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Comparative Study of Solvent Effect by TOPSIS Method in the Oxidation of Acetaldehyde

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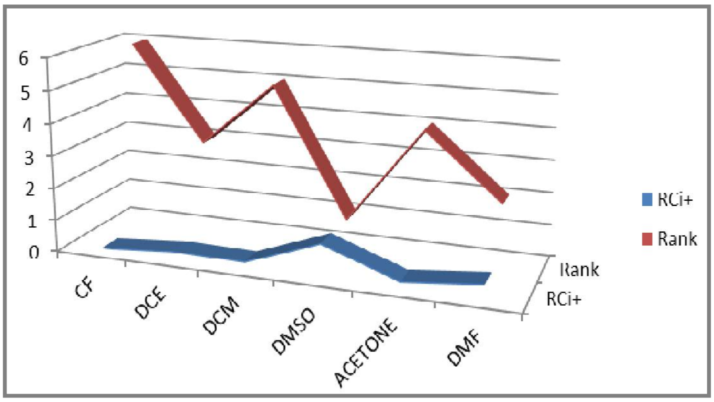
ABSTRACT

The oxidation of acetaldehyde with benzimidazolium fluorochromate, 2,2'bipyridinium chloro-chromate, pyridinium chlorocromate, morpholinium chlorochromate and quinolinium fluorochromate carried out in different solvents like chloroform(CF), 1,2-dichloroethane(DCE), dichloromethane (DCM), dimethyl sulfoxide (DMSO), acetone, dimethyl formamide (DMF) at temperature 298 K. By using the technique for order of preferences by similarity to ideal solution (TOPSIS), solvent effect is analyzed and we found descending order of solvents for fast reaction as DMSO> DMF> DCE> ACETONE> DCM> CF.

Graphical Abstract



Rank of preference order of solvents.

Keywords: Oxidation, acetaldehyde, TOPSIS, solvent effect.

INTRODUCTION

Chromium Cr (VI) reagents have been used as an oxidant for the oxidation of many organic compounds. Many Chromium Cr (VI) containing compounds have been used for the oxidation of various organic functional groups [**1-5, 36-40**]. The oxidation of aldehyde (aliphatic and aromatic) by

PFC [6], BPCC [7], MCC [8], PBC [9], TEACC [10], QBC [11], BPSP [12], BTEACC [13], IFC [14], PFC [15], PBC [16], QFC[17], BPCC [18], PCC [19], BTEACC [20], QBC [21], MCC [22], TPSD [23, 24], IFC [25] QCC [26], TEACC [27] and BIFC [28] in DMSO has been reported. TOPSIS is a broadly applicable numerical method in multiple criteria decision making. TOPSIS method was originally established by Hwang and Yoon [33], and further developed by Yoon [34]. Hwang *et.al.* [35], further published a new approach for decision making under multi objectives.

We have studied kinetic aspect of the oxidation reaction of acetaldehyde with BIFC [28], BPCC [7,18], PCC [19], MCC [8, 22], QFC [17] in different solvents i.e. chloroform(CF), 1,2-dichloroethane(DCE), dichloromethane (DCM), dimethyl sulfoxide (DMSO), acetone, dimethyl formamide (DMF) at temperature 298 K, and best solvent is identified under the different alternatives.

MATERIALS AND METHODS

Materials: The acetaldehyde is commercial product and is used as supplied. BIFC [29], BPCC [2], PCC [1], MCC [30] and QFC [31] prepared by the reported methods and purity is investigated by iodometric method. Solvents are purified by the usual methods of purification [32].

Measurements: The reactions have arranged to be under pseudo-first order conditions by keeping an excess (×10 or greater) of the substrate over the oxidant. The reactions are carried out at constant temperature 298K. The reaction mixture are prepared by mixing requisite amount of substrate and Solvent etc. and allowed to stand in a thermostatic bath for a sufficient length of time to enable the solution to attain the temperature of the bath. The reaction is started by adding a solution of the oxidant, which has also been equilibrated in the thermostat previously, by means of pipette. The reaction flask swirled vigorously to mix the solution. The reactions are followed by monitoring the decrease in [oxidant] spectro-photometrically.

RESULTS AND DISCUSSION

The rate constants k_2 in six solvents compared using TOPSIS method (Table 1).

Table1. Decision matrix of rate constants ($10^4 k_2\ s^{-1}$) for the oxidation of acetaldehyde by different oxidants at 298 K

Solvent \ Oxidant	BIFC	BPCC	PCC	MCC	QFC
CF	15.08	15.5	6.76	27.6	31.6
DCE	19.20	19.6	85.1	31.6	42.7
DCM	17.80	17.4	74.1	34.7	36.3
DMSO	60.70	56.2	262	99.5	123
ACETONE	15.80	18.2	77.6	28.8	38.9
DMF	33.60	28.2	126	56.2	64.6

The normalized matrix is obtained and consequently the normalized value r_{ij} is calculated as follows:

$$r_{ij} = x_{ij} \sqrt{\sum_{i-1}^{m} x_{ij}^2}, i = 1, 2, ..., m, and, j = 1, 2, ..., n$$

Calculate the weighted normalized matrix. The weighted normalized value v_{ij} is calculated as follows:

$$v_{ij} = r_{ij} \times w_j, i = 1, 2, ..., m, and, j = 1, 2, ..., n$$

Where, w_j is the weight of the j^{th} criterion or attribute and $\sum_{j=1}^{n} w_j = 1$.

Table 2. Normalized matrix is constructed using rate constants for the oxidation of Acetaldehyde by different oxidants at 298 K

Solvent \ Oxidant	BIFC	BPCC	PCC	MCC	QFC
CF	0.03901	0.04294	0.00421	0.04237	0.04007
DCE	0.04977	0.05429	0.05295	0.04869	0.05414
DCM	0.04605	0.04820	0.04611	0.05346	0.04603
DMSO	0.15704	0.15569	0.16302	0.15332	0.15596
ACETONE	0.04088	0.05042	0.04828	0.04438	0.04932
DMF	0.08693	0.07812	0.07839	0.08659	0.08115

Positive ideal (A^+) and negative ideal (A^-) solutions.

$$A^+ = \{(\max_i v_{ij} \mid j \in C_b), (\min_i v_{ij} \mid j \in C_c)\} = \{v_j^+ \mid j = 1,2,...,m\}$$

$$A^- = \{(\min_i v_{ij} \mid j \in C_b), (\max_i v_{ij} \mid j \in C_c)\} = \{v_j^- \mid j = 1,2,...,m\}$$

Positive ideal (A^+)

0.15704	0.15569	0.16302	0.15332	0.15596

Negative ideal (A^-)

0.03901	0.04294	0.00421	0.04237	0.04007

The calculation of separation measures in the m-dimensional Euclidean distance is made. The separation measures of the positive ideal solution and the negative ideal solution, respectively, are as follows:

$$S_i^+ = \sqrt{\sum_{j=1}^{m} (v_{ij} - v_j^+)^2}, \qquad i = 1,2,...,m$$

0.27858	0.23503	0.24412	0.24694	0.16775

$$S_i^- = \sqrt{\sum_{j=1}^{m} (v_{ij} - v_j^-)^2}, \qquad i = 1,2,...,m$$

0.05345	0.04462	0.27858	0.04574	0.11261

Relative closeness to the ideal solution defined as follows:

$$RC_i^+ = \frac{S_i^-}{S_i^* + S_i^-}, i = 1,2,...,m$$

Table 3. Rank of preference order of solvents

Solvent	RC_i^+	Rank
CF	0	6
DCE	0.18527	3
DCM	0.15455	5
DMSO	1	1
ACETONE	0.15627	4
DMF	0.40166	2

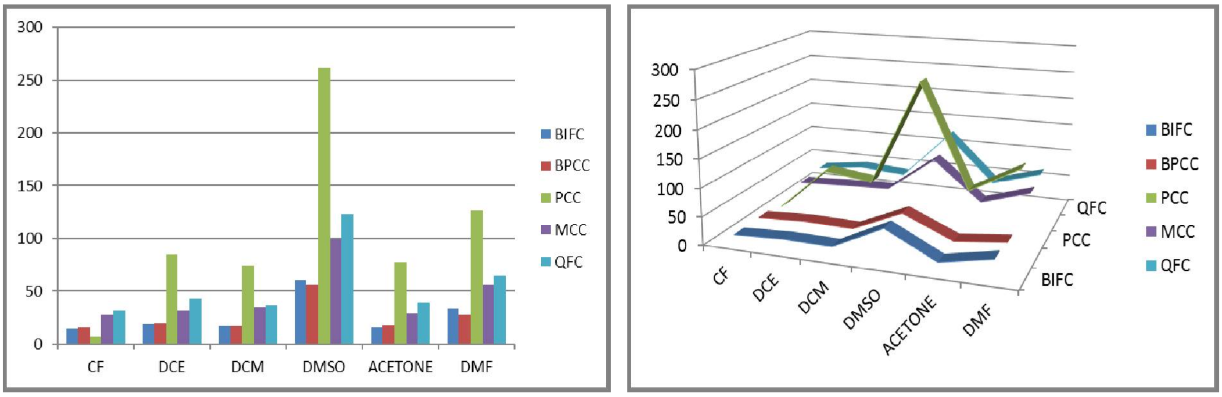


Figure 1 and 2. Decision analysis of rate constants for the oxidation of acetaldehyde by different oxidants at 298 K.

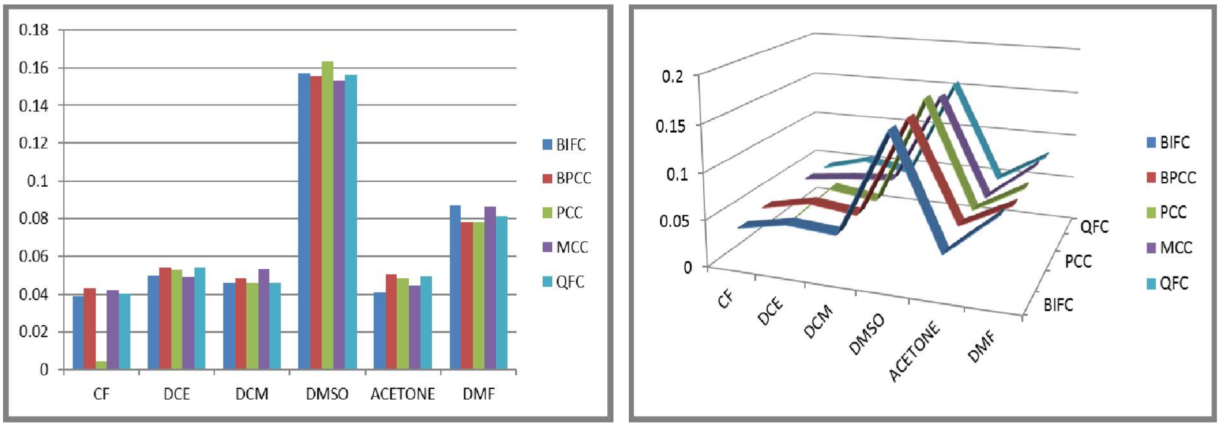


Figure 3 and 4. Normalization of rate constants ($10^4 k_2 s^{-1}$) for the oxidation of acetaldehyde by different oxidants at 298 K.

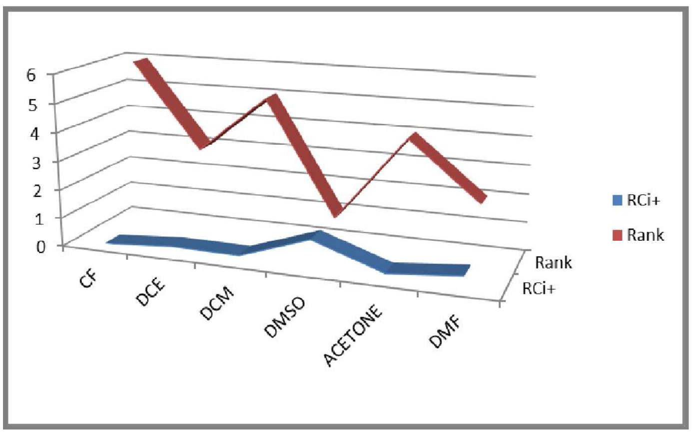


Figure 5. Rank of preference order of solvents.

APPLICATION

Comparative study of solvent effect is one of the important concepts of physical organic chemistry. TOPSIS is the applied method in multiple criteria decision making. It has an importance for the choice of solvent for the chemical reaction.

CONCLUSION

TOPSIS method is useful for selection of best solvent for the oxidation of acetaldehyde by different oxidants. In this study we found the following order of preference for reaction- DMSO> DMF> DCE> ACETONE> DCM> CF.

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