

## PERMANGANATE OXIDATION OF L-ALANINE IN ACIDIC SOLVENT: AUTOCATALYSIS BY INTERMEDIATE Mn(IV) SPECIES

Maria J. INSAUSTI, Fernando MATA-PEREZ and Maria P. ALVAREZ-MACHO

*Departamento de Química-Física,*

*Facultad Ciencias, Universidad de Valladolid, 47005 Valladolid, Spain*

Received January 18, 1993

Accepted May 11, 1993

The kinetics of L-alanine oxidation by permanganate ion in buffer solutions at pH 2.2 have been studied. Both spectrophotometric and kinetic evidence is provided for the existence of an intermediate Mn(IV) species of colloidal nature. An autocatalytic course of the oxidation is discussed.

Among oxidizing agents used in the laboratory, potassium permanganate had been frequently preferred<sup>1</sup>. This gave rise to numerous studies on the behaviour of this ion as an oxidizing agent.

In view of the important role of amino acids in metabolism, kinetic studies on permanganate oxidation of a few amino acids have also been carried out. Thus, it has been found that the oxidation of alanine in strongly acidic solvents<sup>2-5</sup> is catalyzed by Mn(II) species. On the other hand, within the range of physiological pH (that is between pH 6 – 8), it has been shown that the same reaction is autocatalyzed by Mn(IV) species, which is temporarily soluble, as long as phosphate ions are present in the solvent<sup>6-15</sup>. However, opinions are not unanimous in this respect. So, for instance, other workers<sup>6</sup> refer to Mn(III) as the autocatalyst for the permanganate oxidation of phenylalanine.

However, there are no reports on permanganate oxidation of L-alanine in the acid pH region. This led us to study the oxidation at pH about 2.00. The aim was to describe kinetics of the reaction with respect to its possible autocatalytic character, and especially to elucidate the nature of the catalyst.

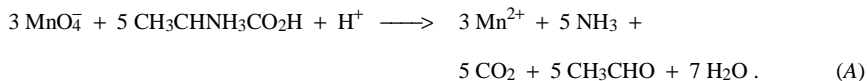
### EXPERIMENTAL

The reagents used were potassium permanganate, potassium chloride and L-alanine from Merck (p.a.), phosphoric acid and potassium dihydrogen phosphate from Panreac (p.a.).

*Kinetic measurements.* Kinetic runs were followed spectrophotometrically using a Spectronic 1201 instrument. The reactor was a special quartz cell (with 1 cm of optical pathway) provided with an internal temperature control system connected to a conventional thermostat (Frigiter model), which ensured temperature stability during the runs within 0.05 °C. The measurements were carried out at 40 °C.

Radiometer 51 pH-meter provided with a combined electrode was used to measure pH. In all the experiments pH was set to 2.2. Reagent concentrations were  $4 \cdot 10^{-4} \text{ mol dm}^{-3}$  for the permanganate and  $5 \cdot 10^{-2} \text{ mol dm}^{-3}$  for L-alanine in an aqueous phosphoric acid-potassium dihydrogen phosphate buffer (ionic strength  $0.05 \text{ mol dm}^{-3}$ ).

*Stoichiometry.* The stoichiometry of the reaction was determined by the analysis of both  $\text{KMnO}_4$  and  $\text{CH}_3\text{CHO}$  species. Permanganate was determined by quenching the known amount of the reaction mixture with the known excess of  $\text{Fe}^{2+}$ , followed by titration of the unreacted  $\text{Fe}^{2+}$  against the standard  $\text{Ce}^{4+}$ . The aldehyde was determined colorimetrically, using chromotropic acid. The  $\text{KMnO}_4/\text{CH}_3\text{CHO}$  ratio was found to be about 3 : 5. Hence, the stoichiometry is as follows:



## RESULTS AND DISCUSSION

### KINETICS

UV spectra (Figs 1 and 2) of the reaction mixtures clearly show a decrease of the absorbance at 525 nm during the reaction. Furthermore, the absorbance at 418 nm first rises, then falls, becoming zero in later stages.

In this range of the UV-VIS spectrum, a number of different oxidation states of manganese show optical absorption<sup>1,16,17</sup>. First, proofs have been given<sup>18,19</sup> that the band at 418 nm is characteristic of Mn(IV) species. It is possible that the formation of both Mn(IV) and Mn(III) species takes place from a transient compound of manganese,

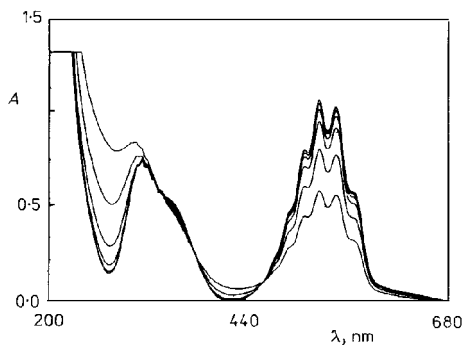


FIG. 1

Successive scans at 8 min intervals for the reduction of permanganate ion ( $4 \cdot 10^{-4} \text{ mol dm}^{-3}$ ) by L-alanine ( $0.05 \text{ mol dm}^{-3}$ ) at  $40^\circ\text{C}$ , pH 2.2 and ionic strength  $0.05 \text{ mol dm}^{-3}$

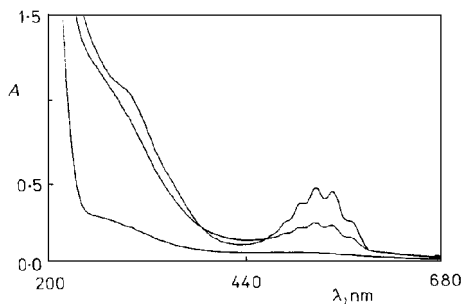


FIG. 2

Successive scans at the end of the reduction of permanganate ion ( $4 \cdot 10^{-4} \text{ mol dm}^{-3}$ ) by L-alanine ( $0.05 \text{ mol dm}^{-3}$ ) at  $40^\circ\text{C}$ , pH 2.2 and ionic strength  $0.05 \text{ mol dm}^{-3}$

such as Mn(VI), which perhaps is formed during the observed induction period. In fact, the spectra of the reaction mixtures (Fig. 1) are consistent with those of both Mn(VI) and Mn(VII) species<sup>1</sup> and support the above assumption. However, there is no evidence that under our experimental conditions Mn(III) exists as an unstable reaction intermediate. This species occurs only in strongly acidic media<sup>20</sup>. So, when the acidity decreases, Mn(III) disproportionates into Mn(IV) and the product<sup>21</sup>, Mn(II).

On the contrary, it is well known that the absorbance at 418 nm,  $A_{418}$ , is a measure of the Mn(IV) produced during the reaction. However, both the plot of  $\ln A_{418}$  vs time and the plot of  $A_{525}$  vs  $A_{418}$  are not linear. These findings exclude that Mn(IV) is the reaction product. On the other hand, the plot of  $A_{525}$  vs time,  $t$  (Fig. 3) has a sigmoid profile, which is characteristic of autocatalytic reactions<sup>22</sup>. Besides, the values of  $A_{418}$  vs  $t$  (Fig. 4, curve 1) first increase, reaching a maximum value, and then fall rapidly to zero. A similar result (a bell profile curve) was found for the experimental reaction rate vs time dependence (Fig. 4, curve 2). Moreover, the maximum values of both the reaction rate and the absorbance at 418 nm,  $A_{418}$ , correspond to the inflection point of the  $A_{525}$  vs time plots (Fig. 3). All these findings are consistent with the assumption that the reaction is autocatalyzed by Mn(IV) species. On the other hand, a detailed analysis of curve 2 in Fig. 4 reveals the existence of an induction period. Comparison of curves 1

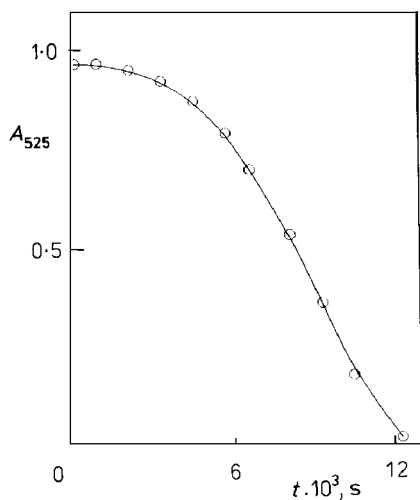


FIG. 3

Absorbance at 525 nm vs time for the oxidation of L-alanine ( $0.05 \text{ mol dm}^{-3}$ ) by potassium permanganate ( $4 \cdot 10^{-4} \text{ mol dm}^{-3}$ ) at  $40^\circ\text{C}$ , pH 2.2 and ionic strength  $0.05 \text{ mol dm}^{-3}$

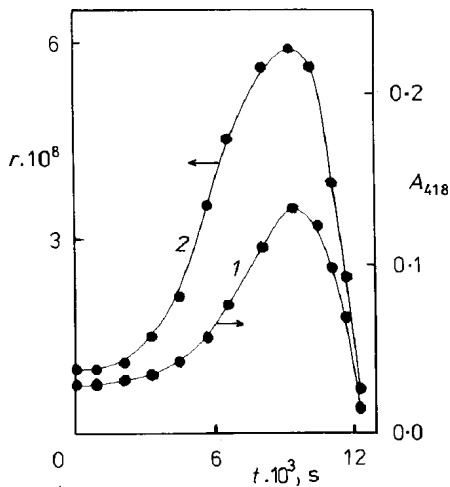


FIG. 4

Absorbance at 418 nm vs time (1) and reaction rate vs time ( $r$ ,  $\text{mol dm}^{-3} \text{ s}^{-1}$ ) (2). Permanganate concentration  $4 \cdot 10^{-4} \text{ mol dm}^{-3}$ , L-alanine concentration  $0.05 \text{ mol dm}^{-3}$ ,  $40^\circ\text{C}$ , pH 2.2 and ionic strength  $0.055 \text{ mol dm}^{-3}$

and 2 (Fig. 4) shows that for the induction period the absorption at 418 nm remains almost constant.

The induction period is very sensitive to changes in the concentration of the equimolar  $\text{H}_3\text{PO}_4\text{-H}_2\text{KPO}_4$  mixture when the other experimental conditions remain constant. The analysis of Fig. 5 reveals that Mn(IV) is a soluble species longer to appear. Its concentration decreases (as reflected in the drop of the maximum absorption at 418 nm) as the concentration of  $\text{H}_3\text{PO}_4\text{-H}_2\text{KPO}_4$  increases. A similar effect of the phosphate buffer concentration has been found<sup>23,24</sup> also for neutral solvents (pH from 6 to 8). However, in those cases the colloidal nature of Mn(IV) species was proved.

In spite of its soluble nature, for the present acidity conditions Mn(IV) species shows the characteristic behaviour of colloids<sup>25,26</sup>. Indeed, at the moment when Mn(IV) species is detectable at 418 nm (Fig. 4, curve 2), the log plot of the absorbance against wavelength gives the straight line with the slope  $-3.90$  which is very close to the theoretical value of Rayleigh's equation (1)

$$\log A = \log (128 \pi^5 \alpha^2 c N l / 3M) - 4 \log \lambda, \quad (1)$$

where  $A$  absorbance of colloid solution,  $\alpha$  polarizability of colloid particles in  $\text{m}^3$ ,  $c$  concentration in  $\text{kg m}^{-3}$ ,  $N$  Avogadro's number,  $l$  length of the cell containing the solution in m,  $M$  statistical molar mass of colloid particles in  $\text{kg mol}^{-1}$  and  $\lambda$  is wavelength in nm.

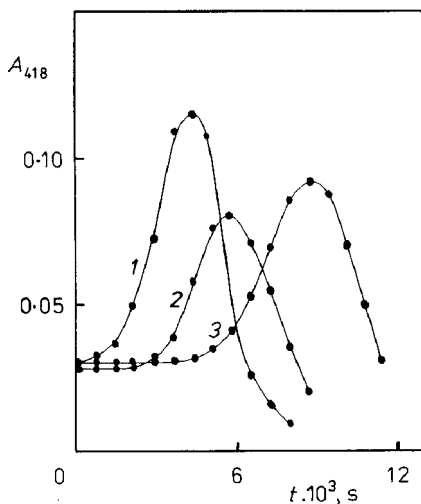


FIG. 5

Absorbance at 418 nm vs time for the oxidation of L-alanine ( $0.5 \text{ mol dm}^{-3}$ ) by permanganate ion ( $4 \cdot 10^{-4} \text{ mol dm}^{-3}$ ) at  $40^\circ\text{C}$ , pH 2.2. Ionic strength: 1 0.05, 2 0.15 and 3  $0.25 \text{ mol dm}^{-3}$

The value of the slope which is now obtained (3.90) is slightly lower than that found<sup>15</sup> for the permanganic oxidation of L-alanine at pH 6 – 9 (5.9). But in that case the colloid flocculated, which was not detected under our experimental conditions. On the contrary, the soluble form of Mn(IV) which was produced at pH 2.2 was finally converted into a Mn(II) species transparent to radiation at both 418 and 525 nm. Such a form of Mn(IV) has already been postulated<sup>27 – 33</sup> as an intermediate. On the other hand the reduction of Mn(IV) to Mn(II) is favoured by solvent acidity<sup>34</sup>. Therefore, the fact that the colloidal Mn(IV) species is converted to Mn(II) at pH 2.2 means only that in this solvent its reduction is fast, compared to its flocculation.

Because of the induction period (Fig. 4), the analysis of  $\ln A_{525}$  vs time plot is not conventional. For this reason, an alternative treatment proposed by Bazsa et al. was used<sup>35 – 37</sup>. Two parallel reaction pathways were considered, one being autocatalytic. For this model, time at the inflection point,  $t_i$ , on the absorbance vs time plots (which evidently corresponds to the maximum reaction rate) is given as:

$$t_i = \frac{p}{k_1 + k_2 [\text{Mn(IV)}]_0}, \quad (2)$$

where  $k_1$  and  $k_2$  are the specific non-catalytic and catalytic reaction rate, respectively,  $[\text{Mn(IV)}]_0$  is the initial catalyst concentration and  $p$  is a mathematical parameter. From our data the ratio  $k_1/k_2 = 1.03 \cdot 10^{-4}$ , which is of the same order of magnitude as that found for neutral solvents<sup>15</sup>.

The interrelation between  $t_i$  and Mn(IV) concentration permits to use the  $t_i$  parameter to study the influence of experimental variables on the autocatalyst, in a similar way to other systems<sup>35 – 37</sup>.

When the initial permanganate concentration was changed from 3 to  $7 \cdot 10^{-4}$  mol dm<sup>3</sup>, the  $t_i$  values have increased, leading to the following equation ( $r_{xy} = 0.9973$ )

$$\log t_i = 3.64 + 0.48 [\text{MnO}_4^-]_0. \quad (3)$$

However, an increase in the initial amino acid concentration results in a decrease of  $t_i$  values. There exists a linear relation ( $r_{xy} = 0.9932$ ) between  $\log t_i$  and  $\log [\text{alanine}]$ . This is consistent with Eq. (2) because both  $k_1$  and  $k_2$  are actually pseudofirst-order rate constants, depending upon the amino acid concentration ( $2$  to  $8 \cdot 10^{-4}$  mol dm<sup>-3</sup>). In fact, the slope found ( $-1.02$ ) confirms the first order of the oxidation with respect to the amino acid.

$$\log t_i = 0.69 - 1.02 \log [\text{alanine}] \quad (4)$$

The influence of the phosphates was also analyzed in detail (Table I). For these purposes, experiments were carried out by changing concentrations of both  $\text{KH}_2\text{PO}_4$  and  $\text{H}_3\text{PO}_4$  while their mutual ratio was maintained constant. Hence, pH is constant but the ionic strength of the solvent is varied. Figure 5 shows that the induction period increases on increasing the phosphate concentration. Nevertheless, this trend was not observed when, for a given phosphate concentration, the ionic strength of the solvent was controlled by the addition of KCl. This result points to that in the formation of the intermediate Mn(IV) species, the phosphates have a specific role similar to that suggested for neutral solvents<sup>13</sup>. On the other hand, the results obtained by using KCl (Table II) prove the existence of the salt kinetic effect under the conditions used.

The values of  $\ln t_i$  vs  $1/T$  (31 to 46 °C) fit well the Arrhenius equation, the activation energy being  $E_a = 72.2 \text{ kJ mol}^{-1}$ , ( $r_{xy} = 0.9998$ , Eq. (5)):

$$\ln t_i = -23.25 + 8636.55 / T. \quad (5)$$

TABLE I

Influence of the buffer concentrations on the inflection time  $t_i$ ;  $[\text{MnO}_4^-] = 4 \cdot 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{alanine}] = 0.05 \text{ mol dm}^{-3}$ , pH 2.2, 40 °C

$[\text{H}_3\text{PO}_4]$	$[\text{KH}_2\text{PO}_4]$	$t_i$ , min
0.043	0.05	77
0.087	0.10	85
0.130	0.15	89
0.174	0.20	101

TABLE II

Influence of the potassium chloride concentration on the inflection time  $t_i$ ;  $[\text{MnO}_4^-] = 4 \cdot 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{alanine}] = 0.05 \text{ mol dm}^{-3}$ ;  $\mu = 0.05 \text{ mol dm}^{-3}$ , pH 2.2, 40 °C

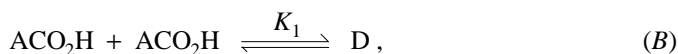
$[\text{KCl}]$	$t_i$ , min
0.0	77
0.1	85
0.2	93
0.3	97
0.4	109

## MECHANISM

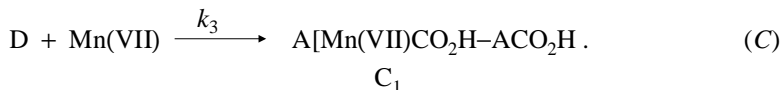
The experimental rate equation indicates that the oxidation of alanine involves two parallel reactions, of which only one produces Mn(IV) which acts as the catalyst. Both mechanisms should lead to the first-order dependence of the reaction rate on the alanine concentration.

In a number of preceding investigations<sup>19,33,38</sup>, homogeneous pathway has been considered as the key for the Mn(IV)-catalyzed mechanism (heterogeneous). Under the present experimental conditions, no findings contradicts this assumption. Hence, two parallel mechanisms have been considered as interdependent. This assumption is the main difference between our contribution and that by Hussain et al.<sup>38</sup> who proposed two quite independent routes.

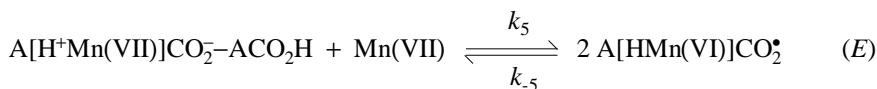
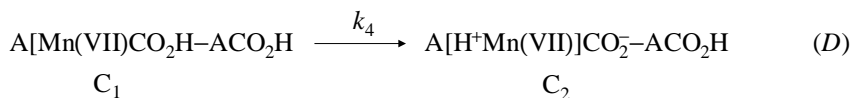
With this in mind, the following scheme can be proposed:

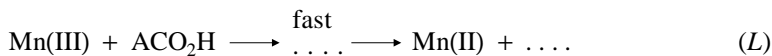
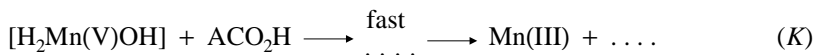
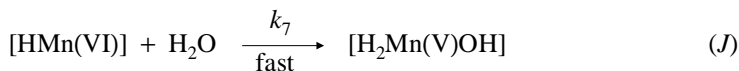
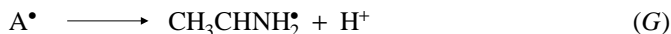
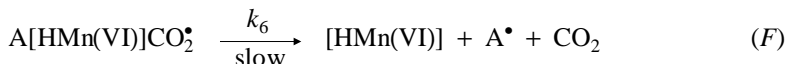


where A is  $\text{CH}_3\text{CH}(\text{NH}_3)$



We believe that the presence of the dimeric species D is justified due to the existence of hydrogen bonding between alanine molecules. On the other hand, it has been assumed<sup>39</sup> that amino acid molecules form a complex with Mn(VII) species. In opinion of Hussain et al.<sup>38</sup>, the formation of such a complex ( $\text{C}_1$ ) should lead to the reaction products through the following steps.

*Non-Catalyzed Mechanism*



An intramolecular hydrogen transfer (Eq. (C)) takes place first, giving the zwitterionic compound  $\text{C}_2$ . The cleavage of the compound  $\text{C}_2$  is explained both by an intramolecular electron transfer<sup>40</sup> to Mn(VII) and by a simultaneous attack by the permanganate ion.

It has been assumed<sup>41</sup> that the process (F) which produces radical species  $\text{A}^{\bullet}$  and  $\text{CO}_2$  is the rate-determining step. The radical  $\text{A}^{\bullet}$  produces a neutral free radical by deprotonation (Eq. (G)). Oxidation of the neutral free radical by permanganate ion (Eq. (E)) gives the ethyliminium ion (imines are known to be intermediates of the permanganate oxidation of amines<sup>42</sup>). Hydrolysis of the ethyliminium ion results in acetaldehyde and ammonium ion formation (Eq. (I)).

In agreement with these considerations, the rate of the reaction  $v = k_6 [\text{AHMn(VI)CO}_2^{\bullet}]$ . This assumption means that  $k_6$  should be smaller than  $k_{-5}$ . On the other hand, the location of different isobestic points allows us to suppose that the whole reaction proceeds uniformly under the steady-state conditions. So, by applying this approximation to the  $\text{A}[\text{HMn(VI)}]\text{CO}_2^{\bullet}$  species, their respective concentrations are found to be the square root of  $k_3[\text{C}_2][\text{Mn(VII)}]$ .



From the steady-state approximation with respect to both  $C_1$  and  $C_2$  compounds it follows that

$$[C_1] = \frac{k_3}{k_4} K_1 [\text{ACO}_2\text{H}]^2 [\text{Mn(VII)}] \quad (6)$$

and

$$\begin{aligned} [C_2] &= \frac{k_4 [C_1]}{k_5 (1 + [C_2]) [\text{Mn(VII)}]} = \frac{k_4 [C_1]}{k_5 [\text{Mn(VII)}]} = \\ &= \frac{k_3 K_1}{k_5} [\text{ACO}_2\text{H}]^2 . \end{aligned} \quad (7)$$

Hence, the theoretical rate equation for the non-catalyzed mechanism is

$$v = k_6 (k_3 K_1)^{1/2} [\text{ACO}_2\text{H}] [\text{Mn(VII)}]^{1/2} , \quad (8)$$

in agreement with the experimental reaction orders. Alternatively to the step (J), Mn(VI) species should be reduced also by the amino acid molecules. This process leads to Mn(VI) species and is the key for the catalyzed mechanism.

#### *Catalyzed Mechanism*



At this moment, one should keep in mind two important features of the catalyzed reaction. First, its reaction rate shows first-order dependence on the Mn(IV) concentration and further the reaction order with respect to alanine and Mn(VII) species is the same as that for the non-catalyzed reaction. Furthermore, there is enough evidence for the colloidal nature of Mn(IV) species also under the conditions used in this work.

However, in order to define the reaction rate relating to the catalyzed mechanism, one has to make a number of other considerations. First, it is necessary to specify

whether the Mn(VII) species, alanine, or both are adsorbed onto colloid Mn(IV) beads. Based on the extensive literature data on the adsorption of ions onto oxyhydrates of Mn(IV), one can conclude that the zwitterionic species  $C_2$  has the greater tendency to be adsorbed than the Mn(VII) species. If, apart from that, one takes into account that the former species is found in great excess in the bulk solution compared to the latter, one can reasonably expect that the majority of active sites on the colloid surface will be occupied by the  $C_2$  species. Provided that the Mn(IV) species acts as an oxidizing agent, one has to decide whether the  $C_2$  species, once adsorbed, is oxidized by Mn(IV) or by Mn(VII). If, for instance, the slow rate of  $N_2H_4/MNO_2$  reaction<sup>43</sup> is taken into account, the reaction between the  $C_2$  species and the adsorbed Mn(IV) can be considered to be negligible. Therefore, we have assumed<sup>18</sup> that the heterogeneous mechanism involves the reaction between the  $C_2$  adsorbed on colloidal Mn(IV) and Mn(VII), the permanganate being supplied from the bulk solution.

In order to determine the concentration of this adsorbate, we have assumed that the adsorption of the  $C_2$  species onto colloidal Mn(IV) fulfills Freundlich isotherm (9)

$$[\text{adsorbate}] = M [\text{Mn(VI)}] a [C_2]^b, \quad (9)$$

where  $a$  and  $b$  (their values are one) are parameters of the isotherm and  $M$  is the mean molar weight of the colloidal adsorbent under the conditions used in this work.

The reaction rate for the catalyzed mechanism shows the same formal dependence (reaction order) on both alanine and Mn(VII) species concentration as that for the non-catalyzed mechanism. Hence, based on the adsorbate genesis one can conclude that the catalyzed mechanism involves a similar sequence of steps as the homogeneous process.

## REFERENCES

1. Stewart R.: *Oxidation Mechanisms: Applications to Organic Chemistry*. Wiley, New York 1964.
2. Kumar R., Saxena L. R.: *J. Indian Chem. Soc.* **47**, 435 (1970).
3. Verma S. R., Reddy M. J., Shastry V. R.: *J. Chem. Soc., Perkin Trans. 2* **1976**, 469.
4. Katgeri S. N., Mahadevappa D. S., Naidu H.: *Bull. Soc. Chim. Fr.*, **1 9/10**, 381 (1979).
5. Shrivastava S. T., Mathur B. L.: *J. Indian Chem. Soc.* **56**, 991 (1979).
6. Andres Ordax F. J., Arrizabalaga A., Martinez de Ilarduya J. I.: *An. Quim.* **80**, 531 (1984).
7. Andres Ordax F. J., Arrizabalaga A., Martinez Perez de Mendiola R.: *Stud. Chem.* **11**, 303 (1986).
8. Perez-Benito J. F., Mata-Perez F., Brillas E.: *Can. J. Chem.* **65**, 2329 (1987).
9. de Andres J., Brillas E., Garrido J. A., Perez-Benito J. F.: *J. Chem. Soc., Perkin Trans 2* **1987**, 2408.
10. Perez-Benito J. F., Rodriguez R. M., de Andres J., Brillas E., Garrido J. A.: *Int. J. Chem. Kinet.* **21**, 71 (1989).

11. Brillas E., Garrido J. A., Perez-Benito J. F., Rodriguez R. M., de Andres J.: *Collect. Czech. Chem. Commun.* **53**, 479 (1988).
12. Rodriguez R. M., de Andres J., Brillas E., Garrido J. A., Perez-Benito J. F.: *New J. Chem.* **12**, 143 (1988).
13. Insausti M. J., Mata-Perez F., Alvarez-Macho M. P.: *Int. J. Chem. Kinet.* **23**, 593 (1991).
14. Insausti M. J., Mata-Perez F., Alvarez-Macho M. P.: *An. Quim.* **87**, 821 (1991).
15. Insausti M. J., Mata-Perez F., Alvarez-Macho M. P.: *An. Quim.* **87**, 877 (1991).
16. Simandi L. I., Jaky M., Savage C. R., Schelly Z. A.: *J. Am. Chem. Soc.* **107**, 4220 (1985).
17. Jaky M., Simandi L. I.: *J. Chem. Soc., Perkin Trans. 2* **1972**, 148.
18. Mata F., Perez-Benito J., Arranz A.: *Z. Phys. Chem. (Leipzig)* **135**, 141 (1983).
19. Hussain M. I., Ahmad F.: *Transition Met. Chem.* **15**, 185 (1990).
20. Davies G.: *Coord. Chem. Rev.* **4**, 199 (1969).
21. Simandi L. I., Jaky M.: *J. Chem. Soc., Perkin Trans. 2* **1973**, 1856.
22. Schmid R., Sapunov V. N.: *Non-Formal Kinetics*. Verlag Chemie, Basel 1982.
23. Mata F., Perez-Benito J.: *Z. Phys. Chem. (Leipzig)* **267**, 120 (1986).
24. Mata-Perez F., Perez-Benito J.: *J. Chem. Ed.* **65**, 2373 (1987).
25. Barrow G. M.: *Quimica Fisica*. Reverte, Barcelona 1968.
26. Ogino T., Hasegawa K., Hoshino E.: *J. Org. Chem.* **55**, 2653 (1990).
27. Simandi L. I., Jaky M.: *J. Am. Chem. Soc.* **98**, 1995 (1976).
28. Jaky M., Simandi L. I.: *React. Kinet. Catal. Lett.* **3**, 397 (1975).
29. Polgar K., Jaky M., Simandi L. I.: *React. Kinet. Catal. Lett.* **5**, 489 (1976).
30. Son N. T., Jaky M., Simandi L. I.: *Inorg. Nucl. Chem. Lett.* **12**, 291 (1976).
31. Jaky M., Simandi L. I., Shafirovich V. I.: *Inorg. Chim. Act.* **90**, 139 (1984).
32. Perez-Benito J. F., Arias C., Brillas E.: *Int. J. Chem. Kinet.* **22**, 261 (1990).
33. Hussain M. I., Ahmad F.: *Int. J. Chem. Kinet.* **22**, 349 (1990).
34. Arndt D.: *Manganese Compounds as Oxidizing Agents in Organic Chemistry*. Open Court, La Salle-Illinois 1981.
35. Bazsa G., Beck M. T.: *Acta Chim. Hung.* **73**, 425 (1972).
36. Pota G., Bazsa G.: *J. Chem. Soc., Faraday Trans. 1* **84**, 215 (1988).
37. Lengyel I., Barna T., Bazsa G.: *J. Chem. Soc., Faraday Trans. 1* **84**, 229 (1988).
38. Hussain M. I., Ahmad F.: *Transition Met. Chem.* **14**, 169 (1989).
39. Rao V. S., Sethuram B., Narneeth Rao T.: *J. Chem. Kinet.* **11**, 165 (1979).
40. Sutter J. R., Park K. P.: *J. Phys. Chem.* **88**, 770 (1984).
41. Garcia Raso A., Deya M. P., Saa M. J.: *J. Org. Chem.* **51**, 4281 (1986).
42. Wei M., Stewart R.: *J. Am. Chem. Soc.* **88**, 1974 (1966).
43. Coeffier G., Brenet J.: *Bull. Soc. Chim. Fr.* **11**, 2835 (1964).

Revised by J. Hetflejš.