Phosphotungustic Acid Catalyzed Oxidation of Some Primary Alcohols (methanol and ethanol) by N-chloroisonicotinamidamide in Aqueous Acetic Acid Medium

Priyanka Singh¹, Sanjay Kumar Singh²


Abstract: Phosphotungustic acid catalyzed oxidation of aliphatic primary alcohols (methanol and ethanol) into aldehydes in aqueous acetic acid medium with N-chloroisonicotinamide was reported. Keggin anion tungustic acid was able to form ternary complex with oxidant species and substrate in pre-equilibrium state. The order with respect to [substrate] changes from first to zero-order. The reaction is first-order in [NCIN] and less than unit order in acid. Acetic acid accelerates the reaction rate. The added products isonicotinamide and salt do not significantly affect the reaction rate, a suitable mechanism proposed with rate law, supported by involved reaction constants and activation parameters.

Key words: Methanol, Ethanol, N-chloroisonicotinamide, Phosphotungustic acid, Oxidation.

1. INTRODUCTION

Recently variety of transition metal ions have been introduced as a catalyst under specific conditions of the reaction in kinetics. One such catalyst is phosphotungustic acid a heteropoly metalates exhibits diverse chemical and electrical properties and efficient catalyst (Keggin anionic frame work) for oxidation. It accommodates in the form of outer sphere with large radius of the surface and its electron changes in an octahedral environment with one co-ordination site occupied by solvent molecule. Several protocols were developed and reviews are published in the recent past, its use at low pH less than 8 envisaged in liquid.

The development of the newer reagent N-chloroisonicotinamide for the oxidation of organic substrates continuous to be of interest. The reagent employed in these investigation, NCIN is a useful, less Toxic, little irritants and acts as a source of halogenium ion deserves further investigation. Literature survey reveals that although several organic compounds hydroxy acids, amines, hydroxy- acids, benzaldehydes etc. The oxidation of aliphatic primary amines by several oxidants such as NCSA, QCC, PBC, CAT, NBSA, etc. have been studied previously. We are interested to explore the mechanism involved in the oxidation of alcohols by halo-oxidants NCIN which is non-complementary nature and possibility of a having reactive intermediates which have been encountered in the reactions. The present investigation aimed to understand the nature of complex formed by catalyst PTA with substrate and reacting species of halogen in aqueous acetic acid media.

2. EXPERIMENTAL

Methanol and ethanol (B.D.H.) were procured and used as such received from the vendor. Analytical grade or guaranteed reagents and demineralized double distilled water were used throughout the kinetic study. The oxidant N-chloroisonicotinamide was used after synthesizing it or its (Across) sample was used and its solution was prepared in 80% acetic acid (B.D.H.). It was standardized by iodometric process and kept in dark place to avoid the action of light and save it from the alteration of its concentration.

The requisite amount of catalyst, phototungustic acid (PTA) yellow crystals was dissolved in enough boiling water acidified with HCl. The solution is followed by addition of few drops of acetone to maintain the pH of the solution.

The purity of PTA has been checked by standard procedure. Various others solutions and indicators used in the kinetic study were used in standard form.

Kinetic Studies

All the catalytic kinetic oxidation were carried out in a black-coated pyrex conical flask at 318 and 313 K under the pseudo first-order condition.

[Substrate] >> [NCIN]

The reaction was initiated by the mixing of the NCIN to the other contents reaction vessel thermostated at their respective desire temperatures. The whole reaction mixture was mixed thoroughly. The progress of the NCIN-alcohol reaction was followed by estimating the values of unreacted NCIN iodometrically in known aliquots of the reaction mixtures periodically at different intervals of time.
The parameters $a_0$ and $(a-x)$ represent the values at zero time and at a given instant of time respectively. The rate constants of reaction in each kinetic run computed by integration method:

$$ k = \frac{2.303}{t} \log \frac{[NCIN]_0}{[NCIN]_t} $$

The rate constants are reproducible with a precision of ±3% error.

4. Results And Discussion

Different ratio of $\Delta[NCIN]$ to $\Delta[alcohol]$ were equilibrated at 318 and 323 K taking same content under pseudo first order conditions for 24 hours. The determination of unconsumed NCIN revealed that one molecule of NCIN was required for the oxidation of each mole of aliphatic primary alcohol. The stoichiometric equation may be formulated as:

$$ R \text{CH}_2\text{OH} + \text{PTA} \xrightarrow{[H^+]} \text{RCHO} + \text{HCl} $$

where, $R = -\text{H}$, and -CH$_3$, for methanol and ethanol respectively.

The corresponding products aldehydes were identified by TLC and forming their 2,4-derivatives characterized by determination of their melting points.

The study reveals that rate of reaction varies as a first power of concentration of NCIN which confirmed by the plot of log $[NCIN]$ vs. Time with unit slope.

The study was performed by varying 5 X concentration of alcohols at pre-fixed conditions of the reaction. The results show that Michaelis-Menten type kinetics operative in mechanism (Table 1) which was further confirmed by graphic plot $\frac{1}{k_{obs}}$ vs. $\frac{1}{[alcohol]}$ with positive slope on ordinate axis in fraction-order (Fig. 1).

**Table 1: Dependence of rate on [alcohol]**

<table>
<thead>
<tr>
<th>$10^2[alcohol]$ (mol dm$^{-3}$)</th>
<th>$10^4 k$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$OH (1)</td>
<td>CH$_3$CH$_2$OH (2)</td>
</tr>
<tr>
<td>1.50</td>
<td>1.33</td>
</tr>
<tr>
<td>2.00</td>
<td>1.68</td>
</tr>
<tr>
<td>2.50</td>
<td>2.16</td>
</tr>
<tr>
<td>3.33</td>
<td>2.76</td>
</tr>
<tr>
<td>4.00</td>
<td>3.02</td>
</tr>
<tr>
<td>5.00</td>
<td>3.51</td>
</tr>
<tr>
<td>6.25</td>
<td>3.98</td>
</tr>
</tbody>
</table>
The acidity on the catalysed rate of oxidation have insignificant effect, likewise neutral salt (NaCl) and isonicotinamide could not show their influence on rate.

The kinetic data have been collected for different composition of solvents, acetic acid and water indicate increasing effect of rate with decrease in dielectric constant of the medium (D) which leads ion-ion dipole type of effect on rate.

PTA (Keggin anions) gets converted into the oxidised form and acts as an outer reagent forming complexes by the replacement of the water molecules of hydrogen is more probable transition state which is more stabilized in the medium. The oxidation of alcohol by heteropoly anions occurred via overlap of the p-system with the tungstate frame work. The proton release during the reaction by PTA do not alter sufficient reaction rate but or responsible for protonation of HOCl. Protonated NCIN is not involved in the reaction mechanism which may be attribute to the negligible effect of variation or H2SO4 on the reaction rate.

In the present investigation PTA show fractional-order kinetics for the reactions (Table 2). The graphic plots of log k vs. log [PTA] with positive intercept on Y-axis proves its ability of forming activated complex between oxidant species and reactant (Fig. 2) showing fractional-order kinetics.

### Table 2: Effect of [PTA] catalyst on rate

<table>
<thead>
<tr>
<th>10^4 [PTA] (mol dm^-3)</th>
<th>CH3OH</th>
<th>CH3CH2OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.25</td>
<td>-</td>
<td>2.10</td>
</tr>
<tr>
<td>1.50</td>
<td>2.47</td>
<td>2.23</td>
</tr>
<tr>
<td>2.00</td>
<td>2.76</td>
<td>2.42</td>
</tr>
<tr>
<td>2.50</td>
<td>2.98</td>
<td>2.61</td>
</tr>
<tr>
<td>3.33</td>
<td>3.10</td>
<td>2.73</td>
</tr>
<tr>
<td>4.00</td>
<td>2.81</td>
<td>2.82</td>
</tr>
<tr>
<td>5.00</td>
<td>3.12</td>
<td>-</td>
</tr>
</tbody>
</table>

In the present reaction series the hydrolic product of NCIN, produces HOCl and its protonated species H2O•Cl have been assumed as the reacting species participating in the reaction mechanism.
Mechanism
Considering the various kinetic results, stoichiometry and reacting species of the oxidant, the mechanism may be outlined in two schemes (non-protonated and protonated paths).

**Scheme-1 (non-protonated path)**

\[
\text{NCIN} + \text{H}_2\text{O} \xrightleftharpoons{k_1} \text{HOCl} + \text{N-isonicotinamide} \quad \text{... (1)}
\]

\[
\text{HOCl} + \text{H}^+ \xrightleftharpoons{k_2} \text{H}_2\text{O}^+\text{Cl}^-
\]

\[
\begin{array}{c}
\text{PTA} \\
\text{H} \quad \text{H} \\
\text{C} \quad \text{O} \\
\text{H} \\
\text{Complex (C}_1^f\text{)}
\end{array} + \text{HOCl} \xrightarrow{K_4} \begin{array}{c}
\text{PTA} \\
\text{H} \quad \text{H} \\
\text{C} \quad \text{O} \quad \text{Cl} \\
\text{H} \\
\text{Complex (X}_1^f\text{)}
\end{array} + \text{H}_2\text{O} \quad \text{... (3)}
\]

\[
\text{S} \\
\text{PTA} \\
\text{R} \\
\text{H}
\]

\[
\begin{array}{c}
\text{R} \\
\text{C} \quad \text{OH} \\
\text{alcohol}
\end{array} + [\text{PW}_{12}\text{O}_{40}]^{3-} \xrightleftharpoons{} \begin{array}{c}
\text{R} \\
\text{C} \quad \text{OH} \\
\text{PTA, Keggin type}
\end{array} \quad \text{... (5)}
\]

\[
\begin{array}{c}
\text{PTA} \\
\text{H} \\
\text{C} \\
\text{O} \quad \text{Cl} \\
\text{H}
\end{array} + \text{H}_2\text{O} \xrightleftharpoons{k_2}\text{slow rds} \begin{array}{c}
\text{PTA} \\
\text{H} \\
\text{C} \\
\text{O} \\
\text{H}
\end{array} \quad \text{... (7)}
\]

\[
\begin{array}{c}
\text{R} \\
\text{C} \quad \text{O} \\
\text{H}
\end{array} \xrightleftharpoons{\text{rerrangement}} \begin{array}{c}
\text{R} \\
\text{C} \\
\text{O} \\
\text{H}
\end{array} \quad \text{... (8)}
\]

\[
\begin{array}{c}
\text{R} \\
\text{C} \\
\text{H}
\end{array} \quad \text{Fast} \quad \begin{array}{c}
\text{H} \\
\text{C} \\
\text{O} \\
\text{H}
\end{array} \quad \text{... (9)}
\]
Rate law was derived as:

\[
    k_{obs} = \frac{\text{Rate}_{[\text{NCIN}][\text{PTA}]}}{[\text{INM}] + K_i + K_i K_4[\text{PTA}] \times [\text{alcohol}]}
\]

The order of reactivity was noticed in the present investigation is:

\[\text{CH}_3\text{CH}_2\text{OH} > \text{CH}_3\text{OH}\]

The present trends in order reactivity was also observed in enthalpy of activation and \(\Delta H^\#\). This can be justified like cumulative effects of several parameters like polar, hydrophobic and hydrophilic interactions etc. Inductive effect, size of the molecule play major role in deciding above order of reactivity. The rate of the ethanol was found faster due to decrease in chain length of methanol (\(\text{CH}_3\text{OH}\)), which has the lowest alcoholic percentage in comparison to ethanol i.e. ethanol has the highest. Beside this, the large negative value of \(\Delta S^\#\) probably suggested the complex formed at the apex point in the transition state is polar and solvated, \(\Delta S^\#\) value loss in transitional energy consequently restricts the rotational freedom of the molecules which favours the carbocationic intermediate formation. From thermodynamic point of view fastest reaction has lowest \(E_a\) and vice versa (Table 3). In addition to this the value of Gibbs free (\(\Delta G^\#\)) energy are very close to each other shows that similar mechanism is operative in them. Overall the study concludes that reactions are entropy controlled.

**Table 3. Activation Parameters**

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>(E_a) (kJ mol(^{-1}))</th>
<th>(\Delta H^#) (kJ mol(^{-1}))</th>
<th>(\Delta G^#) (kJ mol(^{-1}))</th>
<th>(-\Delta S^#) (JK(^{-1}) mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{CH}_3\text{OH}</td>
<td>59.82</td>
<td>58.48</td>
<td>92.50</td>
<td>104.52</td>
</tr>
<tr>
<td>\text{CH}_3\text{CH}_2\text{OH}</td>
<td>55.06</td>
<td>53.44</td>
<td>90.62</td>
<td>115.05</td>
</tr>
</tbody>
</table>

**Conclusion**

Keggin type anion of PTA catalyst shows ability to form ternary complexes with oxidant species and substrates in the pre-equilibrium state. The study follow Michalis-Menten type kinetics with stoichiometry 1:1 the reaction show first-order rate with respect to oxidant and fractional-order each with [PTA] and \(\text{H}^+\) ion. Corresponding products aldehydes are characterized by forming their 2,4-derivatives. The kinetic results and thermodynamic parameters support the proposed mechanism.

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**Conflict of Interest**

The authors declare conflict of no interest whatsoever.

**REFERENCES**