Catalytic Effect of Mn^{2+} on Oxidative Deamination and Decarboxylation of L-isomers of Amino Acids by Permanganate

B.R. SAHU‡, VIJAY R. CHOUREY*, SHAKUNTALA PANDEY† and V.R. SHASTRY†

Government Autonomous Post Graduate College, Dhar-454 001, India

Investigation of catalytic effect of Mn^{2+} on oxidative deamination and decarboxylation of L-isomers of amino acids was carried out by iodometric estimations.

INTRODUCTION

The effect of Mn(II) as a catalyst in the case of oxidation of permanganate is well known.[1-4] The oxidation reactions of L-aspartic acid, L-asparagine, L-glutamine and L-glutamic acid by permanganate in moderately concentrated sulphuric acid media have also been found to be catalysed by the addition of Mn (II) ion. The present paper describes the experimental finding.

EXPERIMENTAL

All the chemicals used in this investigation were of BDH, AnalaR, SM, GR or imported specifications. Redistilled water was used to prepare all the solutions. The progress of reaction was followed by iodometric estimations of the reaction mixture at various time intervals. It has been observed that oxidation reactions of all four amino acids are double stage processess.[5] The reactions have been studied in absence and presence of Mn(II) ion to investigate the catalytic effect of Mn(II). The results are given in Table-1.

RESULTS AND DISCUSSION

It has been pointed out by Moelwyn Hughes[6] that in the presence of the catalyst, the uncatalysed and catalysed reactions proceed simultaneously so that

$$k_1 = k_o + K_c \, [\text{Catalyst}]^* \qquad (1)$$

Successive addition of the catalyst brings about proportionate increase in the observed velocity, 'x' is unity and K_c becomes a bimolecular constant. In the present study it has been found that the value of the rate constant is directly

proportional to the concentration of the catalysts Mn(II) ion (Fig. 1) and therefore 'x' is unity and the relation will be

$$k_1 = k_o + K_c[Mn^{2+}] \qquad (2)$$

where k_1 is the observed pseudo first order rate constant in the presence of the catalyst Mn(II) ion, k_0 is the pseudo first order rate constant for the uncatalysed reaction and Kc is the catalytic constant. The values of K_c obtained from $K_c = k_1 - k_o/[Mn^{2+}]$ are found fairly constant (Table-1).

TABLE-1

CATALYTIC EFFECT OF Mn(II) ON OXIDATION REACTIONS OF L-ISOMERS
OF AMINO ACIDS

$[KMnO_4] = 8.88 \times 10^{-4}$ M, $[H_2SO_4] = 5.0$ M (3.0 M for L-Glutamine),   Temp. = 313 K.

$[MnSO_4] \times 10^4$ M	$k_1 \times 10^3$ min^{-1} (I stage)	$k_1' \times 10^3$ min^{-1} (II-stage)	$k_o \times 10^3$ (Uncatalysed first stage)	$K_c = \dfrac{k_1 - k_0}{[Mn^{2+}]}$
1. For [L-Aspartic acid] = 0.02 M				
0.0	6.48	4.31	6.48	—
2.0	8.25	disappear	6.48	8.85
4.0	10.01	disappear	6.48	8.85
6.0	11.35	disappear	6.48	8.11
8.0	13.05	disappear	6.48	8.20
2. For [L-Glutamic acid] = 0.024 M				
0.0	3.64	6.36	3.64	—
2.0	4.25	disappear	3.64	3.06
4.0	4.83	disappear	3.64	2.97
6.0	5.33	disappear	3.64	2.81
8.0	5.92	disappear	3.64	2.85
3. For [L-Asparagine] = 0.08 M				
0.0	2.83	6.77	2.83	—
2.0	5.43	disappear	2.83	13.06
4.0	8.02	disappear	2.83	13.01
6.0	10.23	disappear	2.83	12.36
8.0	12.63	disappear	2.83	12.26
4. For [L-Glutamine] = 0.02 M				
0.0	3.53	15.98	3.53	—
2.0	5.62	disappear	3.53	10.46
4.0	7.70	disapperar	3.53	10.42
6.0	9.45	disappear	3.53	9.86
8.0	11.51	disappear	3.53	9.87

High increase in the rate of the oxidation of oxalate ion by permanganate has been noticed by the addition of Mn(II) by Malcolm and Noyes.[1]

According to them the main reaction during first stage is rapid oxidation-reduction between Mn(VII) and Mn(II) which produces oxalate complex of Mn(III) and perhaps the other oxidation states of Mn. Nath, et al[2] have also

① [L-ASPARATIC ACID] = 0.02M   TEMP. = 313K
② [L-ASPARAGINE] = 0.08M   [KMnO₄] = 8.88×10⁻⁴M
③ [L-GLUTAMINE] = 0.02M
④ [L-GLUTAMIC ACID] = 0.024M

[H₂SO₄] = 5.0M
              3.0M FOR
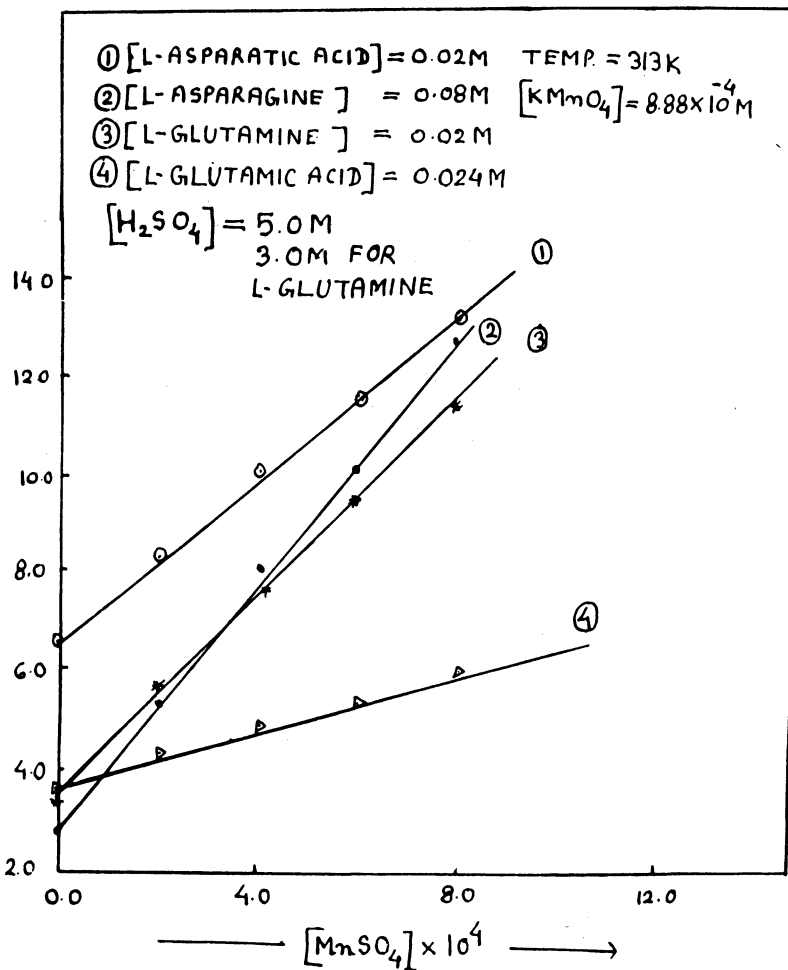   L-GLUTAMINE

Fig. 1.   Velocity constant k_1 against $[Mn^{2+}]$

suggested formation of Mn(III) as an active oxidant in the case of oxidation of pinacol by permanganate, catalysed by Mn(II). This Mn(III) then forms reversible complex with pinacol.

In the present study it is interesting to observe that the second stage processes in all these amino acids disappear by the addition of Mn(II). Similar behaviour has also been reported by Verma.[7]

Thus in the present case of oxidation of amino acids by permanganate in sulphuric acid medium, there are two possibilities: (1) either Mn(II) forms a complex with amino acids which may then be oxidised by permanganate, or (2) firstly Mn(II) may react with Mn(VII) to give Mn(III) which may accelerate the rate of the reaction, being a strong oxidizing agent. Similar views have been put forth by Polissar[3], Waterbury, Hayes and Martin[4].

Experiments have been performed to investigate the oxidation of these amino

acids by Mn(III) under similar conditions and it has been observed that Mn(III) does not oxidise the substrate directly. Hence, we may suggest that the catalytic effect of Mn(II) might be due to the complex formation between Mn(II) and substrate which oxidises in a single stage reaction eliminating second stage processes.

ACKNOWLEDGEMENT

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