Kinetics and mechanism of the oxidation of L-α-amino-*n*-butyric acid in moderately concentrated sulfuric acid medium

Homayoon Bahrami and Mansour Zahedi

Abstract: The reaction kinetics of L-α-amino-*n*-butyric acid oxidation by permanganate ion have been investigated in moderately strong acid medium using a spectrophotometric technique. In all cases studied an autocatalytic effect, due to Mn^{+2} ions formed as a reaction product, was observed. Both catalytic and noncatalytic processes were determined to be first order with respect to the permanganate ion and the amino acid. The overall rate equation for this process may be written as:

$$-d[MnO_4^-]/dt = k'_1[MnO_4^-] + k'_2[MnO_4^-]\cdot[Mn^{+2}]$$

where k'_1 and k'_2 are pseudo-order rate constants for the noncatalytic and catalytic reactions, respectively. The influence of some factors such as temperature and reactant concentration on the rate constants has been studied, and the activation parameters have been calculated. Reaction mechanisms satisfying observations for both catalytic and noncatalytic routes have been presented.

Key words: L-α-amino-*n*-butyric acid, permanganate oxidation, concentrated acidic medium, autocatalysis, free radical intermediates.

Résumé : Faisant appel à une technique spectrophotométrique, on a étudié la cinétique de la réaction d'oxydation de l'acide L-α-aminobutyrique par l'ion permanganate dans un milieu acide relativement fort. Dans tous les cas étudiés, on a observé un effet autocatalytique par les ions Mn^{+2} qui se forment comme produit de la réaction. On a déterminé que les processus tant catalytique que non-catalytique sont tous les deux du premier ordre par rapport à l'ion permanganate et à l'acide aminé. L'équation globale de vitesse pour le processus est de la forme:

$$-d[MnO_4^-]/dt = k'_1[MnO_4^-] + k'_2[MnO_4^-]\cdot[Mn^{+2}]$$

dans laquelle k'_1 et k'_2 sont les constantes de vitesse du premier ordre des réactions respectivement non-catalytique et catalytique. On a étudié l'influence de quelques facteurs, tels que la température et la concentration, sur les constantes de vitesse étudiées et on a calculé les paramètres d'activation. On propose des mécanismes réactionnels pour les voies catalytique et non catalytique qui satisfont les résultats obtenus.

Mots clés : acide L-α-aminobutyrique, oxydation avec du permanganate, milieu acide concentré, autocatalyse, intermédiaires radicalaires.

[Traduit par la Rédaction]

Introduction

Owing to the biological importance of amino acids, the kinetics and mechanistic study of their oxidation has received considerable attention. The permanganate oxidation process of amino acids in strong acid media (1–14), in neutral and weak basic solutions (15–23), and in weak acid media (24–29) has been investigated. The occurrence of autocatalysis effects in weak acid media, neutral aqueous solution, and weak basic media has been extensive (15–29), whereas no rigorous evidence of such an effect has been reported in strong acid media. There have been just two reports (10, 14) of a "double-stage" process vaguely attributed to possible autocatalysis, with no thorough information as far as the autocatalysis effect is concerned.

In autocatalytic pathways in which Mn^{+2} ions have been determined to be responsible for the effect, a mechanism with no free radicals involved has been suggested (28, 29). In the present paper, distinct evidence of the autocatalytic influence of Mn^{+2} for the permanganate oxidation of L-α-amino-*n*-butyric acid in strong acid medium has been presented, and a free radical mechanism has been proposed.

Experimental

All the reagents were from Merck or Sigma. The solutions were prepared with triply distilled and deionized water. The

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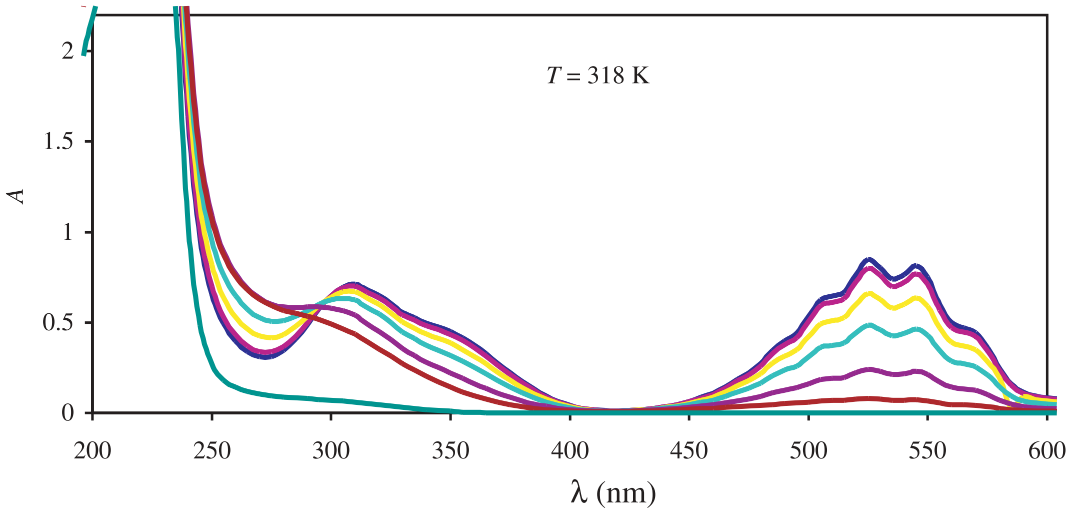
Fig. 1. Spectral changes in the oxidation of L-α-amino-*n*-butyric acid by permanganate ion. [$KMnO_4$] = 4 × 10^{-4} mol dm^{-3}, [L-abu] = 0.1 mol dm^{-3}, [H_2SO_4] = 3.16 mol dm^{-3}, *T* = 318 K. Scanning time intervals = 6 min.



permanganate solutions were prepared and tested by the Vogle method (30). The kinetic progress of the reaction was followed by measuring the absorbance of the permanganate ions at 525 nm with a thermostated (Shimadzu TB-85 ± 0.1 K) Shimadzu (2100 Model) UV–vis spectrophotometer within the temperature range 25–45 °C. For the permanganate molar absorption coefficient at 525 nm and in strong acid solution, a value of 2.26 × 10^3 dm^3 mol^{-1} cm^{-1} was obtained.

In all the kinetic measurements, the amino acid was used in excess (250-fold) relative to permanganate, to insure pseudo-first-order kinetics (28, 29).

Results

Stoichiometry and product analysis

By employing spot tests (31, 32), the final reaction products were detected as ammonium ions and the corresponding aldehyde. For carbon dioxide detection, the standard Vogle method (33) was employed. As well, it is well known (4, 12, 34) that in the reduction process of permanganate ions in strong acid media (as long as the reducing species is in excess), Mn^{+2} ions are the final product.

Our reaction was performed in an excess of amino acid, and we used the procedure outlined below to study the stoichiometry of the reaction; the following equation is proposed as the reaction stoichiometry:

$$[1] \quad 2MnO_4^- + 5CH_3\text{-}CH_2\text{-}CH(NH_3)^+COO^- + 11H^+ \rightarrow 5CH_3\text{-}CH_2\text{-}CHO + 5NH_4^+ + 5CO_2 + 2Mn^{+2} + 3H_2O$$

Procedure

Equal concentrations of known amounts of permanganate and amino acid were mixed and kept at 45 °C temperature for 1 h. For the permanganate concentration determination, a known amount of reaction mixture was quenched by a standard iron(II) solution. The unreacted iron was subsequently titrated by a standard cerium(IV) solution. Aldehyde concentration was determined by a calorimetric procedure using chromotropic acid. We came to the final conclusion that 1 mol of permanganate generates 2.5 mol of aldehyde, as is indicated by the balanced equation, eq. [1] (1, 2, 8).

Rate equation

Figure 1 illustrates the permanganate absorption vs. wavelength curves obtained at 6 min intervals as the reaction proceeded. From previous studies (15–23), Mn(IV) ions absorb in the region 400–650 nm. Figure 1 shows the lack of spectral changes from 400–650 nm, which means that MnO_2 is not a reaction product. Furthermore, since no rise and fall in absorption is observed at 418 nm, it is concluded that Mn(IV) ions do not intervene as possible oxidizing agents unless they are short lived.

The absorbance–time plots are illustrated in Fig. 2. In all the experiments performed, curves with a sigmoid profile (Fig. 2*a*) were obtained. This characteristic suggests the existence of an autocatalytic mechanism. To demonstrate that Mn^{+2} is the species responsible for the autocatalytic effect, kinetic runs were carried out in the presence of the $MnSO_4$ species at the beginning of the reaction. As the initial concentration of Mn^{+2} ions increased, a notable increase in the reaction rate was seen (Fig. 2*b*). Further increases of initial Mn^{+2} concentration and maintaining the Mn^{+2} concentration equal to the permanganate ion concentration led to a complete disappearance of the sigmoid form (Fig. 2*c*). Taking the Mn^{+2} effect on the reaction rate into account, the following rate equation has been proposed:

$$[2] \quad d[MnO_4^-]/dt = k'_1[MnO_4^-] + k'_2[MnO_4^-]\cdot[Mn^{+2}]$$

where k'_1 and k'_2 are pseudo-order rate constants for the noncatalytic and catalytic processes, respectively. The amino acid concentration, which is always kept in large excess, and the constant acid concentration in each experiment are included in these pseudo-order rate constants.

The integrated form of this equation gives:

$$[3] \quad \ln[(k'_1/k'_2 + x)/(a - x)] = (k'_1 + k'_2 a)t - \ln(k'_2 a/k'_1)$$

Fig. 2. Effect of the added initial concentration of ions on the absorbance time plots. [$KMnO_4$] = 4 × 10^{-4} mol dm^{-3}, [L-abu] = 0.1 mol dm^{-3}, [H_2SO_4] = 3.16 mol dm^{-3}, T = 313 K. (*a*) [Mn^{+2}] = 0 mol dm^{-3}; (*b*) [Mn^{+2}] = 2 × 10^{-4} mol dm^{-3}; (*c*) [Mn^{+2}] = 4 × 10^{-4} mol dm^{-3}.

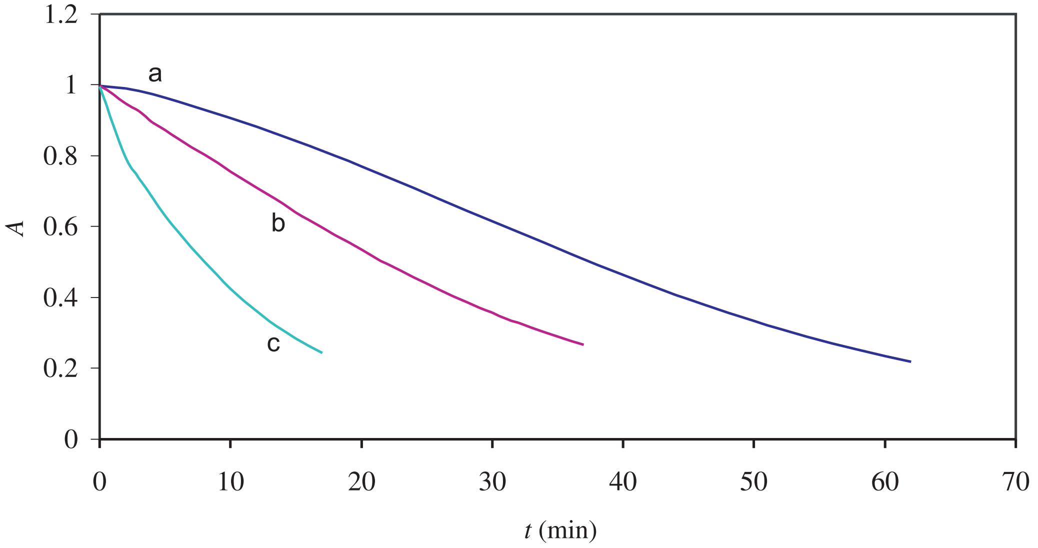
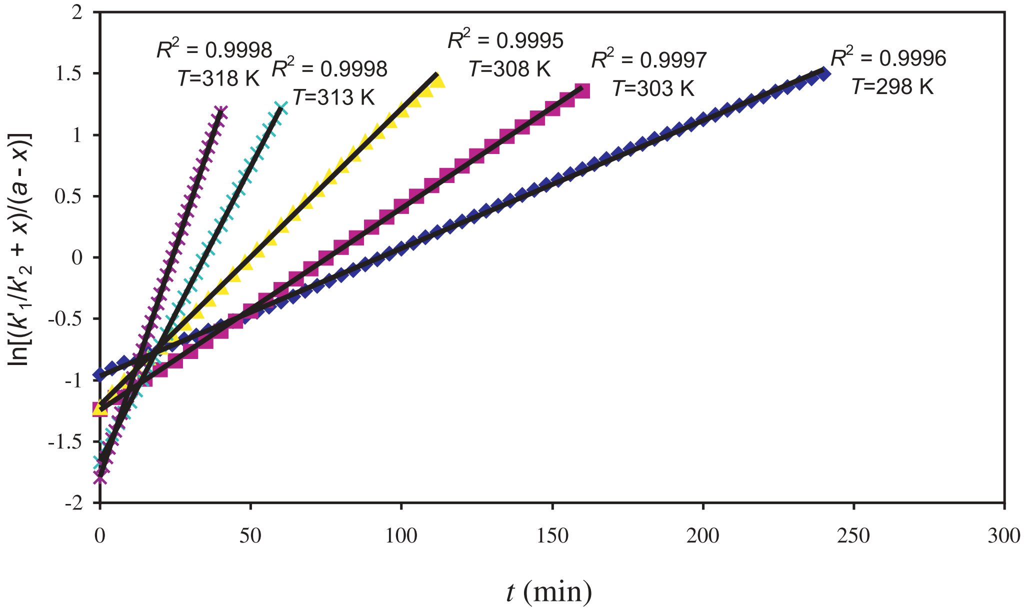


Fig. 3. Integrated rate-law plots for the oxidation of L-α-amino-*n*-butyric acid by potassium permanganate at various temperatures. [$KMnO_4$] = 4 × 10^{-4} mol dm^{-3}, [L-abu] = 0.1 mol dm^{-3}, [H_2SO_4] = 3.16 mol dm^{-3}.



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

For the correct determination of pseudo-constants k'_1 and k'_2, the following procedure has been employed. Because the reaction is slow and the initial Mn^{+2} concentration is sufficiently low, initial guesses of k'_1 values have been obtained by fitting the initial portion of the rate data to a first-order rate equation and assuming no catalytic effect in the early stages of the reaction. Moreover, our kinetic run in the presence of manganese sulfate(II) with a concentration equal to that of the permanganate ion satisfies the following rate equation:

$$[4] \qquad \ln[a(b + x)/b(a - x)] = k'_2\,(a + b)t$$

where b refers to the initial concentration of manganese sulfate(II). The calculated rate constants under this condition have provided a reasonable initial guess for k'_2. Having previously determined preliminary values of k'_1 and k'_2, eq. [3] has then been used for the simultaneous determination of the kinetic data of the reaction by taking advantage of iterative methods (18, 24–29). Figure 3 demonstrates the results of the fitting process of rate data at various temperatures and under the same conditions.

Table 1 gives the final values for k'_1 and k'_2 at various temperatures. Almost perfect fits to the curves in Fig. 3 (R^2 values of 0.9995–0.9998) not only corroborate the validity of the applied kinetic method but also confirm the autocatalytic effect of the Mn^{+2} species.

Fig. 4. Effect of the amino acid concentration on the catalyzed and uncatalyzed pseudo-order rate constants. $[KMnO_4] = 4 \times 10^{-4}$ mol dm^{-3}, $[H_2SO_4] = 3.16$ mol dm^{-3}, $T = 313$ K.

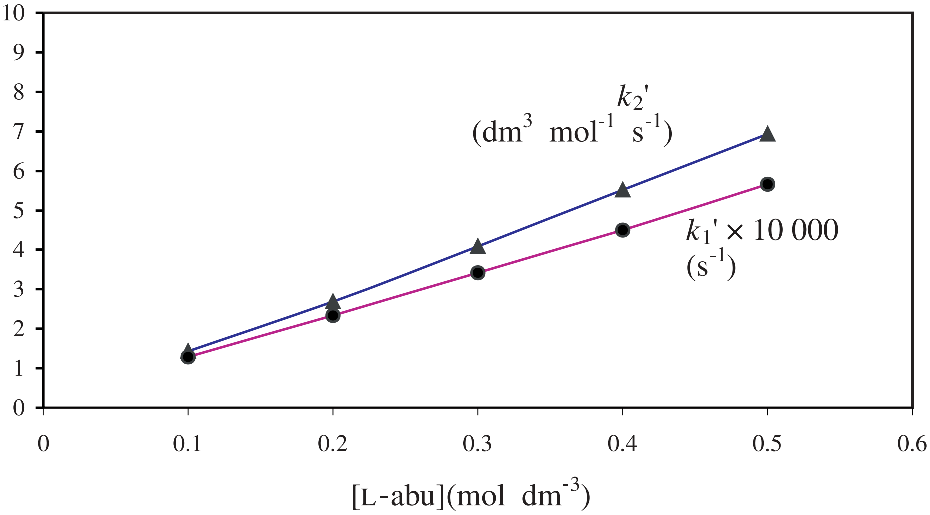


Table 1. Effect of temperature on k_1' and k_2'; $[KMnO_4] = 4 \times 10^{-4}$ mol dm^{-3}; [L-abu] = 0.1 mol dm^{-3}; $[H_2SO_4] = 3.16$ mol dm^{-3}.

T (K)	$k_1' \times 10^5$ (s^{-1})	$k_2' \times 10^2$ (dm^3 mol^{-1} s^{-1})
298	4.12 (±0.02)	27.72 (±0.05)
303	6.16 (±0.04)	49.98 (±0.11)
308	9.12 (±0.09)	81.05 (±0.19)
313	12.78 (±0.09)	142.24 (±0.2)
318	17.79 (±0.09)	239.8 (±0.2)

Note: Values in parenthesis are estimated errors on each of k_1' and k_2'.

Table 2. Variation of k_2' and k_1' vs. the concentration of butyric acid; $[KMnO_4] = 4 \times 10^{-4}$ mol dm^{-3}; $[H_2SO_4] = 3.16$ mol dm^{-3}; $T = 313$ K.

[L-abu] (mol dm^{-3})	k_2' (dm^3 mol^{-1} s^{-1})	$k_1' \times 10^4$ (s^{-1})
0.1	1.43	1.28
0.2	2.81	2.51
0.3	4.35	3.83
0.4	5.67	5.17
0.5	7.05	6.33

Table 3. Effect of Mn(II) on k_2' at 313 K; [L-abu] = 0.1 mol dm^{-3}; $[H_2SO_4] = 3.16$ mol dm^{-3}; $[KMnO_4] = 4 \times 10^{-4}$ mol dm^{-3}.

[Mn(II)]	0	0.0002	0.0004	0.0006
k_2' (dm^3 mol^{-1} s^{-1})	1.43	1.41	1.34	1.19

Dependence of the kinetic parameters

Dependence of reaction rate on [amino acid], $[MnO_4^-]$, and $[Mn^{2+}]$

The pseudo-order rate constants obtained at various amino acid concentrations are summarized in Table 2. Figure 4 shows these results. The plots of $1/k_1'$ and $1/k_2'$ against 1/[L-abu] (L-abu = L-α-amino-*n*-butyric acid) (not shown) gave straight lines that both pass through the origin. These observations confirm first order with respect to the amino acid for both the noncatalytic and catalytic pathways (12).

To investigate the effect of permanganate concentration on the reaction rate, its concentration was varied from 4×10^{-4} to 6×10^{-4} mol dm^{-3} at 313 K, which caused k_1' and k_2' values to be decreased by 14% and 31%, respectively.

Table 3 summarizes the data that have been obtained for k_2' with increasing Mn^{+2} ion concentration. From these results it is evident that when Mn^{+2} concentration is raised, k_2' values decrease. This observation, and the fact that the very slow reaction of Mn^{+2} with MnO_4^- (35, 36) switches to a fast reaction when the amino acid is present, suggest that in the process of permanganate consumption some intermediate complex has probably been formed between Mn^{+2} and the amino acid (24–29).

Dependence of reaction rate on sulfuric acid concentration

The effect of $[H^+]$ has been investigated by means of a series of experiments carried out at various sulfuric acid concentrations. As Fig. 5 indicates, k_1' increases when the acid concentration is raised, whereas k_2' initially decreases and then shows a sharp increase. The region of 3–4 mol dm^{-3} sulfuric acid shows the least variation for k_2'. Thus, this concentration region was determined to be the most appropriate region for the rest of our kinetic studies.

Determination of activation parameters

As a further justification of the method that has been applied to determine the pseudo-order rate constants k_1' and k_2' at various temperatures, calculated values of these parameters have been evaluated by the Eyring equation. Figure 6 demonstrates the agreement of both k_1' and k_2' with the Eyring equation. The thermodynamic activation parameters obtained, energy, enthalpy, and entropy, are reported in Table 4.

Acrylonitrile addition

The presence of free radicals as intermediates was con-

Fig. 5. Effect of the sulfuric acid concentration on the uncatalyzed and catalyzed pseudo-order rate constants. [$KMnO_4$] = 4 × 10^{-4} mol dm^{-3}, [L-abu] = 0.1 mol dm^{-3}, T = 313 K.

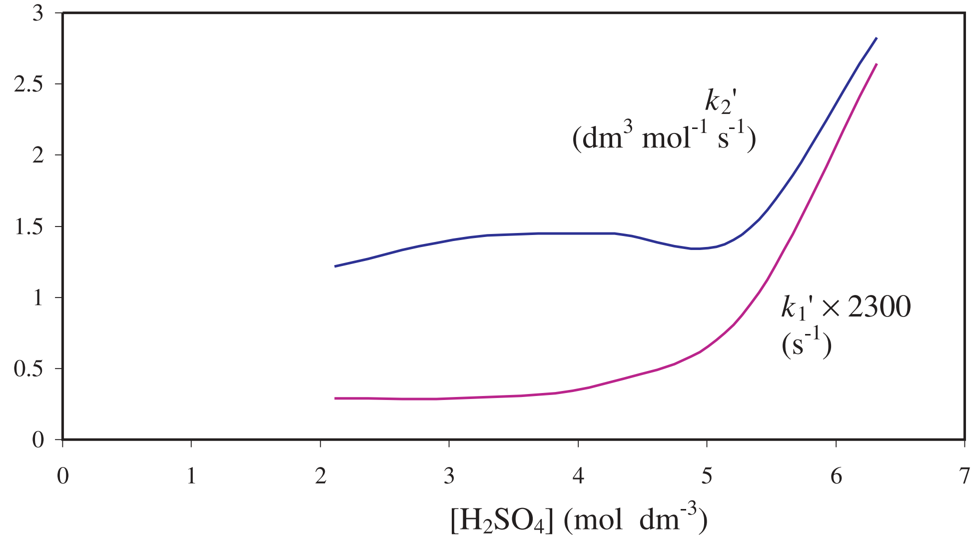


Fig. 6. Eyring plots for the uncatalyzed and catalyzed processes. [L-abu] = 0.1 mol dm^{-3}, [$KMnO_4$] = 4 × 10^{-4} mol dm^{-3}, [H_2SO_4] = 3.16 mol dm^{-3}.

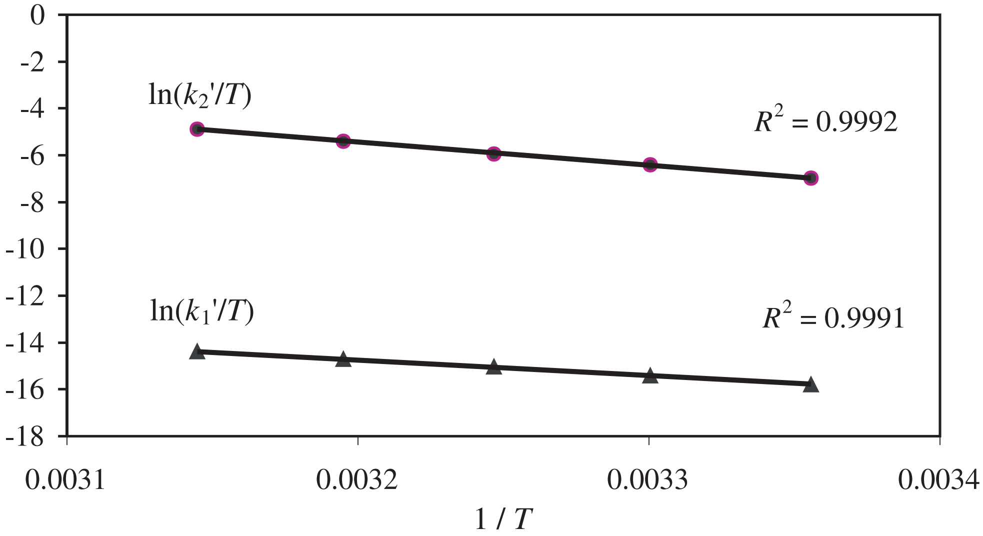


Table 4. Activation parameters; [$KMnO_4$] = 4 × 10^{-4} mol dm^{-3}; [L-abu] = 0.1 mol dm^{-3}; [H_2SO_4] = 3.16 mol dm^{-3}.

	Uncatalyzed process	Catalyzed process
$\Delta S^{\#}$ (J mol^{-1} K^{-1})	–144 (±3)	19 (±4)
$\Delta H^{\#}$ (kJ mol^{-1})	55 (±1)	82 (±1)
E_a (kJ mol^{-1})	58 (±1)	84 (±1)

Note: Values in parenthesis are estimated errors on each thermodynamical parameter.

firmed by addition of acrylonitrile, which led to polymerization, both in the presence and in the absence of manganese sulfate(II).

Discussion

In agreement with the experimental results that have been presented and taking into account the previous literature references, two separate mechanisms for the catalyzed and uncatalyzed pathways are proposed to describe the reaction pathway. Since the existence of intermediate free radicals was confirmed, their involvement in the reaction mechanism has also been considered.

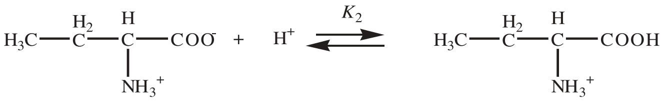
Reaction mechanism for the uncatalyzed process

All the experiments were performed in strong acid media. With the evidence presented pointing to no involvement of other manganese oxidation states, Mn(VII) is the most probable reactive species. Reaction rate enhancement observed by increasing acid concentration suggests the formation of a more powerful oxidant, namely permanganic acid, by the following equilibrium:

$$[5] \qquad MnO_4^- + H^+ \overset{K_1}{\rightleftarrows} HMnO_4$$

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

[6]

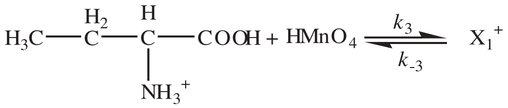


$$H_3C-\overset{H_2}{C}-\overset{H}{\underset{NH_3^+}{C}}-COO^- + H^+ \overset{K_2}{\rightleftharpoons} H_3C-\overset{H_2}{C}-\overset{H}{\underset{NH_3^+}{C}}-COOH$$

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 the permanganic acid and the cationic form of the amino acid is proposed (11, 12, 28).

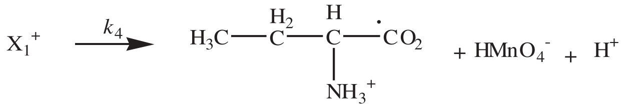
[7]



$$H_3C-\overset{H_2}{C}-\overset{H}{\underset{NH_3^+}{C}}-COOH + HMnO_4 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} X_1^+$$

This complex may rupture according to the following equation:

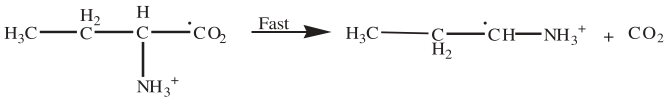
[8]



$$X_1^+ \xrightarrow{k_4} H_3C-\overset{H_2}{C}-\overset{H}{\underset{NH_3^+}{C}}-\dot{C}O_2 + HMnO_4^- + H^+$$

Based on the radical involvement in the reaction mechanism, the iminium cation (24–29) is possibly formed via three steps

[9]



$$H_3C-\overset{H_2}{C}-\overset{H}{\underset{NH_3^+}{C}}-\dot{C}O_2 \xrightarrow{Fast} H_3C-\underset{H_2}{C}-\dot{C}H-NH_3^+ + CO_2$$

[10]

$$H_3C-\overset{H_2}{C}-\dot{C}H-NH_3^+ \xrightarrow{Fast} H_3C-\overset{H_2}{C}-\dot{C}H-NH_2 + H^+$$

[11]

$$H_3C-\overset{H_2}{C}-\dot{C}H-NH_2 + HMnO_4^- \xrightarrow{Fast} H_3C-\overset{H_2}{C}-\overset{H}{C}=NH_2^+ + HMnO_4^{2-}$$

By hydrolysis of the iminium cation, the corresponding aldehyde is obtained (28)

[12]

$$H_3C-\overset{H_2}{C}-\overset{H}{C}=NH_2^+ + H_2O \xrightarrow{Fast} H_3C-CH_2-CHO + NH_4^+$$

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

[13] $5HMnO_4^{2-} + 11H^+ \rightarrow 3MnO_4^- + 2Mn^{2+} + 3H_2O$

Multiplying eqs. [5], [6], [7], [8], [9], [10], [11], and [12] by a factor of five and then summing them with eq. [13] 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 uncatalyzed process is

[14] $-d[Mn(VII)]/dt = k_1'[MnO_4^-]$

[15] $$k_1' = \frac{\alpha_0[H^+]^2[\text{L}-abu]_t}{\beta_0(1+\beta_1[H^+]+\beta_2[H^+]^2)+\alpha_1[H^+]^2[MnO_4]}$$

where $[\text{L-abu}]_t$ represents the total concentration of amino acid; [Mn(VII)] represents the total concentration of permanganate; and where

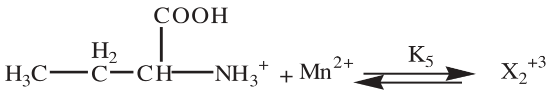
$$\alpha_0 = K_1K_2k_3k_4$$
$$\alpha_1 = K_1K_2k_3$$
$$\beta_0 = k_{-3} + k_4$$
$$\beta_1 = K_1 + K_2$$
$$\beta_2 = K_1K_2$$

The rate law obtained above corresponds to that mechanism explaining the observed experimental behavior: the first-order reaction with respect to both permanganate and amino acid and the change in k_1', the uncatalyzed pseudo-order rate constant, when the permanganate concentration varies.

Reaction mechanism for the catalyzed process

Addition of Mn^{+2} ions led 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 L-α-amino-*n*-butyric acid in a fast step before it is oxidized by permanganic acid in a slow step (15, 16).

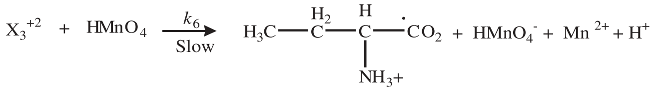
[16]



$$H_3C-\overset{H_2}{C}-\overset{COOH}{CH}-NH_3^+ + Mn^{2+} \overset{K_5}{\rightleftharpoons} X_2^{+3}$$

As the rate determining step, slow attack of permanganic acid on complexes has been proposed (28–29)

[17]



$$X_3^{+2} + HMnO_4 \underset{Slow}{\xrightarrow{k_6}} H_3C-\overset{H_2}{C}-\overset{H}{\underset{NH_3+}{C}}-\dot{C}O_2 + HMnO_4^- + Mn^{2+} + H^+$$

The remaining steps, leading to the final products, resemble those presented for the uncatalyzed pathway above. Again, multiplying eqs. [5], [6], [7], [16], [17], [9], [10], [11], and [12] by a factor of five and summing them up with eq. [12] results in the overall reaction with the correct stoichiometry. Assuming a steady-state approximation for the X_2^{3+} complex in the above mechanism, the following rate equation (28) is derived:

[18] $-d[Mn(VII)]/dt = k_2'[Mn^{2+}][MnO_4^-]$

$$k'_2 = \frac{\beta_0\delta_0[\text{L-abu}]_t[\text{H}^+]^2}{\beta_0(1+\beta_1[\text{H}^+]+\beta_2[\text{H}^+]^2)+\alpha_1[\text{H}^+][\text{MnO}_4^-]+\beta_0\delta_1[\text{H}^+][\text{Mn}^{+2}]+\beta_0\delta_2[\text{H}^+]^{2+}[\text{Mn}^{+2}]} \qquad [19]$$

where the notation employed in eq. [14] is conserved, and in addition

$$\delta_0 = K_1K_2K_5k_6$$

$$\delta_1 = K_2K_5$$

$$\delta_2 = K_1K_2K_5$$

This rate law, along with the one proposed for the uncatalyzed process, is in accord with all experimental results presented in this article; namely, first-order dependence on Mn^{+2} ions, permanganate ions, and the amino acid and inverse dependence of k'_2 on permanganate and Mn^{+2} ion concentrations, as shown in the k'_2 expression.

Owing to the complexity of the proposed mechanism, evaluation of the values of the rate constants corresponding to the reaction rate-determining steps for both processes has not been possible. Thus, the activation parameters reported are associated with reaction pseudo-rate constants k'_1 and k'_2, and these values cannot be attributed to any particular reaction step.

Conclusions

The kinetics of the permanganate oxidation process of L-α-amino-*n*-butyric acid in strong acid media was investigated using a spectrophotometric technique. Addition of manganese sulfate(II) to the reaction mixture raised the reaction rate. The sigmoid profile observed for permanganate absorption variation at 525 nm vs. time was completely transformed to a linear one under conditions of $[\text{KMnO}_4]$ = [Mn(II)]. In the presence of manganese sulfate(II), by increasing the amino acid concentration, the reaction rate was increased. Thus, we report the first conclusive evidence of an autocatalytic oxidation process of an amino acid in strong acid media in which Mn^{+2} species are responsible for the effect. The pseudo-order rate constants obtained for both the catalytic and noncatalytic pathways when the amino acid was in excess obeyed the Eyring relation. The presence of free radicals was confirmed, and mechanisms satisfying experimental observations for both catalytic and noncatalytic pathways were presented.

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