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Comparative Study of Solvent Effect for Mandelic acid Oxidation by Different Oxidants

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ABSTRACT

The mandelic acid oxidation has been carried out by benzimidazolium fluorochromate (BIFC), morpholinium fluorochromate (MFC), benzimidazolium dichromate (BIDC), morpholinium chlorochromate (MCC) and tetraethylammonium chlorochromate (TEACC) using different solvents as dimethyl sulphoxide (DMSO), dimethyl formamide (DMF), chloroform (CF), acetone, dichloromethane (DCM) and 1,2-dichloroethane (DCE) at 308K, which results in the corresponding oxoacids formation. By using the TOPSIS method, we analysed the solvent effect and found the order by the solvent's performance score for the reaction as DMSO>DMF>DCE>ACETONE>DCM>CF. The oxidation with all the oxidants resulted in the formation of corresponding oxo acid. The mechanism involved the construction of a cyclic chromate ester in a fast pre-equilibrium and then the decomposition of the ester in a subsequent slow step via a cyclic concerted symmetrical transition state leading to the formation of corresponding oxo acid in all the cases.

Keywords: Oxidants, Solvents, Solvent effect, Mandelic acid, TOPSIS method.

INTRODUCTION

αα-Hydroxy acids are chemical molecules that include hydroxyl and carboxylic groups. Some important members of α-hydroxy acids like glycolic acid, mandelic acid, lactic acid, malic acid, citric acid and tartaric acid are obtained from sugarcane, milk, apple, citrus fruits, grape wine and bitter almonds, respectively. These α-hydroxy acids and their derivatives have a large application area like biological, vital, cosmetic and organic synthesis. We have used mandelic acid for our oxidation study. Studying various organic compounds' oxidation in non-aqueous environments is crucial in synthetic organic chemistry. For this study, many Cr(VI) derivatives have been reported[1-5]. The oxidation study of α-hydroxy acids by PBC[6], PDC[7], PCC[8], IDC[9], QCC[10], PzCC[11], MCC[12], TEACC[13], IFC[14], PipCC[15], MFC[16], BIDC[17] etc. has been reported in DMSO. We have studied oxidation reactions of mandelic acid by BIFC, MFC, BIDC, MCC and TEACC in 6 different solvents as dimethyl sulphoxide (DMSO), dimethyl formamide (DMF), chloroform (CF), acetone, dichloromethane (DCM) and 1,2-dichloroethane (DCE) at temperature 308K. αα-Hydroxy acids either oxidised as alcohols, which results in the formation of corresponding oxoacids or undergo oxidative decarboxylation, which gives ketone. We have identified the best solvent under the different alternatives using the TOPSIS method[18] and proposed a suitable mechanism.

Hwang and Yoon[19] invented the TOPSIS approach, which Yoon[20] subsequently enhanced. Hwang *et al.,*[21] also published a new approach to multi-objective decision-making.

MATERIAL AND METHOD

Material

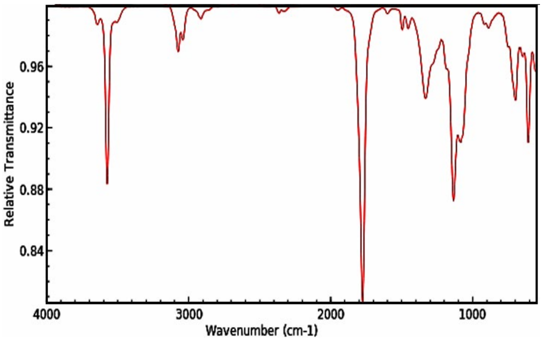
We have used A. R. (analytical reagent) grade mandelic acid. The reported method was used to prepare BIFC[22], MFC[23], BIDC[24], MCC[25] and TEACC[26] and their purity was determined using an iodometric approach. Solvents were purified using standard procedures[27].

Kinetic Experiments

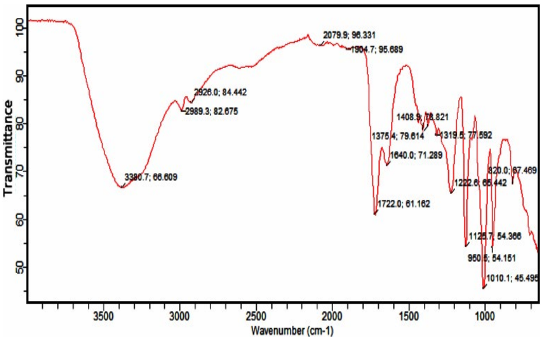
Pseudo, first-order constant, was obtained using a significant excess (*15 times or more) of the substrate over oxidants. For our research, we used six different solvents. The study of reactions was done at a constant temperature of 308K. The reaction mixtures were prepared by mixing the appropriate amount of solvent, substrate etc. and keeping them at a constant temperature in a thermostatic water bath. The reaction was started by introducing an oxidant solution previously stored in the water bath. The decrease in the concentration of oxidants was monitored spectrophotometrically. For carrying out our experiments, we have used the UV-Vis spectrophotometer model (AIMIL India model MK2) in which we have selected λ_{max} 364 nm, 356 nm, 365 nm, 350 nm and 352 nm, respectively, for BIFC, MFC, BIDC, MCC and TEACC as these oxidants showed (absorbance) λ_{max} at 364 nm, 356 nm, 365 nm, 350 nm and 352 nm.

RESULTS AND DISCUSSION

We have done the oxidation of mandelic acid by different oxidants using six solvents, which results in the formation of corresponding oxoacids. The product is also confirmed by spectral analysis. FTIR spectra of mandelic acid oxidation by BIFC in DMSO solvent have been given, and similar results have been obtained with other oxidants and solvents. A suitable mechanism has been proposed which involves the formation of a chromate ester in a fast pre-equilibrium and then the decomposition of the ester in a subsequent slow step via a cyclic concerted symmetrical transition state leading to the formation of corresponding oxo acid in all the cases. A suitable mechanism for all the oxidants has been given. We have used the TOPSIS approach to compare the rate constants k_2 in six solvents for specific oxidants to find out which solvent is best suited for the oxidation of mandelic acid.

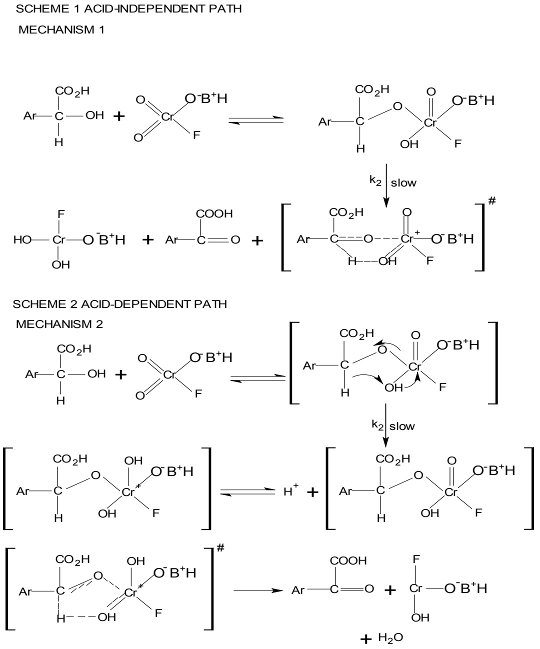


FTIR Spectrum of mandelic acid



FTIR Spectrum of corresponding oxyacids formed by oxidation of mandelic acid by BIFC in DMSO

Mechanism



Where B = BI-Benzimidazolium, M-Morpholinium, TEA-Tetraethylammonium

TOPSIS Study:

Table 1: At 308 K decision matrix of rate constants (10^4 k_2 s^{-1}) for the mandelic acid oxidation by given oxidants

Oxidant Solvent	BIFC	MFC	BIDC	MCC	TEACC
DMSO	62.9	72.4	52.4	74.6	68.2
DMF	31.7	46.6	28.9	40.4	39.2
CF	20.5	23.4	15.0	19.9	19.2
ACETONE	22.8	25.1	16.3	24.1	25.8
DCM	21.6	30.3	17.2	22.8	23.6
DCE	23.8	27.8	19.1	26.5	28.9

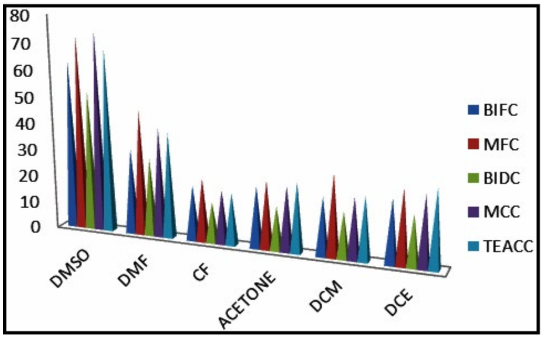


Fig. 1. Decision matrix of the rate constants for mandelic acid oxidation by given oxidants

Calculations of the Normalized Matrix

Calculations of the Normalized matrix X_{ij} done by this formula:

$$\overline{X}_{ij} = \frac{X_{ij}}{\sqrt{\sum_{j=1}^{n} X_{ij}^2}}$$

i = 1,2,…,m
j = 1,2,…,n

Table 2: Normalized matrix calculated using rate constants (10^4 k_2 s^{-1}) for the mandelic acid oxidation by given oxidants at 308 K

Oxidant Solvent	BIFC	MFC	BIDC	MCC	TEACC
DMSO	0.0091	0.0070	0.0111	0.0079	0.0079
DMF	0.0045	0.0045	0.0061	0.0043	0.0046
CF	0.0029	0.0023	0.0032	0.0021	0.0022
ACETONE	0.0033	0.0024	0.0034	0.0026	0.0029
DCM	0.0031	0.0029	0.0036	0.0024	0.0027
DCE	0.0034	0.0027	0.0040	0.0028	0.0034

Calculations of the weighted normalized matrix

Calculations of the weighted normalized matrix V_{ij} done through this formula:

$$V_{ij} = \bar{X}_{ij} \times W_j$$

i = 1,2,…,m
j = 1,2,…,n

Table 3: Weighted normalized matrix calculated using normalized matrix for the mandelic acid oxidation by given oxidants at 308 K

Oxidant Solvent	BIFC	MFC	BIDC	MCC	TEACC
DMSO	0.0018	0.0014	0.0022	0.0016	0.0016
DMF	0.0009	0.0009	0.0012	0.0009	0.0009
CF	0.0006	0.0005	0.0006	0.0004	0.0004
ACETONE	0.0007	0.0005	0.0007	0.0005	0.0006
DCM	0.0006	0.0006	0.0007	0.0005	0.0005
DCE	0.0007	0.0005	0.0008	0.0006	0.0007

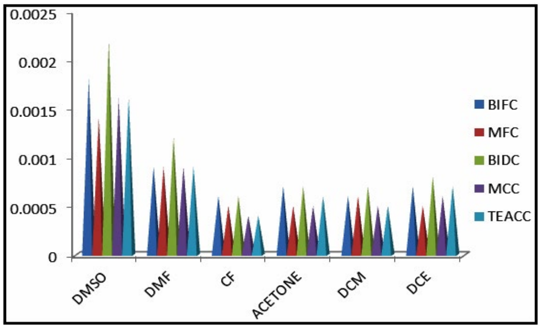


Fig. 2. Weighted normalised matrix of the rate constants for mandelic acid oxidation by given oxidants

Calculations of the positive ideal and negative ideal values

Max V_{ij} is V^+ (positive ideal value), and Min V_{ij} is V^- (negative ideal value).

Positive Ideal Values V^+:

0.0018	0.0014	0.0022	0.0016	0.0016

Negative Ideal Values V^-:

0.0006	0.0005	0.0006	0.0004	0.0004

Calculations of the Euclidean distance from positive ideal values and negative ideal values

Calculations of the Euclidean distance from positive ideal values (S_i^+) done by this formula:

$$S_i^+ = \left[\sum_{j=1}^{m} \left(V_{ij} - V_j^+ \right)^2 \right]^{0.5}$$

DMSO	DMF	CF	ACETONE	DCM	DCE
0	0.0017	0.0028	0.0025	0.0026	0.0024

Calculations of the Euclidean distance from negative ideal values (S_i^-) done by this formula:

$$S_i^- = \left[\sum_{j=1}^{m} \left(V_{ij} - V_j^- \right)^2 \right]^{0.5}$$

DMSO	DMF	CF	ACETONE	DCM	DCE
0.0028	0.0011	0	0.0003	0.0002	0.0004

Calculate the performance score

Calculations of performance score P_i is done as follows:

$$P_i = \frac{S_i^-}{S_i^+ + S_i^-}$$

DMSO	DMF	CF	ACETONE	DCM	DCE
1	0.393	0	0.11	0.07	0.14

Table 4: Rank by the performance score of the solvents

Solvent	Pi	Rank
DMSO	1	1
DMF	0.393	2
CF	0	6
ACETONE	0.11	4
DCM	0.07	5
DCE	0.14	3

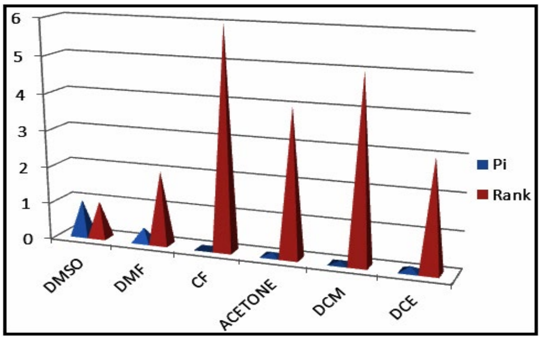


Fig. 3. Rank by the performance score of the solvents

CONCLUSION

In this study, we have done the oxidation of mandelic acid by different oxidants. The resultant product was corresponding oxoacids. The mechanism involved the formation of a cyclic chromate ester in a fast pre-equilibrium and then the decomposition of the ester in a subsequent slow step via a cyclic concerted symmetrical transition state leading to the formation of corresponding oxo acid in all the cases. The comparative study of the solvent effect is an essential concept of physical organic chemistry. The TOPSIS method is helpful for this study. This is the multiple criteria decision-making method. In this study, we have done the oxidation of mandelic acid by different oxidants and solvents and based on the TOPSIS method, the following order by the performance score of the solvents for the reaction-DMSO>DMF>DCE>ACETONE>DCM>CFwas obtained. Thus it was concluded that the oxidation of mandelic acid by different oxidants gives the best results when DMSO is used as a solvent.

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Conflict of interest

The authors declare no conflict of interest in the present work.

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