



## Isolation and Characterisation of Oxidation Product of Glycollic Acid by Chromic Acid in Tetrahydrofurane and Tertiary Butyl Alcohol Medium

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(Received: August 05, 2012; Accepted: September 03, 2012)

### ABSTRACT

The complexes of composition  $[\text{Cr}_2(\text{OH})_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_4]$  and  $[\text{Cr}_2(\text{OH})_2(\text{C}_2\text{O}_4)(\text{CHO}\cdot\text{COO})_2(\text{H}_2\text{O})_4]$  were isolated by oxidation of glycollic acid with chromic acid in aqueous tetrahydrofuran and tertiary butyl alcohol medium using different chromic acid and glycollic acid ratios. The products isolated were characterised from the elemental analysis, magnetic susceptibility and infrared spectral studies. The substrate having higher oxidation states of chromium could not be isolated in solid form.

**Key words :** Chromic acid, Glycollic acid, Oxidised Cr (III) complexes.

### INTRODUCTION

The kinetics of oxidation of glycollic acid has been studied in detail by chromic acid oxidation methods<sup>1-3</sup>. The oxidation of glycollic acid to glyoxylic acid using a microbial cell transformant as catalyst has been reported<sup>4</sup>. A little work has been done on the isolation and characterization of intermediate complexes formed during the redox reactions. In present investigation we have isolated and characterized the stable complexes formed during the oxidation reactions.

### EXPERIMENTAL

The glycollic acid (E. Merck) and chromium trioxide (E. Merck) were used in the

reaction. The solvents used tetrahydrofuran (THF) and Tertiary butyl alcohol (TBA) Anal'R grade reagent were used.

The estimation of C and H was obtained from CDRI, Lucknow. Chromium was estimated volumetrically. The FTIR data was recorded on FTIR spectrophotometer from CDRI, Lucknow.

### Procedure

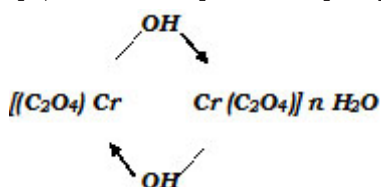
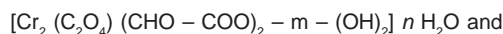
1.2 ml of glycollic acid (0.737 M solution) in THF was taken in each case but different amounts of  $\text{CrO}_3$  in TBA were taken and reaction was carried out in TBA + THF (1:1) medium at 25°C. The amount of  $\text{CrO}_3$  taken were 1.5g (1M solution) (GTH-1), 1g (0.667 M solution) (GTH – 4) and 0.5g (0.334 M solution) (GTH – 5). The solid compounds were

obtained in each case and products formed were collected.

The elemental analysis suggested the proposed formulation (Table 1) of the chromium complexes formed.

### RESULTS AND DISCUSSION

The variations of the amount of oxidant ( $\text{CrO}_3$ ) for fixed amount of glycollic acid changes the extent of formation of oxalic and glyoxylic acid contents in the reaction process. The composition of products formed were found between



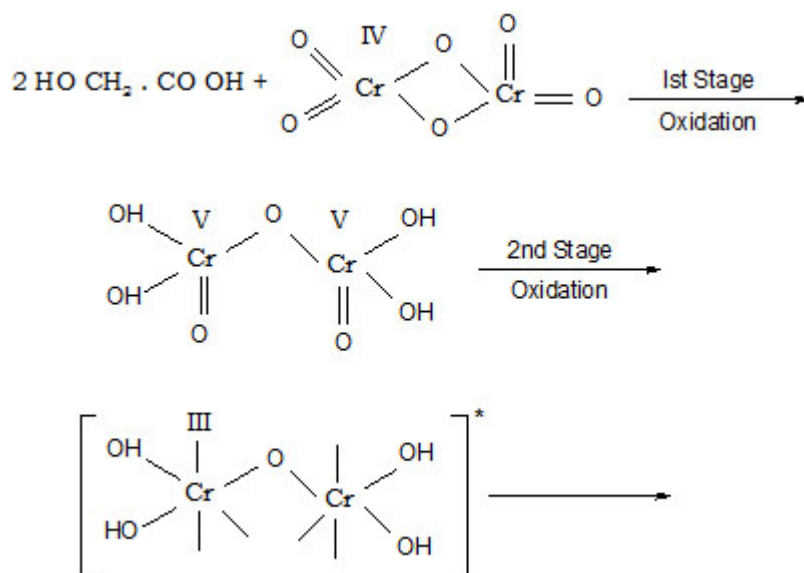
The products formed were partially soluble in cold water and more in hot condition. The solubility of complex in water to some extent can be attributed to interaction of water molecules with complex carboxylate group. It has been found that product

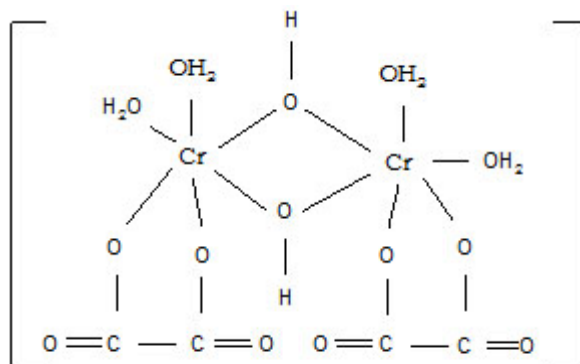
formed in excess of  $\text{CrO}_3$  has composition  $\text{Cr}_2 (\text{C}_2\text{O}_4)_2 - \mu - (\text{OH})_2 .8 \text{H}_2\text{O}$  (GTH - 1). The complex formed in appropriate amount of glycollic acid has composition  $\text{Cr}_2 (\text{C}_2\text{O}_4)_2 - \mu - (\text{OH})_2 .10 \text{H}_2\text{O}$  (GTH - 4). In lower proportion of oxidant the complex  $\text{Cr}_2 (\text{C}_2\text{O}_4) - (\text{CHO} . \text{COO})_2 - \mu - (\text{OH})_2 .4 \text{H}_2\text{O}$  (GTH - 5) is formed. The glycollic acid is a weak acid containing one primary alcoholic group and the reaction proceeds by oxidation of alcoholic part ( $\text{HO} - \text{CH}_2 -$ ) to formyl group ( $-\text{CHO}$ ) and that coordinates with excess of oxidant which further gets oxidised into oxalic acid. The further oxidation of oxalic acid to  $\text{CO}_2$  was not achieved as evidenced by formation of hydroxoquo Cr (III) oxalate  $\text{Cr}_2 (\text{C}_2\text{O}_4)_2 \mu(\text{OH})_2 . n \text{H}_2\text{O}$  in good yield.

In presence of less oxidant,  $\text{CrO}_3$ , the glyoxylic acid ( $\text{CHO} . \text{COOH}$ ) and oxalate containing mixed Cr (III) complex has been isolated (GTH - 5).

The presence of aldehydic group in this complex has been confirmed by Tollen's Reagent test and IR spectral band of (C-H) bending band at  $1460.2 \text{ cm}^{-1}$ .

The oxidation of  $\text{HO} . \text{CH}_2 . \text{COOH}$  (glycollic acid) proceeds as shown below :

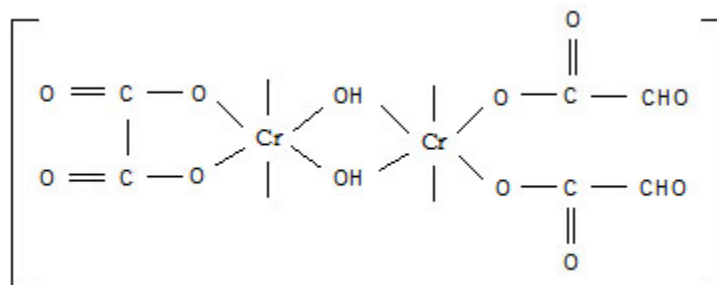




**Final Product**

**Fig. 1:**

If oxidant  $\text{CrO}_3$  is in less than proper molar ratio, the  $\text{CHO} - \text{COOH}$  remains coordinated as bridging carboxylic acid group as shown :-



**Fig. 2:**

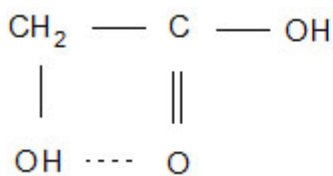
The proportion of complex B varies with amount of oxidant and glycollic acid in experiment. Therefore, the complex B has slightly higher carbon and chromium (III) percentage than that of complex A.

The magnetic susceptibility of complex has been recorded and it was found in the range of 3.52 – 3.67 BM at room temperature, which substantiated the oxidation state +3 of chromium. The complex does not contain chromium in higher

oxidation state as they fail to liberate  $\text{I}_2$  in acidic medium.

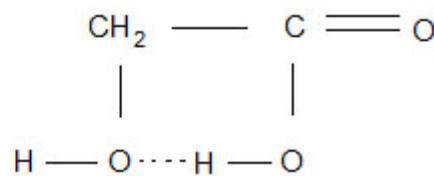
**I.R.**

Glycollic acid contains alcoholic group ( $-\text{OH}$ ) and carboxylic group ( $-\text{COOH}$ ) adjacent to hydroxyl group carbon and thus it has both free carboxylic group ( $-\text{COOH}$ ) and hydrogen bonded alcoholic group ( $-\text{OH}$ ), which is bonded strongly by Ketonic group ( $>\text{C}=\text{O}$ ) oxygen. (Fig. C & D).



**Fig. 3:**

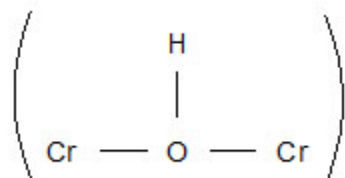
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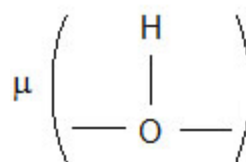
**Fig. 4:**

Due to the presence of both species in free glycollic acid<sup>6</sup>, it shows  $\nu$  (OH) frequency as a broad band between 3600 – 2615  $\text{cm}^{-1}$  region. Due to the predominance of species D, it shows very strong Ketonic group  $\nu$  (CO) stretching band at 1732  $\text{cm}^{-1}$  and (CO) vibration<sup>6</sup> as weak band at 1637  $\text{cm}^{-1}$ . The ( $\text{CH}_2$ ) I.R. vibration of glycollic acid enveloped in strong hydrogen bonded (OH) frequency. The  $\delta$ ( $\text{CH}_2$ ) of methylinic group<sup>7</sup> is observed at 1431  $\text{cm}^{-1}$  and sym (COO) as weak band at 1355  $\text{cm}^{-1}$ . The (C – C) stretching was located in free glycollic acid at 1224  $\text{cm}^{-1}$ , while (C – O) phenolic at 1087  $\text{cm}^{-1}$ . The weak I.R. band at 991  $\text{cm}^{-1}$  and 883  $\text{cm}^{-1}$  are attributed to  $\text{CH}_2$  group wagging and rocking vibrations. The I.R. band at 659  $\text{cm}^{-1}$  and 474  $\text{cm}^{-1}$  are deformation bands.

The oxidation products of glycollic acid display entirely different I.R. vibrations from glycollic acid. The I.R. spectral characteristic of complex is similar to oxalic acid and complex containing hydrogen bonded water molecules. The broad I.R. band between 3600 – 2900  $\text{cm}^{-1}$  supports plenty of water molecules coordinated and attached with hydrogen bonding with oxalic acid carbonyl group. The band at 2363  $\text{cm}^{-1}$ , which is sharp and medium suggests the presence of bridging – OH group



in complexes isolated in each experimental conditions. The broad and very strong I.R. band between 1730  $\text{cm}^{-1}$  and 1550  $\text{cm}^{-1}$  is mixture of  $\delta$   $\text{CH}_2\text{O}$ ,  $\nu$  as (C=O) and (C=O – H – O – H) present in complex. The  $\nu$  of (C=O) group is also very strong and located at 1404  $\text{cm}^{-1}$  in complexes. The (C – C) of oxalic acid was observed at 1272  $\text{cm}^{-1}$  and (C – O) at 1079  $\text{cm}^{-1}$ . I.R. band at 935  $\text{cm}^{-1}$  is due to



The bands at 805, 765, 611, 502 and 468  $\text{cm}^{-1}$  are attributed to various deformation vibrations in complexes. The strong band at 548  $\text{cm}^{-1}$  can be attributed to  $\nu$  (Cr –  $\text{OH}_2$ ) stretching.

Thus, from the evidence of magnetic susceptibility data, elemental analysis and infrared spectral band position, the oxidation of glycollic acid by  $\text{CrO}_3$  in neutral solvents tetra-hydrofuran and tertiarybutyl alcohol to oxalic acid has been established. The formation of intermediate product glyoxylic acid (OHC – COOH) and the formation of their chromium (III) complexes have been substantiated.

**Table 1: Elemental analysis of chromium complexes (%)**

Compound	Found (Calculated)		
	C	H	Cr
GTH – 1	10.31	3.73	23.40
$\text{Cr}_2(\text{C}_2\text{O}_4)_2 - \mu - (\text{OH})_2 \cdot 8 \text{H}_2\text{O}$	(10.38)	(3.89)	(23.37)
GTH – 4	9.80	4.44	21.54
$\text{Cr}_2(\text{C}_2\text{O}_4)_2 - \mu - (\text{OH})_2 \cdot 10 \text{H}_2\text{O}$	(9.60)	(4.41)	(21.68)
GTH – 5	16.30	2.71	23.80
$\text{Cr}_2(\text{C}_2\text{O}_4)_2(\text{CHO} \cdot \text{COO})_2 - \mu - (\text{OH})_2 \cdot 4 \text{H}_2\text{O}$	(16.07)	(2.68)	(24.11)

**Table 2: FTIR absorption bands in cm<sup>-1</sup>**

Glycollic acid	3358	2615	1732	1637	1431	1355
					1224	1087
					991	883
					659	474
GTH – 1	3395	2363	1707	1684	1407	1272
					1089	934
					810	773
					699	544
GTH – 4	3406	2362	1683	–	1407	1275
					1080	933
					811	773
					–	544
GTH – 5	3362	2363	1590	1460	1404	1272
					1091	935
					809	765
					612	549

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