# Kinetic Study of the Oxidation of L-Phenylalanine by Potassium Permanganate in Acid Medium

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#### Abstract

The kinetics of permanganate oxidation of L-phenylalanine in acid medium at a constant ionic strength has been investigated spectrophotometrically. An autocatalytic reaction was observed being autocatalyzed by a soluble form of Mn(IV).

The reaction appears to involve a parallel consecutive reaction process in which Mn(IV) is formed as an intermediate and Mn(II) as a reaction product. A tentative mechanism consistent with the kinetics is discussed. © 1995 John Wiley & Sons, Inc.

#### Introduction

Permanganate ion has several advantages as an analytical reagent [1]. Above all, it is a strong, vividly colored oxidant, serving as its own indicator. Though permanganate is extensively used as an oxidizing agent, the kinetics of oxidation of  $\propto$ -amino acids in a moderately acid medium have received little attention [2–8]. Also, the oxidation of  $\propto$ -amino acids by permanganate ion has been studied in perchloric and sulphuric medium [9–16]. A careful view of these articles indicates that permanganate oxidation of L-phenylalanine (Ph-A) has been investigated in strong acid medium [10,15] and in a neutral medium [17–18] but no studies have been found in moderate acid medium.

Hence, the aim of this work is to study the kinetics of the oxidation of Lphenylalanine by permanganate ion at pH about 2.00 in order to verify its autocatalytic character and to gain a better understanding of the autocatalytic oxidation mechanism.

# **Experimental**

The reagents used were potassium permanganate, potassium chloride, manganese(II) sulphate, and L-phenylalanine from Merck p.a., and phosphoric acid and potassium dihydrogen phosphate from Panreac p.a. All the experiments were performed in aqueous media (water twice distilled). The experimental conditions were of the order of  $10^{-4}$  mol dm<sup>-3</sup> for permanganate ion and  $10^{-2}$  mol dm<sup>-3</sup> for phenylalanine, in aqueous solution of buffer mixtures of phosphoric acid and potassium dihydrogen phosphate (ionic strength 0.05 mol dm<sup>-3</sup>).

Kinetic runs were followed spectrophotometrically using a Spectronic 1201 (200-800 nm). The progress of the reaction was followed at 525 nm and 418 nm.

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The reactor was a special quartz cell (with 1 cm of optic pathway), supplied with an internal system of thermostation connected to a conventional thermostat, Frigiter model, which ensures temperature stability during the reaction runs with an error of  $\pm 0.05$  °C.

The pH of solutions was measured by a Radiometer 51 instrument.

Under these conditions a previous study of the stoichiometry of the reaction by conventional methods [19,20] allowed us to use the following equation:

(1) 
$$5C_6H_5CH_2CH(NH_2) + CO_2H + 2MnO_4^- + 6H^+ \longrightarrow$$
  
 $2Mn^{+2} + 5NH_3 + 5CO_2 + 3H_2O + 5C_6H_5CH_2CHO$ 

### Results

The plot of  $A_{525}^{cor}$  vs. time (Fig. 1(a)), shows a sigmoid profile which is characteristic of autocatalytic reactions. As it is known [21] not only permanganate ion absorbs at 525 nm, but also Mn(IV). Under these circumstances, we must correct the absorbance values in order to determine the true values of permanganate concentration. With the help of a correction factor (R\*) [5,8], we can estimate the absorbance of Mn(IV) at 525 nm. In the latter stages of the reaction, the ratio between  $A_{525}$  and  $A_{418}$  becomes constant, and can be taken as a measure of the absorbance to Mn(IV) at 525 nm using

(2) 
$$A_{525}^{cor} = A_{525}^{obs} - A_{418}^{obs} R^{\prime}$$

where  $R^* = (A_{525}^{obs}/A_{428}^{obs})_{inf}$ .

The absorbance at 418 nm initially rises then falls and finally, tends to become zero (Fig. 1(b)). It is well known that the absorbance at 418 nm is a measure of Mn(IV) [22–24] produced during the reaction. Plots of ln A<sub>418</sub> vs. time or A<sub>525</sub> vs. A<sub>418</sub> are nonlinear, a result which has to be taken as a fact that Mn(IV) is not the end product.



Figure 1. Absorbance at (a) 525 nm and (b) 418 nm vs. time for the oxidation of L-phenylalanine (0.04 M) by potassium permanganate ( $4 \times 10^{-4}$ M) at 40°C, pH 2.3, and ionic strength 0.05 M.

Moreover, as shown in Figure 2 for a typical kinetic run, all the experiments displayed a bell-shaped profile when the reaction ate is plotted against time. The rate values were determined from the experimental data as the result of minus the derivative of the permanganate concentration with respect to time. It is clear that, if the rate presents both an acceleration and a decay period, a product concentration against time plot is necessarily S-shaped, when the reaction is autocatalytic [25].

All these findings are consistent with the fact that the reaction is autocatalyzed by Mn(IV), Mn(II) is a reaction product.

A differential rate law can be used for an autocatalytic reaction is as follows:

(3) 
$$-dc/dt = k_1c + k_2c(c_0 - c)$$

its associated integrate rate law is:

(4) 
$$\ln\left[(k_1 + k_2c_0 - k_2c)/c\right] = \ln\left(k_1/c_0\right) + (k_1 + k_2c_0)t$$

where c and  $c_0$  are the concentrations of permanganate ion at time t and at the beginning of the reaction, while  $k_1$  and  $k_2$  are the pseudo-rate constants of the non-catalytic and catalytic pathways, respectively. For the simultaneous determinations of pseudo-rate constants  $k_1$  and  $k_2$ , an iterative method [26,27] was applied. A plot of the left-hand side of eq. (49) against time then yields a straight line (see Fig. 3).

The values of the rate constants corresponding to several initial permanganate concentrations have been compiled in Table I. We can see that both  $k_1$  and  $k_2$  are independent of the initial permanganate concentration.

The dependence of the rate constants on the phenylalanine concentration is shown in Figure 4 (a); we can see that  $1/k_1$  against 1/[Ph-A] plot is linear. These indications suggest that the oxidation reaction involves an intermediate complex formation between substrate phenylalanine and oxidant [10,28],  $k = 2.8 \times 10^{-4}$  (rate constant of complex decomposition) and K = 10.59 (equilibrium constant of complex).



Figure 2. Reaction ate vs. time plot for the oxidation of L-phenylalanine (0.04 M) by potassium permanganate ( $4 \times 10^{-4}$  M) at 40°C, pH 2.3, and ionic strength 0.05 M.



Figure 3. Integral rate-law plot for the oxidation of L-phenylalanine (0.04 M) by potassium permanganate ( $4 \times 10^{-4}$  M) at 40°C, pH 2.3, and ionic strength 0.05 M.

On the other hand Figure 4 (b) shows that for  $1/k_2$  vs. 1/[Ph-A] Langmuir isotherm is fulfilled, which parameters are K = 8.40 and  $k_0MS = 10.18$ , where K is the equilibrium constant of adsorption, M is the molar mass, and S is the specific surface of absorption.

Additions of potassium chloride to the solution do not significantly affect the rate constant, so both  $k_1$  and  $k_2$  are independent of the ionic strength of the medium. However, when the concentration of  $KH_2PO_4$  and  $H_3PO_4$  was changed while keeping the pH of solution constant, the Brönsted-Bjerrum equation [29] is obeyed for  $k_2$ .

(5) 
$$\log k_2 = 0.53 + 0.84\sqrt{I}/(1+\sqrt{I})$$
  $r_{xy} = 0.9999$ 

The dependence of both  $k_1$  and  $k_2$  on temperature follows the Arrhenius equation (Fig. 5), the corresponding activation energies are  $E_{\rm al} = 42.88 \text{ kJ/mol}$  and  $E_{\rm a2} = 79.60 \text{ kJ/mol}$ , respectively.

A series of experiments has been carried out to determine the dependence of the rate constants  $k_1$  and  $k_2$  on the pH of the medium. Table II shows the results obtained.

$10^4 [KMnO_4]/M$	$10^5 k_1 / \mathrm{s}^{-1}$	$k_2/{ m M}^{-1}~{ m s}^{-1}$
3	7.9	4.6
4	8.0	4.7
5	7.9	4.5
6	7.9	4.6
7	8.0	4.6

TABLE I. Rate constants at several initial permanganate concentrations. L-Phenylalanine = 0.04 M; I = 0.05; pH = 2.3, and T = 40 °C.



Figure 4. Dependence of the rate constants on the reductant concentration for the oxidation of L-phenylalanine by potassium permanganate (4  $\times$  10<sup>-4</sup> M) at 40°C, pH 2.3, and ionic strength 0.05 M.



Figure 5. Arrhenius plots for the oxidation of L-phenylalanine (0.04 M) by potassium permanganate (4  $\times$  10<sup>-4</sup> M) at pH 2.3 and ionic strength 0.05 M.

pH	$10^5 k_1/{ m s}^{-1}$	$k_2/{ m M}^{-1}~{ m s}^{-1}$	
1.84	8.1	5.53	
1.93	8.0	5.36	
2.01	8.0	5.25	
2.18	8.1	4.96	
2.30	8.0	4.70	
2.43	8.0	4.45	
2.63	8.0	4.16	
2.81	8.1	3.91	

TABLE II. pH influence of the rate constants. [KMnO<sub>4</sub>] =  $4 \times 10^{-4}$  M; [L-phenylalanine] = 0.04 M; and  $T = 40^{\circ}$ C.

It can be seen that  $k_1$  remains constant and  $k_2$  deceases linearly when the pH is increased.

On the other hand, some experiments were performed in the presence of Mn(II) sulphate, according to the study realized by Perez-Benito et al. [30]. It was observed that  $k_1$  increases when Mn(II) concentration rises but  $k_2$  remains constant (Table III). As shown in Figure 6 the profile is the same both in the presence and absence of Mn<sup>+2</sup>. Equation (6) indicates that there exists a linear relationship between log  $(k_1 - k_1^0)$  and log [Mn<sup>+2</sup>]:

(6) 
$$\log(k_1 - k_1^0) = 0.24 + 1.01 \log[\text{Mn}^{+2}]$$
  $r_{xy} = 0.9999$ 

where  $k_1^0$  (4.9 × 10<sup>-5</sup>) is the value of the corresponding rate constant in the absence of Mn<sup>+2</sup>. These findings mean that Mn<sup>+2</sup> ion is catalyst of the permanganatephenylalanine reaction, it is well-known that the ability of this ion to react with permanganate ion according to the following stoichiometry (Guyard's reaction) is [31]:

(7)  $2MnO_4^- + 3Mn^{+2} + 2H_2O \implies 5MnO_2 + 4H^+$ 

# DISCUSSION

The experimental rate equation points out that the phenylalanine oxidation involves two parallel reactions, only one of which produces Mn(IV) which acts as an autocatalyst. In a number of preceding investigations [8,32,33] a homogeneous pathway is considered to be the key for Mn(IV)-catalyzed process. Both processes should lead to a first-order with respect to permanganate.

Similar to the permanganate oxidation of L-alanine and glycine [34,35], two parallel mechanisms, have been considered here as interdependent.

TABLE III. Rate constants at several initial Manganese (II) concentrations. [KMnO<sub>4</sub>] =  $4 \times 10^{-4}$  M; [L-phenylalanine] = 0.02 M; I = 0.05 M; pH = 2.3; and T = 40°C.

$10^4 \; [{\rm Mn^{+2}}]/{ m M}$	$10^4 k_1/{ m s}^{-1}$	$k_2/{ m M}^{-1}~{ m s}^{-1}$
1	1.45	3.00
2	2.97	3.00
3	4.46	3.00
4	5.97	3.00
5	7.50	3.00



Figure 6. Absorbance at 525 nm vs. time for the oxidation of L-phenylalanine (0.02 M) by potassium permanganate (4  $10^{-4}$  M) at 40°C and pH 2.3. Manganese (II) concentration: (a) 0.0; (b)  $0.5 \times 10^{-4}$ ; (c)  $1 \times 10^{-4}$ ; and (d)  $2 \times 10^{-4}$  M.

L-phenylalanine amino acid at such high hydrogen ion concentration is assumed to be completely protonated.

Noncatalyzed Process

(8) 
$$C_6H_5CH_2CH(NH_3)^+CO_2H + Mn(VII) \iff C_6H_5CH_2CHMn(VII)NH_3CO_2H C_1$$

(9) 
$$C_1 \xrightarrow{\text{slow}} C_6H_5CH_2CHNH_3[HMn(VI)]CO_2^{-1}$$

(see ref. [36] for intramolecular electron transfer to  $Mn(\mbox{VII}))$ 

(10) 
$$C_6H_5CH_2CHNH_3[HMn(VI)]CO_2^+ + H_2O \xrightarrow{fast} CO_2 + C_6H_5CH_2CHNH_3[H_2Mn(V)]OH$$

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(11) 
$$C_6H_5CH_2CHNH_3[H_2Mn(V)]OH + C_6H_5CH_2CH(NH_3)^+CO_2H + H^+ \xrightarrow{fast} CO_2 + 2C_6H_5CH_2COH + 2NH_4^+ + Mn^{+3} + 3H_2OH^{+1}$$

(12) 
$$C_6H_5CH_2CH(NH_3)^+CO_2H + 2Mn^{+3} + H_2O \xrightarrow{\text{tast}} 2Mn^{+2} + C_6H_5CH_2COH + NH_4^+ + CO_2 + 2H^+$$

According to those mechanisms the rate of disappearance of permanganate ion through the noncatalytic pathway is:

$$r_1 = k_9[\mathrm{C}_1]$$

the concentration of C1 compound obtained from the formation equilibrium is:

$$[C_1] = \frac{K_8[Ph-A][Mn(VII)]}{1 + K_8[Ph-A]}$$

In agreement with these considerations, the calculated reaction rate is:

$$r_1 = rac{k_9 K_8 [\text{Ph-A}] [\text{Mn}(\text{VII})]}{1 + K_8 [\text{Ph-A}]}$$

where

$$\frac{k_9K_8[\text{Ph-A}]}{1+K_8[\text{Ph-A}]}$$

is identified with the pseudoconstant of the noncatalytic pathway,  $k_1$ .

When Mn(VI) produced is not complexed, the alternative to the step (10) is the reduction of Mn(VI) with the amino acid. This process leads to Mn(IV) species, the key for the catalyzed mechanism.

(13) 
$$C_1 \longrightarrow HMn(VI) + C_6H_5CH_2CHNH_3CO_2^{-1}$$

Autocatalyzed Process

(13) 
$$\operatorname{HMn}(\operatorname{VI}) + \operatorname{C}_{6}\operatorname{H}_{5}\operatorname{CH}_{2}\operatorname{CH}(\operatorname{NH}_{3})^{+}\operatorname{CO}_{2}\operatorname{H} + \operatorname{H}_{2}\operatorname{O} \longrightarrow \ldots \longrightarrow \operatorname{Mn}(\operatorname{IV})$$

It has been assumed [8,10,32,33] that protonated amino acid form a complex with  $MnO_4^-$  species. The results obtained (when the dependence of the rate constants on the phenylalanine concentration has been studied) support this idea.

The decomposition of this complex appears to be rate-determining. Moreover, it has been reported that carbon dioxide, aldehydes, and ammonium [5,9,10,37,38] are all obtained from the permanganate oxidation of amino acids.

Furthermore, Mn(VI) is unstable in acid medium and is rapidly reduced to Mn(IV). The formed Mn(IV) is a reactive intermediate. At the moment this intermediate is formed the catalytic pathway is involved. This Mn(IV) is the soluble form of colloidal manganese dioxide, would be stabilized in solution by the existence of bonds  $MnO_2 - H_2PO_4^{-1}$  on their surface [39,40]. In the first place, the phenylalanine is absorbed onto the colloidal manganese dioxide [20]. This fact is confirmed by the experimental findings  $(1/k_2 \text{ vs. } 1/[Phe]$  plot is lineal, and Langmuir isotherm is fulfilled). Therefore, we have assumed [39] that the catalytic process occurs by means of a reaction between this absorbate (formed by Mn(IV) an L-phenylalanine) and the permanganate ion, this adsorbate has an apparent negative charge due to the stabilization of Mn(IV) by  $H_2PO_4^{-1}$  ions. The collision between two negative ions is confirmed by the Brönsted-Bjerrum equation.

The reaction rate for the catalyzed process shows the same formal dependence (kinetic orders) with respect to the concentration of Mn(VII) species as for noncatalytic process. Hence, we can conclude that from the absorbate genesis the catalyzed process follows a sequence which is similar to that steps of the noncatalytic reaction.

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