Oxidative Transformation of Mandelic acid by Pyridinium dichromate 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 pyridinium dichromate 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 pyridinium dichromate (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 studied\(^4\). Oxidation of lactic, malic and mandelic acids by cromic acid.

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Materials and Method

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

\[ \text{IR} = \lambda_{\text{max}} \text{(KBr)} = 3250, 1660, 1500, 1340, 110, 950, 870, 770 \text{ cm}^{-1} \]

Preparation of Solutions:

Pyridinium dichromate 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 \((2 \times 10^{-2} \text{ M})\). The results at the effect of substrate concentration on the rate constant are summarized in (Table 1). A plot at log k v/s lag [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 favers 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 step. 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 pyridinium dichromate (PDC) varied in the range \((1 \times 10^{-3} \text{ to } 4 \times 10^{-3} \text{ mol/dm}^{-3} \text{ at } 303k)\).

Effect of \([H^+]\) Ion:

To study effect of hydrogen ion p-toluenesulphonic acid was used. The rate of oxidation was studied from \([H^+] = 0.02 \text{ M} \text{ to } 1.6 \text{ M}\). It was observed that rate increases with increase in hydrogen ion concentration. logk 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. Plat 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 KJ mol^{-1} and the entropy value is negative (-20.99 Jmol^{-1} 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:

\[ \text{[PTSA]} = 3 \times 10^{-3} M \quad \text{[PDC]} = 3 \times 10^{-3} M \quad T = 303K \]

| [sub] \(10^{-2} M\) | [PTSA] \(10^{-3} M\) | Water-DMSO% in v/v | \(K \times 10^5 \text{ sec}^{-1}\) |
|---------------------|---------------------|---------------------|---------------------|
| 2.0                 | 3                   | 0                   | 5.73               |
| 3.0                 | 3                   | 0                   | 8.58               |
| 4.0                 | 3                   | 0                   | 12.86              |
| 5.0                 | 3                   | 0                   | 16.39              |
| 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                 | 10                  | 23.03              |
| 2.0                 | 3                   | 20                  | 16.08              |
| 2.0                 | 3                   | 30                  | 11.7               |
| 2.0                 | 3                   | 40                  | 79.78              |
| 2.0                 | 3                   | 50                  | 7.95               |

VARIATION OF RATE WITH PERATOLEOUNE SULPHONIC ACID

Log k vs log \([H^+]\)

Table 2

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

| Temp. (in k) | \(k \times 10^5 \text{ sec}^{-1}\) |
|--------------|-----------------------------------|
| 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 $\Delta E_a^\#$ $\text{kJ mol}^{-1}$ | Entropy of activation $\Delta S^\#$ $\text{J mol}^{-1} \text{K}^{-1}$ | Free Energy activation $\Delta G^\#$ $\text{kJ mol}^{-1}$ | Enthalpy of activation $\Delta H^\#$ $\text{kJ mol}^{-1}$ |
|----------------|------|------------------------------------------------------------|-------------------------------------------------|------------------------------------------------|-------------------------------------------------
| 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. Glasston\(^9\) 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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