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Kinetics of thermolysis of some transition metal perchlorate complexes with 1,4-diaminobutane ligand☆

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Abstract

Three metal perchlorate complexes of general formula $[M(dab)_2](ClO_4)_2 \cdot xH_2O$ (where M = Zn, Cu and Ni; dab = 1,4-diaminobutane) have been prepared and characterized by gravimetry, infrared spectroscopy (IR) and elemental analysis. Thermolysis has been studied by thermogravimetry (TG) in air and simultaneous thermogravimetry–differential thermogravimetry–differential thermal analysis (TG–DTG–DTA) and differential scanning calorimetry (DSC) in N_2 atmosphere. Isothermal gravimetry over the temperature range of initial decomposition of the complexes has been done to evaluate the kinetics. Both model fitting and isoconversional methods have been used for the evaluation of the kinetics. Model fitting gives a single value of activation energy (E) whereas the isoconversional method yields a series of E values which vary with extent of conversion. Ignition with varying amounts of the complexes was measured to see the response to rapid heating. The thermal stability order of the complexes is $[Zn(dab)_2](ClO_4)_2 \gg [Cu(dab)_2](ClO_4)_2.2H_2O \approx [Ni(dab)_2](ClO_4)_2$.

Keywords: 1,4-Diaminobutane; Metal perchlorate complex; Thermolysis; Kinetics; Ignition delay

1. Introduction

When 1,4-diaminobutane (dab), a neutral bidentate ligand, complexes to metal ions having ClO_4^- as counterion, the resultant complex undergoes self-propagative decomposition reactions due to presence of both oxidizing (ClO_4) and reducing (dab) groups in the same molecule [1,2]. On the basis of their sensitivity, amine complexes lie between primary and secondary explosives [3,4]. These complexes may have applications in propellants, explosives and pyrotechnics. Some energetic transition metal complexes [5–8] and salts of NTO (5-nitro-2,4-dihydro-3H-1,2,4-triazole-3-one) [9] have proved to be potential ballistic modifiers for composite solid propellants. In previous studies, we have reported the thermolysis, kinetics and decomposition mechanism of some hexammine metal perchlorates [6,10], bis(ethylenediamine) metal nitrates [8,11] and perchlorates [12] and bis(propylenediamine) metal nitrates [13]. Hexammine metal perchlorate complexes were found to be potential burning rate modifiers for composite solid propellants. We report here the preparation, characterization, kinetics and mechanism of thermolysis of bis(1,4-diaminobutane) metal perchlorate complexes. Simultaneous thermogravimetry–differential thermogravimetry–differential thermal analysis (TG–DTG–DTA), DSC, TG, isothermal gravimetry and ignition delay measurements have been done to investigate the effect of slow and fast heating of complexes under various conditions.

2. Experimental

2.1. Materials

AR grade commercially available chemicals were used as received, zinc carbonate (Thomas Baker), copper car-

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bonate (BDH), nickel carbonate (Thomas Baker), 70% perchloric acid and methanol (Ranbaxy), ethanol (Hayman), 1,4-diaminobutane (Merck) and silica gel TLC grade (Qualigens).

2.2. *Preparation of the complexes*

Hexahydrated metal perchlorates were obtained by treating metal carbonates with 70% perchloric acid, washing the salts with petroleum ether, recrystallizing from distilled water and drying over fused calcium chloride. The metal perchlorate complexes were prepared by treating an ethanolic solution of metal perchlorate hexahydrates with an ethanolic solution of 1,4-diaminibutane in desired [14–18]. The precipitated complexes were washed with methanol, recrystallized and dried over fused calcium chloride.

2.3. *Thermal decomposition studies*

TG was done at 5 °C/min in static air (sample mass ≈ 30 mg) on indigenously fabricated TG apparatus [19]. Iso-thermal gravimetry was performed in static air with the same TG apparatus (mass ≈ 30 mg). Simultaneous TG–DTG–DTA curves were recorded on a Pyris Diamond Star system in flowing nitrogen (flow rate 100 mL/min, sample mass 3–5 mg, heating rate 10 °C/min). DSC was done in inert atmosphere (flowing nitrogen at a rate of 50 mL/min) on a Mettler Toledo Star system (sample mass 2–4 mg, heating rate 10 °C/min). Ignition delay was recorded with the tube furnace technique [20–23] (mass 20 and 7 mg).

3. Results

3.1. *Characterization*

The purity of complexes was checked by thin layer chromatography. The mass percent of metal was estimated gravimetrically [24]. The mass percent of other elements (C, H and N) was obtained on an Heraeus Carlo Erba 1108 instrument. The complexes were characterized by their infrared spectra (impact 400, KBr pellet). Results are reported in Table 1.

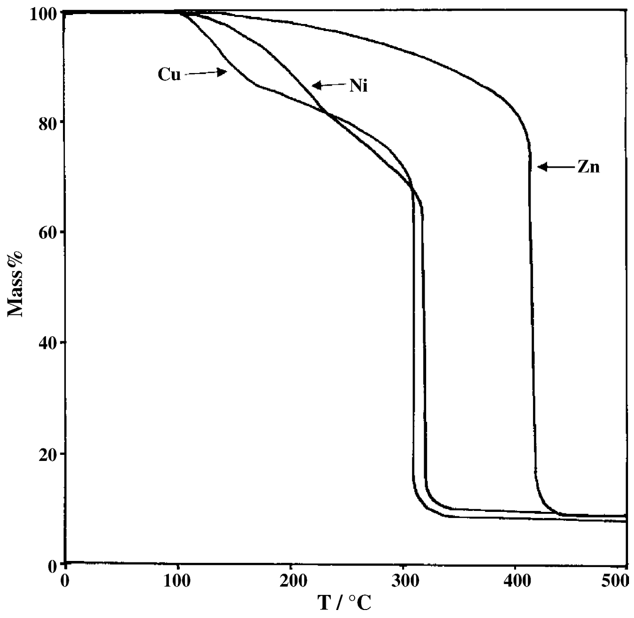

Fig. 1. TG curves of complexes in air atmosphere.

3.2. *TG*

TG curves obtained in air are shown in Fig. 1. In all the three complexes, the initial rate of thermolysis is slow but later thermolysis is fast.

3.3. *Simultaneous TG–DTG–DTA in flowing N_2 atmosphere*

Simultaneous TG–DTG–DTA curves are presented in Fig. 2 Complexes of Zn and Ni decompose in single step giving a corresponding DTG peak and exothermic peak in DTA. The copper complex decomposes in two steps in the temperature range 60–92 and 153–262 °C giving mass losses of 7.2 and 76%, respectively. TG and DTA data show the stability of the complexes decreases in the order $[Zn(dab)_2](ClO_4)_2 \gg [Cu(dab)_2](ClO_4)_2{\cdot}2H_2O \approx [Ni(dab)_2](ClO_4)_2$.

3.4. *DSC in flowing N_2 atmosphere*

DSC curves for all the three complexes are analogous to their corresponding DTA curves having exothermic peak

Table 1
Physical, elemental and spectral parameters of the complexes

Compound	Color	% observed (calculated)				IR (ν cm^{-1})								
		C	H	N	M	N–H str.	N–H bend	C–H str.	C–H bend	H_2C–NH_2	Cl=O	Cl–O	ClO_4	M–N
$[Zn(dab)_2](ClO_4)_2$	White	22.1 (21.8)	5.3 (5.4)	13.3 (12.7)	14.4 (14.8)	3271	1457	2926	1384	1088	1117	673	629	469
$[Cu(dab)_2](ClO_4)_2{\cdot}2H_2O$	Blue	20.7 (20.2)	5.4 (5.9)	12.6 (11.8)	12.9 (13.3)	3243	1466	2950	1442	1084	1116	690	630	480
$[Ni(dab)_2](ClO_4)_2$	Sky blue	21.8 (22.)	5.8 (5.5)	13.4 (12.9)	13.8 (13.5)	3314	1467	2910	1446	1087	1119	712	628	496

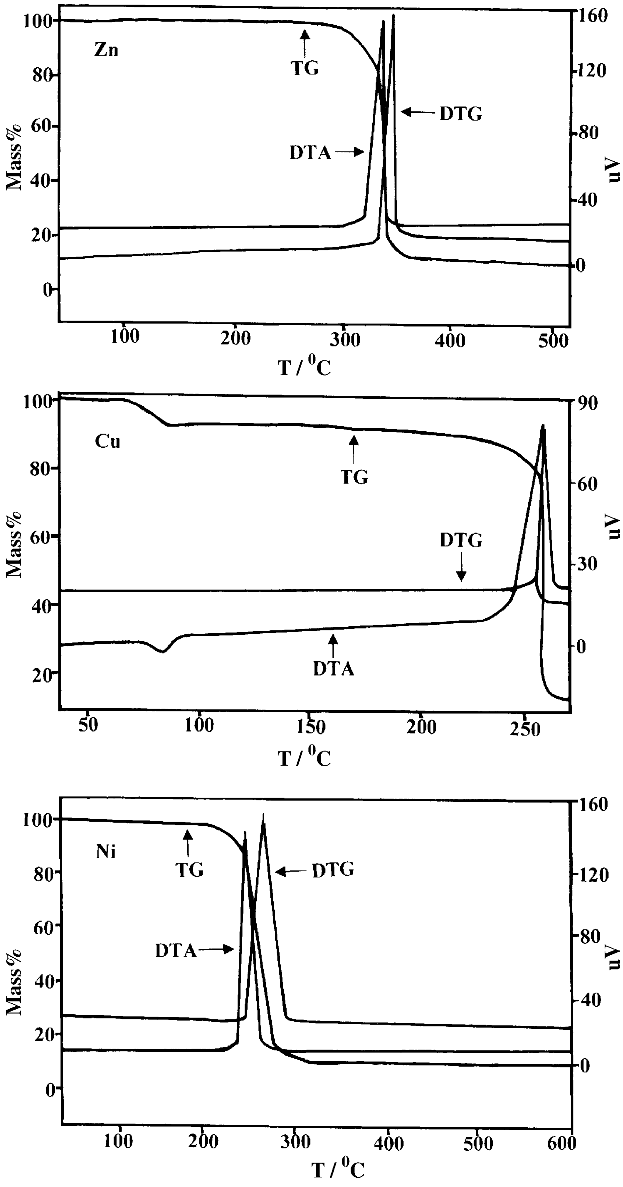

Fig. 2. Simultaneous TG–DTG–DTA curves of complexes in N_2 atmosphere.

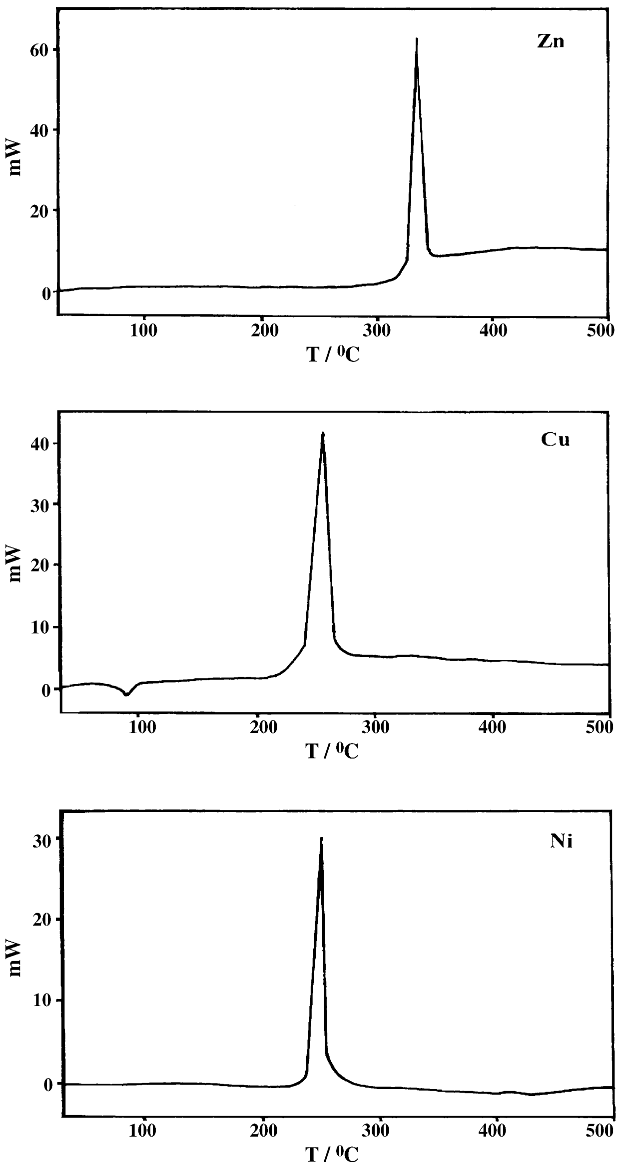

Fig. 3. DSC thermograms of complexes in N_2 atmosphere.

temperature at 336, 245 and 245 °C for Zn, Cu and Ni compound, respectively (Fig. 3.). For Cu complex, one additional endotherm is present at 86 °C due to loss of water.

3.5. *Isothermal gravimetry*

Mass loss was recorded at five temperatures in the decomposition range for early thermolysis (~33% weight loss), Fig. 4.

3.6. *Kinetic evaluation of isothermal gravimetry data*

The kinetics of the early decomposition of the complexes ($\alpha = 0.33$) has been evaluated by model fitting [13,19] as well as by the model-free isoconversional method [25]. Each model results in nearly the same activation energy (E). The average E for Zn, Cu and Ni complexes are 176, 43 and 144 kJ/mol, respectively. Application of the isoconversional method results in a series of E values (Fig. 5), which vary with extent of conversion (α). The E for Zn is higher than Cu and Ni complex.

3.7. *Ignition delay measurements*

Ignition delay (τ) at various temperatures was recorded with different amounts (20 and 7 mg) to see the self-heating effect of sample particles in comparison to the glass ignition tube (Table 2). Zn complex does not ignite in less than 10 min at 350 °C, so ignition delay is recorded at 420,435, 450,465 and 480 °C. The ignition delay for all the complexes is less for sample mass 7 mg, compared with that of

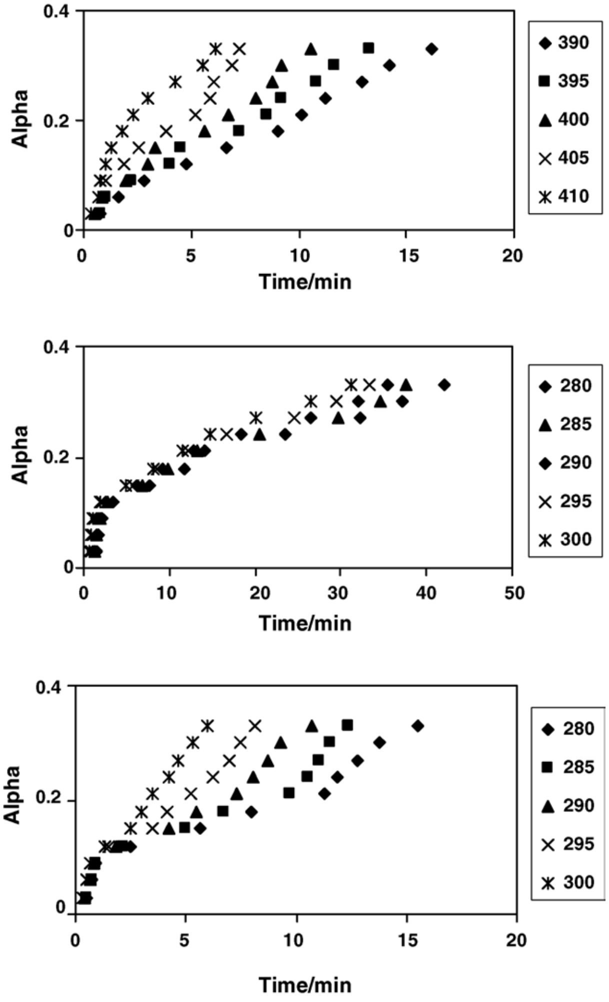

Fig. 4. Isothermal TG thermograms of complexes in air atmosphere.

20 mg. τ for Cu and Ni complexes is nearly the same which shows equal thermal stability. Thus, the thermal stability order is $[Zn(dab)_2](ClO_4)_2 \gg [Cu(dab)_2](ClO_4)_2\cdot 2H_2O \approx [Ni(dab)_2](ClO_4)_2$.

The τ was fitted to [26–28]:

$$\tau = A\ \exp \frac{E^*}{RT}$$

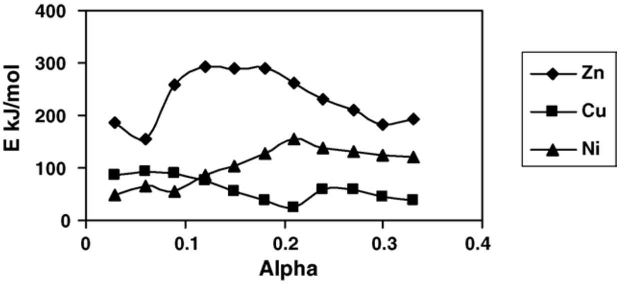

Fig. 5. Variation of activation energy with extent of conversion (α).

where E^* is the activation energy for thermal ignition, A, the pre-exponential factor and T is the absolute temperature. E^* was determined from the slope of a plot of ln(τ) versus $1/T$, see Table 2. The activation energy (E^*) is not varying much with the variation of sample mass.

4. Discussion

The analytical data presented in Table 1 agree with the calculated mass percent of each element. Also, the characteristic absorption frequencies of atoms/groups match the standard texts [29,30]. Zn and Ni complexes are anhydrous whereas Cu complex is hydrated. TG curves obtained in static air atmosphere (Fig. 1) show that Zn and Ni complexes decompose in one step.

A comparison of the TG curves, in air and in nitrogen shows that in N_2 the mass loss is sudden while in air, initial mass loss (∼20%) is slow. This is because of slow heating rate (5 °C/min) in air and fast heating rate (10 °C/min) in N_2. Also, a large sample mass (∼30 mg) was used in air and a small mass in N_2 (4–5) mg. Initial 20% weight loss (in case of Cu 27%) corresponds to one dab molecule (for Cu $2H_2O$ and one dab molecule). During data recording, the characteristic odor of dab was observed. After the removal of these moieties, the residue left is $[M(dab)](ClO_4)_2$ which ignites at elevated temperatures giving a sharp mass loss (60%) and gaseous products. Finally the metal oxide is left as residue, although in curve less residue is shown (10%) because some of residue is thrown outside the crucible. Due to fast heating rate in inert atmosphere, the mass loss is sudden (∼80%) leaving residue

Table 2
Ignition delay (τ), ignitionn temperature (T_E) and activation energy for thermal explosion (E^*) of complexes (sample mass 7 mg)

Compound[a]	Mass (mg)	τ (s) at various temperatures										E^* (kJ/mol)	r
		320	340	360	380	400	420	435	450	465	480		
1	20	–	–	–	–	–	140 ± 1	136 ± 1	126 ± 1	110 ± 1	104 ± 1	22.5	0.9974
	7	–	–	–	–	–	131 ± 1	127 ± 1	121 ± 1	109 ± 1	98 ± 1	22.4	0.9789
2	20	139 ± 1	121 ± 1	105 ± 1	84 ± 1	64 ± 1	–	–	–	–	–	31.6	0.9816
	7	127 ± 1	110 ± 1	86 ± 1	72 ± 1	55 ± 1	–	–	–	–	–	34.7	0.9920
3	20	150 ± 1	121 ± 1	92 ± 1	74 ± 1	56 ± 1	–	–	–	–	–	40.8	0.9974
	7	142 ± 1	112 ± 1	81 ± 1	67 ± 1	52 ± 1	–	–	-	–	–	41.9	0.9979

[a] 1: $[Zn(dab)_2](ClO_4)_2$; 2: $[Cu(dab)_2](ClO_4)_2\cdot 2H_2O$; 3: $[Ni(dab)_2](ClO_4)_2$.

of metal oxides (19%). Thus, the mechanism of thermolysis may be proposed as:

$$[M(dab)_2](ClO4)_2xH_2O \rightarrow [M(dab)_2](ClO4)_2 + xH_2O$$

$$[M(dab)_2](ClO4)_2 \rightarrow [M(dab)](ClO4)_2 + dab$$

$$[M(dab)](ClO4)_2 \rightarrow MO + \text{gaseous products}$$

The formation of monoligand intermediates has been seen earlier during thermal studies of bis(ethylenediamine)-copper chloride/bromide monohydrates [31], bis(ethylenediamine)metal nitrate [8,11] complexes.

Comparison of the DTA and DSC exothermic peak temperatures (Table 2) shows the decreasing trend as $[Zn(dab)_2](ClO_4)_2 \gg [Cu(dab)_2](ClO_4)_2{\cdot}2H_2O \approx [Ni(dab)_2](ClO_4)_2$ for early thermolysis ($\alpha = 0.33$).

Analysis of kinetics from isothermal TG data using model fitting method, values of E obtained from different models for particular sample are nearly equal irrespective of the equations used. It is difficult to assign a single value of E to a particular process taking place in such a complex solid state decomposition. Model-free isoconversional method shows that the thermolysis of these complexes is not as simple as indicated by model fitting method. As can be seen from Fig. 5, the value of E changes with α but in all the α range, E for Zn complex is higher than Cu and Ni which indicates the stability of Zn complex is higher than Cu and Ni. Except in lower α range, E for Ni is greater than Cu indicating the greater stability of Ni over Cu complex.

To examine the effect of rapid heating on the complexes, ignition delay was measured. A perusal of Table 2 reveals that, at a particular temperature, τ for Cu and Ni complex are nearly the same. This shows their similar thermal stability. Thus, the thermal stability order is same as indicated earlier. This thermal stability order can be directly correlated with the cation size. Comparison of τ data for 20 and 7 mg of sample for all three complexes indicates that it is lower for 7 mg. This emphasizes that the self-propagative heating effect of sample particles are less than the contact heating to the ignition tube wall. Although the τ are different for different sample masses, activation energies for ignition (E^*) are almost the same.

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