Catalytic Activity of Tungstate & Molybdate Ions in the Epoxidation of Maleic Acid

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The kinetics of epoxidation of maleic acid by hydrogen peroxide in the presence of sodium tungstate or sodium molybdate have been studied. Tungstate-catalysed epoxidation of maleic acid to cis-epoxysuccinic acid is faster than that for molybdate catalysis. The reaction is first order with respect to maleic acid and catalyst and zero order with respect to hydrogen peroxide. A reaction mechanism has been proposed.

EPOXIDES have shown a growing industrial importance, particularly in the polymer field. Although organic peracids\(^1\) are generally used for the epoxidation of alkenes, compounds having strong electron withdrawing substituents close to the double bond are not readily epoxidized by organic peracids\(^2\). However, epoxidation in these cases is brought about\(^3\) by hydrogen peroxide in the presence of inorganic compounds of metals such as W, Mo, V, Os, Ti, Zr, Th, Nb, Ta, Cr, Ru and Se. Mudget and Young\(^4\) made a qualitative comparison of osmic, tungstic, molybdic, tantalic, titanic, and selenious acids as catalysts for the epoxidation by direct addition of hydrogen peroxide to ethylenic compounds. Later Payne and Williams\(^5\) achieved the epoxidation of \(\alpha,\beta\)-unsaturated acids and aldehydes in the presence of sodium tungstate and selenium dioxide.

This paper presents a quantitative and comparative kinetic study of tungstate and molybdate ion catalysed epoxidation of maleic acid by hydrogen peroxide in ethanol water mixture.

Materials and Methods

All the chemicals used were of reagent (BDH) grade quality. Maleic acid solution was standardized using bromate-bromide procedure\(^6\). The ionic strength of the reaction mixture was maintained by the addition of sodium perchlorate. The \(pH\) of the reaction mixture was adjusted by adding triethanolamine.

The progress of the reaction up to 75% completion was followed as reported earlier\(^7\). The plots of [hydrogen peroxide] versus time were found to be linear and the rates were determined from the slopes of these plots. Pseudo-zero order rates are reported as \(k_{obs}\).

The presence of cis-epoxysuccinic acid was confirmed by the method of Jungnickel et al.\(^8\).

Results and Discussion

The plots of [hydrogen peroxide] against time indicate zero order dependence of rate on [hydrogen peroxide] in either case. The values of \(k_{obs}\) increase with the increase in [maleic acid] (Table 1) and [catalyst] (Table 2). This is indicative of the first order dependence of rate on the catalyst as well as on the maleic acid concentrations.

Preliminary studies have shown that under the experimental conditions, hydrogen peroxide does not bring about epoxidation of maleic acid in the absence of catalyst (tungstate or molybdate) and also the catalyst alone without hydrogen peroxide fails to bring about the epoxidation. In aqueous solutions, tungstate and molybdate ions hydrolyse into the acid anions as in Eq. (1) and (2).

\[
\text{MO}_4^{2-} + \text{H}^+ \rightleftharpoons \text{HMO}_4^- \quad \ldots(1)
\]

<table>
<thead>
<tr>
<th>[Maleic acid] (\times 10^4) (M)</th>
<th>(k_{obs}) (mole litre(^{-1}) min(^{-1})) (\times 10^8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium tungstate</td>
<td>Sodium molybdate</td>
</tr>
<tr>
<td>2.67</td>
<td>8.70</td>
</tr>
<tr>
<td>4.66</td>
<td>15.20</td>
</tr>
<tr>
<td>5.33</td>
<td>17.30</td>
</tr>
<tr>
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<td>26.00</td>
</tr>
<tr>
<td>10.65</td>
<td>34.70</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>[Catalyst] (\times 10^4) (M)</th>
<th>(k_{obs}) (\times 10^4) (mole litre(^{-1}) min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium tungstate</td>
<td>Sodium molybdate</td>
</tr>
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<td>5.00</td>
<td>8.65</td>
</tr>
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<td>10.00</td>
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<tr>
<td>15.00</td>
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<td>20.00</td>
<td>34.62</td>
</tr>
<tr>
<td>25.00</td>
<td>43.23</td>
</tr>
</tbody>
</table>
pH and not the unionized peroxyacid attack the double

\[ \text{HMO}_2 + \text{H}_2\text{O} \rightarrow \text{HMO}_2 + \text{H}_2\text{O} \]  \hspace{1cm} (3)

We have reported earlier that the formation of \( \text{HMO}_2 \) is maximum around \( pH \) 4.7 to that of \( \text{HMO}_4 \) around \( pH \) 3.6. The rates of epoxidation catalysed by tungstate or molybdate increase with increasing \( pH \) and are maximum (Table 3) at the \( pH \) at which \( \text{HMO}_4 \) formation is maximum and thereafter the rates decrease with further increase in \( pH \). This clearly suggests that peroxyacid anions are the epoxidizing agents. At this stage it looks instructive to argue why negatively charged peroxyacid anion rates decrease with further increase in \( pH \).

This explains the order of the reaction with respect to substrate, catalyst and the oxidant. The \( pH \) dependence of the process as given in Table 3 can be very well explained by Eq. (9). At higher \( pH \), equilibrium 2 becomes insignificant. Therefore, the term \( K_1 K_4 [\text{H}^+]^2 \) in Eq. (9) can be dropped to give Eq. (10).

\[
\text{Epoxidation rate} = \frac{k' [\text{H}_2\text{A}][\text{HMO}_4]_{\text{cat}}}{1 + K_1 [\text{H}^+] + K_4 [\text{H}^+]^2} \hspace{1cm} (9)
\]

we get

\[
\text{Epoxidation rate} = \frac{k' [\text{H}_2\text{A}][\text{HMO}_4]_{\text{cat}}}{1 + K_1 [\text{H}^+] + K_4 [\text{H}^+]^2} \hspace{1cm} (10)
\]
The plot between $1/k_{obs}$ and $1/[H^+]$ (at higher pH where equilibrium 2 is insignificant) is linear. At low pH the term $K_1K_2[H^+]^2$ becomes significant and its value increases rapidly with the increase in $[H^+]$ and the rate thus decreases with the decrease in pH in the lower pH range.

A comparison of the epoxidation rates (Table 4) of maleic and citraconic acids shows that the presence of methyl group at the site of double bond is rate enhancing. This points to an electrophilic addition and is generally observed in the corresponding reaction of olefins with organic peracids and in other three center-type additions9,10.

An increase in the ionic strength from 3·0-8·0M (NaClO4) did not affect the rate in both the cases. But the epoxidation rate decreased as the percentage of water in ethanol-water mixture decreased i.e. with the lowering of the dielectric constant of medium (Table 5). Solvent and salt effects were studied to gain an insight into the nature of the transition state of the oxygen transfer from the peracids to the double bond of the olefinic substrate.

The higher rate of the tungstate-catalysed epoxidation as compared with the molybdate-catalysed is due to the greater stability of the peroxy anion of tungstate since within the same group of the periodic table, the stability of peroxy anion increases with increasing atomic weight11,12.

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References