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Comparative Study by TOPSIS Method for the Solvent Effect in the Oxidation of Benzaldehyde

Abstract

The oxidation of benzaldehyde with pyridiniumchlorocromate, 2,2'bipyridinium chlorochromate, morpholiniumchlorochromate, quinoliniumfluorochromate and benzimidazoliumfluorochromatecarried out in different solvents like chloroform(CF), 1,2-dichloroethane(DCE), dichloromethane (DCM), dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), acetone, at temperature 308 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>DCM >ACETONE > CF.

Keywords: Oxidation, Benzaldehyde, TOPSIS, Solvent Effect.

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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[1-5,36,37,38]. The oxidation of aldehyde (aliphatic & 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.

Review of Literature

We have studied kinetic aspect of the oxidation reaction of benzaldehyde with PCC[19], BPCC[7,18], MCC[8,22], QFC[17], BIFC[28] in different solvents i.e. chloroform(CF), 1,2-dichloroethane(DCE), dichloromethane (DCM), dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), acetoneat temperature 308 K, and best solvent is identified under the different alternatives.

Aim of the Study

The major objective of the study is to find most suitable solvent for the oxidation of benzaldehyde by Cr (VI) reagents, using the technique for order of preferences by similarity to ideal solution (TOPSIS).

Materials and methods

Materials

The benzaldehyde is commercial product and is used as supplied. PCC[1],BPCC[2], MCC[30],QFC[31] and BIFC[29]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 benzaldehyde over the oxidant. The reactions are carried out at constant temperature 308 K. The reaction mixture are prepared by mixing requisite amount of benzaldehyde 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: Decision matrix is constructed using rate constants (10^4 k_2 s^{-1}) for the oxidation of benzaldehyde by different oxidants at 308 K

	PCC	BPCC	MCC	QFC	BIFC
CF	62.2	11.2	22.2	25.2	10.0
DCE	80.8	15.0	27.5	36.3	14.4
DCM	68.6	13.2	30.5	31.6	12.5
DMF	118	24.7	46.2	52.6	28.2
DMSO	246	51.4	78.5	125	54.6
ACETONE	70.2	12.8	24.8	32.9	11.4

Calculate the normalized matrix. 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 (10^4 k_2 s^{-1}) for the oxidation of Benzaldehyde by different oxidants at 308 K.

Oxidant / Solvent	PCC	BPCC	MCC	QFC	BIFC
CF	0.040473	0.035684	0.042160	0.033656	0.030255
DCE	0.052576	0.047791	0.052225	0.048480	0.043567
DCM	0.044638	0.042056	0.057922	0.042203	0.037818
DMF	0.076782	0.078695	0.087737	0.070250	0.085318
DMSO	0.160072	0.163762	0.149078	0.166943	0.165190
ACETONE	0.045679	0.040781	0.047097	0.043940	0.034490

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^+)

0.160072	0.163762	0.149078	0.166943	0.165190

Negative ideal (A^-)

0.040473	0.035684	0.042160	0.033656	0.030255

Calculate the separation measures using the m-dimensional Euclidean distance. The separation measures of each alternative from the positive ideal solution and the negative ideal solution, respectively, are as follows:

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

0.279486	0.251418	0.261210	0.183481	0.266125

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

0.028131	0.020897	0.098065	0.279486	0.014183

Calculate the relative closeness to the ideal solution. The relative closeness of the alternative A_i with respect to A^+ is defined as follows:

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

Table 3: Rank of preference order of solvents

	RC_i^+	Rank
CF	0	6
DCE	0.100630	3
DCM	0.074073	4
DMF	0.348309	2
DMSO	1	1
ACETONE	0.050598	5

Figure 1

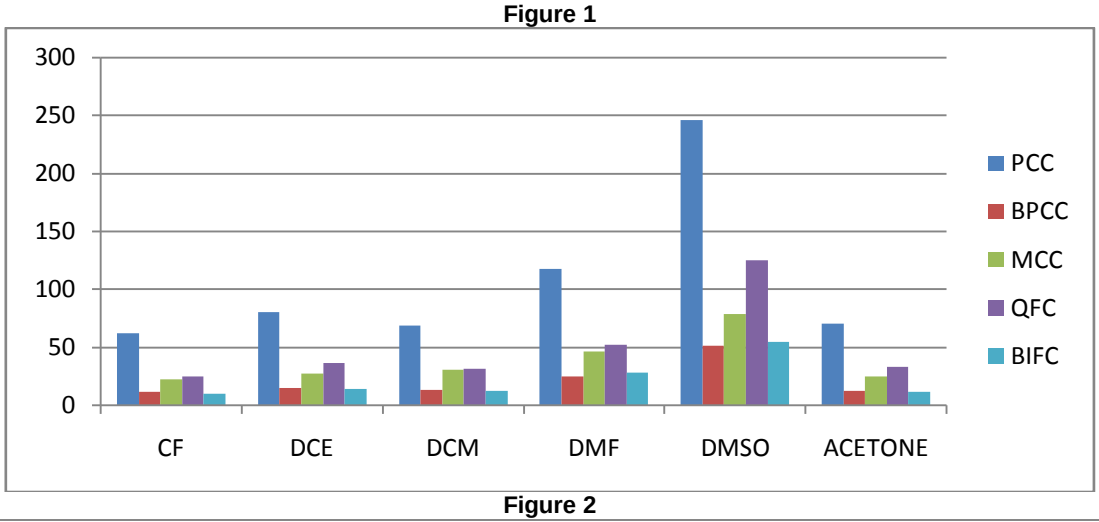


Figure 2

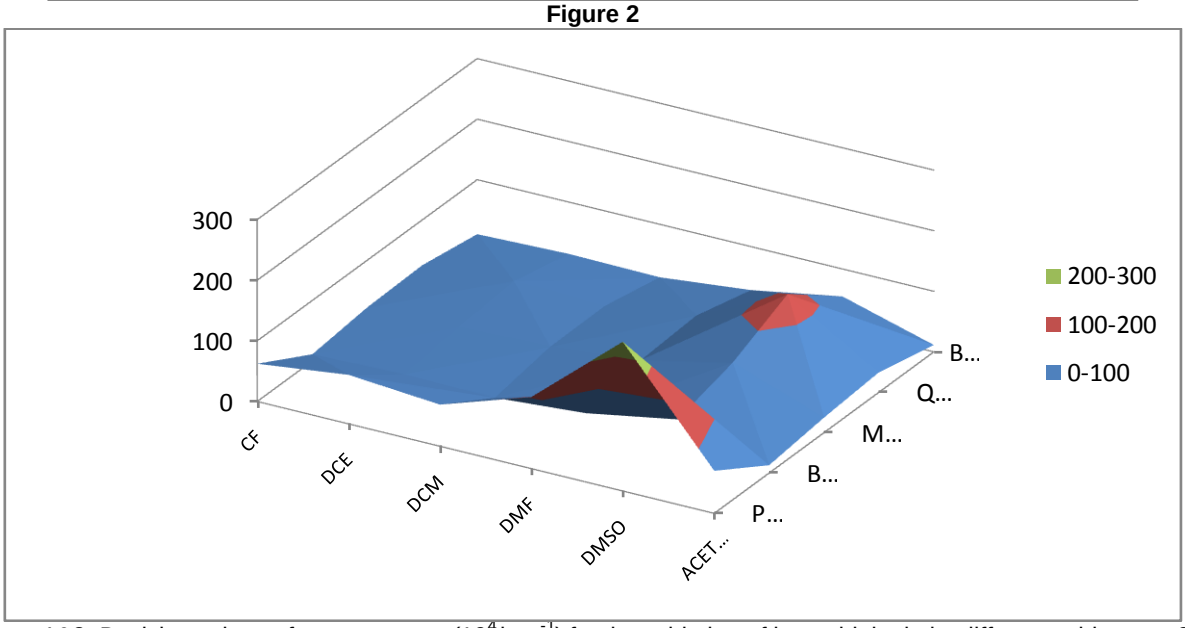


Figure 1&2: Decision values ofrate constants ($10^4 k_2$ s^{-1}) for the oxidation of benzaldehyde by different oxidants at 308 K.

Figure 3

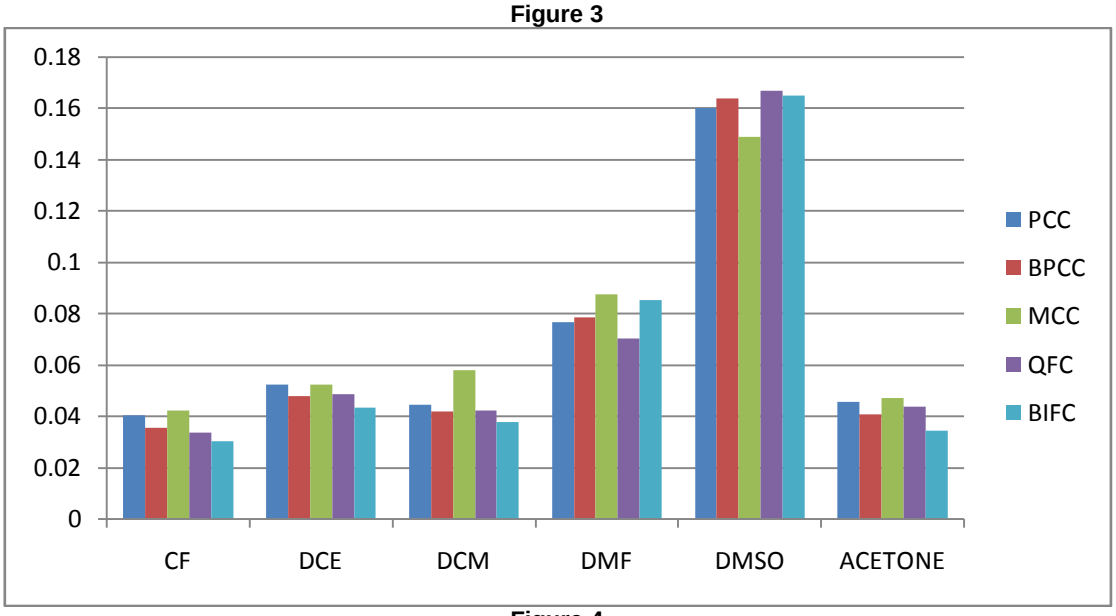


Figure 4

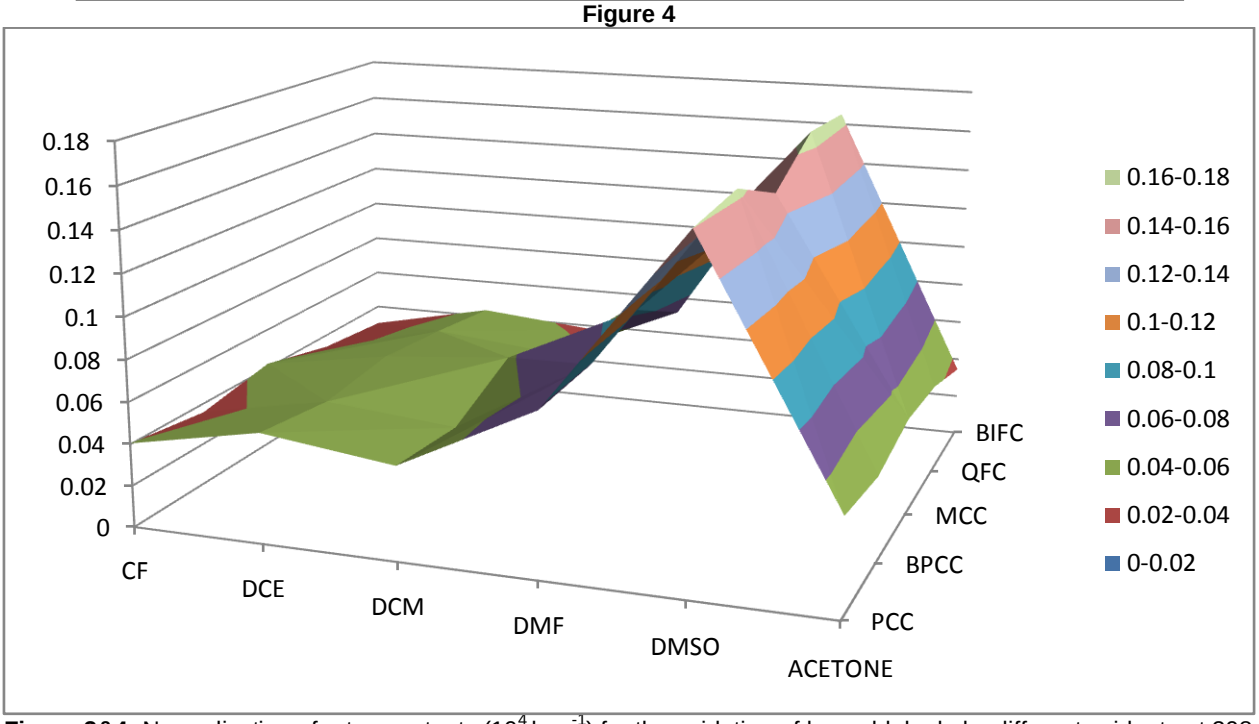
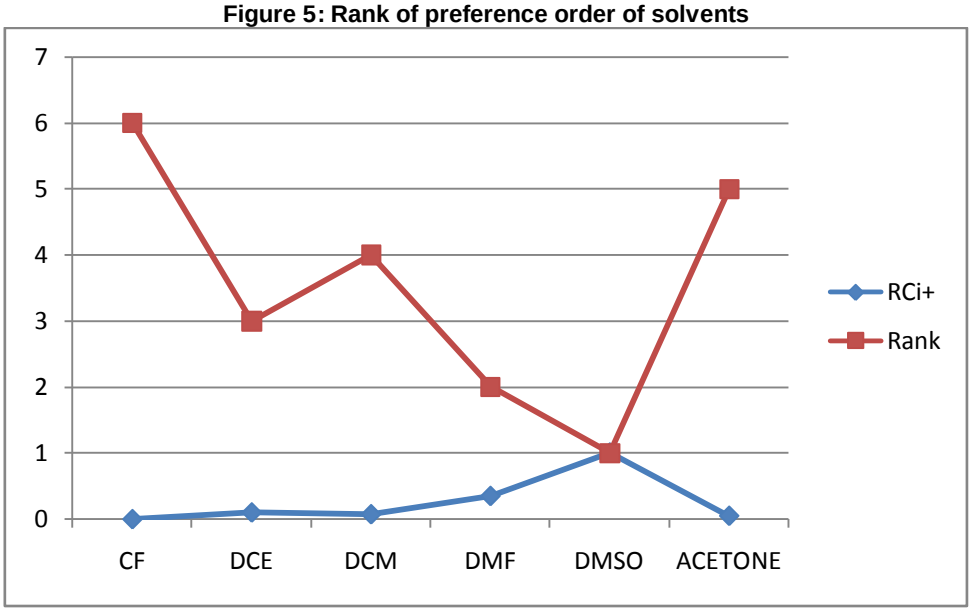


Figure 3&4: Normalization of rate constants (10^4 k_2 s^{-1}) for the oxidation of benzaldehyde by different oxidants at 308 K.

Figure 5: Rank of preference order of solvents



Conclusion

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. In this study we found the following order of preference of solvents for theoxidation of benzaldehyde- DMSO> DMF> DCE> DCM> ACETONE> CF. DMSO is found to be the most preferred solvent for the oxidation of benzaldehyde while chloroform is least preferred for the same reaction.

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