Kinetics and Mechanism of the Oxidation of L-α-Amino*n*-Butyric Acid by Permanganate in Acid Medium

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ABSTRACT

The kinetic study of the oxidation of L- α -amino- π -butyric acid by permanganate ions has been carried out in buffered acid medium at pH = 1–3, using a spectrophotometric technique. An auto-catalytic effect has been observed in all cases due to Mn²⁺ ions formed as a product of the reaction. A first-order reaction with respect to the amino acid and the permanganate ions in both processes, catalyzed and uncatalyzed was obtained. The influence of several factors (pH, temperature, ionic strength, and reactants concentration) on the rate constants has also been investigated. In this article we propose a reaction mechanism in accordance with the experimental results obtained. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The study of the oxidation of amino acids has received considerable attention in previous literature due to the importance of the degradation of these compounds in biological systems. Many kinetic chemical studies have been reported on the oxidation of amino acids using different oxidants [1-14]. The kinetic study of amino acids and permanganate systems has been the subject of many articles, especially during the last ten years. The acid medium has been the determining factor of the kinetic behavior for permanganate oxidation and their final products. The permanganate oxidation of these compounds has been widely studied in strong acid medium [15–25], where no noticeable auto-catalytic effects were found. However, in neutral medium or weakly alkaline, the literature consulted agrees as to the appearance of the cited auto-catalytic effect [26–33]. The purpose of this article is to analyze the permanganic oxidation of L- α -amino-*n*-butyric acid (L-abu) in weak acid medium (1 < pH < 3), as no references to such process has been found.

EXPERIMENTAL

All the reactants used were p. a. Merck or Sigma. The solutions were prepared in buffered medium with phosphoric acid and potassium dihydrogenphosphate with tridistilled water deionized and boiled. In each

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case the phosphoric acid and potassium dihydrogenphosphate concentrations were those necessary for fixing the pH and ionic strength required. The permanganate solutions were prepared and tested by the Vogel method [34]. The pH of the solutions was measured with a pH-meter Crison micro pH 2002.

KINETIC MEASUREMENTS

The kinetic progress of the reaction was followed by measuring the absorbance of the permanganate ions at 525 nm. A Perkin-Elmer Mod. 552 spectrophotometer, supplied with a conventional thermostatic bath (\pm 0.1 K), was used. For the absorption molar coefficient, a value of 2300 dm³ mol⁻¹ cm⁻¹ was obtained.

RESULTS

Stoichiometry

The following reaction products were detected by spot tests [35,36]: carbon dioxide, ammonium ions, and the corresponding aldehyde. On the other hand, it is well known [18,25,37] that in the reduction of permanganate ions in acid medium and in excess of reducing species, the Mn^{2+} ion is the final product.

Our experiments were performed in an excess of aminoacid. Under these conditions, a previous study of the stoichiometry of the reaction by conventional methods, identifying the reaction products [36], allowed us to deduce the following equation:

$$2MnO_4^- + 5CH_3CH_2CH(N^+H_3)COO^- + 11H^+ \longrightarrow 5CH_3CH_2CHO + 5NH_4^+ + 5CO_2 + 2Mn^{2+} + 3H_2O \quad (1)$$

Rate Equation

In all the experiments carried out, curves with a sigmoid profile for the absorption-time plots have been obtained. This characteristic suggests the existence of an autocatalytic mechanism and supports the rate law:

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

where k'_1 and k'_2 are rate pseudo-constants. This equation has been integrated obtaining the expression:

$$\ln \frac{k_1'/k_2' + x}{a - x} = (k_1' + k_2' a) t - \ln \frac{a}{k_1'/k_2'}$$
(3)

which means that there should be a linear dependence between $\ln[k'_1/k'_2 + x)/(a - x)]$ and the reaction time. In this equation "a" represents the initial concentration of permanganate and "x" is the amount of MnO_4^- which has reacted up to time "t."

For the simultaneous calculation of pseudo-constants k'_1 and k'_2 an iterative method has been used, which is described in a precedent work [38]. This method has been previously applied successfully in other auto-catalytic reactions [26–28]. Figure 1 is an



Figure 1 Representative plots of the rate law. [L-abu] = 0.10 mol dm⁻³; I = 0.20 mol dm⁻³; pH = 2.16; and T = 318 K. [KMnO₄]: (**I**) 5.0×10^{-4} mol dm⁻³; (+) 7.0×10^{-4} mol dm⁻³; and (*) 9.0×10^{-4} mol dm⁻³.



Figure 2 Effect of the amino acid concentration on the rate pseudo-constants. $[MnO_4^{-1}] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$; I = 0.20 mol dm⁻³; pH = 2.16; T = 318 K; (III) k_1' ; and $(+) k_2'$.

example representing the rate law after convergence. This linear behavior is in good agreement with the proposed rate equation.

Dependence of the Kinetic Parameters

The determination of the rate pseudo-constants for experiments carried out in different concentrations of amino acid shows first-order in such species, for both catalyzed and uncatalyzed pathways (Fig. 2).

The variation of the initial concentration of permanganate shows a negative effect on the values of both k'_1 and k'_2 (Table I).

Likewise, in order to analyze the effect of the ionic strength of the medium on the pseudo-constants, plots of Brönsted-Bjerrum's equation have been carried out (Fig. 3). It can be noticed that both plots are straight lines with negative slopes. The effect of pH has been investigated by means of a series of experi-

Table I Rate Pseudo-Constants at Several Permanganate Concentrations [L-abu] = 0.10 mol dm⁻³; I = 0.20 mol dm⁻³; pH = 2.16; and T = 318K

[MnO ₄ ⁻] ^a	k' ^b	k' ^c
5.0	5.03	10.48
6.0	4.77	9.22
7.0	4.50	6.90
8.0	4.32	6.04
9.0	4.22	5.07

⁴ Concentration in mol dm⁻³ \times 10⁴.

^h Rate constants in $s^{-1} \times 10^5$.

^c Rate constants in dm³ mol⁻¹ s⁻¹.

ments carried out for different values of pH. Figure 4 shows that the profiles of both pseudo-constants reach a maximum close to pH = 2.

It has been verified that both k'_1 and k'_2 obey the Arrhenius equation, which corroborates the validity of the iterative method used. The thermodynamic activation parameters obtained, energy, enthalpy, and entropy, are shown in Table II.

In order to demonstrate that the Mn^{2+} is the responsible agent in the autocatalytic process and to show the validity of the kinetic calculation employed, kinetic runs were performed in presence of the Mn^{2+} species at the beginning of the reaction. As the initial concentration of Mn^{2+} ions increased, a tendency of the sigmoid form of the absorbance-time plot to disappear was observed. Simultaneously, a notable increase in the reaction rate was seen (Fig. 5).

When the initial concentration of the Mn^{2+} is sufficiently low, k'_1 and k'_2 can be calculated simultaneously, whereas for high initial concentrations of the mentioned species, the contribution of the uncatalyzed process is negligible with respect to the catalyzed one. Therefore in these conditions, only this last process will be considered. The constancy obtained in the values of k'_1 and k'_2 , corroborates the validity of the applied kinetic method.

DISCUSSION

In agreement with the experimental behavior and taking into account the bibliographic references, two mechanisms are proposed to interpret the reaction pathways, catalyzed and uncatalyzed, separately.



Figure 3 Effect of the ionic strength on the rate pseudo-constants. [L-abu] = 0.10 mol dm⁻³; [MnO₄⁻] = 5.0×10^{-4} mol dm⁻³; pH = 2.16; T = 318 K; (\blacksquare) log k'_1 ; and (+) log k'_2 .

Reaction Mechanism of the Uncatalyzed Process

All the experiments were carried out in acid medium. Therefore, we can take the following equilibrium into account.

$$MnO_4^- + H^+ \stackrel{K_1}{\longrightarrow} HMnO_4$$
 (4)

Bailey and Carrington [39] have determined the equilibrium constant $K_1 = 2.99 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1}$. As

we have worked on an interval of
$$1 < pH < 3$$
, the permanganic acid concentration is negligible with respect to the permanganate ions concentration.

On the other hand, it is well-known that in aqueous solutions the following equilibria between the cationic, zwitterionic, and anionic forms of L-aminobutyric acid take place:

$$CH_{3}CH_{2}CH(NH_{2})COO^{-} + H^{+} \underbrace{\overset{K_{2}}{\longleftarrow}}_{CH_{3}CH_{2}CH(N^{+}H_{3})COO^{-}} (5)$$



Figure 4 Effect of the pH on the rate pseudo-constants. $[MnO_4^{-1}] = 5.0 \times 10^{-4} \text{ mol } dm^{-3};$ [L-abu] = 0.10 mol dm⁻³; I = 0.20 mol dm⁻³; pH = 2.16; T = 318 K; (\blacksquare) k'_1 ; and (+) k'_2 .

Table II Activation Parameters $[KMnO_4] = 5.0 \times 10^{-4}$ mol dm⁻³; |L-abu| = 0.10 mol dm⁻³; I = 0.20 mol dm⁻³; pH = 2.16; and T = 313-333 K

	$\Delta S^{\#a}$	$\Delta H^{\#b}$	Eac
Uncatalyzed process	-210.0	37.4	40.1
Catalyzed process	-18.6	66.3	69.1

^a Entropy of activation in J mol⁻¹ K⁻¹.

^h Enthalpy of activation in kJ mol⁻¹.

* Energy of activation in kJ mol⁻¹.

$$CH_{3}CH_{2}CH(N^{+}H_{3})COO^{-} + H^{+} \xleftarrow{K_{3}} CH_{3}CH_{2}CH(N^{+}H_{3})COOH \quad (6)$$

Provided that $pK_2 = 9.66$ and $pK_3 = 2.30$ [40] we can conclude that, in the pH range used (1 < pH < 3), the anionic species concentration is negligible as opposed to the zwitterion concentration, so that, cationic species and zwitterionic species co-exist in the reactive medium. None of them should be rejected when considering our rate equation.

Hence, it can be supported that the observed reaction is due to the oxidation of the zwitterionic and cationic forms by permanganate ion.

Likewise, the formation of an addition complex between the permanganate ion and the zwitterion is proposed.

$$MnO_4^{-} + CH_3CH_2CH(N^+H_3)COO^{-} \xleftarrow{k_4}{k_{-4}} X_1^{-}$$
(7)

In the same way, the formation of another addition complex between the permanganate ion and the cationic form of the amino acid is admitted.

$$MnO_4 - + CH_3CH_2CH(N^+H_3)COOH \xrightarrow{k_5} X_2 \quad (8)$$

Similar complexes have been proposed by other authors [15,16] about amino acid oxidation processes.

We can also admit the inter-conversion between both complexes by means of the corresponding protonation and deprotonation step.

$$X_1^{-} + H^+ \stackrel{k_6}{\underset{k_{-6}}{\longrightarrow}} X_2$$
 (9)

These complexes could experiment an irreversible rupture.

$$X_{1}^{-} \xrightarrow{k_{7}} CH_{3}CH_{2}CH = N^{+}H_{2} + CO_{2} + HMnO_{4}^{2-} (10)$$

$$X_{2} \xrightarrow{k_{8}} CH_{3}CH_{2}CH = N^{+}H_{2} + CO_{2} + HMnO_{4}^{2-} + H^{+} (11)$$

Given that the species Mn(V) is very unstable in acid medium, it is converted into Mn(II) and Mn(VII) by means of a rapid step.

$$5 \text{ HMnO}_{4}^{2-} + 11 \text{ H}^{+} \xrightarrow{\text{fast}} 3\text{MnO}_{4}^{-} + 2 \text{ Mn}^{2} + 8 \text{ H}_{2}\text{O} \quad (12)$$



Figure 5 Effect of the added initial of Mn^{2+} ions on the absorbance time plots. [KMnO₄] = 5.0 $\times 10^{-4}$ mol dm⁻³; [L-abu] = 0.10 mol dm⁻³; I = 0.20 mol dm⁻³; pH = 2.16; T = 318 K; [Mn²⁺]: (III) 0.0 mol dm⁻³; (+) 5.0 $\times 10^{-5}$ mol dm⁻³; and (*) 1.25 $\times 10^{-4}$ mol dm⁻³.

Finally, by hydrolysis of the iminic cation, the correspondent aldehyde is obtained [20,21,24,26,27].

$$CH_{3}CH_{2}CH = N^{+}H_{2} + H_{2}O \xrightarrow{fast} CH_{3}CH_{2}CHO + NH_{4}^{+}$$
(13)

In agreement with this mechanism, and admitting the steady-state approximation for the X_1^- and X_2 species, the rate equation obtained for the uncatalyzed process is:

$$v = -\frac{d[Mn(VII)]}{dt} = [MnO_4^{-}][L - abu]_T$$

$$\frac{\alpha_0 + \alpha_1[H^+] + \alpha_2[H^+]^2}{\beta_0 + \beta_1[H^+] + \beta_2[H^+]^2} \quad (14)$$

$$+ [MnO_4^{-}]\{\tau_0 + \tau_1[H^+] + \tau_2[H^+]^2\}$$

where $[L-abu]_{T}$ represents the total concentration of amino acid, [Mn(VII)] the total concentration of Mn(VII) and where:

$$\begin{aligned} \alpha_0 &= (k_{-5} + k_{-8} + k_{-6}) k_4 k_7 \\ \alpha_1 &= K_3 k_5 k_{-6} k_7 + K_3 k_5 k_8 (k_{-4} + k_7) + k_4 k_6 k_8 \\ \alpha_2 &= K_3 k_5 k_6 k_8 \\ \beta_0 &= (k_{-4} + k_7) (k_5 + k_6 + k_8) \\ \beta_1 &= K_3 (k_{-4} + k_7) (k_5 + k_8) + k_6 (k_5 + k_8) \\ &+ K_3 k_6 (k_{-4} + k_7) \\ \beta_2 &= K_3 k_6 (k_5 + k_8) \\ \tau_0 &= k_{-4} (k_5 + k_{-6} + k_8) \\ \tau_1 &= K_3 k_5 k_{-6} + K_3 k_5 (k_{-4} + k_7) + k_4 k_6 \\ \tau_2 &= K_3 k_5 k_6 \end{aligned}$$

The rate law corresponding to that mechanism explains the experimental behavior observed: the firstorder reaction with respect to amino acid and permanganate ions; the decreasing in k'_1 values when the permanganate concentration increases (Table I) and a qualitative interpretation for the k'_1 vs. pH plot observed (Fig. 4).

Reaction Mechanism of the Catalyzed Process

To interpret the catalyzed pathway of oxidation, a possible reaction mechanism is proposed. In such mechanism, the formation of addition complexes between the Mn^{2+} ions and the zwitterionic and cationic forms are postulated [26–28].

$$CH_{3}CH_{2}CH(N^{+}H_{3})COO^{-} + Mn^{2+} \underbrace{\underset{k_{-9}}{\longleftarrow}}_{k_{-9}} X_{3}^{2+}$$
(15)

CH₃CH₂CH(N⁺H₃)COOH + Mn²⁺
$$\frac{k_{10}}{k_{-10}} X_4^{3+}$$
 (16)

As rate-determining steps, the attack of the permanganate ion on the complexes formed [26-28] is accepted.

$$MnO_{4}^{-} + X_{3}^{2+} \xrightarrow{k_{12}} CH_{3}CH_{2}CH = N^{+}H_{2} + CO_{2} + HMnO_{4}^{2-} + Mn^{2+}$$
(17)
$$MnO_{4}^{-} + X_{4}^{3+} \xrightarrow{k_{13}} CH_{3}CH_{2}CH = N^{+}H_{2} + CO_{2} + HMnO_{4}^{2-} + Mn^{2+} + H^{+}$$
(18)

Like in the uncatalyzed process, the dismutation of Mn(V) into Mn(VII) and Mn(II) [eq. (12)] and the hydrolysis of iminic cation [eq. (13)], give rise to the products.

If the steady-state approximation for the X_3^{2+} and X_4^{3+} species is admitted, the mechanism proposed leads to the following rate equation:

$$v = -\frac{d[Mn(VII)]}{dt}$$

$$= \frac{[MnO_4^+][Mn^{2+}][L - Abu]_T \{\delta_0 + \delta_1[H^+]\}}{\{MnO_4^-](\epsilon_0 + \epsilon_1[H^+]) + \eta_0 + \eta_1[H^+]\}}$$

$$= \frac{\{[MnO_4^-](\epsilon_0 + \epsilon_1[H^+]) + \eta_0 + \eta_1[H^+]\}}{\{\alpha_0 + \alpha_1[H^+] + \alpha_2[H^+]^2 + [MnO_4^-](\beta_0 + \beta_1[H^+] + \beta_2[H^+]^2)\} \{\theta_0 + \theta_1[MnO_4^-] + \theta_2[MnO_4^-]^2\}} (19)$$

where the adopted notation of eq. (14) is conserved and in addition:

$$\delta_{0} = (k_{-5} + k_{8} + k_{-6}) (k_{-4} + k_{7})$$

$$\delta_{1} = k_{6}(k_{-5} + k_{8})$$

$$\varepsilon_{0} = k_{9}k_{12}k_{13}$$

$$\varepsilon_{1} = K_{3}k_{10}k_{12}k_{13}$$

$$\eta_{0} = k_{9}k_{-10}k_{12}$$

$$\eta_{1} = K_{3}k_{-9}k_{10}k_{13}$$

$$\theta_{0} = k_{-9}k_{-10}$$

$$\theta_{1} = k_{-9}k_{13} + k_{-10}k_{12}$$

$$\theta_{2} = k_{13}k_{12}$$

This rate law, together with the one obtained for the uncatalyzed process, is in agreement with all experimental results presented in this article: the first-order reaction in the permanganate ions, Mn^{2+} ions, and with respect to amino acid; the qualitative dependence for the k'_2 vs. pH found (Fig. 4) and the decreasing in k'_2 values with the permanganate concentration increases (Table I).

Unfortunately, it has not been possible to evaluate the values of the rate constants corresponding to the reaction determining steps, given the complexity of the mechanisms proposed for both processes. Therefore, the activation parameters summarized in Table II, are associated with the apparent rate constants k'_1 and k'_2 , and their values can not be attributed to none of the specific reaction steps. Taking this into account and, in spite of the correct agreement of the Arrhenius equation experimentally observed, it does not seem suitable to carry out a particular interpretation of the cited experimental results.

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