

## Conclusive Evidence for Delayed Autocatalytic Behavior of Mn(II) Ions at a Critical Concentration

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The kinetics of the permanganic oxidation process of glycine, L-alanine and L-leucine in strong acid media were investigated using a spectrophotometric technique. Conclusive evidence has proven that the autocatalytic activity of Mn(II) in these reactions in strong acidic media is analogous to that of weak acid media, but in the former, Mn(II) ions should acquire a critical concentration for them to show autocatalytic characteristics. This critical concentration depends on the nature of the amino acid used. Considering the delayed autocatalytic behavior of Mn(II) ions, we herein present the rate equations and mechanisms satisfying observations for both catalytic and noncatalytic routes. The correspondence of the pseudo-order rate constants of the catalytic and noncatalytic pathways to Eyring law verify both the critical concentration as well as the delayed autocatalytic behavior concepts. In general, the onset of delayed behavior can be attributed to the concentration ratio of Mn(II) to amino acid which can be of a certain value for any particular amino acid.

**Keywords:** Glycine, L-alanine and L-leucine, Permanganate oxidation, Concentrated acidic medium, Delayed autocatalysis, Free radical intermediate

### INTRODUCTION

Kinetics and mechanistic study of amino acid oxidation by permanganate in a strong acid medium has received considerable attention since the 1970s [1-21]. In most of these studies, the reaction has been considered to be a process that follows perfect second order kinetics at constant  $[H^+]$  and with no autocatalytic effect. There are two reports of a double-stage process in which every stage is shown to have kinetic identical to a pseudo-first order reaction [10,14].

In our previous studies [19,20], we reported the presence of an autocatalytic effect, with  $Mn^{2+}$  as the autocatalytic agent. Also, in a more recent work [21] we showed that this delayed

autocatalytic phenomenon exists for the oxidation of L-norleucine structural isomers. As a major conclusion in the latter work, it was found that the delayed behavior requires a critical ratio of the concentration of  $Mn^{2+}$  to that of L-leucine of about  $2 \times 10^{-3}$ . In contrast to our observations, Verma *et al.* [1] has reported a non-autocatalytic behavior in the oxidation of leucine, glycine and alanine by permanganate in a strong acid medium. In the present investigation, reexamination of the oxidation of the above three amino acids under the stated conditions seems necessary. Thus, in this work, our previous results for leucine have been expanded, reanalyzed and improved. Conclusive evidence shows that the oxidations of these three amino acids are in fact autocatalyzed, with  $Mn^{2+}$  as the autocatalytic agent. However, it should be noted that, for  $Mn^{2+}$  to show delayed autocatalytic characteristics, it should

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acquire a critical concentration. This critical concentration depends on the nature of the amino acid used. In our view, the conclusions of previous reports, stating that the oxidation of amino acids in a moderately concentrated acidic medium is non-autocatalytic, are dependent on three major factors. First, either the process was not followed long enough (well after 50% completion). Second, they may have just sufficed to the sigmoid profile of the concentration-time curves rather than following complete curves of rate-time data. Third, they may not have reached the critical concentration of the autocatalytic moiety as explained above. The results presented in this paper strongly support the idea of delayed autocatalytic behavior of Mn(II) in the oxidation processes of amino acids and should encourage researchers to take more caution while studying such processes.

## EXPERIMENTAL

All the reagents were purchased from Merck or Sigma. The solutions were prepared with triply distilled water that was deionized and boiled. The permanganate solutions were prepared and tested by the Vogel method [22]. The kinetic progress of the reaction was followed by measuring the absorbance of the permanganate ions at 525 nm with a thermostated (Eyela SB-11,  $\pm 0.1$  K) UV-Vis spectrophotometer (Shimadzu model 1601 PC) within the temperature range of 25-45 °C. At 525 nm in a strong acid solution, a permanganate molar absorption coefficient of  $2.26 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  was obtained. In all the kinetic measurements, the amino acid was used in excess relative to permanganate. The reaction products were analyzed and identified by GC-MS using a Thermoquest-Finnigan gas chromatograph coupled to a TRACE ion trap detector, with helium as a carrier gas, an ionization voltage of 70 eV, and ion source and interface temperatures of 200 °C. In a mass range of  $m/z$  40-90, the above analysis was performed with a stationary phase in a fused silica capillary column (DB-1, 60 m  $\times$  0.25 mm i.d.; film thickness 0.25  $\mu\text{m}$ ). The operating conditions included injector and detector temperatures of 280 and 300 °C, respectively, and an oven temperature program ranging from 50 to 250 °C at a rate of 5 °C  $\text{min}^{-1}$ , finally held at 250 °C for 10 min.

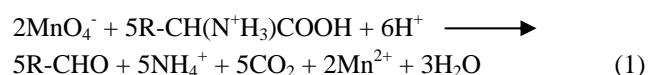
For all amino acids studied, after the completion of the

reaction (absorbance  $< 0.01$ ), the following reaction products were detected: ammonium ions [23], carbon dioxide [24] and the corresponding aldehyde. For aldehyde isolation, the acidic medium was neutralized with sodium hydroxide (3 N). The solution was extracted twice with diethyl ether ( $2 \times 15 \text{ ml}$ ). The organic layer was dried (sodium sulfate), concentrated under reduced pressure, and the residue identified based on GC retention times and computer matching of mass spectra using the Wiley Registry, NIST mass spectral library. Also, the corresponding aldehyde was isolated as its 2,4-dinitrophenylhydrazone derivatives. The melting points of the mentioned derivatives were confirmed by comparing them with reference compounds [25]. Reaction mixtures containing various ratios of amino acid to  $\text{MnO}_4^-$  were mixed in the presence of 3.16 M  $\text{H}_2\text{SO}_4$ , then equilibrated for 24 h at room temperature.

## RESULTS AND DISCUSSION

### Stoichiometry and Product Analysis

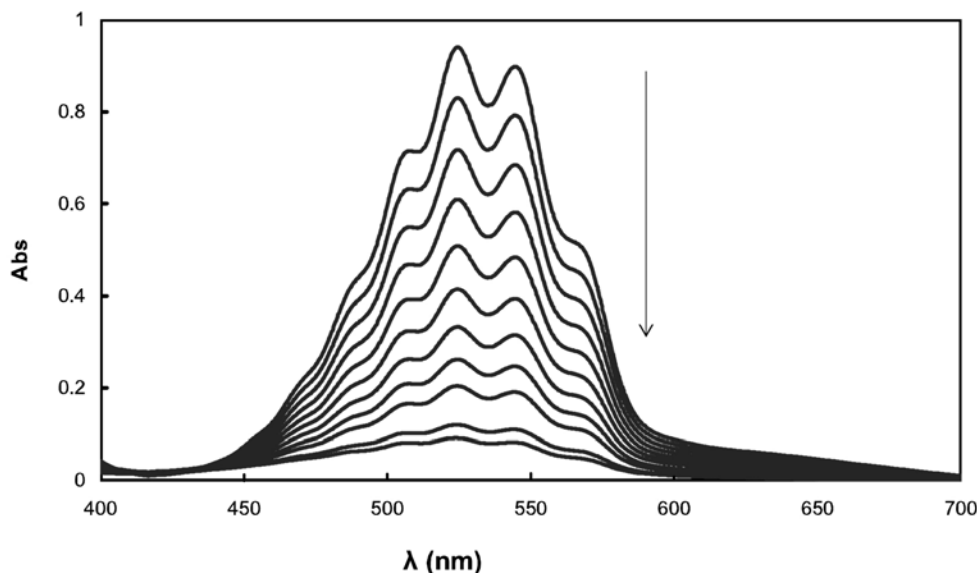
Our estimate of the unreacted  $\text{MnO}_4^-$  shows that 1 mol of  $\text{MnO}_4^-$  consumes 2.5 mol of the amino acid [12]. Moreover, under our reaction conditions, the obtained aldehyde is not oxidized further and the response to the corresponding acid test is negative. In view of these results and taking into account that the reduction final product of permanganate in acid medium and in large excess of reducing species is the  $\text{Mn}^{2+}$  ion [1,3,11,26], the following equation was obtained:



where R = -H for glycine, R = -CH<sub>3</sub> for L-alanine and R = -H<sub>2</sub>C-CH(CH<sub>3</sub>)-CH<sub>3</sub> for L-leucine.

### Rate Equation

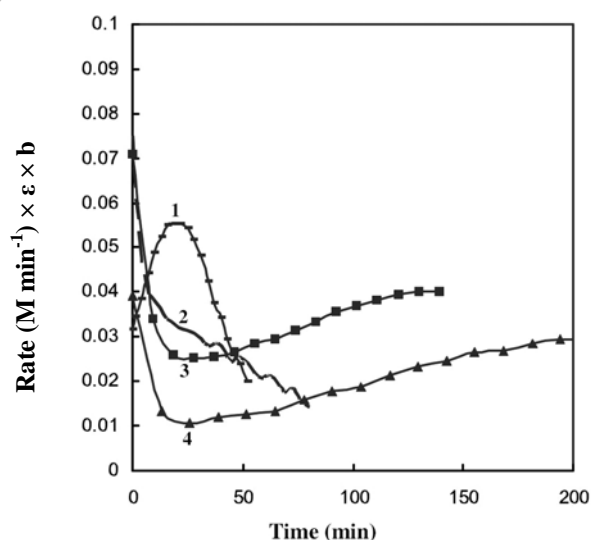
Figure 1 illustrates the permanganate absorption vs. wavelength curves for L-leucine oxidation, obtained at four-minute intervals as the reaction proceeded. From previous studies [27-35], it is known that  $\text{MnO}_2$  absorbs in the 400 to 650 nm region. The absorption profiles suggest that  $\text{MnO}_2$  is not a reaction product. Furthermore, the maximum absorption



**Fig. 1.** Spectral changes with wavelength at various times in the oxidation of L-leucine by permanganate ion.  $[\text{KMnO}_4] = 4 \times 10^{-4} \text{ M}$ ,  $[\text{L-leucine}] = 0.1 \text{ M}$ ,  $[\text{H}_2\text{SO}_4] = 3.16 \text{ M}$ ,  $T = 323 \text{ K}$ , scanning time intervals = 4 min.

about 0.458 and 0.108 of its absorption at 525 nm (permanganate  $\lambda_{\text{max}}$ ) [36]. Thus, if Mn(IV) and Mn(III) species exist as stable moieties in the reaction medium, the absorption profile of permanganate over time must have changed from what is observed in Fig. 1, especially in the region of 525-527 nm, in order to contain the absorption features of the former ion. It is worth motioning here that it has been shown that, for Mn(III) to be generated as a product of the direct reaction between permanganate and Mn(II), an acidic medium with a pH of about 1-2 is required [37]. Furthermore, it has been reported that, for Mn(III) to become stable in the latter medium, species such as  $\text{C}_2\text{O}_4^{2-}$  [38] and  $\text{P}_2\text{O}_7^{4-}$  [39] are necessary. Therefore, we must conclude that under our present conditions, Mn(IV) and Mn(III) ions can neither be yielded *via* direct permanganate-Mn(II) reaction, nor are they stable even if they are generated by an amino acid-permanganate reaction. Additionally, the same results have been obtained for glycine and L-alanine, with all amino acids treated with 3.2 to 7 M  $\text{H}_2\text{SO}_4$ .

In Fig. 2, reaction rate-time curves for glycine, L-alanine and L-leucine are compared with that of L- $\alpha$ -amino-n-butyric acid. The oxidation of L- $\alpha$ -amino-n-butyric acid in a strong acidic medium by permanganate has been studied elsewhere [20]. The curve of the reaction rate *vs.* time for the latter acid



**Fig. 2.** Comparison of reaction rates over time.  $[\text{KMnO}_4] = 4 \times 10^{-4} \text{ M}$ ,  $[\text{H}_2\text{SO}_4] = 3.16 \text{ M}$ : (1) [2-amino-butyric acid] = 0.1 M,  $T = 313 \text{ K}$ ; (2) [leucine] = 0.1 M,  $T = 298 \text{ K}$ ; (3) [glycine] = 0.9 M,  $T = 308 \text{ K}$ ; (4) [alanine] = 0.6 M,  $T = 308 \text{ K}$ ,  $\epsilon = 2.26 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ,  $b = 1 \text{ cm}$ .

wavelengths for Mn(IV) and Mn(III) ions lie in the 400-460 nm region. It has been reported that permanganate absorption at the maximum wavelength of the aforementioned species is

shows that the rate increases from the onset of the reaction, whereas such increases in the reaction rates for glycine and L-alanine after an initial decrease occur at 45% and 35% of their corresponding reaction progression, respectively. For the case of L-leucine, however, there is no increase in the reaction rate even up to 60% of reaction progression, although some oscillations are observed after that stage. Figure 3 illustrates rate-time curves for L-alanine at a considerable initial concentration of Mn(II). From Fig. 3 it is obvious that the maximums of the curves of the reaction rates over time move to the earlier stage of reaction as the  $\text{Mn}^{2+}$  concentration increases. Trends for glycine that are similar to those of L-alanine have been observed, so we conclude that  $\text{Mn}^{2+}$  is the autocatalytic agent.

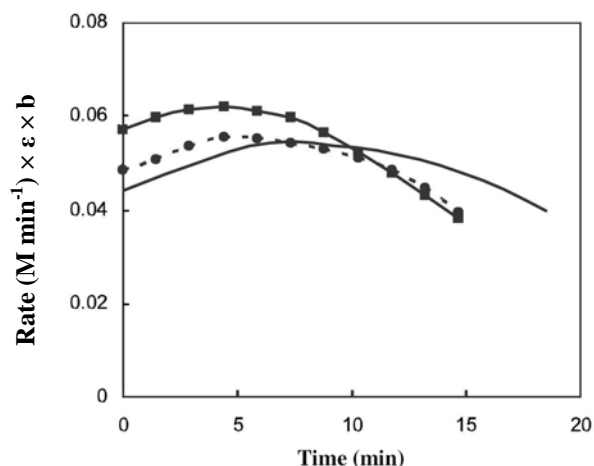
Although, as has been stated elsewhere [40,2], a sigmoidal profile for absorbance-time plot can be taken as an evidence for an autocatalytic process, such profiles were not observed in our experiments, which have proven to follow a "autocatalytic behavior". However, such sigmoidal profiles can not be seen and judged as autocatalytic activity in cases where the latter behavior starts in the later stages of the process. As such, it would therefore be impossible to fit the kinetics data from the initiation of the reaction to its point of 70% completion with only a single rate equation. Thus, for the delayed autocatalytic reactions mentioned above, such an autocatalytic effect could not be detected if the reaction is not followed to at least to the point of 70% completion. This phenomenon has led to the false conclusion in some reports of the existence of a "double-stage" process without any autocatalytic role for  $\text{Mn}^{2+}$  [10,14].

According to the above discussion, the following rate equation is proposed for glycine, L-alanine and L-leucine at the points of 45%, 35% and 60% reaction completion, respectively:

$$\frac{-d[\text{MnO}_4^-]}{dt} = k_1' [\text{MnO}_4^-] \quad (2)$$

with further reaction progress, we obtain the following equation for glycine and L-alanine:

$$\frac{-d[\text{MnO}_4^-]}{dt} = k_1' [\text{MnO}_4^-] + k_2' [\text{MnO}_4^-][\text{Mn}^{+2}] \quad (3)$$



**Fig. 3.** Effect of the added initial concentration of Mn(II) ions on the reaction rate-time plots. [L-alanine] = 0.5 M,  $[\text{KMnO}_4] = 4 \times 10^{-4}$  M,  $[\text{H}_2\text{SO}_4] = 3.16$  M,  $T = 313$  K. Concentration of  $\text{Mn}^{2+}$  ion is (---) 0.0012 M, (■) 0.0016 M and (●) 0.0020 M,  $\epsilon = 2.26 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ,  $b = 1$  cm.

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 at a large excess, and the constant sulfuric acid concentration in each experiment are included in these pseudo-order rate constants. The integrated forms of the equations give:

$$\ln \frac{a}{(a-x)} = k_1' t \quad (4)$$

$$\ln \frac{[(k_1'/k_2') + x]}{(a-x)} = (k_1' + k_2' a) t - \ln(k_2' a / k_1') \quad (5)$$

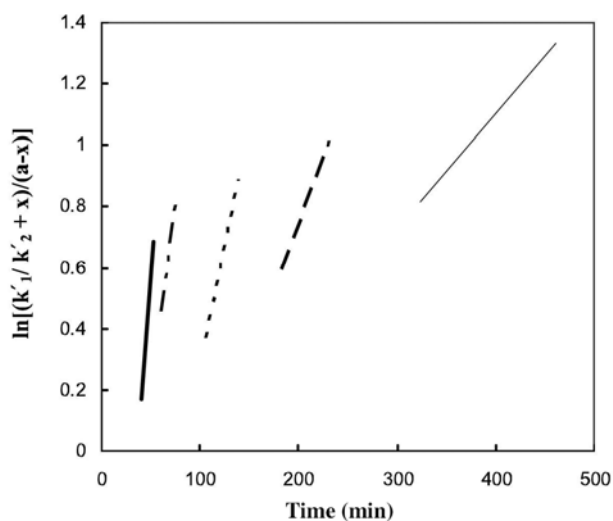
where **a** represents the initial concentration of permanganate and **x** the amount of permanganate ion consumed to time **t**.  $k_1'$  values are obtained by fitting the rate data to a first-order rate equation for L-leucine, the results of which are mentioned in Table 1. Initial estimation of  $k_1'$  for glycine and L-alanine is made by fitting the initial 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.

Moreover, our kinetics, which run in the presence of manganese(II) sulfate with a greater concentration than that of the permanganate ion, satisfy the following rate equation:

**Table 1.** Effect of Temperature on  $k_1'$  and  $k_2'$ <sup>a</sup>

T (K)	$k_1' \times 10^5 \text{ (s}^{-1}\text{)}$			$k_2' \times 10^2 \text{ (M}^{-1} \text{s}^{-1}\text{)}$	
	Glycine <sup>b</sup>	L-Alanine <sup>c</sup>	L-Leucine <sup>d</sup>	Glycine <sup>b</sup>	L-Alanine <sup>c</sup>
298	2.64 ( $\pm 0.04$ ) <sup>e</sup>	1.74 ( $\pm 0.01$ )	23.33 ( $\pm 0.21$ )	13.50 ( $\pm 0.10$ )	9.26 ( $\pm 0.03$ )
303	3.72 ( $\pm 0.06$ )	2.03 ( $\pm 0.02$ )	35.50 ( $\pm 0.21$ )	25.69 ( $\pm 0.15$ )	16.17 ( $\pm 0.05$ )
308	5.65 ( $\pm 0.08$ )	2.59 ( $\pm 0.02$ )	51.01 ( $\pm 0.32$ )	50.45 ( $\pm 0.20$ )	26.77 ( $\pm 0.06$ )
313	8.5 ( $\pm 0.12$ )	3.18 ( $\pm 0.05$ )	70.83 ( $\pm 0.36$ )	86.67 ( $\pm 0.29$ )	48.32 ( $\pm 0.13$ )
318	12.40 ( $\pm 0.17$ )	3.83 ( $\pm 0.07$ )	100.33 ( $\pm 0.52$ )	148.17 ( $\pm 0.43$ )	81.44 ( $\pm 0.18$ )

<sup>a</sup>[KMnO<sub>4</sub>] =  $4 \times 10^{-4}$  M, [H<sub>2</sub>SO<sub>4</sub>] = 3.16 M. <sup>b</sup>[Glycine] = 0.9 M. <sup>c</sup>[Alanine] = 0.6 M. <sup>d</sup>[Leucine] = 0.1 M. <sup>e</sup>Values in parentheses are estimated errors on each of  $k_1'$  and  $k_2'$  value.



**Fig. 4.** Integrated rate-law plots for the oxidation of glycine by potassium permanganate at various temperatures. [glycine] = 0.9 M, [KMnO<sub>4</sub>] =  $4 \times 10^{-4}$  M, [H<sub>2</sub>SO<sub>4</sub>] = 3.16 M: (—) Linear, T = 298 K,  $R^2 = 0.9995$ ; (— —) Linear, T = 303 K,  $R^2 = 0.9996$ ; (- - -) Linear, T = 308 K,  $R^2 = 0.9991$ ; (- · -) Linear, T = 313 K,  $R^2 = 0.9993$ ; (— — —) Linear, T = 318 K,  $R^2 = 0.9995$ .

$$\ln \frac{a(b+x)}{b(a-x)} = k_2' (a+b)t \quad (6)$$

where **b** represents the initial concentration of manganese(II) sulfate.

The calculated rate constants under these conditions

provide a reasonable initial guess for  $k_2'$ . Having previously determined preliminary values for  $k_1'$  and  $k_2'$ , Eq. (5) is used for the simultaneous determination of the kinetic data of the region of reaction-rate increase by taking advantage of iterative methods [27-31,40-45]. Figure 4 demonstrates the typical results of the fitting process of rate data for glycine at various temperatures under the same conditions.

Table 1 gives the final values for  $k_1'$  and  $k_2'$  at various temperatures. Almost perfect fits to the data in Fig. 4 ( $R^2$  values of 0.9991-0.9996) not only corroborate the validity of the applied kinetics method, but also confirm the autocatalytic effect of the Mn<sup>2+</sup> species and points to such delayed activity at certain critical concentrations of Mn<sup>2+</sup>.

### Dependence of Reaction Rate on [Amino Acid], [MnO<sub>4</sub><sup>-</sup>] and [Mn<sup>2+</sup>]

The pseudo-order rate constants obtained at various amino acid concentrations are summarized in Table 2 and illustrated in Fig. 5. The plots of  $1/k_1'$  and  $1/k_2'$  against  $1/[\text{amino acid}]$  (not shown) gave straight lines that pass through the origin. These observations confirm first order with respect to the amino acid for both the noncatalytic and catalytic pathways [12].

The effect of permanganate concentration is mentioned in Table 3. Taking a closer look at Table 3, it is obvious that  $k_1'$  values are decreased with increasing permanganate concentrations, but  $k_2'$  values are not changed appreciably. Table 4 summarizes the data obtained for  $k_2'$  by increasing the Mn<sup>2+</sup> ion concentration in the process of glycine and L-alanine oxidation. From these results, it is evident that when Mn<sup>2+</sup> concentration is raised,  $k_2'$  values decrease. This observation,

**Table 2.** Variation of  $k_1'$  and  $k_2'$  vs. the Amino Acid Concentration<sup>a</sup>

[Amino acid] (M)	$k_1' \times 10^5$ (s <sup>-1</sup> )			$k_2' \times 10^2$ (M <sup>-1</sup> s <sup>-1</sup> )	
	Glycine <sup>b</sup>	L-Alanine <sup>c</sup>	L-Leucine <sup>d</sup>	Glycine <sup>b</sup>	L-Alanine <sup>c</sup>
0.1	-	-	35.50	-	-
0.2	-	1.38	67.00	-	39.17
0.3	-	2.04	102.50	-	58.77
0.4	-	2.80	133.50	-	75.50
0.5	4.67	3.61	188.67	47.00	96.40
0.6	5.52	4.50	-	59.18	121.26
0.7	6.51	-	-	68.67	-
0.8	7.70	-	-	78.53	-
0.9	8.50	-	-	86.67	-

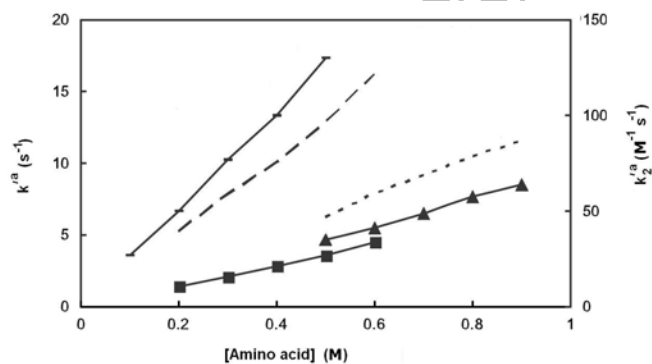
<sup>a</sup>[KMnO<sub>4</sub>] =  $4 \times 10^{-4}$  M, [H<sub>2</sub>SO<sub>4</sub>] = 3.16 M. Error on k values is less than 1%. <sup>b</sup>T = 313 K. <sup>c</sup>T = 323 K. <sup>d</sup>T = 303 K.

**Table 3.** Effect of KMnO<sub>4</sub> on  $k_1'$  and  $k_2'$ <sup>a</sup>

[KMnO <sub>4</sub> ] (M)	$k_1' \times 10^5$ (s <sup>-1</sup> )			$k_2' \times 10^2$ (M <sup>-1</sup> s <sup>-1</sup> )	
	Glycine <sup>b</sup>	L-Alanine <sup>c</sup>	L-Leucine <sup>d</sup>	Glycine <sup>b</sup>	L-Alanine <sup>c</sup>
0.0004	12.40	4.50	100.33	148.17	121.26
0.00052	8.86	3.03	98.20	148.87	121.83

<sup>a</sup>[H<sub>2</sub>SO<sub>4</sub>] = 3.16 M; error on k values is less than 1%. <sup>b</sup>[Glycine] = 0.9 M, T = 318 K.

<sup>c</sup>[L-Alanine] = 0.6 M, T = 323 K. <sup>d</sup>[L-Leucine] = 0.1 M, T = 313 K.



**Fig. 5.** Effect of amino acid concentration on the catalyzed and uncatalyzed pseudo-order rate constants. [KMnO<sub>4</sub>] =  $4 \times 10^{-4}$  M, [H<sub>2</sub>SO<sub>4</sub>] = 3.16 M, (a)  $k_1'^a = k_1' \times 10^5$  for glycine and L-alanine,  $k_1'^a = k_1' \times 10^4$  for L-leucine, (b)  $k_2'^b = k_2' \times 10^2$  for glycine and L-alanine: (—) alanine, T = 323 K, catalytic; (---) glycine, T = 313 K, catalytic; (▲) glycine, T = 313 K, noncatalytic; (■) alanine, T = 323 K, noncatalytic; (- - -) leucine, T = 303 K, noncatalytic.

**Table 4.** Effect of Mn(II) on the Reaction Rate ( $k_2'$ )<sup>a</sup>

[Mn(II)] (M)	$k_2' \times 10^2$ (M <sup>-1</sup> s <sup>-1</sup> ) <sup>b</sup>	
	Glycine	L-Alanine
0	47.00	40.33
0.0004	46.50	39.83
0.0008	45.33	37.83
0.0012	42.33	35.50
0.0016	39.50	34.58

<sup>a</sup>[KMnO<sub>4</sub>] =  $4 \times 10^{-4}$  M, [H<sub>2</sub>SO<sub>4</sub>] = 3.16 M, [amino acid] = 0.5 M, T = 313 K. <sup>b</sup>Error on k values is less than 1%.

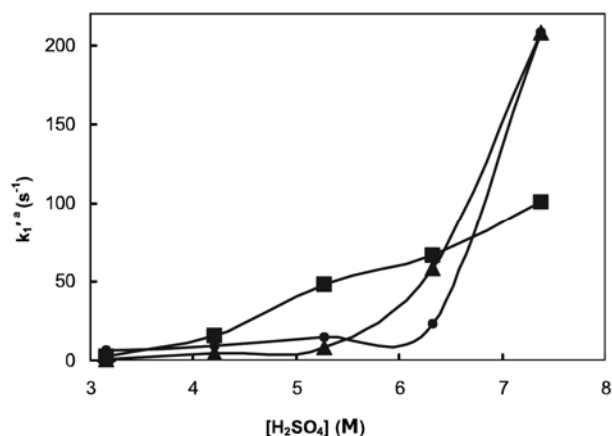
and the fact that the very slow reaction of Mn<sup>2+</sup> with MnO<sub>4</sub><sup>-</sup> [46-47] switches to a fast reaction when the amino acid is present, suggest that in the process of permanganate consumption some intermediate complex is probably formed between Mn<sup>2+</sup> and the amino acid [41-45].

## 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. These experiments show that the autocatalytic effect in the oxidation of glycine and L-alanine is destroyed at sulfuric acid concentrations higher than 4.5 M. As Fig. 6 indicates,  $k_1'$  increases when the acid concentration is raised. The range of 3-4 M sulfuric acid shows the least variation for  $k_1'$ . Thus, this concentration range was determined to be most appropriate for the rest of our kinetic studies.

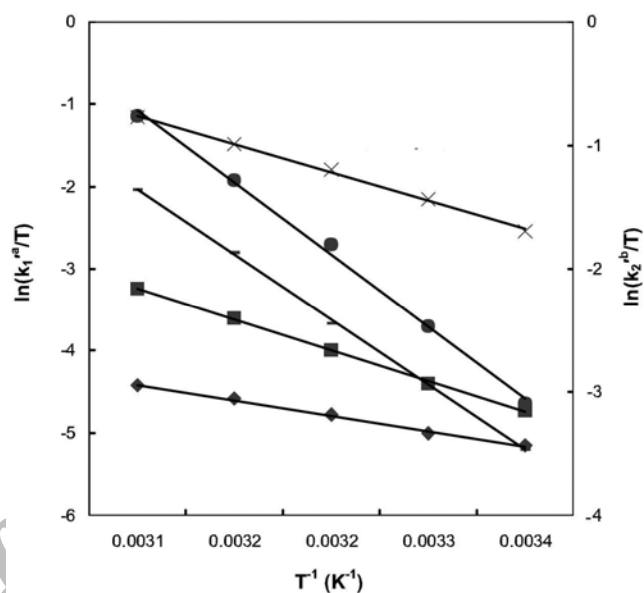
## Determination of Activation Parameters

In order to further justify the method determining the



**Fig. 6.** Effect of the sulfuric acid concentration on the uncatalyzed pseudo-order rate constants.  $[KMnO_4] = 4 \times 10^{-4}$  M,  $[glycine] = 0.6$  M,  $T = 308$  K,  $[L-alanine] = 0.3$  M,  $T = 323$  K,  $[L-leucine] = 0.1$  M,  $T = 298$  K,  $k_1'^a = k_1' \times 10^5$  for glycine and L-alanine,  $k_1'^a = k_1' \times 5000$  for L-leucine: (■) glycine, (●) alanine and (▲) leucine.

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 7 demonstrates the agreement of both  $k_1'$  and  $k_2'$  with the Eyring equation. The thermodynamic activation parameters, energy, enthalpy and entropy, are reported in Table 5.



**Fig. 7.** Eyring plots for the catalyzed and uncatalyzed processes.  $[KMnO_4] = 4 \times 10^{-4}$  M,  $[H_2SO_4] = 3.16$  M,  $[glycine] = 0.9$  M,  $[L-alanine] = 0.6$  M,  $[L-leucine] = 0.1$  M, (a)  $k_1'^a = k_1' \times 10^5$ , (b)  $k_2'^b = k_2' \times 100$ : (■) glycine, noncatalytic,  $R^2 = 9987$ ; (◆) alanine, noncatalytic,  $R^2 = 9953$ ; (×) leucine, noncatalytic,  $R^2 = 9989$ ; (●) glycine, catalytic,  $R^2 = 9982$  and (◼) alanine, catalytic,  $R^2 = 9991$ .

## Acrylonitrile Addition

The presence of free radicals as intermediates was confirmed by addition of acrylonitrile, which led to polymerization both in the presence and in the absence of manganese sulfate(II) [12].

## Reaction Mechanism

In agreement with the experimental results that have been presented and taking into account the previous literature, 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.

**Table 5.** Activation Parameters for the Uncatalyzed and Catalyzed Oxidation of Amino Acids<sup>a</sup>

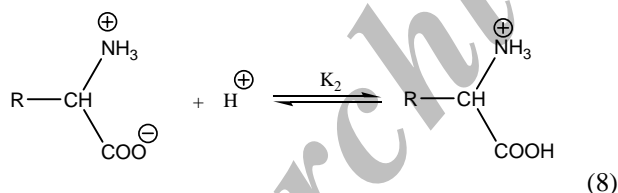
Activation parameter	Uncatalyzed process			Catalyzed process	
	Glycine <sup>b</sup>	L-Alanine <sup>c</sup>	L-Leucine <sup>d</sup>	Glycine <sup>b</sup>	L-Alanine <sup>c</sup>
$\Delta S^\ddagger (\text{J mol}^{-1} \text{ K}^{-1})$	$-134 \pm 5$	$-239 \pm 3$	$-132 \pm 3$	$47 \pm 7$	$8 \pm 5$
$\Delta H^\ddagger (\text{kJ mol}^{-1})$	$59.2 \pm 1.5$	$28.9 \pm 0.9$	$54.3 \pm 1.0$	$91.9 \pm 2.2$	$81.1 \pm 1.6$
$E_a (\text{kJ mol}^{-1})$	$61.8 \pm 1.5$	$31.4 \pm 0.9$	$56.9 \pm 1.0$	$94.7 \pm 1.9$	$83.7 \pm 1.5$

<sup>a</sup>[KMnO<sub>4</sub>] =  $4 \times 10^{-4}$  M, [H<sub>2</sub>SO<sub>4</sub>] = 3.16 M. <sup>b</sup>[Glycine] = 0.9 M, <sup>c</sup>[L-Alanine] = 0.6 M. <sup>d</sup>[L-Leucine] = 0.1 M.

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 with the increasing acid concentration suggests the formation of a more powerful oxidant, namely permanganic acid, by the following equilibrium:

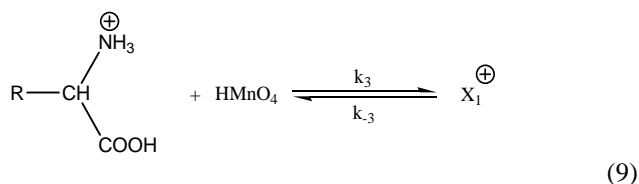


At the high acid concentration used, protonation of the zwitterionic form of the amino acid gives

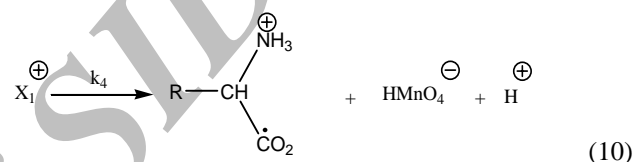


A mechanism consistent with the observed kinetic data includes the following steps.

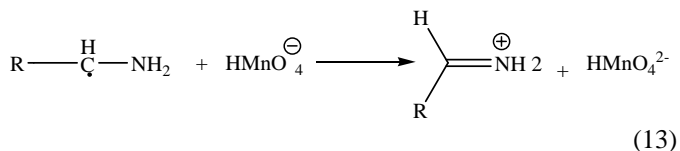
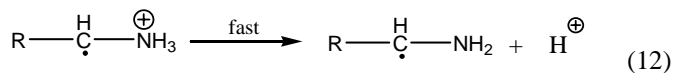
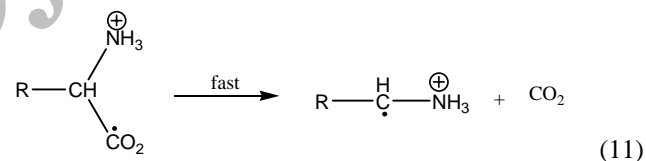
In agreement with the experimental results, the formation of an additional complex between the permanganic acid and the cationic form of the amino acid is proposed [11,12,45], as:



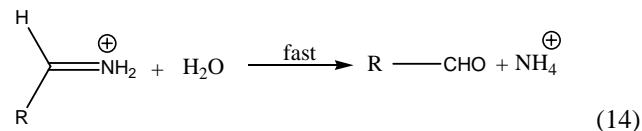
This complex may rupture according to the Eq. (10) as a rate determining step:



Based on the radical involvement in the reaction mechanism, the iminium cation [41-45] is possibly formed *via* three steps:



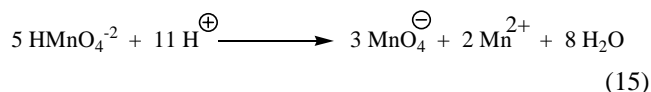
By hydrolysis of the iminium cation, the corresponding aldehyde is obtained [44], as:



Knowing the fact that the species Mn(V) is very unstable in strong acidic media, it will be converted to Mn(II) and Mn(VII) by means of rapid disproportionation steps, which are included in the following equation:



## Conclusive Evidences for Delayed Autocatalytic Behavior of Mn(II) Ions



Multiplying Eqs. (7-14) by a factor of five and then summing them with Eq. (15) results in the overall reaction and satisfies the stoichiometry. In agreement with the above scheme, assuming a steady-state approximation for  $\text{X}_1^+$ , the rate equation obtained for the uncatalyzed process is:

$$\frac{-d[\text{Mn(VII)}]}{dt} = k_1' [\text{Mn(VII)}] \quad (16)$$

$$k_1' = \frac{\alpha_0 [\text{H}^+]^2 [\text{amino acid}]_t}{\beta_0 (1 + \beta_1 [\text{H}^+] + \beta_2 [\text{H}^+]^2) + \alpha_1 [\text{H}^+]^2 [\text{Mn(VII)}]} \quad (17)$$

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

$$\alpha_0 = K_1 K_2 k_3 k_4$$

$$\alpha_1 = K_1 K_2 k_3$$

$$\beta_0 = k_{-3} + k_4$$

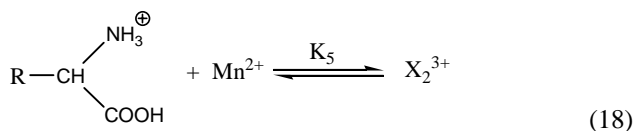
$$\beta_1 = K_1 + K_2$$

$$\beta_2 = K_1 K_2$$

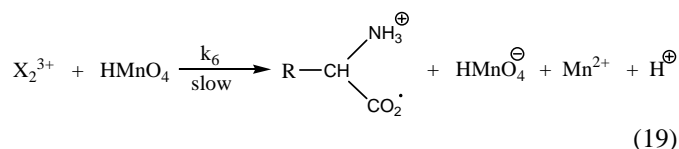
The rate law obtained above corresponds to the mechanism that explains the observed experimental behavior: the first-order reaction with respect to both permanganate and the amino acid and the change in  $k_1'$ , the uncatalyzed pseudo-order rate constant, when the permanganate concentration varies.

### Reaction Mechanism for the Catalyzed Process

Addition of  $\text{Mn}^{2+}$  ions led to an increase in the reaction rate, while the evidence presented also suggests that an adduct might be formed between  $\text{Mn}^{2+}$  and the protonated amino acid, in a fast step before it is oxidized by permanganic acid in a slow step [27-28].



As the rate-determining step, slow attack of permanganic acid on complexes has been proposed [40-41], as:



The remaining steps, leading to the final products, resemble those presented for the uncatalyzed pathway above. Again, multiplying Eqs. (7, 8, 18, 19, 11-14) by a factor of five and summing them up with Eq. (15) results in the overall reaction with the correct stoichiometry. Assuming a steady-state approximation for the  $\text{X}_2^{3+}$  complex in the above mechanism, the following rate equation [41] is derived:

$$\frac{-d[\text{Mn(VII)}]}{dt} = k_2' [\text{Mn}^{+2}] [\text{Mn(VII)}] \quad (20)$$

$$k_2' = \frac{\delta_0 [\text{H}^+]^2 [\text{amino acid}]_t}{1 + \beta_1 [\text{H}^+] + \beta_2 [\text{H}^+]^2 + \delta_1 [\text{H}^+] [\text{Mn}^{+2}] + \delta_2 [\text{H}^+]^2 [\text{Mn}^{+2}]} \quad (21)$$

where the notation employed in Eq. (17) is conserved, and in addition:

$$\delta_0 = K_1 K_2 K_5 k_6$$

$$\delta_1 = K_1 K_2$$

$$\delta_2 = K_1 K_2 K_5$$

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  $\text{Mn}^{2+}$  ions, permanganate ions, and the amino acid and inverse dependence of  $k_2'$  on  $\text{Mn}^{2+}$  ion concentrations, as shown in the  $k_2'$  expression.

As stated elsewhere, in order to have a steady state concentration of the  $\text{X}_2^{3+}$  complex, it is necessary that a given ratio of  $\text{Mn}^{2+}$  to amino acid exists in the medium. It is also well apparent that in order to achieve a rate equation for a particular reaction, a steady-state concentration of intermediate(s) due to some equilibrium steps in the reaction path must be generated [48,49]. Since a steady-state concentration of the  $\text{X}_2^{3+}$  complex can be considered only at a

certain ratio of  $Mn^{2+}$  to amino acid, the autocatalytic equation can not be applied until such ratio is created. Based on the above discussion, it can be judged that the autocatalytic effects can be ignored at the early stages of the reaction of L-leucine, for example, although it can have perturbing influences on the non-catalytic stage for some amino acids. This fact led us to evaluate not only  $k_2'$ , but also  $k_1'$ , more accurately from the data obtained for the autocatalytic stage of the reaction for glycine and L-alanine.

Owing to the complexity of the proposed mechanism, the evaluation of the values of the rate constants corresponding to the 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 permanganic oxidation process of glycine, L-alanine and L-leucine in strong acid media were investigated using a spectrophotometric technique. Upon investigating rate-time curves it was concluded that, after passing a determined portion of the reaction time for glycine and L-alanine, a parallel reaction is encountered. 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. By increasing the concentration of  $Mn(II)$ , observing the increase in reaction rates and fitting the kinetic data into appropriate rate expressions, it is determined that this species is the autocatalytic agent. For the autocatalytic activity to initiate its action, a critical concentration of the mentioned species is required. This critical concentration, in addition to the nature of the amino acid used, depends on the amount of sulfuric acid present in the matrix.

It has been shown that, in order to have a steady-state concentration of the  $X_2^{3+}$  complex, it is necessary that a given ratio of  $Mn^{2+}$  to amino acid exist in the medium. It is also clear that, in order to achieve a rate equation for a particular reaction, a steady-state concentration of intermediate(s) due to

some equilibrium steps in the reaction path must be generated. A steady-state concentration of the  $X_2^{3+}$  moiety can only be considered at a certain ratio of  $Mn^{2+}$  to amino acid; therefore, the autocatalytic equation can not be applied until such ratio is created. In most of the research carried out on this particular subject, the autocatalytic effect has neither been investigated nor reported. This may be due to the "critical concentration" phenomenon, which is required for the initiation of the delayed autocatalytic effect.

The correspondence of the pseudo-order rate constants of the catalytic and noncatalytic pathways to the Eyring law presented in this work verifies this claim.

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