Asian Journal of Chemistry Vol. 11, No. 3 (1999), 873–877

Studies in Oxidation of Gallic Acid with Potassium Dichromate

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Oxidation of gallic acid with $K_2Cr_2O_7$ has been investigated. The present paper deals with the characterisation of product obtained during the oxidation in solid state. The analytical and spectral study of the oxidation product indicates that it a trinuclear complex of Cr(III) containing OH^- and O^{2-} bridge and pyruvate ion ligand. The potentiometric titration in aqueous solution was also carried out. A tentative mechanism of the reaction is proposed on the basis of results.

INTRODUCTION

The oxidation of gallic acid has been a subject of extensive study[1–4]. In our earlier communication[5], it was reported that the reaction between gallic acid and potassium permanganate occurred in solid state when the two were triturated. The reaction was highly exothermic. Similar but less violent reaction occurs when the process is carried with potassium dichromate. Therefore the nature of reaction products was identified and confirmed by potentiometric works. A simple mechanism for the cleavage gallic acid by $K_2Cr_2O_7$ has been proposed in this paper.

EXPERIMENTAL

In a dry mortar and pestle a mixture of gallic acid and $K_2Cr_2O_7$ in the ratio of about 1:3 by weight was taken and triturated for 1/2 h. During the trituration the orange colour changed to brown. The mixture was then treated with water when it started frothing with the evolution of heat and a dark brown solid was obtained. The solid was insoluble in water and so it was separated by filtration and purified by repeated washing with water till it was free from excess dichromate. The purified sample was dried and kept in desiccator till completely dry.

The potentiometric titrations were carried out by the usual method[6, 7]. The e.m.f. of the cell was measured on a stretched wire potentiometer having ten metre length wire by Poggendroff's compensation method. A spot galvanometer sensitive to 2 millivolt was used in the null point detector. Potassium dichromate (AnalaR) used in the work was powdered, heated in an air oven at 140–150°C for 1 h and cooled in a desiccator before use.

RESULTS AND DISCUSSION

In the reaction between gallic acid and $K_2Cr_2O_7$, an insoluble brown substance is produced which is found to be chromium complex containing some potassium. The dark brown complex has been characterised on the basis of physico-chemical investigation.

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TABLE-1

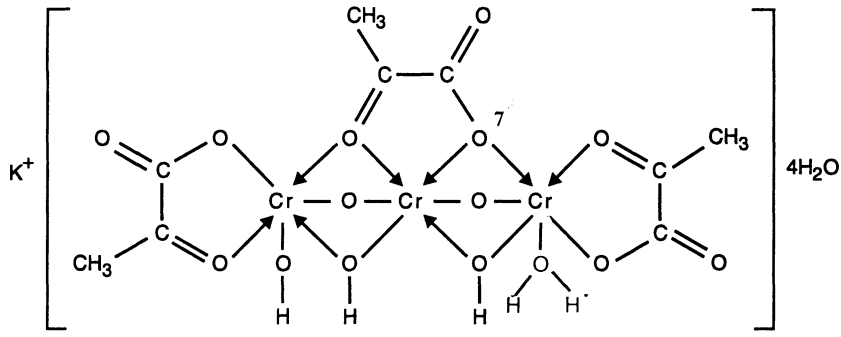
Gallic acid solution added to $K_2Cr_2O_7$ solution in H_2SO_4		$K_2Cr_2O_7$ solution added to gallic acid solution in H_2SO_4	
Conc. of H_2SO_4	Inflection point $K_2Cr_2O_7 : C_7H_6O_5$	Conc. of H_2SO_4	Inflexion point $K_2Cr_2O_7 : C_7H_6O_5$
1 N	2.51 : 1	3 N	2.80 : 1
3 N	2.60 : 1	5 N	2.76 : 1
6 N	2.63 : 1	6 N	2.90 : 1
9 N	2.91 : 1		

The elemental analysis of dark brown compound corresponds to formula $C_9H_{22}O_{19}Cr_3K$. For Cr^{3+}, μ_{eff} should be 3.87 B.M. In present course of investigation, subnormal magnetic moment value was observed which indicates that there is antiferromagnetic coupling between adjacent Cr^{3+} ions at room temperature.

The dark brown complex displays a broad band near 3550–3350 cm^{-1}. A broad band (hump) in the region 3550–3350 cm^{-1} is generally observed in case of aquo complexes and is due to ν(OH) of water molecule (coordinated and/or uncoordinated) and ν(OH) of hydroxy groups[8, 9]. The separation of ν(O—H) of water and ν(O—H) of hydroxy group could not be observed in the spectrum and probably these two couple together to yield a broad hump at around 3550–3350 cm^{-1}. The presence of H_2O molecule and/or O—H group might have been confirmed by the comparison of IR spectra of the sample in low frequency region with its deuterated sample but due to our limited resourcess, this study could not be undertaken. The spectrum of brown solid displays two distinct >C=O stretching vibrations located near 1665 cm^{-1} and 1640 cm^{-1} as fairly strong absorption bands. The occurrence of two distinct ν(C=O) vibration unambiguously suggests the presence of two different types of carbonyl (>C=O) group. The vibration at around 1665 cm^{-1} is attributed to (>C=O) stretching vibration of carbonyl group whereas ketonic ν(C=O) is located around 1640 cm^{-1}. In general acid carbonyl group and keto carbonyl group display ν(C=O) band around 1730 cm^{-1} and 1700 cm^{-1} respectively. In the proposed structure of Cr(III) compiex, the lowering of carbonyl ν(C=O) vibration can be attributed to resonance involving α, β-unsaturation[8, 9] whereas the red shift of keto ν(C=O) vibration can be attributed to resonance involving α, β-unsaturation as well as involvement of >C=O group in coordination to metal atom[8, 9]. The spectrum indicates a weak and broad band at around 1590 cm^{-1}. This may be assigned to δ H_2O and indicates the presence of water molecule in the complex. The presence of medium and broad band near 1380 cm^{-1} can be attributed to δ CH_3. The band of medium intensity in far IR region near 465 cm^{-1} is due to ν(Cr—O) and suggests (Cr—O) linkage in the compound.

The loss in weight at 120 and 200°C corresponds to H_2O and $4H_2O$ and this may be assumed to be coordinated in inner and outer spheres respectively.

The above physico-chemical evidences and discussions can be used to propose following tentative structure for dark brown solid.



In both potentiometric titrations, *i.e.*, gallic acid added to $K_2Cr_2O_7$ in the presence of H_2SO_4 and reverse, inflexions were observed as recorded in Table-1 at different concentrations of H_2SO_4.

On addition of gallic acid to potassium dichromate solution in H_2SO_4, the orange colour gradually turned brown and at the inflexion point the colour became distinctly greenish-blue indicating the conversion of Cr(VI) to Cr(III) in the reaction. In all the titrations in different concentrations of H_2SO_4 only one inflexion corresponding to nearly 2.66 mole of $K_2Cr_2O_7$ per mole of gallic acid (Table-1) was observed, which is suggestive of stoichiometry.

$$8Cr_2O_7^{-2} + 3C_7H_6O_5 + 61H^+ \rightarrow 3CH_3COO^- + 16Cr^{3+} + 15CO_2 + 35H_2O$$

According to the above equation,

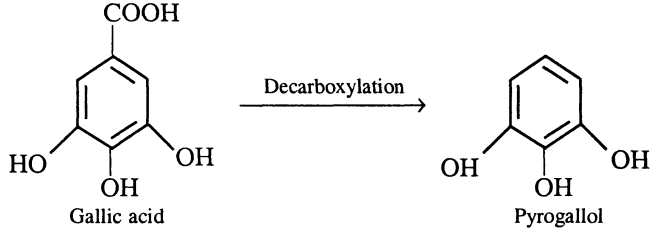
$$K_2Cr_2O_7 : C_7H_6O_5 = 2.66 : 1$$

In reverse titration when $K_2Cr_2O_7$ solution was added to the solution of gallic acid in increasing amount the orange colour first obtained changed to bluish green and finally at the inflexion point it became greenish blue. At the inflexion point the molar ratio of gallic acid and $K_2Cr_2O_7$ was again found to be nearly $K_2Cr_2O_7$: $C_7H_6O_5 = 2 : 66 : 1$ in all titrations (Table-1).

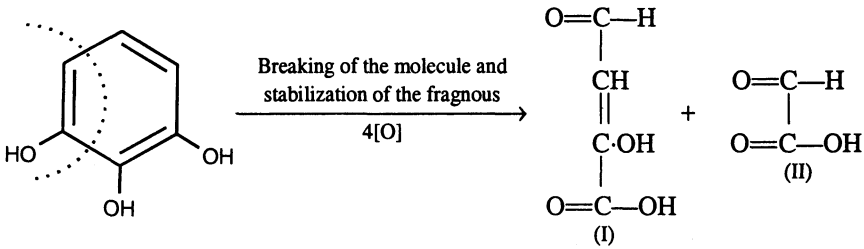
Mechanism of cleavage of gallic acid by potassium dichromate

The reaction between $K_2Cr_2O_7$ and $C_7H_6O_5$ in the presence of water or H_2SO_4 is highly exothermic. This might be due to some violent reaction taking place between them leading to breaking of gallic acid molecule. A simple mechanism for cleavage of gallic acid molecule has been proposed which explains the results of reaction between $K_2Cr_2O_7$ and $C_7H_6O_5$ in presence of water and various concentrations of sulphuric acid. The mechanism involves the following steps:

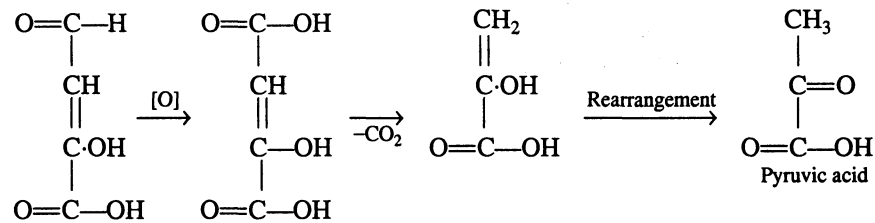
(1) Gallic acid easily gives out CO_2 and is converted into pyrogallol.



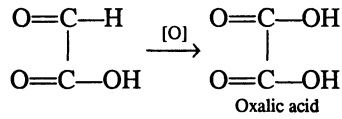
(2) This is followed by breaking of the molecule and stabilization of the fragments by taking oxygen in the oxidation process and can be given as follows:



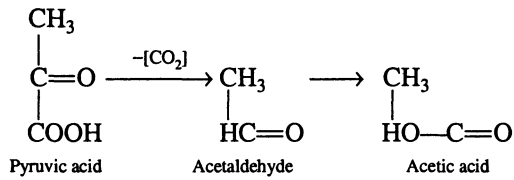
(3) The fragment (I) undergoes further oxidation asnd rearrangement process forming pyruvic acid as given below:

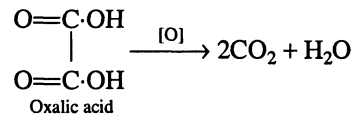


(4) The fragement (II) oxidizes to oxalic acid by oxidation and can be represented as



(5) Finally pyruvic acid and oxalic acid both undergo oxidation, the former giving acetic acid and CO_2 and the latter CO_2 and H_2O as given below;

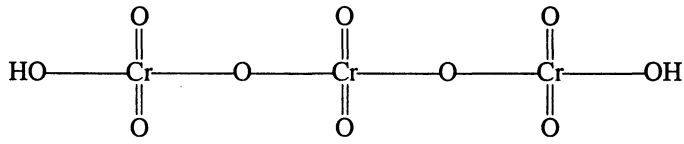




It has been reported that Cr^{6+} ions show strong tendency to condense and form polynuclear chain[10].

$$CrO_4^{2-} \rightarrow Cr_2O_7^{2-} \rightarrow Cr_3O_{10}^{2-} \rightarrow Cr_4O_{13}^{2-}$$

A trinuclear chain of chromium of the type



may be supposed to be formed in this case. According to the above mechanism in step 1 to 3, six atoms of oxygen are needed for the formation of pyruvic acid and oxalic acid from gallic acid. This oxygen is readily available from the trinuclear chromium chain reducing Cr^{6+} to Cr^{3+}. Pyruvic acid obtained in the oxidation of gallic acid forms a trinuclear complex with Cr^{3+} whose structure has been proposed above. As no Cr^{3+} ions are left, oxalic acid obtained from the cleavage of gallic acid fails to form a complex and escapes when repeatedly washed to make the pyruvic complex pure. The stoichiometry at the inflexion point corresponds to 2.66 moles of $K_2Cr_2O_7$ per mole of $C_7H_6O_5$ and the solution turns greenish blue indicating the formation of Cr^{3+}. It is well known that

$$2.66 \text{ moles of } K_2Cr_2O_7 \equiv 8(O)$$

In steps 1 to 5 of the mechanism, the total number of oxygen atoms needed in the cleavage of a molecule of gallic acid is exactly 8. Since the colour of the solution at the inflexion point is characteristic of Cr^{3+}, it is expected that Cr^{6+} is reduced to Cr^{3+} in the process of cleavage of gallic acid.

ACKNOWLEDGEMENTS

The authors expresses thank to Dr. S.N. Prasad, Retired Professor, Chemistry Deptt., B.R.A., Bihar University, Muzaffarpur for encouragement and valuable discussion. The facilities for providing IR, UV from CDRI, Lucknow are thankfully acknowledged.

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(*Received*: 13 January 1999; *Accepted*: 3 April 1999) AJC-1712