Kinetics of thermolysis of some transition metal nitrate complexes with 1,6-diaminohexane ligand[☆]

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Abstract

Metal nitrate complexes of general formula $[M(dah)_2](NO_3)_2$ (where M = Zn, Cu and Ni; dah = 1,6-diaminohexane) have been prepared and characterized by elemental analysis, infrared spectroscopy (IR) and gravimetric method. The thermal decomposition has been studied using thermogravimetry (TG). Simultaneous thermogravimetry–differential thermogravimetry–differential thermal analysis (TG–DTG–DTA) and differential scanning calorimetry (DSC) were done in N_2 atmosphere.

Isothermal TG of initial decomposition of all these complexes, have been carried out to evaluate the kinetics of early thermolysis. Both, model fitting and isoconversional method have been used for the evaluation of the kinetics of thermal decomposition. Model fitting method have given the single value of activation energy (E) whereas, isoconversional method yields a series of E-value, which vary with extent of conversion. Ignition of the complexes was measured to see the response towards rapid heating with varying amounts. The thermal stability of the complexes was found to be in the order as $[Zn(dah)_2](NO_3)_2 > [Cu(dah)_2](NO_3)_2 \approx [Ni(dah)_2](NO_3)_2$.
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1. Introduction

Recently interest has been increased in the thermal decomposition studies of the transition metal complexes containing both monodentate and bidentate amine ligands [1–6]. When these complexes has $NO_3{}^-$ or $ClO_4{}^-$ as counterion, exhibits the properties of high energetic compounds. On thermal treatment, these complexes undergo highly exothermic self-propagative decomposition reactions [7]. Thus, these complexes release chemical energy in the form of heat and produce gaseous products and solid residues [8]. These complexes find applications in propellants, explosives and pyrotechnic compositions. Moreover, these transition metal amine complexes decompose to respective metal oxides which find enormous applications in the preparation of environmental sensors for the detection of trace level pollutants such as H_2S, CO, NO_x, and NH_3, etc. [9–12]. One of the most important technological applications of such energetic complexes is their incorporation in composite solid propellant as burning rate modifiers [13–20].

In the last few years, we have reported the studies on thermolysis, kinetics and mechanism of some hexammine metal perchlorates [21,22], bis(ethylenediamine) metal nitrates [18,23], bis(propylenediamine) metal nitrates [24], bis(1,4-diaminobutane) metal nitrates [25] and perchlorates [26]. Hexammine metal perchlorates [21,22] and bis(ethylenediamine) metal nitrates [18,23] were found to be potential additives for composite solid propellants. Thus, in the light of above enormous applications, we report here the preparation, characterization, kinetics and mechanism of thermolysis of bis(1,6-diaminohexane) metal nitrate complexes. Non-isothermal TG, simultaneous TG–DTA, DSC and ignition delay measurements have been carried out to examine the effect of slow and rapid heating of complexes in different complexes. Isothermal TG at five different temperatures has been used to evaluate the kinetics of thermolysis.

2. Experimental

2.1. Materials

Following AR grade commercially available chemicals were used as received: zinc carbonate (Thomas baker), basic cupric carbonate, nickel carbonate (Qualigens), 70% nitric acid (BDH), ethanol (Hyman), 1,6-diaminohexane (Merck), silica gel, iodine (s.d. fine chemicals) and petroleum ether (Merck).

2.2. Preparation and characterization of the complexes

The complexes were prepared and characterized by following the same procedure as bis(propylenediamine) metal nitrates [24]. Physical, elemental and spectral data are presented in Table 1.

2.3. Thermal decomposition studies

Dynamic TG in static air is done at the heating rate of 10 °C/min (sample mass ≈33 mg) using the indigenously fabricated TG apparatus [27]. Isothermal TG has been done using the same TG at appropriate decomposition temperatures. Simultaneous TG–DTG–DTA curves of the complexes were obtained on Pyris Diamond Star system in flowing N_2 (flow rate 100 mL/min, heating rate 10 °C/min). DSC was obtained on Mettler Toledo Star system in flowing nitrogen (flow rate 50 mL/min, heating rate 10 °C/min). TG, TG–DTG–DTA and DSC curves are presented in Figs. 1–3, respectively. Ignition delay of the complexes (D_i) were recorded using tube furnace technique [28]. The sample (mass 20 and 7 mg, 100–200 mesh) was taken in an ignition tube (length = 5 cm, diameter = 0.4 cm), inserted into the tube furnace (TF) with the help of a bent wire. The time interval between the insertion 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 for the insertion of the ignition tube into the TF was kept constant throughout each run. The accuracy
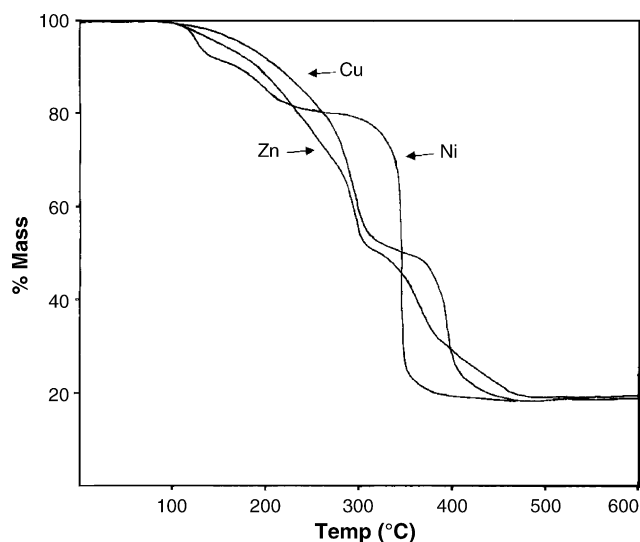

Fig. 1. TG curves of complexes in air atmosphere.

Table 1
Physical, elemental and spectral parameters of the complexes

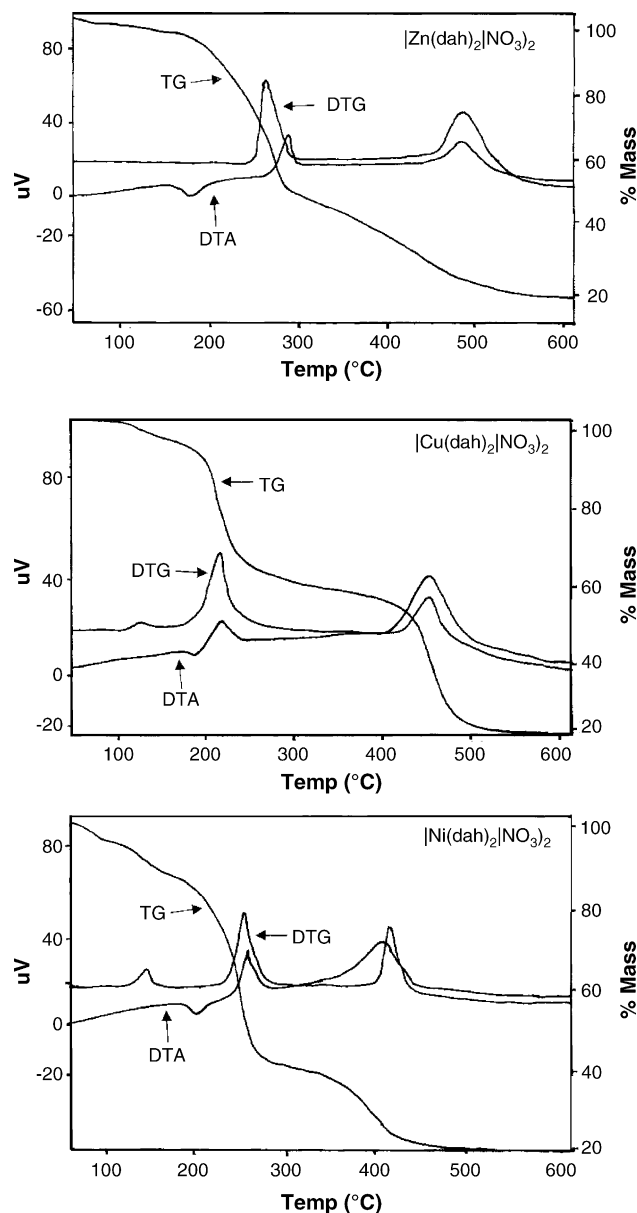| Compound | Color | % Observed (calculated) | | | | | IR ν (cm^{-1}) | | | | | | |
		C	H	N	Metal	M–N	N–H (str.)	N–H (bend)	–NH$_2$	H$_2$N–CH$_2$	C–H (str.)	C–H (bend)	NO$_3^-$
[Zn(dah)$_2$(NO$_3$)$_2$]	White	33.5 (34.2)	7.1 (7.5)	13.8 (13.3)	14.9 (15.5)	544	3273	1590	2925	1018	2855	1438	1383
[Cu(dah)$_2$(NO$_3$)$_2$]	Blue	34.8 (34.3)	7.9 (7.6)	13.6 (13.3)	15.6 (15.2)	571	3238	1589	2926	1032	2855	1443	1383
[Ni(dah)$_2$(NO$_3$)$_2$]	Sky blue	35.3 (34.6)	7.5 (7.7)	12.9 (12.5)	14.4 14.1)	523	3309	1528	2935	1087	2852	1420	1383

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

of temperature measurement of TF was $\pm 1\,^\circ$C. Each run was repeated five times and mean D_i values are reported in Table 2.

2.4. Kinetic analysis

Isothermal TG data taken at appropriate temperatures have been used to evaluate the kinetics of early thermolysis. Kinetics is evaluated using the model fitting [29] as well as isoconversional method by Vyazovkin and Wight [30]. The following equation is found to hold under isothermal condition:

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

where α is the extent of conversion, E_α the activation of energy at a particular α, R the gas constant and T_i the absolute temperature. Thus, the values of E_α were evaluated at various α_i. Isothermal
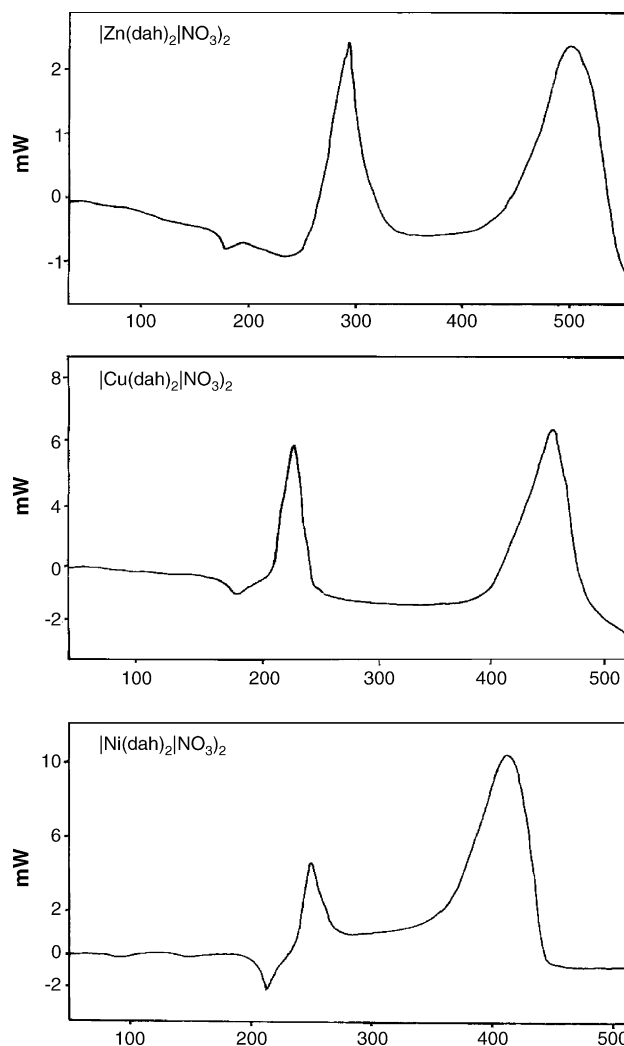

Fig. 3. DSC thermograms of complexes in N_2 atmosphere.

TG curves are shown in Fig. 4. The dependencies of E_α on extent of conversion are presented in Fig. 5.

The kinetics of fast decomposition is evaluated from the ignition delay (D_i). The D_i data were found to fit in the following equation [31,32]:

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

where E^* is the activation energy for ignition, A the Arrhenius factor and T is the absolute temperature. The values of E^* were obtained from the slope of $\ln D_i$ versus $1/T$.

3. Results and discussion

The complexes were characterized by infrared [33,34] (Perkin-Elmer RXI Spectrometer), elemental analysis (Heraeus Carlo Erba 1108 Instrument) and gravimetric methods [35]. The molecular/empirical formula of the complexes was deduced by fitting the observed percent mass of the various elements with that of calculated (Table 1). The IR spectral data (Table 1) also signalize the proposed molecular formula of the complexes. N–H frequency for ligand decreases from 3350–3400 to
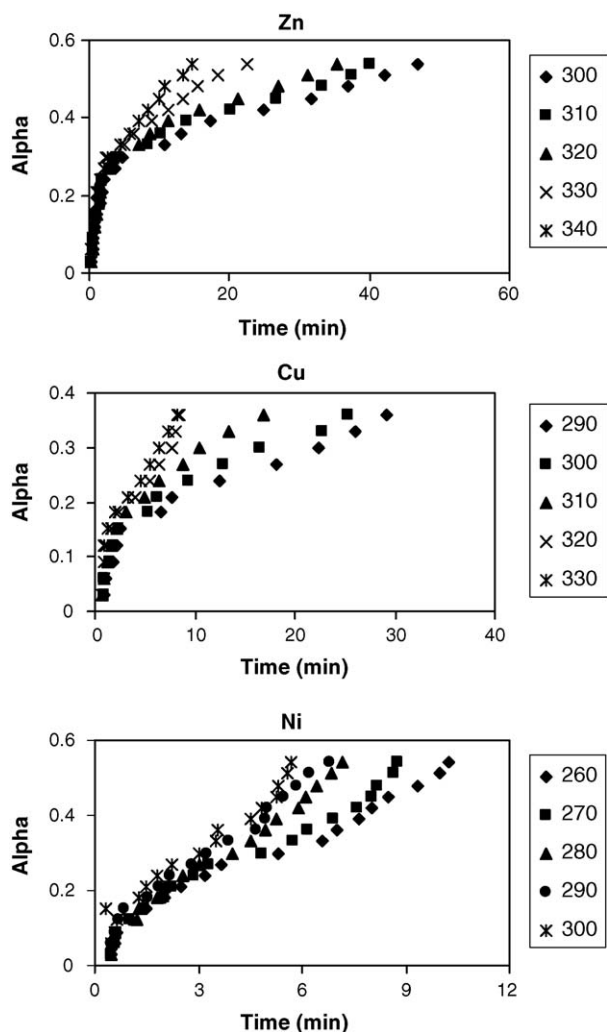
Fig. 4. Isothermal TG graph of the complexes.

$3238–3273\,cm^{-1}$ after complexation to metal ion. M–N stretching frequency in the range $571–523\,cm^{-1}$ confirms the metal to ligand bond formation.

TG thermogram taken in static air (Fig. 1) and in flowing N_2 (Fig. 2) reveals that zinc complex decomposes in two steps. Although these two steps are not well distinguish, but the presence of two DTG peak supports the two-step process. First step (~54% mass loss) is rapid but second step is gradual (~25% mass loss). Finally, the residue left corresponds to the ZnO

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

(~19%). Both the steps are exothermic as in DTA and DSC, two exothermic peaks are obtained at ~288 and 490 °C, respectively. Just before the first exotherm an endotherm is present at ~196 °C which shows that there is partial removal/breaking of ligand molecule after which the compound decomposes exothermically. Copper complex also decomposes in the same way as zinc complex. Both the steps (~42 and 38% mass loss, respectively) are rapid and exothermic. Corresponding to these two steps, two exotherms are obtained in DTA and DSC at ~230 and 470 °C, respectively. Prior to the first exotherm an endotherm is obtained at ~197 °C. Finally, the residue obtained corresponds to ZnO (~19%). Nickel complex also decomposes in two steps. In the first step ~43% and in second step ~20% mass losses are observed. Finally, the left residue corresponds to the NiO (19%). An endotherm is obtained at ~218 °C which is due to partial removal/degradation of ligand (~12% mass loss).

Thus, all the three complexes decompose more or less in same pattern. Owing to the first step mass loss (~54, 42 and 43% for Zn, Cu and Ni, respectively) reveals the partial removal of ligand molecule (ligand ~56%). After this, the residue mainly consists of metal nitrate. In three of the cases, first exothermic peak is sharp and second one is spread over a wide range of temperature (Figs. 2 and 3) which may be due to the simultaneous decomposition of 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 [24] and 1,4-diaminobutane [25].

In the thermolysis of bis(ethylenediamine)metal nitrates [18,23], bis(propylenediamine) metal nitrates [24] and bis(1,4-diaminobutane)metal nitrate [25] complexes monoligand intermediate, $[M(ligand)](NO_3)_2$ is formed. But in the present case, there is no indication for the formation of such monoligand intermediate. This may be due to the enlarged chain of the ligand molecule due to which the carbon chain may break randomly instead of removal of ligand molecule, as there is nine membered chelate rings.

The kinetic analysis applying model fitting approach using isothermal TG data, gave an average activation energy 92.2, 105.3 and 38.7 kJ/mol upto $\alpha = 0.54$, 0.39 and 0.54, respectively. Application of isoconversional method to the isothermal TG data shows that the solid-state decomposition of these complexes is not as simple as indicated by the model fitting method. The value of activation energy varies with extent of conversion, α (Fig. 5). As the solid-state thermolysis is so complex, it is not easy to correlate the variation of E-value to a particular process. However, the activation energy increases as the thermolysis proceed. This is so because, in this range the removal/breaking of ligand molecule occurs ($\alpha = 0.54$, ligand $\approx 56\%$). In other words, we may say that the bond breaking processes exceeds the bond making processes.

Metal nitrate complexes with ethylenediamine ligand are insensitive to impact upto 110 cm height with 2 kg weight [23]. All these complxes are quite stable at room temperature but they ignite with a noise and light with fumes under sudden high heating. Ignition delay data (Table 2) shows that time for ignition at affixed temperature in the order Ni $\approx$ Cu < Zn either the sample mass is 20 or 7 mg. Thus, thermal stability will be in same order.

Table 2
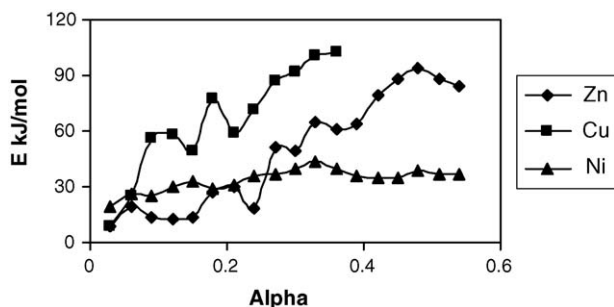Ignition delay (D_i), activation energy for thermal ignition and correlation coefficient (r) for the complexes

Compound	OB	Mass (mg)	D_i (s) at various temperatures					E^* (kJ/mol)	r
			350 ± 1	370 ± 1	390 ± 1	410 ± 1	430 ± 1		
$[Zn(dah)_2(NO_3)_2]$	−132.8	20	104 ± 1	93 ± 1	84 ± 1	65 ± 1	49 ± 1	33.7	0.9654
		7	98 ± 1	87 ± 1	78 ± 1	63 ± 1	48 ± 1	30.9	0.9668
$[Cu(dah)_2(NO_3)_2]$	−127.9	20	100 ± 1	89 ± 1	77 ± 1	60 ± 1	46 ± 1	35.2	0.9778
		7	84 ± 1	73 ± 1	59 ± 1	51 ± 1	45 ± 1	29.3	0.9972
$[Ni(dah)_2(NO_3)_2]$	−129.3	20	102 ± 1	88 ± 1	68 ± 1	59 ± 1	49 ± 1	34.0	0.9961
		7	82 ± 1	68 ± 1	54 ± 1	50 ± 1	41 ± 1	30.9	0.9930

OB, oxygen balance.

The higher stability of Zn complex may be attributed to the filled d^{10} electronic configuration of Zn^{2+} ion. The thermal stability order may be compared with the ionization potential of the metals. The first ionization potential of Ni, Cu and Zn are 7.64, 7.72 and 9.39 eV, respectively, which have the same order as their thermal stability. The activation energy for ignition is nearly the same for all the three complexes. The sample mass has been varied (20 and 7 mg) to see the self-heating effect of the sample particles in comparison to contact heating through ignition tube wall. From Table 2, it is clear that, for any of the complex the time for ignition is less when sample mass is 7 mg. This indicates that the self-heating of the sample particles is slow in comparison to ignition tube wall. This effect is also seen earlier in the complex, bis(1,4-diaminobutane) metal perchlorate [26].

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 two common exothermic peaks due to ignition of the complex residue giving sudden weight loss in TG. 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 $Ni \approx Cu < Zn$. These complexes are being used as burning rate modifier for solid propellants.

Acknowledgements

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