Metabolic pathways of amino-acids involve separation of the amino group from the amino acid carbon skeleton and thereafter conversion of the carbon chain to products which also arise in the metabolism of fats and carbohydrates. These are then completely oxidized. The general path for the oxidation of α-amino acids is as follows.

\[
\text{RCH COOH} + \text{oxidase} \xrightarrow{\text{RC-COOH} + \text{H}_2\text{O}} \text{RC -COOH} + \text{NH}_3
\]

The α-keto acid produced above may be converted to carbohydrate which is the major source of glycogen obtained by glycogenesis.

The available literature on amino acid oxidation mostly concerns with the enzymatic activities. There are casual references on its oxidation by inorganic oxidants. Most of these deal with the analysis of intermediates and the end products in the oxidation of α-amino acids with \( \text{KMnO}_4 \), \( \text{Cr (vi)} \) and \( \text{H}_2\text{O}_2 \). The mechanistic aspect of the reaction seems to have been untouched. Persulphate and chloramine-T oxidation of
glycine, DL-α-alanine and α-valine has just been reported.

The literature on permanganate as well as manganic oxidation is voluminous and in either case, the role of Mn$^{2+}$ is very complicated and has still not been clearly understood. Thus, to have a better understanding of the reaction, the oxidation of four simple amino acids, viz., glycine, DL-α-alanine and DL-iso and normal valine have been studied in detail in presence of low as well as high concentration of Mn(II).

The kinetics of oxidation of glycine, DL-α-alanine and DL-iso and normal valine by Mn(III)-sulphate in sulphuric acid medium has been investigated. All the four amino acids have been found to follow a similar kinetics. The nature of the reaction is very much dependent on the concentration of Mn(II) present in the reaction mixture. The results are summarised as follows.

Oxidation of amino acids with Mn(III) sulphate in the presence of low (below 0.01M) concentration of Mn(II)

The reaction showed a first order dependence on Mn(III) when the initial concentration of Mn(II) present in the reaction
mixture was less than 0.01M, however, this limit for 
DL-n-valine was significantly high (0.1M). The reaction 
rate was independent of the Mn(II) concentration, so 
long as its concentration was within the concentration 
range mentioned above.

The reaction showed first order dependence on amino 
acid and an inverse first order dependence on hydrogen ion 
concentration. The rate was independent of ionic strength 
except for a negative salt effect for DL-iso and normal-
valine.

Oxidation of amino acids with Mn(III) sulphate in 
the presence of high concentration of Mn(II).

In the presence of larger concentration (above 0.1M) of 
Mn(II), the reaction showed a second order dependence on 
Mn(III) with an inhibitory effect of Mn(II).

The reaction showed first order dependence on amino acid 
and an inverse first order on hydrogen ion concentration and 
a negative salt effect.

In view of the above the most probable reaction sequence 
is as follows.

\[
\text{Mn}^{3+} + \text{HA}^+ \xrightarrow{k_1} \text{Mn}^{2+} + \text{H}^+ \quad \text{--- Fast ---} \quad (1)
\]

\[
\text{Mn}^{2+} \xrightarrow{k_2} \text{Mn}^{3+} + \text{A}^+ \quad \text{--- Slow ---} \quad (2)
\]
A' + Mn^{3+} \xrightarrow{k_3} \text{Product} + Mn^{2+} \quad \text{--- fast --- (3)}

(where HA' stands for the protonated amino acid molecule and A' for the free radical).

It is, therefore, expected that when Mn^{2+} concentration is low, the rate determining step is the forward reaction of equation (2). On the other hand, when Mn^{2+} concentration is highly increased the concentration of A' becomes too low making the reaction (3) rate determining step.

Thus at lower concentration of Mn(II) in the reaction mixture, the reaction rate is given as follows.

Reaction rate = k_+ k_2 \frac{[\text{Mn}^{3+}][\text{HA}']}{[H^+]} (A)

where \( k_{\text{obs}} = k_+ k_2 k_1 \frac{[\text{HA}']}{[H^+]} \).

This explains the results on the manganic oxidation of four amino acids studied viz., glycine, DL-α-alanine and DL-iso and normal-valine in presence of low concentration of Mn^{2+}. 
In presence of high concentration of \( \text{Mn}^{2+} \) in the reaction mixture, step (3) becomes rate controlling.

Reaction rate = \( k_3 [A^-] [\text{Mn}^{3+}] \)

Applying steady state to \([A^-]\) and \([\text{Mn} A^{3+}]\) we have,

\[
\text{Reaction rate} = \frac{k_{+1} k_{+2} k_3 [\text{HA}^+] [\text{Mn}^{3+}]^2}{k_{-1} k_{-2} [H^+] [\text{Mn}^{2+}] + k_{-1} k_3 [\text{Mn}^{2+}] [H^+] + k_3 k_{+2} [\text{Mn}^{3+}]} 
\]

The last two terms of the denominator are negligible in comparison to the first, and the above reduces to the following,

\[
\text{Reaction rate} = \frac{k_{+1} k_{+2} k_3 [\text{HA}^+] [\text{Mn}^{3+}]^2}{k_{-1} k_{-2} [H^+] [\text{Mn}^{2+}]} \quad \text{(B)}
\]

Further, as the concentration \( \text{HA}^+ \) and \( \text{Mn}^{2+} \) are very much in excess over that of \( \text{Mn}^{3+} \), the concentration of \( \text{HA}^+ \) and \( \text{Mn}^{2+} \) can thus be assumed to remain constant in a given run. The expression (B), thus simplifies to,

\[
\text{Reaction rate} = k_{\text{obs}} [\text{Mn}^{3+}]^2
\]

where \( k_{\text{obs}} = k_1 k_{+2} k_3 \frac{[\text{HA}^+]}{[H^+] [\text{Mn}^{2+}]} \)

This explains the observations on the oxidation of amino acids in presence of higher concentration of \( \text{Mn}^{(II)} \).
Under both the conditions of investigation viz., low and high concentration of Mn(II) in the reaction mixture, the formation of NH₃, keto acid, aldehyde and the corresponding carboxylic acids have been detected. The mechanism may be schematically written as below.

\[
R\text{-CH} + \text{COOH} + \text{Mn}^{3+} \rightarrow \text{RCH} + \text{C-OH} + \text{H}^+ \quad (1)
\]

\[
\text{RCH} \rightarrow \text{C-OH} \quad \text{Fast} \quad \text{RCHO} \quad \text{Mn}^{3+} \quad \text{CO}_2 \quad \text{RCOOH.}
\]

\[
\text{RCH} \rightarrow \text{C-OH} + \text{Mn}^{2+} \quad (2)
\]

\[
\text{RC} + \text{C} + \text{H}_2\text{O} \rightarrow \text{H-O-C-C-OH} + \text{NH}_3 + \text{Mn}^{2+} + \text{H}^+ \quad \text{Fast}
\]

\[
\text{R} + \text{C} + \text{OH} + \text{Mn}^{3+} \rightarrow \text{H-O-C-C-OH} + \text{NH}_3 + \text{Mn}^{2+} + \text{H}^+ \quad \text{Fast}
\]

\[
\text{R} + \text{C} + \text{OH} + \text{Mn}^{3+} \rightarrow \text{H-O-C-C-OH} + \text{NH}_3 + \text{Mn}^{2+} + \text{H}^+ \quad \text{Fast}
\]

\[
\text{R} + \text{C} + \text{OH} + \text{Mn}^{3+} \rightarrow \text{H-O-C-C-OH} + \text{NH}_3 + \text{Mn}^{2+} + \text{H}^+ \quad \text{Fast}
\]

\[
\text{R} + \text{C} + \text{OH} + \text{Mn}^{3+} \rightarrow \text{H-O-C-C-OH} + \text{NH}_3 + \text{Mn}^{2+} + \text{H}^+ \quad \text{Fast}
\]

\[
\text{R} + \text{C} + \text{OH} + \text{Mn}^{3+} \rightarrow \text{H-O-C-C-OH} + \text{NH}_3 + \text{Mn}^{2+} + \text{H}^+ \quad \text{Fast}
\]

\[
\text{R} + \text{C} + \text{OH} + \text{Mn}^{3+} \rightarrow \text{H-O-C-C-OH} + \text{NH}_3 + \text{Mn}^{2+} + \text{H}^+ \quad \text{Fast}
\]

\[
\text{R} + \text{C} + \text{OH} + \text{Mn}^{3+} \rightarrow \text{H-O-C-C-OH} + \text{NH}_3 + \text{Mn}^{2+} + \text{H}^+ \quad \text{Fast}
\]