ISSN XXXX XXXX © 2019 IJESC

Research Article Volume 9 Issue No.3

Study of the Products Obtained by Treating Glycine with Ditertiary Butyl Chromate in Water

Poonam Singh[1], Dr. Anita Gupta[2], Dr. H. O. Pandey[3]
Department of Chemistry
Ranchi University, Ranchi, India

Abstract:
Di-tert-butyl chromate (TBC) was prepared by dissolving calculated quantity of pure and dry chromium trioxide (CrO_3) in tert-butyl alcohol (TBA). Glycine was treated with TBC in different substrate: oxidant (TBC) molar ratio in water as solvent. The solid products obtained were isolated, washed, dried, purified and collected as GY11, GY21, GY23. The formula of these products have been worked out on the basis of elemental analysis, thermo gravimetric weight loss studies and FTIR peaks.

Keywords: FTIR, Glycine, Peaks, TBA, TBC, Water

I. INTRODUCTION

TBC has been used as oxidant by several workers. They have used this oxidant for the oxidation of various types of organic compounds. In most of these studies, solid complexes of chromium have been obtained. G.DMishra *et.al.* [1-11] have used TBC for oxidizing various organic compounds. In the present work, we have used glycine with TBC in various substrates: oxidant ratios in water. Microwave is being used as a heat source for chemical synthesis[12]. In his article "Controlled microwave heating in modern organic synthesis" Kappe agrees that microwave is the Bunsen burner of the 21st century[13]. Microwave heating under controlled conditions offers distinct advantages over conventional heating. Chromium (VI) based reagents have been extensively used in organic synthesis[14-15]. TBC has proved to be a potent and versatile oxidizing agent. It was prepared for the first time by Weinhaus but Oppenauer[16] introduced it as a new oxidizing agent.

II. CHEMICAL USED:

Chromium trioxide (CrO_3), TBA, Water, Glycine, Potassium persulphate ($K_2S_2O_8$), Acetone etc. (Chemical used were all A.R.Grade.)

Experimental Procedure

(a) GY 11 (substrate : oxidant :: 1:1 molar ratio) :
TBC was prepared by dissolving 1 gm of pure and dry CrO_3 in 10 ml of TBA. 0.76 gm of Glycine was dissolved in water to get substrate solution (SS-1). Exothermic reaction took place when TBC was added to SS-1 leading to the formation of black precipitate which turned to grayish black product when washed several times with acetone and dried. This was labeled as GY11.

(b) GY21 (substrate: oxidant :1:0.5 molar ratio):
TBC was prepared by dissolving 0.5 gm of pure and dry CrO_3 in 10 ml of TBA. 0.76 gm of Glycine was dissolved in water to get substrate solution (SS-2). Exothermic reaction took place when TBC was added to SS-2 leading to the formation of black precipitate. The product turned into grayish black product when washed several times with acetone and dried. This was labeled as GY21.

(b) GY23 (substrate: oxidant :: 2:3 molar ratio):
TBC was prepared by dissolving 1.5 gm of pure and dry CrO_3 in 10 ml of TBC. 0.76 gm of Glycine was dissolved in water to get substrate solution (SS-3). TBC solution was now added to SS-3 solution. After 5 minutes it got heated which showed the exothermic nature of the reaction. The reaction mixture was now left overnight. The solid product obtained thus was washed successively with acetone and water. The black colour solid was labeled as sample GY 23.

III. RESULTS AND DISCUSSION:

The quantitative analysis of carbon, hydrogen & nitrogen were performed instrumentally. The chromium content was estimated volumetrically. The proposed formula, percentage composition of the complex was experimentally found as well as calculated theoretically.

(a) GY11: Table 1 shows the comparison of observed and calculated elemental percentage.
Colour - Greyish black

Table.1. Composition of gy11

Element	Observed %	Calculated %
Nitrogen	8.148	7.36
Carbon	15.68	18.947
Hydrogen	3.69	4.210
Chromium	26	27.368
Oxygen	46.482	42.105

Empirical Formula : $Cr_2N_2C_6H_{16}O_{10}$

Proposed Formulation:
$CrO.2[HCHO.NH_2.CH_2.COOH].3H_2O$

The FTIR peaks also support the presence of the bonds and groups present in proposed formulation. (Table 2).

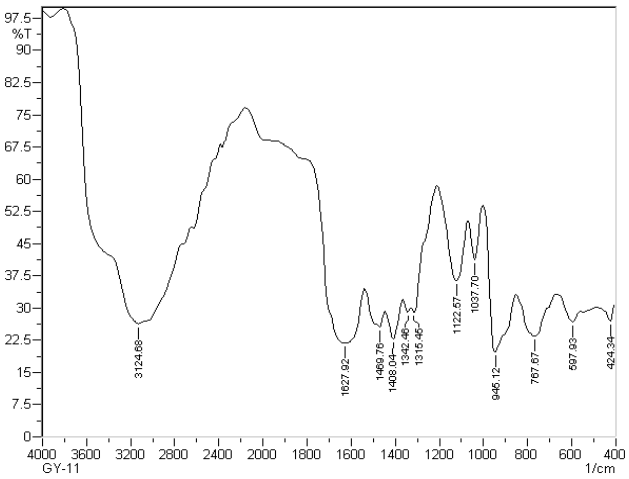


Table.2. FTIR peak of complex GY11

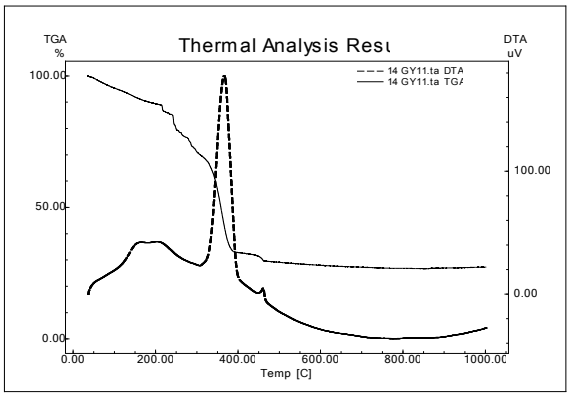
Peak at	Nature of Peaks	Group Assignment
3124.68	Broad	Ar-NO_2, C-H stretching
1627.92	Middle	C=O stretching (aldehyde), (-C=C-) Alkene
1469.76	Medium	C-H stretching, C=C stretching
1408.04	Weak	C=O stretching
1342.46	Sharp	COO^- group
1315.45	Sharp	-O-NO_2 (nitrates)
1122.57	Sharp	C-O of alcohol, COOH, aldehyde
1037.70	Weak	C-C stretching
945.12	Weak	CO coordinated water
767.67	sharp	HCOOH
597.93	Weak	Cr-O bonding
424.34	Weak	Cr-O bonding

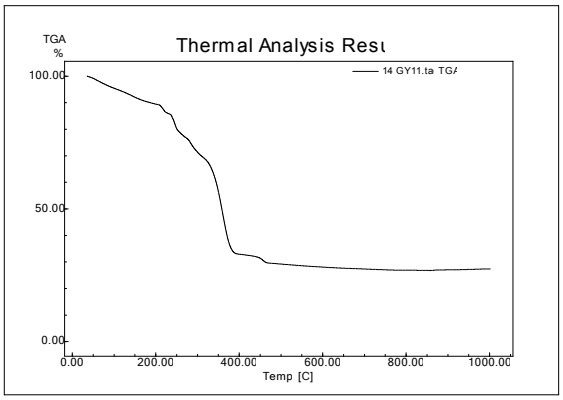
The DTA-TGA curves of the complex GY 11 show the expected loss pattern for the proposed formulation. The three stages of the loss as supported by DTA curves occur at 35 ^{0}C and 510^{0}C. The 1st and 3rd losses of 10.97% (theoretical 9.479 %) and 3.673% (theoretical 4.73 %) correspond to the escape of two and one water molecules in the temperature range of 35-210^{0}C & 410 to 510^{0}C respectively. The second experimental loss of 56.318%(theoretical 55.26%) is attributed to two molecules of formic acid, amino group and ethanoic acid leaving behind the oxide of Cr (Table III,weight loss pattern).

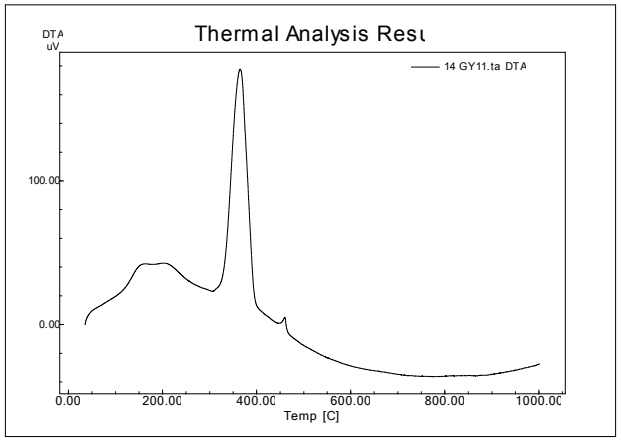
Table.3. Weight Loss Pattern

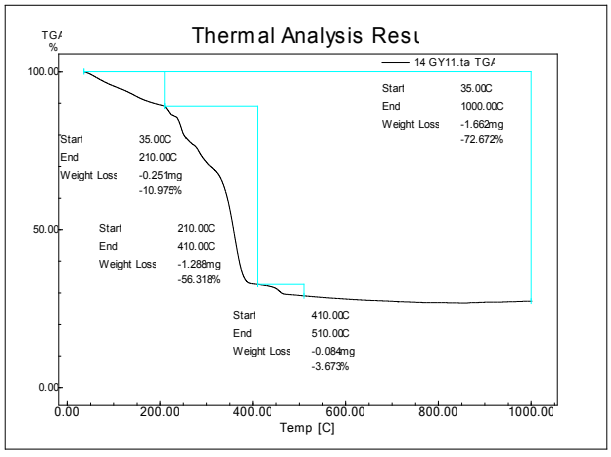
Temperture	Weight loss pattern	Percentage loss	
		Experimental	Theortical
35^{0}C-210^{0}C	2 CrO-2HCHO-2NH_2-2CH_2HCOOH-3H_2O	10.97	9.479
	-2H_2O		
210^{0}C-410^{0}C	2CrO-2HCHO-2NH_2-2CH_2HCOOH-H_2O	56.318	55.26
	-2HCHO.2NH_2.2CH_2HCOOH		
410^{0}C-510^{0}C	2 CrO.H_2O	3.673	4.73
	-H_2O		
	2 CrO		

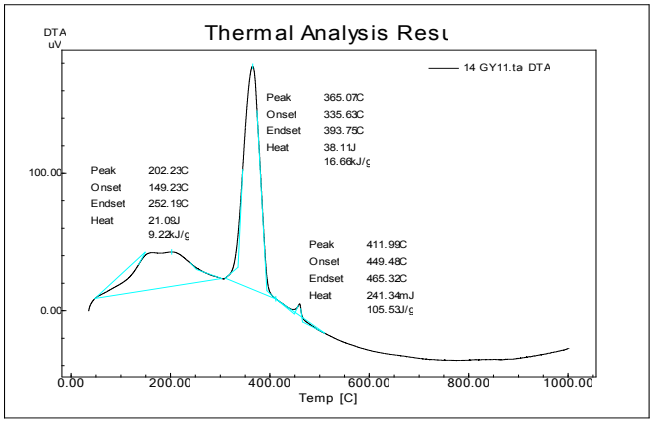
DTA-TGA curves of complex GY11











IV. RESULTS AND DISCUSSION:

(b) GY21: Table 4 shows the comparison of observed and calculated elemental percentage.
Colour - Greyish black

Table.4. Composition of Gy21

Element	Observed %	Calculated %
Nitrogen	11.58	6.008
Carbon	19.91	20.60
Hydrogen	4.618	3.00
Chromium	20.8	22.31
Oxygen	45.10	48.068

Empirical Formula: $Cr_2 N_2 C_8H_6O_{14}$
Proposed Formulation:
$2\ CrO.2[COOH.NO.CH_2COOH]H_2O$

The FTIR peaks also support the presence of the bonds and groups presents in proposed formula (Table 5).

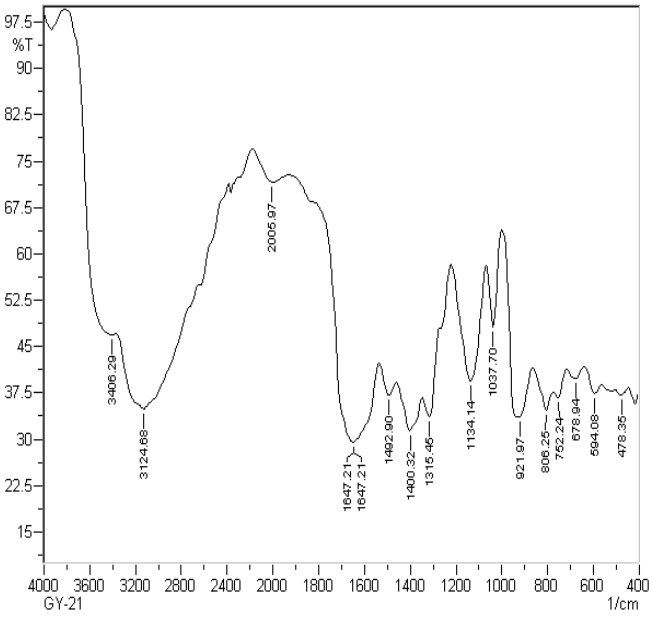


Table.5. FTIR peak of complex GY21

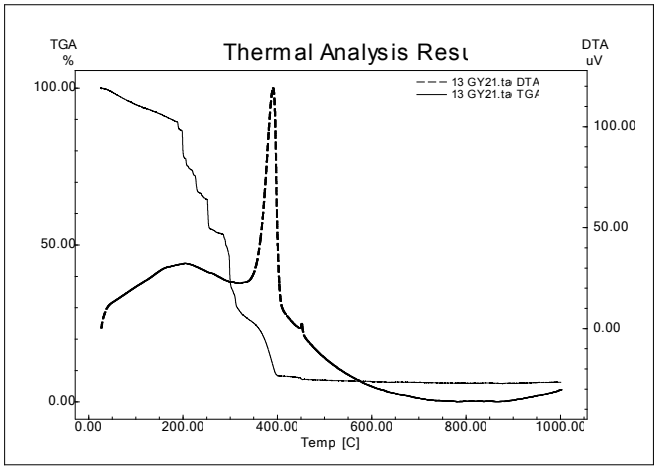
Peak at	Nature of Peaks	Group Assignment
3406.29	Broad	Ar-NO_2, C-H stretching
3124.68	Broad	Ar-NO_2, C-H stretching
2005.97	Broad	CR=CR,C-H stretching
1647.21	Middle	C=O stretching (aldehyde), (-C=C-) Alkene
1492.90	Medium	C-H stretching, C=C stretching
1400.32	Weak	C=O stretching
1315.45	Sharp	-O-NO_2 (nitrates)
1134.14	Sharp	C-O of alcohol, COOH, aldehyde
1037.70	Weak	C-C stretching
921.97	Weak	CO coordinated water
806.25	Weak	O-H Rocking (due to water)
752.24	sharp	HCOOH
678.94	Weak	Cr-O bonding
594.08	Weak	Cr-O bonding
478.35	Weak	Cr-O bonding

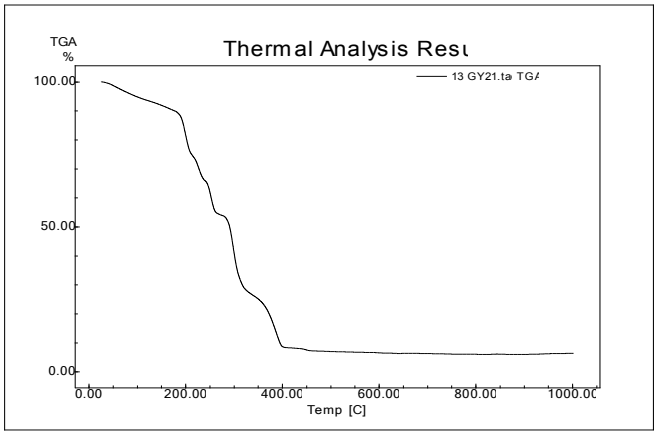
The DTA- TGA curves of the complex GY 21 show the expected loss pattern for the proposed formulation. The loss in mass starts from the very beginning. The three stages of the loss as supported by DTA curves occur between186 ^{0}C and 500^{0}C. The 1st loss of 80.56% (theoretical 77.89 %) is due to loss of molecules of formic acid, acetic acid and nitric oxide. The second experimental loss of 1.35% (theoretical 4.73 %) is attributed to escape of a water molecule leaving behind the oxide of Cr

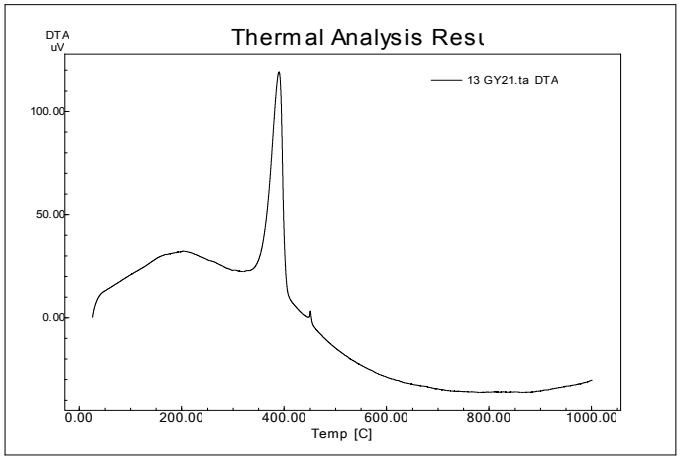
Table.6. Weight Loss Pattern

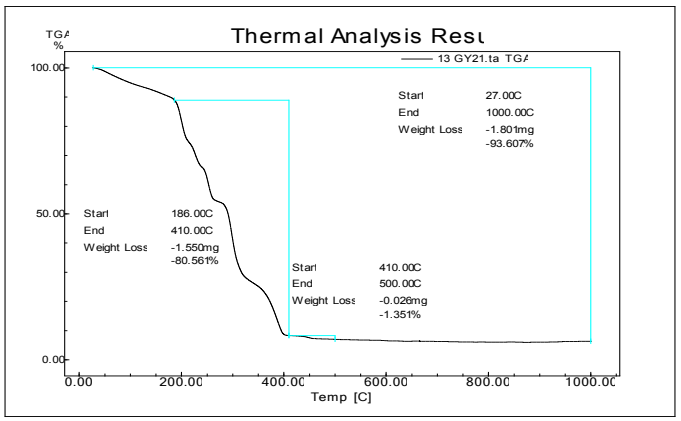
Temperture	Weight loss pattern	Percentage loss	
		Experimental	Theortical
186 ^{0}C- 410 ^{0}C	2 CrO.2 [HCOOH.NO.CH_3 COOH].H_2O	80.56	77.89
	-2[HCOOH.2NO.2CH_3COOH]		
410 ^{0}C- 500 ^{0}C	2 CrO H_2O	1.35	4.73
	-H_2O		
	2 CrO		

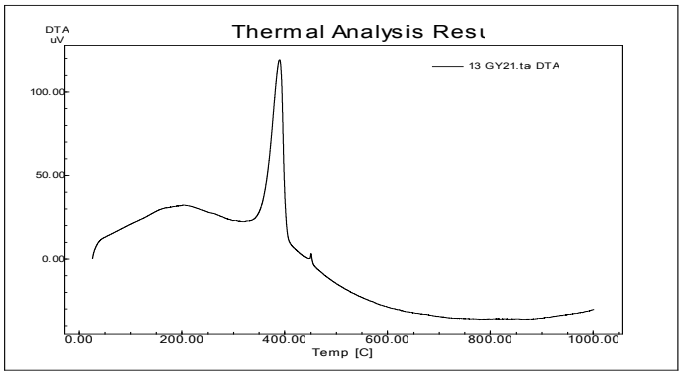
DTA-TGA curves of complex GY 21

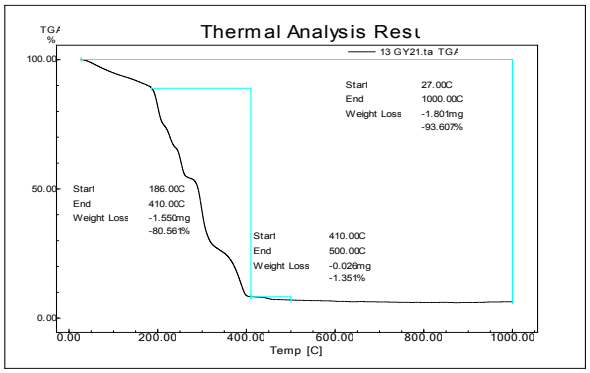












V. RESULTS AND DISCUSSION:

(c)GY23: Table 7 shows the comparison of observed and calculated elemental percentage.
Colour - Black

Table.7. Composition of Gy23

Element	Observed %	Calculated %
Nitrogen	6.105	7.29
Carbon	9.986	12.5
Hydrogen	2.603	3.15
Chromium	31.2	27.08
Oxygen	49.129	50.0

Empirical Formula: $Cr_2N_2C_4H_{12}O_{12}$

Proposed Formulation:
CrO. 2[CHO NO COOH]. H_2O

The FTIR peaks also support the presence of the bonds and groups presents in proposed formula (Table 8).

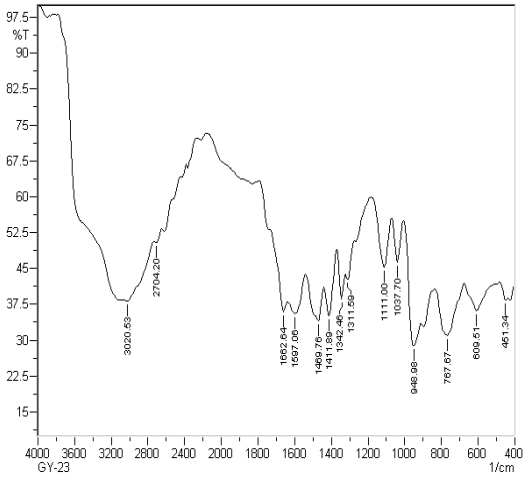


Table.8. FTIR peak of complex GY23

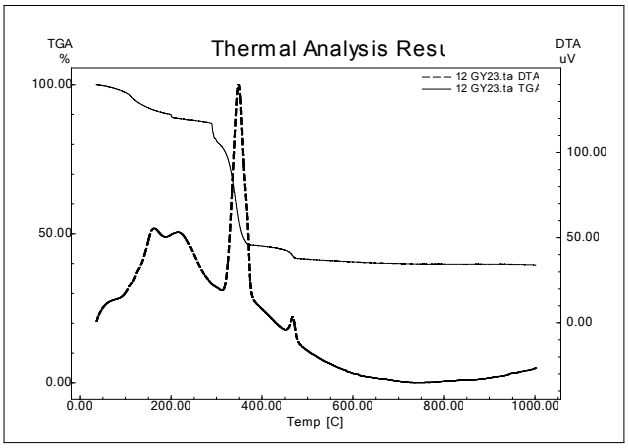
Peak at	Nature of Peaks	Group Assignment
3020.53	Broad	Ar-NO_2, C-H stretching
2704.20		
1662.64	Middle	C=O stretching (aldehyde), (-C=C-) Alkene
1597.06	Sharp	C-O of alcohol, COOH, aldehyde
1469.76	Medium	C-H stretching, C=C stretching
1411.89	Weak	C=O stretching
1342.46	Sharp	COO^- group
1311.59	Sharp	-O-NO_2 (nitrates)
1111.00	Sharp	C-O of alcohol, COOH, aldehyde
1037.70	Weak	C-C stretching
948.98	Weak	CO coordinated water
767.67	sharp	HCOOH
609.51	Weak	Cr-O bonding
451.34	Weak	Cr-O bonding

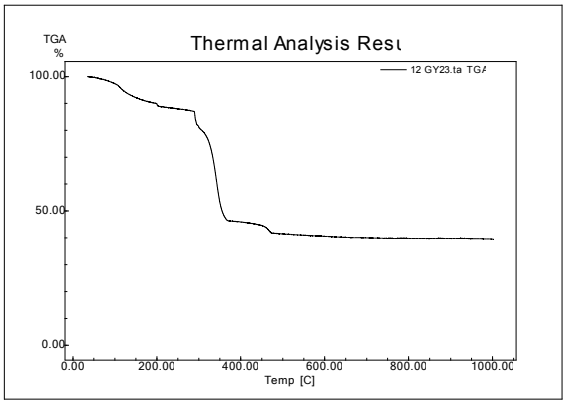
The DTA-TGA curves of the complex GY 23 show the expected loss pattern for the proposed formulation. The three stages of the loss as supported by DTA curves occur at 36 ^{0}C and 550^{0}C. The 1st loss of 12.91% (theoretical 15.625 %) is due to loss of molecule of nitric oxide. The second major experimental loss of 40.27 % (theoretical 38.54%) is attributed to loss of two molecules of formic acid. The third experimental loss of 5.15 % (theoretical 4.687%) is attributed to escape of water molecule leaving behind the oxide of Cr.

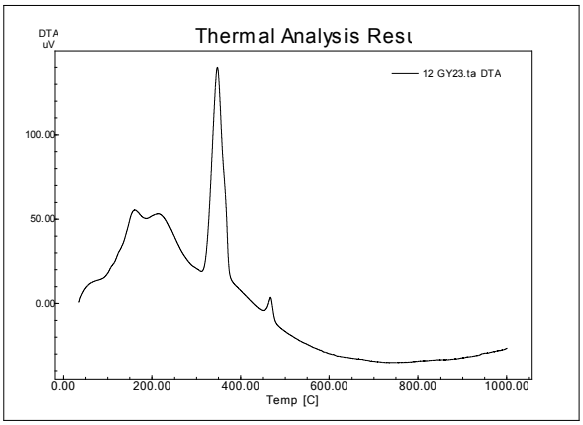
Table.9. Weight Loss Pattern

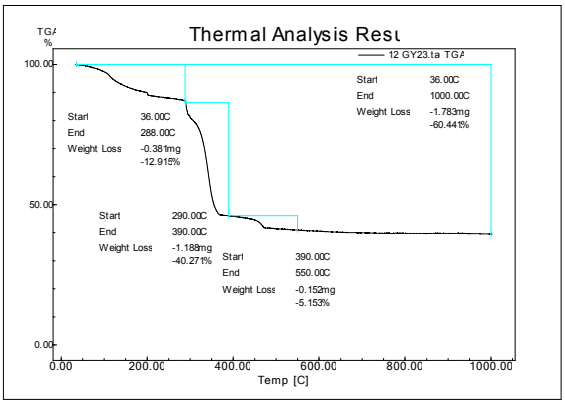
Temperture	Weight loss pattern	Percentage loss	
		Experimental	Theortical
36 ^{0}C - 288 ^{0}C	2 CrO.2 [HCHO.NO.HCOOH].H_2O	12.91	15.625
	-2 NO		
290 ^{0}C- 390 ^{0}C	2 CrO 2 HCHO 2HCOOH	40.27	38.54
	-2HCHO.2HCOOH		
390 ^{0}C - 550 ^{0}C	2CrO.H_2O	5.15	4.687
	- H_2O		
	CrO		

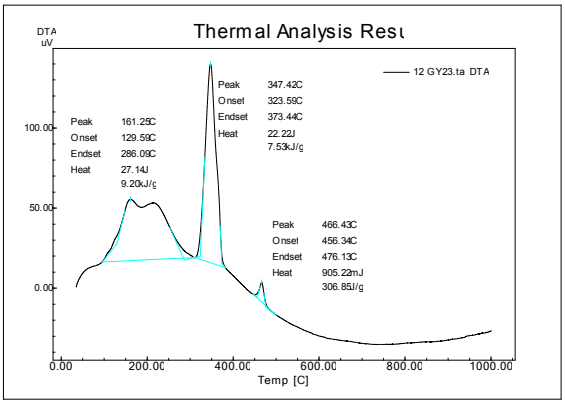
DTA-TGA curves of complex GY 23











VI. CONCLUSION

The reaction conditions in table show that the formation of compounds/ complexes of chromium with glycine is difficult. The chemical oxidation of glycine under mechanical stirring and

microwave condition leads to different product including nitro derivatives. The degradative oxidation of the substrate takes place when the ratio of oxidant is more as substantiated by the presence of smaller fragments in case of GY-23. The formation of amino compound in higher ratio of oxidant is supported by its presence in GY -23 as ligand. This is not observed in other cases where the extent of oxidation is less. Extent of degradative oxidation increases as the proportion of oxidant is raised, as the lower fragment HCOOH is observed in GY-23. It is also supported by the fact that some of the complexes like GY-21 & GY-23 is formed with the unoxidised ligand along with other side products (where the oxidant ratio is less compared to GY-23). Again the solubility of the products in water is more in those cases when Glycine itself is present as ligand. The number of water molecule in the products GY-23 is more whereas it is less in products GY-11 and GY-21. This may be due to the fact greater extent of oxidation leads to the formation of smaller organic moiety and greater number of water molecule.

VII. REFERENCES

[1]. G.D. Mishra, (1985). J. Inst. Chem. (Ind.) Pp. 57.

[2]. G.D.Mishra, R.Prasad, S.P. Singh and S.Mishra, (1988). J. Inst. Chem. (Ind.) Pp. 60.

[3]. G.D.Mishra, H.O.Pandey, and N.N. Mishra, (1990). J. Inst. Chem. (Ind.) 62,37

[4].G.D.Mishra, N.Drivedi, N.N.Mishra, and H.O.Pandey, (1991). J. Inst. Chem. (Ind.)62,67

[5]. G.DMishra, S.N.Tiwari, and N.N.Mishra, (1991). J. Inst. Chem. (Ind.)63,217 .

[6]. G.D.Mishra, S.N.Tiwari ; N.Dwivedi and M.Alam, (1991). J. Inst. Chem. (Ind.) 63,166

[7]. G.D.Mishra, M,Alam, R.Thakur, and N.N.Mishra, (1991). J. Inst. Chem. (Ind.)63,(6)217

[8]. G.D.Mishra, H.C. Mishra, and L.N.Choubey, (1985).J. Inst. Chem. (Ind.) Soc LX, 521

[9]. G.D.Mishra, R.K. Singh, and B.H.P. Pingua, (1999). J. Chemtracks, 1:172

[10]. H.C Mishra, G.Mishra, and L.N. Choubey, (1983).J. Inst. Chem. (Ind.) Soc. Vol. LX

[11]. G.Mishra, and N.K Tiwari, (2005). J. Chemtracks 7, 163, 168

[12]. D. Adam, (2003). Nature 421,571

[13]. C.O. Kappe, Angew, (2004) Chem.Int. Ed. 43,6250

[14]. F. Freeman, (1986) In Organic Synthesis by oxidation with metal compounds : Mijs. W.J. ; de Jonge, C.R.H.I Eds. Plenum Press : New York, pp. 68-81

[15]. Neeraj, A.K. Pandey and G.D. Mishra, (2009) J. Chemtracks 11(2),

[16]. R.V. Oppenaeur and H.Obermuch, (1949). Assoc.quim. Argent,37,246

ACKNOWLEDGEMENT

I would like to use this auspicious occasion to offer my special thanks and deep sense of gratitude to my supervisor Dr. Anita Gupta, Assistant Professor ,SSM college, Ranchi for fruitful discussion, and systematic guidance throughout the course of investigation. My acknowledgement is also due to Dr. H.O. Pandey, Head of Department of Chemistry, Ranchi University for inspiration and humble co-operation. I am thankful to Dr. S.K.Swain, Research officer and Dr. S.K. Sao, Technical Superintendents for carring out the instrumental analysis, FTIR curves obtained by Fourier Transform Infrared Spectrometer and TGA- DTA Thermo gravimetric mass at **BIT Mesra, Ranchi** I express a deep sense of gratitude to my Husband Shree Arun Sinha,my daughter Ms. Abhigya,my parents, Parents in-laws, other family members. Last but not the least, I wish to express my sincere thanks to my subordinate Ms. Sonali for her valuable contribution and co-operation in compiling the thesis. I cannot forget the immense contribution of house assistant, Ms.Shandya and Ms.Bina who took care of my household work during this period.