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## **Influence of Manganese(II) and Fluoride Ions on the Kinetics and Mechanism of Oxidation of DL- $\alpha$ -Alanine by Permanganate Ion in Acid Perchlorate Media**

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The kinetics of permanganate oxidation of DL- $\alpha$ -alanine in aqueous perchloric acid solution, at a constant ionic strength of  $2.0 \text{ mol dm}^{-3}$ , was investigated spectrophotometrically. The reaction was found to be second-order overall kinetics in the concentration of both reactants in the slow initial stage, but the second-order kinetics are not, however, maintained throughout the relatively fast final stage of reaction. Addition of  $\text{Mn}^{2+}$  ion was found to accelerate the oxidation reaction, whereas a retardation in the reaction rate was observed on addition of  $\text{F}^-$  ion. This fact leads to the prediction that Mn(III) and/or Mn(IV) play an important role in the reaction kinetics. A tentative mechanism consistent with the kinetics is discussed.

The oxidation of DL-alanine by permanganate ion was studied by Verma *et al.*<sup>1</sup> in concentrated solutions of sulphuric and perchloric acids ( $3\text{--}5 \text{ mol dm}^{-3}$ ). The mechanism proposed by them could not explain the influence of the added salts, such as  $\text{Mn}^{2+}$ , on the reaction kinetics. Our preliminary experiments on this reaction at moderate  $[\text{H}^+]$  suggested that the reaction mechanism is different from that proposed by Verma and co-workers. The reaction was, therefore, reinvestigated in detail in order to shed more light on the mechanism of oxidation of amino acids by that oxidant.

### **EXPERIMENTAL**

#### ***Materials and Method***

Crystalline DL- $\alpha$ -alanine and potassium permanganate used were of Analar (BDH). All other reagents were of analytical grade and their solutions were prepared by using doubly distilled conductivity water. The temperature was controlled within  $\pm 0.1^\circ\text{C}$ .

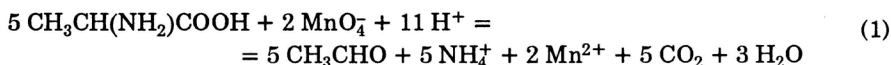
The preparation and analysis of the stock solutions, and the procedure for the kinetic runs were the same as described previously.<sup>2,3</sup>

All kinetic measurements were performed under pseudo first-order conditions where the amino acid was maintained in a large excess over the permanganate ion concentration. The course of reaction was followed by monitoring the decrease in absorbance of permanganate ion at 525 nm, its absorption maximum, as a function of time. It was verified that there is no interference from other reagents at this wavelength.

## RESULTS

### *Stoichiometry and Products Analyses*

The reaction mixtures containing varying ratios of the amino acid to  $\text{MnO}_4^-$  ion were mixed in the presence of  $1.0 \text{ mol dm}^{-3}$   $\text{HClO}_4$  adjusted to constant ionic strength of  $2.0 \text{ mol dm}^{-3}$ , and equilibrated for 24 hours at room temperature. Estimation of the unreacted  $[\text{MnO}_4^-]$  showed that 1 mole of  $\text{MnO}_4^-$  consumed  $2.5 \pm 0.1$  moles of the amino acid. Verma<sup>1</sup> and Rao *et al.*<sup>4</sup> maintained that ammonia and acetaldehyde were products of the oxidation reaction. That result was substantiated by simple qualitative analyses of the products conforming to the stoichiometric equation



Similar reaction products were observed during the oxidation of amino acids by  $\text{MnO}_4^-$ -ion<sup>7,8</sup> or by other oxidants.<sup>9,10</sup>

### *Reaction-Time Curves*

The reaction-time curves were found to be of inverted S-shape throughout the entire range of reaction. The initial rates were relatively slow at early stages, followed by an increase in the reaction rate at longer times. As the reaction is of autocatalytic nature, the behaviour of oxidation obeys the rate expression  $(A_t - A_\infty) = B_0 \exp(-k_s t) + P_0 \exp(-k_f t)$ . Here,  $k_s$  and  $k_f$  are the first order rate constants for the slow and fast reactions, while  $B_0$  and  $P_0$  represent the absorbance change for the slow and the fast reacting species, respectively. The rate constants (Table I) were obtained by drawing a straight line through the slow time linear portion ( $k_s$ ) of the first order plot and extrapolating the line back to zero time ( $B_0$ ). The rate of oxidation,  $k_f$ , for the fast oxidation reaction was obtained from plots of the form  $-\ln [(A_t - A_\infty) - (A'_t - A_\infty)]$  vs. time. The quantity  $(A_t - A_\infty)$  represents the experimental point and  $(A'_t - A_\infty)$  represents the extrapolated point at time  $t'$ <sup>11,12</sup> (Figure 1).

### *Dependence of Reaction Rate on $[\text{MnO}_4^-]$ and $[\text{Amino Acid}]$*

The log (absorbance)-time plots for the initial stages of reaction indicate that the reaction is first order with respect to permanganate ion. The order with respect to the amino acid in this initial stage was found from the measurements of the rates of several ratios of amino acid and fixed permanganate concentrations. The constancy of the second-order rate constants,  $k'_s$ , derived from dividing  $k_s$  by [amino acid] indicates that the rate of oxidation is also first-order in amino acid (Table I).

The second-order kinetics is, however, never maintained as the reaction proceeds throughout the autoacceleration period, and this behaviour is followed by a more complex kinetics.

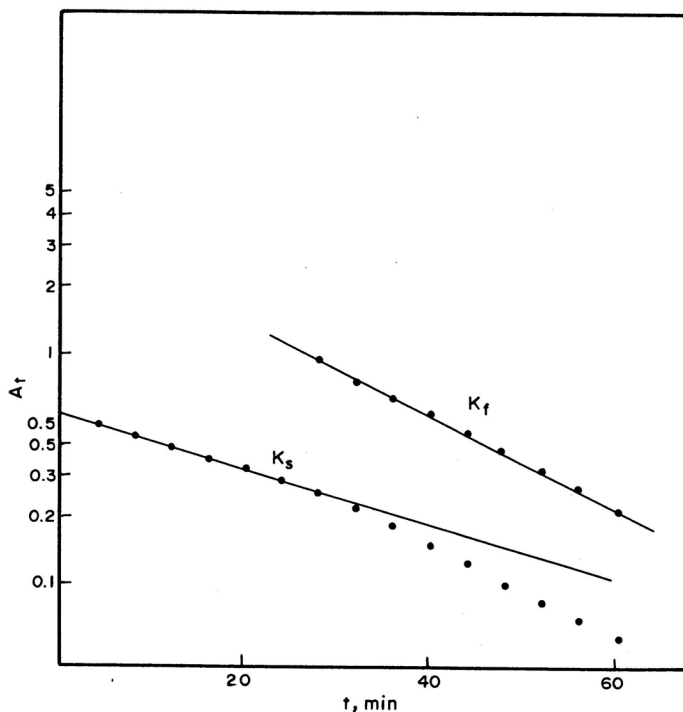


Figure 1. Semi-log plot of  $A_t$  vs. time.  $[\text{MnO}_4^-] = 2.8 \times 10^{-4}$ ,  $[\text{DL-alanine}] = 6 \times 10^{-2}$ ,  $[\text{H}^+] = 1.0$ ,  $I = 2.0 \text{ mol dm}^{-3}$  at temp. =  $25^\circ\text{C}$ .

TABLE I

Rates of oxidation of DL-alanine by permanganate ion.  $[\text{MnO}_4^-] = 2.8 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 1.0 \text{ mol dm}^{-3}$ ,  $I = 2.0 \text{ mol dm}^{-3}$  and temp. =  $25^\circ\text{C}$

$10^2$ [amino acid] mol dm <sup>-3</sup>	$10^4 k_s$ s <sup>-1</sup>	$10^4 k_f$ s <sup>-1</sup>	$10^3 k'_s$ dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	$10^2 k'_f$ dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>
4.5	2.58	4.58	5.67	10.17
6.0	3.35	5.83	5.50	9.67
7.5	4.27	7.02	5.67	9.33
10.0	5.68	9.00	5.67	9.00
12.5	6.88	10.63	5.50	8.50
15.0	8.50	12.33	5.67	8.17

### Dependence of Reaction Rate on Added Salts

It is well known that acidified  $\text{MnO}_4^-$  is reduced by  $\text{Mn}^{2+}$  to give  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions,<sup>13</sup> which are removed by fluoride ions through complex formation.<sup>14</sup> If  $\text{MnO}_4^-$  ions are primarily responsible for the oxidation, a reduction in the initial rate should be observed in the presence of added  $\text{Mn}^{2+}$  ions which reduce the concentration of  $\text{MnO}_4^-$  ions.<sup>15</sup> If, on the other hand, intermediate manganese ions are the active oxi-

dizing species, the addition of  $Mn^{2+}$  should cause acceleration of the reaction rate. Similarly, the addition of  $F^-$  ions should retard the reaction if the intermediate manganese ions are mainly responsible for the oxidation, but should cause no significant change if  $MnO_4^-$  ions are the principal oxidizing entities.<sup>16</sup>

The experimental observation indicated that the reaction rate was increased with increasing the  $Mn^{2+}$  ion with complete disappearance of the induction period even at low  $[Mn^{2+}]$  while a decrease in the rate was observed on addition of  $F^-$  (Table II).

TABLE II

*Effect of adding salts on the autoacceleration rate of oxidation of DL-alanine by permanganate ion- $[MnO_4^-] = 2.8 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[DL\text{-alanine}] = 0.1 \text{ mol dm}^{-3}$ ,  $[H^+] = 1.0 \text{ mol dm}^{-3}$ ,  $I = 2.0 \text{ mol dm}^{-3}$  and temp. = 25 °C*

$10^3[NaF]$ mol $dm^{-3}$	$10^4 k_f$ $s^{-1}$	$10^3 [Mn^{2+}]$ mol $dm^{-3}$	$10^4 k_f$ $s^{-1}$
0.0	9.00	0.0	9.00
2.5	7.22	2.5	12.18
5.0	5.35	5.0	20.17
10.0	3.73	7.5	34.05

### *Dependence of Reaction Rate on Ionic Strength*

No primary effect was observed within the concentration limits demanded for the application of Brønsted-Bjerrum equation. At higher concentrations of added  $NaClO_4$ , the values of  $k_s$  and  $k_f$  were found to increase with the rise of the ionic strength. The values of  $k_s$  and  $k_f$  at  $I = 3.0$  and  $4.0$  and fixed of  $[H^+] = 1.0$ ,  $[MnO_4^-] = 2.8 \times 10^{-4}$ ,  $[DL\text{-alanine}] = 0.1 \text{ mol dm}^{-3}$  and  $30 \text{ °C}$  are  $6.83 \times 10^{-4}$  and  $7.83 \times 10^{-4}$ , and  $1.02 \times 10^{-3}$  and  $1.12 \times 10^{-3} \text{ s}^{-1}$ , respectively. Indeed, the plots of the logarithms of the rate constants against the ionic strength of Brønsted-Bjerrum equation were fairly linear with positive intercepts.

### *Dependence of Reaction Rate on $[H^+]$*

In order to examine the influence of  $[H^+]$  on the reaction rate, some kinetic runs were performed in  $HClO_4$  of  $0.75\text{--}2.0 \text{ mol dm}^{-3}$ , in the same concentration range as used previously.<sup>2,3</sup> The ionic strength was kept constant at  $2.0 \text{ mol dm}^{-3}$  by adding sodium perchlorate. It was found that the rate of oxidation increased with increasing  $[H^+]$  (Table III).

### *Oxidation of DL-alanine by Manganese(III)*

Manganese(III) perchlorate solutions are known to be reasonably stable in the presence of an excess of manganese(II), otherwise the  $Mn^{3+}$  disproportionates with the precipitation of manganese dioxide.<sup>17</sup>

Manganese(III) perchlorate solutions were prepared by addition of acid permanganate solution to sufficient acidified manganese(II), as described elsewhere.<sup>7</sup> The

TABLE III

Effect of  $[H^+]$  on the reaction rates of oxidation of DL-alanine by permanganate ion.  
 $[MnO_4^-] = 2.8 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[DL\text{-alanine}] = 7.5 \times 10^{-2} \text{ mol dm}^{-3}$ ,  
 $I = 2.0 \text{ mol dm}^{-3}$  and temp. = 30 °C

$[H^+]$ mol dm <sup>-3</sup>	$10^4 k_s$ s <sup>-1</sup>	$10^4 k_f$ s <sup>-1</sup>
0.75	5.63	9.55
1.00	6.13	10.50
1.25	6.75	11.55
1.50	7.38	12.65
1.75	8.15	13.87
2.00	9.00	15.27

prepared solutions were usually stable for a few days even when subsequently diluted so that the hydrogen ion concentration became about 1.5 mol dm<sup>-3</sup>.

The oxidation kinetics of DL-alanine by manganese(III) ion was followed spectrophotometrically under a nitrogen atmosphere at a wavelength of 290 nm, the absorption maximum of Mn<sup>3+</sup> ion, as a function of time. These kinetic measurements were carried out under pseudo first-order conditions where the amino acid was present in a large excess over that of [Mn<sup>3+</sup>]. The experimental results showed that the reaction was first-order with respect to manganese(III) concentration, as indicated by the linearity of log (absorbance)-time plots for more than three half-lives of reaction completion, while a fractional order was observed in [DL-alanine] (Table IV).

TABLE IV

Rate constants for the oxidation of DL-alanine by manganese(III).  $[Mn^{2+}] = 0.1$ ,  
 $[Mn^{3+}] = 5.3 \times 10^{-4}$ ,  $[H^+] = 1.0$ ,  $I = 2.0 \text{ mol dm}^{-3}$  and temp. = 25 °C\*

$10^2[DL\text{-alanine}]$ , mol dm <sup>-3</sup>	5.00	7.50	10.00	15.00	20.00
$10^3 k_{\text{obs}}$ , s <sup>-1</sup>	2.35	3.22	4.10	5.35	6.18
$10^2 k$ , dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	4.70	4.29	4.10	3.57	3.09

\*  $k_{\text{obs}}$ , the observed pseudo-first order rate constant;  $k$ , the second-order rate constant.

## DISCUSSION

In acid solutions, amino acids tend to exist predominantly as the protonated species  $RCHN^+H_3COOH$  (Zwitterion).<sup>18</sup> By analogy to the chemistry of potassium permanganate under our experimental conditions,<sup>19</sup> it is reasonable to assume that  $HMnO_4$  species are generated as follows



where  $K_2$  is the protonation constant ( $2.99 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1}$  at 25 °C).<sup>19</sup>

The hydrogen ion dependency of the reaction rate (non-integral order) may suggest that at least one reaction path involving the protonated species is contributed in

the slow stage of reaction. Again, the positive salt effect further indicates reaction between an ion and a neutral molecule.<sup>20</sup>

Therefore, for the initial induction period two competitive reactions in the rate-determining step may be suggested



where  $\text{LH}^+$  is the protonated alanine. Hence, the rate constant can be expressed as a function of the substrate and  $\text{H}^+$  concentration:

$$\text{Rate} = \frac{k_a K_1 + k_b K_1 K_2 [\text{H}^+][\text{LH}^+][\text{MnO}_4^-]_{\text{T}}}{1 + K_2 [\text{H}^+]} \quad (5)$$

where  $[\text{MnO}_4^-]_{\text{T}}$  is the total analytical concentration of permanganate ion. Assuming that under our experimental conditions  $K_2[\text{H}^+] \ll 1$  in Eq. (5) the second order rate constant of the initial induction period can be rewritten as follows,

$$\text{Rate} \propto k_s' = k_a' + k_b' [\text{H}^+]^n \quad (6)$$

where  $k_a' = k_a K_1$ ,  $k_b' = k_b K_1 K_2$  and  $n = 0.5$ . Equation (6) requires the plot of  $k_s'$  against  $[\text{H}^+]^{0.5}$  to be linear. Our data satisfy this requirement (Figure 2). The values of  $k_a'$  and  $k_b'$  (Table IV) were calculated by the least-squares method.

Unfortunately, the values of  $k_a$  and  $k_b$  could not be evaluated because  $K_1$  and  $K_2$  were not known at different temperatures. Although some attempts were made to evaluate these constants at various temperatures from the experimental data, the results were not encouraging. The activation parameters of  $k_a'$  and  $k_b'$  paths of the induction period were evaluated using Eyring's equation (Table V).

Several factors may be responsible for the negative entropy of activation, *e.g.* the charge and the ordering of the solvent molecules around the activated complexes. In general, ordering is affected by the charge of the activated complex. If the activated complex is uncharged, the ordering of the solvent molecules around the activated complex should be less than around the separate reactant ions and this will tend to make the entropy of activation less negative than for the activated complex with a positive charge. It seems quite likely that the entropies of activation for  $k_a'$  and  $k_b'$  paths are

TABLE V  
Activation parameters of DL-alanine oxidation by permanganate ion

Pathway	$\Delta S^\ddagger$	$\Delta H^\ddagger$	$\Delta G^\ddagger$	Ref.
	$\text{J K}^{-1} \text{mol}^{-1}$	$\text{kJ mol}^{-1}$	$\text{kJ mol}^{-1}$	
$k_a'$	$-123.91 \pm 6.02$	$58.99 \pm 1.74$	$95.91 \pm 3.53$	This work 1
$k_b'$	$-55.15 \pm 2.21$	$69.54 \pm 1.77$	$86.02 \pm 2.43$	
$k_b'$	$-55.13$	$70.35$	$86.18$	

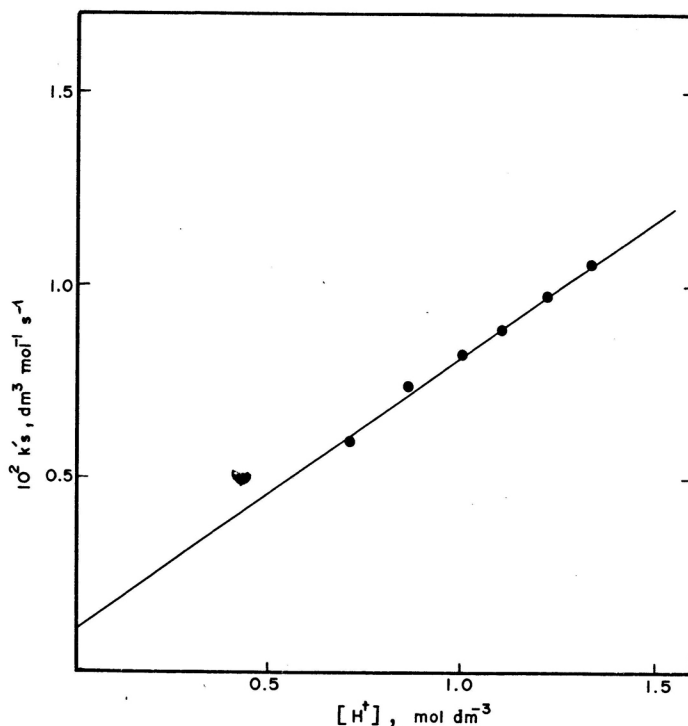


Figure 2. Hydrogen ion dependency for the induction period.  $[\text{MnO}_4^-] = 2.8 \times 10^{-4}$ ,  $[\text{DL-alanine}] = 7.5 \times 10^{-2}$ ,  $I = 2.0 \text{ mol dm}^{-3}$  and temp. = 30 °C.

not consistent with this behaviour. Consequently, the less negative entropy of activation for  $k_b$ ' path as compared with  $k_a$ ' path may be interpreted by the contribution of the positive  $\Delta S^\ddagger$  for the protonation of  $\text{MnO}_4^-$  ion in the former path, but not in the latter one because  $\Delta S^\ddagger$ ' values are composite quantities of entropy terms.

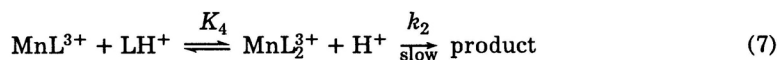
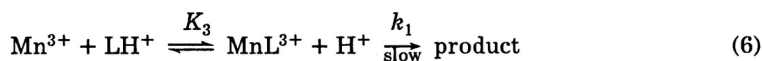
It was observed that for a group of  $\text{MnO}_4^-$  reaction  $\Delta S^\ddagger$  is negative for the reactions which proceed *via* complex formation, *i.e.*, inner sphere mechanism,<sup>21,22</sup> while the  $\Delta S^\ddagger$  values for the outer-sphere reactions tend to be more positive<sup>23</sup> (*cf.* Table VI). The entropy of activation for  $\text{MnO}_4^-$  DL-alanine reaction falls within the observed range of the former case. Again, redox reactions involving the same oxidant and proceeding by a similar mechanism should show an isokinetic relationship.<sup>24</sup> A plot of  $\Delta H^\ddagger$  vs.  $\Delta S^\ddagger$  was fairly linear, which was consistent with the suggested mechanisms for these redox reactions.

Disappearance of the induction period even at low  $[\text{Mn}^{2+}]$  and the decrease in the reaction rate on addition of  $\text{F}^-$  ion may suggest that  $\text{Mn}^{3+}$  and/or  $\text{Mn}^{4+}$  are the principle reactive species throughout the autoacceleration period. However, the oxidation of DL-alanine by manganese(III) as well as the continuous increase in the oxidation rate with increasing the added  $\text{Mn}^{2+}$  to the  $\text{MnO}_4^-$ -alanine redox reaction indicate conclusively that  $\text{Mn}^{3+}$  but not  $\text{Mn}^{4+}$  is the sole oxidant in this final stage. Attempts were made to allow a spectrophotometric detection of the  $\text{Mn}^{3+}$  ion intermediate as the

TABLE VI  
Activation parameters for some organic-permanganate reactions

Reaction	$\Delta S^\ddagger$	$\Delta H^\ddagger$	$\Delta G^\ddagger$	Ref.
	J K <sup>-1</sup> mol <sup>-1</sup>	kJ mol <sup>-1</sup>	kJ mol <sup>-1</sup>	
DL-alanine	-55	70	86	This work
$\beta$ -Phenylalanine	-160	34	82	4
Glycine	-116	48	83	2
DL-Valine	-105	51	82	2
DL-Alanine	-53	70	86	2
L-Arginine	-127	50	88	8
Glycol	-120	41	77	24
Glycolic acid	-92	58	86	24
Tartaric acid	-119	45	80	29
Lactic acid	-58	59	76	30

reaction proceeded in the oxidation of DL-alanine by  $MnO_4^-$  ion. Unfortunately, experimental conditions makes the detection unsuccessful. Consequently, the most probable reaction mechanism is



The intermediate complex ions,  $MnL^{3+}$  and  $MnL_2^{3+}$ , are formed and subsequently undergo further decomposition to give the reaction products. The variation of the rate constant either for the autoacceleration period or the oxidation of DL-alanine by manganese(III) with the change of the substrate and hydrogen ion concentrations may be expressed by the relationship

$$\text{Rate} = \frac{(k_1 K_3 [H^+]^{-1} + k_2 K_3 K_4 [H^+]^{-2}) \cdot [LH^+][Mn^{3+}]_T}{1 + K_3 [H^+]^{-1} [LH^+] + K_3 K_4 [H^+]^{-2} [LH^+]^2} \quad (8)$$

where  $[Mn^{3+}]_T$  denotes the total analytical concentration of manganese(III). Under our experimental conditions of low  $[LH^+]$ ,  $K_3 K_4 [LH^+]^2 [H^+]^{-2} \ll (1 + K_3 [LH^+] [H^+]^{-1})$  and, hence, reaction (7) may be neglected.

Then reaction (6) is considered as the sole rate determining-step and equation (8) can be recast to the form

$$\text{Rate} = \frac{k_1 K_3 [H^+]^{-1} [LH^+] [Mn^{3+}]}{1 + K_3 [H^+]^{-1} [LH^+]} \quad (9)$$

According to equation (9), at constant  $[H^+]$  a plot of  $1/\text{rate}$  versus  $1/[\text{substrate}]$  should be linear (Figure 3). The good linearity obtained beside the positive intercept on  $1/\text{rate}$  axis may be considered as a kinetic evidence for the formation of an inter-



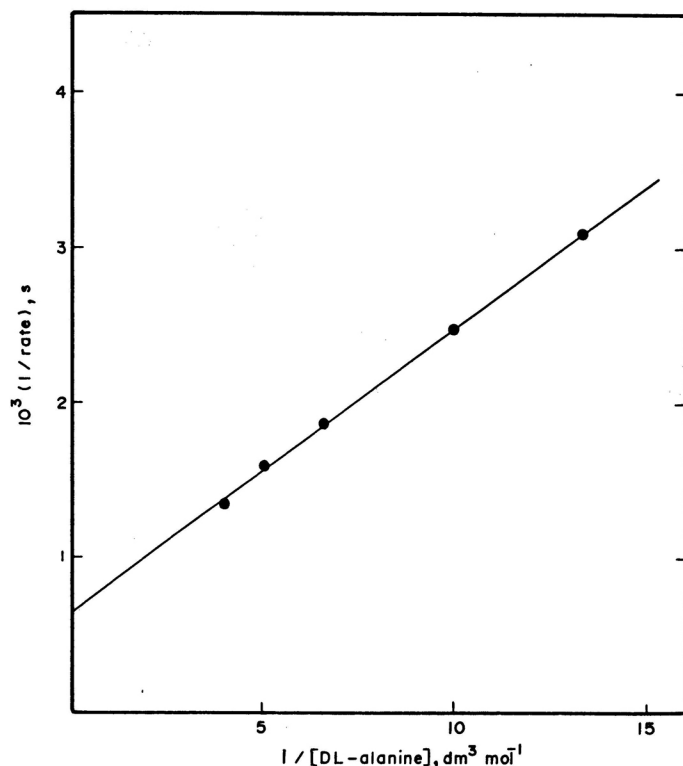


Figure 3. Plot of  $1/\text{rate}$  vs.  $1/[\text{DL-alanine}]$  in the oxidation of DL-alanine by manganese(III).  $[\text{Mn}^{3+}] = 5.3 \times 10^{-4}$ ,  $[\text{Mn}^{2+}] = 0.1$ ,  $[\text{H}^+] = 1.0$ ,  $I = 2.0 \text{ mol dm}^{-3}$  and temp. =  $25^\circ\text{C}$ .

mediate complex ion in accordance with the Michaelis-Menten kinetics.<sup>25</sup> Again, the plot of  $1/\text{rate}$  against  $[\text{H}^+]$  at constant substrate should give a straight line, as it is observed experimentally with respect to the oxidation of DL-alanine by  $\text{MnO}_4^-$  ion. The value of  $K_3$  was found to be 2.63 at  $[\text{H}^+] = 1.0$ ,  $I = 2.0 \text{ mol dm}^{-3}$  and  $25^\circ\text{C}$ . Similar reaction mechanisms for the oxidation of some organic substrates by  $\text{MnO}_4^-$  have been reported elsewhere.<sup>26-28</sup>

The positive catalytic effect of  $\text{Mn}^{2+}$  on the rate of reaction may reflect the one-electron transfer mechanism. However, this pathway is not favoured from the energetic points of view for the  $\text{Mn(VII)/Mn(VI)}$  (+0.56 V) and  $\text{Mn(VII)/Mn(V)}$  (+1.1 V) couples.<sup>29</sup> The protonation of permanganate ion shifts the  $\text{Mn(VII)/Mn(VI)}$  couple to a more positive value (+1.3 V) which makes  $\text{HMnO}_4$  a stronger oxidizing agent than  $\text{MnO}_4^-$  ion.

In view of these facts it may be possible to suggest that the oxidation of DL-alanine by permanganate ion proceeds by a successive one-electron transfer mechanism of inner-sphere nature throughout two distinct stages. In the initial slow stage, manganese(III) is formed as a transient species. Then, the formed Mn(III) is attacked by the substrate to give the reaction products *via* intermediate complexes formation through-

out the autoacceleration period. The mechanism of oxidation can be illustrated by Scheme (I).

Unfortunately, it was not possible to obtain a direct evidence of the intermediate complex ions, but the reason could be that the subsequent oxidation of the intermediates is slow in comparison with their formation.

#### REFERENCES

1. R. S. Verma, M. J. Reddy, and V. R. Shastry, *J. Chem. Soc., Perkin II.* (1976) 469.
2. N. M. Girgis, R. M. Hassan, and A. S. El-Shahawy, *Bull. Fac. Sci., Assiut Univ.* **16** (1987) 41.
3. R. M. Hassan, M. A. Mousa, and M. H. Wahdan, *J. Chem. Soc., Dalton Trans.* (1988) 605.
4. V. S. Rao, B. Sethuram, and T. N. Rao, *Ind. J. Chem. Kinet.* **11** (1975) 165.
5. A. I. Vogel, *"Practical Organic Chemistry"*, Longmans, London, 1962, p. 325.
6. A. I. Vogel, *"A Text Book of Quantitative Inorganic Analysis"*, Longman, London, 1962, p. 787.
7. U. D. Mudliar, V. R. Chourey, R. A. Verma, and V. R. Shastry, *J. Ind. Chem. Soc.* **LX** (1983) 561.
8. K. B. Reddy, B. Sethuram, and T. N. Rao, *Ind. J. Chem.* **20A** (1981) 395.
9. M. Z. Barakat, M. F. Abdel Wahab, and M. M. Elsadag, *J. Chem. Soc.* (1956) 4685.
10. M. S. Ramachandran and T. S. Vivekanandam, *Bull. Chem. Soc. Jpn.* **60** (1987) 3397.
11. K. W. Hicks and M. A. Hurless, *Inorg. Chim. Acta* **74** (1983) 229.
12. R. M. Hassan, M. H. Wahdan, and A. Hassan, *Europ. Polym. J.* **24** (1988) 281.
13. W. A. Waters, *Quart. Rev.* **12** (1955) 227.
14. H. F. Launer, *J. Amer. Chem. Soc.* **54** (1932) 2297.
15. P. S. Radhakrishnamurti and M. D. P. Rao, *Ind. J. Chem.* **15A** (1977) 524.
16. P. Nath, K. K. Banerji, and G. V. Bokove, *Ind. J. Chem.* **8** (1970) 1113.
17. D. R. Rosseinsky, *J. Chem. Soc.* (1963) 1181.
18. A. E. Martell and R. M. Smith, *Critical Stability Constants*, Vol. I, Plenum Press, New York, 1974.
19. N. Bailey, A. Carrington, T. A. K. Lott, and M. C. R. Symons, *J. Chem. Soc.* (1960) 290; *Chem. Rev.* **63** (1963) 443.
20. C. H. Rochester, *"Progress in Reaction Kinetics"*, Pergamon Press, Oxford, 1971, p. 145.
21. F. M. Moore and K. W. Hicks, *Inorg. Chem.* **14** (1975) 413.
22. K. W. Hicks, *J. Inorg. Nucl. Chem.* **38** (1976) 1381.
23. F. Frees, *J. Amer. Chem. Soc.* **103** (1981) 1194.
24. L. Leffler and E. Grunwald, *Rates and Equilibria of Organic Reactions*, Wiley, New York, 1963, pp. 324 and 342.
25. L. Michaelis and M. L. Menten, *Biochem. Z.* **49** (1918) 49.

26. K. K. Senkupta, D. K. Khamrui, and D. C. Mukherjee, *Ind. J. Chem.* **13** (1975) 348.
27. G. V. Bakore and R. Shanker, *Ind. J. Chem.* **1** (1963) 108.
28. M. M. Girgis, S. A. El-Shatoury, and Z. H. Khalil, *Canad. J. Chem.* **63** (1985) 3317.
29. G. Millazzo, S. Caroll, and V.K. Sharma, *Tables of Standard Potential*, John Wiley and Sons, New York, 1978; W. Latimer, *Oxidation Potentials*, 2nd Edn., Prentice-Hall, Englewood Cliffs, New Jersey, 1952.

#### SAŽETAK

**Utjecaj Mn(II) i F<sup>-</sup> iona na kinetiku i mehanizam oksidacije DL- $\alpha$ -alanina s permanganatom u vodenoj perklornoj kiselini**

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Istraživana je kinetika oksidacije DL- $\alpha$ -alanina s permanganatom u kiselim otopinama 2.0 M ionske jakosti. Prisutnost Mn(II) iona katalizira, a fluorid iona usporava reakciju koja se odvija u dva stupnja. Raspravlja se o mehanizmu reakcije koja uključuje Mn(III) i Mn(IV) vrste.