Comparative Study of Solvent Effect for tryptophan Oxidation by Different Oxidants

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Research Article

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Additional Declarations:
No competing interests reported.

Tables 1 to 7 are available in the Supplementary Files section.
Comparative Study of Solvent Effect for tryptophan Oxidation by Different Oxidants

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ABSTRACT

Quinaldinium fluorochromate (QnFC), imidazolium fluorochromate (IFC), quinoxalinium dichromate (QxDC), imidazolium chlorochromate (ICC), and quinaldinium chlorochromate (QnCC) have all performed tryptophan oxidation at 308K using various solvents, including dimethyl sulphoxide (DMSO), dimethyl formamide (DMF), acetone, dichloromethane (DCM) and 1,2-dichloroethane (DCE). This has led to the formation of the corresponding indole-3-acetaldehyde. We examined the solvent effect using the Technique for Order of Preference by Similarity to Ideal Solution (TOPSIS) method, and the solvent performance score for the reaction revealed the following order: DMSO>DMF>DCE>DCM>ACETONE. Corresponding indole-3-acetaldehyde were formed as a result of the oxidation process with all of the oxidants.

Keywords: Oxidants, Solvents, Solvent effect, tryptophan, TOPSIS method.

Introduction:

Many organic compounds have been oxidized by using chromium compounds in both aqueous and non-aqueous media. It has been demonstrated that chromium reagents, in particular Cr (VI) reagents, are adaptable and capable of oxidizing nearly all oxidisable organic functional groups. To carry out this transformation, a variety of reagents and experimental techniques have been developed. Reagents containing chromium (VI) reactive species are particularly popular for the oxidation of alcohols to carbonyl compounds.

Spectrophotometric analysis has been used to examine the kinetics of chromic acid oxidation of L-tryptophan in H$_2$SO$_4$ medium at a constant ionic strength of 0.6 mol dm$^{-3}$ and at 25 °C. Quinaldinium fluorochromate(QnFC), imidazolium fluorochromate( IFC), quinoxalinium dichromate(QxDC), imidazolium chlorochromate(ICC), and quinaldinium chlorochromate (QnCC) have all been studied for their reactions to thiomallic acid oxidation at a temperature of 308 K in five different solvents dimethyl sulphoxide (DMSO), dimethyl formamide (DMF),acetone, dichloromethane (DCM) and 1,2-dichloroethane (DCE). Using the TOPSIS method we have determined which solvent is optimal among the various options and have suggested a workable mechanism. The TOPSIS method was created by Hwang and Yoon, and Yoon improved it later. Hwang and colleagues have also presented a novel method for multi-objective decision-making.
EXPERIMENTAL

Material

Tryptophan of the analytical reagent (A. R.) grade has been used. Iodometric analysis was used to ascertain the purity of QnFC$^{13}$, IFC$^{14}$, QxDC$^{15}$, ICC$^{16}$, and QnCC$^{17}$, which were prepared using the described procedure. Standard protocols were followed to purify the solvents$^{18}$.

Kinetic Experiments

A considerable excess of the substrate over oxidants (*15 times or more) was used to obtain the pseudo-first-order constant. We used five different solvents in our research. The reactions were studied at a fixed temperature of 308 K. The right amounts of solvent, substrate, etc. were combined to create the reaction mixtures, which were then maintained at a steady temperature in a thermostatic water bath. An oxidant solution that had been kept in the water bath beforehand was introduced to initiate the reaction. Using spectrophotometry, the drop in oxidant concentration was tracked. We utilized the AIMIL India model MK2 UV-Vis spectrophotometer to conduct our experiments, and we chose $\lambda_{\text{max}}$ 470 nm for QnFC, IFC, QxDC, ICC, and QnCC, respectively, because these oxidants

Stoichiometry and analysis of products:

For twenty-four hours, the reaction mixture with an excess of oxidant over tryptophan was kept at room temperature with DMSO present. One mole of tryptophan consumed one mole of the oxidant, according to an estimation of the unreacted oxidant.

Stoichiometry

By adding more [QnFC] than [Tryptophan] and letting the reaction run to completion, the stoichiometry of the reaction [QnFC]:[Tryptophan] was found. Using iodometry, the unreacted Quinaldinium fluorochromate was estimated. It was determined by measuring the amount of unreacted Quinaldinium fluorochromate that one mole of oxidant consumed one mole of substrate. It was discovered that the stoichiometry between tryptophan and QnFC was 1:1.

Analysis of products:

Tryptophan (0.1 M) in DMSO and Quinaldinium fluorochromate (0.1 M) in DMSO made up the reaction mixture. The medium was kept in check with 0.15 M para toluene sulphonic acid. After that, the reaction mixture was given a small warmup and allowed to finish the reaction for roughly 48 hours. The reaction mixture was dried over anhydrous sodium sulfate and extracted
with ether after 48 hours. The product was obtained by cooling the ethereal layer after it had been repeatedly cleaned with water and allowed to evaporate on a water bath.

The primary product, indole-3-acetaldehyde, was used to analyze the product. It was identified by spot test\textsuperscript{19}, and its 2,4-dinitrophenylhydrazine derivative was quantitatively estimated\textsuperscript{20}. It was determined that other products had been mentioned\textsuperscript{21, 22}. Previous reports of comparable oxidation products under various experimental settings range from \textsuperscript{23 - 26}. Conversely, the addition of manganese(II) sulfate to the reaction mixture resulted in a decrease in the oxidation rate, which verified the formation of Cr III species\textsuperscript{27,28}. This oxidant produced such a product in the majority of organic substrate oxidation reactions. The identical process was used for QnCC, ICC, QxDC, and IFC. Five products in total were examined in this study.

RESULTS AND DISCUSSION

We have oxidized tryptophan with five different oxidants and solvents, forming corresponding indole-3-acetaldehyde in the process.

In all cases, corresponding indole-3-acetaldehyde are formed through the formation of a chromate ester in the ester through a cyclic concerted symmetrical transition state, according to a suitable mechanism that has been proposed. For each oxidant, an appropriate mechanism has been provided.

**Mechanism:** Mechanism and Rate law

![Mechanism Diagram]

Chromate ion: Chromium(III) oxide
Chromic acid: Chromium(VI) oxide
Scheme 1: Mechanistic scheme of the oxidation of tryptophan by Chromium(VI)
Technique for Order of Preference by Similarity to Ideal Solution (TOPSIS) Method:

We have used the TOPSIS approach to compare the rate constants $k_2$ in five solvents for specific oxidants to find out which solvent is best suited for the oxidation of tryptophan. TOPSIS as one of MCDM methods considers both the distance of each alternative from the positive ideal and the distance of each alternative from the negative ideal point. In other words, the best alternative should have the shortest distance from the positive ideal solution (PIS) and the longest distance from the negative ideal.

In this study there are 5 oxidants and 5 solvents that are ranked based on TOPSIS method. Table-1 describes the criteria Table-2 shows the decision matrix.

The Steps of the TOPSIS Method:

**STEP 1: Normalize the decision-matrix.**

The following formula can be used to normalize.

$$ r_{ij}(x) = \frac{x_{ij}}{\sqrt{\sum_{i=1}^{m} x_{ij}^2}} \quad i = 1, \ldots, m \ ; j = 1, \ldots, n $$

Table-3 shows the normalized matrix.

**STEP 2: Calculate the weighted normalized decision matrix.**

According to the following formula, the normalized matrix is multiplied by the weight of the criteria.

$$ v_{ij}(x) = w_j r_{ij}(x) \quad i = 1, \ldots, m \ ; j = 1, \ldots, n $$

Table-4 shows the weighted normalized decision matrix.

**STEP 3: Determine the positive ideal and negative ideal solutions.**

The aim of the TOPSIS method is to calculate the degree of distance of each alternative from positive and negative ideals. Therefore, in this step, the positive and negative ideal solutions are determined according to the following formulas.

$$ A^+ = (v_1^+, v_2^+, \ldots, v_n^+) $$
$$ A^- = (v_1^-, v_2^-, \ldots, v_n^-) $$

So that

$$ v_j^+ = \{(\max v_{ij}(x) | j \in j_1), (\min v_{ij}(x) | j \in j_2)\} \quad i = 1, \ldots, m $$
$$ v_j^- = \{(\min v_{ij}(x) | j \in j_1), (\max v_{ij}(x) | j \in j_2)\} \quad i = 1, \ldots, m $$

where $j_1$ and $j_2$ denote the negative and positive criteria, respectively.

Table-5 shows both positive and negative ideal values.
STEP 4: Distance from the positive and negative ideal solutions

TOPSIS method ranks each alternative based on the relative closeness degree to the positive ideal and distance from the negative ideal. Therefore, in this step, the calculation of the distances between each alternative and the positive and negative ideal solutions is obtained by using the following formulas.

\[
d_i^+ = \sqrt{\sum_{j=1}^{n} [v_{ij}(x) - v_j^+(x)]^2}, \quad i = 1, \ldots, m
\]

\[
d_i^- = \sqrt{\sum_{j=1}^{n} [v_{ij}(x) - v_j^-(x)]^2}, \quad i = 1, \ldots, m
\]

In Table 6 shows the distance to the positive and negative ideal solutions.

STEP 5: Calculate the relative closeness degree of alternatives to the ideal solution

In this step, the relative closeness degree of each alternative to the ideal solution is obtained by the following formula. If the relative closeness degree has value near to 1, it means that the alternative has shorter distance from the positive ideal solution and longer distance from the negative ideal solution.

\[
C_i = \frac{d_i^-}{d_i^+ + d_i^-}, \quad i = 1, \ldots, m
\]

In Table 7 shows the relative closeness degree of each alternative to the ideal solution and its ranking. The (figure-1) shows the ci values of solvents

Conclusion:

We performed the oxidation of tryptophan by various oxidants in this investigation. Corresponding indole-3-acetaldehyde were the end product. The process involved the fast pre-equilibrium formation of a cyclic chromate ester, followed by the ester's slow step-by-step breakdown via a cyclic concerted symmetrical transition state, which in every case resulted in the formation of corresponding indole-3-acetaldehyde. In physical organic chemistry, the comparative analysis of the solvent effect is a fundamental concept. For this study, the TOPSIS method is useful.

This is the method of making decisions based on multiple criteria. We oxidized tryptophan in this study using a variety of oxidants and solvents. Using the TOPSIS method, we were able to determine the order of the solvents' performance score in relation to the reaction: DMSO>DMF>DCE>DCM>ACETONE. Thus, it was determined that using DMSO as a solvent produced the best results when oxidizing tryptophan using various oxidants.
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Conflict of interest

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


29.
Figures

Figure 1

Rank by the performance score of the solvents

Supplementary Files

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- table.docx