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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 $[Zn(dah)_2](NO_3)_2 > [Cu(dah)_2](NO_3)_2 \approx [Ni(dah)_2](NO_3)_2$.

Keywords: 1,6-Diaminohexane; Metal nitrate complex; Thermolysis; Kinetics; Ignition delay

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.

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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

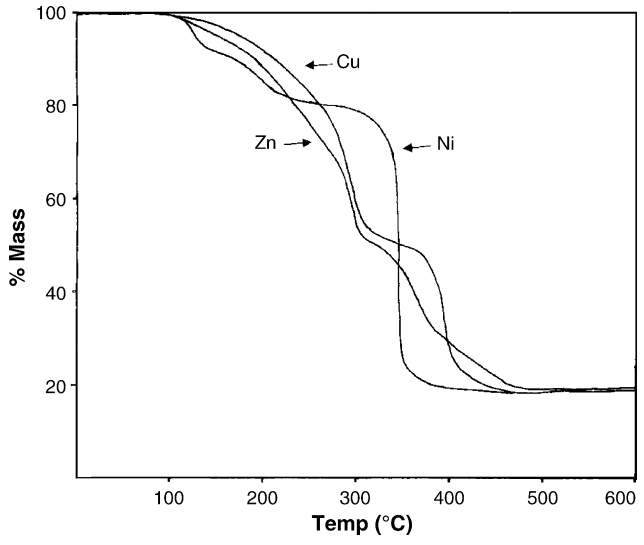

Fig. 1. TG curves of complexes in air atmosphere.

Table 1
Physical, elemental and spectral parameters of the complexes

Compound	Color	% Observed (calculated)				IR ν (cm^{-1})							
		C	H	N	Metal	M–N	$-NH_2$	N–H (str.)	N–H (bend)	H_2N-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	2925	3273	1590	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	2926	3238	1589	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	2935	3309	1528	1087	2852	1420	1383