

Thermolysis of some transition metal nitrate complexes with 1,4-diamino butane ligand

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Abstract

Four complexes are prepared and characterized having molecular formula $[\text{Zn}(\text{dab})_2](\text{NO}_3)_2$, $[\text{Cu}(\text{dab})_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, $[\text{Ni}(\text{dab})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and $[\text{Mn}(\text{dab})_2](\text{NO}_3)_2$, where dab: 1,4-diaminobutane. Thermolyses of these complexes were investigated by simultaneous thermogravimetry (TG), derivatives thermogravimetry (DTG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). The kinetics of the thermolysis at early stages is investigated using isothermal TG by applying model-fitting and isoconversional method. Thermolytic process is slow in inert (N_2) and is fast in air atmosphere due to oxidative nature. To investigate the response of these complexes under the condition of rapid heating, ignition delay (D_1) has been measured. Thermal stability of the complexes was found to increase in the order $\text{Mn} < \text{Cu} < \text{Ni} < \text{Zn}$.

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1. Introduction

Keen interest has recently been devoted to thermolysis of studies of transition metal complexes in solid state containing monodentate and bidentate ligands [1–6]. 1,4-Diaminobutane acts as bidentate neutral ligand. This compound when complexed with metal ions having NO_3^- ion as counter anion exhibits highly energetic properties because it undergoes highly exothermic decomposition due to the presence of both reducing and oxidizing group [7,8]. The nature of explosivity of such compounds is reported to lie between primary and secondary explosives [9,10]. These transition metal complexes undergo exothermic decomposition to give ultra fine metal oxides which may have interesting electrical, magnetic and catalytic properties [11]. Some semiconducting oxides such as CuO, MnO, ZnO, etc. are used in the preparation of environmental sensors for the detection of trace level pollutants

such as H_2S , CO, NO_x , NH_3 , etc. [12–15]. Nano sized metal oxides formed in situ during thermolysis may be better substitute for this application in place of aged one. The energetic metal complexes are insensitive to impact up to 110 cm with 2 kg weight [16,17] and have been proved to be potential ballistic modifiers for composite solid propellants [18–25]. During the combustion of propellants, these complexes produce highly reactive metal oxides which catalyse the burning rate of the propellant better than the oxide which are aged. Also, the exothermic decomposition of these complexes is supportive for burning rate enhancement and enhancement of surface temperature.

Recently, we have undertaken studies on the thermolysis and kinetics of some hexammine metal perchlorates [23,11], bis(ethylenediamine) metal nitrates [26] and bis(diethylenetriamine) metal nitrate [17] and bis(propylenediamine) metal nitrate [16] complexes. Hexamine metal perchlorates [22,23] and bis(ethylenediamine) metal nitrates have been found to be potential additives for composite solid propellants. In continuation of these investigations, we are reporting here the preparation, characteri-

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zation and thermal decomposition of bis(1,4-diaminobutane) metal nitrate complexes. Slow thermal decomposition has been studied by thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). Rapid decomposition is studied by ignition delay measurement. The kinetics of thermolysis has also been evaluated.

2. Experimental

2.1. Materials

The following AR grade commercially available chemicals were used as received: zinc carbonate (Thomas Baker), basic cupric carbonate, nickel carbonate (Qualigens), manganese carbonate, 70% nitric acid (BDH), ethanol (Hyman), 1,4-diaminobutane (Merck), silica gel, iodine (s.d. fine chemicals) and petroleum ether (Merck).

2.2. Preparation and characterization of the complexes

Complexes were prepared and characterized by following the same procedure as bis(propylenediamine) metal nitrates were prepared [16]. Physical, elemental and spectral data are presented in Table 1.

2.3. Thermal decomposition studies

Non-isothermal TG in static air atmosphere is done at a heating rate of 10 °C/min (sample mass 30 mg) using the indigenously fabricated TG apparatus [27]. Isothermal TG has also been done using the same above said TG apparatus at appropriate temperature of decomposition. Simultaneous TG–DTG–DTA thermograms of the complexes were obtained on Pyris Diamond Star system in flowing nitrogen atmosphere (flow rate 100 mL/min) at a heating rate of 10 °C/min. DSC thermograms were obtained on Mettler Toledo Star system in flowing nitrogen atmosphere (flow rate 50 mL/min) at 10 °C/min heating rate. TG curves taken in air, simultaneous TG–DTG–DTA and DSC curves are shown in Figs. 1–3, respectively. The ignition delays (D_i) of the complexes were measured using the tube furnace technique [28]. The sample (mass 20 mg, 100–200 mesh) was taken in an ignition tube (length = 5 cm and diameter = 0.4 cm) clamped with a bent wire and inserted manually into the tube furnace (TF). The time interval between the insertion of the ignition tube into the TF and the moment of visible ignition, noted with the help of a stop watch, gave the value of ignition delay in seconds (s). The time taken for the insertion of the ignition tube was also kept constant throughout the measurements. The accuracy of temperature measurement of TF was ± 1 °C. Each run was repeated four times and mean D_i values are reported in Table 2.

Table 1
Physical, elemental and spectral parameters of the complexes

Complex	Color	% observed (calculated)				IR ν (cm^{-1})							
		C	H	N	Metal	M–N	–NH ₂	N–H (str.)	N–H (bend)	H ₂ N–CH ₂	C–H (str.)	C–H (bend)	NO ₃ [–]
[Zn(dab) ₂](NO ₃) ₂	White	26.62 (27.05)	6.12 (6.72)	22.41 (23.67)	14.92 (15.47)	591	2922	3227	1574	1041	2854	1448	1383
[Cu(dab) ₂](NO ₃) ₂ ·H ₂ O	Blue	25.88 (26.76)	6.13 (6.69)	21.30 (20.48)	17.10 (16.36)	550	2925	3231	1590	1052	2855	1436	1383
[Ni(dab) ₂](NO ₃) ₂ ·2H ₂ O	Sky blue	26.82 (26.40)	6.0 (6.60)	24.2 (23.11)	16.8 (17.3)	542	2948	3237	1582	1061	2862	1423	1383
[Mn(dab) ₂](NO ₃) ₂	Brown	25.93 (26.27)	5.91 (6.56)	23.12 (22.98)	17.43 (17.89)	494	2980	3244	1578	1068	2886	1410	1383

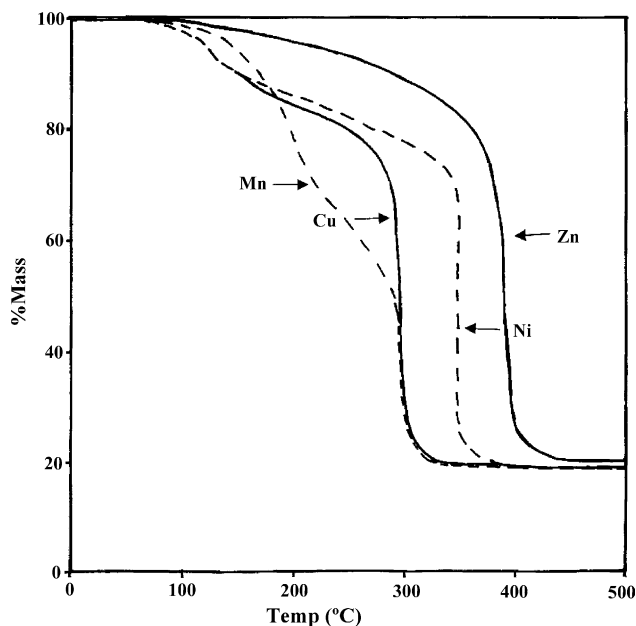


Fig. 1. TG curves of complexes in air atmosphere.

2.4. Kinetic analysis

Kinetics of thermolysis is evaluated from isothermal TG taken at appropriate temperature using the model fitting [29]

as well as isoconversional method given by Vyazovkin and Wight [30].

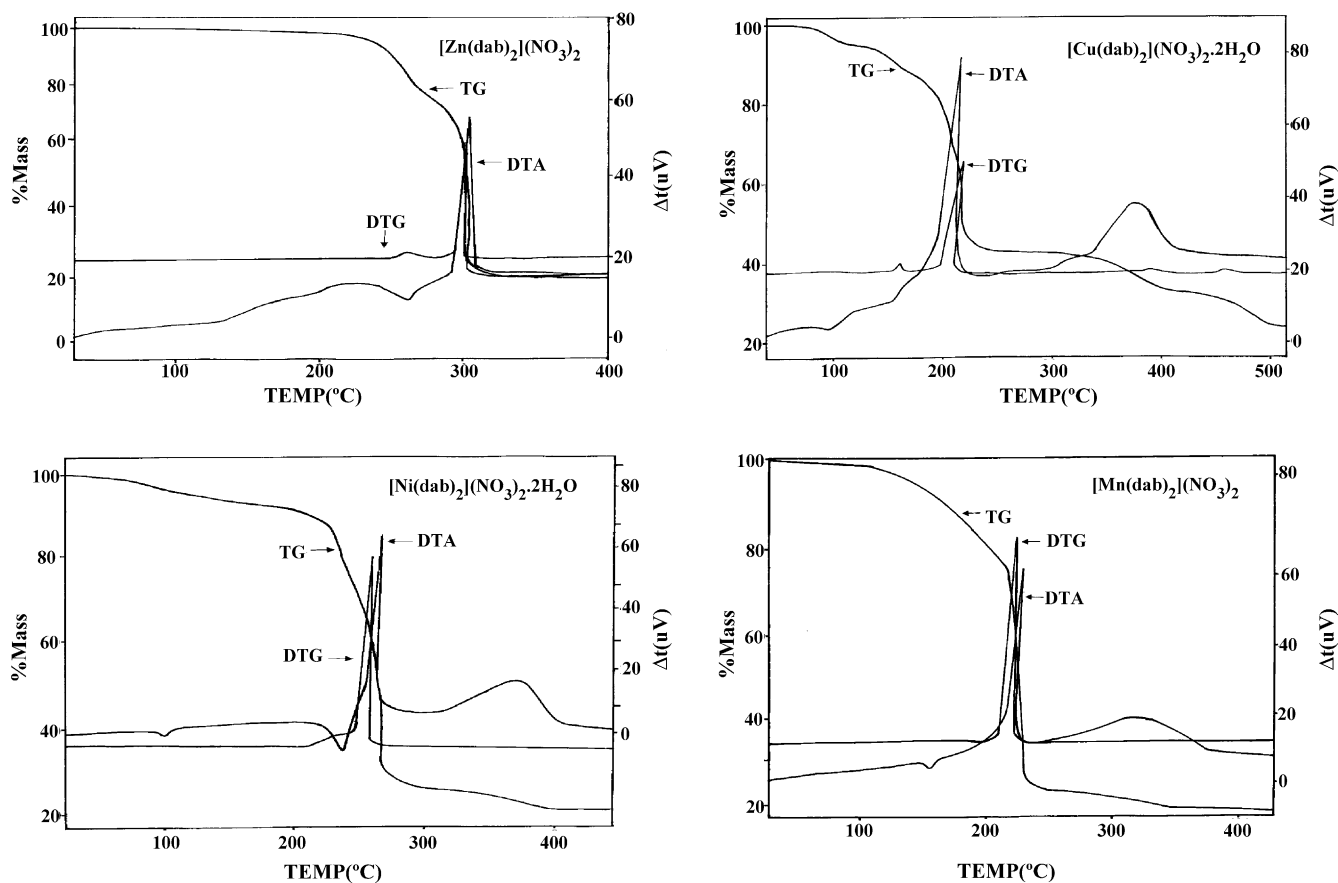
Under isothermal condition the following equation is found to hold:

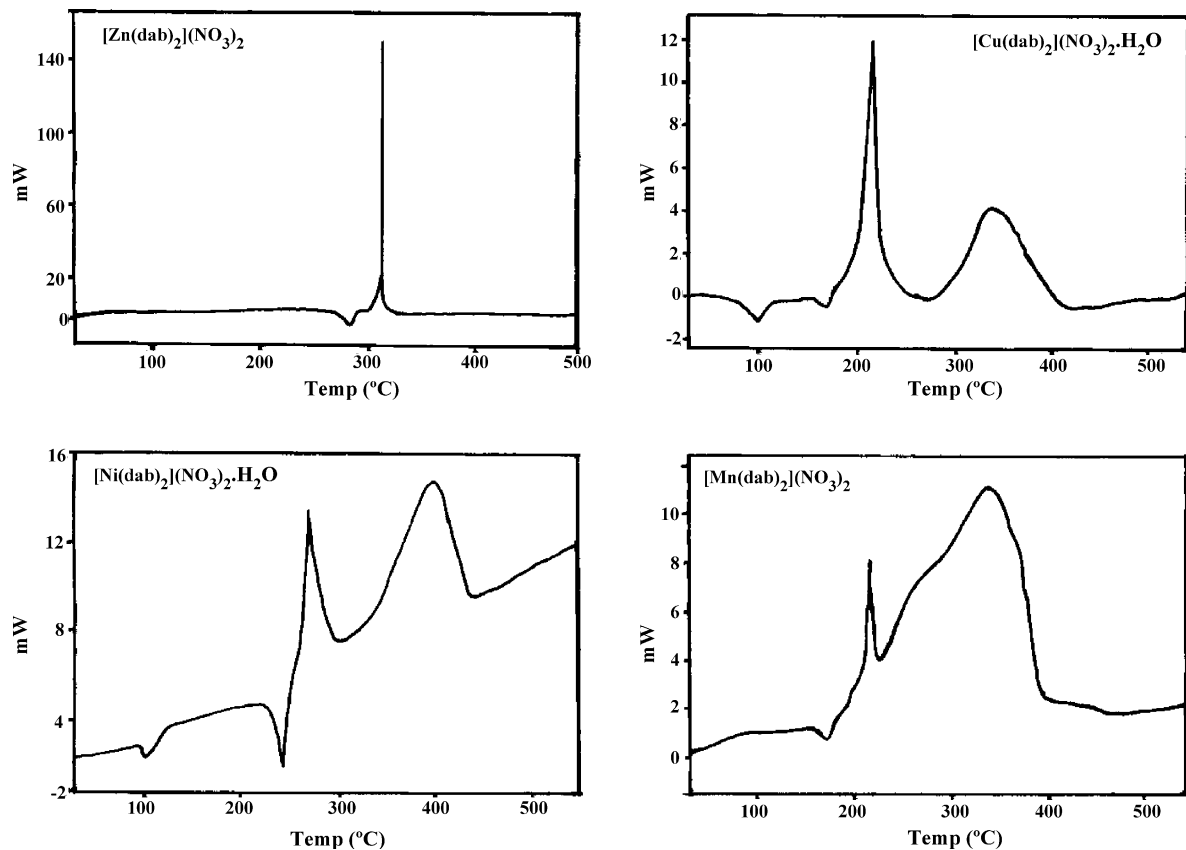
$$-\ln t_{\alpha,i} = \ln \left[\frac{A}{g(\alpha)} \right] - \frac{E_{\alpha}}{RT_i}$$

where α is the extent of conversion, E_{α} the activation of energy at a particular α , R the gas constant and T_i is the absolute temperature. E_{α} is evaluated from the slope of the plot of $-\ln t_{\alpha,i}$ against $1/T_i$. Thus, the values of E_{α} were evaluated at various α_i . Isothermal TG curve and the dependencies of E_{α} on extent of conversion are shown in Fig. 4. Kinetic analysis of fast decomposition is evaluated from ignition delay data, D_i . The D_i data were found to fit in following equation [31,32]

$$D_i = A e^{E^*/RT}$$

where E^* is the activation energy for ignition and T is the absolute temperature. The values of E^* were obtained from the slope of $\ln D_i$ versus $1/T$, which is shown in Fig. 5.

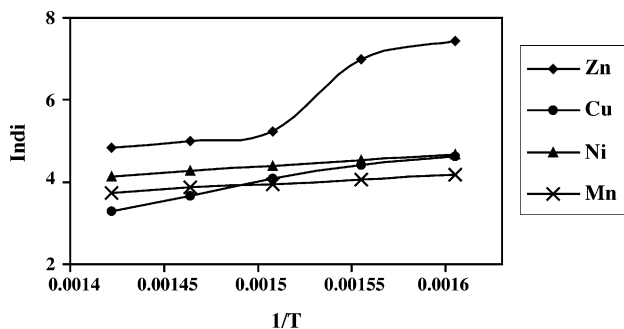
Fig. 2. Simultaneous TG-DTG-DTA curves of complexes in N_2 atmosphere.

Fig. 3. DSC thermograms of complexes in N_2 atmosphere.Table 2
Ignition delay (D_i), activation energy for thermal ignition and correlation coefficient (r) for the complexes

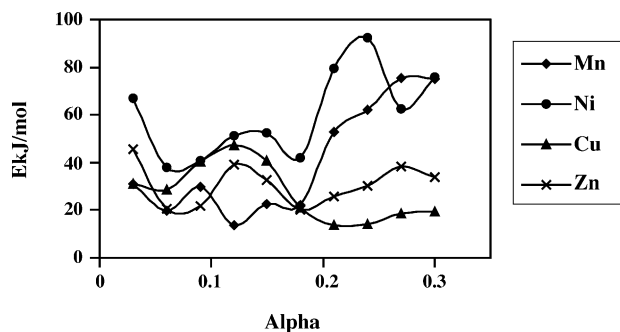
Complex	D_i (s) at temperature ($^{\circ}C$)					E (kJ/mol)	r
	350	370	390	410	430		
$[Zn(dab)_2](NO_3)_2$	1680	1098	188	148	127	131.0	0.9960
$[Cu(dab)_2](NO_3)_2 \cdot H_2O$	103	82	60	39	27	45.1	0.9920
$[Ni(dab)_2](NO_3)_2 \cdot 2H_2O$	108	92	81	71	62	52.5	0.9995
$[Mn(dab)_2](NO_3)_2$	65	58	52	48	42	40.7	0.9968

3. Results and discussion

The complexes were characterized by gravimetric methods [33], infrared [34,35] (Perkin-Elmer RXI Spectrometer)

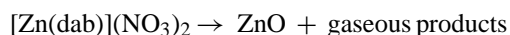
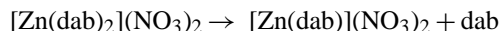
Fig. 4. Graph of $\ln D_i$ vs. $1/T$.

and elemental analysis (Heraeus Carlo Erba 1108 Instrument). The molecular/empirical formula of the complexes was deduced by fitting the observed percentage weights of the various elements with that of calculated (Table 1). The IR

Fig. 5. Variation of activation energy with extent of conversion (α).

spectral data (Table 1) also signalize the proposed molecular formula of the complexes. After the coordination of ligand to metal ion, the N–H stretching frequency decreases from 3350–3400 cm^{-1} to 3216–3242 cm^{-1} . IR signal for M–N stretching in the range 490–550 cm^{-1} confirms the metal to ligand bond formation.

From the TG thermogram taken in static air (Fig. 1) and in flowing N_2 atmosphere (Fig. 2), it is clear that zinc complex undergoes decomposition in two steps. First step (24.8 wt.% loss) is due to the removal of one dab ligand molecule and is slow process (220–280 °C). In second step (299–305 °C), the residue ignited at ~298 °C giving a sharp weight loss (~54.2%). Corresponding to these two steps, two DTG peaks were also observed. First step is endothermic as in DTA and DSC endothermic peak is obtained at 262 and 279 °C, respectively. The second of decomposition is fast and exothermic as evidenced by DTA (303 °C) and DSC peak (318 °C) (Figs. 2 and 3). Finally, the left out residue (~21%) may be attributed to ZnO . Thus, the decomposition pathway for this complex may be proposed as:

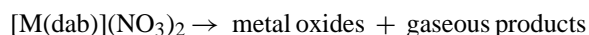
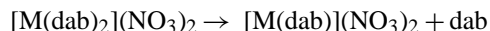
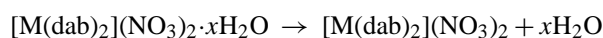


Nickel and copper complex decomposes in four steps (Figs. 1 and 2). In case of copper complex, the first step (85–121 °C) is due to the loss of one H_2O molecule (~4.6 mass% loss). This step is endothermic as an endotherm is obtained in DTA and DSC at 110 °C (Figs. 2 and 3). Now, the anhydrous complex, $[\text{Cu}(\text{dab})_2](\text{NO}_3)_2$, decomposes and after giving a small weight loss, it ignited at 210 °C giving an exotherm at 218 °C in DTA and DSC. Just prior to this exotherm, an endotherm is obtained at ~172 °C, which is due to small weight loss prior to sudden weight loss. The small weight loss seems to be the partial removal of ligand molecule. After the ignition of the complex, the left residue decomposes slowly (307–470 °C) exothermically. Finally above 500 °C, the left residue may be attributed to copper oxide (~24%).

Decomposition of nickel complex follows the pattern of copper complex. First step (82–150 °C) is due to the dehydration of the complex (~8.4 mass% loss) and is endothermic (DTA; DSC, peak 103 °C). In second step (200–268 °C), the dehydrated complex decomposes and after a small weight loss it ignites and a sharp weight loss is observed (66.5%). For this ignition, an exotherm is obtained at 268 °C. Before this exotherm, an endotherm (240 °C) is present for the slow decomposition (partial removal of dab molecule) of the dehydrated complex. After the ignition of the complex, the left residue decomposes slowly (315–420 °C) exothermically. Finally above 500 °C, the left residue may be attributed to nickel oxide (~24%).

Manganese complex decomposes in three steps. In the first step (125–216), one ligand leaves off giving a weight loss (~23%) and an endotherm in DTA and DSC curves at ~160 °C. In second step, the moiety $[\text{Mn}(\text{dab})](\text{NO}_3)_2$ ig-

nited and gives a sharp weight loss (~51%), and an exothermic peak in DTA and DSC (peak temperature ~220 °C). The ignited residue even decomposes slowly exothermically (242–385). Finally, the manganese oxides are left as decomposition product. Observed percentage mass losses are in agreement with those calculated, which confirms the assumed composition of the group expelled [33,36,37]. Except Zn complex, where only one exothermic peak is present, all other complexes show two exothermic peaks in DTA as well as in DSC curves. First exothermic peak is sharp and second one is spread over a wide range of temperature (310–470 °C), which may be due to simultaneous decomposition of the metal nitrate and oxidation of the metal-to-metal oxide. Same type of observation is also seen in the thermal decomposition of nitrate complexes of transition metals with propylenediamine [16]. Thus, the plausible mechanistic pathway for the decomposition for copper, nickel and manganese complexes may be given as:



where M = Cu, Ni and Mn; $x = 1, 2$ and 0 for Cu, Ni and Mn complexes, respectively.

Mono (1,2-diaminobutane) metal nitrate species is formed as intermediate and separation of stages in case of Zn and Mn complexes is due to relatively higher thermal stability of this monoligand intermediate in comparison to that of other complexes. The formation and stability of such monoligand intermediate compounds have been seen earlier during thermal studies of bis(ethylenediamine) copper chloride/bromide monohydrates [37,5], bis(ethylenediamine) copper nitrate [25,26] and bis(ethylenediamine) metal perchlorate complexes [29]. Corresponding metal oxides were obtained as final decomposition products at the end of thermal reactions. Such observation has also been made earlier during thermal studies of amine complexes of copper(II) nitrate [29,26], nickel(II) nitrate [26,38,39] and bis(ethylenediamine) metal perchlorate complexes [29].

Change of atmosphere affects decomposition modes of the complexes. The rate of decomposition of all these complexes is fast in air than in N_2 . The comparison of TG taken in air and in N_2 shows that the steps are not very clear in air atmosphere. This change in mode of decomposition is due to oxidative nature of air atmosphere.

The analysis of the kinetics using model-fitting method from isothermal TG results the average activation energy 76.2, 17.2, 56.0 and 88.8 kJ/mol up to $\alpha = 0.36, 0.33, 0.56$ and 0.33 for Zn, Cu, Ni and Mn complexes, respectively. The higher value of E for Zn and Mn complexes is because in these complexes there is no associated water molecule and the weight loss occurs due to the removal of dab ligand molecule, which needs greater energy due to its chelation to

metal ion. In the case of Ni complex also, the overall activation energy is high due to removal of both water and dab molecule ($\alpha = 0.56$).

Applying isoconversional method to the isothermal TG indicates that the decomposition of these complexes is not as simple as indicated by the model-fitting approach. The value of activation energy, E , varies with α (Fig. 4). By taking into account the complexity of the solid-state thermolysis, it is not easy to correlate the variation of E value to a particular process. Initially, the activation energy is high due to endothermic nature of the initiation of the thermal decomposition process. After this high value E decreases (α up to 0.06), then again it increases (α up to 0.12). The increase of E value in this range is because diaminobutane molecule is detaching from the complex and is breaking into smaller fragments giving gaseous products. After this increase, E again decreases (α up to 0.18) which may be due to the overall compensating effect of various bond breaking and bond making processes. Now, after $\alpha = 0.18$, E again increases because at this stage the ignition of $[M(\text{dab})](\text{NO}_3)_2$ residue is started which is thermally stable and needed high energy for their decomposition. The mechanism of thermolysis changes as reaction proceeds.

All these complexes are quite stable at room temperature but they ignite with noise and fumes under rapid heating. Ignition delay data (Table 2) show that the time required for ignition at a fixed temperature increases in the order $\text{Mn} < \text{Cu} < \text{Ni} < \text{Zn}$. The activation energy for ignition (Table 2) for Zn, Cu, Ni and Mn complexes, respectively, 131.0, 45.1, 52.5 and 40.7 kJ/mol, which is in the same order as their ignition delay. Thus, the thermal stability of the complexes increases in the same order. The stability order of these complexes can be correlated to the increasing ionization potentials of the metals ($\text{Mn} < \text{Ni} < \text{Cu} < \text{Zn}$). Among these, the thermal stability of Zn complex is much higher than the other. This may be attributed to the filled d^{10} electronic configuration of Zn^{2+} ion. Higher stability of Ni complex than Cu complex is also found earlier with propylenediamine ligand [16].

4. Conclusion

TG, DTG, DTA and DSC studies in N_2 and in air atmosphere represents the nature of thermal decomposition of complexes. All these complexes give a common exothermic peak due to ignition of the complex residue giving sudden weight loss in TG. The rate of thermolysis is comparatively high in air to that in inert atmosphere. Kinetic analysis from isothermal TG applying model-fitting method results a single value of E , which cannot be assigned to a particular process. On the other hand, isoconversional method explains well the complexity of the reaction as it results a series of E values as a function of extent of conversion. The thermal stability of the complexes as indicated by ignition delay increases in the order $\text{Mn} < \text{Cu} < \text{Ni} < \text{Zn}$.

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