Oxidation of 1, 2-Propandiol by Tripropylammonium
Fluorochromate: A Kinetic and Mechanistic Study

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Abstract: The Kinetics of oxidation of 1, 2-propandiol by tripropylammonium
fluorochromate [TPAFC] has been studied Spectrophotometrically catalyzed by sulphuric
acid in aqueous acetic acid medium in the temperature range 292-318K. The reaction is first
order with respect to both 1, 2-propandiol and TPAFC. The activation parameters for the slow
step were computed and calculated. Effect of ionic strength and dielectric constant of medium
has also been studied. A suitable mechanism has been proposed.

Key words: 1, 2-propandiol, tripropylammonium fluorochromate, oxidation, kinetics.

INTRODUCTION:– Organic halochromates have long been used as mild and selective
oxidizing reagents in synthetic organic chemistry¹-¹². tripropylammonium fluorochromate
(TPAFC) is one such compound used for the oxidation of organic substrate¹³-¹⁶. There seem to
be no report on the oxidation of 1, 2-propandiol by TPAFC. Therefore, in continuation of our
earlier work on the oxidation studies of different alcohols¹⁷-¹⁹, we report here the kinetics and
mechanism of acid catalyzed oxidation of 1, 2-propandiol by TPAFC in acetic acid medium.

EXPERIMENTAL SECTION:– All the chemicals and reagents were of analytical grade. All
the solutions used in the study were prepared by using distilled acetic acid²⁰ and doubly
distilled water. tripropylammonium fluorochromate was prepared by the following method:
chromium (VI) oxide (15.0g, 0.150 mol) was dissolved in water in a polyethylene beaker and
40% hydrofluoric acid (11.3 ml, 0.225 mol) was added with stirring at 0⁰C. To the resultant
orange solution, tripropylamine (28.3 ml, 0.150 mol) was added drop wise with stirring to
this solution over a period of 30 minutes and stirring was continued for 30 minutes at 0°C. The orange colored precipitate was filtered, washed with petroleum ether and dried in vacuum for 2 hours at room temperature. Yield was 28 g (97%); mp was 142°C.

The tripropylammonium fluorochromate was stored in polyethylene bottle for long period of time. TPAFC was soluble in water, DMF, acetonitrile, acetone and DCM and was sparingly soluble in benzene, chloroform and hexane.

DETERMINATION OF STOICHIOMETRY AND PRODUCT ANALYSIS:-

The stoichiometry of the reaction was determined by carrying out several sets of experiment with varying amount of (TPAFC) largely in excess over 1, 2-propandiol in 20% acetic acid by using 0.1N H2SO4. The remaining (TPAFC) was then analyzed Spectrophotometrically. The result indicated that 1 mole of 1, 2-propandiol react with 1 mole (TPAFC).

\[
\text{R-CH}_2\text{-OH} + [\text{C}_3\text{H}_7]_3\text{NH(CrO}_3\text{F)} + [\text{C}_3\text{H}_7]_3\text{NH(CrO}_3\text{H}_2\text{F)}
\]

Where \( R = \text{CH(OH)CH}_3 \)

The product analysis was carried out under kinetic conditions. In a typical experiment, 1, 2-propandiol (0.05 mol) and TPAFC (0.01 mol) were made up to 50 ml in 20% acetic acid and kept in dark for about 24 hours to ensure the completion of the reaction. The solution was then treated with an excess (200 ml) of a saturated solution of 2, 4-dinitrophenylhydrazine in 2 mol dm\(^{-3}\) HCl and kept overnight in a refrigerator. The precipitated 2, 4-dinitrophenylhydrazone (DNP) was filtered off, dried, weighed, recrystallized from ethanol and weighed again. The yield of DNP before and after recrystallisation was 2.0 g (90%) and 1.7 g (75%) respectively. The DNP was found identical with the DNP of 2-hydroxyl-1-propanal by meting point. The products were also characterized by TLC, IR, and NMR spectra.

KINETIC MEASUREMENTS:-

The reactions were followed under pseudo-first-order conditions by keeping large excess (\( x \geq 10 \) or greater) of the 1, 2-propandiol over TPAFC. The temperature was kept constant to +/- 0.1 K. The solvent was acetic acid. The reactions were followed by monitoring the decrease
in the concentration of TPAFC Spectrophotometrically at 345 nm for 80% completion of the reaction. The pseudo-first-order rate constants \( k_{\text{obs}} \), were evaluated from the linear \((r=0.990-0.999)\) plots of log [TPAFC] against time. Duplicate kinetic runs showed that the rate constants were reproducible to within +/- 3%.

**RESULT AND DISCUSSION:**

The results of oxidation of 1, 2-propanediol by TPAFC are represented in table 1-7.

**Effect of variation of concentration 1, 2-propanediol:** The oxidation of 1, 2-propanediol (1, 2-PD) with TPAFC in 20% of acetic acid in presence of sulphuric acid yields acetone. By keeping constant [TPAFC] and \([H_2SO_4]\), the increase in [1, 2-propanediol] increases the rate of reaction (Table-1). The plot of log of \( k_{\text{obs}} \) versus log [1, 2-propanediol] for different initial concentration of 1, 2-propanediol is linear with unit slope demonstrate the first order dependence of rate on 1, 2-propanediol (Figure: 1).

<table>
<thead>
<tr>
<th>([1,2-PD])</th>
<th>0.01M</th>
<th>0.02M</th>
<th>0.03M</th>
<th>0.04M</th>
<th>0.05M</th>
<th>0.06M</th>
<th>0.07M</th>
<th>0.08M</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k \times 10^3\text{sec}^{-1} )</td>
<td>1.12</td>
<td>1.56</td>
<td>2.00</td>
<td>2.44</td>
<td>2.88</td>
<td>3.32</td>
<td>3.76</td>
<td>4.20</td>
</tr>
</tbody>
</table>

**Table 1: Effect of variation of [1, 2-propanediol] on reaction rate**

\([\text{TPAFC}]= 0.001 \text{ M, } [\text{H}_2\text{SO}_4] = 0.1 \text{ N, Temperature}=303\text{K, AA} = 20\% (v/v)\)

**Effect of variation of concentration of TPAFC:**

At constant [1, 2-propanediol] and [\(H_2SO_4\)], the in [TPAFC] increases the rate of reaction(Table-2). The plot of log \( k_{\text{obs}} \) verses log [TPAFC] for different initial concentration of TPAFC is linear with unit slope present the first-order dependence of rate on TPAFC.
Table 2: Effect of variation of [TPAFC] on reaction rate

\[
\text{[1, 2-propandiol]} = 0.01 \text{ M}, \ [\text{H}_2\text{SO}_4] = 0.1 \text{ N}, \ \text{Temp.} = 303K, \ \text{AA} = 20\% \ (v/v)
\]

**Effect of variation of concentration of H\(^+\):**

In order to study the effect the H\(^+\) ion concentration on the rate of oxidation reaction of 1, 2-propandiol, the dependence of reaction rate has been investigated at different initial concentration of H\(_2\)SO\(_4\). The rate of reaction increases with increase in [H\(_2\)SO\(_4\)] (Table-3). The plot of log \(K_{obs}\) verses log [H+] are also straight line with slope less than unity, Indicating a fractional order dependence on [H\(^+\)].

Table 3: Effect of variation of [H\(_2\)SO\(_4\)] on reaction rate

\[
\text{[TPAFC]} = 0.001 \text{ M}, \ [\text{1, 2-propandiol}] = 0.01 \text{ M}, \ \text{Temp.} = 303K, \ \text{AA} = 20\% \ (v/v)
\]

**Effect of ionic strength:**

In the present investigation effect of salt on the rate of reaction is carried out. The salts selected are KCl, KBr, and KI. These will give effect of anion particularly halides on the rate of reaction. The divalent and trivalent cationic salt were also used such as CaCl\(_2\), Ca(NO\(_3\))\(_2\), Al(NO\(_3\))\(_3\) and K\(_2\)SO\(_4\). The experiments were carried out under pseudo- first- order condition. These results were used to determine first order rate constant. The rate constants for the oxidation of 1, 2-propandiol in presence of different salt are shown in (Table 4). From table it is clear that, the rate increases with increase in cationic charge and decreases with increase in anionic charge\(^{21}\).

Table 4: Effect of variation of [salts] on reaction rate
Effect of solvent composition:-

At fixed [AP], [TPAFC] and [H⁺], the rate of oxidation of 1, 2-propandiol with TPAFC increases with decrease in polarity of solvent (Table 5). This is due to polar character of transition state as compared to the reactant. The plot of log k_{obs} verses 1/D is linear with positive slope indicating ion- dipole type of reaction.22

<table>
<thead>
<tr>
<th>Acetic acid</th>
<th>10 %</th>
<th>20 %</th>
<th>30 %</th>
<th>40 %</th>
<th>50 %</th>
<th>60 %</th>
<th>70 %</th>
<th>80 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>k x 10³sec⁻¹</td>
<td>0.82</td>
<td>1.12</td>
<td>1.31</td>
<td>1.48</td>
<td>1.66</td>
<td>1.83</td>
<td>2.01</td>
<td>2.18</td>
</tr>
</tbody>
</table>

Table 5: Effect of variation of Acetic Acid % on reaction rate

Effect of temperature:-

The study of effect of temperature on rate of oxidation of 1, 2-propandiol by TPAFC has been subjected to different temperature range 293K to 313K by keeping the concentration of 1, 2-propandiol and reagent constant. Rate constants are given in Table 6. The plots of log of K_{obs} verses 1/T are linear (Figure: 2)

<table>
<thead>
<tr>
<th>Temperatures (K)</th>
<th>293</th>
<th>298</th>
<th>303</th>
<th>308</th>
<th>313</th>
<th>318</th>
</tr>
</thead>
<tbody>
<tr>
<td>k x 10³sec⁻¹</td>
<td>0.31</td>
<td>0.71</td>
<td>1.12</td>
<td>1.56</td>
<td>1.94</td>
<td>2.35</td>
</tr>
</tbody>
</table>

Table 6: Effect of variation of Temperatures on reaction rate

Figure: 2: Arrhenius plot of oxidation of 1, 2-propandiol
Activation parameters are presented in (Table 7). The negative values of entropy of activation reflect that the transition state is more rigid than initial state. The nearly constant ΔG value indicates that similar mechanism is operative for the oxidation of 1, 2-propandiol.

<table>
<thead>
<tr>
<th>Activation parameters</th>
<th>ΔEa KJ mole⁻¹</th>
<th>ΔH# KJ mol⁻¹</th>
<th>ΔS# JK⁻¹ mole⁻¹</th>
<th>ΔG# KJ mole⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>43.33</td>
<td>40.81</td>
<td>-166.93</td>
<td>91.39</td>
</tr>
</tbody>
</table>

Table 7: Activation Parameters

[TPAFC] = 0.001 M, [1,2-PD] = 0.01 M. [H₂SO₄] = 0.1 N, Temp. =303 K, AA = 20 %

Energy-entropy relationship:-

The values of entropy of activation also suggested that the reaction is entropy as well as enthalpy controlled. The values of free energies of activation of reaction were found to be more or less similar. These trends also support the identical reaction mechanism being followed in these reactions²³.

CONCLUSION:-

The rate constants of the slow step involved in the mechanism were evaluated and activation parameters were also computed. The negative value of ΔS# provides support to the formation of rigid transition state. The overall mechanism described here is consistent with product and kinetic studies.

Mechanism of oxidation of 1, 2-propanediol by TPAFC:-
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REFERENCES:-