Journal of Thermal Analysis and Calorimetry, Vol. 76 (2004) 507–519

THERMAL STUDIES ON ENERGETIC COMPOUNDS
Part 30. Kinetics and mechanism of bis(diethylenetriamine)metal nitrate complexes

G. Singh[*] *and D. K. Pandey*

Chemistry Department, DDU Gorakhpur University, Gorakhpur-273 009, India

(Received July 15, 2003; in reviser form October 30, 2003)

Abstract

The nitrate complexes of copper, nickel and zinc with diethylenetriamine (dien) i.e. $[Cu(dien)_2](NO_3)_2$, $[Ni(dien)_2](NO_3)_2 \cdot 2H_2O$ and $[Zn(dien)_2](NO_3)_2$ have been prepared and characterised. Thermal studies were undertaken using TG-DTG, DSC, ignition delay (t_{id}) and ignition temperature (IT) measurements. Impact sensitivity was measured using drop mass technique. The kinetic parameters for both non-isothermal and isothermal decomposition of the complexes were evaluated by employing Coats–Redfern (C–R) method and Avrami–Erofeev (A–E) equations (n=2 and 3), respectively. The kinetic analysis, using isothermal TG data, was also made on the basis of model free isoconversional method and plausible mechanistic pathways for their decomposition are proposed. Rapid process was assessed by ignition delay measurements. All these complexes were found to be insensitive towards impact of 2 kg mass hammer up to the height limit (110 cm) of the instrument used. The heat of reaction (ΔH) for each stage of decomposition was determined using DSC.

Keywords: decomposition kinetics, DSC, metal nitrate complexes, TG-DTG

Introduction

Nitrates [1–4] are powerful oxidizing agents and decompose exothermally at elevated temperatures to give oxygen as one of the major products. Of the various classes of high energetic compounds (HECs) available, transition metal complexes find applications in explosives, propellant formulations and pyrotechnique compositions. The explosivity of such type of HECs is reported to lie between those of primary and secondary explosives [5]. Thermal characterisation of these complexes helps in knowing the thermal stability, safety in handling and storage. The kinetic analysis permits a deeper-insight into the mechanism of thermal decomposition of new HECs. Earlier we have reported thermal characterisation and explosion of various HECs [6–12]. Very recently, we have undertaken investigations [13] on some bis(ethylenediamine)metal(II) nitrates. Kinetics and mechanistic

---

[*] Author for correspondence: E-mail: gsingh4us@yahoo.com

1388–6150/2004/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

aspects of thermal decomposition of bis(diethylenetriamine)metal(II) nitrates are not reported yet. Thus, an attempt has been made in this paper to prepare, characterize and investigate the mechanism for thermal decomposition of such type of complexes.

Experimental procedure

Materials

The following chemicals (obtained from the sources given in parentheses) were used as received: Carbonates of copper (BDH), nickel and zinc (Thomas Baker), 70% HNO_3 and methanol (Ranbaxy), ethanol (Hayman), diethylenetriamine (s.d. fine chemicals), and silica gel TLC grade (Qualigens).

Preparation and characterizations of complexes

Firstly, the metal nitrates were prepared by a procedure similar to the one as reported earlier [14] but with slight modification, by treating corresponding metal carbonates (MCO_3) with 70% nitric acid (HNO_3) at room temperature (RT). The metal nitrates thus obtained were washed with petroleum ether, recrystallised from distilled water and dried over fused $CaCl_2$ in desiccator. The bis(diethylenetriamine)metal nitrate complexes were prepared by reacting ethanolic solution of corresponding metal nitrates with diethylenetriamine in stoichiometric amount.

$$\mathrm{MCO_3{+}HNO_3(70\%){\rightarrow}M(NO_3)_2 \xrightarrow{+\mathrm{dien}}}$$
$$\mathrm{[M(H_2N{-}CH_2CH_2{-}NH{-}CH_2CH_2{-}NH_2)_2](NO_3)_2{\cdot}}n\mathrm{H_2O}$$
$$\text{bis(diethylenetriamine)metal nitrate}$$

where M=Cu, Ni, Zn and n=0, 2, respectively.

The crystalline complexes with different colours, were washed with methanol. All these nitrates were recrystallised from their aqueous solution, dried over fused $CaCl_2$ and their purity was checked by thin layer chromatography (TLC). These complexes were characterised by gravimetric method [15], infrared [16, 17] (Impact 400) and elemental analysis (Fission Instrument DP 200 series 2). TLC, IR and elemental data are summarized in Table 1.

Thermal characterisation

The details of thermal characterisation of complexes are given below.

Simultaneous TG-DTG

TG-DTG curves were obtained on DuPont 2100 Thermal Analysis instrument in nitrogen atmosphere (flow rate 60 mL min^{-1}) at a heating rate of 10°C min^{-1} and DSC curves are given in Fig. 1. The temperature of inception T_i, temperature of completion T_f, DTG peak temperature T_s and percentage mass loss of each stage of decomposition are presented in Table 2.

Table 1 Physical, TLC, elemental and spectral parameters of bis(diethylenetriamine)metal nitrates

No.	Compound	Colour	TLC *	Elemental analysis/% observed (calculated)				IR/cm^{-1}					
			R_f	C	H	N	Metal	ν_{dien}	νM–N	$\nu H_2N–CH_2$	νNO_3	νCH_2	νNH_2
1	$[Cu(dien)_2](NO_3)_2$	dark blue	0.75	23.7 (24.4)	5.9 (6.6)	27.6 (28.5)	15.5 (16.1)	1035m	428s	1035m	1340s	1457m	445s
2	$[Zn(dien)_2](NO_3)_2\ 2H_2O$	violet	0.68	23.9 (24.6)	5.8 (6.7)	28.2 (28.8)	14.7 (15.2)	1095m	445s	1080m	1360s	1490m	450s
3	$[Zn(dien)_2](NO_3)_2$	white	0.71	23.7 (24.3)	5.8 (6.6)	27.5 (28.4)	15.9 (16.5)	1055m	440s	1110m	1400s	1495m	490s

* R_t is retention factor; eluent=*n*-butanol:chloroform:gl. acetic acid (2:1:1); locating reagent: iodine

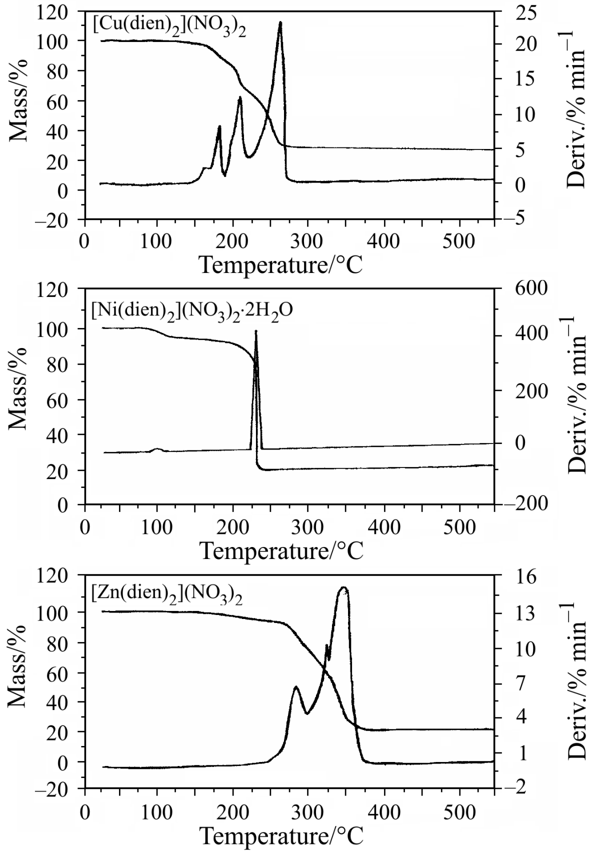

Fig. 1 TG-DTG curves of bis(diethylenetriamine)metal complexes recorded at a heating rate of 10°C min^{-1} in flowing nitrogen atmosphere (flow rate 60 mL min^{-1})

DSC

This study was performed on V4.OB DuPont 2100 in an inert atmosphere (N_2, flow rate 60 mL min^{-1}) at a heating rate of 10°C min^{-1} and DSC curves are reported in Fig. 2. DSC peak temperatures and ΔH values are summarised in Table 2.

Non-isothermal TG

To determine the effect of atmosphere change on isothermal and non-isothermal TG on these complexes (weighing≈20 mg, 100–200 mesh, heating rate 2°C min^{-1}) were undertaken in static air using home made thermogravimetric analyser (TGA) [16] in our laboratory. As the complex of Ni metal was found to cause repeated explosion during TG studies, it was thought of interest to perform TG on all of the present complexes by diluting the samples with alumina (1:1 ratio) in same experimental conditions to have a comparison of thermal behaviour of all the complexes. The kinetics of non-isothermal decomposition of

Table 2 Thermoanalytical data on complexes

Comp. No.	Stage	TG(N_2)						DSC(N_2)		
		T_i/ C	T_s/ C	T_f/ C	Mass loss/%		Expelled group	Peak temperature/°C		ΔH/J g^{-1}
					obs.	calc.		endo*	exo	
1	I	170	181	183	12.3	13	0.5 dien	180	–	387.5
	II	200	208	212	24	25	0.5 dien	187	–	387.5
	III	248	260	267	42	43	1 dien+NO_x	–	238	1079
2	I	82	94	106	7.8	8.4	$2H_2O$	103	–	120.8
	II	155	175	190	23	24	1 dien	211	–	126.5
	III	229	230	231	73.5	74	1 dien+NO_x	–	254	395.2
3	I	240	283	290	25	26.2	1 dien	285	–	58.8
	II	326	348	400	55	54	1 dien+NO_x	–	314	937.5

*Data taken from TG in static air atmosphere

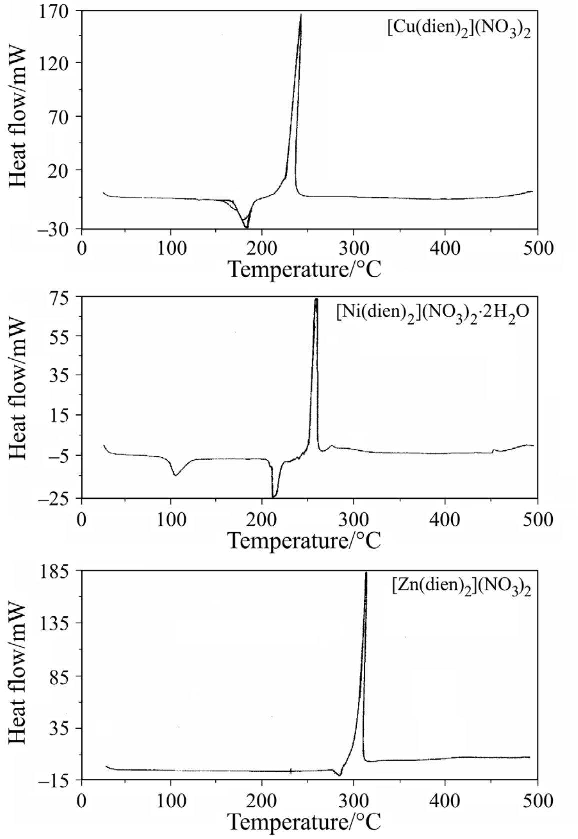

Fig. 2 DSC curves of complexes obtained at a heating rate of 10°C min^{-1} in flowing nitrogen atmosphere (flow rate 60 mL min^{-1})

the complexes was estimated using this TG data by C–R equation [19–21]. The calculated parameters such as activation energy (E_a), order parameter (n), pre-exponential factor (A) and correlation coefficient (r) are reported in Table 3.

Table 3 Kinetic parameters for non-isothermal decomposition of complexes obtained from Coats–Redfern (C–R) method

Comp. No.	Decomposition stage	n	E_a/kJ mol^{-1}	lg$A$	r
1	I	0.0	105.3	3.6260	0.9957
	II	0.0	123.2	4.2670	0.9969
	III	0.0	79.5	2.6518	0.9954
2	I	0.0	88.6	3.3429	0.9976
	II	0.0	72.8	2.0644	0.9898
	III	0.0	55.3	1.9878	0.9995
3	I	0.0	127.9	1.9755	0.9897
	II	0.0	120.2	1.5442	0.9981

Isothermal TG

The isothermal TG on these complexes (sample mass≈20 mg, 100–200 mesh) was carried out in static air using above said apparatus [18]. The kinetics for isothermal decomposition of these complexes were evaluated using isothermal TG data which were fitted in nine mechanism based kinetic models [22, 23]. Avrami–Erofeev equations (1 and 2) were found to be the best-fit models leading to straight-line plots.

$$[-\ln(1-\alpha)]^{1/2}=kt \tag{1}$$

$$[-\ln(1-\alpha)]^{1/3}=kt \tag{2}$$

The correlation coefficient value (r) were also determined using the following relation,

$$r=\frac{\sum xy}{\sqrt{\sum x^2 \sum y^2}} \tag{3}$$

where x and y are values at abscissa and ordinates, respectively. The calculated values for rate constant (k), E_a and r are reported in Table 4.

Table 4 Kinetic parameters and correlation coefficients (r) for isothermal decomposition of complexes

Comp. No.	Avrami–Erofeev (n=2)						
	Rate constant ($k\cdot10^{-3}$/min^{-1}) at (T/K)					r	E_a/kJ mol^{-1}
1	9.9 (493)	15.6 (503)	32.0 (513)	42.3 (523)	75.5 (533)	0.9887	86.8
2	6.0 (478)	8.2 (483)	15.8 (488)	34.0 (493)	43.4 (498)	0.9989	72.5
3	7.5 (573)	15.2 (593)	28.4 (613)	49.2 (633)	65.0 (653)	0.9952	114.8
	Avrami–Erofeev (n=3)						
1	7.9 (493)	16.1 (503)	30.0 (513)	41.7 (523)	73.6 (533)	0.9987	88.1
2	7.4 (478)	14.9 (483)	21.7 (488)	35.8 (493)	42.5 (498)	0.9988	70.8
3	6.5 (573)	12.5 (593)	27.8 (613)	48.2 (633)	66.6 (653)	0.9992	112.9

Model free isoconversional method [24] (Eq. (4)) was also employed to make kinetic analysis for isothermal decomposition of these complexes.

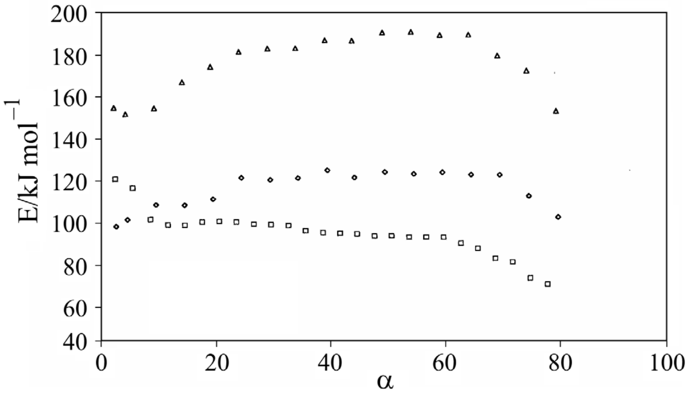

Fig. 3 Dependencies of E on extent of conversion (α) obtained from isoconversional method. ◇ – $[Cu(dien)_2](NO_3)_2$, □ – $[Ni(dien)_2](NO_3)_2{\cdot}2H_2O$ and △ – $[Zn(dien)_2](NO_3)_2$

$$-\ln t_\alpha = \ln\left[\frac{A}{g(\alpha)}\right] - \frac{E_\alpha}{RT} \tag{4}$$

where t is time, α is extent of conversion, A is pre-exponential factor, E_α indicates activation energy at various α, R represents gas constant and T is absolute temperature. The values of E_α were calculated from the slope of $-\ln t$ *vs.* $1/T$ plots and dependencies of E_α on the α values are demonstrated in Fig. 3.

Ignition delay (t_{id}) and ignition temperature (IT) measurements

The time interval between the insertion of the sample tube into the TF and the appearence of smoky flame was taken to be the t_{id}. t_{id} and *IT* were measured using tube furnace (TF) [25] technique. The ignition tube (length=5 cm and diameter=0.4 cm) containing sample (mass 20 mg, 100–200 mesh) clamped with a bent wire was inserted manually into the TF. Each experiment was repeated three times and mean t_{id} values are reported in Table 5. The accuracy of the temperature measurement of TF was ±1°C. The ignition delay data was fitted in following equation [26–28] to obtain the value of activation energy for thermal ignition (E*) reported in Table 5.

$$t_{id} = B\exp\frac{E^*}{RT} \tag{5}$$

where B is constant, E* is the activation energy for ignition and T is the absolute temperature.

Impact sensitivity measurement

An impact apparatus for high explosive was used to carry out this experiment. The description of the device and experimental setup are reported elsewhere [7].

Table 5 Ignition delay (t_{id}), ignition temperature (*IT*) and activation energy for thermal ignition (E^*) of complexes

Comp. No.	t_{id}/s at various temperatures/°C							*IT*/°C for t_{id} of 25 s	E^*/kJ mol^{-1}
	300	325	350	375	400	425	450		
1	147 0.5	128 1.0	92 0.0	66 0.1	52 0.5	31 0.5	22 1.0	430	37.0
2	126 0.3	98 0.1	72 0.4	56 0.9	29 1.0	23 0.5	17 1.0	405	32.6
3	179 0.5	149 0.0	125 0.5	85 0.7	57 1.0	34 0.8	24 0.0	445	47.0

Results and discussion

The analytical data presented in Table 1, clearly indicate that there is a good agreement between percentage of observed and calculated values of each element and hence confirming the metal complex formation. IR spectral data (Table 1), on the other hand, also signalize the proposed molecular formulae of the complexes. The simultaneous TG-DTG traces obtained in inert atmosphere of nitrogen (Fig. 1) and TG taken in static air (with alumina) show multistage decomposition of the complexes. The nature of the thermal curves for the complexes of copper and zinc metals were found to be same both in nitrogen and air (diluted with alumina). The copper complex was decomposed in three stages whilst zinc complex in two stages. However, different decomposition patterns were observed for nickel complex in different experimental conditions. Two step decomposition was seen in simultaneous TG-DTG analysis (Fig. 1). However, three stages appear when TG is performed on this complex diluted with alumina in static air (Table 2). It seems that a higher heating (10°C min^{-1}) applied in simultaneous analysis is responsible for rapid decomposition and hence causing second and third steps to occur simultaneously. The TG data given in Table 2 indicate that there is a close agreement between the observed and calculated mass losses corresponding to different decomposition stages of all the complexes. This showed the assumed composition of expelled groups in corresponding stages to be reasonably correct. All these complexes generally undergo decomposition processes; dehydration and/or partial deammination and finally oxidative decomposition to yield corresponding metal oxides as final decomposition product. A similar type of decomposition trend is observed during the course of TG analysis of the complexes in air atmosphere.

From the thermal data reported in Table 2, the complexes appear to decompose in following stages:

$$[\mathrm{Cu(dien)_2}](\mathrm{NO_3})_2 \rightarrow [\mathrm{Cu(dien)_{1.5}}](\mathrm{NO_3})_2 \rightarrow [\mathrm{Cu(dien)}](\mathrm{NO_3})_2 \rightarrow \mathrm{CuO}+\text{gaseous products}$$

$$[\mathrm{Ni(dien)_2}](\mathrm{NO_3})_2\cdot 2\mathrm{H_2O} \rightarrow [\mathrm{Ni(dien)_2}](\mathrm{NO_3})_2 \rightarrow [\mathrm{Ni(dien)}](\mathrm{NO_3})_2 \rightarrow \mathrm{NiO}+\text{gaseous products}$$

$$[\mathrm{Zn(dien)_2}](\mathrm{NO_3})_2 \qquad [\mathrm{Zn(dien)}](\mathrm{NO_3})_2 \rightarrow \mathrm{ZnO}+\text{gaseous products}$$

Firstly, in the case of $[\mathrm{Cu(dien)_2}](\mathrm{NO_3})_2$, the first two stages of mass losses involve the partial deammination, in which, out of the two ligand molecules (dien), one is expelled out. In the first step only 0.5dien molecule is lost. The mass loss (T_s=181°C) between the temperature range 170–183°C corresponds to removal of half ammine molecule leading to appearance of first endothermic peak at 180°C in DSC curve (Fig. 2). In second stage, the precursor $[\mathrm{Cu(dien)_{1.5}}](\mathrm{NO_3})_2$, formed as intermediate during the course of thermolysis of parent complex, undergoes further deammination (T_s=208°C) to loss 0.5dien molecule yielding monodien complex. This process can also be observed as endotherm in DSC at 187°C. The partial losses of such type of moieties were also observed by Prabhumirashi *et al.* [29] in the study of chloro complexes of copper with tetra-methylenediamine and chloroanilines. The monodien species thus formed undergoes final stage of decomposition giving copper oxide as decomposition product. In this stage, simultaneous loss of second dien molecule with counter anion (NO_3^-) takes place and the process appears to be exothermic (238°C) in DSC trace. As the first two endothermic processes are overlapping in DSC curve, ΔH value (Table 2) was calculated for the overall endothermic process.

TG data of $[Ni(dien)_2](NO_3)_2\cdot 2H_2O$ (in static air) presented in Table 2 show that the first stage of mass loss in temperature range 95–110°C involves the complete dehydration of the complex, which is also evident from an endothermic peak at 103°C in DSC curve. On further heating, the anhydrous $[Ni(dien)_2](NO_3)_2$ undergoes partial deammination (160–190°C) and one dien molecule is lost. An endotherm with peak temperature 211°C is also indicating the said process. In the third step, exothermic decomposition takes place, which corresponds to removal of counter anion (deanionation) with second dien molecule as discussed above.

The first step of decomposition (T_s=283°C) of $[Zn(dien)_2](NO_3)_2$ corresponds to loss of one dien molecule and second step involves oxidative decomposition (T_s=348°C) to ZnO and the process appeared as exotherm at 314°C in DSC.

Thus, from the TG-DTG and DSC analysis, the various decomposition processes taking place are understood. In order to evaluate kinetic parameters, different methods have been employed. The model fitting method was used to estimate kinetics of non-isothermal as well as isothermal decomposition. The parameters obtained for non-isothermal decomposition (Table 3) are quite comparable with those obtained for isothermal decomposition (Table 4). The activation energy of these complexes was found to be in order:

$$[Zn(dien)_2](NO_3)_2 > [Cu(dien)_2](NO_3)_2 > [Ni(dien)_2](NO_3)_2\cdot 2H_2O$$

The lower activation energy value in the case of nickel complex may be due to loosely held water of crystallisation at outer sphere and hence causing less thermal stability. The model fitting method is for overall thermal decomposition process of the complexes and this fails to explain the complexity of decomposition reactions. Model free isoconversional method, on the other hand, permits the calculation of E_α pertaining to each value of α and thus one can examine the dependencies of E_α on extent of conversion. As E of the complexes are different, the mechanism of decomposition is also different. It is clear from Fig. 3 that the initial and final E_α values for decomposition of copper and zinc complexes were found to be lower. However, nearly constant values were obtained between these two stages. In the case of nickel complex, E_α value is decreasing initially which became constant in α range 12 to 63 and finally a gradual decrease is observed. Thus, it can be inferred that isoconversional method explains the complexity of decomposition reaction.

Although, these complexes are stable at room temperature and insensitive to the impact test applied, they get ignited when subjected to a sudden high temperature. Therefore, it was found interesting to know kinetics of rapid analysis by means of ignition delay measurements. It is observed that E^* values are nearly one third of the E_a values. *IT* was measured to have a comparison of thermal stability of these complexes. E^* and *IT* of these complexes (Table 5) were found to decrease in order:

$$[Zn(dien)_2](NO_3)_2 > [Cu(dien)_2](NO_3)_2 > Ni(dien)_2](NO_3)_2{\cdot}2H_2O$$

Thus, based on *E** and *IT*, thermal sensitivity of zinc complex is less than that of nickel and copper complexes.

Conclusions

Thermal analysis of these complexes occurs in multistages. Dehydration (of hydrated complex) or deammination followed by exothermic decomposition at higher temperatures giving corresponding metal oxides seems to be the general mechanism of thermal decomposition. Rate controlling process of thermolysis involves random nucleation. Kinetic analysis made both by slow analysis (using TG data) and rapid one (using ignition delay data) indicates the higher thermal stability of zinc complex while nickel complex is very sensitive to heat. However, all these complexes were found to be insensitive to the impact and thus are safe to handle and store.

* * *

Thanks are due to Head of Chemistry Department, DDU Gorakhpur University, Gorakhpur for laboratory facility, Dr. Santosh Kumar Pandey, New Custom House Laboratory, Mumbai for IR and elemental analysis and DRDO, New Delhi for financial assistance.

References

1 B. T. Fedoroff, Encyclopedia of Explosives and related Items, Picatinny Arsenal, New Jersey, Vol. I, 1960, pp. A311–379.
2 J. H. Koper, O. G. Jansen and P. J. Vanden Berg, Explosivestoffe, 8 (1970) 181.
3 B. Pacewska, M. Keshr and O. Kluk, J. Therm. Anal. Cal., 74 (2003) 595.
4 Q. S. M. Kwok and D. E. G. Jones, J. Therm. Anal. Cal., 74 (2003) 57.
5 W. Friendrich and P. Vervoost, C. A., 21 (1924) 1184.
6 G. Singh and I. P. S. Kapoor, Combust. Flame, 92 (1993) 283.
7 G. Singh, I. P. S. Kapoor, S. M. Mannan and J. P. Agrawal, Combust. Flame, 97 (1994) 355.
8 G. Singh, I. P. S. Kapoor and S. M. Mannan, Thermochim. Acta, 262 (1995) 117.
9 G. Singh, I. P. S. Kapoor and S. M. Mannan, J. En. Mater. Sci., 13 (1995) 141.
10 G. Singh, I. P. S. Kapoor and S. K. Tiwari, Indian J. Chem., 7 (2000) 236.
11 G. Singh, I. P. S. Kapoor S. K. Tiwari and S. P. Felix, Indian J. Eng. Mater. Sci., 7 (2000) 167.
12 G. Singh, I. P. S. Kapoor and S. Jacob, J. Sci. Indust. Res., 59 (2000) 575.
13 G. Singh and D. K. Pandey, Prop. Expl. Pyro., 28 (2003) 231.
14 K. C. Patil and V. R. Pai Vernekar, Thermochim. Acta, 15 (1976) 257.
15 Vogel's Text Book of Quantitative Inorganic Analysis, Longman, London 1985, 4th Ed.
16 K. Nakamoto, Infrared and Raman spectra of Inorganic and Coordination Compounds, Wiley and Sons, New York 1978, p. 206.
17 C. W. Robert, Hand Book of Physics and Chemistry, CRC Press, Florida, 66 (1996) 197.
18 G. Singh and R. R. Singh, Res. Ind., 23 (1978) 92.
19 A. W. Coats and J. P. Redfern, Nature, 20 (1964) 88.
20 A. W. Coats and J. P. Redfern, Polym. Lett., 3 (1965) 917.

21 S. A. Fakiaha, K. H. Halawani and K. M. El-Salaam, J. Thermal Anal., 39 (1993) 913.
22 V. Satava, Thermochim. Acta, 2 (1971) 423.
23 C. M. Wyandt and D. R. Flanagan, Thermochim. Acta, 196 (1992) 379.
24 S. Vyazovkin, Thermochim. Acta, 355 (2000) 155.
25 G. Singh, S. K. Vasudeva and I. P. S. Kapoor, Indian J. Tech., 29 (1991) 589.
26 N. Semenov, Chemical Kinetics and Chain Reactions, Clarendon Press, Oxford 1935, Chap. 18.
27 E. S. Freeman and S. Gardon, J. Phys. Chem., 60 (1956) 867.
28 J. Zim and R. N. Rogers, J. Phys. Chem., 66 (1962) 2646.
29 L. S. Prabhumirashi, S. R. Nayak and J. K. Khoje, Paper presented in Seventh National Symposium on Thermal Analysis (R. E. C. Srinagar), 1989, p. 92.