Kinetics and mechanism of oxidation of benzyl alcohol and cyclohexanol by quinolinium fluorochromate

Suresh D. Dhage*1, S. B. Patwari2 and Swanand Mukhedkar3

1Department of Chemistry, SSJES, Arts, Comm. and Science College, Gangakhed, Parbhani (M.S.), India
2Department of Chemistry, Lalbahadur Shastri College, Dharmabad, Dist. Nanded, (M.S.) India
3Department of Chemistry, Shahir Annabhau Sathe College, Mukhed, Dist. Nanded (M.S.) India

ABSTRACT

The kinetics of oxidation of cyclic alcohols like Benzyl alcohol and Cyclohexanol by Quinolinium Fluorochromate (QFC) has been studied in acetonitrile-nitrobenzene (1:1,v/v) medium. The reaction is first order with respect to oxidant and the rate is almost independent of the substrate concentration. The reactions are catalysed by an acid. The decrease in dielectric constant, increases the rate of reaction. The effect of temperature and solvent composition were studied and the various activation parameters are evaluated. Based on the experimental results, a probable reaction mechanism was proposed.

Keywords: Kinetics, Oxidation, Benzyl alcohol, Cyclohexanol, Quinolinium fluorochromate

INTRODUCTION

The selective oxidation of alcohols to the corresponding aldehydes is a frequently used transformation in organic synthesis and hence variety of methods has been developed. Among them Chromium (VI) containing reagents have been extensively studied1. The most popular of them, the collins reagent, showed several difficulties. It should be used in large excess and it is unstable and it shows a poor selectivity in oxidation of alcohols to their aldehydes2.

Quinolinium Fluorochromate (QFC) has been used as a mild and selective oxidising agent in synthetic organic chemistry3. It oxidises secondary alcohols to corresponding ketones in dimethyl sulphoxide (DMSO)4,5 and also oxidises atrolactic acid to ketones6.

It has been reported that, this complex converts alcohols into aldehyde products at room temperature and it is a better oxidant than Pyridinium Chlorochromate, Pyridinium Fluorochromate7.

In the present work, we report the kinetics of oxidation of Benzyl alcohol and cyclohexanol by Quinolinium Fluorochromate and evaluate the reaction rate constants at different temperature and discuss the probable mechanism.
EXPERIMENTAL SECTION

Materials:
All chemicals used were reagent grade materials from Merck. The solvents were purified and dried by distillation over P₂O₅. Quinolinium Fluorochromate (QFC) was prepared by the procedure described in literature³ and its purity was checked by the melting point, TLC and iodometric method.

The reaction products Benzaldehyde and Cyclohexanone were characterized by spectral analysis and estimated as their 2,4-dinitrophenyl hydrazones.

Kinetic Measurements (Methods):
For kinetic measurements, the reactions were performed under pseudo-first order conditions by maintaining a large excess (X ≥ 5) of alcohol over QFC. The reactions were carried out at constant temperature (+ 0.1K) and progress of reaction were followed by iodometric estimation of unreacted chromium (VI). The medium of reaction was always 1:1 (v/v) acetonitrile : nitrobenzene. This medium was chosen as a solvent, because acetonitrile did not react with QFC. The reaction mixture were homogeneous for the total period of kinetic investigation.

The rate constants were determined from the plot of log [oxidant] against time. Dielectric constant for the varying proportions of acetonitrile-nitrobenzene mixture were estimated from the dielectric constants of pure solvents⁸ (Table 3). A constant ionic strength could not be maintained owing to the non-aqueous nature of the reaction medium.

The effect of temperatures on reaction rate were studied with varying temperatures of 303, 308, 313 and 318 K respectively for both alcohols. The activation parameters were evaluated by the standard procedure⁹ (Table-4).

RESULTS AND DISCUSSION

Stoichiometry and Product analysis:
The stiochiometry of various oxidations studied and well estimated by the reaction of respective alcohol with an excess of oxidant (QFC) followed by estimating the unreacted Cr (VI). In some cases, however, an excess of alcohols were used and followed by the estimation of the carbonyl product. The stoichiometry of the reactions with Benzyl alcohol and cyclohexanol can be represented as follows

\[
3RCH₂OH + 2Cr^{(VI)} \rightarrow 3RCHO + 6H^+ + 2Cr^{(III)} \quad \text{...... (1)}
\]

\[
2C₆H₁₂OH + 2Cr^{(VI)} \rightarrow 3C₅H₁₀CO + 6H^+ + 2Cr^{III} \quad \text{......(2)}
\]

The oxidation of benzene alcohol and cyclohexanol by QFC in 1:1 (v/v) acetonitrile-nitrobenzene leads to the formation of Benzaldehyde and Cyclohexanone respectively in very high yields showing no indication of further oxidation of carbonyls.

Effect of variation of [QFC] on reaction rate:
Like the analogous pyridinium chlorochromate₁₀-₁₂, these two alcohols studied were found to be first order with respect to time, because the first order rates were constant at different times. The reactions were also first order with respect to oxidant (QFC) as the rate constants were found to be practically unchanged for most of the reaction times with varying concentration of oxidants as showing table 1.

Effect of variation of [Substrate] on reaction rate:
As the concentration of substrates (alcohols) increases, there is increase in the rate constants as shown in table 2.

The plot of log k v/s log [Substrate] shows that the rate of reaction increases with substrate concentration, indicating that, the complex formation takes place between substrate and oxidant.
Table 1: Oxidant Dependence of the reaction rate:

<table>
<thead>
<tr>
<th>[QFC] × 10^3 mol dm^-3</th>
<th>k_1 × 10^4 sec^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Benzyl alcohol] 0.01 mol dm^-3</td>
<td>7.52</td>
</tr>
<tr>
<td>[Cyclohexanol] 0.01 mol dm^-3</td>
<td>7.52</td>
</tr>
<tr>
<td>1</td>
<td>7.52</td>
</tr>
<tr>
<td>2</td>
<td>7.52</td>
</tr>
<tr>
<td>3</td>
<td>7.52</td>
</tr>
<tr>
<td>4</td>
<td>7.52</td>
</tr>
</tbody>
</table>

Table 2: Substrate Dependence of the reaction rate:

<table>
<thead>
<tr>
<th>Substrate</th>
<th>[QFC] = 0.001 mol dm^-3; T = 303 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Benzyl alcohol]</td>
<td>7.52</td>
</tr>
<tr>
<td>[Cyclohexanol]</td>
<td>8.06</td>
</tr>
</tbody>
</table>

Table 3: Dependence of Reaction Rate on Solvent Composition:

<table>
<thead>
<tr>
<th>Nitrobenzene (%)</th>
<th>Acetonitrile (%)</th>
<th>Dielectric constant</th>
<th>[Benzyl alcohol] 0.02 mol dm^-3 k_1 × 10^4 sec^-1</th>
<th>[Cyclohexanol] 0.02 mol dm^-3 k_1 × 10^4 sec^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>70</td>
<td>36.50</td>
<td>1.75</td>
<td>3.61</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>36.20</td>
<td>3.83</td>
<td>5.98</td>
</tr>
<tr>
<td>70</td>
<td>30</td>
<td>35.90</td>
<td>7.62</td>
<td>10.89</td>
</tr>
</tbody>
</table>

Effect of solvent:
The reaction has been studied under various composition of solvent mixture as shown in table 3. It has been observed that, the reaction rate increases with decreases in dielectric constant of medium suggesting that, the more polar solvents may require larger reaction times for the oxidation reactions.

Table 4: Dependence of rate on temperature and activation parameters for the oxidation of alcohols by QFC:

<table>
<thead>
<tr>
<th>Substrate</th>
<th>k_1 × 10^4 (sec^-1)</th>
<th>ΔH^* (KJmol^-1)</th>
<th>ΔS^* (JK mol^-1 K^-1)</th>
<th>ΔG^* (KJmol^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzyl alcohol</td>
<td>7.52</td>
<td>7.60</td>
<td>8.12</td>
<td>2.99</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>8.34</td>
<td>8.72</td>
<td>9.12</td>
<td>5.22</td>
</tr>
</tbody>
</table>

Further, the nearly constant values of free energies of activation suggests that, a similar mechanism is operative in both oxidations. Free energies of the acid catalysed reactions appear to be lower, as there has been pronounced
increase in the rate of catalysed reaction suggesting that a protonated Cr\textsuperscript{VI} species may be involved in the rate determining step in presence of an acid. This is in accord with the involvement of such species well established in Chromium(VI) Oxide oxidations\textsuperscript{16}.

**MECHANISM**

In the view of the above results, the following reaction mechanism is proposed. The oxidation of alcohols proceeds via hydride-ion transfer involved in the rate determining step. The oxidation of alcohols results in the formation of corresponding carbonyl compounds.

![Scheme 1](image1.png)

It is possible that the hydride transfer may take place either through the prior formation of chromate (Scheme 1), or directly (Scheme 2). The present data also suggest, like the similar oxidations involving chromic acid\textsuperscript{16}, a chromate formation in the rate-determining step (Scheme 1).

**CONCLUSION**

At the end of this research work, we conclude that, in the kinetics of oxidation of Benzyl alcohol and Cyclohexanol by Quinolinium Fluorochromate (QFC), it has been found that the reaction was first order with respect to oxidant and rate is almost independent of substrate concentration. The reactions are catalyzed by an acid. The decrease in dielectric constant increases the rate of reaction significantly. The rate of reaction increases with temperature and the various activation parameters are evaluated. A suitable mechanism is proposed involving the hydride ion transfer in rate determining step.

**REFERENCES**