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THERMAL AND KINETIC STUDIES ON SOME HYDRAZINIUM AND BIS-HYDRAZINE METAL CARBOXYLATES

R. RAGUL and B. N. SIVASANKAR*

Department of Chemistry, Government Arts College, Udhagamandalam, THE NILGIRIS – 643002 (T.N.) INDIA

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ABSTRACT

Hydrazinium formate hemi hydrate, $HCOON_2H_5.0.5H_2O$ and its metal complexes viz., $[(N_2H_5)_2M(HCOO)_4]. H_2O$ where M = Co, Ni or Zn have been prepared and subjected to controlled thermal degradation in air. The thermogravimetry has been used to investigate the thermal decomposition kinetics of the above compounds. This analysis has been extended to the corresponding acetate and glycinate complexes, $[(N_2H_5)_2M(CH_3COO)_4]$ and $[(N_2H_5)_2M(NH_2CH_2COO)_4]$ where M = Co, Ni or Zn. The kinetic parameters were evaluated using the Coast-Redfern equation. The thermal reactivity and their kinetics have been compared with the corresponding bis-hydrazinium metal carboxylates.

Key words: Hydrazinium metal carboxylates, Bis-hydrazinium metal carboxylates, Metal oxides, Metal powders, Thermal kinetics.

INTRODUCTION

Hydrazinium metal carboxylate complexes have been recently reported and gains much interest due to their structure and thermal reactivity[1-5]. Metal complexes containing positively charged ligands are rare in contrast with those containing negatively charged and neutral ligands[6-8]. Hydrazinium metal carboxylates are expected to decompose at lower temperature due to the presence of hydrazine moiety, which is an endothermic compound. Further, the catalytic activity of the intermediates formed during thermal decomposition enhances the thermal reactivity of these complexes.

During our research on hydrazine metal carboxylates, we have reported the synthesis and characterization of number of hydrazinium metal formates[9], acetates[10] and glycinates[11] as precursor to metal oxides and fine metal powders. Since these complexes are new to the literature, their thermal decomposition kinetics have not been studied so far. Also bis-hydrazine metal formates[12] and acetates[13] are known to the literature and recently we have reported hydrazine metal glycinates[11]. For these complexes the thermal kinetic parameters have also not been reported. As far as we are aware, the only report available on thermal kinetics is on hydrazinium metal ethylenediamminetetraacetates[14]. Hence, in this paper, we have reported the thermal decomposition kinetics on hydrazinium metal carboxylates and bis-hydrazine metal carboxylates. We made an attempt to compare the thermal reactivity and thermal kinetics of hydrazinium metal carboxylates with the respective bis-hydrazine metal carboxylates.

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*Author for correspondence; E-mail: sivabickol@yahoo.com

EXPERIMENTAL

All the chemicals used were of analytical grade and the solvents were distilled before use. Hydrazine hydrate (99-100%) was used as such in all the reactions.

Hydrazinium formate hemi hydrate, hydrazinium metal formates, acetates and glycinates were prepared by the methods described earlier[9-11]. Bis-hydrazine metal formates, acetates and glycinates have been prepared by the following methods to obtain these complexes with high purity.

Preparation of bis-hydrazine metal formates

These complexes were prepared by adding an aqueous solution (100 mL) containing a mixture of formic acid (2.28 mL, 0.06 mol) and hydrazine hydrate (4.5 mL, 0.09 mol) to an aqueous solution (100 mL) of the respective metal nitrate hexa hydrate [0.03 mol, 8.73 g of $Co(NO_3)_2.6H_2O$ or $Ni(NO_3)_2.H_2O$ or 8.918 g of $Zn(NO_3)_2.H_2O$]. The resulting solution was kept at room temperature and the respective complexes precipitated were filtered, washed with ethanol and dried over P_2O_5.

Preparation of bis-hydrazine metal acetates

These complexes were prepared by the same procedure as above except substituting formic acid by acetic acid (3.6 mL, 0.06 mol).

Previously these complexes were prepared by the reaction of respective solid metals formates or acetate hydrates with excess of hydrazine hydrate. To avoid the lack of homogeneity, in the present method these complexes were precipitated from the aqueous solution.

Preparation of bis-hydrazine nickel glycinate

An aqueous solution (50 mL) containing a mixture of glycine (3 g, 0.04 mol) and hydrazine hydrate (2 mL, 0.04 mol) was added to an aqueous solution of nickel nitrate hexa hydrate (2.91 g 0.01 mol). The resulting solution was kept at room temperature for about one hour. The violet complex precipitated was filtered, washed with ethanol and dried in air.

Preparation of bis-hydrazine cobalt and zinc glycinates

The above method adopted for the nickel complex always resulted in the formation of tris-hydrazine in the case of cobalt and zinc ions[15]. Hence these complexes were prepared by reacting respective solid metal glycinate hydrates with excess hydrazine hydrate[11]. The composition of these complexes was determined on the basis of hydrazine and metal analyses[16].

Physico-chemical techniques

The simultaneous TG-DTA experiments in air were carried out using a Netzsch Thermal analyzer STA-409. The thermal analyses were carried out in static air with the heating rate of $10^oC\ min^{-1}$ using aluminium crucible as sample holder and aluminium oxide as reference material. About 10 mg of the samples were used to carry out the thermal experiments. The final products obtained were confirmed by their chemical analyses and X- ray powder diffraction.

RESULTS AND DISCUSSION

The hydrazinium formate hemi hydrate has been used in the preparation of hydrazinium metal formate mono hydrates. In the case of acetate and glycinate complexes, an aqueous solution containing a mixture of hydrazine hydrate and glacial acetic acid or glycine in 1 : 1 ratio have been used as ligands.

The complexes are slightly hygroscopic and hence stored in vacuum desiccator over P_2O_5. The complexes are all soluble in water and insoluble in alcohol and other common organic solvents. The bis-hydrazine complexes have been prepared by the reaction of a mixture of respective acid and hydrazine hydrate with the corresponding metal nitrate hydrates in aqueous medium. However, the bis-hydrazine cobalt and zinc glycinates were prepared by the reaction of the respective solid metal glycinates with hydrazine hydrate. The chemical analyses and conductivity measurements conform to the desired composition of the complexes. The room temperature magnetic moments of the complexes coupled with the electronic spectra confirm the octahedral coordination around the metal ions.

As expected the hydrazinium ions are coordinated to the metal ions in all the cases, shown by a band in the region 990-1015 cm^{-1}, allowing the monodendate coordination of carboxylate ions. This is also shown by the bands at 1660-1620 cm^{-1} and 1380 cm^{-1} for asymmetric and symmetric stretching respectively in the infrared spectra of these complexes[17]. The bis-hydrazine complexes are octahedral as reported earlier.

The complexes show isomorphism within the individual series, shown by their X-ray powder diffraction patterns.

Thermal degradation

$HCOON_2H_5.0.5\ H_2O$

Hydrazinium formate hemi hydrate is a highly crystalline, colourless substance and melts sharply at 162°C. DTA shows an endotherm corresponding to melting and there is no signal in DTG. The starts decomposing at 220°C without leaving any residue indicating complete decomposition to give gaseous products. The DTG peak temperature is 259°C and DTA shows an endotherm at 259°C. The activation energy is 146.75 KJ mol^{-1} and the negative entropy of activation may be due to the more ordered structure of the activated complex than the ground state.

$[(N_2H_5)_2Co(HCOO)_4].H_2O$

The cobalt complex undergoes decomposition without melting. The first stage is dehydration in the temperature range 75-105°C. TG shows a weight loss of 6% which is very well coincides with the calculated loss of 5.57%. This stage is found to be endothermic as evident from DTA which shows an endotherm at 95°C. The dehydration takes place at low temperature, which clearly excludes the possibility of coordination of water molecule. The energy of activation is very low, which is also in accordance with easy dehydration. The entropy of activation is very low. The anhydrous complexes decomposes exothermically in the temperature range 130-180°C with the DTA peak at 162°C to expel N_2H_4 and HCOOH moieties to give $N_2H_5Co(HCOO)_3$ as intermediate. This intermediate is assigned on the basis of TG weight loss. Attempt to prepare $N_2H_5Co(HCOO)_3$ by the reaction of ligand and cobalt nitrate hexa hydrate in 3 : 1 ratio was unsuccessful. Hence, we tried to isolate this complex after the completion of second stage. However, due to the continuous decomposition the residue removed was found to have indefinite composition. Hence, we were not able to characterize this compound. The activation energy is low (75.67 KJ mol^{-1}), which may be due to the thermal susceptibility of hydrazine moiety in the complexes. The lower entropy values indicate that the anhydrous complex is more orderly arranged in the activated state. In the third stage, the intermediate gives cobalt formate which is also exothermic. The activation energy is high, which is expected because after the removal of one or two ligands, further expulsion of ligand is difficult. The entropy of activation is higher than the previous stages. The residue from the third stage, cobalt formate is thermally stable and decomposes in the temperature range 270-340°C. The TG weight loss observed accounts for the formation of Co_3O_4 as the final residue. The final product was also confirmed by X-ray powder diffraction. The Ea value, 350.94 KJ mol^{-1} is also an indication of stability of cobalt formate. The entropy of activation is very high, which excludes the formation of p-type CoO.

$[(N_2H_5)_2Ni(HCOO)_4].H_2O$

In the case of nickel complex, dehydration takes place at higher temperature (105-162^oC) than the cobalt complex, which is mostly observed for coordinated water. However, the spectral and X-ray powder diffraction studies[9] clearly indicates the isomorphism between the hydrazinium metal formate hydrates, which rejects the water coordination. The lower activation energy for this first stage, 39.58 KJ mol^{-1} in the nickel complex indicates that the water molecule in a complex is outside the coordination sphere. The anhydrous nickel complex decomposes similar to the cobalt complex and the residue at this stage is $N_2H_5Ni(HCOO)_3$ which we could not isolate due to its continuous decomposition.

The activation energy is low for this stage also and the entropy of activation is lower for both first and second stages similar to the cobalt complexes. Unlike cobalt complex, the intermediate $N_2H_5Ni(HCOO)_3$ decomposes in one step to give nickel metal as the final residue in the temperature range 250-290^oC. The activation energy for this stage is high which may be due to the simultaneous formation and decomposition of nickel formate, though there is no distinct step in TG.

$[(N_2H_5)_2Zn(HCOO)_4].H_2O$

In the case of zinc complex the first stage is dehydration as expected with low activation energy. But the anhydrous complex straight away gives ZnO by total decomposition of the complex. The activation energy for the second stage is very high, which indicates due to coordinative saturation of the anhydrous complex, chemisorption is not taking place.

$[(N_2H_5)_2Co(CH_3COO)_4]$

Hydrazinium cobalt acetate undergoes single step decomposition exothermically in the temperature range 240-300^oC to give Co_3O_4. The TG weight loss and X-ray powder pattern of the residue are in accordance with its composition. The higher Ea value indicates the higher thermal stability of the complex. The positive entropy indicates the disorderness of the activated complex formed before decomposition.

$[(N_2H_5)_2Ni(CH_3COO)_4]$

Nickel complexes decompose in three stages. In the first stage one ligand molecule, hydrazinium acetate is expelled from the system to give $N_2H_5Ni(CH_3COO)_3$ which further decomposes to give $NiCO_3$ and then to NiO. All the stages are exothermic.

The energy of activation for the second stage is very high and for the third stage is low, which may be due to the catalytic activity of NiO formed during the decomposition.

$(N_2H_5)_2Zn(CH_3COO)_4]$

In this case the first stage is endothermic decomposition where one molecule of acetic acid is expelled from the complex to give an adduct, which further decomposes exothermically to give $ZnCO_3$ and finally ZnO as the final residue.

The low Ea value for the final stage may be due to the catalytic activity of p-type ZnO formed during this stage[14].

$[(N_2H_5)_2Co(NH_2CH_2COO)_4]$

The glycinate complex decomposes in two stages to give metal powder as the final residue and the cobalt glycinate being the intermediate. The first stage is endothermic with the expulsion of two molecules of hydrazinium glycinate and the second stage is exothermic. The formation of cobalt metal as the final residue is also observed in the case of tris-hydrazine metal glycinate[15] and bis-hydrazine metal glycinates[11].

The low activation energy and negative entropy of activation for the second stage may be due to the chemisorption of oxygen on coordinatively unsaturated intermediate.

$(N_2H_5)_2Ni(NH_2CH_2COO_4]$

The decomposition and its kinetics are almost similar for cobalt and nickel complexes. The decomposition temperatures are also in the same range.

$[(N_2H_5)_2Zn(NH_2CH_2COO)_4]$

This complex decomposes in three stages. In the first stage, zinc glycinate hydrazinate is formed. This intermediate decomposes to $ZnCO_3$, which finally gives zinc metal. The energy of activation for the first two stages are very low and the negative entropy indicates the ordered arrangement and the negative entropy indicates the ordered activated states for the complex and the intermediate. The thermal kinetic data of all the formate, acetate and glycinate complexes are summarized in Table 1, 2 and 3, respectively.

Table 1: Thermal and kinetic data of hydrazinium formate and its metal complexes $[(N_2H_5)_2 M (HCOO)_4]H_2O$

Compd.	Stage	TG temp. range (°C)	Weight loss (%) Found (Calc.)	Residue	E_a KJ mol^{-1}	S KJ mol^{-1} K^{-1}	A S^{-1}
Ligand	I	220-280 259*(+)	99 (100)	-	146.75	-164.05	29876.78
M=Co	I	75-105 95*(+)	06 (05.57)	$(N_2H_5)_2$ Co$(HCOO)_4$	96.10	-169.12	11231.18
	II	130-180 162*(-)	32 (29.75)	N_2H_5 Co$(HCOO)_3$	75.67	-225.51	15.05
	III	180-270 218*(-)	56 (57.02)	Co $(HCOO)_2$	173.46	-151.22	129055.3
	IV	270-340 292*(-)	74 (75.13)	Co_3O_4	350.94	-10.72	3.24×10^{12}
M=Ni	I	105-162 136*(+)	06 (05.57)	$(N_2H_5)_2$ Ni$(HCOO)_4$	39.58	-250.62	0.69
	II	165-250 220*(-)	30 (29.77)	N_2H_5 Ni$(HCOO)_3$	24.28	-265.21	12.32
	III	250-290 270*(-)	82 (81.73)	Ni	313.62	-31.60	2.53×10^{11}
M=Zn	I	110-150 136*(+)	06 (05.49)	$(N_2H_5)_2$ Zn$(HCOO)_4$	39.58	-250.62	0.69
	II	220-280 240*(-)	76 (75.61)	ZnO	313.62	-31.60	2.53×10^{11}

DTA peak temperature (°C)
* Endothermic signal in DTA (+)
Exothermic signal in DTA (-)

Table 2: Thermal and kinetic data of hydrazinium metal acetate complexes [$(N_2H_5)_2$ M $(CH_3COO)_4$]

Compd.	Stage	TG temp. range (^{o}C)	Weight loss (%) Found (Calc.)	Residue	E_a KJ mol^{-1}	S KJ mol^{-1} K^{-1}	A S^{-1}
M=Co	I	240-300 270*(-)	76 (77.78)	Co_3O_4	569.01	199.34	1.52 x 10^{23}
M=Ni	I	275-300 270*(-)	25 (25.52)	$(N_2H_5)_2$ $Ni(CH_3HCOO)_4$	137.65	-182.05	3627.89
	II	300-340 305*(-)	68 (67.11)	$NiCO_3$	907.57	401.47	1.13 x 10^{34}
	III	340-400 365*(-)	78 (79.31)	NO	207.33	-143.02	44.92
M=Zn	I	180-280 265*(+)	16 (16.33)	$(N_2H_5)_2$ $Zn(HCOO)_4$	60.81	-241.92	2.58
	II	280-325 290*(-)	66 (65.90)	$ZnCO_3$	370.00	2.63	1.16 x 10^{13}
	III	380-500 465*(+)	76 (77.87)	ZnO	85.31	-242.74	3.21

DTA peak temperature (^{o}C)*
Endothermic signal in DTA (+)
Exothermic signal in DTA (-)

Table 3: Thermal and kinetic data of hydrazinium metal glycinate complexes [$(N_2H_5)_2$ M $(NH_2CH_2COO)_4$]

Compd.	Stage	TG temp. range (^{o}C)	Weight loss (%) Found (Calc.)	Residue	E_a KJ mol^{-1}	S KJ mol^{-1} K^{-1}	A S^{-1}
M=Co	I	180-290 230*(+)	50 (50.86)	$Co(NH_2CH_2COO)_2$	165.85	-143.19	347130.8
	II	290-470 440*(-)	86.40 (86.01)	Co	110.73	-232.57	10.55
M=Ni	I	150-400 200*(+)	53 (51.88)	$Ni(NH_2CH_2COO)_2$	286.42	-107.77	3.34 x 10^{7}
	II	400-460 410*(-)	86.50 (86.05)	Ni	40.97	-264.72	0.1464
M=Zn	I	150-270 210*(+)	42 (42.59)	$Zn(NH_2CH_2COO)_2.N_2H_4$	69.64	-232.23	1.73
	II	280-500 380*(-)	67 (67.88)	$ZnCO_3$	45.41	-269.43	0.12
	III	510-590 530*(+)	85.20 (84.71)	Zn	245.44	-159.77	75429.63

DTA peak temperature (^{o}C)*
Endothermic signal in DTA (+)
Exothermic signal in DTA (-)

[M(HCOO)$_2$(N$_2$H$_4$)$_2$]

As already reported, the cobalt complex decomposes in two stages to give Co_3O_4 at 447°C and the intermediate being cobalt formate. The nickel formate gives a mixture of nickel metal and nickel oxide at 223°C. Zinc complex decomposes similar to the cobalt complex to give zinc oxide as the final residue.

Bis-hydrazine metal formates decompose at higher temperature than the corresponding hydrazinium metal formate monohydrates. This is because of the fact that the first stage of decomposition in bis-hydrazine complexes is endothermic. The exothermic decomposition is expected when the hydrazine and the metal complex decompose simultaneously. If this is the case then such complexes decompose at lower temperatures.

Unlike metal oxalate hydrazinates[18], metal formate hydrazinates do not exhibit autocatalytic decomposition/combustion behavior. This may be due to the loss of hydrazine endothermically at lower temperature before the exothermic decomposition of the metal formates.

In the case of nickel complex alone this happens and the decomposition temperature is comparable with the hydrazinium nickel formate.

The activation energies for the bis-hydrazine metal formates are in the range 20-67 KJ mol^{-1} for all the stages and the entropy values are in the range, -223 to 280 KJ mol^{-1} K^{-1}. In the nickel complex the lower degradation temperature may be attributed to the formation of nickel metal as one of the degradation products which catalyses further decomposition. Though when compared to the zinc complex the activation energy is 16.10 KJ mol^{-1}, higher for nickel complex, unlike zinc complex where the zinc formate is formed as the intermediate, nickel complex directly gives the mixture of nickel and nickel oxide which enhances further decomposition.

[M(CH$_3$COO)$_2$(N$_2$H$_4$)$_2$]

Acetate complexes due to the exothermic decomposition of first stage decompose at lower temperature than the corresponding formate complexes and also than the respective hydrazinium complexes.

When the acetate complexes are closely analyzed it is seen that the hydrazine adducts decompose at lower temperatures than the hydrazinium complexes which is attributed to the exothermic decomposition of adducts. In the case of hydrazinium zinc acetate, the first step is endothermic and in both hydrazinium nickel and zinc acetates the intermediate is respective metal carbonates, which are known to decompose at higher temperature. But adducts always give respective acetates as intermediates.

The hydrazinium cobalt acetate gives Co_3O_4 at almost same temperature range as bis-hydrazine cobalt acetate. This is quite expected because this hydrazinium complex decomposes exothermically in single step to give the final residue as already observed in the case of nickel formate hydrazinate and the degradation temperature is lower than any other similar type of complexes. The kinetic data indicates the kinetic energy for all the degradation stages are higher than the formate adduct indicating the thermal stability of the acetate adduct. In the case of bis-hydrazine nickel and zinc acetates and hydrazinium nickel and zinc acetates the Ea values are comparable. However, for hydrazinium cobalt acetate Ea value is much higher than the corresponding bis-hydrazine complex. This is why the degradation starts at higher temperature (240°C) than adduct which starts decomposing at 160°C. But once the decomposition starts, the hydrazinium complex shows auto decomposition behavior and the oxide formed at 300°C whereas the adduct decomposes in three stages to give Co_3O_4 at 315°C. The entropy for all the stages is negative and comparatively higher than the corresponding formate complexes. But in the case of hydrazinium metal acetates there is a large variation in entropy for different stages which may be due to the nature of intermediates formed.

$M(NH_2CH_2COO)_2(N_2H_4)_2$

Bis-hydrazine metal glycinate complexes decompose at very low temperature than the both bis-hydrazine metal formates and acetates. This is mainly due to the fact that after the exothermic removal of one hydrazine, the monohydrazine intermediate decompose vigorously and exothermically to give the end product. The decomposition of zinc complex is violently exothermic. In the hydrazinium metal glycinates the formation of metal glycinates and carbonates as intermediates and the exothermic degradation in the first stage of decomposition resulted in the formation of end products at far higher temperatures than the bis-hydrazine complexes. In the case of zinc, though mono-hydrazinate intermediate is formed by hydrazinium complex, that gives only zinc through zinc carbonate and no direct decomposition is observed. Fortunately, in bis-hydrazine zinc glycinate the decomposition is single step.

The activation energies for the adducts are lower than the hydrazinium complexes except zinc complex. Similar to most of the other complexes the negative entropy is observed for all the stages. The thermal and kinetic data of the bis-hydrazine metal formates, acetates and glycinates are summarized in table 4, 5 and 6, respectively. The simultaneous TG-DTA traces of cobalt complexes are shown in Figs. 1-6.

Table 4: Thermal and kinetic data of bis-hydrazine metal formate complexes $[(N_2H_5)_2 M (NH_2CH_2COO)_4]$

Compd.	Stage	TG temp. range (°C)	Weight loss (%) found (Calc.)	Residue	E_a KJ mol^{-1}	S KJ mol^{-1} K^{-1}	A S^{-1}
M=Co	I	100-204 161*(+)	28 (30.05)	$Co(HCOO)_2$	65.78	-223.22	19.76
	II	204-447 280*(-)	62.50 (63.50)	Co_3O_4	33.63	-272.73	65.28 x 10^{-3}
M=Ni	I	116-223 217*(-)	66 (64.87)	Ni + NiO	37.64	-260.61	24.86 x 10^{-2}
M=Zn	I	110-324 168*(+)	29 (29.17)	$Zn(HCOO)_2$	21.54	-279.09	42.23 x 10^{-3}
	II	280-500 380*(-)	61 (62.90)	ZnO	66.11	-257.26	54.79 x 10^{-2}

DTA peak temperature (°C)*
Endothermic signal in DTA (+)
Exothermic signal in DTA (-)

Table 5: Thermal and kinetic data of bis-hydrazine metal acetate complexes [M $(CH_3COO)_2(N_2H_4)_2$]

Compd.	Stage	TG temp. range (^{o}C)	Weight loss (%) Found (Calc.)	Residue	E_a KJ mol^{-1}	S KJ mol^{-1} K^{-1}	A S^{-1}
M=Co	I	160-190 180*(-)	20 (19.92)	$Co(CH_3COO)_2$	157.98	-130.97	13.60 x 10^{5}
	II	190-220 222*(-)	27 (26.56)	$Co(CH_3COO)_2$	228.80	-73.01	15.84 x 10^{8}
	III	220-315 305*(-)	66 (66.69)	CO_3O_4	93.57	-219.14	42.99
M=Ni	I	190-245 230*(-)	52 (51.10)	$Ni+Ni(CH_3COO)_2$	163.89	-135.77	84.72 x 10^{4}
	II	245-335 330*(-)	69 (68.97)	NiO	154.35	-179.58	52.27 x 10^{2}
M=Zn	I	150-195 170*(-)	26 (25.87)	$Zn(CH_3COO)_2$	117.36	-172.01	95.50 x 10^{2}
	II	195-310 280*(-)	46 (46.49)	$ZnO+(CH_3COO)_2$	143.44	-177.61	60.73 x 10^{2}
	III	310-450 410*(-)	69 (67.10)	ZnO	74.05	-248.09	15.63 x 10^{-1}

DTA peak temperature	(^{o}C)*
Endothermic signal in DTA	(+)
Exothermic signal in DTA	(-)

Table 6: Thermal and kinetic data of bis-hydrazine metal glycinate complexes [M $(NH_2CH_3COO)_2(N_2H_4)_2$]

Compd.	Stage	TG temp. range (^{o}C)	Weight loss (%) Found (Calc.)	Residue	E_a KJ mol^{-1}	S KJ mol^{-1} K^{-1}	A S^{-1}
M=Co	I	90-190 140*(-)	12 (11.82)	$Co(NH_2CH_2COO)_2$ (N_2H_4)	45.42	-245.81	12.43 x 10^{-1}
	II	190-220 205*(-)	79.50 (78.26)	Co	150.02	-152.66	10.56 x 10^{4}
M=Ni	I	125-235 150*(-)	12.50 (11.83)	$Ni(NH_2CH_2COO)_2$ (N_2H_4)	51.36	-244.43	15.02 x 10^{-1}
	II	235-255 250*(-)	79.20 (78.33)	Ni	172.32	-139.59	55.63 x 10^{4}
M=Zn	I	240-270 260*(-)	77.40 (76.45)	Zn	186.68	-135.26	95.48 x 10^{4}

DTA peak temperature	(^{o}C)*
Endothermic signal in DTA	(+)
Exothermic signal in DTA	(-)

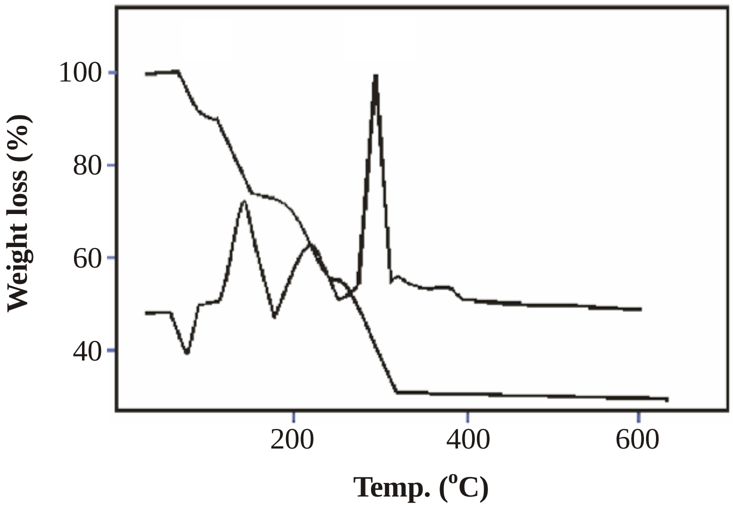

Fig. 1: Simultaneous TG-DTA of Hydrazinium cobalt formate hydrate

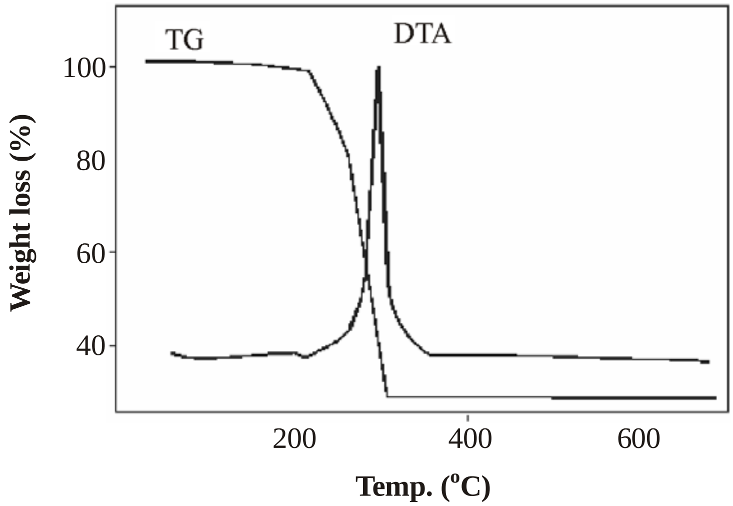

Fig. 2: Simultaneous TG-DTA of Hydrazinium cobalt acetate

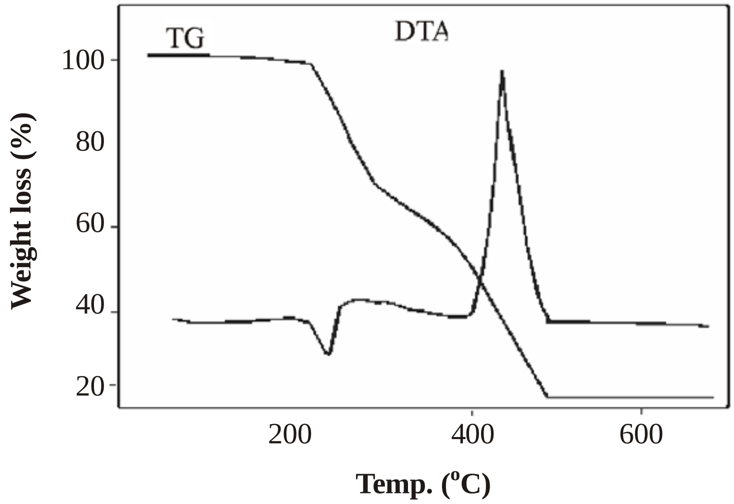

Fig. 3: Simultaneous TG-DTA of Hydrazinium cobalt glycinate

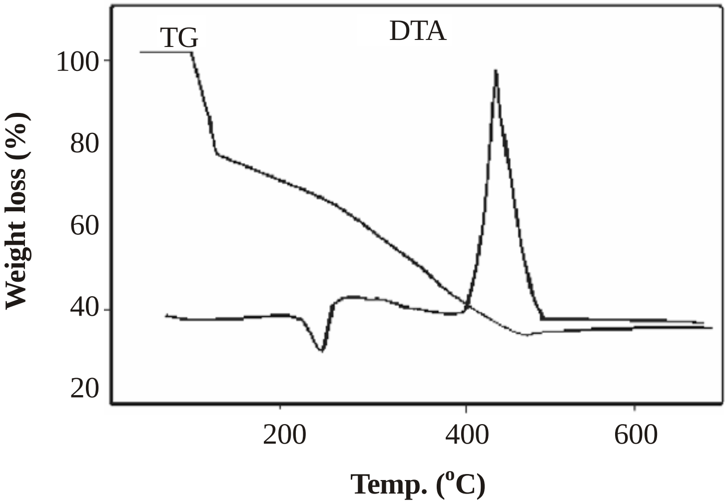

Fig. 4: Simultaneous TG-DTA of bis-hydrazine cobalt formate

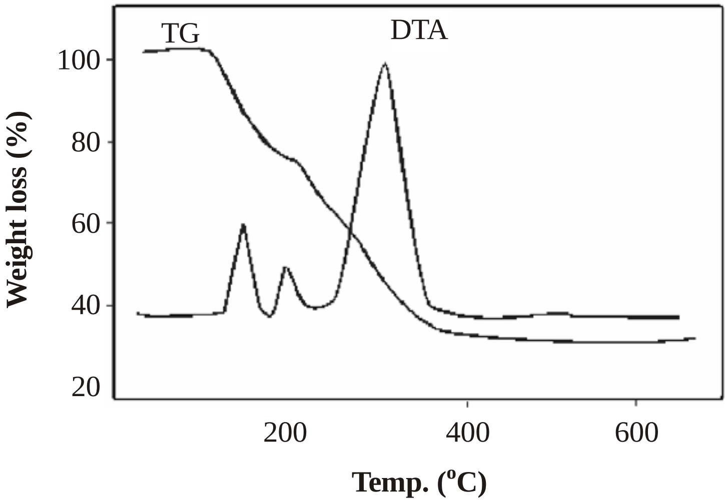

Fig. 5: Simultaneous TG-DTA of bis-hydrazine cobalt acetate

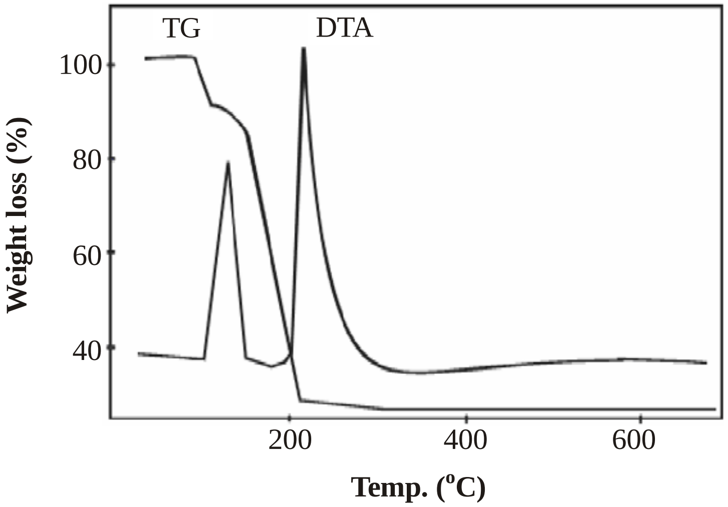

Fig. 6: Simultaneous TG-DTA of bis-hydrazine cobalt glycinate

CONCLUSIONS

The following observations have been made on the basis of our investigations.

(i) For the bis-hydrazine complexes the hydrazine and metal contents were found to be much more in coincidence with the theoretical values which indicates the high purity of the complexes prepared by the present method. However, the TG curves are almost identical with the literature report.

(ii) Hydrazinium complexes, though crystalline and structurally interesting, when we deal with thermal reactivity, they generally decompose at higher temperatures than the respective bis-hydrazine complexes.

(iii) Though the formate and acetate complexes resulted in the formation of respective metal oxide during thermal degradation, the glycinate complexes always give the respective metal powder as the end residue.

(iv) Though the decomposition temperatures are higher for hydrazinium complexes, due to its higher crystallinity and its crystallization from the aqueous solution rather than the precipitation, the hydrazinium complexes are supposed to be more suitable for the preparation of mixed metal complexes and inturn for the preparation of mixed metal oxide with high purity.

(v) In all the cases, due to the presence of hydrazine moiety the activation energy are low and the entropy for most of the stages are found to be negative.

(vi) The activation energy for the formate complexes are lower than that of the acetate complexes.

(vii) The activation energies for the glycinate adducts are found to be lower than the corresponding hydrazinium complexes.

(viii) In the case of hydrazinium metal formates the Ea for the final stage is lower than the corresponding adducts.

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