Kinetics of silver(I) catalysed peroxydisulphate oxidation of benzylphenylglycollic acids

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Ag(I) catalysed peroxydisulphate oxidation of benzylphenylglycollic and substituted benzylphenylglycollic acids in acetic acid-water mixture (30% v/v) at constant ionic strength is first order each in peroxydisulphate and [Ag(I)] and independent of [reductant]. Addition of ionic strength is first order each in peroxydisulphate acids in acetic acid-water mixture (30% v/v) at constant ionic strength. The rates of reaction, thus indicating negative salt effect. For example under the conditions [peroxydisulphate]=1×10^{-3} mol dm^{-3}, [substrate]=5×10^{-4} mol dm^{-3}, [Ag^{+}]=1×10^{-5} mol dm^{-3} and temp.=35°C increase in ionic strength from 0.04 to 0.1 mol dm^{-3} decreased k_{1}×10^{3} from 1.21 to 0.52 min^{-1} when KNO_{3} was used and 1.36 to 0.67 min^{-1} when K_{2}SO_{4} was used.

The rate of the reaction was inhibited by added allyl acetate, an efficient scavenger for the sulphate radical ion SO_{4}^{2-} (ref. 5). When the allyl acetate concentration was increased to 0.03 mol dm^{-3}, oxidation was completely checked showing a free radical chain mechanism.

The effect of temperature on the rate of the reaction was studied at 30, 35 and 40°C and activation parameters calculated (Table 1). The reactivities of different substituents follow the order: 4-OCH_{3} > 4-CH_{3} > H > 4-Cl > 2,4-dichloro. It is observed that even under conditions when the reaction shows zero order dependence on [substrate], there is considerable difference in the values of k_{1}. It is also evident that electron-donating substituents on the benzene nucleus increase the rate while electron-withdrawing groups retard it. The logarithm of the rate constants at 35°C correlated well with σ^{+} values. A similar correlation between log k_{1} and σ^{+} has been observed by us in the alkaline hexacyanoferrate (III) oxidation of BPGAs. The above order of reactivities is in agreement with the negative values of ρ^{+} (−0.5).

From the results of Table 1 it is evident that both ΔH^{1} and ΔS^{1} are important in controlling the rates of reaction, though the enthalpy factor versus time for over 75-80% of the reaction and also by the non-variation in the rate constant values at varying [peroxydisulphate] in the range of 0.0001 mol dm^{-3} to 0.001 mol dm^{-3}.

Varying [BPGA] from 1.0×10^{-4} to 10.0×10^{-4} mol dm^{-3} at 35°C did not affect the rate constant showing that the reaction is zero order in [BPGA].

The reaction rate increased with increase in [Ag(I)]. At [Ag(I)] in the range of 1.0×10^{-5} mol dm^{-3} to 10.0×10^{-5} mol dm^{-3}, the plot of log [Ag(I)] versus log k_{1} was linear with unit slope indicating that the reaction is first order in [Ag(I)]. Further, a plot of k_{1} against [Ag(I)] passed through the origin showing that the uncatalysed decomposition of peroxydisulphate was negligible.

Increase in the ionic strength decreased the rate of reaction, thus indicating negative salt effect. For example under the conditions [peroxydisulphate]=1×10^{-3} mol dm^{-3}, [substrate]=5×10^{-4} mol dm^{-3}, [Ag^{+}]=1×10^{-5} mol dm^{-3} and temp.=35°C increase in ionic strength from 0.04 to 0.1 mol dm^{-3} decreased k_{1}×10^{3} from 1.21 to 0.52 min^{-1} when KNO_{3} was used and 1.36 to 0.67 min^{-1} when K_{2}SO_{4} was used.

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Table 1—Reaction rate constants and Arrhenius parameters for the peroxydisulphate oxidation of BPGA

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$k_1 \times 10^3$ min$^{-1}$</th>
<th>$E_a$ kJ mol$^{-1}$</th>
<th>$-\Delta S^i$ J mol$^{-1}$ k$^{-1}$</th>
<th>$\Delta H^i$ kJ mol$^{-1}$</th>
<th>$\Delta G^i$ kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-CH$_3$</td>
<td>1.25</td>
<td>1.58</td>
<td>1.99</td>
<td>19.98</td>
<td>242.71</td>
</tr>
<tr>
<td>H</td>
<td>0.75</td>
<td>1.01</td>
<td>1.31</td>
<td>24.08</td>
<td>232.68</td>
</tr>
<tr>
<td>4-Cl</td>
<td>0.51</td>
<td>0.67</td>
<td>1.07</td>
<td>34.68</td>
<td>203.98</td>
</tr>
<tr>
<td>2,4-dichloro</td>
<td>0.24</td>
<td>0.36</td>
<td>0.75</td>
<td>38.54</td>
<td>194.26</td>
</tr>
<tr>
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<td>1.01</td>
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</tr>
<tr>
<td>4-Cl</td>
<td>0.32</td>
<td>0.50</td>
<td>0.75</td>
<td>38.54</td>
<td>194.26</td>
</tr>
</tbody>
</table>

Such a postulation has been rejected by Anderson and Kochi$^7$ for it does not explain the critical role played by alkyl radicals and the catalysis of Cu(II). Further, the value of $\rho^+ (-0.5)$ supports the possibility of a benzylphenylmethanol radical$^10$ and eliminates the possibility of the formation of the same cation$^11$.

The catalytic effect of silver ions may be explained by considering Ag$^{2+}$ and SO$_4^{2-}$ as the reactive species. This is in accordance with the observations of Subbaraman and Santappa$^{12}$, and Higginsen and Marshall$^{13}$ that one-electron transfer is more likely in oxidation-reduction system between transition metal ion and an ion derived from a non-transition element.

All the experimental evidences lead to rate law (2)

$$\frac{d[S_2O_8^{2-}]}{dt} = k[S_2O_8^{2-}][Ag^+] \quad \ldots \quad (2)$$

The rate-determining step should not therefore involve any BPGA molecule but only S$_2$O$_8^{2-}$ and Ag$^+$ ions which yield intermediates capable of readily oxidising the substrate in subsequent fast steps. This is further supported by the negative value of $\Delta S^i$.

On the basis of the above observations a radical chain mechanism (Scheme 1) has been proposed.

$$\begin{align*}
Ag^+ + S_2O_8^{2-} & \rightarrow Ag^2+ + SO_4^{2-} + SO_4^{2-} \\
Ag^+ + SO_4^{2-} & \rightarrow Ag^2+ + SO_3^{2-}
\end{align*}$$

$$\begin{align*}
C_6H_5CH_2COOH & \rightarrow OH + Ag^{II} \quad \rightarrow C_6H_5CH_2COOH + Ag^{II} \\
C_6H_5CH_2COOH & \rightarrow OH + C_6H_5CH_2COOH + Ag^{II} \\
C_6H_5CH_2COOH & \rightarrow OH + C_6H_5CH_2COOH + Ag^{II}
\end{align*}$$

SCHEME 1
Table 2—Comparison of the rates of BPGA with lactic acid and mandelic acid [peroxydisulphate] = 1.6 x 10^{-4} mol dm^{-3}; [substrate] = 5.0 x 10^{-4} mol dm^{-3}; [Ag(I)] = 1.0 x 10^{-4} mol dm^{-3}; \mu = 0.1 mol dm^{-3}; Temperature = 35°C; Solvent = acetic acid-water (30% V/V)

<table>
<thead>
<tr>
<th>Substrate</th>
<th>( k_1 \times 10^3 \text{ min}^{-1} )</th>
<th>( E_a )</th>
<th>( \Delta S^\circ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lactic acid</td>
<td>0.63</td>
<td>34.68</td>
<td>-202.06</td>
</tr>
<tr>
<td>Mandelic acid</td>
<td>0.55</td>
<td>35.22</td>
<td>-201.46</td>
</tr>
<tr>
<td>Benzylphenylglycollic acid</td>
<td>0.67</td>
<td>32.61</td>
<td>-208.44</td>
</tr>
</tbody>
</table>

which is in agreement with the observed stoichiometry and kinetic data.

Applying the steady state conditions Scheme 1 leads to rate Law 3.

\[
\frac{-d[\text{S}_2\text{O}_8^{2-}]}{dt} = \frac{k_1k_2k_4}{k_5} \left[ \text{Ag}^+ \right] \left[ \text{S}_2\text{O}_8^{2-} \right] \]

results in the expression

\[
-k_1[\text{S}_2\text{O}_8^{2-}] + k_4[\text{C}_6\text{H}_5-\text{CH}_2-C-\text{C}_6\text{H}_5-OH]
\]

Although by the steady state hypothesis the concentration of \( \text{C}_6\text{H}_5-\text{CH}_2-C-\text{C}_6\text{H}_5-OH \) is a constant, this may vary from reductant to reductant giving rise to variation in the rate constant \( k_4 \) for the different variation in \( k_1 \) for

\[
k = \left[ \frac{k_1k_2k_4}{k_5} \right]^{1/2}
\]

Acknowledgement

The authors are grateful to the UGC, New Delhi for financial assistance.

References