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Study on Solvent Effect by TOPSIS Method in Oxidation of Aliphatic Alcohol

M. H. Gagare[1]*, Dr. S. D. Dhage[2]

[1]Research Scholar, Dept. of Chemistry, Maharashtra Udaygiri Mahavidyalaya, Udgir-413512 Dist-Latur, Maharashtra, India

[2]Department of Chemistry, SSJES's Arts, Comm. And Science College, Gangakhed-431514, Dist-Parbhani, Maharashtra, India

ABSTRACT

In this article, the oxidation of aliphatic alcohol with benzimidazolium fluorochromate (BIFC), piridinium chlorocromate (PCC), bipyridinium chlorochomate (BPCC), imidazolium fluorochromate (IFC), quinolinium fluorochromate (QFC) carried out in different solvents like dicloroethane (DCE), acetone, dimethyl sulfoxide (DMSO), dimethyl formide (DMF), dichloromethane (DCM), chloroform (CF) at temperature 308 K. we analysed the solvent effect and found the decreasing order sequence of solvents for fast reaction by using the technique for order of preferences by similarity to ideal solution (TOPSIS) method.

Keywords: - Solvent effect, oxidation, TOPSIS, Aliphatic alcohols

I. INTRODUCTION

In the oxidation of organic compounds with reagent there are Chromium Cr(VI) reagents most commonly used as a oxidant. Many Chromium Cr (VI) containing reagents have been used for the oxidation of various organic substrates [1-5]. Many researchers has been reported the oxidation of aliphatic aldehydes and aromatic aldehydes by, QBC [6], BPCC [7], MCC [8], IFC [9], TEACC [10], PFC [11], BPSP [12], BTEACC [13], PBC [14], PFC [15], PBC [16], QBC [17], BPCC [18], PCC [19], BTEACC [20], QFC[21], MCC [22], BIFC [23], IFC [24] QCC [25], TEACC [26] and TPSD [27, 28] in the solvent DMSO. The technique for order of preferences by similarity to ideal solution (TOPSIS) method is a broadly useful numerical technique in multi- criteria decision making problems. TOPSIS method was originally introduced by Hwang and Yoon [30], and further developed by Yoon [31]. Hwang *et.al.* [32], also published a modified new approach for decision making problems under multi objectives. In this article, we have studied kinetic aspect of the oxidation of aliphatic alcohol with imidazolium fluorochromate (IFC) [33], quinolinium fluorochromate (QFC) [34], benzimidazolium fluorochromate (BIFC) [35], piridinium chlorocromate (PCC) [36], bipyridinium chlorochomate (BPCC) [37] carried out in different solvents like dicloroethane (DCE), acetone, dimethyl sulfoxide (DMSO), dimethyl formide (DMF), dichloromethane (DCM), chloroform (CF) at temperature 308 K. and suitable solvent is selected for the different alternatives.

II. MATERIALS AND METHODS

Materials: The aliphatic alcohol is commercial product and is used as supplied. BIFC [29], BPCC [7], PCC [19], IFC [24] and QFC [21] are prepared by the stated methods and purity is studied by iodometric method. Solvents are purified by the standard methods of purification [32].

Measurements:

The reactions have been set up to occur under pseudo-first-order conditions by keeping an excess (×10 or greater) of the substrate over the oxidant. The reactions are carried out at a constant temperature 308K. The required amount of substrate, solvent, etc. is combined to create the reaction mixture, which is then left in a thermostatic bath for the amount of time necessary for the solution to reach the bath's temperature. The reaction started by adding a solution of the oxidant, which had been previously equilibrated in the thermostat by means of a pipette. To mix the solution, the reaction flask was vigorously whirled. The reactions are tracked by spectro-photometrically measuring the decrease in [oxidant].

Result and Discussion by using TOPSIS Method

The study of solvent effect on oxidation is an important concept in Physical Organic chemistry. The TOPSIS method is very useful in multiple criteria decision making problem. The rate constants ($10^4 k_2 s^{-1}$) of oxidation of aliphatic alcohols by five reagents BIFC, BPCC, PCC, IFC and QFC in different solvents like dicloroethane (DCE), acetone, dimethyl sulfoxide (DMSO), dimethyl formide (DMF), dichloromethane (DCM), chloroform (CF) at temperature 308 K.

Table-1. Decision Matrix of rate constants ($10^4 k_2 s^{-1}$) for the Oxidation of Aliphatic alcohol by the oxidants BIFC, BPCC, PCC, IFC and QFC at 308 K.

Reagent / Solvent	IFC	QFC	BIFC	PCC	BPCC
DCE	5.1	70.9	36.1	13.8	35.8
DMSO	6.2	151.1	75.2	26.8	76.1
DMF	5.5	132.0	65.9	22.4	65.1
DCM	4.9	92.1	46.1	15.9	45.9
CF	5.7	79.8	40.9	12.5	41.0

Step-1. The normalized value y_{ij} is calculated as

$$y_{ij} = x_{ij} \Big/ \sqrt{\sum_{i=1}^{m} x_{ij}^2} \ , \ i = 1,2,\dots,m \ , \ j = 1,2,\dots,n$$

We obtained the normalized value matrix as follows:

Table-2. Normalized value Matrix of rate constants ($10^4 k_2 s^{-1}$) for the Oxidation of Aliphatic alcohol by the oxidants BIFC, BPCC, PCC, IFC and QFC at 308 K.

Reagent / Solvent	IFC	QFC	BIFC	PCC	BPCC
DCE	0.4148	0.2891	0.2938	0.3235	0.2914
DMSO	0.5042	0.6162	0.6120	0.6283	0.6193
DMF	0.4473	0.5383	0.5363	0.5251	0.5298
DCM	0.3985	0.3756	0.3752	0.3728	0.3736
CF	0.4636	0.3254	0.3328	0.2931	0.3337

Step-2. The weighted normalized value W_{ij} is calculated as

$$W_{ij} = y_{ij} * W_j \,,\ i = 1,2,\dots,m\,,\ j = 1,2\,,\dots,n$$

Where W_j is weight of the j[th] attribute or criterion and $\sum_{j=1}^{n} W_j = 1$

Now we obtained the weighted normalized value matrix for assigning equal weight for each criterion as follows:

Table-3. Weighted Normalized value Matrix of rate constants ($10^4 k_2 s^{-1}$) for the Oxidation of Aliphatic alcohol by the oxidants BIFC, BPCC, PCC, IFC and QFC at 308 K.

Reagent / Solvent	IFC	QFC	BIFC	PCC	BPCC
DCE	0.0830	0.0578	0.0588	0.0647	0.0583
DMSO	0.1008	0.1233	0.1224	0.1257	0.1239
DMF	0.0895	0.1077	0.1073	0.1050	0.1060
DCM	0.0797	0.0752	0.0751	0.0746	0.0747
CF	0.0927	0.0651	0.0666	0.0586	0.0667

Step-3. Now we calculate positive ideal solution (PIS) (A_+) and Negative ideal solution(NIS) (A_-)

$$PIS = A_+ = \{W_1^+, W_2^+, W_3^+, \dots .. W_j^+\}$$

Where $W_j^+ = \left\{\left(\max_i \frac{W_{ij}}{} j\epsilon J\right), \left(\min_i \frac{W_{ij}}{} j\epsilon J'\right)\right\}$

$$NIS = A_- = \{W_1^-, W_2^-, W_3^-, \dots .. W_j^-\}$$

Where $W_j^- = \left\{\left(\min_i W_{ij} / j\epsilon J\right), \left(\max_i W_{ij} / j\epsilon J'\right)\right\}$,

Where $J = Beneficial\ Attribute, J' = Nonbeneficial\ Attribute$

Table 4. Positive ideal solution (PIS)A_+

Reagent / Solvent	IFC	QFC	BIFC	PCC	BPCC
DCE	0.0830	0.0578	0.0588	0.0647	0.0583
DMSO	0.1008	0.1233	0.1224	0.1257	0.1239
DMF	0.0895	0.1077	0.1073	0.1050	0.1060
DCM	0.0797	0.0752	0.0751	0.0746	0.0747
CF	0.0927	0.0651	0.0666	0.0586	0.0667

Therefore, the Positive ideal solution

$$PIS = A_+ = \{0.1008, 0.1233, 0.1224, 0.1257, 0.1239\}$$

Table 5. Nigative ideal solution $(NIS)A_-$

Reagent / Solvent	IFC	QFC	BIFC	PCC	BPCC
DCE	0.0830	0.0578=W_2^-	0.0588W_3^-	0.0647	0.0583W_5^-
DMSO	0.1008	0.1233	0.1224	0.1257	0.1239
DMF	0.0895	0.1077	0.1073	0.1050	0.1060
DCM	0.0797 W_1^-	0.0752	0.0751	0.0746	0.0747
CF	0.0927	0.0651	0.0666	0.0586W_4^-	0.0667

Therefore, the Negative ideal solution

$$NIS = A_- = \{0.0797, 0.0578, 0.0588, 0.0586, 0.0583\}$$

Step 4:- Calculate the Separation measures from PIS and NIS of each alternatives by using Euclidean distance formula.

$$S_i^+ = \sqrt{\sum_{j=1}^{n}(W_j^+ - W_{ij})^2}, \qquad i = 1,2,3,\ldots,m$$

$$\mathbf{S_i^+ = [0.1112, 0.0, 0.03205, 0.85728, 0.10517\,]}$$

$$S_i^- = \sqrt{\sum_{j=1}^{n}(W_j^- - W_{ij})^2}, \qquad i = 1,2,3,\ldots,m$$

$$\mathbf{S_i^- = [0.0069, 0.1152, 0.0842, 0.0286, 0.0168]}$$

Step 5:- Computation of the Relative closeness to the ideal solution defined as:

$$C_i^+ = \frac{S_i^-}{S_i^+ + S_i^-} \quad , i = 1, 2, 3, 4, 5$$

Hence we get the relative closeness to the ideal solution as

$C_1^+ = 0.0585$
$C_2^+ = 1.0000$
$C_3^+ = 0.7243$
$C_4^+ = 0.2468$
$C_5^+ = 0.1379$

Table 6. Rank of preference order for selection of solvents

Solvent	C_i^+	Rank Preference
DCE	0.0585	5
DMSO	1.0000	1
DMF	0.7243	2
DCM	0.2468	3
CF	0.1379	4

Fig. 1 and 2. Graphical analysis of rate constants for the oxidation of aliphatic alcohol by different oxidants at 308 K.

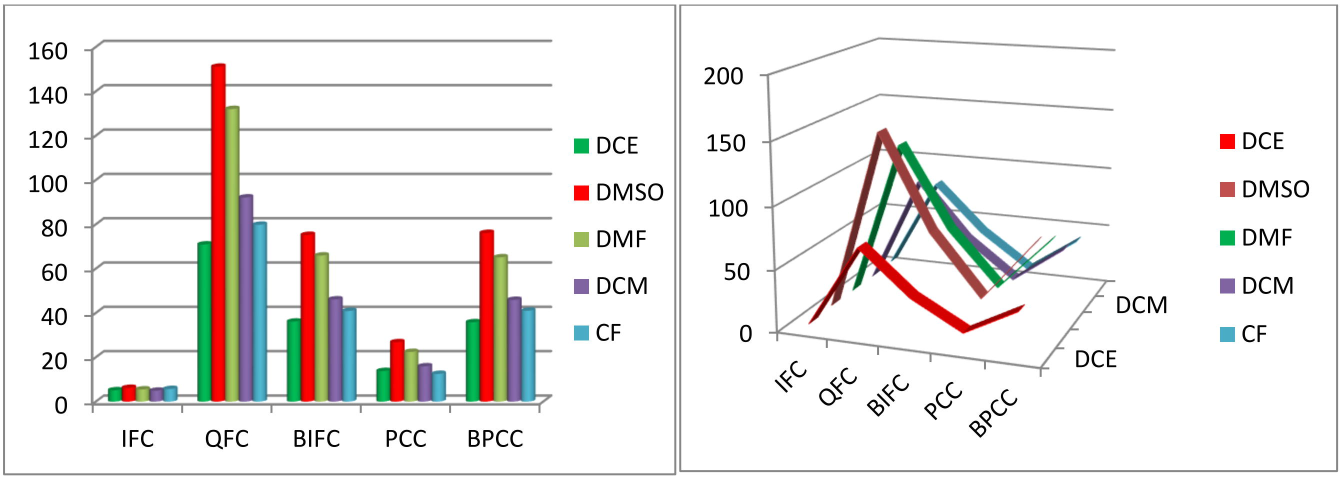


Fig. 3 and 4. Graphical analysis for normalization of rate constants (10^4 k2 s-1) for the oxidation of aliphatic alcohol by different oxidants at 308 K.

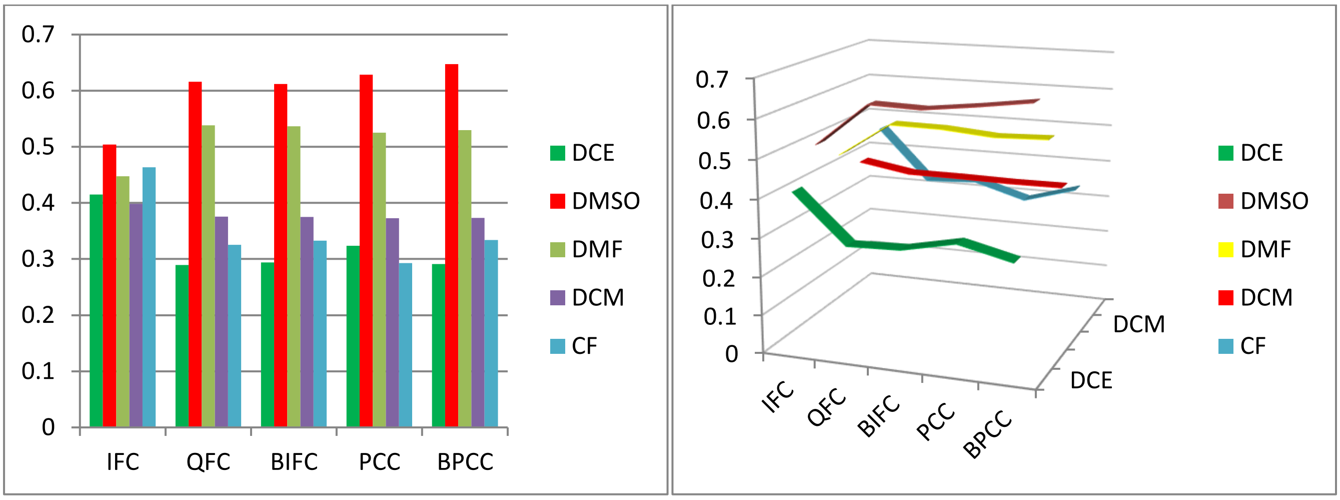
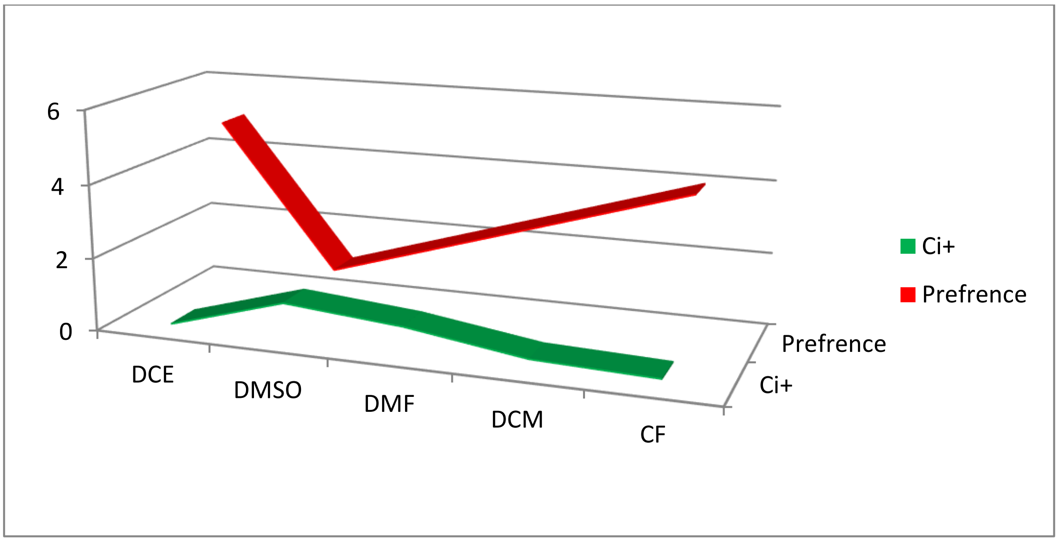


Fig.5. Rank of preference order for selection of solvents



III.CONCLUSION

Solvent effect is one of the important concepts in kinetic study of oxidation reaction. In this paper we discuss the application of TOPSIS method for the selection of the most suitable solvent for the oxidation of oxidant by using hypothetical data. We have examined that the DMSO is the most suitable solvent for the oxidation of aliphatic alcohols with given oxidant according to the above mentioned parameters.

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