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Studies in Oxidation of Gallic Acid

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Oxidation of gallic acid with $KMnO_4$ has been investigated and the oxidation product has been characterised by means of physico-chemical methods which include analytical, spectral IR and ^1H NMR, magnetic and potentiometric measurements. Mechanism for the cleavage of gallic acid by $KMnO_4$ has been proposed.

INTRODUCTION

The oxidation of gallic acid has been a subject of extensive study[1-4]. However, the permanganate oxidation in solid state has not been reported so far. The present paper deals with the characterisation of product obtained during the above reaction in solid state. The potentiometric titration in aqueous solution was also carried out. A tentative mechanism of the reaction is proposed on the basis of results.

EXPERIMENTAL

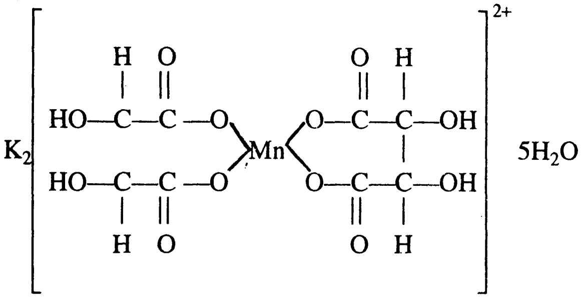
The chemicals used were AR grade of E. Merck. Gallic acid and potassium permanganate in molar ratio 1:3; were triturated and after the vigorous reaction with spark, the reaction product was extracted with water. The insoluble portion was hydrated MnO_2. Soluble portion was found to contain K_2CO_3 (which was separated by chromatography) and a reddish brown compound.

The elemental analysis and magnetic moment of reddish brown compound was determined. IR was measured in CsI disc. The potentiometric titration of gallic acid with $KMnO_4$ and its reverse titration were carried out by Pogendroff's compensation method.

RESULTS AND DISCUSSION

The elemental analysis of reddish brown compound corresponds to formula $K_4[Mn(C_4H_4O_6)_2]\cdot 5H_2O$. The magnetic moment data (6.26 BM) indicates it to be a high spin complex with antiferromagnetic coupling[5].

The complex displays a broad band near 3400–3150 cm^{-1} indicative of presence of water molecule[6, 7] which is also indicated by a band at 1600 cm^{-1} for its bending mode. The (>C=O) stretching mode has been observed at *ca.* 1665 cm^{-1}. The lowering in >C=O stretching (normally at 1730 cm^{-1} in esters) is indicative of its involvement in co-ordination with Mn^{2+}. (The strong band at 3060 cm^{-1} may be attributed to C—H stretching mode and four bands in the region 800–600 cm^{-1} are tentatively assigned as ν(C—C), ν(>C=O), plane-deformation and out-of-plane deformation bands[8].) In far IR region band at 445 cm^{-1} may be due to ν(Mn – O). The loss of water molecule was observed at 70°C with gradual change in colour. This suggests the presence of uncoordinated water molecule. A tentative structure has been assigned to the complex as—



The ^1H NMR spectrum of deuterated sample shows only one peak at δ6.36 corresponding to C—H proton. The proton of O—H group had probably undergone exchange with deuterium of solvent and hence its signal was not observed. The deshielding due to carboxylic oxygen and hydroxylic oxygen causes the increases in δC—H value; however, existence of hydrogen bonding may not be ruled out.

In both potentiometric titrations *i.e.* gallic acid added to $KMnO_4$ in presence of H_2SO_4 and reverse, two inflexions were observed as recorded in Table 1 at different concentrations of sulphuric acid.

TABLE-1
GALLIC ACID ADDED TO $KMnO_4$ SOLUTION IN SULPHURIC ACID

Concentration of $KMnO_4$	First inflexion $KMnO_4$: Gallic acid	Final inflexion $KMnO_4$: Gallic acid
0.10 N	6.64 : 1	4.20 : 1
0.25 N	6.53 : 1	3.96 : 1
0.50 N	6.32 : 1	3.87 : 1
0.75 N	6.22 : 1	4.17 : 1
1.00 N	6.22 : 1	4.07 : 1
3.00 N	6.12 : 1	3.84 : 1
5.00 N	6.12 : 1	3.92 : 1

In the former titration a dark brown substance was separated with the disappearance of pink colour of $KMnO_4$ at first inflexion which disappeared at the final inflexion. It was characterised as $MnO_2 \cdot 2H_2O$ and its amount decreases with increase in concentration of H_2SO_4.

The inflexion corresponds to 6.66 moles $KMnO_4$ per mole gallic acid with formation of $MnO_2 \cdot 2H_2O$ (dark brown substance) may be represented as

$$20MnO_4^- + 3C_7H_6O_5 + 20H^+ \longrightarrow 20MnO_2 + 15CO_2 + 16CO + 19H_2O \quad (1)$$

The second inflexion corresponds to further oxidation of gallic acid with disappearance of MnO_2 as

$$MnO_2 + C_7H_6O_5 + 20H^+ \longrightarrow 10Mn^{2+} + 5CO_2 + 13H_2O \quad (2)$$

The final result corresponds to 4:1 $KMnO_4$/gallic acid stoichiometry as

$$4MnO_4^- + C_7H_6O_5 + 12H^+ \longrightarrow 4Mn^{2+} + 5CO_2 + 9H_2O \quad (3)$$

The shift in first inflexion by concentration change of H_2SO_4 (ranging from 0.1 N to 5 N) is presumably due to the formation of MnO_2 and Mn^{2+} both at intermediate concentration in place of equation (1).

$$6MnO_4 + C_7H_6O_5 + 8H^+ \longrightarrow MnO_4 + Mn^{2+} + 5CO + 7H_2O \quad (4)$$

However, equations for the oxidation corresponding to second inflexion and overall oxidation remain unchanged.

The surprising observation in reverse titration with same final result is worth mention such as

(a) a faster reaction rate.
(b) formation of an intense cherry red colour at first inflexion corresponding to ratio 2.8:1 ($KMnO_4$/gallic acid).
(c) final ratio being 4:1 as suggested earlier with disappearance of cherry red colour.

The various equations to satisfy the above observations may be tentatively proposed as:

The oxidation of gallic acid to tartaric acid by permanganate followed by formation of a Mn(II) tartarate complex at first inflexion.

$$28MnO_4^- + 10C_7H_6O_5 + 64H^+ \rightarrow 5[Mn(C_4H_4O_6)_2]^{2-} + 3CO_2 + 42H_2O + 23Mn^{2+} \quad (5)$$

It corresponds to stoichiometry $KMnO_4/C_7H_6O_5 = 2.8 : 1$ as observed. However, the complex further reduces MnO_4^- according to equation.

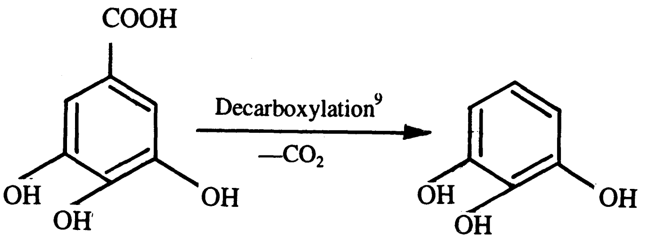
$$12MnO_2 + 5[Mn(C_4H_4O_6)_2]^{-2} + 56H^+ \rightarrow 17Mn^{2+} + 20CO_2 + 20CO + 48H_2O \quad (6)$$

which gives the overall changes reported by eqn. (3) with stoichiometry 4:1.

Mechanism of cleavage of gallic acid by $KMnO_4$ (gallic acid added to $KMnO_4$)

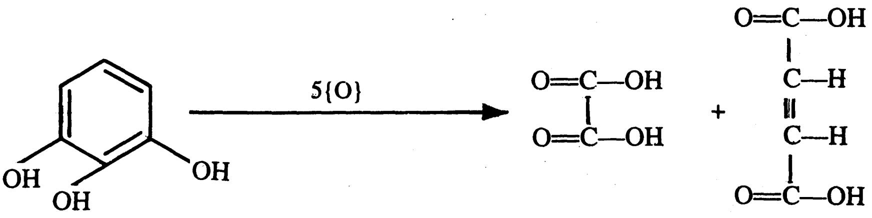
Reduction of MnO_4^- to MnO_2 during first inflexion represented by equation (1) with molar ratio 6.66:1 ($KMnO_4$/gallic acid) corresponds to 10 available oxygen atoms consumed per mole of gallic acid. The proposed cleavage of gallic acid on this basis is as

Step I

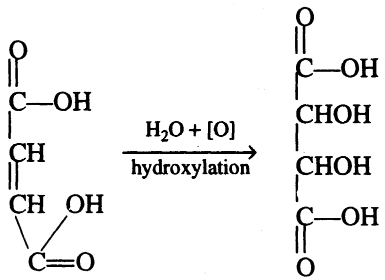


Pyrogallol

Step II

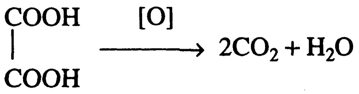


Oxalic acid Maleic acid



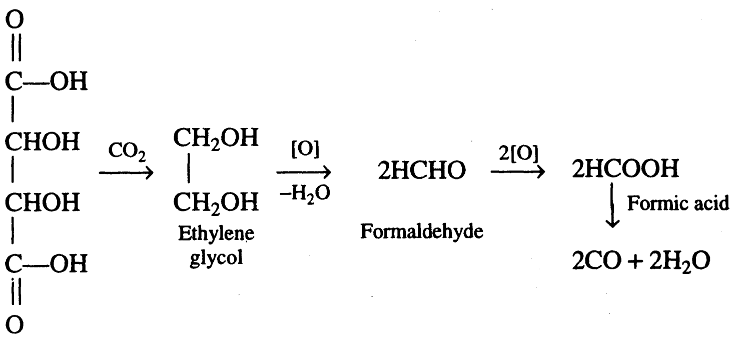
Tartaric acid

Step III



$$\begin{array}{c}COOH\\ |\\ COOH\end{array} \xrightarrow{[O]} 2CO_2 + H_2O$$

Step IV



$$\begin{array}{l}O\\ \|\\ C—OH\\ |\\ CHOH\\ |\\ CHOH\\ |\\ C—OH\\ \|\\ O\end{array} \xrightarrow{CO_2} \begin{array}{c}CH_2OH\\ |\\ CH_2OH\end{array} \xrightarrow[-H_2O]{[O]} 2HCHO \xrightarrow{2[O]} \begin{array}{c}2HCOOH\\ \downarrow\\ 2CO + 2H_2O\end{array}$$

This also suggests formation of 6.66 mole of MnO_2 per mole of gallic acid which further oxidises gallic acid. According to above proposed cleavage 6.66 moles of MnO_2 are equivalent to 6.66 moles of available oxygen atom which oxidise 0.66 moles of gallic acid during second inflexion. The ratio thus comes to 6.66:1.66 *i.e.* 4:1.

In reverse titration when gallic acid is in excess first and second inflexion with molar ratio 2.8:1 and 4:1 corresponds to 7 and 10 available oxygen atoms respectively. The cleavage along with complex formation is believed due to complex formation.

Step V

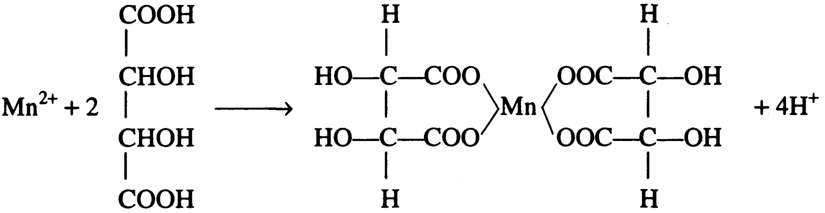
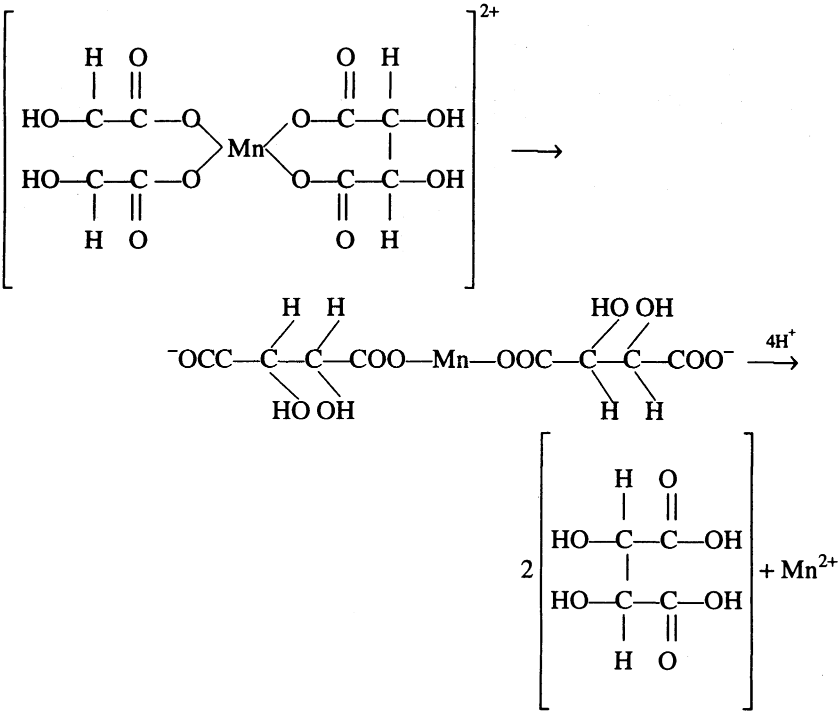


TABLE 2
REVERSE TITRATION KMnO4 ADDED TO GALLIC ACID SOLUTION IN SULPHURIC ACID

Concentration of H_2SO_4	First inflexion	Final inflexion
0.75 N	2.80:1	3.80:1
2.00 N	2.88:1	4.06:1
5.00 N	2.84:1	3.98:1

In place of step IV, which in fact involves 7 available oxygen atoms, the final step VI may be
which again suggests the consumption of 10 available oxygen atoms.



The proposed mechanism is in accordance with the observed stoichiometries corresponding to first and second inflexion during direct and reverse titration of gallic acid with $KMnO_4$.

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