyclic structure from non cyclic structure or the activated state is more polar than the reaction. Negative 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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