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INDUCTIVE AND MECHANISTIC STUDIES OF OXIDATION OF CARBOXYLIC AND HYDROXY-CARBOXYLIC ACIDS IN Fe(II)-Mn(VII) REACTION: EFFECT OF MANGANESE(II)

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An attempt is made to explore the mechanism of induced oxidation of carboxylic and hydroxy-carboxylic acids in Fe(II)-Mn(VII) redox reaction. The manganese(VII)-carboxylic acid reactions induced by iron(II) may involve the participation of Mn(VI), Mn(IV) and Mn(III) as transient species. The probable mechanism is that Mn(VI) formed in the primary step by one equivalent process, oxidises the carboxylate ion to a ketonic product along with the formation of Mn(IV). The intermediate Mn(IV) also oxidises the carboxylate ion to a ketonic product with the formation of Mn(III).

INTRODUCTION

A series of induced oxidation reactions have been discovered after Schonbein[1] in which the sulphite induced air oxidation of arsenite solution. Kessler[2] introducd the term induced oxidation and a prerequisite in an induced oxidation system is at least one of the reactants which undergoes two or more electron change. Adrian[3] made a detailed study of the oxidation of citric acid by acid permanganate and concluded that a keto-carboxylic acid is an intermediate oxidation product which finally oxidised to formaldehyde/formic acid and carbon dioxide. In the oxidation of oxalic acid by elementary oxygen in presence of manganese(II) at 100–108°C, Baczko and Schroer[4] noticed the induction period was independent of oxygen pressure and suggested a chain mechanism for manganese(II) catalysis and also concluded the formation of CO_2^-, COOH and HO_2^- as transient species - which might further convert to give H_2O_2. In the permanganate treated oxalic acid reduction of $HgCl_2$, Mahon and Lal[5] observed the formation of CO_2^- ions as per the following mechanism

$$Mn(C_2O_4)_2^- \rightarrow MnC_2O_4 + CO_2 + CO_2^- \quad (1)$$

Bhale and Bhagwat[6] studied the permanganate oxidation of citric acid in presence of sulphuric acid and observed that with the increase of $[KMnO_4]$ and separately $[H^+]$, the rate of oxidation of citric acid was relatively faster and moreover the added $MnSO_4$ further enhanced the rate of oxidation. Shafigullin[7] observed the formation of Mn(IV) along with Mn(III) in the oxidation of oxalic acid by acid permanganate and also observed an induction period in the above study and attributed the same to the formation of MnO_2 which was finally reduced to lower oxide on reaction with more permanganate. Bhale *et al.*[8] studied the acid permanganate oxidation of tartaric acid and observed the reaction rate increased in presence of added manganese(II). In order to understand the gradual reduction of Mn(VII) to Mn(II), Gupta and Awasthi[9] attempted the reduction of permanganate and separately MnO_2 by citric acid and further suggested that the addition of Mn(II) causes the formation of Mn(VI) and Mn(III) as transient species according to the following mechanism.

$$MnO_4^- + Mn^{++} \rightarrow MnO_4^{--} + Mn^{+++} \qquad (2)$$

Bakore *et al.*[10-12] made a detailed investigation into the kinetics of oxidation of α-hydroxy and other hydroxy-carboxylic acids by acid permanganate and concluded that the rate of oxidation of these carboxylic acids increased with the development of some induction period but, however, this was reduced appreciably by the addition of manganese(II). Zalesskii and Samitov[13] studied the oxidation of oxalic acid by acid permanganate and noticed the development of an induction period. Dutta *et al.*[14] made a systematic study of the induced oxidation of oxalate/oxalic acid by acid permanganate with molecular oxygen as inductor and concluded the generation of oxalate radicals or ascorbate radicals (in case of ascorbic acid) during the course of induced oxidation.

Potassium permanganate is widely used as an oxidising agent for both preparative and analytical purposes. The basic stoichiometry in the Fe(II)-Mn(VII) redox reaction can be represented as follows:

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn(II) + 5Fe^{3+} + 4H_2O \qquad (3)$$

In assigning the mechanism of oxidation of organic compounds with acid permanganate different pathways can be visualised. One pathway may be the dehydrogenation of the organic molecule or transfer of an oxygen atom or atoms from acid permanganate. However the oxidation of organic compounds usually occurs in sequential steps but the final products are almost always different from the resultants by an even number of electrons. During the course of oxidation with acid permanganate different oxidation states of manganese may be visualised depending upon the nature of electron transfer. During the course of induced oxidation reaction with manganese(VII), hexavalent, tetravalent, trivalent and bivalent manganese are needed to account for different types of oxidation reactions with organic compounds.

The standard redox potential for Mn(VII)/Mn(II), Mn(VII)/Mn(IV), Mn(IV)/Mn(II) and Mn(III)/Mn(II) in acid medium are 1.51, 1.70, 1.23 and 1.51 V respectively. Further, the reducing agents which preferentially lose one electron reduce Mn(VII) to Mn(VI). The subsequent steps of the reaction depend on the other properties of the reducing agent. If the reducing agent loses two electrons, the following steps finally showing Mn(II) formation may be possible.

Here H_2A and A are the recuced and oxidised forms of the reduing agent or any organic molecule.

$$2Mn(VII) + H_2A \rightarrow 2Mn(IV) + A + 2H^+ \qquad (4)$$

$$2Mn(VI) + H_2A \rightarrow Mn(IV) + A + 2H^+ \qquad (5)$$

$$2Mn(IV) + H_2A \rightarrow 2Mn(III) + A + 2H^+ \qquad (6)$$

$$2Mn(III) + H_2A \rightarrow 2Mn(II) + A + 2H^+ \qquad (7)$$

When manganese(VII) or acid permanganate solution acts on a mixture of the reducing agents 'A' and 'B' (e.g., Fe^{2+} and $C_2O_4^{2-}$) of which 'A' preferentially loses one electron whereas 'B' preferentially loses two electrons, the reaction is a combination of two schemes. Such a type of reaction may be classified under the phenomenon called induced oxidation. It was already established that no reaction occurred between permanganate and oxalate for upto a week if traces of Mn(II) were removed, whereas in the presence of Fe(II) salt the same oxalate ion is rapidly oxidised. In this paper the authors have attempted a detailed study of iron(II) induced oxidation of oxalic, malic, tartaric, citric and mandelic acids by manganese(VII) in presence of manganese(II) with the aim of exploring the mechanistic steps involved in the induced oxidation reactions.

EXPERIMENTAL

Reagents

A *c.a.* 0.05N Mohr's salt solution in 2.5N sulphuric acid was prepared by dissolving the required amount of Mohr's salt in one litre of 2.5N sulphuric acid. Further the normality was checked from time to time through a potentiometric titration against a standard dichromate solution and also separately using diphenylamine sulphonate (D.P.A.S.) as an internal indicator. For the preparation of manganese(VII) solution about 3.25 gm A.R. potassium permaganate was taken and dissolved in one litre double distilled water and the solution was boiled gently for 15-30 mins and then cooled to the laboratory temperature. This solution was filtered through a sintered glass funnel and stored in a dark-brown coloured glass bottle. The above permanganate solution was standardised against a standard sodium oxalate solution (0.05N) prepared from A.R. sodium oxalate. Carboxylic acids viz., oxalic, malic, tartaric, citric and mandelic acids employed in these investigations were of analytical grade. The solutions of the above carboxylic acids were standardised by a cerate oxidimetric method furnished by Rao *et al.*[15] Further the manganese(II) used in these studies was of A.R. grade $MnSO_4.H_2O$.

Procedure

Requisite volumes of 0.05M iron(II) solution and 10 N H_2SO_4 were taken in a 100 ml beaker and the reaction mixture was diluted to 50 ml with double distilled water. In every titration the concentration of iron(II) was 0.005N while that of sulphuric acid was 2.0 N. The titration was performed potentiometrically using 'Oxford portable direct reading potentiometer with a built-in standard cadmium cell of 1.0185 V and provided with a spot galvanometer and an indicator platinum electrode'. The potentials are recorded for each addition of 0.1 ml manganese(VII) solution. First differential potentiometric approach making use of the plot *viz.*, $\Delta E/\Delta V$ *vs.* V was used to locate the correct end-point and correspondingly the correct volume of manganese(VII) was found out. The induced oxidation of carboxylic and hydroxy- carboxylic acids in Fe(II)-Mn(VII) redox reaction was followed potentiometrically employing 10^{-3} M stock carboxylic acid solution for every 50 ml of the reaction mixture. The volumes of carboxylic acids employed were 2.5, 5.0, 7.5, 10.0, 12.5, 15.0, 17.5 and 20 ml of the above stock carboxylic acid solution.

Another series of titrations were also performed in presence of manganese(II). In every case the induction factor is calculated from the ratio of the number of equivalents of oxidised carboxylic acid to the number of inductor equivalents (oxidised Fe(II)). Indirectly the inducttion factor is ascertained from the ratio of the volumes of potassium permanganate (0.025N) consumed with respect to iron(II) with and without the addition of carboxylic acids.

RESULTS AND DISCUSSIONS

It is noticed that with the increase in the ratio of number of moles of any carboxylate ion to the number of moles of iron(II), the induction factor progressively increases. These induction factors are evaluated from the first differential potentiometric plots, *viz.*, $\Delta E/\Delta V$ *vs.* V.

An asymptotic approach of these induction factors shows that 'X' and 'Y' attain experimental limiting values, X = 0.004 and Y = 0.123 for the ratio of [oxalic acid] : [Fe(II)], (0.08 : 1.0). This observation of progressive increase of induction factor for a very low mole ratio may explain that there is a very rapid induced oxidation of oxalic acid with the addition of more and more manganese(VII) solution. Such a rapid induced oxidation observed in oxalic acid may be due to the formation of transient Mn(VI), Mn(IV) and Mn(III) species and finally formation of Mn(II) during the course of induced oxide reaction. Further the manganese(II) formed in the reaction mixture may cause an autocatalytic effect on the induced oxidation of oxalic acid. The study of variation of induction factor is also undertaken at different [manganese(II)] i.e. from 0.01 to 0.08M, however employing the same concentrations of oxalic acid and iron(II). From these studies it is observed that the induction factor is practically unaffected. Such a strange observation may be explained on the basis that the extraneous or separately added manganese(II) may not cause further autocatalytic effect on the induced oxidation of oxalic acid.

Further in the case of hydroxy-carboxylic acids viz., malic, tartaric, citric and mandelic acids similar observations were made when a series of potentiometric titrations were performed without the addition of manganese(II). The asymptotes obtained in Fig. 1 have 'X' and 'Y' limits (X = 0.112, Y = 0.103) for a mole ratio of [malic acid] : [Fe(II)], (0.2 : 1.0). It is further noticed that Mn(II) has a pronounced inhibitory effect on the induction factor. The relevant asymptotic curves viz., B_1, B_2 B_3 and B_4 accounting for the effect of 0.01M, 0.02M, 0.04M and 0.08M [Mn(II)] are also furnished in Fig. 2. As is evident from Fig. 2 for an eight-fold increase of [Mn(II)], the induction factor decreases to half of its original value. (At 0.01M [Mn(II)] the I.F. was 0.0975 while at 0.08M [Mn(II)] it was 0.0465 for the same mole ratio of [malic acid] : [Fe(II)].

In the case of tartaric acid the 'X' and 'Y' limits of the asymptotes are 0.04 and 0.155 respectively for a mole ratio of [tartaric acid] : [Fe(II)] (0.8 : 1.0). Further it is observed that manganese(II) has a significant inhibitory effect on the induction factors. This is also evident from the asymptotes of B-series. As is evident from these asymptotes for a four-fold increase of [Mn(II)] the induction factor decreases to about half of its original value 0.001M [Mn(II)], the induction factor was 0.125 while at 0.004M [Mn(II)] it was 0.0475 for the same mole ratio of [tartaric acid] : [Fe(II)]). The asympotote 'A' has 'X' and 'Y' limits (X = 0.25 and Y = 0.128 for a very high mole ratio of [citric acid] : [Fe(II)] (9.0 : 1.0). (Fig. 3) Even in this case it is observed that Mn(II) has a pronounced inhibitory effect on the observed values of induction factors. Further even with the use of a very low concentration of Mn(II) e.g., 0.002M the lowering of induction factors by about half of its original value is observed. At 0.002M [Mn(II)] the I.F. was 0.0685 while without [Mn(II)] it was 0.1275 for the same mole ratio of [citric acid] : [Fe(II)] (9.0 : 1.0). The asymptotes B_1 and B_2 vide Fig. 3 have 'X' and 'Y' limits of 0.785 and 0.091 respectively.

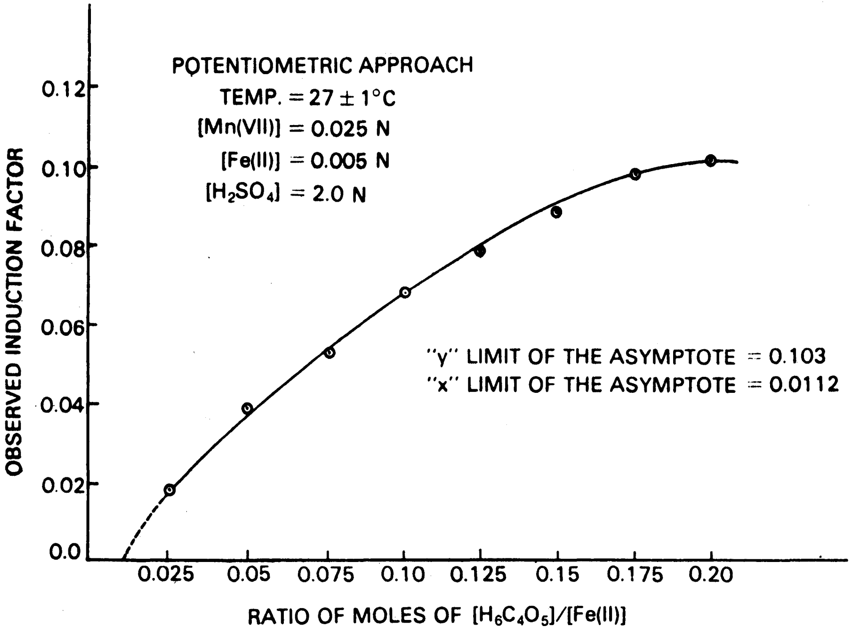


Fig. 1 An asymptotic approach to an induction factor of 0.1025 oxidtion of varying amounts of Malic Acid by 0.025N Mn(VI)-reaction induced by 0.005N Fe(II) in the presence of 2.0N H_2SO_4.

Among the asymptotes of mandelic acid, the asymptote 'A', the 'X' limit is 0.02 while 'Y' limit is 0.166 for a mole ratio of [Mandelic acid] : [Fe(II)] (0.4 : 1.0). In *B*-series 'X' limit of the asymptotes B_1 and B_2 is 0.0255 while 'Y' limit is 0.0816 for the same mole ratio in presence of 0.001M and 0.002M [Mn(II)]. The use of even such lower concentrations of manganese(II) e.g., 0.002M causes the lowering of induction factor by one-third of its original value. At 0.002M [Mn(II)], the induction factor was 0.053 while without [Mn(II)], the I.F. value was 0.166 for the same mole ratio of [Mandelic acid] : [Fe(II)] (0.4 : 1.0).

In the induced oxidation of carboxylic/hydroxy-carboxylic acids in iron(II)-manganese(VII) redox system the possibility of the formation of Mn(VI), Mn(IV) and Mn(III) as transient species can be anticipated. As these investigations were carried out in the presence of atmospheric oxygen one would normally expect the interference of oxygen in these induced oxidation reactions. Further our separate detailed investigations carried out in presence of inert atmosphere (N_2

atmosphere) as well as atmospheric oxygen reveal that atmospheric oxygen has practically negligible effect on these induced oxidation reactions. This observation is also in consonance with that of Mahon and Lal[5].

The overall mechanism of induced oxidation of a carboxylic acid e.g., oxalic acid may be represented as follows:

$$\mathrm{Fe(II)} + \mathrm{Mn(VII)} \rightarrow \mathrm{Fe(III)} + \mathrm{Mn(VI)} \qquad (1)$$

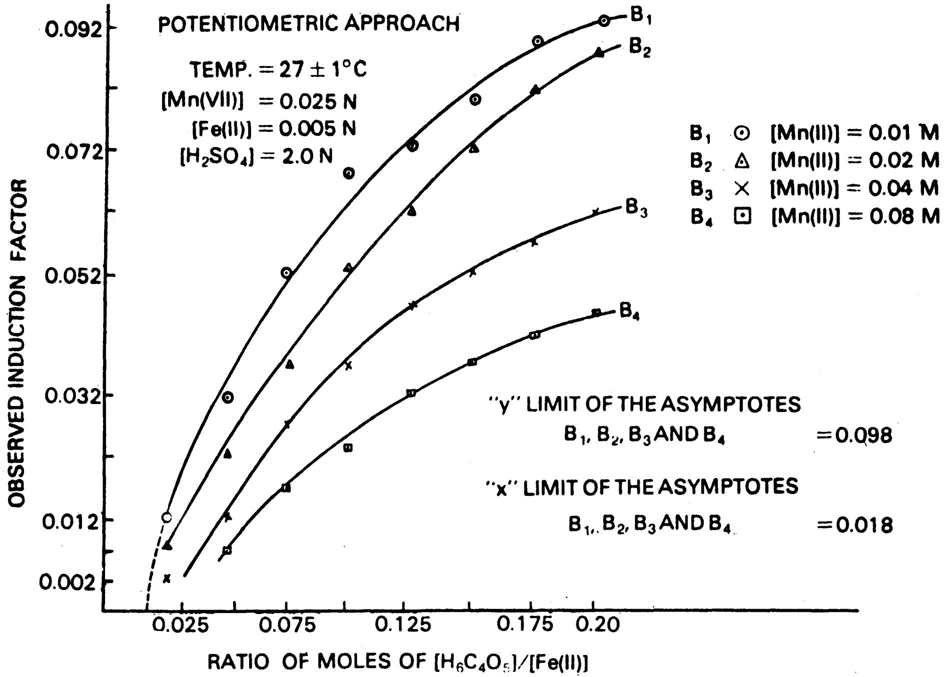


Fig. 2. An asymptotic approach to an induction factor of 0.0975 oxidation of varying amounts of Malic Acid by 0-.025N Mn(VII)-reacation induced by -0.005N Fe(II) in presence of 2.0N H_2SO_4, effect of Mn(II).

$$\mathrm{Mn(VI)} + 2\mathrm{Fe(II)} \rightarrow 2\mathrm{Fe(III)} + \mathrm{Mn(IV)} \qquad (2)$$

$$\mathrm{Mn(VI)} + C_2O_4^{2-} \rightarrow \mathrm{Mn(IV)} + 2CO_2. \qquad (3)$$

$$2\mathrm{Mn(IV)} + C_2O_4^{2-} \rightarrow 2\mathrm{Mn(III)} + 2CO_2 \qquad (4)$$

Mn(III) formed may be converted into Mn(II) in either of these routes.

$$\mathrm{Mn(III)} + 2C_2O_4^{2-} = \mathrm{Mn}(C_2O_4)_2^- \qquad (5)$$

$$\mathrm{Mn}(C_2O_4)_2^- \rightarrow \mathrm{Mn(II)} + C_2O_4^{2-} + CO_2 + CO_2^- \qquad (6)$$

$$\mathrm{Mn}(C_2O_4)_2^- + CO_2^- \rightarrow \mathrm{Mn(II)} + 2C_2O_4^{2-} + CO_2 \qquad (7)$$

In a similar manner in the induced oxidation of malic, tartaric, citric and mandelic acids in Fe(II)-Mn(VII) redox system, the possibility of formation of Mn(VI), Mn(IV), Mn(III) and finally Mn(II) is possible. The systematic mechanistic steps of induced oxidations of these hydroxy-carboxylic acids in Fe(II)-MN(VII) system can be represented as follows:

$$\mathrm{Fe(II)} + \mathrm{Mn(VII)} \rightarrow \mathrm{Fe(III)} + \mathrm{Mn(VI)} \qquad (8)$$

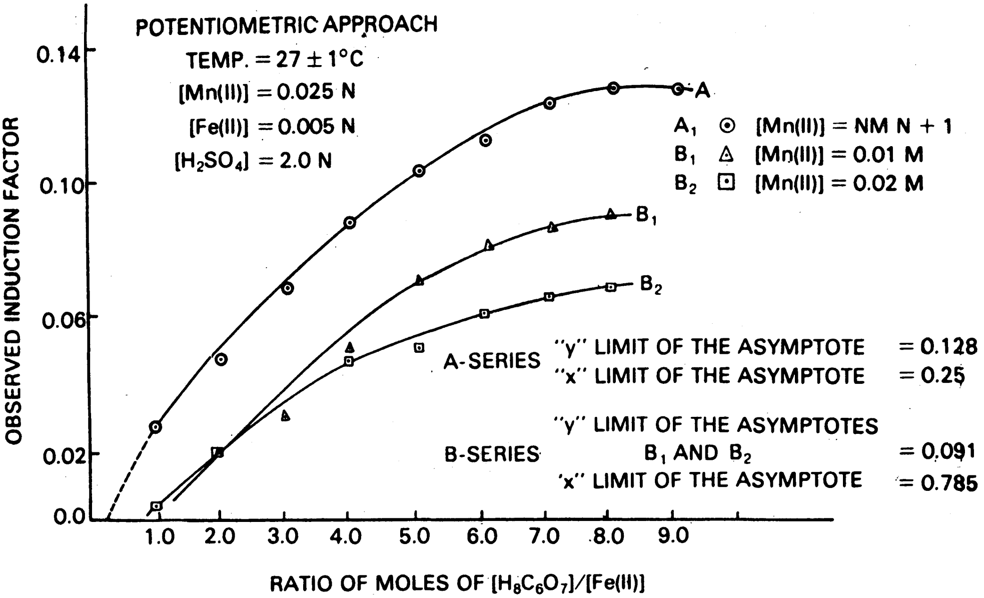
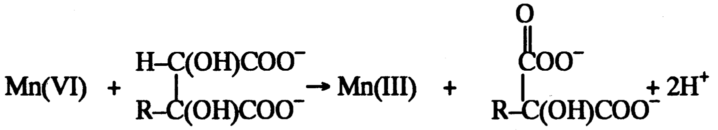
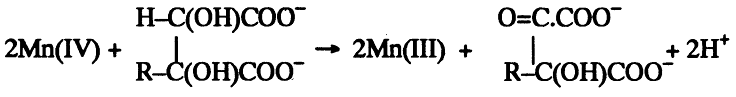


Fig. 3. An asymptotic approach to an induction factor of 0.127 oxidation of varying amounts of Malic Acid by 0-.025N Mn(VII)-reaction induced by -0.005N Fe(II)
A–Series Citric Acid Alone B–Series Effect of Mn(II)

$$\mathrm{Mn(VI) + 2Fe(II) \rightarrow 2Fe(III) + Mn(IV)} \qquad (9)$$

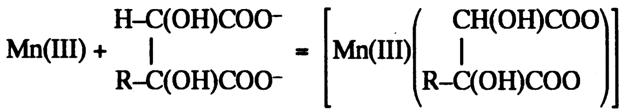


$$\mathrm{Mn(VI)} + \begin{array}{l} \mathrm{H{-}C(OH)COO^-} \\ \quad | \\ \mathrm{R{-}C(OH)COO^-} \end{array} \rightarrow \mathrm{Mn(III)} + \begin{array}{l} \quad \mathrm{O} \\ \quad \| \\ \quad \mathrm{COO^-} \\ \quad | \\ \mathrm{R{-}C(OH)COO^-} \end{array} + 2\mathrm{H^+} \qquad (10)$$

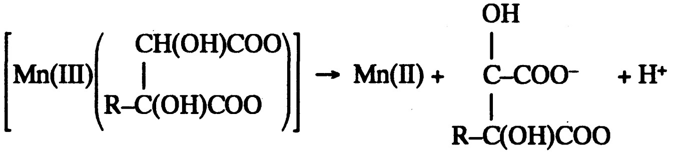


$$2\mathrm{Mn(IV)} + \begin{array}{l} \mathrm{H{-}C(OH)COO^-} \\ \quad | \\ \mathrm{R{-}C(OH)COO^-} \end{array} \rightarrow 2\mathrm{Mn(III)} + \begin{array}{l} \mathrm{O{=}C.COO^-} \\ \quad | \\ \mathrm{R{-}C(OH)COO^-} \end{array} + 2\mathrm{H^+} \qquad (11)$$

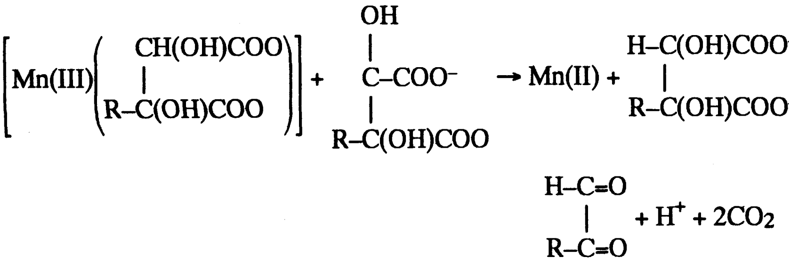
Mn(III) formed may be converted into Mn(II) as follows:



$$\mathrm{Mn(III)} + \begin{array}{l} \mathrm{H{-}C(OH)COO^-} \\ \quad | \\ \mathrm{R{-}C(OH)COO^-} \end{array} = \left[\mathrm{Mn(III)}\left(\begin{array}{l} \mathrm{CH(OH)COO} \\ | \\ \mathrm{R{-}C(OH)COO} \end{array}\right)\right] \qquad (12)$$



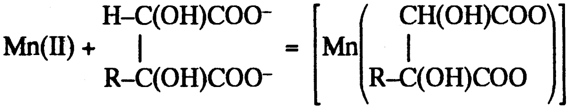
$$\left[\mathrm{Mn(III)}\left(\begin{array}{l} \mathrm{CH(OH)COO} \\ | \\ \mathrm{R{-}C(OH)COO} \end{array}\right)\right] \rightarrow \mathrm{Mn(II)} + \begin{array}{l} \quad \mathrm{OH} \\ \quad | \\ \quad \mathrm{C{-}COO^-} \\ \quad | \\ \mathrm{R{-}C(OH)COO} \end{array} + \mathrm{H^+} \qquad (13)$$



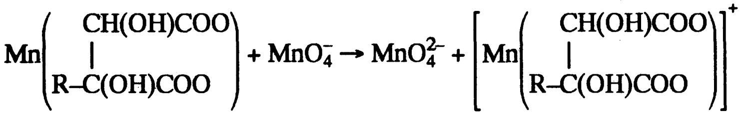
$$\left[\mathrm{Mn(III)}\left(\begin{array}{l}\mathrm{CH(OH)COO}\\ |\\ \mathrm{R{-}C(OH)COO}\end{array}\right)\right] + \begin{array}{c}\mathrm{OH}\\ |\\ \mathrm{C{-}COO^-}\\ |\\ \mathrm{R{-}C(OH)COO}\end{array} \rightarrow \mathrm{Mn(II)} + \begin{array}{l}\mathrm{H{-}C(OH)COO^-}\\ |\\ \mathrm{R{-}C(OH)COO^-}\end{array} + \begin{array}{l}\mathrm{H{-}C{=}O}\\ |\\ \mathrm{R{-}C{=}O}\end{array} + H^+ + 2CO_2 \quad (14)$$

where 'R' stands for 'H' or 'CH_2COOH' group or 'CH(OH)COOH' group or 'phenyl' group and sometimes '(OH)' or 'CH(CH)OOO$^-$' may be replaceable with a 'H' atom so as to represent all carboxylic acids under study.

Further the oxidation of (manganese(II)-hydroxy acid) complex by MnO_4^- into (manganese(III)-hydroxy acid) complex can also be visualised as per the following steps



$$\mathrm{Mn(II)} + \begin{array}{l}\mathrm{H{-}C(OH)COO^-}\\ |\\ \mathrm{R{-}C(OH)COO^-}\end{array} = \left[\mathrm{Mn}\left(\begin{array}{l}\mathrm{CH(OH)COO}\\ |\\ \mathrm{R{-}C(OH)COO}\end{array}\right)\right] \quad (15)$$



$$\mathrm{Mn}\left(\begin{array}{l}\mathrm{CH(OH)COO}\\ |\\ \mathrm{R{-}C(OH)COO}\end{array}\right) + MnO_4^- \rightarrow MnO_4^{2-} + \left[\mathrm{Mn}\left(\begin{array}{l}\mathrm{CH(OH)COO}\\ |\\ \mathrm{R{-}C(OH)COO}\end{array}\right)\right]^+ \quad (16)$$

The (manganese(III)-hydroxy acid) complex formed in the above step disproportionates into a free radical and manganese(II) as explained in step (13).

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