RESEARCH PAPER

Kinetics and mechanism of the permanganate-induced autocatalytic dehydration reaction of L-\(\gamma\)-amino-\(n\)-butyric acid to give 2-pyrrolidone through a radical intermediate in moderately concentrated acidic medium

Homayoon Bahrami\(^a\), Moghadas Bigdeli\(^a\), Mehdi D. Davari\(^a\), Mansour Zahedi\(^a\),* and Ali A. Moosavi-Movahedi\(^b\)

\(^a\)Department of Chemistry, Faculty of Sciences, Shahid Beheshti University, G.C., Evin, 19839-6313, Tehran, Iran
\(^b\)Institute of Biochemistry and Biophysics, University of Tehran, Tehran, Iran

*E-mail: m-zahedi@cc.sbu.ac.ir

ABSTRACT

The reaction kinetics and mechanism of the permanganate ion oxidation of L-\(\gamma\)-amino-\(n\)-butyric acid (GABA) in moderately concentrated sulfuric acid medium has been investigated spectrophotometrically.

The product of this reaction is 2-pyrrolidone, which is a 5-membered lactam structure compound (gamma-butyrolactam). Conclusive evidence indicates autocatalytic activity for Mn(II) in this reaction, analogous to that of some \(\alpha\)-amino acids. It has been shown that such activity appears when a certain concentration ratio of Mn(II) to GABA is built up in the medium, termed the \textquotedblleft critical ratio\textquotedblright. The magnitude of this ratio depends on the sulfuric acid concentration. In considering the \textquotedblleft delayed autocatalytic behaviour\textquotedblright of Mn(II) ions, rate equations satisfying our observations for both the catalytic and non-catalytic routes have been presented. The reaction shows a first-order dependence on permanganate ion concentration both in the catalytic and non-catalytic pathways, and an apparent first-order dependence on Mn\(^{2+}\) ions in the catalytic pathway. Also, it was found that the variation in the apparent rate constants of the catalytic and non-catalytic pathways \textit{versus} the GABA concentration follows saturation curves. The correspondence of the pseudo-order rate constants of the...
catalytic and non-catalytic pathways to the Arrhenius and Eyring laws have verified the “critical ratio” as well as the “delayed autocatalytic behaviour” concepts.

The activation parameters associated with both pathways have been computed and discussed. Mechanisms for both catalytic and non-catalytic routes involving radical intermediates, as well as a product having a lactam skeleton, are reported.

**KEYWORDS:** L-γ-amino-n-butyric acid (GABA), permanganate ion, oxidation, kinetics, mechanism, delayed autocatalysis, critical ratio, 2-pyrrolidone, gamma-butyrolactam

### 1. INTRODUCTION

Gamma-aminobutyric acid (GABA) is a non-essential amino acid formed from glutamic acid with the help of vitamin B6. GABA is found in almost every region of the brain, and is formed through the activity of the enzyme glutamic acid decarboxylase (GAD). GAD catalyses the formation of GABA from glutamic acid. GAD requires vitamin B6 (pyridoxal phosphate) as a cofactor, which can be used to regulate the levels of GABA. GABA is the primary inhibitory neurotransmitter in the central nervous system to block the transmission of an impulse from one cell to another. In humans, GABA acts at inhibitory synapses in the brain and spinal cord [1–5].

2-Pyrrolidone is a five-membered lactam. It is a colourless liquid used as a high-boiling non-corrosive polar solvent for a wide variety of industrial applications. It is also an intermediate in the manufacture of polymers such as polyvinylpyrrolidone and polypyrrolidone. The lactam structure has an important role in antibiotics, such as penicillin [6,7].

Several methods reported for the synthesis of 2-pyrrolidone suffer from one or other limitation such as requiring harsh conditions, volatile environment-tally-unfriendly organic solvents, long reaction times and low yields. Accordingly, we have developed a simple approach for producing this important class of pyrrolidones (Scheme 1). The kinetics and mechanism of the oxidation of amino acids in moderately concentrated acid media have been extensively studied [8–24]. In most of these studies, the reaction has been considered as a process that follows perfect second-order kinetics at constant \([H^+]\) and without
any autocatalytic effect. There are two reports of a “double stage” process in which every stage is shown to have kinetics identical to a pseudo-first order reaction [20,24]. In our previous studies [8,9], we have reported the presence of autocatalytic effect in which Mn\(^{2+}\) is the autocatalytic agent while in a recent work, it was shown that such autocatalytic activity features a delay which shows up once a critical ratio of Mn(II) to amino acid is built up, depending on the nature of the amino acid used [10]. Thus the autocatalytic activity of Mn(II) has been observed in the oxidation of L-proline [25] as well as of sarcosine [26].

In the present study, the effect of substitution of the amine at the carbon chain of an \(\alpha\)-amino acid in permanganate oxidation has been investigated, thus we have chosen L-\(\gamma\)-amino-\(n\)-butyric acid (GABA) as substrate.

Besides the importance of the kinetic and mechanistic study of such a process, product analysis revealed that the permanganate oxidation of GABA can be regarded as a novel method for the synthesis of a valuable pyrrolidone skeleton. The advantages of such a synthesis can be stated as having smooth conditions, water as solvent, a high yield and a single-step procedure.

2. EXPERIMENTAL PROCEDURES

Materials

All reagents were from Merck or Fluka. All reagents were of analytical grade and their solutions were prepared by dissolving the requisite amount of samples in tridistilled, deionized and boiled water. All weighing was performed on a Shimadzu AW220 electronic balance (± 0.0001 g). The preparation and analysis of the stock solutions and process for kinetic runs were the same as described earlier [8–10]. Permanganate solutions were prepared and tested by the Vogel method [27].

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Kinetic measurements

The measurements of the kinetic progress of reaction, and the techniques employed were those of references [25,26].

Products analysis

In order to analyze and identify the reaction products, the oxidation of GABA was performed at constant temperature in acidic medium. In the course of reaction, the solution’s colour changed from violet to colourless meaning that Mn\(^{2+}\) ions are produced as the major manganese moiety. Oxygen gas was generated during reaction, as confirmed by a flame test. After completion of the reaction, the products were isolated and identified using IR, \(^1\)H NMR, \(^{13}\)C NMR and MS spectra as well as melting point. The main product (2-pyrrolidone) that was isolated is a monomer of L-\(\gamma\)-amino-\(n\)-butyric acid molecule having a lactam skeleton. It is noteworthy that no CO\(_2\) gas was detected as a product of reaction. Thus we have supplemented the usual synthetic routes to this important class of 2-pyrrolidones with a simple, single-step oxidation process in aqueous medium, giving a high yield, under mild conditions. So, a significant result of this paper is the ability to replace environmentally-unfriendly organic solvents with environmentally friendly H\(_2\)O, to omit organic solvents, and to increase reaction rates and product yields.

Procedure for direct synthesis of product

A solution of GABA (0.515 g, 5 mmol), KMnO\(_4\) (0.078 g, 0.5 mmol), concentrated H\(_2\)SO\(_4\) (98%) (3.16 mol dm\(^{-3}\)), was stirred for 24 hours until the colour of KMnO\(_4\) disappeared. At the end of reaction, the solution was neutralized over a period of 2 h with barium hydroxide. The organic phase was subsequently distilled in vacuo. The sole organic product was confirmed by a single spot on TLC. The residue was extracted with chloroform and crystallized from chloroform and \(n\)-hexane (yield ca. 80%). Analysis of the product gave the following:

2-pyrrolidone. Colourless crystal at \(<25^\circ\)C; m.p. 25\(^\circ\)C; IR(KBr) 3225(N\(=\)H, aliphatic), 1717(C\(=\)O), 1313(CO\(=\)N), 1107(C\(=\)N) cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 2.76(2H, t, CH\(_2\)\(-\)N), 2.08(2H, t, CH\(_2\)\(-\)CO), 1.65(2H, quintet, C\(–\)CH\(_2\)\(-\)C); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 177.50(CON), 138.62(C\(–\)CH\(_2\)\(-\)N), 31.20(C\(–\)CH\(_2\)\(-\)CO), 22.1(C\(–\)CH\(_2\)\(-\)C); MS, \(m/z\), 85(M), 56(M-29), 41(M-44). The \(^{13}\)C NMR spectrum showed 4 types of carbons, while
the MS spectrum verified that the compound mass equals that of the proposed product. As an assurance, it was observed that when the oxidizing agent was absent from the medium, no cyclization occurred, meaning that sulfuric acid alone cannot lead to the product. As another blank test, the reaction was performed with Mn(II) present while KMnO₄ was absent, and as a result no cyclization occurred.

**Reaction stoichiometry**

Reaction mixtures containing various ratios of GABA to MnO₄⁻ were mixed in the presence of 3.16 mol dm⁻³ H₂SO₄ and then equilibrated for 24 hours at room temperature. Estimation of the unreacted MnO₄⁻ showed that 1 mole of MnO₄⁻ consumed 5 moles of the amino acid [22]. In view of these results, and taking into account that the final product of reduction of permanganate in acid medium and in a large excess of reducing species is the Mn²⁺ ion [11,13,21,28], the following equation was deduced:

$$\text{2MnO}_4^- + 10\text{NH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COO}^- + 6\text{H}^+ \rightarrow \text{HN} + 13\text{H}_2\text{O} + 2\text{Mn}^{2+} + \frac{5}{2}\text{O}_2$$ (1)

**Acrylonitrile addition**

The reaction mixture was mixed with acrylonitrile monomer and kept for 2 hours in an inert atmosphere. The presence of free radicals as intermediates was confirmed by the observed polymerization, both in the presence and in absence of manganese sulfate(II). Blank experiments of either MnO₄⁻, or GABA alone, with acrylonitrile, did not induce polymerization under the same conditions as those induced with reaction mixtures. Initially-added acrylonitrile decreases the rate, indicating the intervention of free radicals, as was the case in earlier work [8 – 24].

3. RESULTS AND DISCUSSION

**Rate equation**

As mentioned above, measurements of the course of reaction, and the data analysis, are similar to those reported elsewhere [25,26] and Mn(VII) was the sole species giving its absorption profile during reaction.
Therefore it is concluded that under our present conditions, Mn(IV) and Mn(III) ions are neither yielded via direct the permanganate – Mn(II) reaction, nor are they stable even if generated by the amino acid-permanganate reaction.

In Figure 1 a typical plot of permanganate concentration versus time is shown. Since Figure 1 does not appear to be a perfect sigmoidal profile, it might be concluded that an autocatalysis reaction has not occurred. However, the rate-time plot of Figure 2, shows a bell-shaped curve which becomes evident after 35% of the reaction. Such an observation is clear evidence of delayed autocatalytic behaviour for this reaction, as has been reported elsewhere [10].

Figure 3 illustrates the rate of change of permanganate concentration versus time curves in order of increasing initial concentration of Mn(II), from which it is obvious that the reaction half life is decreased by adding increasing amounts of Mn$^{2+}$. In addition, the increasing rate component (bell-shaped) of these curves is gradually annihilated when the Mn$^{2+}$ is increased to 0.0008 M. From these observations it could be concluded that Mn$^{2+}$ is the autocatalytic agent. As has been reported before [10], and is clear from Figures 2 and 3, for Mn$^{2+}$ to show such a “delayed autocatalytic characteristic” it should reach a certain concentration, which we call the “critical concentration”. It should be noted that some experiments were carried out when the following reactants, KMnO$_4$, Mn(II), and H$_2$SO$_4$ were present while the GABA was absent. The result
Figure 2 Reaction rate versus time plot. \([\text{KMnO}_4] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}\), \([\text{H}_2\text{SO}_4] = 3.16 \text{ mol dm}^{-3}\), \([\text{GABA}] = 0.5 \text{ mol dm}^{-3}\), \(T = 313 \text{ K}\).

Figure 3 Effect of added initial concentration of \(\text{Mn}^{2+}\) ions on reaction rate-time plots.* Time values divided by 3 for clarifying delayed autocatalysis. \([\text{GABA}] = 0.5 \text{ mol dm}^{-3}\), \([\text{KMnO}_4] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}\), \([\text{H}_2\text{SO}_4] = 3.16 \text{ mol dm}^{-3}\), \(T = 308 \text{ K}\).
was that the rate of consumption of permanganate was much slower than when GABA was present. This observation confirms that permanganate consumption stems from the oxidation of GABA rather than the direct reaction of permanganate with Mn(II), which is known to be very slow. Thus regarding the product analysis section, the generation of 2-pyrrolidone can only be understood in terms of the direct reaction between GABA and permanganate which is catalysed by Mn(II) ions, as shown above.

From the above discussion, the following rate equation is proposed for the oxidation of GABA until the autocatalytic behaviour of Mn$^{2+}$ emerges:

$$-\frac{d[MnO_4^-]}{dt} = k_1'[MnO_4^-]$$

(2)

As reaction proceeds, the following equation for GABA oxidation becomes significant:

$$-\frac{d[MnO_4^-]}{dt} = k_1'[MnO_4^-] + k_2'[MnO_4^-][Mn^{2+}]$$

(3)

where $k_1'$ and $k_2'$ are pseudo-order rate constants for the non-catalytic and catalytic processes, respectively. The GABA concentration, which is always kept in large excess, and the constant sulfuric acid concentration in each experiment, are included in these pseudo-order rate constants. The integrated forms of these equations give, respectively:

$$\ln\frac{a}{(a-x)} = k_1't$$

(4)

$$\ln\frac{k_1'/k_2' + x}{a-x} = (k_1' + k_2'a)t - \ln\frac{k_2'a}{k_1'}$$

(5)

where $a$ represents the initial concentration of permanganate and $x$ is the amount of permanganate ion consumed to time $t$.

Initial estimation of $k_1'$ for GABA was made by fitting the early portion of the rate data to a first-order rate equation. This is because there is no catalytic effect in the early stages of the reaction. Having obtained preliminary values of $k_1'$ and $k_2'$, Equation 5 was used for the determination of the kinetic data for the region of reaction rate increase by utilising iterative methods [8–10,25–26,29] and such data are summarized in Table 1. Figure 4 demonstrates the typical results of the fitting process of rate data for GABA at various temperatures and under the conditions...
same conditions. Almost perfect fits to the data in Figure 4 (R² values of 0.9991 – 0.9993) not only corroborate the validity of the applied kinetic method, but also confirm the autocatalytic effect of the Mn²⁺ species and points to such delayed activity at certain critical concentrations of Mn²⁺. Note that estimated errors for $k_{1}'$ and $k_{2}'$ are 1 – 2% and 0.5 – 1% throughout all experiments, respectively.

**Dependence of reaction rate on GABA**

The rate constant values are summarized in Table 2 for variation in L-γ-amino-n-butyric acid concentration. From Table 2, it is clear that the onset of autocatalytic activity is further delayed if the GABA concentration is increased. It can therefore be concluded that the initiation of autocatalytic activity not only depends on the
Mn\(^{2+}\) concentration but also on that of GABA. Thus, the delayed autocatalytic effect can only occur at a certain concentration ratio of Mn\(^{2+}\) to GABA, namely the “critical ratio”.

The pseudo-order rate constants obtained at various GABA concentrations are given pictorially in Figure 5. Also, it was found that the variation of the apparent rate constants of catalytic and non-catalytic pathways against the GABA concentration shows the saturation curves.

### Table 2

<table>
<thead>
<tr>
<th>[GABA] (mol dm(^{-3}))</th>
<th>(k_1^{a})</th>
<th>(k_2^{b})</th>
<th>Extent of reaction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>3.91</td>
<td>124.8</td>
<td>35%</td>
</tr>
<tr>
<td>0.4</td>
<td>55.85</td>
<td>151.7</td>
<td>43%</td>
</tr>
<tr>
<td>0.5</td>
<td>6.34</td>
<td>166.4</td>
<td>44%</td>
</tr>
<tr>
<td>0.6</td>
<td>8.93</td>
<td>191.7</td>
<td>49%</td>
</tr>
<tr>
<td>0.7</td>
<td>8.63</td>
<td>192.5</td>
<td>51%</td>
</tr>
</tbody>
</table>

![Figure 5](https://www.prkm.co.uk)

**Figure 5** Effect of GABA concentration on reaction rate-time plots. [KMnO\(_4\)] = 4.0 \times 10^{-4} mol dm\(^{-3}\), [H\(_2\)SO\(_4\)] = 3.16 mol dm\(^{-3}\), T = 318 K, \(k_1^{a} = 10^5 (s^{-1})\), \(k_2^{b} (dm^3 mol^{-1} s^{-1})\).
Dependence of reaction rate on sulfuric acid concentration

The effect of \([H^+]\) was investigated by varying the sulfuric acid concentrations. The data of Table 3 indicate that as the acid concentration is increased, delay in the onset of autocatalytic behaviour is increased. At high concentrations of acid (about 6 mol dm\(^{-3}\)), the autocatalytic effect is suppressed. Figure 6 depicts changes in \(k_1^0\) and \(k_2^0\) versus sulfuric acid concentration. As this figure indicates, \(k_1^0\) increases when the acid concentration is raised. The region 3.16 – 4.27 mol dm\(^{-3}\) of sulfuric acid shows the least variation for \(k_1^0\). Thus, this concentration region was determined to be the most appropriate for the rest of our kinetic studies. In addition, it is apparent from the same figure that \(k_2^0\) decreases with

<table>
<thead>
<tr>
<th>[H(_2)SO(_4)] (mol dm(^{-3}))</th>
<th>(k_1^0)</th>
<th>(k_2^0)</th>
<th>Extent of reaction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.16</td>
<td>3.40</td>
<td>91.14</td>
<td>49%</td>
</tr>
<tr>
<td>4.27</td>
<td>9.23</td>
<td>150.4</td>
<td>54%</td>
</tr>
<tr>
<td>5.33</td>
<td>17.47</td>
<td>192.2</td>
<td>64%</td>
</tr>
<tr>
<td>6.40</td>
<td>79.50</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>7.47</td>
<td>357.2</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Figure 6  Effect of sulfuric acid concentration on catalysed and uncatalysed pseudo-order rate constants. \([\text{KMnO}_4]=4.0 \times 10^{-4} \text{ mol dm}^{-3}\), \([\text{GABA}]=0.5 \text{ mol dm}^{-3}\), \(T=308 \text{ K}\); \(k_1^0 = k_1^0 \times 10^5 \text{ (s}^{-1}\)), \(k_2^0 = k_2^0 \times 100 \text{ (dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\)).
increasing sulfuric acid concentration. Overall, it can be stated that the autocatalytic behaviour of Mn\(^{2+}\) in the oxidation process also depends on the sulfuric acid concentration.

**Activation parameters**

The pseudo-order rate constants \(k_1'\) and \(k_2'\) were determined at various temperatures employing Equation 5 and under similar conditions with respect to GABA, sulfuric acid and permanganate concentrations, and are summarized in Table 1. Figures 7 and 8 demonstrate the adherence of both \(k_1'\) and \(k_2'\) with the Arrhenius equation, showing linear relations with \(R^2\) coefficients ranging from 0.9991 to 0.9993. Such an observation justifies the method applied in our kinetic study of GABA oxidation. The activation parameters (energy, enthalpy, and entropy) have been obtained and are reported in Table 4. These reveal that although the catalytic pathway requires a higher activation energy, owing to the less negative activation entropy, the reaction rate for this pathway is greater (see value for \(\Delta G^\circ\)).

![Figure 7](image-url)  
**Figure 7** Arrhenius plots for catalysed and uncatalysed processes. 
\([\text{KMnO}_4] = 4.0 \times 10^{-4}\) mol dm\(^{-3}\), \([\text{H}_2\text{SO}_4] = 3.16\) mol dm\(^{-3}\), \([\text{GABA}] = 0.5\) mol dm\(^{-3}\).
Reaction mechanism

The experimental results indicate two separate mechanisms for the catalysed and uncatalysed pathways. Since the existence of intermediate free radicals was confirmed, their involvement in the reaction mechanism has also been incorporated.

Reaction mechanism for the uncatalysed process

All the experiments were performed in moderately concentrated sulfuric acid media and are considered as acid-catalysed reactions. Therefore, it is possible that $H^+$ is consumed and later generated in various steps. With the evidence pointing to no involvement of other manganese ions except Mn(VII) in the GABA as reaction media.

**Table 4** Activation parameters for GABA oxidation by $\text{MnO}_4^-$ $[\text{KMnO}_4] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 3.16 \text{ M}$, $[\text{GABA}] = 0.5 \text{ mol dm}^{-3}$, $T = 298 – 318 \text{ K}$

<table>
<thead>
<tr>
<th>Reaction routes</th>
<th>$E_a$</th>
<th>$\Delta H^{#}$</th>
<th>$\Delta S^{#}$</th>
<th>$\Delta G^{#}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(kJ mol$^{-1}$)</td>
<td>(kJ mol$^{-1}$)</td>
<td>(J mol$^{-1}$ K$^{-1}$)</td>
<td>(kJ mol$^{-1}$)</td>
</tr>
<tr>
<td>Catalysed processes</td>
<td>50 ($\pm 0.7$)</td>
<td>47 ($\pm 0.7$)</td>
<td>$-92$ ($\pm 2$)</td>
<td>76 ($0.7$)</td>
</tr>
<tr>
<td>Uncatalysed processes</td>
<td>48 ($\pm 2$)</td>
<td>45 ($\pm 2$)</td>
<td>$-183$ ($\pm 8$)</td>
<td>102 ($2$)</td>
</tr>
</tbody>
</table>

Values in parenthesis are estimated errors on each parameter.
oxidation process, MnO$_4^-$ is the most probable reactive species. The increase in reaction rate with acidity suggests the formation of a more powerful oxidant, namely permanganic acid, by the following equilibrium:

$$\text{MnO}_4^- + H^+ \rightleftharpoons \text{HMnO}_4$$ (6)

At the high acid concentration used, protonation of the zwitterionic form of GABA gives:

$$\text{NH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COO}^+ + H^+ \rightleftharpoons \text{NH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$$ (7)

A mechanism consistent with the observed kinetic data includes the following steps. In agreement with the experimental results, the formation of an addition complex between permanganic acid and the cationic form of GABA is proposed [21,22,29].

$$\text{HMnO}_4 + \text{NH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH} \rightleftharpoons \frac{k_3}{k_4} \text{X}_1^+$$ (8)

This complex may break down according to the following equation:

$$\text{X}_1^+ \rightleftharpoons \frac{k_4}{k_3} \text{NH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COO}^- + \text{HMnO}_4^- + H^+$$ (9)

Based on the involvement of radicals in the reaction mechanism, a dimer species is formed in the following steps:

$$\text{NH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COO}^- \xrightarrow{\text{fast}} \text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COO}^- + H^+$$ (10)

$$2 \text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COO}^- \xrightarrow{\text{fast}} \text{N}\ddot{\text{H}}\text{H}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \dddot{\text{C}} - \text{O} - \text{O} - \dddot{\text{C}} - \text{CH}_2 - \text{CH}_2\text{CH}_2 - \text{N}\ddot{\text{H}}$$ (11)

Due to an internal rearrangement of the aforementioned dimer, two molecule of 2-pyrrolidone and one molecule of peroxide are produced.
Hydrogen peroxide decomposition proceeds as follows:

$$\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \frac{1}{2} \text{O}_2$$  \hspace{1cm} (15)

Knowing that the species Mn(VI) is very unstable in strongly acidic media, it will be converted into Mn(II) and Mn(VII) by means of a rapid disproportionation.

$$5\text{HMnO}_4^- + 3\text{H}^+ \rightarrow 4\text{MnO}_4^- + \text{Mn}^{2+} + 4\text{H}_2\text{O}$$  \hspace{1cm} (16)

Multiplying Eqns (6), (7), (8), (9), and (10) by a factor of 10 and Eqns (11), (12), (13), (14), and (15) by a factor of five and Eqn (16) by a factor of two, and then summing them with each other results in the overall reaction with the stiochiometry satisfied. In agreement with the above scheme, assuming a steady state approximation for $X_1^+$, the rate equation obtained for the uncatalysed process is
\[
-\frac{d[Mn(VII)]}{dt} = k_1'[MnO_4^-] 
\]

\[
k_1' = \frac{\alpha_0[GABA][H^+]^2}{\beta_0(1 + \beta_1[H^+] + \beta_2[H^+]^2) + \alpha_1[H^+]^2[Mn(VII)]} 
\]

\[
\alpha_0 = K_1K_2k_3k_4 \\
\alpha_1 = K_1K_2k_3 \\
\beta_0 = k_{-3} + k_4 \\
\beta_1 = K_1 + K_2 \\
\beta_2 = K_1K_2 
\]

where [GABA]_t represents the total concentration of GABA and [Mn(VII)] represents the total concentration of permanganate.

The rate law obtained above corresponds to that mechanism explaining the observed experimental behaviour: namely (i) the first-order reaction with respect to permanganate concentration and (ii) the variation of the apparent rate constants of the non-catalytic pathways against GABA to give a saturation curve.

**Reaction mechanism for the catalysed process**

Addition of Mn\(^{2+}\) ions leads to an increase in the reaction rate, while the evidence presented also suggests that an adduct might be formed between Mn\(^{2+}\) and the protonated GABA:

\[
\text{NH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH} + \text{Mn}^{2+} \overset{k_5}{\longrightarrow} \text{X}_2^{3+} 
\]

As the rate-determining step, the slow attack of permanganic acid on the above complex is proposed [25,26].

\[
\text{X}_2^{3+} + \text{HMnO}_4^- \overset{k_6}{\longrightarrow} \text{H}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COO}^- + \text{HMnO}_4^- + \text{Mn}^{2+} + \text{H}^+ 
\]

The remaining steps, leading to the final products, resemble those presented for the uncatalysed pathway above. Again, multiplying Eqns (6), (7), (19), (20), and (10), by a factor of 10 and Eqns (11), (12), (13), (14), and (15) by a factor of five and Eqn (16) by a factor of two, and then summing them up with each other results in the overall equation with the correct stoichiometry.

Assuming a steady-state approximation for the X\(_2^{3+}\) complex in the above mechanism, the following rate equation [00] is derived:

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\[
-k \frac{d[Mn(VII)]}{dt} = k_1 [MnO_4^-] + k_2 [MnO_4^-][Mn^{2+}]
\]

This rate law is in accord with all experimental results; namely, the first-order dependence on $Mn^{2+}$ ions and the permanganate ion concentrations. Also, the above equation explains the variation of the apparent rate constants of the catalytic pathway against $[\text{GABA}]$ to give the saturation curve.

4. CONCLUSIONS

In order to study the influence of permanganate ion on the oxidation of GABA, the kinetics of this reaction in moderately concentrated sulfuric acid medium was investigated spectrophotometrically. It is well known that the oxidation of primary $\alpha$-amino acids with KMnO$_4$ in water produce simple aldehydes. Here, by using GABA under the same conditions, an interesting product, namely 2-pyrrolidone, was formed. The well-known and important gamma-butyrolactam were thus obtained in a single-step preparation and was completely characterized by IR, mass, $^1H$ NMR, $^{13}C$ NMR spectral analyses, as well as its melting point.

Other major goals of this paper were to replace the environmentally-unfriendly organic solvents with environmentally-friendly $H_2O$, i.e. to omit organic solvents, and to increase reaction rates and product yields. By investigating rate-time curves it is concluded that when a particular portion of the reaction time for GABA oxidation has passed, a parallel reaction is encountered similar to that of primary $\alpha$-amino acids studied in our previous works. The results show that this process can be considered as a delayed autocatalytic reaction. By increasing the concentration of Mn(II), which accelerates the reaction, and also by

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fitting the kinetic data into appropriate kinetics equations, it is demonstrated that
this species is the autocatalytic agent. It has been shown that the initiation of
autocatalytic activity not only depends on the Mn$^{2+}$ concentration but also on
that of GABA. Thus, delayed autocatalytic effect can only occur at a certain ratio
of concentrations of Mn$^{2+}$ to GABA, namely the “critical ratio”. Moreover, the
delayed autocatalytic phenomenon vanishes at concentrations of sulfuric acid
greater than 6 M, i.e. the amount of sulfuric acid in the medium plays a critical
role.

The pseudo-order rate constants obtained for both the catalytic and non-
catalytic pathways, when GABA was in excess, obeyed the Arrhenius and Eyring
relations. The activation parameters associated with the pseudo-rate constants $k_1'$
and $k_2'$ were computed and discussed. It is clear that the results obtained in the
present work accommodate the presence of radical intermediates as well as the
formation and decomposition of permanganate-GABA and Mn$^{2+}$-GABA
complexes in these reactions.

Based on above facts, plausible mechanisms for the catalytic and non-
catalytic pathways involving the formation of a dimer between two GABA
molecules have been proposed and discussed. The rate laws derived are in
excellent agreement with the experimental results.

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6. REFERENCES

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