ELSEVIER

Thermochimica Acta 397 (2003) 237–247

thermochimica acta

www.elsevier.com/locate/tca

Thermal degradation kinetics of Co(II), Ni(II), and Zn(II) hydrazinesulfinates in air, oxygen and nitrogen atmospheres

B.N. Sivasankar[a,*], L. Ragunath[b]

[a] *Department of Chemistry, Government Arts College, The Nilgiris, Udhagamandalam 643002, Tamilnadu, India*
[b] *Department of Chemistry, Sri Ramakrishna Engineering College, Coimbatore 641022, Tamilnadu, India*

Received 22 May 2001; received in revised form 25 June 2002; accepted 22 July 2002

Abstract

Cobalt, nickel and zinc hydrazinesulfinate complexes of the molecular formula $M(N_2H_3SOO)_2$ where M=Co, Ni and Zn, respectively, have been prepared and characterized by analytical and spectral techniques. The thermal decomposition of these complexes have been studied in three different atmospheres, viz. static air, oxygen and nitrogen. In static air, cobalt and zinc complexes give respective metal sulfites while the nickel complex yield nickel sulfate. In oxygen atmosphere, cobalt complex gives a mixture of oxide and sulfate while the nickel and zinc complexes yield the respective metal oxide. In the nitrogen atmosphere, the complexes decompose to yield a mixture of metal sulfide and metal sulfite in the case of cobalt and nickel while zinc complex gives ZnO. The above complexes have also been subjected to sudden heating at high temperatures ca. 500 °C, i.e. combustion, which resulted in the formation of metal oxide in the case of cobalt while the nickel complex gives nickel sulfide as the final product. However, the zinc complex gives mixture of zinc oxide and zinc sulfate. The kinetic parameters were evaluated for these complexes using Coats–Redfern equation. The parameters have been studied on the basis of TG-data and in most of the cases, the decomposition is found to follow first order kinetics.

Keywords: Metalhydrazinesulfinates; Thermal kinetics; Combustion experiments; Metal oxides; Metal sulfides

1. Introduction

Hydrazine complexes have received considerable attention for the past few years due to the coordinating ability and thermal sensitivity of hydrazine. Metal complexes containing hydrazine have been exploited in the preparation of metal compounds in pure form by their decomposition at low temperatures. This low temperature decomposition has been attributed to the endothermic nature of N–N bond, which releases enormous amount of heat energy during its thermal cleavage. This energy is in fact responsible for the decomposition of other parts of the complex to metal oxides [1–5], metal powders [6,7], and mixed metal oxides [8–10].

During the course of our research work we have reported the synthesis and characterization of a number of metal hydrazine complexes containing carboxylates [11–13], hydrazine carboxylates [14,15], hydrazine sulfinates as anions. Further, the hydrazinesulfinate complexes with transition metal ions are new to the literature [16] and no detailed studies on thermal degradation and thermal kinetics have been carried out so far. Also no combustion studies have been reported for the hydrazine complexes except mixed metal sulfite hydrazinates [17]. Hence, as a continuation of our earlier studies, we have studied the thermal decomposition of Co(II), Ni(II) and Zn(II)

---

[*] Corresponding author.

0040-6031/02/$ – see front matter © 2002 Published by Elsevier Science B.V.
PII: S0040-6031(02)00395-7

hydrazinesulfinates in different atmospheres such as air, oxygen and nitrogen and their decomposition kinetics. The combustion has also been studied in air at ca. 500 °C. In this paper, we wish to report the results of the above investigation.

2. Experimental

All the chemicals used were of AnalaR grade and 99–100% hydrazine hydrate was used in all the reactions. The solvents were distilled before use.

2.1. Preparation of complexes

The metal hydrazinesulfinates of the type $M(N_2H_3SOO)_2$, where M=Co, Ni or Zn were prepared by passing sulfurdioxide gas to an aqueous solution (25 ml) containing the respective metal nitrate hydrates (0.01 mol) and hydrazine hydrate (1.5 ml, 0.03 mol). On passing sulfurdioxide, the precipitate initially formed by adding hydrazine hydrate to the metal nitrate solution slowly dissolved and the complexes were formed simultaneously.

The compounds formed were filtered, washed with water (25 ml), then with alcohol (15 ml) and dried in air. The compositions of the complexes were determined by chemical analyses as $M(N_2H_3SOO)_2$, where M=Co, Ni or Zn.

Simultaneous TG–DTA of the complexes in static air was recorded on a TGF-5000 RH, thermo balance of ULVAC RICO, Japan. General V2.2A Dupont 9900 instrument was used to record the TG–DTA in oxygen atmosphere. The thermal experiments in nitrogen atmosphere were carried out using Perkin-Elmer series DTA 7 instrument. In these experiments platinum cups were used to hold about 10 mg of the samples. The heating rate employed was 10 K min^{-1}. The combustion studies have been carried out by decomposing the complexes in a pre-heated silica crucible at about

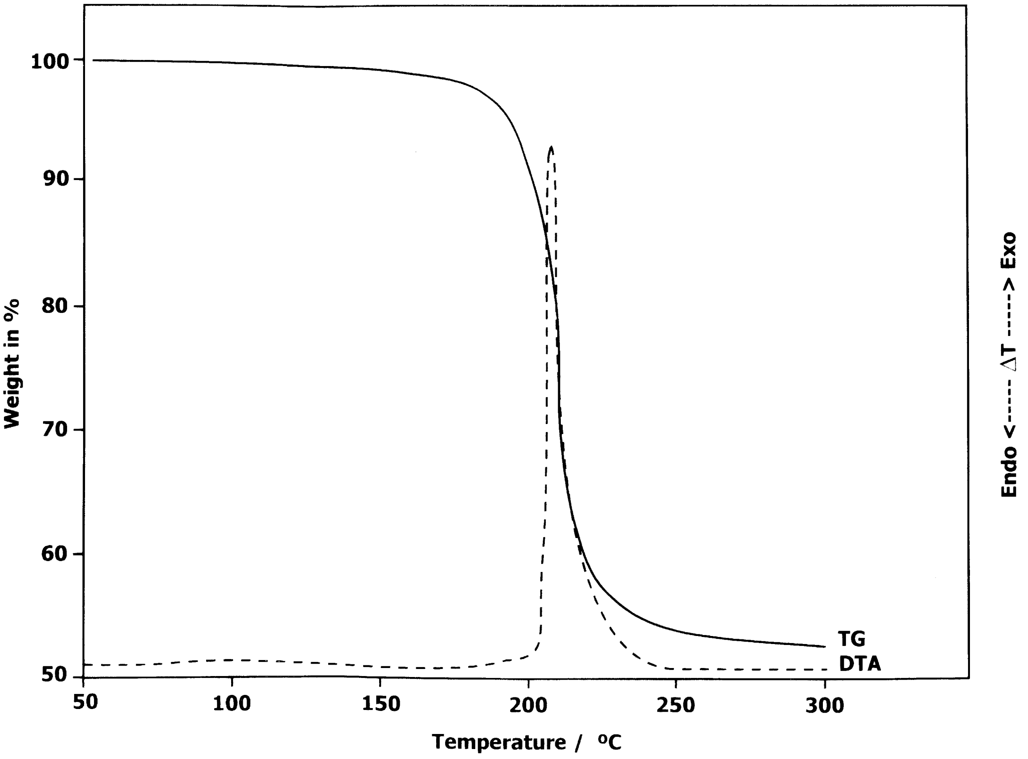

Fig. 1. Simultaneous TG–DTA traces of $Co(N_2H_3SOO)_2$ in air.

500 °C in static atmosphere and the end products were analyzed for their composition.

The evaluation of kinetic parameters, viz. order, energy of activation (E_a), entropy of activation (ΔS) and pre-exponential factor (A) using Coats–Redfern equation was based on a computer program which was developed for use on a Busybee, PC/XT computer (HCL Ltd.).

3. Results and discussion

The metal hydrazinesulfinate complexes were prepared by passing sulfurdioxide gas through an aqueous solution containing respective metal salt and hydrazine hydrate in appropriate ratio. The complexes are stable in air and insoluble in water and organic solvents.

The analytical, magnetic, spectral (electronic and infrared) and X-ray powder data indicate that the complexes are of low spin type with four coordinated geometry [16].

3.1. *Thermal decomposition*

The simultaneous TG–DTA traces of Co, Ni and Zn complexes in air are given in Figs. 1–3, respectively. The curves in oxygen atmosphere are shown in Figs. 4–6, respectively, for the Co, Ni and Zn complexes. Figs. 7–9 are the thermal traces for the above complexes in nitrogen atmosphere. The intermediates and the final products formed during the thermal analyzes were analyzed and confirmed by hydrazine and metal analyses, infrared spectra and X-ray powder diffraction.

3.1.1. *Cobalthydrazinesulfinate*

In air, this complex undergoes one-step decomposition to give the cobalt sulfite as the end product. The TG curve shows a weight loss of 44.60% corresponding to this degradation and one sharp exotherm is observed in DTA trace.

In oxygen atmosphere, the thermal curves show two-step decomposition. In first stage, the complex

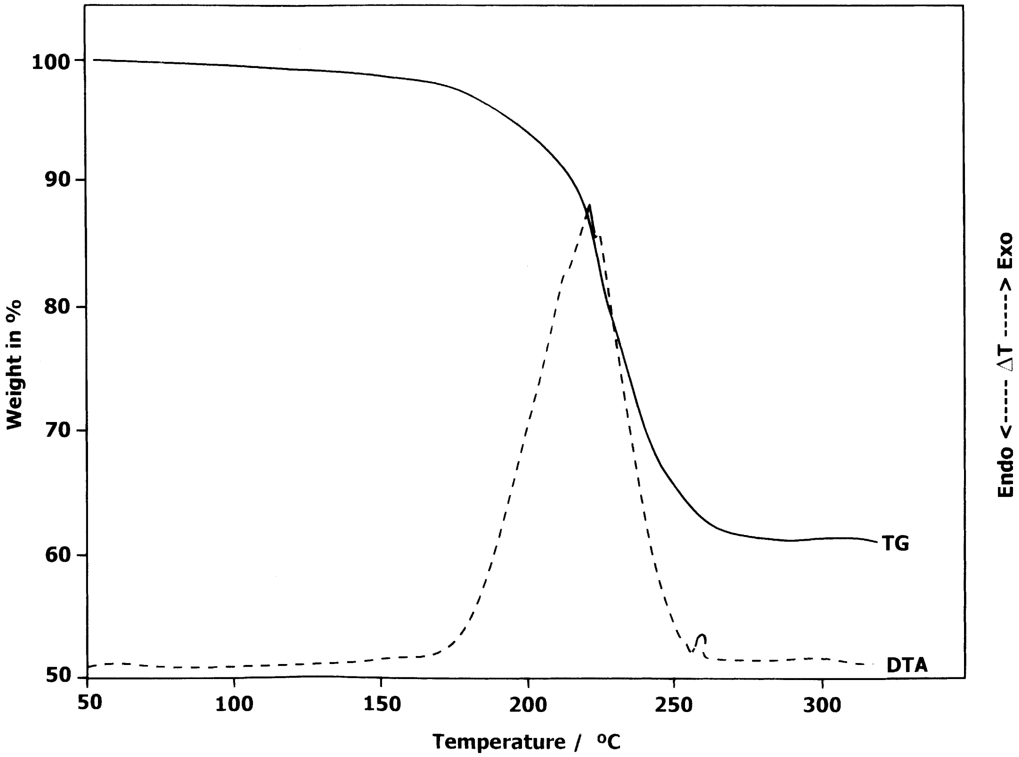

Fig. 2. Simultaneous TG–DTA traces of $Ni(N_2H_3SOO)_2$ in air.

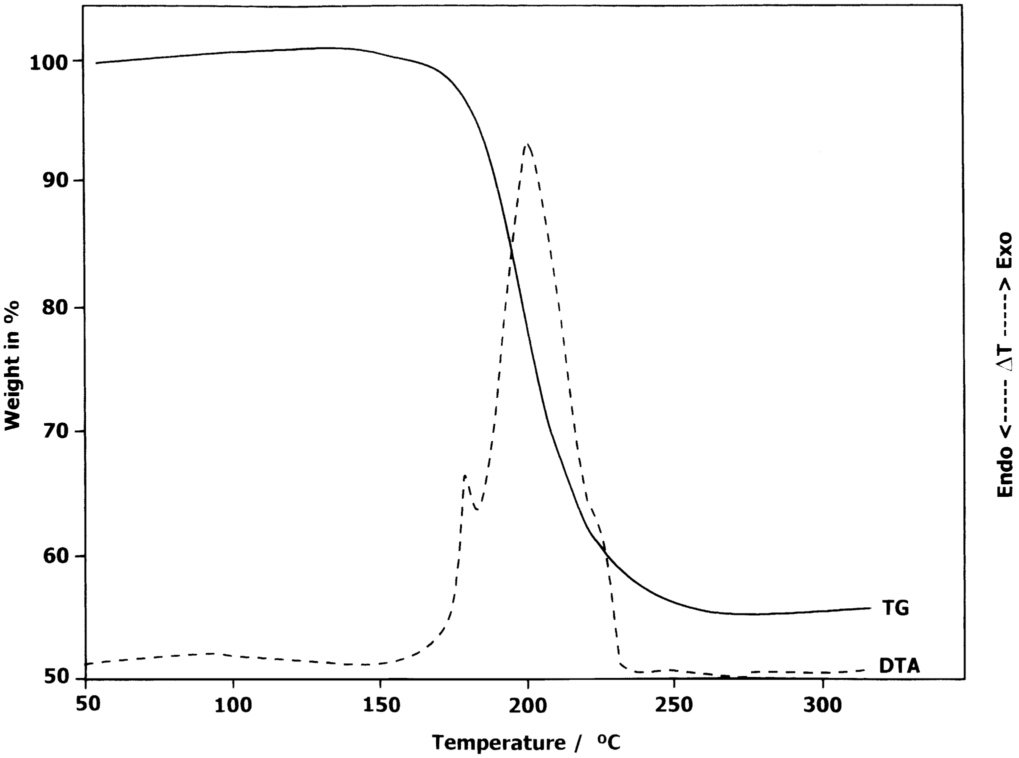

Fig. 3. Simultaneous TG–DTA traces of $Zn(N_2H_3SOO)_2$ in air.

decomposes to give cobalt sulfite dihydrazinate, in the temperature range 60–120 °C, which further decomposes at higher temperature (300–400 °C) to yield a mixture of cobalt sulfate and cobaltic oxide. The observed weight losses very well coincides with the values calculated for the intermediate and the final product.

Two-step decomposition is observed for this cobalt complex in nitrogen atmosphere also. Though the TG shows almost continuous weight loss in the temperature range (50–220 °C), a break is seen at 160 °C. The DTA curve also shows splitting confirming the two-step process. On the basis of TG weight loss, the cobalt sulfite dihydrazinate and a mixture of cobalt sulfate and cobaltic oxide are proposed as an intermediate and final products, respectively.

Both in air and oxygen atmospheres, the oxidative decomposition takes place which is quite expected. In all the three atmospheres, the decompositions are exothermic in nature. The TG and DTA data for the cobalt complex in three different atmospheres are shown in Table 1.

The proposed reactions in air, oxygen and nitrogen atmospheres are given as Eqs. (1)–(3), respectively.

$$\mathrm{Co(N_2H_3SOO)_2 + 2O_2 \rightarrow CoSO_3 + 2N_2 + 3H_2O + SO_2} \quad (1)$$

$$\mathrm{3Co(N_2H_3SOO)_2 + 7O_2 \rightarrow CoSO_4 + Co_2O_3 + 6N_2 + 5SO_2 + 9H_2O} \quad (2)$$

$$\mathrm{2Co(N_2H_3SOO)_2 \rightarrow CoSO_3 + CoS + 2SO_2 + 4N_2 + 5H_2 + H_2O} \quad (3)$$

The thermal kinetics data (Table 2) for the cobalt complex shows that all the stages follow first order kinetics. The energy of activation (E_a), calculated in air (104.6 kJ/mol) shows that the overall rate of thermal degradation is high in air. However, in other two atmospheres, the first stage is very fast when compared to the second stage, that too in nitrogen atmosphere, the

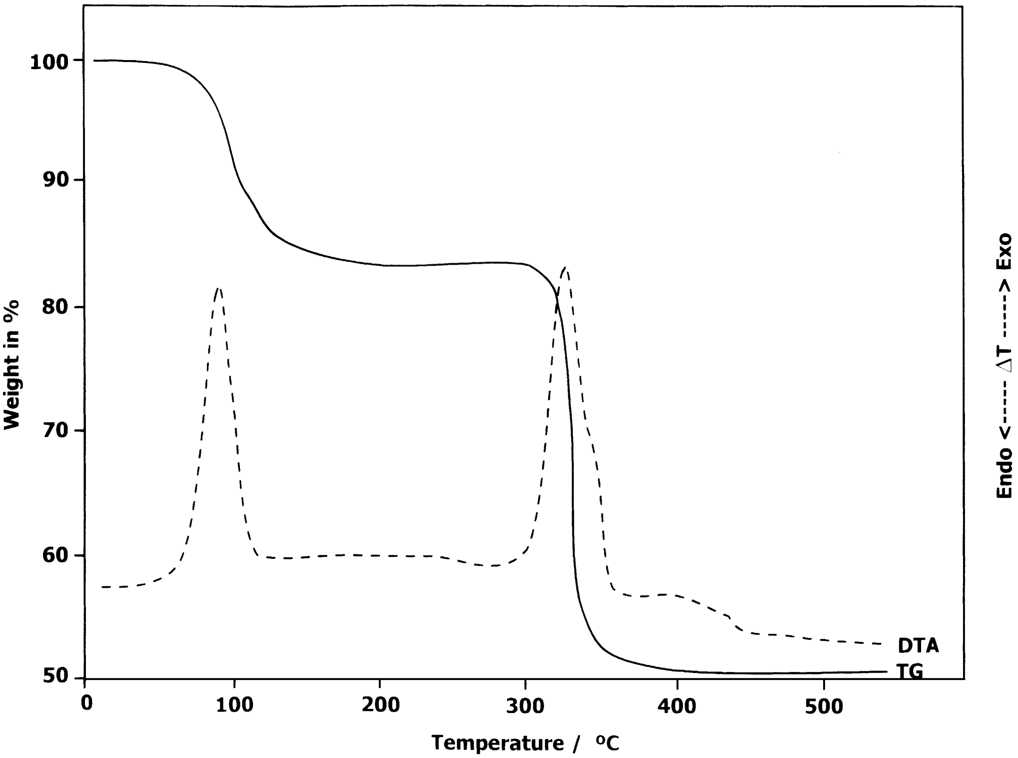

Fig. 4. Simultaneous TG–DTA traces of $Co(N_2H_3SOO)_2$ in oxygen.

Table 1
Thermal data of cobalt hydrazinesulfinate

Atmosphere	DTA peak temperature (°C)	TG temperature range (°C)	Weight loss (%)		End product
			Found	Calculated	
Air	215 (exo)[a]	150–280	44.60	44.18	$CoSO_3$
Oxygen	80 (exo)[a]	50–140	17.00	18.48	$CoSO_3{\cdot}2N_2H_4$
	320 (exo)[a]	290–400	50.00	52.25	$CoSO_4 + Co_2O_3$
Nitrogen	75 (exo)[a]	50–175	16.00	18.48	$CoSO_3{\cdot}2N_2H_4$
	187 (exo)[a]	175–250	53.00	53.85	$CoSO_3 + CoS$
Combustion	–	~500	65.00	66.71	Co_2O_3

[a] Exo: exothermic.

activation energy is very low (20.5 kJ/mol) showing the increased rate of decomposition which may be due to the catalytic activity of cobalt sulfite hydrazinate.

3.1.2. Nickel hydrazinesulfinate

The thermal and kinetic degradation data of the nickel complex in various atmospheres is summarized in Tables 3 and 4, respectively. The complex decomposes in one step in static air at the temperature range 177–276 °C with the weight loss of about 37.30% to give the nickel sulfate as the final product. The DTA shows an exotherm at 225 °C corresponding to this decomposition.

In oxygen atmosphere, the complex decomposes in two stages as in the case of cobalt complex. The nickel sulfite dihydrazinate is the intermediate and the nickel

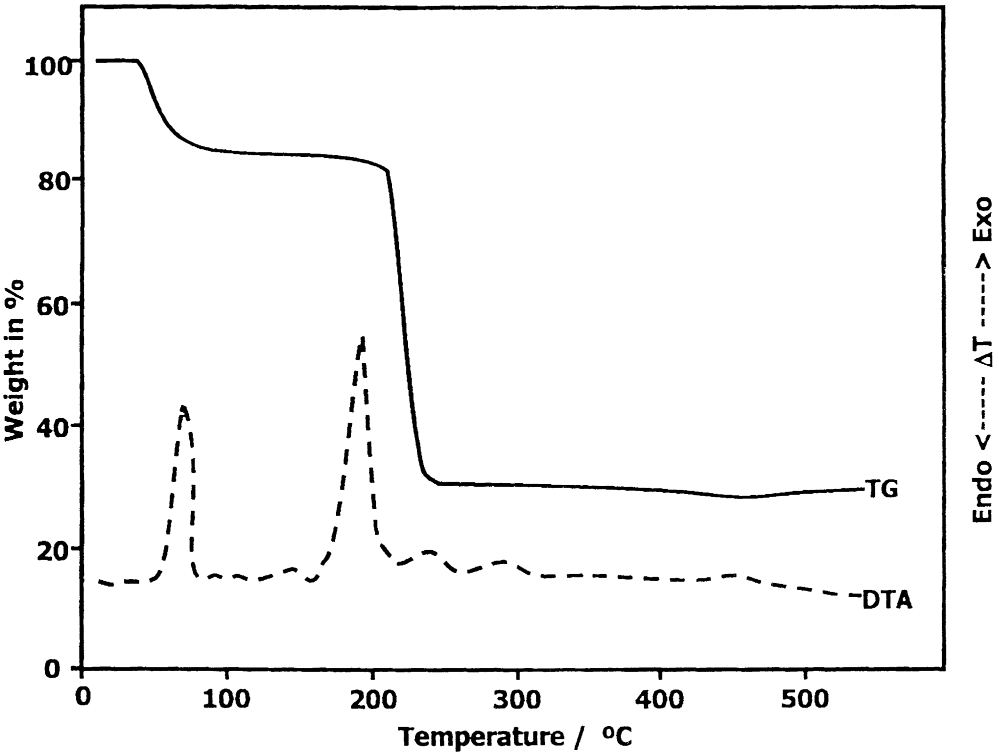

Fig. 5. Simultaneous TG–DTA traces of $Ni(N_2H_3SOO)_2$ in oxygen.

Table 2
Kinetic data of cobalt hydrazinesulfinate

Atmosphere	Stage	n order	E_a (kJ/mol)	S (kJ/(mol K))	A (s^{-1})
Air	I	0.89	104.6	−132.17	6.06×10^5
Oxygen	I	0.90	85.9	−109.35	8.31×10^6
	II	0.90	212.9	8.03	7.60×10^{12}
Nitrogen	I	0.93	20.5	−308.76	1.32×10^{-3}
	II	0.90	151.8	−1.64	2.59×10^{12}

Table 3
Thermal data of nickel hydrazinesulfinate

Atmosphere	DTA peak temperature (°C)	TG temperature range (°C)	Weight loss (%)		End product
			Found	Calculated	
Air	225 (exo)[a]	177–276	37.30	37.75	$NiSO_4$
Oxygen	75 (exo)[a]	30–90	16.00	18.50	$NiSO_3{\cdot}2N_2H_4$
	190 (exo)[a]	170–230	68.00	68.69	NiO
Nitrogen	240 (exo)[a]	175–275	52.50	53.89	$NiSO_3 + NiS$
Combustion	–	~500	64.00	63.54	NiS

[a] Exo: exothermic.

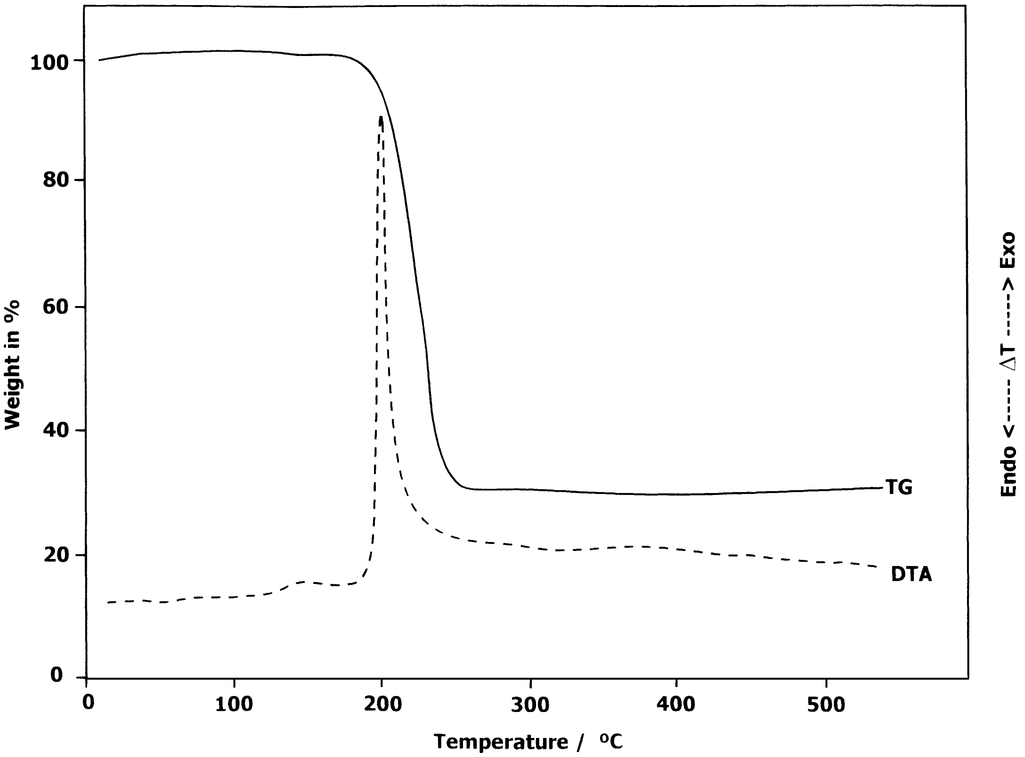

Fig. 6. Simultaneous TG–DTA traces of $Zn(N_2H_3SOO)_2$ in oxygen.

Table 4
Kinetic data of nickel hydrazinesulfinate

Atmosphere	Stage	n order	E_a (kJ/mol)	S (kJ/(mol K))	A (s^{-1})
Air	I	0.89	82.3	−184.18	1.51×10^3
Oxygen	I	0.90	73.2	−116.13	4.25×10^6
	II	0.90	238.9	157.31	3.31×10^{20}
Nitrogen	I	0.89	37.3	238.9	1.65×10^{-2}

oxide is the final residue. The temperature range is 50–230 °C and DTA shows two exotherms at 75 and 190 °C for the above two stages.

In nitrogen atmosphere, the complex give the mixture of nickel sulfide and nickel sulfite in one step. The weight loss observed from the thermal traces is well in agreement with the theoretical value. Though the formation of metal sulfide as end product is rare, in the present case nickel sulfide as residue is not surprising because metal sulfite hydrazinates have also been reported to yield metal sulfide [17]. Since the present complexes mostly undergo decomposition via metal sulfite hydrazinates, formation of nickel sulfide is not totally unexpected.

The proposed reactions in air, oxygen and nitrogen atmospheres are given as Eqs. (4)–(6), respectively.

$$2Ni(N_2H_3SOO)_2 + 5O_2 \rightarrow 2NiSO_4 + 4N_2 + 6H_2O + 2SO_2 \quad (4)$$

$$Ni(N_2H_3SOO)_2 + 2O_2 \rightarrow NiO + 2N_2 + 2SO_2 + 3H_2O \quad (5)$$

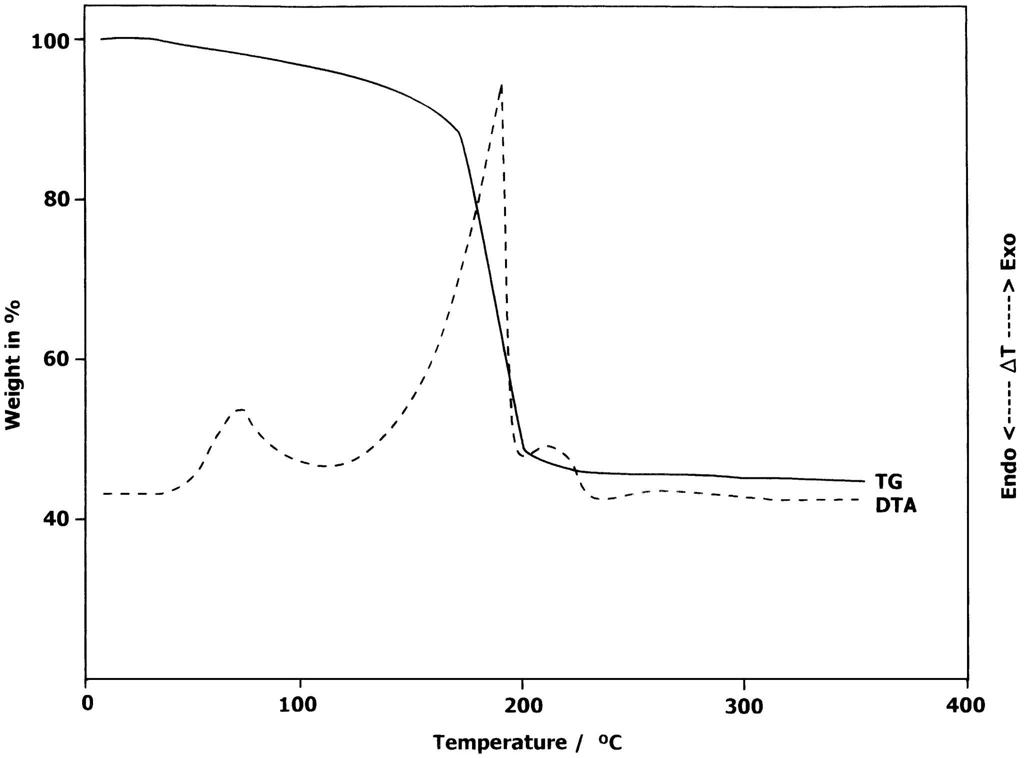

Fig. 7. Simultaneous TG–DTA traces of $Co(N_2H_3SOO)_2$ in nitrogen.

$$2Ni(N_2H_3SOO)_2 \rightarrow NiSO_3 + NiS + 2SO_2 + 4N_2 + 5H_2 + H_2O \qquad (6)$$

For nickel complexes also the order is in the range 0.89–0.9 indicating the first order kinetics for the thermal degradation. The activation energy is very low in nitrogen atmosphere as in the case of cobalt complex indicating the high thermal reactivity of the nickel complex. In many instances, nickel complexes are found to be more reactive and in some cases explosion was observed during heating [6,12]. In the present case, the observed low value of activation energy may also be attributed to the catalytic activity of the nickel sulfide which formed during the thermal degradation, enhances further degradation. In oxygen atmosphere, the first step has the less activation energy (73.2 kJ/mol) than the second step (238.9 kJ/mol) indicating the relative stability of the intermediate, nickel sulfite dihydrazinate than the starting complex.

3.1.3. Zinc hydrazinesulfinate

In static air, zinc complex decompose in single step in the temperature range 158–292 °C to give zinc sulfite. The DTA shows one exotherm corresponding to this decomposition. The weight loss observed in TG trace, 44.70%, is in accordance with the theoretical value, 44.18%.

In both oxygen and nitrogen atmosphere, the zinc complex undergoes one-step decomposition. However, in these two atmospheres zinc oxide is formed as the residue. The temperature range for the decomposition is 170–250 °C in oxygen atmosphere and 200–350 °C in nitrogen atmosphere. The thermal and kinetic data for the zinc complex is summarized in Tables 5 and 6, respectively.

The proposed reactions in air, oxygen and nitrogen atmospheres are given as Eqs. (7)–(9), respectively.

$$Zn(N_2H_3SOO)_2 + 2O_2 \rightarrow ZnSO_3 + 3H_2O + SO_2 + N_2 \qquad (7)$$

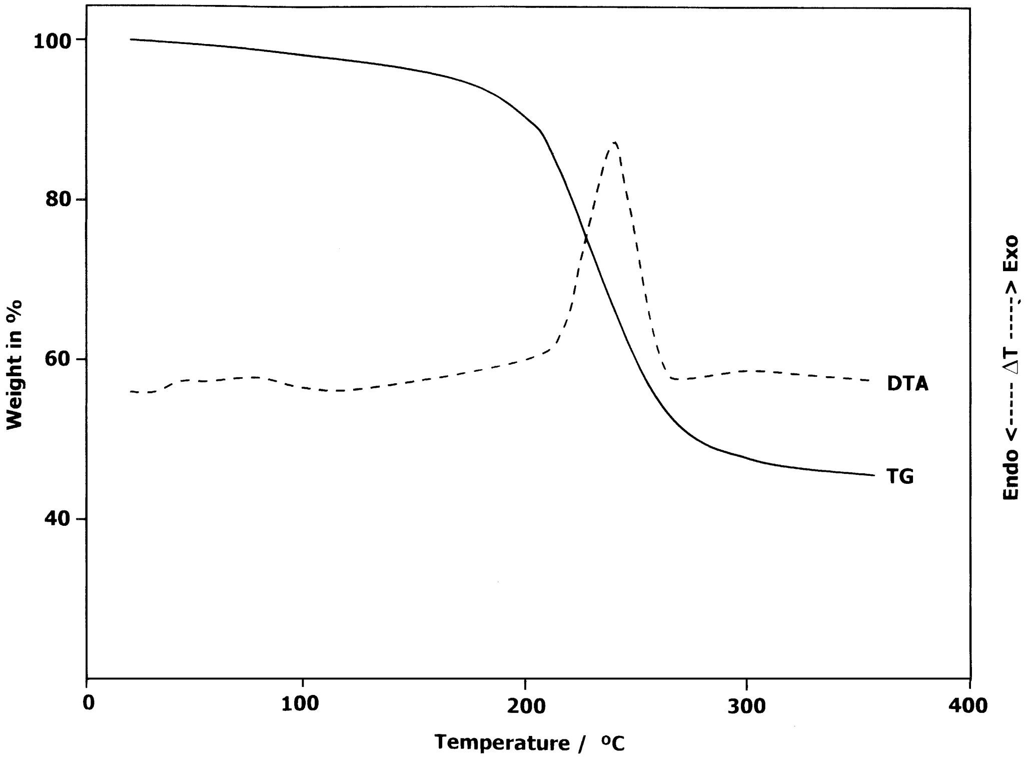

Fig. 8. Simultaneous TG–DTA traces of $Ni(N_2H_3SOO)_2$ in nitrogen.

Table 5
Thermal data of zinc hydrazinesulfinate

Atmosphere	DTA peak temperature (°C)	TG temperature range (°C)	Weight loss (%)		End product
			Found	Calculated	
Air	200 (exo)[a]	158–292	44.70	44.18	$ZnSO_3$
Oxygen	200 (exo)[a]	170–250	69.00	68.16	ZnO
Nitrogen	275 (exo)[a]	200–350	68.00	68.16	ZnO
Combustion	–	~500	51.00	52.50	$ZnSO_4$ + ZnO

[a] Exo: exothermic.

Table 6
Kinetic data of zinc hydrazinesulfinate

Atmosphere	Stage	n order	E_a (kJ/mol)	S (kJ/(mol K))	A (s^{-1})
Air	I	0.90	52.5	−244.21	1.65×10^0
Oxygen	I	0.90	116.4	−104.55	1.40×10^7
Nitrogen	I	0.89	91.2	−178.60	2.94×10^3

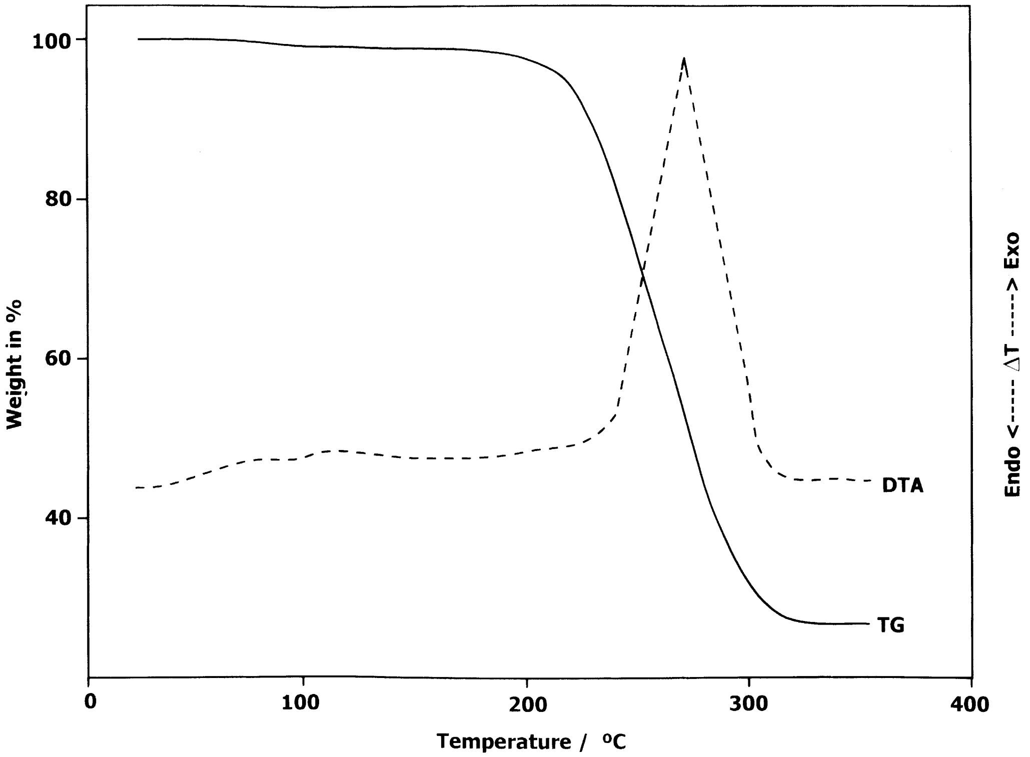

Fig. 9. Simultaneous TG–DTA traces of $Zn(N_2H_3SOO)_2$ in nitrogen.

$$Zn(N_2H_3SOO)_2 + 2O_2 \rightarrow ZnO + 2N_2 + 2SO_2 + 3H_2O \quad (8)$$

$$Zn(N_2H_3SOO)_2 \rightarrow ZnO + SO_2 + SO + 2N_2 + 3H_2 \quad (9)$$

As observed for previous two complexes, the degradation of zinc complex in all the three atmospheres also follow first order kinetics ($n = 0.89$–0.9). In air, the rate of decomposition is more which is obvious from the energy of activation ($E_a = 52.5\,\mathrm{kJ/mol}$) which is the lowest value among the three atmospheres.

3.2. Combustion studies

Combustion data (Tables 1, 3 and 5) shows that cobalt complex gives cobaltic oxide, nickel complex yields nickel sulfide and zinc complex resulted in a mixture of zinc sulfate and zinc oxide as the decomposition residue. The combustion products were confirmed by analytical and X-ray powder diffraction studies.

References

[1] J.E. House, A.J. Vandenbrook, Thermochim. Acta 150 (1989) 79.
[2] K.C. Patil, C. Nesamani, P.R. Paiverneker, Synth. React. Inorg. Met. Org. Chem. 12 (1982) 383.
[3] J. Macek, A. Rahten, J. Slivnik, Proc. Eur. Symp. Ther. Anal. 1 (1976) 161.
[4] P. Ravindranathan, K.C. Patil, Thermochim. Acta 71 (1983) 53.
[5] G.V. Mahesh, K.C. Patil, Thermochim. Acta 99 (1986) 188.
[6] B.N. Sivasankar, S. Govindarajan, Thermochim. Acta 244 (1994) 235.
[7] J. Macek, R. Hrovat, B. Novosel, J. Therm. Anal. 40 (1993) 335.
[8] P. Ravindranathan, K.C. Patil, J. Solid State Chem. 66 (1987) 20.
[9] B.N. Sivasankar, S. Govindarajan, Z. Naturforsch. 49b (1994) 950.

[10] P. Ravindranathan, K.C. Patil, Am. Ceram. Soc. Bull. 66 (1987) 688.

[11] B.N. Sivasankar, S. Govindarajan, Synth. React. Inorg. Met. Org. Chem. 25 (1995) 31.

[12] B.N. Sivasankar, S. Govindarajan, J. Therm. Anal. 46 (1996) 117.

[13] B.N. Sivasankar, S. Govindarajan, Synth. React. Inorg. Met. Org. Chem. 24 (1994) 1573.

[14] B.N. Sivasankar, S. Govindarajan, Indian J. Chem. 33A (1994) 329.

[15] B.N. Sivasankar, S. Govindarajan, Synth. React. Inorg. Met. Org. Chem. 25 (1995) 127.

[16] B.N. Sivasankar, S. Govindarajan, Synth. React. Inorg. Met. Org. Chem. 24 (1994) 1583.

[17] J.S. Budkuley, Ph.D. Thesis, Indian Institute of Science, Bangalore, 1987.