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Research Paper

KINETICS OF THERMOLYSIS OF NICKEL PERCHLORATE COMPLEX WITH 2-AMINOPYRIDINE LIGAND

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Trinuclear nickel perchlorate complex with 2-aminopyridine and water ligand of the general formula $[\text{Ni}_3(\text{C}_5\text{H}_6\text{N}_2)_2(\text{H}_2\text{O})_{10}](\text{ClO}_4)_6$ have been prepared and characterized by elemental analysis, FT-IR spectroscopy, gravimetric method and thermogravimetry. On the basis of thermogravimetry, structure of the complex have been suggested in which four water molecules are bridged between Ni atoms and six are terminally coordinated. Thermal behaviour of complex has been investigated by thermogravimetry (TG) and differential thermal analysis (DTA). The complex decomposes in two steps. Kinetics for thermal decomposition of complex has been studied using isothermal TG data by applying model fitting and isoconversional method. Response of the complex towards rapid heating has been investigated by explosion delay measurements and evaluating the kinetics of explosion using these data.

Keywords: 2-Aminopyridine, Perchlorate complex, Thermolysis, Explosion delay and kinetics

INTRODUCTION

Many complexes of transition metals having organic ligand and NO_3^- or ClO_4^- ions (Kumar *et al.*, 2012, 2012; Singh *et al.*, 2008, 2009; Dalvi *et al.*, 2008; Konar *et al.*, 2003;) have shown self catalyzed exothermic thermolysis, and may find application in rocket propellants (Singh *et al.*, 2003, 2005), explosives and pyrotechnics (Fedoroff and Sheffield, 1966; Kopper and Jansen, 1970). These complexes when decompose gives corresponding metal oxide

(Kumar *et al.*, 2012) which may have exciting catalytic, magnetic and electrical ownership (Sawant *et al.*, 2002). Transition metal oxides are good burning rate enhancer for composite solid propellants (Kung, 1998; Shen *et al.*, 1993; Solymosi, 1977; Jacob and Whitehead, 1969; Patil *et al.*, 1975). Thermal investigation of energetic complexes assists to perceive cleanly the safety in handling, thermal stability and storage. Kinetic studies furnish an easy access into the mechanism of thermal decomposition of

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a new energetic material. 2-Aminopyridine acts as a bidentate (El-ajaily *et al.*, 2009; Deshpande *et al.*, 2010; Li and Yuan, 2012) or as a monodentate (Mei *et al.*, 2009; Kozlevcar *et al.*, 2001).

In recent years, the study of polynuclear complexes of transition metals has endured dreadful progress due to their various applications and structural captivations. In this work, we submit an account of preparation, characterization and thermolytic studies of nickel perchlorate complex with 2-aminopyridine ligand. The complex is trinuclear and have coordinated water molecules along with 2-aminopyridine. Kinetic evaluation using isothermal TG data has been studied. Kinetics of fast decomposition (explosion) of complex has also been incorporated in this paper.

MATERIALS AND METHODS

Materials

Following analytical grade reagents nickel

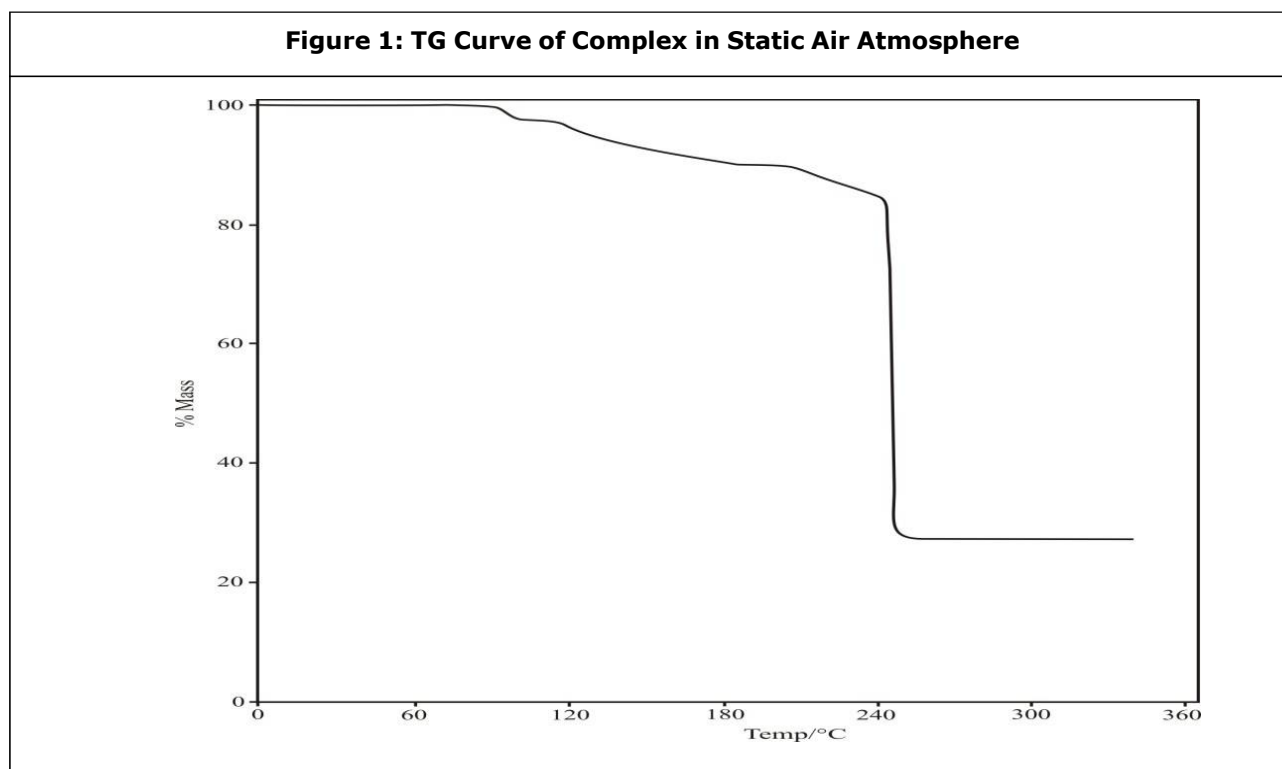
carbonate, perchloric acid, 2-aminopyridine (s.d. fine), ethanol (Changshu Yangyuan Chemical China), petroleum ether (Merck) were used without further purification.

Preparation and Characterisation of Complex

The complex was prepared by two step procedure. In first step nickel perchlorate was obtained by reacting nickel carbonate with 60% perchloric acid followed by recrystallization. Precipitate of reported complex was formed when ethanolic solution of 2-aminopyridine and nickel perchlorate reacts. Precipitate was washed 3 times with ethanol and dried in hot air oven. The complex was characterized by gravimetric estimation (Vogel *et al.*, 1995), infra red (Miller and Wilkins, 1952; Robert, 1996; Nakamoto, 1978) (Perkin Elmer FT-IR spectrometer) and elemental analysis (Thermo Finnigan Flash EA 1112 CHNS analyzer). Various characterisation data are presented in Table 1.

Table 1: IR Frequencies And Elemental Analysis Data of the Complex

IR ν (cm ⁻¹)	Assignments	Element %, Observed/Calculated	
414, 469	M-N	C	10.36/10.68
627	ClO ₄ ⁻	N	4.75/4.98
772	Pyridine ring	H	2.70/2.67
1090	ClO ₄ ⁻	Ni	14.82/15.67
1330	Aryl C-NH ₂		
1490	Aryl C=C		
1572	N-H def.		
1625	Aryl C=N		
2951	C-H str.		
3363	N-H str.		
3430	O-H str.		

Figure 1: TG Curve of Complex in Static Air Atmosphere

Thermogravimetric (TG) in Air

Dynamic TG (Figure 1) was undertaken using an indigenously fabricated TG apparatus (Singh and Singh, 1978) in static air atmosphere. Gold crucible was used as sample holder (sample mass 20 mg, heating rate 10 °C/min)

Simultaneous TG-DTG-DTA

These curves were obtained at heating rate of 10 °C/min in flowing N₂ atmosphere (sample mass ~ 4 mg, N₂ flow rate 100 ml/min) in open crucible (Perkin Elmer Pyris Diamond TG/DTA). The curves are shown in Figure 2.

Isothermal TG

Isothermal TG (Figure 4) a complex was taken under static air using the same indigenously fabricated TG apparatus as mentioned earlier (Sample mass 10mg, particle size 200 mesh) at temperatures 160, 170, 180 ,190, 200°C for 30% weight loss.

Kinetic Analysis of isothermal TG data

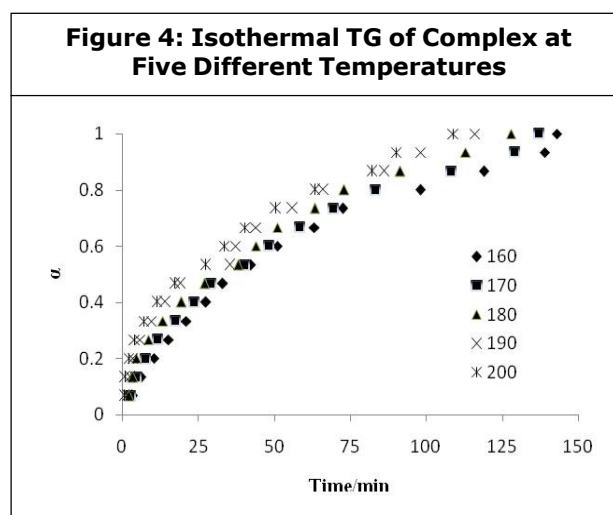
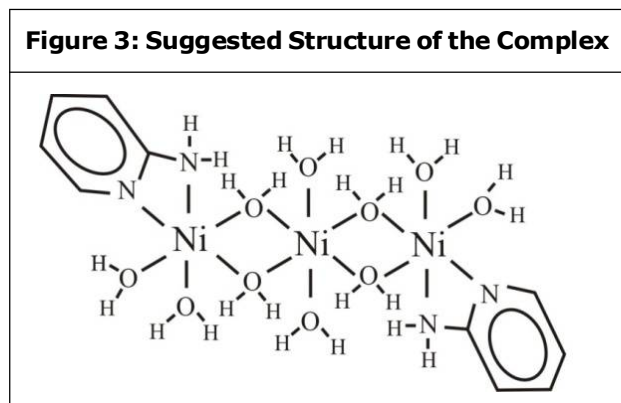
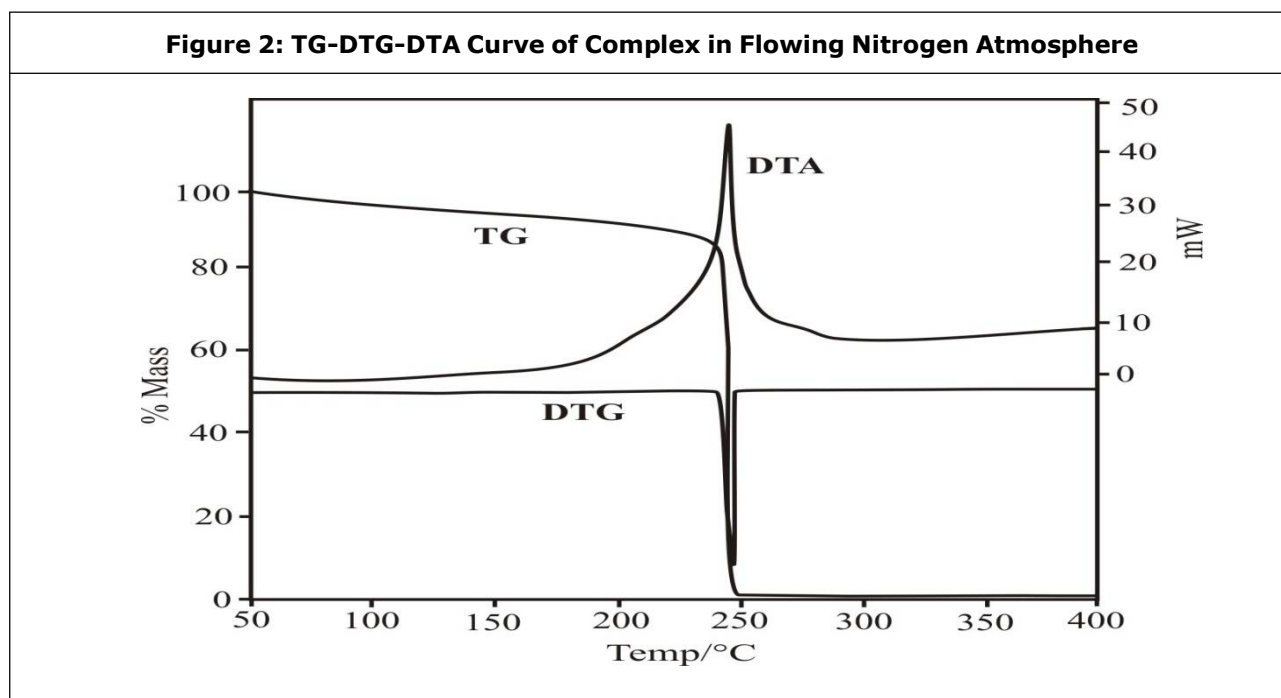
Usually a single step kinetic equation is employed for the kinetic analysis of solid state thermal decomposition (Brown and Dollimore, 1997; Kumar *et al.*, 2012)

$$d\alpha/dt = k(T)f(\alpha) \quad \dots(1)$$

where α is the extent of conversion, t is the time and T is absolute temperature. $k(T)$ is rate constant and $f(\alpha)$ is the reaction model (Table 3) (Brown and Dollimore, 1997; Kumar *et al.*, 2012). The Arrhenius equation can describe satisfactorily the temperature dependence of $k(T)$. Substituting the value of $k(T)$ in Arrhenius equation, gives

$$d\alpha/dt = A \exp(-E/RT).f(\alpha) \quad \dots(2)$$

where A is the Arrhenius factor, E is the activation energy and R the gas constant.



Model Fitting Method

Equation (1) when rearranged and integrated, yield the following equation:

$$g_j(\alpha) = k_j(T) t \quad \dots(3)$$

where $g(\alpha) = \int_0^\alpha [f(\alpha)]^{-1} d\alpha$ is the integrated form of reaction models (Table 3). Equation (3) gives the rate constant $k(T)$ when a particular model is substituted in it. For a model, the rate constant at various temperatures T_i and Arrhenius parameters can be determined by using logarithmic form of following Arrhenius equation:

$$\ln k_j(T_i) = \ln A_j - E_j / RT_i \quad \dots(4)$$

Arrhenius parameters are shown in Table 3.

Isoconversational Method

This method makes possible to evaluate the activation energy as a function of extent of conversion (Vyazovkin and Wight, 1997, 1999) (Figure 5) which indicate towards multistep kinetics. According to isoconversational method, the reaction model is not dependent on temperature

Table 2: TG-DTA Data of the Complex

Step	TG		DTA	
	Temperature Range/°C	% Decomposition	Peak Position/°C	Nature of Peaks
I	95-240	15	—	—
II	243-248	58	247	Exo

Table 3: Activation Energy (E), Arrhenius Factor and Correlation Coefficients (R) for the Isothermal Decomposition of the Complex

S.No.	Model	lnA	Slope	E/kJmole ⁻¹	r	Mean Dev	SD
1	Power law ^{3/4}	2.330	1627.9	13.5	0.9929	2.890	3.047
2	Power law ^{2/3}	2.102	16.37.3	13.2	0.9931	2.782	2.934
3	Power law ^{1/2}	1.798	1654.8	13.7	0.9933	2.684	2.793
4	Power law ^{-1/2}	1.215	1726.5	14.3	0.9944	2.433	2.566
5	Power law ⁻¹	1.140	1748.2	14.5	0.9947	2.418	2.550
6	Mampel (1-á)	-0.359	1986.8	16.5	0.9922	1.921	2.027
7	a-e ^{3/4}	1.934	1666.4	13.8	0.9946	2.729	2.877
	a-e ^{2/3}	0.649	1994.7	16.6	0.9901	2.434	2.567
9	a-e ^{1/2}	0.278	1997.4	16.6	0.9908	2.251	2.375
10	cs	1.158	1872.2	15.9	0.9937	2.559	2.689
11	T-d-diff	0.959	2040.1	16.9	0.9926	2.637	2.781
12	cc	1.234	1793.4	14.9	0.9941	2.513	2.650
13	P-T	-0.941	1977.1	16.4	0.9998	1.619	1.710
14	G-B	2.191	1853.9	15.4	0.9944	3.056	3.222

Figure 5: A Plot of Activation Energy (E) vs α

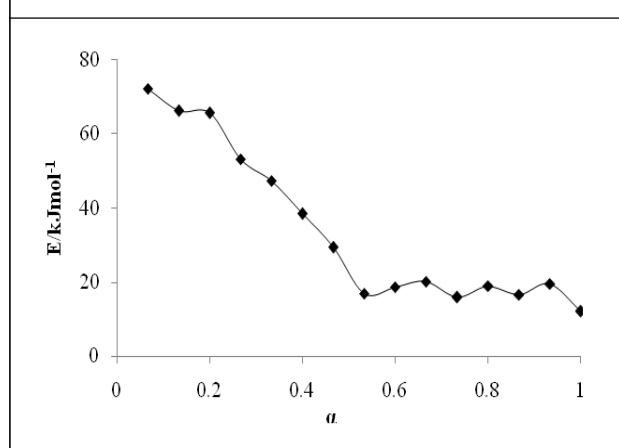
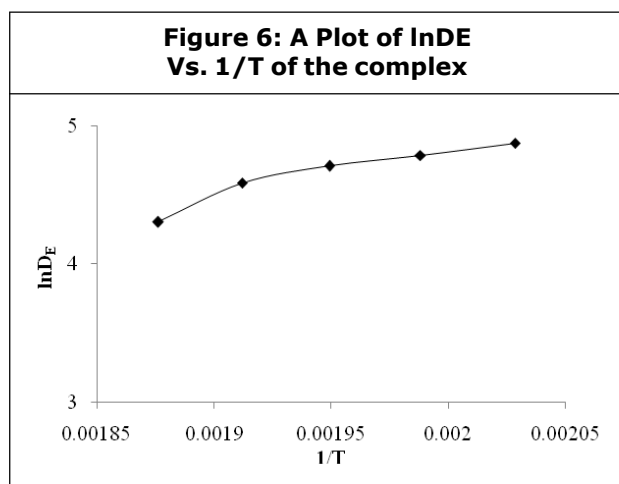


Table 4: Explosion Delay, Activation Energy for Thermal Explosion (E*) and Correlation Coefficient (r) of Complex

D _E /s at Temperature/°C					E*/kJ mol ⁻¹	r	lnk
220 ±1	230 ±1	240 ±1	250 ±1	260 ±1			
131	120	111	98	74	29.2	0.9518	-2.196

or heating rate. If we combine equation (3) and (4), we have

$$-\ln t_{\alpha_i} = \ln [A_{\alpha}/g(\alpha)] - E_g/RT_i \quad \dots(5)$$



E_{α} is obtained from the slope of plot of $-\ln t_{\alpha,i}$ vs $1/T$.

Explosion Delay Measurements

Explosion delay (D_E) measurement was performed using tube furnace technique (Singh *et al.*, 1991), (sample mass ~10mg) at temperatures 220, 230, 240, 250, and 260°C with temperature accuracy of $\pm 1^\circ\text{C}$ (Table 4). The D_E data was fitted in the equation (Kumar *et al.*, 2012)

$$D_E = A \exp E^*/RT \quad \dots(6)$$

where E^* is the activation energy for explosion, A plot of D_E vs $1/T$ is presented in Figure 6.

RESULTS AND DISCUSSION

Elemental and Spectral Description

The analytical data given in Table 1, present a good agreement between calculated and observed percentage of the element C, H, N and Ni which certify the proposed molecular formula of the complex. In the IR spectra, a broad band at 3430 cm^{-1} is due to O-H stretching vibration indicating the presence of coordinated water molecules in the complex. A peak at 1090 cm^{-1} is specific of a non-coordinated ionic perchlorate and a sharp peak around 627 cm^{-1} indicate the

presence of ClO_4^- ion having Td symmetry i.e. not coordinated to nickel. Peak at 414 and 469 cm^{-1} is due to M-N stretching (Miller and Wilkins, 1952; Robert, 1996; Nakamoto, 1978) which confirms the nickel to ligand coordination. Other peaks shown in Table 1 are according to standard text.

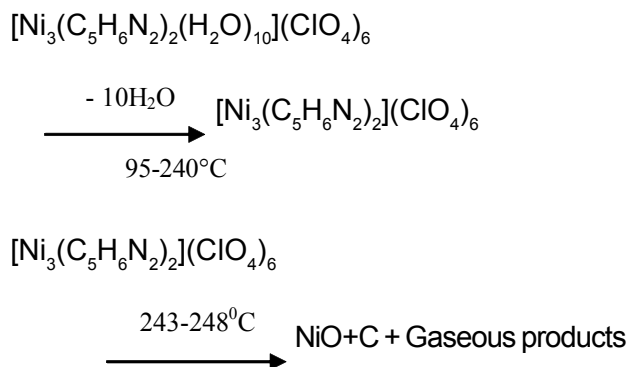
Thermal Analysis

Thermogravimetric curve (TG) obtained in static air (Figure 1) shows that the complex decomposes in two steps. First step is slow (95 - 240°C) and second is rapid (243 - 248°C). First step of mass loss is due to loss of $10\text{H}_2\text{O}$ molecules ($\sim 15\%$ mass; calculated % mass of $10\text{H}_2\text{O} = 14.7\%$). A close view of TG data shows that this first step is completed via two less distinct stages. In first stage, four water molecules leave the complex in the temperature range 95 - 180°C ($\sim 7\%$ mass) and in second stage, rest of six water molecules also leave the complex in the temperature range 200 - 240°C ($\sim 9\%$ mass) giving anhydrous complex. At 243°C the left residue ignited and given a sharp weight loss ($\sim 58\%$) which forms the second step of TG curve. Finally a residue ($\sim 28\%$) is left which may be due to nickel oxide (calculated 19%) and carbon (10.5% calculated).

In flowing nitrogen atmosphere also, the complex decomposed in two steps (Figure 2) of which first step is gradual and second is very rapid similar to static air TG. A DTG peak has been recorded for rapid step. Since first step is very gradual, no DTG peak has been obtained for this. In DTA thermogram (Figure 2), during 1st step of decomposition the curve is below the baseline (0.0) which indicates the endothermic elimination of water molecules. An exothermic peak at 247°C in DTA curve has been obtained due to ignition of

residual mass (dehydrated complex) after first step decomposition.

Thus, the tentative mechanism of thermolysis of the complex may be given as:



Owing to the TG, the complex may contain $4\text{H}_2\text{O}$ molecule (~6%) as bridged ligand between two Ni atoms and $6\text{H}_2\text{O}$ molecule (~9%) may terminally coordinated, two on each Ni-atom. One 2-aminopyridine ligand coordinated to each terminal Ni-atoms in a bidentate fashion. Thus, each Ni-atom will be hexacoordinated and giving a trinuclear chain in which H-bonds between coordinated H_2O molecules could not be omitted (Figure 3). Several bridged polynuclear complexes of Ni with various ligands has also been reported in open literature in which Cl^- , Br^- , OH^- and CO or other ligands bridges between Ni-atoms

Very recently trinuclear and tetranuclear complexes of Ni have been reported (Xiao *et al.*, 2011). In these complexes Ni is octahedrally coordinated and O-atom of 3,5-dichloro-2-hydroxy-benzylaminoacetic acid bridges between two Ni-atoms. A dinuclear perchlorate complex of Ni in which nickel (II) are bridged by alkoxide oxygen (Konar *et al.*, 2012). Water bridged dinuclear cationic complexes of first row transition series are also reported in literature (Wilcox,

1996) in which cationic complexes are crucial in the model studies of metallocatecholases and metallohydrolases.

The kinetic analysis of 30% decomposition of initial mass which includes elimination of all the water molecules and 2-Apy ligands, has been studied using isothermal TG data in static air by applying model fitting and isoconversional method (Vyazovkin and Wight, 1997, 1999). Each model results approximately same activation energy (Table 3, average $E = 15.2 \text{ kJ mole}^{-1}$). Since solid state decomposition is a complex process, isocoversional method ((Vyazovkin and Wight, 1997, 1999) has been applied to estimate the activation energy which will be independent of models. A perusal of Figure 5 shows that the activation energy changes with α (degrees of conversion). Thus, this method evaluate the effective activation energy having a separate value at different α which explore the multistep kinetics for such a complex solid state process. It is not easy to assign a benign value of activated energy to a particular process.

Complex is stable at room temperature, but in response to sudden high temperature it explodes. The activation energy of explosion was found to be 29.2 kJmole^{-1} (Table 4). Exponential dependence of explosion delay on temperature was found. This shows that reactant changes significantly during pre-explosion reactions. The process of explosion is not a process of steady state. Freeman and Gorden (Freeman and Gorden, 1956) derived following equation:

$$D_E = Ae^{\Delta H^*/RT}$$

where ΔH^* is the heat of activation and comparable to activation energy, E^* (equation 6).

CONCLUSION

Trinuclear nickel complex has been synthesized and characterized. Complex decomposes in two steps of which first step is slow and second is fast. Corresponding to second step an exothermic DTA peak has been obtained. Model fitting method applied on isothermal TG data yields a single value of activation energy whereas isoconversional method gives a series of E values at different α . Explosion delay exponentially depends on temperature.

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REFERENCES

1. Brown M E, Dollimore D and Galway A K (1997), *Reaction in the solid state, comprehensive chemical kinetics*, Vol. 22, Elsevier, Amsterdam, the Netherlands.
2. Deshpande M Mrunalini, Junne B Subhash, Saraf V Devdatta and Kulkarni A Prafullakumar (2010), "Synthesis and spectral analysis of some new lanthanide complexes derived from 2,4 and 2, 5-dihydroxy acetophenones and screened their antimicrobial activity", *J Chem Pharm Res.*, Vol. 2(3), pp. 453-458.
3. Dalvi A A, Satpati A K and Palrecha M M (2008), "Simultaneous determination of Pt and Rh by catalytic adsorptive stripping voltametry using hexamethylenetetramine (HMTA) as complexing agent", *Talanta*, Vol. 75, pp. 1382-1387.
4. El-ajaily M M, El-mashaty F I, El-zeweay R S and Maihub AA (2009), "New Co(III) mixed ligand complexes effect on the germination and root length of wheat", *International Journal of Chem Tech Research*, Vol. 1, No. 1, pp. 80-87.
5. Fedoroff B T and Sheffield O E (1966), "Encyclopedia of explosives and related items", Vol. 5, Picatinny Arsenal Dover NJ, pp. F217-F223.
6. Freeman E S and Gorden S (1956), "The application of the absolute rate theory of the ignition of propagatively reaction system: thermal ignition of the system: lithium nitrate - magnesium sodium nitrate", *J Phys Chem.*, Vol. 60, pp. 867-871.
7. Jacob P W M and Whitehead H M (1969), "Decomposition and combustion of ammonium perchlorate", *Chem Rev.*, Vol. 69, pp. 551-389.
8. Konar Saugata, Jana Atanu, Das Kinsuk, Ray Sangita, Chatterjee Sudipta and Kar Susanta Kumar (2012), "Complexes of a functionally modified pyrazole derived ligand – mononuclear Zinc(II), dinuclear nickel(II) and a rare pentanuclear cadmium (II) complex with a TBP core and their photoluminescence studies", *Polyhedron*, Vol. 47, pp. 143-150.
9. Konar S, Mukherjee P S, Drew M G B, Ribas J and Chaudhary N R (2003), "Synthesis of two new 1D and 3D networks of Cu(II) and Co(II) using malonate and urotropin as

- bridging ligands: Crystal structure and magnetic studies”, *Inorg Chem.*, Vol. 42, pp. 2545-2552.
10. Koper J H, Jansen O G, and Van der Berg P J (1970), “A reaction mechanism for the decomposition of ammonium nitrate (Delft, technische Hogeschool, Delft Netherlands)”, *Explosivstoffe*, pp. 181-183.
 11. Kozlevcar Bojan, Lah Nina, Zlindra Daniel, Leban Ivan and Segedin Primoz (2001), “Copper(II) benzoate, and acetates with 2-aminopyridine”, *Acta Chim Slov.*, Vol. 48, pp. 363-374
 12. Kumar Dinesh, Kapoor I P S, Singh Gurdip, and Frohlich Roland (2012), “Preparation, characterisation and kinetics of thermolysis of nickel and copper nitrate complexes with 2,2'-bipyridine ligand”, *Thermochim Acta.*, Vol. 545, pp. 67-74.
 13. Kumar Dinesh, Kapoor I P S, Singh Gurdip, Goel Nidhi and Singh Udai P (2012), “Preparation, characterisation and thermal behaviour of polymeric complex of cadmium hexamethylene tetramine nitrate”, *Solid State Sci.*, Vol. 14, pp. 495-500.
 14. Kung H H, (1998), “Transition metal oxides, surface chemistry and catalysis”, Vol. 45, Elsevier, Amsterdam.
 15. Li Li and Fugen Yuan (2012), “Synthesis and structural characterisation of the heteroleptic nickel 2-aminopyridine complex of (acac)(CH₃COO)Ni(2-NH₂Py)₂”, *Synthesis and Reactivity in Inorganic, Metal-organic, Nano-metal Chemistry*, Vol. 42, No. 2, pp. 205-208.
 16. Mei Luo, Ming Tang Hai, Rong Li Qian, Jie Sun, Zhong Yang Shen and Liang Li Xue (2009), “The synthesis of N-Zn, N-Cu complexes involving 2-aminopyridine and ethylenediamine ligands and application to the Henry reaction”, *J Chem Sci.*, Vol. 121, No. 4, pp. 435-440.
 17. Miller F A, and Wilkins C H (1952), “Infrared and characteristic frequencies of inorganic ions”, *Anal Chem.*, Vol. 24, No.8, pp. 1253-1294.
 18. Nakamoto K (1978), *Infrared and Raman spectra of inorganic and coordination compounds*, Wiley and Sons, pp. 206-208.
 19. Patil K C, Pai Verneker V R, Jain S R (1975), “Role of metal perchlorate amines on ammonium perchlorate decomposition”, *Combust Flame*, Vol. 25, pp. 387-388.
 20. Robert C W (1996), *Hand book of physics and chemistry*, Vol. 66, C R C Press, Florida.
 21. Sawant S Y, Kannan K R and Verneker V M S (2002), “Thirteenth national symposium on thermal analysis”, BARC, Mumbai.
 22. Semenov N (1935), *Chemical kinetics and chain reactions*, Clarendon Press Oxford (Chapter 18).
 23. Shen S M, Chen S , Wu B H (1993), “The thermal decomposition of ammonium perchlorate (AP) containing a burning rate modifier”, *Thermochim Acta.*, Vol. 223, pp. 135-142.
 24. Singh G, Baranwal B P, Kapoor I P S, Kumar D, Singh C P and Frohlich R (2008), “Some transition metal nitrate complexes with hexamethylenetetramine Part LV: Preparation, X-ray crystallography and thermal decomposition”, *J Therm Anal Calorim.*, Vol. 91, 3, pp. 971-977.

25. Singh G, Kapoor I P S and Vasudeva S K, (1991), "Thermolysis of AP-PS additive mixture II", *Indian J Technol.*, Vol. 29, pp. 584-589.
26. Singh G, Pandey D K, (2003), "Studies on energetic compounds part 27: kinetics and mechanism of thermolysis of bis(ethylenediamine) metal nitrate and their role in the burning rate of solid propellants", *Propellant Explos Pyrotech.*, Vol. 28, pp. 231-239.
27. Singh G, Pandey D K, (2005), "Studies on energetic compounds, part 43: effect of some BEMP complexes on the combustion and condensed phase thermolysis of HTPB-AP composite solid propellants", *Ind J Chem Technol.*, Vol. 12, pp. 175-180.
28. Singh Gurdip, Kapoor Inder Pal Singh, Kumar Dinesh, Singh Udai P, and Goel Nidhi, (2009), "Preparation, X-ray crystallography and thermal decomposition of transition metal perchlorate with perchlorate and 2,2'-bipyridyl ligands", *Inorg Chim Acta.*, Vol. 362, pp. 4091-4098.
29. Singh G, and Singh R R, (1978), "Indigenously fabricated apparatus for thermogravimetric analysis", *Res Ind.* Vol. 23, pp. 92-93.
30. Solymosi F (1977), *Structure and stability of salts of halogens oxyacid in the solid phase*, John Wiley and sons, New York, pp. 195.
31. Vogel A I, Basset J editors (1995), *Vogel's text book of quantitative inorganic analysis*, 4th edition, London.
32. Vyazovkin S and Wight C A (1997), "Isothermal and non-isothermal kinetics in solids: in search of ways towards consensus", *J Phy Chem.*, Vol. A10, pp. 8279-8284.
33. Vyazovkin S and Wight C A (1999), "Model free and model fitting approaches to kinetic analysis of isothermal and non-isothermal data", *Thermochim Acta.*, Vol. 340-341, pp. 53-58.
34. Wilcox D E (1996), "Binuclear metallohydrolases", *Chem Rev.*, Vol. 96 (7), pp. 2435-2458.
35. Xiao Yu, Zhang Shu Hua, Li Guang Zhao, Wang Yin Guang and Feng Chao (2011), "Synthesis, crystal structure and magnetic properties of cubane and linear trinuclear nickel complexes formed by 3,5-dichloro-2-hydroxybenzylaminoacetic acid", *Inorg Chim Acta.*, Vol. 366, pp. 39-43.



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