Kinetics and mechanism of oxidation of amyl alcohol by pyridinium bromochromate

M. Vellaisamy and R. Santhi

Department of Chemistry, Rajah Serfoji Government College, Thanjavur, Tamilnadu, India

ABSTRACT

The kinetics of oxidation of amyl alcohol (AA) by pyridinium bromochromate (PBC) has been studied in 50% acetic acid - water (v/v) medium in the presence of perchloric acid at 303K. The reaction is first order each in pyridinium bromochromate and amyl alcohol. The reaction is not depends on the hydrogen ion concentration. It shows zero order with respect to hydrogen ion concentration. The rate of oxidation increases with decrease in dielectric constant of solvent suggests ion-dipole interaction. Increase in ionic strength by the addition of sodium perchlorate has no effect on the rate constant. There is no polymerization with acrylonitrile and absence of free radical was proved. Amyl aldehyde has been identified as a product of oxidation. The rate of the reaction has been conducted at four different temperatures and activation parameters were calculated. From the observed kinetic results, a suitable mechanism with rate law has been proposed.

Keywords: Amyl alcohol, kinetics, oxidation and pyridinium bromochromate

INTRODUCTION

Chromium compounds have been used in aqueous and non aqueous medium for the oxidation of a variety of organic compounds[1]. Chromium especially, Cr (VI) reagents have been proved to be versatile reagents and capable of oxidizing almost all the oxidizable organic functional groups[2-4]. Numerous reagents and experimental procedures have been developed to carry out this transformation[5], in particular reagents containing chromium (VI) reactive species are widely used for the oxidation of alcohols to carbonyl compounds [6-7]. Pyridinium bromochromate is not hygroscopic and also not suffered from photosensitivity. The literature survey reveals that the kinetics of oxidation of amyl alcohol by pyridinium bromochromate has not yet been studied. Hence, in the present investigation, the oxidation of amyl alcohol by pyridinium bromochromate in aqueous acetic acid medium and the correspondent mechanistic aspects are reported.

MATERIALS AND METHODS

Analar Grade of amyl alcohol was distilled at 138.5°C and used. The pyridinium bromochromate was prepared by literature method[8]. Acetic acid was purified[9] by standard method and the fraction distilling at 118°C, was collected. All other chemicals used were of AR grade. The solutions were prepared in triple distilled water.
Kinetic Measurements

The kinetic studies were carried out under pseudo first order conditions in 50% acetic acid 50% water medium with the concentration of the amyl alcohol in large excess compared to that of the oxidant. All reactant solutions were placed in thermostated water bath for one hour to attain a temperature of 30°C. Appropriate quantities of the reagent solutions were mixed in a 250cm$^3$ conical flask already placed in the thermostated bath. The reaction rate was followed by measuring the decrease in absorbance at 470nm for up to 80% of the reaction by systronics UV-Visible spectrophotometer. The reaction was completed when the pyridinium bromochromate solution turned from yellow to green. The reactions were followed by determining the concentration of the unreacted PBC, for known intervals of time. The pseudo first order rate constants $k_1$ computed from the linear plots of log absorbance versus time by the least squares method were reproducible within ± 2%.

Stoichiometry and product analysis

The reaction mixture containing an excess of oxidant over amyl alcohol were kept at room temperature in the presence of perchloric acid for 24 h. Estimation of the unreacted oxidant showed that one mole of amyl alcohol consumed one mole of the oxidant.

CH$_3$CH$_2$CH$_2$CH$_2$OH+CrO$_2$BrOPYH$^+$ →CH$_3$CH$_2$CH$_2$CH$_2$CHO+(OH)$_2$CrBrOPYH$^+$

Amyl alcohol(0.1mol) in acetic acid and Pyridinium bromochromate (0.1mol) in water were mixed with perchloric acid and kept at room temperature for one day to ensure completion of the reaction. Then the reaction mixture was extracted with chloroform. The chloroform layer was then dried over anhydrous sodium sulphate and then evaporation of the chloroform layer gave the liquid product. From the infrared, GC-MS spectral data, it was confirmed that the product obtained was amyl aldehyde.

RESULTS AND DISCUSSION

Oxidation of amyl alcohol by pyridinium bromochromate has been conducted in 50 % acetic acid and 50% water medium at 303 K under pseudo – first order conditions and the observed results were discussed. The order of the reaction with respect to pyridinium bromochromate was found to be unity as shown by the linearity of log absorbance versus time plot. (Table 1). At constant concentration of substrate and perchloric acid, the increase in concentration of pyridinium bromochromate did not affect the rate of reaction (Table 1) The linear constancy in the value of $k_1$ irrespective of the concentration of the pyridinium bromochromate confirms the first order dependence on pyridinium bromochromate. The varying the concentration of amyl alcohol at 303 K and keeping all other reactant concentration as constant and the rates were measured (Table 1). The rate of oxidation increased progressively on increasing the concentration of amyl alcohol indicating first order dependence with substrate. The plot of log $K_{ob}$ versus log [amyl alcohol] gave the slope of 0.90(r=0.999), shows that the oxidation reaction was first order with respect to amyl alcohol.

The reaction was followed with different concentrations of perchloric acid and keeping all the concentrations as constant and rate were measured. There is no change in the rate of the reaction with the increasing the concentration of H$^+$. It indicates that the reaction is not depends on the hydrogen ion concentration. The change in ionic strength by the addition of sodium perchlorate has no effect on the rate constant (Table 1) indicating the involvement of neutral molecule in the rate determining step.

The effect of solvent composition on the reaction rate was studied by varying the concentration of acetic acid 50% - 65%. The reaction rate increases with the increase in the proportion of acetic acid in the medium (Table 1). When the acetic acid content increases in the medium , the acidity of the medium increased where as the dielectric constant of the medium is decreased suggesting ion-dipole interaction[10,11]. The clear mixture containing amyl alcohol and pyridinium bromochromate when allowed to stand with a drop of acrylonitrile[12] no turbidity is formed suggesting the non involvement of free radicals in this reaction.

The rate constants were measured at four different temperature and the activation parameters were computed from a plot of $\ln K_2/T$ versus $1/T$ of the Eyring’s equation[13] and it was found to be linear. The negative value of entropy of activation $\Delta S^*$ indicates a polar transition state with extensive charge separation which promote high degree of solvation of the transition state compared to the reactants. The rate constant and thermodynamic parameters are tabulated in Table 2.
Mechanism and Rate law

The order with respect both PBC and Isoamyl alcohol was first order. The addition of sodium perchlorate or acrylonitrile had an insignificant effect on the rate of the reaction. The rate of the reaction decreases with addition of Mn$^{2+}$ indicate that the reaction proceed by two electron transfer process. The observed stoichiometry for the reaction was 1:1 and the oxidation product is amyl aldehyde. Based on the experimental results, a probable mechanism and rate law for the oxidation of amyl alcohol by pyridinium bromochromate is given below in scheme1.

Mechanism

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3\text{CHO} + (\text{OH})_2\text{CrBrO}^+\text{PyH}^+ & \xrightarrow{K} \text{CH}_3\text{CH}_2\text{CH}_2\text{CHO} + \text{OH}^- + \text{Br}^- \\
\end{align*}
\]

Rate law

The above mechanism leads to the following rate law

\[
\text{Rate} = -\frac{d[\text{PBC}]}{dt} = \text{K}_k[\text{PBC}][\text{sub}]
\]

The proposed mechanism and the derived rate law fit well to the experimental observations

**Table 1:** Rate constant for the oxidation of amyl alcohol by pyridinium bromochromate at 303K.

<table>
<thead>
<tr>
<th>[AA] x 10$^{-2}$ mol dm$^{-3}$</th>
<th>[PBC] x 10$^{-3}$ mol dm$^{-3}$</th>
<th>[HClO$_4$] x 10$^{-7}$ mol dm$^{-3}$</th>
<th>[ACOH - H$_2$O] % (v/v)</th>
<th>[NaClO$_4$] x 10$^{-4}$ mol dm$^{-3}$</th>
<th>[MnSO$_4$] x 10$^{-4}$ mol dm$^{-3}$</th>
<th>K x 10$^{-4}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5 - 4.0</td>
<td>2.5</td>
<td>1.0</td>
<td>50</td>
<td>0.0</td>
<td>0.0</td>
<td>9.91 - 12.31</td>
</tr>
<tr>
<td>2.5</td>
<td>2.5 - 3.5</td>
<td>1.0</td>
<td>50 - 65</td>
<td>0.0</td>
<td>0.0</td>
<td>9.91 - 4.88</td>
</tr>
<tr>
<td>2.5</td>
<td>2.5</td>
<td>1.0 - 2.5</td>
<td>50</td>
<td>0.0</td>
<td>0.0</td>
<td>9.91 - 9.50</td>
</tr>
<tr>
<td>2.5</td>
<td>2.5</td>
<td>1.0</td>
<td>50</td>
<td>0.0 - 7.5</td>
<td>0.0</td>
<td>9.91 - 9.78</td>
</tr>
<tr>
<td>2.5</td>
<td>2.5</td>
<td>1.0</td>
<td>50</td>
<td>0.0</td>
<td>0.0 - 3.5</td>
<td>9.91 - 6.90</td>
</tr>
</tbody>
</table>

**Table 2:** Dependence of rate constant on temperature and activation parameters

<table>
<thead>
<tr>
<th>[PBC] = 2.5 x 10$^{-7}$ mol dm$^{-3}$</th>
<th>[AA] = 2.5 x 10$^{-2}$ mol dm$^{-3}$</th>
<th>Solvent = 50% CH$_3$COOH-H$_2$O (v/v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (K)</td>
<td>$k_k$ x 10$^{-4}$ (s$^{-1}$)</td>
<td>Activation Parameters</td>
</tr>
<tr>
<td>----------------</td>
<td>-----------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>303</td>
<td>9.91</td>
<td>$\Delta H^\ddagger$ = 3.5058kJmol$^{-1}$</td>
</tr>
<tr>
<td>308</td>
<td>10.31</td>
<td>$\Delta S^\ddagger$ = -117.292JK$^{-1}$mol$^{-1}$</td>
</tr>
<tr>
<td>313</td>
<td>12.44</td>
<td>$\Delta G^\ddagger$ = 38.95kJmol$^{-1}$</td>
</tr>
<tr>
<td>318</td>
<td>13.65</td>
<td>$E_a$ = 6.0261kJmol$^{-1}$ at 303 K</td>
</tr>
</tbody>
</table>

**CONCLUSION**

The reaction is first order each in [substrate] and [oxidant]. Zero order with respect to [H$^+$]. The stoichiometry was found to be one mole of amyl alcohol consuming one mole of pyridinium bromochromate. The main product of the reaction was found to amyl aldehyde. The negative values of $\Delta S^\ddagger$ provided support for the formation of a rigid
activated complex. The mechanism proposed for this oxidation reaction is in accordance with the observed kinetic facts.

Acknowledgements
The authors are thankful to Dr. D. Ilangeswaran for his kind help, head of the department of chemistry and principal of Rajah Serfoji Government College (Autonomous), Thanjavur for providing facilities.

REFERENCES