Oxidation Studies: Part VIII — Kinetics of Ag⁺-catalysed Co(III) Oxidation of Amino Acids

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Ag⁺-catalysed oxidation of amino acids such as glycine, α-alanine, β-alanine, aspartic acid, glutamic acid and threonine by Co(III) in sulphuric acid has been found to be first order in [Co(III)], and fractional in [amino acid] and [Ag(I)]. The rate law obtained has been explained by assuming the formation of an adduct between amino acid and Ag(I) in a fast-step. This adduct is assumed to react with Co(III) in a slow step to yield Ag2⁺-substrate adduct which ultimately undergoes internal oxidation in a fast step to give the products. The bimolecular rate constant (k) for the slow step and the activation parameters are presented and discussed.

\[ \text{Fig. 1 — Plots of } \log [\text{glycine}] \text{ versus } t (\text{curve-A}), \log k' \text{ versus } \log [\text{glycine}] (\text{curve-B}), \log k' \text{ versus } \log [\text{Ag(I)}] (\text{curve-C}), \text{ and } 1/k' \text{ versus } 1/[\text{glycine}] (\text{curve-D}) \text{ at } 20^\circ \text{C and } [\text{Co(III)}] = 5 \times 10^{-3} \text{M; } [\text{H}^+] = 2.0 \text{M; and } \mu = 5.0 \text{M} \text{ for curve-A; } [\text{glycine}] = 0.5 \text{M; } [\text{Ag(I)}] = 4 \times 10^{-4} \text{M; for curve-B; } [\text{Ag(I)}] = 4 \times 10^{-4} \text{M; for curve-C; } [\text{glycine}] = 0.1 \text{M; for curve-D; } [\text{Ag(I)}] = 4 \times 10^{-4} \text{M} \]

Materials and Methods

All the amino acids used were of E. Merck or BDH grade. Other chemicals used were of analar grade. Co(III) sulphate was prepared by the anodic oxidation of Co(II) sulphate. Solutions of amino acids, in H₂SO₄ containing AgNO₃ and Co(III) in H₂SO₄ were taken in flasks covered with black cloth and placed in a thermostat for half an hour before mixing. The course of reaction was followed by estimating the unreacted Co(III) at different time intervals by quenching 10 ml aliquots of the reaction mixture with excess of KI solution followed by titrating the liberated iodine against thiosulphate solution using starch as indicator. Aldehydes, ammonia and carbon dioxide were identified as the products of oxidation by their characteristic tests. Aldehydes were estimated gravimetrically as their 2,4-DNP derivatives. It was found that for every two moles of Co(III) consumed one mole of aldehyde was formed.

Results and Discussion

Under the condition [amino acid] > [Co(III)] in the presence of Ag(I), the order in [Co(III)] was unity as seen from the linear plot of log a/(a-x) versus t (Fig. 1, curve-A). From the slope of the plot of log k' versus log [amino acid] (Fig. 1, curve-B), the order in [amino acid] was found to be fractional. The orders of reaction in glycine, α-alanine, β-alanine, glutamic acid, aspartic acid and threonine were 0.54, 0.55, 0.97, 0.64, 0.66 and 0.60 respectively. The rate of oxidation of amino acid increased with increasing [Ag(I)] (Table 1).

SANTAPPA et al. reported that glycine reacts very slowly with Co(III) in sulphuric acid medium. In view of the recent work on Ag(I)-catalysed oxidation of amino acids by Ce⁴⁺ and persulphate, it was thought of interest to find out whether Ag(I) could be used as a catalyst in Co(III) oxidation of organic substrates. In the present paper the kinetics of oxidation of glycine, α-alanine, β-alanine, aspartic acid, glutamic acid and threonine by Co(III) in the presence of Ag(I) under varying conditions are presented and a possible mechanism has been discussed.
The order of reaction in [Ag(I)] was found to be fractional in all the cases, viz, 0.71, 0.20, 0.16, 0.50, 0.70 and 0.51 for glycine, \( \alpha \)-alanine, \( \beta \)-alanine, aspartic, glutamic acid and threonine, respectively. These orders were obtained from the slope of the plots of \( \log k' \) versus \( \log [Ag^+] \) (Fig. 1, curve-C). The concentration of Ag(I) was found to be unchanged at the end of the reaction as indicated by the constant thio cyanate titre value.

The rate of oxidation of amino acid was found to be retarded by the increase in \( [H^+] \) at constant \( \mu \), indicating the presence of the equilibrium \( Co^{3+} + H_2O \leftrightarrow CoOH_2^+ + H^+ \), and that COOH\(^2+\) is probably the active species. The rates remained unaffected by increasing \( [SO_4^-] \), which excluded the possibility of CoSO\(_4\) being the reactive species.

The fractional order in [substrate] indicates the complex formation of substrate with either Ag(I) or Co(III). Spectrophotometrically it was found that there is no complex formation between Co(III) and substrate. Since Ag(I) is known to form colourless adducts with oxygen containing compounds, it will not be unreasonable to assume the formation of an adduct between Ag(I) and amino acid before the oxidation by COOH\(^2+\) occurs in the slow step to yield Ag(II)-substrate adduct and Co(II) species, probably in the form of CoOH\(^+\) (ref. 6). Involvement of Ag(II) species was confirmed by bipyridyl test. Thus, taking the oxidation of glycine as an example, the following mechanism may be written:

\[
\begin{align*}
H_4CNH_2COOH + Ag^+ & \rightleftharpoons (\text{adduct})^* \quad \text{(fast)} \\
(\text{Adduct})^* + \text{COOH}^2+ & \rightarrow (\text{Adduct})^{2+} + \text{COOH}^+ \quad \text{(slow)} \\
(\text{Adduct})^{2+} & \rightarrow H_4CNH_2COO^+ + Ag^+ + H^+ \quad \text{(fast)} \\
H_4CNH_2COO^- & \rightarrow H_2CNH_2CO_2H + \text{H}_2\text{O} \quad \text{(fast)} \\
H_4CNH_2 + \text{COOH}^+ & \rightarrow \text{HCHO} + \text{NH}_3 + H^+ + \text{COOH}^* \quad \text{(fast)}
\end{align*}
\]

The fast step (i) is followed by a slow step (ii) where (adduct\(^*)\) changes to (adduct\(^{2+}\)). The (adduct\(^{2+}\)) undergoes internal oxidation (step (iii)) giving the radical H\(_4\)CNH\(_2\)COO which on disproportionation [step (iv)] followed by oxidation with CoOH\(^2+\) (step (v)) gives the products.

From the above mechanism the following rate equation could be derived as:

\[
-\frac{d[Co(III)]}{dt} = kK[Co(III)][Ag(I)][H_4CNH_2COOH] \quad \text{(1)}
\]

or

\[
-2.303 \frac{d \log [\text{Co(III)}]}{dt} = k' = \frac{kK[Ag(I)][H_4CNH_2COOH]}{1 + K[Ag(I)] + K[H_2CNH_2COOH]} \quad \text{(2)}
\]

where \( k' \) is the observed rate constant, \( k \) is the bimolecular rate constant [step (ii)], and \( K \) is the formation constant of the adduct [step (i)]. Equation (1) accounts for the first order dependence in [Co(III)] and fractional order in [amino acid] and [Ag(I)]. Taking the reciprocal of Eq. (2) at constant [Ag(I)], we get Eq. (3).

\[
1 = \left[ H_4CNH_2COOH \right] \left( \frac{kK[Ag(I)] + 1}{k} \right) + \frac{1}{k[Ag(I)]} \quad \text{(3)}
\]

From Eq. (3) it is clear that the plots of \( 1/k' \) versus \( 1/[\text{amino acid}] \) should be linear with an intercept. Such plots were obtained in the present work (Fig. 1, curve-D) for all the amino acids indicating that the proposed mechanism is most probable. Values of \( k \) for all the amino acids were calculated from the intercept of the above linear plots at different temperatures to evaluate the thermodynamic parameters at 20\(^\circ\) (Table 2).

The data in Table 2 clearly show that the rate of oxidation of amino acids to a great extent depends on the structure of the amino acid. Thus, the rate of oxidation is reduced when \( R \) in the amino acid.

### Table 1 — EFFECT OF VARYING [Ag(I)] ON \( k' \)

<table>
<thead>
<tr>
<th>([Ag(I)] \times 10^4) M(^*)</th>
<th>Glycine(a)</th>
<th>( \alpha )-Alanine(b)</th>
<th>( \beta )-Alanine(c)</th>
<th>Aspartic acid(d)</th>
<th>Glutamic acid(e)</th>
<th>Threonine(f)</th>
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<tr>
<td>0</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.920</td>
<td>0.380</td>
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<td>1</td>
<td>13.5</td>
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<td>22.3</td>
<td>11.5</td>
<td>15.3</td>
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<td>2</td>
<td>18.9</td>
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<td>25.1</td>
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<td>16.6</td>
<td>16.1</td>
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<td>—</td>
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<td>30.8</td>
<td>24.1</td>
<td>21.9</td>
</tr>
<tr>
<td>4</td>
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<td>28.0</td>
<td>—</td>
<td>27.0</td>
<td>36.8</td>
<td>34.8</td>
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<td>27.0</td>
<td>36.8</td>
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<td>6</td>
<td>42.2</td>
<td>32.8</td>
<td>—</td>
<td>49.7</td>
<td>—</td>
<td>36.8</td>
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<td>7</td>
<td>—</td>
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</tr>
</tbody>
</table>

\( \* \) for the oxidation of threonine.

(a) \([\text{Glycine}] = 0.2M\).
(b) \([\text{\( \alpha \)-Alanine}] = 0.05M\).
(c) \([\text{\( \beta \)-Alanine}] = 0.05M\).
(d) \([\text{Aspartic acid}] = 0.05M\).
(e) \([\text{Glutamic acid}] = 0.05M\).
(f) \([\text{Threonine}] = 0.01M\).
Table 2—Various Thermodynamic Parameters Obtained for Co(III) Oxidation of Amino Acids in the Presence of Ag(I)

<table>
<thead>
<tr>
<th></th>
<th>ΔE^f</th>
<th>ΔH^f</th>
<th>ΔG^f</th>
<th>ΔS^f</th>
<th>e.u.</th>
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<td>Glycine</td>
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<td>α-Alanine</td>
<td>24.1</td>
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<td>16.7</td>
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<td>β-Alanine</td>
<td>34.5</td>
<td>33.9</td>
<td>15.5</td>
<td>62.7</td>
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<td>Glutamic acid</td>
<td>26.1</td>
<td>25.5</td>
<td>15.5</td>
<td>34.2</td>
<td></td>
</tr>
<tr>
<td>Aspartic acid</td>
<td>29.6</td>
<td>29.1</td>
<td>15.3</td>
<td>46.8</td>
<td></td>
</tr>
<tr>
<td>Threonine</td>
<td>29.0</td>
<td>13.7</td>
<td>52.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

acid (RCHNH₂COOH) is methyl group (α-alanine) instead of H (as in glycine). If R contains any other functional group like OH. COOH as in threonine, aspartic and glutamic acids, the rate is found to increase. Thus, the oxidation of amino acids by Co(III) in the presence of Ag(I) seems to be entropy controlled. This was also confirmed by calculating the isokinetic temperature from the slope of the linear plot of ΔH^f versus ΔS^f which was found to be 263°K. Since, in the present work the experimental temperature (278-298°K) is much above the isokinetic temperature, it clearly indicates the oxidation of amino acids to be entropy controlled.

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References